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Development and chemo-mechanical characterization of eco-compatible extenders containing REOB and recycled tyres' rubber for the production of greener bituminous binders

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To my lovely family, Mom, Dad, Silvia and Tommaso,
You are my strength to overcome difficulties,
You are my courage to face new challenges,
You are my happiness, always!

Keywords

Recycling

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Extended abstract

According to the concepts of circular economy and sustainability, the present experimental research has sought to use recycled products as partial substitutes of traditional road construction materials, such as virgin bitumen and natural aggregates. The use of by-products or wastes that underwent recovery or recycling processes aims to reduce the environmental impact of human and economic activities. In fact, it has two beneficial aspects as it reduces the use of the land in landfilling of wastes and decreases the use of virgin materials and resources, both renewable and non-renewable.

More than 2.5 billion tons of waste are produced in Europe every year. The construction and the related activities such as mining, quarrying and manufacturing generate the largest amount of wastes followed by the activity connected to wastes collection and materials recovery. Several waste products are high valued materials that cannot be landfilled without exploiting their full potential. The present research aims to create a more sustainable asphalt pavement including recycled and/or recovered materials at the binder and asphalt mixture levels. Selected recycled materials and by-products have been used as partial replacement for virgin bitumen and natural aggregates to obtain or, where possible, to improve the performances of the final asphalt mixture compared to those of traditional road materials. In case that bituminous binders and asphalt products with high percentages of recycled materials can behave similarly or better than the reference materials with no environmental-related issues, this research would represent the starting point to promote the use of alternative solutions for pavements, encouraging higher recycling and recovery rates of wastes.

Among all available recycled materials and/or by-products, rubber (R) from end-of-life tyres (ELTs) and re-refined engine oil bottom (REOB) have been employed as constituents of bitumen extenders in order to replace the 25%wt. of neat bitumen from petroleum resources. The granular rubber derives from materials' recovery of ELTs, which are produced in large amount worldwide; only in Italy the production exceeds 210,000 tons in one year. While, REOB is usually identified as a by-product of refinery processing of exhausted engine oils to produce regenerated lubricants; recently, in Italy, the yearly collection of waste lubricant oils counts more than 180,000 tons which results in about 23% of by-products. Consequently, the feasible use of R and REOB in asphalt pavement application allows the manufacturing of eco-friendly bituminous materials mitigating the issues of their disposal. Behind the remarkable environmental benefits of using R and REOB, these recycled products represent two high quality materials. Tyres are high-tech safety products and R from ELTs consists of elastomeric compounds that underwent vulcanisation process. This process cross-links the long polymer chains of natural rubber that cannot move independently relative to each other anymore resulting in a more elastic and resilient material. This leads to improve the petroleum bitumen quality in terms of permanent deformation, thermal cracking, fatigue damage, temperature susceptibility and aging when added as bitumen modifiers. The REOB is highly compatible with bitumen being a petroleum-based material. Also, the addition of liquid phase in bituminous matrix may enhance the thermal cracking resistance of bituminous products at both, the binder and asphalt mixture levels, and mitigate the drawbacks of using polymers like high stiffness and viscosity. With the final goal to increase the quantity of recycled materials into the asphalt products creating more sustainable pavements, recycled aggregates have been used in the aggregate skeleton of asphalt mixes. The recycled materials from reclaimed asphalt pavement (RAP), construction and demolition waste or urban/industrial waste are added in asphalt concretes halving the quantity of the virgin natural aggregates of the considered asphalt mixtures.

The use of recycled materials and/or by-products is more challenging if compared to that of traditional and virgin ones as they are characterized by high variability. This aspect results from numerous characteristics like original chemical composition of virgin materials, experienced ageing processes during their in-service life, recycling and, especially, refinery processes. Therefore, the present research focused at first on the two recycled materials and their interaction during the production of extenders. In fact, R and REOB are the constituents of bitumen extenders that are used to partially substitute the neat bitumen. Two REOBs coming from two distinct refinery plants have been supplied for this study, while one powdered R has been supplied and used. The first experimental analysis on R-REOB compounds was divided into two consecutive steps in order to: (i) establish the mass proportion of the recycled materials (optimum R-REOB ratio) maximizing their use for the production of extenders, and, then, (ii) to evaluate the effect of the processing temperature on the chemo-rheological responses of the R-REOB blends defining the proper production procedure.

A characterization protocol has been developed to identify the optimum mass proportion of R and REOBs combining spectroscopic techniques and microscopic analysis. In detail, nuclear magnetic resonance (NMR) devices and scanning electron microscope (SEM) were employed. The characterization protocol were found meaningful to define the optimum mass proportion of materials and two optimal ratios, namely1:1 and 1:2, were identified and considered for the production of extenders. Then, the Fourier transform infrared (FTIR) spectrometer and dynamic shear rheometer (DSR) have been used to better understand the behaviour of R-REOB blends produced at three test temperatures, namely 130, 160 and 180 °C. The processing temperature was found to affect the final chemo-rheological behaviour of extenders with a lesser extent than R content (i.e. R-REOB ratio), and type of REOB. Therefore, subsequent investigations on bituminous binders and asphalt mixtures were performed by using the R-REOB extenders produced at 160 °C and 180 °C only. The higher production temperatures may also speed up the interactions between the materials. In addition, other two considerations have supported this decision as polymer modified bitumen is usually produced at temperatures equal or higher 160 °C and the highest value, 180 °C, corresponds to the production temperature of both REOBs. Consequently, eight extenders manufactured with two R-REOB ratios (1:1 or 1:2) and, alternatively one of the available REOBs, at two production temperatures (160-180 °C) was used to partially replace standard bitumen and produce extended bitumens.

The eight extenders were used to produce eight corresponding extended bitumens replacing 25%wt. of a 50/70 penetration grade bitumen (Pen 50/70), which is also the reference material. The rheological and chemical properties of the innovative bituminous binders have been determined by means of DSR and FTIR devices. The rheological characterization included the storage stability of the R-REOB-modified bitumens at high temperatures since the solid particles of the added polymer tend to settle in time, resulting in a poorer storage stability of polymer-modified bitumens. Moreover, the durability of the extended bitumens was investigated because it represents a crucial aspect to assess their feasible use as road construction materials and to promote their use. The eight innovative bituminous binders underwent a laboratory ageing protocol to simulate the ageing phenomenon that an asphalt pavement experience at the end of its service life. In particular, two methodologies were applied consecutively to simulate the short- and long-term ageing of asphalt mixtures during production and paving, and their use in-situ, respectively. Then, the rheological and chemical investigations were repeated to evaluate if and how much the innovative binders deteriorate.

Considering the extended bitumens as composite materials, the rheological behaviour of the R-REOB-modified bitumens can be predicted by the use of analytical methods. In particular, the self-consistent (SC) micromechanical model based on the homogenization theory was adopted to predict the complex shear modulus of extended bitumens based on physical properties of individual constituents' and their microstructural aspects. The comparison between experimental and modelled data revealed that the present model better predicts the response of extended bitumens with the equal mass proportions of recycled materials. This response is reasonable, as the incorporation of REOB softened the rigid R particles disregarding one of the hypothesis. The chosen model can be successfully used as a fundamental baseline to preliminary determine the response of R-REOB-modified bitumens with different recipes when the constituents have been tested. However, the percentage of R should be sufficiently high. Thus, the input data needs further investigations to define the correct values and/or other the use of other models can be evaluated for the prediction of G* values. An analytical method that can predict the rheological parameters of R-REOB-modified bitumens based on constituents' information is useful to complete a preliminary analysis on new bituminous binder recipes with low time-consuming. Then, the subsequent experimental analysis will focus on the combinations that have met the desired requirements only.

The last phase of this study addresses to the mechanical characterization and environmental impacts of the eight asphalt mixes with a high percentage of recycled materials that is equal to 48.65% by the weight of the mix. In fact, wearing layer asphalt concretes were produced with the developed extended bitumens and 50% of recycled aggregates by the weight of total aggregates (CAM mixes). The considered CAM mixtures were analysed in terms of volumetric and mechanical behaviours to preliminary assess their feasible use as road construction materials. The stiffness modulus (ITSM), indirect tensile strength (ITS) and moisture susceptibility (ITSR) of the eight CAM asphalt mixes were measured and compared to reference mixes, which are the CAM mix with Pen 50/70 and a traditional wearing course mix mainly made with virgin materials. In addition, the assessment of potential leaching of contaminants from construction products into soil, surface water and ground water have been planned. The environmental impacts of new materials are crucial when recycled products are involved.

The importance of material characterization is well known. When recycled materials are used, this aspect becomes even more crucial due to the variability of products. The experimental activities carried out during the doctoral course underlined the importance of characterizing the new materials and, also, their interactions. In fact, the final bituminous materials have often shown intermediate behaviours to those of constituents. The replacement of Pen 50/70 for R-REOB extenders strongly affects the chemo-rheological responses of the resulting innovative bituminous binders and CAM asphalt mixtures overall the boundary conditions considered. The presence of R improves the elasticity of the final products. The R creates a polymer network within the bituminous matrix that mainly changes the response of materials at high test temperatures. The incorporation of REOB, that is a liquid phase, softens the final bituminous binders and asphalt materials. The influence of this by-product is more marked at low test temperatures. Thus, the extenders can improve the rheo-mechanical behaviours of new innovative bituminous materials at the extreme conditions. The addition of R-REOB compounds balances the effect of individual recycled products; the R mitigates the possible excessive softening effect of REOB at high temperatures resulting in high permanent deformation resistance, while REOB mainly palliates the possible thermal cracking distresses at low temperatures. However, the use of recycled products increases the susceptibility of bituminous material under damaging conditions. The partial substitution of Pen 50/70 with R-REOB compounds can results in final bituminous products more prone to age than the reference bitumen. The ageing tendency can be increased by the presence of functional groups typically associated to the uptake of oxygen molecules. Nonetheless, the ageing phenomenon requests further investigations for its assessment and, possibly, to distinguish the ageing rate of extended and neat bitumens. The use of recycled materials results in additional functional groups related to oxidative ageing in fresh conditions, but they may not accelerate or even hinder the ageing phenomenon of final bituminous products. Lastly, the extended bitumens exhibit a limited storage stability albeit the formation of R-polymer network were visible after separation conditioning.

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Introduction

1.1 Waste management and circular economy

In recent decades, a growing attention to the environment and an increased awareness of the depletion of non-renewable resources led to more sustainable approaches in all sectors, including the construction activities and the production of materials. The main challenge of our society is to reconcile the development and the environment; all nations should strive to balance the aspiration and efforts for improving the quality of life and economic growth with the limited natural resources and environmental impacts. Nowadays, the concept of sustainability represents a policy concept, which has its main aspiration in the Brundtland Report of 1987 (Kuhlman and Farrington 2010). This report defines the sustainable development as an approach that fulfils the demands of present generations without compromising the needs of future generations (World Commission on Environment and Development 1987). Since that interpretation, the concept of sustainability has evolved from a two-dimensional point of view that compared the development with the environment to a three-dimensional concept that includes, but distinguishes, the social and economic developments and the environment conservation (Kuhlman and Farrington 2010). Regardless the strict definition, a sustainable development tries to cope the contradiction between the aims of welfare for the population and environmental protection (Kuhlman and Farrington 2010). In this regard, the economy is moving from an open-ended system to a circular one, where a relationship between resources and wastes exists (Andersen 2007). An open-ended or linear economy converts natural resources into residual products, i.e. the materials at the end of their use, or waste via production and consumption to create utility. On the other hand, circular economy aims to reintroduce the residual products or wastes into the production cycle in order to tend to have no net effect on the environment (Andersen 2007) (Murray et al. 2017). Hence, it has two beneficial aspects as it reduces the use of the environment as a landfill for wastes and decreases the use of virgin materials and resources, both renewable and non-renewable, for economic activities (Andersen 2007). Nonetheless, the circular economy implicitly promotes the high efficiency of the processes, reducing the consumption of energy and the carbon emissions (United Nations Environmental Programme 2006); even though the climate change does not represent its primary focus (Williams 2019). A schematic representation of linear and circular economy is illustrated in Fig. 1.1.

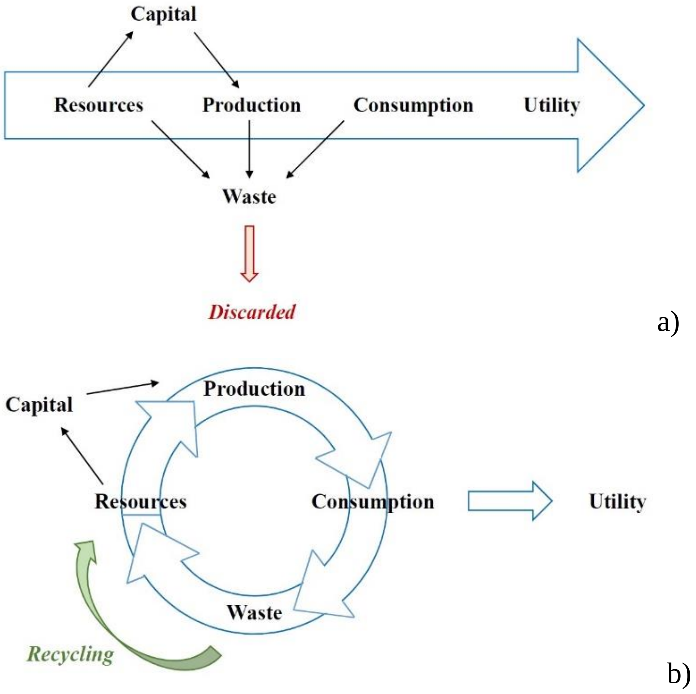


Fig. 1.1. Two economy systems: a) liner economy b) circular economy (Adapted from Andersen 2007).

The proper waste management and circular economy represent two priorities of the European policy. Pursuing the objective of sustainable development, the European Commission has implemented, and continues to develop, legislative and non-legislative measures to achieve the targeted waste management and true circular economy. At the beginning of 2020, the latest European Action Plan for circular economy has been disseminated and replaced the previous EU Action Plan that dates back in 2015. This EU Action Plan aims to accelerate the transition towards a sustainable economy providing a future-oriented agenda that promotes initiatives able to establish a sustainable product policy framework, strives to reduce the EU consumption footprint and doubles its circular material use rate (European Commission 2020). Thus, the circular economy promotes the European commitments on sustainability by gaining some of Sustainable Development Goals (SDGs) introduced by the United Nations in 2015 (Eurostat - EU Commission 2020a).

In order to monitor the trend of waste generation and the effect of European waste policy, the Eurostat produces statistical analysis regularly, every two years. The latest available information dates back in 2018 and the information on waste production by economic activity per year are reported in Table 1.1 (Eurostat - EU Commission 2020b). The statistical measurements highlight that the 28 European countries produced almost 2.6 billion tons of waste in total, and in Italy, the production of waste exceeded 172 million of tons in 2018. Among Europe, the construction activity followed by mining and quarrying, manufacturing, and activity related to wastes collection and materials recovery generate the largest quantity of wastes. A slightly different trend can be observed in Italy where most of wastes are produced by construction activity followed by waste collection and materials recovery, households and manufacturing activities. It is crucial to exploit more the waste products used in the various economic activities, especially those coming from the construction sector and those that have the highest waste production rate. Certainly, preventing the production of waste is the first action that must be strengthened followed by the re-use of products that have not been classified as waste yet according to the waste hierarchy defined by Europe (European Parliament and Council 2008). However, once materials acquire the status of waste, they must be valorised undergoing to recycling or recovery processes in order to reuse them and to minimize the final quantities of waste products to be disposed (European Parliament and Council 2008). The recycle and recovery rate of waste materials has to be increased overcoming the widely misconception that recycled and/or recovered products may have lower quality than new virgin materials.

Table 1.1. Generation of waste in 2018 classified by economic activity (Eurostat - EU Commission 2020b)

Waste generated	Europe (28 countries) [tons]	Italy [tons]
Agriculture, forestry and fishing	20,600,000	332,554
Mining and quarrying	622,850,000	1,349,011
Manufacturing	257,740,000	28,408,150
Electricity, gas, steam and air conditioning supply	81,690,000	2,278,285
Water collection, treatment and supply; sewerage; remediation activities and waste management services	30,350,000	6,107,626
Waste collection, treatment and disposal activities; materials recovery	242,090,000	36,071,525
Construction	972,560,000	60,829,199
Services (except wholesale of waste and scrap)	125,920,000	5,064,541
Wholesale of waste and scrap	29,400,000	1,903,601
Households	216,250,000	30,164,517
Total	2,599,440,000	172,509,009

According to the current trend and environmental strategies of the EU, the transportation infrastructure scientific society has focused on innovative and eco-friendly road materials encouraging the use of raw materials that come from recycling and recovery processes in asphalt mixtures. The use of these materials turns the detriment of non-renewable resources into environmental benefit, as the biologically non-degradable products are used again for the same or different purposes than their original one (Fernandes et al. 2018). In order to create a more sustainable asphalt concrete it is possible to include the recycled and/or recovered materials in the main components of the mixture that is bituminous binder and aggregate skeleton. These products can be used either as modifiers/additives for improving the performances of the final bituminous material or as replacement for virgin constituents themselves.

Waste polymers, resins, emulsion and engine or bio-oils can be used at binder level as modifiers or additives to decrease the amount of petroleum bitumen in the asphalt mix or can represent an alternative for bitumen itself (Aziz, Md M.A. et al. 2015). Depending on the type and quantity of waste materials that have been added or substituted for standard bitumen, the resulting bituminous binder will be named differently (Airey 2017). When referring to bitumen modifiers or, alternatively, modified bitumen, it is mainly about polymers that are incorporated into neat bitumen up to 10% by the total weight of binder. Instead, the addition of oils into neat bitumen in quantity from 7% to 15%wt. that act as bitumen fluxes or rejuvenators leads to produce fluxed/rejuvenated bitumens. When any recycled material and/or by-product replaces standard bitumen from 25% up to 75% by the total weight of binder, the resulting binder is named extended bitumen. When the bitumen substitution exceeds 75% by the total weight of binder, this turns into the generation of alternative binders as the amount of petroleum bitumen is very limited (Airey 2017).

The recycled and recovered materials that come from construction and demolition waste or urban and industrial waste can be introduced in asphalt concrete mixtures instead of using mineral and virgin aggregates only. The recycled materials include reclaimed asphalt concrete from existing pavements RAP), construction and demolition waste, steel slags, ceramics, etc. This short list is not exhaustive as numerous materials can be used as raw aggregates. The incorporation of recycled raw materials can represent a feasible alternative for the construction of urban paved roads if specific evaluations are performed and it is a way to introduce recycled materials and by-products in construction and maintenance processes (Ossa et al. 2016) (Pasandín and Pérez 2015) (Martinho et al. 2018). Several studies and common practices concentrate the secondary raw aggregates in the lower layers of the asphalt pavement, but the use of these materials in the upper layers represent a more valuable solution (Huang et al. 2007).

Nowadays, researchers worldwide seek to overcome the limited percentages of recycled materials commonly used either at binder or at asphalt mixture level and to use them in the highest-valuable products. Nevertheless, these materials may become a resource only if they allow obtaining road pavement materials with at least the same properties as traditional ones and the final product has to be cost effective. Moreover, specific and necessary evaluations should be performed in order to take into account the concerns related to the use of recycled raw materials such as the variability of the products themselves, their handling and mixing characteristics with virgin materials, their environmental features and the leaching potential (Huang et al. 2007) (Kluttz 2012). The adequate methods to specifically characterize the new bituminous binders and asphalt mixture represents a worth discussion. The current test methods may need to be improved, especially, for the evaluation of highly-modified bituminous binders.

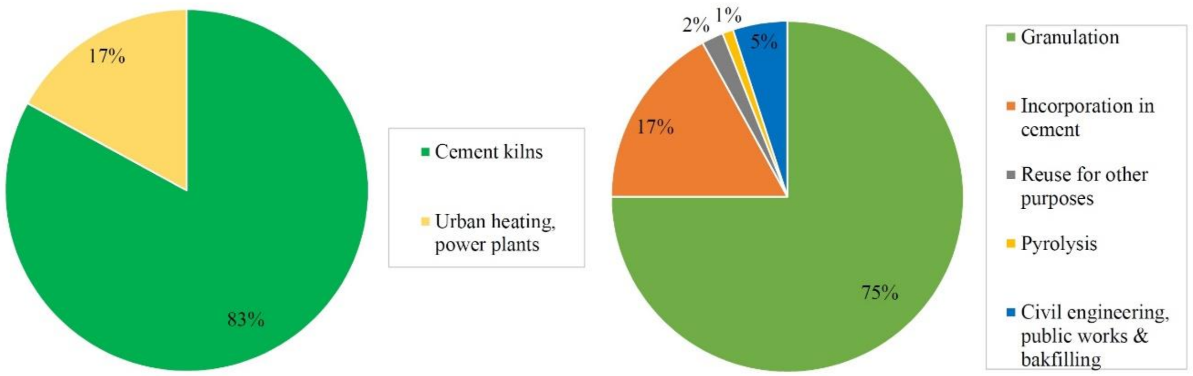
1.2 Two recycled materials as potential bitumen extenders

The use of synthetic and natural polymers as bitumen modifiers can be found as early as 1843 when the process of bitumen modification was patented (Thompson and Hoiberg 1979). In the last decades of the 20th century, modified bitumen by virgin or recycled polymers became widely used due to improvements of the petroleum bitumen quality, which in turn help to increase the resistance of asphalt concrete against the most common pavement distresses such as permanent deformation, thermal cracking, fatigue damage, temperature susceptibility and aging (Becker et al. 2001) (Yildirim 2007). One of the major areas of improvement in polymer-modified bitumen is the elastic recovery (Yildirim 2007). The properties of a bituminous binder are strictly related to those of the starting crude oil and in turn to its refinery process. As a consequence, the bitumen modification has been used by road industry to overcome the use of not well-performing starting crude oils that are available on the market and/or the difficulties related to the control of the refinery process (Becker et al. 2001). The addition of a small amount of polymers (<4%wt.) can extend the useful temperature range for the modified bitumen, which turns to enhance the engineering properties of asphalt mixtures; while, increasing their quantity over 7%wt. leads to change the behaviour of the resulting bituminous binder (Becker et al. 2001). Different type of polymers are used for modifying bitumen. Among all polymers currently used for paving applications, the modifiers can be divided into two categories (Bahia et al. 2001):

- elastomers, such as styrene butadiene styrene (SBS), which is the most common polymer belonging to this category, styrene isoprene (SIS), styrene ethylbutylene (SEBS), styrene butadiene rubber latex (SBR), natural rubber, etc.;
- plastomers, ethylene vinyl acetate (EVA), ethylene propylene diene monomer (EDPM), polyisobutylene, polyethylene, polypropylene, etc.

Both categories include virgin and recycled materials. Some studies have revealed similar performance of virgin and recycled polymers once introduced in road pavements (Kalantar et al., 2012) (Mturi et al. 2014). The possible achievement of similar performance together with the environmental benefits, such as the use of waste materials, and their advantageous price in comparison to the virgin materials have promoted the use of waste polymers over time. Among the available products on the market, rubber from end-of-life tyres (ELTs) is one of the most widely used waste polymer as bitumen modifier (Dondi et al. 2014). In the standard in force, the ELTs are defined as tyres no longer suitable for their original use (EN 14243-1, 2019). Various studies have demonstrated that recycled rubber represents an engineering resource and a possible solution to reuse waste tyres in road materials mitigating the issue of their disposal. As a matter of fact, the ELTs represent a considerable and problematic source of waste; in 2017, the 28 European countries plus Norway, Serbia, Switzerland and Turkey generated 3.42 million tons of ELTs, and Italy produced 334,500 tons of this material alone (ETRma, 2019).

Tyres are high-tech safety products and consist of elastomeric compounds, fabric and steel parts. In detail, the elastomeric compound is the results of the vulcanisation process of natural rubber, which allows the material to meet the end requirements acquiring greater elastic response and becoming a more resilient product (Lo Presti 2013). The process of vulcanisation cross-links the long polymer chains of natural rubber and the chains cannot move independently relative to each other anymore (Lo Presti 2013). Thus, the vulcanisation process changes the chemical structure of the base material to obtain a product with high, specific and desired physical performances. Due to the high value of this product, waste tyres cannot be landfilled without exploiting their full potential; rather they have to be recovered by the use of any recovery operations and be used as recycled material or as a source of energy. In this regard, the European Commission released a legislation that has banned the disposal of ELTs in 1999 (Council of European Union 1999) and have supported several projects to promote research on recycling and treatment of waste tyres since that date. The recovery of ELTs includes energy recovery, where the tyres are used as an alternative to fossil fuels, chemical processing, such as pyrolysis, thermolysis and gasification, and material recovery, where shredded tyres can be used in various civil engineering applications, for instance flooring for playgrounds, shock absorbing mats, paving blocks and rubberized asphalt pavements (Lo Presti 2013). The European association of tyre and rubber manufacturers' declared that about 1.18 million tons of tyres went through energy recovery and about 1.96 million tons of ELTs were treated through material recovery in 2017 (European Tyre & Rubber manufacturers' association 2019). The latter data includes the amount of ELTs used for chemical processing such as pyrolysis. The detailed management and ELTs uses related to both, energy and material, recovery are reported in Fig. 1.2.



a) b)

Fig. 1.2. Management of ELTs in 2017 in European area: a) Energy recovery, b) Material recovery (Adapted from European Tyre & Rubber manufacturers' association 2019).

In Italy, the national consortium of companies in the field of tyres and their recycling manages a portion of the total amount of wasted materials that has been previously mentioned per year. More than 210,000 tons of ELTs were recovered in 2019, of which 43% have been used for energy recovery and 57% for material recovery (Ecopneus Scpa 2020a). The material recovery by granulation (i.e. size reduction) allows using waste rubber in many industrial sectors including asphalt paving as showed in Fig. 1.3.

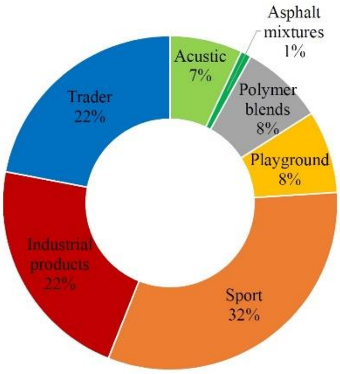


Fig. 1.3. Industrial and commercial application sectors of powder and crumb rubber in Italian market in 2019 (Adapted from Ecopneus Scpa 2020).

Various researches have obtained promising results from the incorporation of rubber particles in various industrial and civil applications worldwide. Nevertheless, the diffusion of innovative technologies have not been fully exploited in Italy yet. In particular, the readily available procedures to manufacture rubberised bituminous binders or rubber asphalt mixes are still limited and have not been promoted even if the applications have exhibited good performances at binder and asphalt mixture levels as it will be shown later on. Several technologies are available to reduce the ELTs in pieces of different sizes (i.e. ambient and cryogenic grinding or wet grinding and hydro jet size reduction) and two main techniques can be used to incorporate rubber particles into bituminous materials that is the dry process and the wet process (Lo Presti 2013). The former introduces crumb rubber particles of different dimensions as a substitute for a portion of mineral aggregates of the mixture, while, the latter adds rubber particles into the bituminous binder as bitumen modifier. The rubber particles used for wet process (crumb or powder) have usually smaller dimensions than the materials used for dry process. Nowadays, both techniques have become popular and they are commonly used. However, the present dissertation will mainly focus on the wet process.

The addition of rubber by the wet process leads to change the physical properties and the rheological behaviour of the resulting bituminous binder at all boundary conditions (Ziari, Goli, Amini 2016) (Ma et al. 2017). During the wet process, the rubber particles and neat bitumen are thoroughly mixed allowing them to react with the aim to benefit of the engineering properties of both constituents materials (Lo Presti 2013). The response of rubber-modified bitumen depends on size of rubber particles and base binder properties (Ziari, Goli, Amini, 2016) (Zhang et al. 2016). Nonetheless, the rheological response of bitumen-rubber blend is affected by processing conditions like time, temperature and frequency, which in turn influence the mechanical behaviour of the resulting asphalt concrete (Lo Presti and Airey 2013). The reaction that regulates their interactions has not been fully understood yet, but can be ascribed to two simultaneous processes: the absorption of the lightest fractions of bitumen that causes rubber swelling, and the digestion of the polymer into bitumen (Lo Presti 2013).

In general, the presence of recycled rubber lowers the penetration value and increases the softening point, viscosity, ductility and elastic response of the resulting binder compared to the base bitumen (Ma et al. 2017). Other studies have found an enhanced elastic response of rubber-modified bitumen than base bitumen (Zhang et al. 2016), or even than SBS-modified bitumen; this result was ascribed to the higher elastomer content of rubber compared to SBS polymers that led to a reduction of the phase angle (δ) values (Mturi et al. 2014). However, the better elastic performance of rubberised binder compared to those of SBS-modified bitumen is not always confirmed (Ma et al. 2017). Many studies highlighted the beneficial effect of rubber introduced in bituminous binders, which can improve their response at high temperatures. In terms of stiffness, these binders exhibited increased complex shear modulus (G^*), which provides better resistance to permanent deformation than the base binder (Mturi et al. 2014). Another research has investigated the high-temperature performance of rubber-modified bitumen by the use of the Multiple Stress Creep and Recovery (MSCR) test, which has confirmed the positive changes provided by rubber particles; the percentage of elastic and recoverable deformation of rubber-modified bitumen was greater than that of the original bitumen (Zhang et al. 2016). Other results found a higher Superpave rutting resistance parameter ($G^*/\sin\delta$) of rubber-modified bitumen than SBS-modified bitumen (Ding et al. 2017) (Ma et al. 2017). At intermediate test temperature, about 20 °C, the results showed lower values of both rheological parameters (G^* and δ) compared to the base binder leading to a more flexible binder that can exhibit greater resistance to fatigue cracking and crack reflection (Mturi et al. 2014). Despite that, the introduction of rubber generally leads to minor changes at low temperatures. As a matter of fact, SBS- and rubber-modified bitumen had similar low-temperature cracking behaviour based on Bending Beam Rheometer (BBR) analysis (Ding et al. 2017) (Ma et al. 2017).

The behaviour of various type of asphalt mixtures confirms the results obtained at binder level. The similar or higher rutting resistance and a more evident low-temperature cracking resistance of asphalt mixes with rubberised binder than SBS-modified bitumen has been found in stone mastic asphalt (SMA) application (Ding et al. 2017) and porous asphalt mixtures (Sangiorgi et al. 2017). Moreover, the asphalt concretes produced with rubberised bitumen have shown a good fatigue life. The gap-graded and continuous graded asphalt mixes exhibited a better fatigue resistance than the reference mix with standard bitumen (Wang et al. 2013). Another study on continuous graded mix found similar crack growth of rubber-modified and SBS-modified mixtures when modifiers have been adequately added; the incorporation of 8% of rubber can replace 4% of SBS polymers (Kök and Çolak 2011). Of course, the rubber quantity, size dimension, sample preparations and test conditions affect the obtained results (Kök and Çolak 2011) (Wang et al. 2013).

Despite the many advantages of the use of rubberised bitumen, the addition of rubber leads to an overall increase in binder viscosity (Ziari, Goli, Amini 2016), which can discourage practitioners from their use. The viscosity of rubber-modified binders was found to be much greater than that of the standard SBS-modified bitumens (Ma et al. 2017). Therefore, more attention has to be paid to the viscosity of rubberised binders since it demands higher production and compaction temperatures (Ziari, Goli, Amini 2016) (Ma et al. 2017), which in turn produce higher greenhouse gas emissions (Amini & Imaninasab 2018). The study of Ma et al. (2017) revealed that the rubberised mix can behave similarly or better than SBS-modified mixture when production temperature was raised to 170-180 °C, while the common production temperature of SBS asphalt concretes is 160 °C. The properties of rubber-modified asphalt mixture degraded and became worse than the properties of SBS-modified concrete when production temperature was lowered to 150-160 °C (Ma et al. 2017). The high production temperature represents a drawback that should not be neglected. Furthermore, it should be considered that bituminous binders' viscosity would increase in time during in service conditions (Huang 2008). All bituminous materials undergo an increment in the amount and apparent molecular weight of the asphaltene fraction during oxidative ageing (Huang 2008). However, some studies demonstrated that the presence of rubber particles yields higher values of phase angle of aged rubber-modified bitumen compared to unaged neat bitumen, which resulted in enhanced resistance to oxidative ageing (Huang 2008) (Nivitha et al. 2016). A previous study indicated that polymer modifiers did not much contribute to the oxidation products in the modified bituminous binders during aging conditions (Nivitha et al. 2016). Even though, a reduction of the proportional elastic contribution at higher temperatures has been observed by Mturi et al. (2014), the elastic response of aged modified binders remained much greater than that of unmodified binders. This can be ascribed to the physico-chemical interaction between standard bitumen and rubber (Nivitha et al. 2016).

The new candidates to reduce the viscosity of the rubber-modified bitumen are oils from various origins (i.e., petroleum or bio-based oils, waste or refined used oils). The addition of oils to neat bitumen leads to reduce the resulting consistency of bituminous binders regardless the origin of oil itself, since a softer fraction with different chemical components is introduced (Golalipour and Bahia 2014). Moreover, previous studies have highlighted the mitigation effect of different type of oils when added to a polymer-modified bitumen (Fini et al. 2019) (Amini and Imaninasab 2018). Acting as bitumen fluxes (Airey 2017), the oil modification increases the penetration of bituminous binders, while decreases their softening point; moreover, an overall reduction of the viscosity of modified bitumens is observed (Lei et al. 2017) (Ingrassia et al. 2020a). As a consequence, the incorporation of oil alters the rheological response and thermal behaviour of the resulting bituminous binders. Oil-modified bitumens exhibited enhanced low-temperature and fatigue performance (Lei et al. 2017) and some researchers suggest that the oils can be used as a possible rejuvenator for aged bituminous binders (Lei et al. 2017) (Ingrassia et al. 2020b). Conversely, all oils tend to negatively affect the high-temperature performances of bituminous binders, especially when overdosed (Lei et al. 2017) (Li et al. 2017) (Ingrassia et al. 2020b). Hence, the addition of any type of oil has to be designed to balance, on one hand, the positive reduction of the consistency of the resulting binder, and, on the other hand, the detrimental effect at high temperature, avoiding the over-softening of the bituminous material. All waste and recycled oils available in the market are environmentally friendly additives, which can help to substitute virgin materials and to save non-renewable resources. Recently, the use of by-products from re-refining of exhausted motor oils has been exhibited a heightened level of interest, even though the blending between bituminous binders and this by-product has been in practice since 1980s (Asphalt Institute 2016).

The non-distillable fraction from re-refining of wasted motor oils is the by-product of recycling procedures of waste lubricating oils to produce second-hand or refined/regenerated lubricants. Thus, the residuum of the oil refinery represents the by-product of the recycling application and its use means doubling the application and effects of circular economy. The lubricating oils are used in every day mechanical processes to allow functioning of engines and mechanisms; consequently, the used oils with lower properties represent the largest amount of liquid, non-aqueous hazardous waste in the world (GEIR 2016). The European commission together with the European association of waste oil re-refining industries (Groupement Européen de l'Industrie de la Régénération, GEIR) promote the recycling (i.e. material recovery) of waste lubricating oils instead of using them for energetic recovery. In detail, waste oil recycling is covered in the EU framework of wastes by the Directive 2008/98/EC (European Parliament and Council 2008). Thanks to recycling, waste oil turns into valuable refined lubricants and it seems that oils can undergo refining process indefinitely (GEIR 2016). As supported by the GEIR association, waste oil regeneration should remain a priority of the European waste management policy because it allows (GEIR 2008):

- the conservation of oil resources guaranteeing a sufficient supply of lubricants;
- the reduction of environmental impacts compared to the primary production of lubricants and to incineration;
- the support of economical contribution due to the growth of refining industry.

Despite the introduction of waste hierarchy by European legislation and the beneficial effects on environment, only 13% of all lubricating oils used in Europe in 2016 came from recycling of waste oils. The remaining 87% by the total used oils were virgin and they came from crude oil refining, mostly imported and produced by major global players (GEIR 2016). Against the European mean trend, there are some best-practice examples that include Greece, Spain, Portugal and Italy (GEIR 2016).

In Italy, about 400,000 tons of lubricating oils were introduced in the market in 2018, of which about 213,000 tons were consumed during in-service operations and 186,554 tons were collected for recycling and, eventually, for disposal (CONOU 2019). Thus, the companies belonging to the national consortium of lubricating oils management collected 47% of the total collectable waste oils (CONOU 2019). In the recent years, almost 99% of the total amount of collected waste oils undergo refining process, while about 1% of used oils are recovered for producing energy or sent for thermal destruction because of contamination (CONOU 2019). From the 99% of collected waste oils, the Italian refinery industries produced 123,000 tons of second-hand lubricants, 42,000 tons of other products such as light oils, diesel oils, bitumen that includes the fraction of non-distillable residuum, and waste products in percentages as detailed in Fig. 1.4. The residuum of refining of lubricating oils is usually, but inadequately, called 'bitumen' by non-experts of bitumen and asphalt sector. Over the years, the terminology used for additives derived from recycled engine oils has not been consistent (Asphalt Institute 2016). The term that strictly refers to the residual distillation products from a vacuum tower in a re-refinery of used lubricating oils and worldwide use is Re-refined Engine Oil Bottom (REOB). This term has been adopted by the American Institute of Bitumen and has been used throughout the present dissertation. This by-product is compositionally different than bitumen that comes from a vacuum tower of a crude oil refinery (Asphalt Institute 2016). A correct and greater use of REOBs contributes to lower the environmental impact of oils' supply chain and their use in road paving materials can represent one possible green solution.

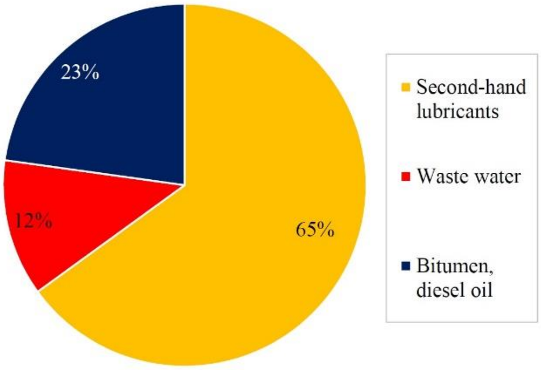


Fig. 1.4. Products of oil refinery (Adapted from CONOU 2019).

The first research effort into the use of REOB in bituminous materials dates back in 1992 and it was done in New Zealand (Herrington 1992). This residual products from re-refining of exhausted motor oils has been used by binder suppliers as a softening agent of bituminous materials in America and Canada as reported in several studies (Wielinski et al. 2015) (Asphalt Institute 2016). The distillation oil bottom represents an economical additive able to extend both, low and high, continuous temperature performance grades (PG) of neat bitumen compared to the use of a softer bitumen that can have a lower value of high temperature PG only (Rubab et al. 2011). Furthermore, it has been found that REOB broadens or relatively does not change the grade spans of the final binder starting from a polymer-modified bitumen, and this modification at a reduced cost to the reseller confirms its extensive use (Paliukaite et al. 2016).

Despite refined waste oils have been used for almost four decades, a limited number of studies focused on the impact of REOBs on bituminous materials, and the obtained data are ambiguous. The first study on REOB-modified bitumen showed that the viscosity of extended bitumen by the use of REOB is slightly less than the viscosity of standard bitumen after RTFOT short-ageing (Herrington 1992). Moreover, it concluded that the addition of REOB up to 10% lowered the temperature susceptibility of the resulting binder (Herrington 1992). Conversely, another study found an increased temperature susceptibility of REOB-modified bitumens than neat bitumen as the master curves were steeper than that of the unmodified bitumen (Golalipour and Bahia 2014). The authors ascribed this trend to the increased molecular mobility caused by oil modification (Golalipour and Bahia 2014). In general, the introduction of REOB alters the thermal susceptibility of the resulting bituminous binder significantly, and this turns into different rheological responses of REOB-modified bitumens. Moreover, base properties of oil affect the final behaviour of the binders even at the same oil content and vary the degree of influence (Golalipour and Bahia 2014) (Li et al. 2017). The rheological analysis demonstrated that REOB reduces the stiffness of the bituminous materials, which can damage the high temperature performances, but improves low temperature performances (Golalipour and Bahia 2014). The study of Karki and Zhou (2019) on REOB-modified binders confirmed the softening effect of the oily fraction regardless the type of REOB used since the crossover frequency increased with an increase in REOB dosage. Some experimental studies have found a reduced risk of low temperature cracking thanks to the oil modification as the presence of REOB lowered the temperature at which cracking occurs (Karki and Zhou 2019) or decreased the thermal stress when temperatures drops (Golalipour and Bahia 2014). On the other hand, the bituminous binders with REOB showed a reduced capacity of relaxing stress and strain increasing the REOB dosage since the R-values obtained from master curves modelling increased (Karki and Zhou 2019). Another study found a significant reduction of thermal and fatigue resistances of final binders at about ambient temperatures by adding REOB in neat bitumen in the range of 6-8% (Paliukaite et al. 2016). The negative effect of REOBs on the fatigue life of modified binders has been exhibited in a third study also. However, the presence of REOB did not detrimentally affect the fatigue crack resistance, which conversely showed an improvement when the residuum content is equal or lower than 6% (Li et al. 2017). Only increasing the concentration of REOB up to 15%, the binder strength and strain tolerance at intermediate temperature could be significantly influenced (Li et al. 2017). Oxidative hardening of the bituminous binders represents another controversial topic. A recent study demonstrated a reduction of oxidative ageing rate of REOB-modified bitumens increasing the amount of REOB itself. However, the carbonyl areas of bituminous binders' expanded with an increase in REOB dosage irrespective of aging levels (Karki and Zhou 2019), so REOB did not act as a rejuvenator. On the other hand, various studies claim that the presence of REOB increases the oxidative ageing rate of these fluxed bitumens (Herrington 1992) (Rubab et al. 2011) (Mogawer et al. 2017). Some authors ascribed this detrimental effect to the presence of large amounts of metal catalysts, such as iron, copper and chromium, and/or oxidized engine oil components (Rubab et al. 2011). Then, higher oxidation rates means more rapid gelation and subsequent thermal cracking as the asphaltenes formed during ageing are less soluble when REOB is present (Rubab et al. 2011). This is the reason why REOB-modified bitumens after ageing processes exhibited lower phase angle values (Rubab et al. 2011).

At mixture level, the moderate content of REOB seemed to be unaffected on fatigue cracking resistance, while higher REOB content (up to 15%wt.) significantly influenced the strength and strain tolerance of the resulting binder. Moreover, a large amount of oil may jeopardize the thermal cracking performance of binders (Li et al. 2017). Other study found that the presence of REOB is not detrimental in terms of rutting resistance, while they showed an insufficient stripping and cracking resistance (Mogawer et al. 2017). Regarding stiffness and tensile resistance of asphalt mixes, a study of Li et al. (2017) observed a negative effect of REOB in terms of tensile strength. On the other hand, the dynamic modulus was the least sensitive to the presence of REOB as expected since the bituminous binders were designed with the same PG grades (Li et al. 2017). Another study observed that blending neat bitumen with REOB at a rate of 9% did not compromise neither asphalt mixture stiffness nor ageing (Wielinski et al. 2015). Conversely, a high amount of REOB seems to be detrimental for the final product, because of reduced adhesiveness to the aggregates leading to stripping and ravelling (Asphalt Institute 2016).

The literature review has shown conflicting opinions on REOBs usage; some have reported the negative impacts, while others have reported positive or indifferent impacts on bituminous binders and asphalt concrete behaviour. It is important to underline that the behaviours of REOB-modified bitumens are related to base properties of constituents as previously mentioned. Hence, the variable chemical composition of REOBs due to the intrinsic variability of waste oils and the difficulties related to the control of the refinery process may result in disagreed results. Deeply investigations of the constituent materials and their effects on the final bituminous products are crucial to minimize the related risks considering the maximum level that can be used and the variability of oil residues. As a precaution, many transportation agencies of American States like Colorado, Connecticut, Illinois, Maine, Massachusetts, Michigan, New Hampshire, New York, Rhode Island and Vermont have completely banned the use of REOBs in their pavement projects, while other agencies in states as Texas, South Carolina and Georgia have imposed a maximum allowable content (Karki and Zhou 2019). However, as a response of the imposed restrictions, REOB has been sometimes used to replace a portion of standard bitumen without any declaration. A research of the Federal Highway Administration (FHWA) found that 20% of the total tested samples contained this by-product with no awareness of many American States Departments of Transportation (DOT) (Asphalt Institute 2016). The conscious REOB modification is crucial for optimizing the management of this waste with respect to better target sustainable destinations. Furthermore, in-depth studies of refinery process are necessary for improving the quality of both constituents, bitumen and REOB, and the resulting bituminous products, and for maximizing the feasible use of recycled raw materials. Indeed, many researchers have highlighted that REOB modifications are heavily dependent on the type of both constituents REOB and bitumen with no general rules (Paliukaite et al. 2016) (Li et al. 2017) (Karki and Zhou 2019).

In the recent past, a limited number of studies have evaluated the addition of both recycled materials, rubber from ELTs and REOB, in partial replacement of neat bitumen obtaining promising results. Two distinct studies proved that the addition of REOB can reduce the viscosity of neat bitumens (Fernandes et al. 2018) and rubber-modified bitumens (Amini and Imaninasab 2018). In the temperature range of 120-180 °C, the viscosity lowered on average of about 32% and 46% when REOB is incorporated in the high percentage of 42.5% and 59.5%, respectively (Amini and Imaninasab 2018). The rheological analysis of bitumens modified by rubber and REOB exhibited better responses at both high and low temperatures. All observed binders presented high values of complex shear modulus, i.e. stiffness, at high temperature and similar or lower G* values at low temperature (Fernandes et al. 2018). It means that the substitution of standard bitumen for 20% of rubber and 15% of REOB can improve the binder resistances against rutting and cracking, respectively (Fernandes et al. 2018). A deeper investigation into the effects of constituents revealed that REOB negatively influences the high temperature performance, but the introduction of rubber mitigates the binders' response satisfying the limit of the Superpave rutting parameter. Moreover, both studies confirmed that rubber-REOB modified bitumens were less prone to rutting by the use of MSCR test. At opposite conditions, the incorporation of REOB had an almost negligible effect, while rubber positively influenced the resulting binders based on data from bending beam rheometer (BBR) (Amini and Imaninasab 2018). However, the formulation of new modified binders has to be carefully evaluated as different type of oils and polymers turns into different properties of the final binders and the changes vary with a different rate (Fernandes et al. 2018). The bitumen modification by the use of REOBs may represent a solution capable of reducing the viscosity of the rubberised bitumen and improving their low temperature performances. On the other hand, the presence of rubber may mitigate the detrimental effect of REOB on high temperature performances and relaxation capability of stresses and strains.

The present research project focuses on the potential use of rubber from ELTs and REOB as more sustainable bitumen extenders since they are used to replace 25%wt. of bitumen at least. The study has tried to exploit the main and positive properties of these recycled materials that is the elastic behaviour of rubber and softening effect of REOB in order to palliate their each other drawbacks. The incorporation of polymers into neat bitumen, albeit from waste ELTs, improves the elastic response of the resulting bituminous binder and asphalt concrete, and stiffens the materials. The more pronounced elasticity and stiffness may turns into enhanced resistance against permanent deformations. However, the increment of stiffness should be controlled avoiding detrimental effects on cracking resistance. Moreover, the presence of solid particles increases the viscosity of the R-modified bitumen. The addition of a liquid phase such as REOB may mitigate the increase of both properties, viscosity and stiffness, of the modified bituminous binder. The REOB acts as a softening agent that may improve the response of bituminous binder and asphalt mix at low temperature. Nonetheless, the addition of this recycled product should compensate the effects of R without over softens the bituminous materials.

1.3 The feasible use of secondary raw aggregates in partial replacement of virgin materials

An asphalt mixture consists of 95%wt. of aggregates and 5%wt. of bituminous binders, approximately. Hence, great amounts of virgin materials are needed for the production of road pavements. With respect to mineral aggregates, the natural material comes from non-renewable resources (rocks). The production of raw aggregates includes rock blasting, quarrying, hauling, crushing and screening. A case study in China revealed that the production of raw aggregates for the construction of road pavement layers generates 43.18% of the total CO_2 equivalent, which represents an expression of the greenhouse gas (GHG) emissions (Ma et al. 2016). The construction of road pavement layer has included the production of raw materials (aggregates and bituminous binders), production of asphalt mixtures, and transportation, paving and rolling of asphalt concretes (Ma et al. 2016). Thus, the production of raw aggregates represents a considerable source of energy consumption and GHG emissions. The use of recycled raw aggregates instead of virgin ones allows the preservation of environment reducing the extraction of aggregates and decreasing the carbon footprint of asphalt mix production. Furthermore, natural source of aggregates are already scarce in some territories as local quarry sites for aggregates are expected to be exhausted soon (Hossain et al. 2016). Several recycled materials and by-products can be used as raw materials to replace virgin aggregates in the production of asphalt concrete after undergoing specific recycling processes and characterizations, which are necessary for mixes production's themselves. Among available wastes, the reclaimed asphalt pavement (RAP), construction and demolition (C&D) waste and solid waste materials are the main sources of recycled raw aggregates. In detail, RAP aggregates mainly consists of removed asphalt concretes from existing infrastructures and, to a minor extent, of wasted or rejected mixes during the production processes; while, recycled aggregates from C&D waste originate from construction, renovation and demolition of structures. Solid waste materials can also be used as raw aggregates for production of asphalt concrete. Depending on the origins of the wastes and/or by-products, recycled materials can consist of steel slags, plastic, rubber, glass, etc. These type of aggregates may substitute virgin natural aggregates giving a significant contribution to the circular economy (Martinho et al. 2018). Moreover, the use of waste can mitigate the disposal issues of many waste products.

Previous studies have obtained promising results thanks to the use of recycled materials and/or by-products, but their usage needs to be encouraged (Martinho et al. 2018). In fact, negative concerns related to mechanical performance, environmental impact and additional costs do not promote their use in asphalt mixtures. The negative concerns together with the widely spread perception that these materials have lower quality than new products lead to a lacking confidence in incorporating high content of RAP (Australian Asphalt Pavement Association - AAPA 2018)(Brock and Richmond 2006), or in using C&D waste (Pasandín and Pérez 2015) or raw aggregates from solid waste (Huang et al. 2007). In general, the issues that can inhibit the use of recycled raw aggregates are related to (Pasandín and Pérez 2015) (Martinho et al. 2018) (Tarsi et al. 2020):

- quality and homogeneity of aggregates;
- undefined mix design and lack in specifications;
- variable performance of the resulting asphalt mixtures.

Being made up of aggregates and aged bituminous binder, RAP aggregates consist of valuable non-recoverable materials, and are suitable candidates to reduce the demand of both virgin materials, aggregates and bitumen. The RAP material can be used as substitute of virgin materials in the new formulation of asphalt concrete or as recycled aggregates to produce unbound layers of pavements (Southern African Bitumen Association - SABITA 2019). However, the latter option does not exploit the full potential of the material as the former does, since it ignores the aged bituminous binder that coats the recycled aggregates. Due to the origin of RAP aggregates as they derive from milling operations of asphalt pavement layers, this type of aggregates presents a high content of fine particles (Kandhal and Mallick 1997) (Copeland 2011). Moreover, RAP material can undergo crushing process to reduce the aggregates size, especially when the material comes from a full-depth pavement demolition; and this process leads to enhance the amount of fines (Kandhal and Mallick 1997) (Copeland 2011). These characteristics negatively affect the homogeneity of RAP. Furthermore, the finer particles contain higher amount of aged binder, due to their higher surface area (Newcomb et al. 2007). Still, finer particles tend to retain moisture (Kandhal and Mallick 1997) (Brock and Richmond 2006); the RAP material itself does not drain as virgin aggregates do (Kandhal and Mallick 1997) (Copeland 2011). Hence, for properly use RAP material, it is crucial to control and assess the quality and homogeneity of

RAP aggregates and stockpiles. The optimization of RAP management can ensure the consistency of the input material and the good quality of the final products. The main resource of RAP material is the presence of bituminous binder. Albeit aged, a portion of bituminous binder that coats RAP aggregates is available and acts as a binder in the new formulation (Al-Qadi et al. 2007) (Lo Presti et al. 2019). However, the definition of the degree of blending and the diffusion that will occur between the virgin and aged binders represents one of the main obstacles to the design asphalt mixtures with high and very high contents of RAP, as there are no overall well-defined procedures for their determination (Zaumanis and Mallick 2015) (Lo Presti et al. 2019). Furthermore, increasing the RAP content may require the addition of softening agents and/or rejuvenators to restore the properties of the aged binder (Al-Qadi et al. 2007). The introduction of any recycling agent represents an additional variable in the mix design, requiring the selection of a compatible agent and its dosage. Focusing on hot mix asphalt (HMA) mixes, the increase of RAP content in new formulations implies a potential increase in the stiffness of the final asphalt mixes (Copeland 2011) (Willis et al. 2012), which is mainly dependent on the stiffness of the RAP binder (Al-Qadi et al. 2007). A stiffer asphalt concrete might be less resistant against cracking due to fatigue, thermal shock and cracking reflection, representing the main reason for the reluctance of road agencies to the use of RAP mixtures (Willis et al. 2012). Several studies highlighted that the presence of aged binder in well-designed asphalt concretes allows the resulting mix to be less susceptible to water damage and less prone to permanent deformations (Karlsson and Isacsson 2006) (Zhou et al. 2011) (Zaumanis and Mallick 2015). As a result, the optimization of RAP management, the deeply characterization of recycled aggregates and the definition of correct mix design can ensure the production of asphalt mixes with high or very high-content of RAP balancing the stiffness effect of RAP itself and the softening effect of recycling agent. Nonetheless, the technology of traditional asphalt plants can limit the maximum amount of RAP that can be incorporated into the asphalt mixtures. The possibility to use novel technological solutions can allow the introduction of RAP content up to 100% without lowering the quality of the products.

The aggregates from C&D waste mainly consists of concrete and stone. Being not combustible materials and undergoing to demolition, the C&D waste can neither be reused in building construction nor used in energy recovery (Pasandín and Pérez 2015). Several studies on the use of this material for producing hot mix asphalt (HMA) obtained promising results despite the higher water absorption than virgin aggregates (Zhu et al. 2012). In fact, the cement mortar around natural aggregates is porous (Martinho et al. 2018). This specific aspect turns into higher quantity of bituminous binder for producing asphalt concretes to compensate the binder absorption (Zhu et al. 2012). In general, the asphalt mixtures that contain C&D waste showed a variable water susceptibility (Pasandín and Pérez 2015). The moisture damage resistance was found to be related to the content of aggregates from C&D waste and nature of all aggregates used, virgin and recycled (Pasandín and Pérez 2015). Consequently, some researchers have found that the asphalt mixes with C&D waste are more prone to stripping (Pasandín and Pérez 2015). However, the study of Ossa et al. (2016) found the suitability of introducing the construction and demolition waste aggregates in quantity up to 20%; the resulting asphalt mixtures showed good performances in terms of stripping and rutting. Previous researchers have found controversial results on water damage and permanent deformation resistances. Some studies determined similar or better resistances of C&D asphalt mixes than traditional mixtures made with virgin materials only (Paranavithana and Mohajerani 2006) (Pérez et al. 2012). While, others claimed that the presence of C&D waste increased the stripping and rutting potential of the resulting asphalt mixes (Mills-Beale and You 2010). In general, the employment of C&D waste allows to reduce the stiffness of the final asphalt mixture (Paranavithana and Mohajerani 2006) (Mills-Beale and You 2010). This response was ascribed to the lower resistance of the attached cement-mortar (Paranavithana and Mohajerani 2006).

Solid waste recycled aggregates can derive from different industrial by-products or type of waste and the origin of materials influence the final properties of asphalt products. The steel slags represent the most common artificial aggregates used in Portugal (Martinho et al. 2018), but it is widely used around Europe. The high density and water absorption are two distinct properties of this material. In fact, their use implicates a large binder consumption that is much higher with respect to natural aggregates (Martinho et al. 2018). These characteristics can discourage the use of steel slag in asphalt mixtures even though the mechanical performances of asphalt concrete that contain steel slags were satisfactory. In detail, steel slags should be used in place of coarse aggregates in wear layers of pavement due to their mechanical strength and skid resistance (Huang et al. 2007). Another recycled raw aggregate is represented by waste glass. Crushed glass with particle dimensions lower than 4.75 mm can replace a portion of fine aggregates in asphalt mixes (Huang et al. 2007). This dimension does not imply any safety risk (Huang et al. 2007). Waste polymers such as rubber from ELTs or low-density polyethylene can also be used as substitute of mineral aggregates. In general, the presence of polymers increase the cracking resistance of the final mix, but other properties can be enhanced depending on the type of polymer used (Huang et al. 2007). However, the dimension of particles needs to be correctly evaluated to meet the gradation requirements (Huang et al. 2007).

In general, when assessing the performance of asphalt pavements containing recycled solid waste materials, some conditions need to be studied and specified unambiguously such as the mixture type as different mix requires different properties, particle size of the solid waste materials and the replacement rate, nature and processing techniques of the recycled materials (Huang et al. 2007).

From the literature review, it can be concluded that the use of recycled raw aggregates requires an extensive characterization of the materials themselves in order to exploit their beneficial aspects. In fact, the mechanical response of the final asphalt mix depends on the origin and properties of the recycled aggregates used. The design and production of asphalt concrete with a high content of recycled raw aggregates is more challenging than traditional ones as recycled aggregates can considerably differ from traditional mineral aggregates. On the other hand, the use of these type of materials can mitigate the disposal issues of non-degradable wastes reducing the demand of landfill space and can reduce the use of virgin and non-renewable resources. The present study employed recycled aggregates as partial substitution of natural materials in the production of asphalt concrete mixes.

1.4 Research objectives

The present research pursues for a greater use of recycled raw materials in bituminous binders and aggregate skeleton with the aim to partially substitute virgin bitumen and mineral aggregates instead of using them as modifiers or additives only. In accordance with sustainability and circular economy principles, the aim of this thesis is to define and characterize more eco-friendly bituminous and asphalt materials for paving that can be suitable and efficient from both performance and economic point of view. Specifically, the recycled materials coming from recovery operations of wastes and the by-products of urban and industrial processes are used to partially replace traditional and virgin materials of road infrastructures, which derive from non-renewable resources such as petroleum bitumen and natural aggregates. Rubber from ELTs and REOB are adopted to partially substitute neat bitumen; while recycled aggregates are used to replace 50%wt. of virgin ones. Therefore, the sustainable approach that aims to use the recycled materials and by-products is applied and carried out in two ways, at the binder and asphalt mixture levels. To this end, this experimental research pursues the following objectives:

- to evaluate the chemical and physical interactions between rubber particles and REOBs developing a characterization protocol of the rubber-REOB blends (i.e. extenders) that allows for the determination of the optimum mass proportion of constituents;

- to characterize the extenders from the chemical and rheological point of view in order to define the rubber-REOB blends with the best performances and to further and deeply investigate their effects when used as bitumen replacement;
- to formulate and produce extended bitumens defining their storage stability that represents useful information for a possible further use of the innovative materials in an asphalt production plant evaluating the potential tools needed for storing them;
- to characterize the extended bitumens from chemical and rheological point of view in fresh conditions and verify the possibility to predict their behaviour by using an analytical method based on the responses and geometrical arrangements of constituents; also, to determine their ageing susceptibility with the aim to establish whether these eco-friendly binders can be considered proper replacements for standard bitumen;
- to manufacture asphalt mixtures with extended bitumens and recycled aggregates and analyse their mechanical performances and their potential leachate to verify their feasible application in road pavements avoiding environmental impacts.

1.5 Thesis outline

The present dissertation is organized in six chapters, as subsequently described, which intend to cover the fundamental aspects of the experimental research activities that have been carried out during the doctoral course. Each of them contains a specific literature review according to the corresponding topics and materials investigated which has helped the author in defining the experimental plan and has supported the discussion as a starting point for further analysis.

Chapter 1 presents an introduction of the experimental research that defines the state-of-art of recycled products usage as partial replacement for virgin materials employed in asphalt industry, which mainly come from non-renewable resources. Furthermore, advantages and disadvantages of their incorporation in materials for road pavements have been highlighted. In addition, the present chapter includes problem statement, research objectives and thesis outline. Part of this chapter contains published materials from the articles *'Rheo-mechanical analysis of bitumens produced with green binder extenders'* authored by Giulia Tarsi, Francesco Mazzotta and Cesare Sangiorgi (https://doi.org/10.1201/9781351063265) and *'The challenges of using reclaimed asphalt pavement for new asphalt mixtures: A review'* authored by Giulia Tarsi, Piergiorgio Tataranni and Cesare Sangiorgi (http://dx.doi.org/10.3390/ma13184052).

Chapter 2 presents the recycled materials used in this dissertation, the definition of optimum bitumen extenders and their characterization including three primary subsections. The first one involves in the rheological and chemical characterization of the two recycled products used as bitumen substitutes (powdered rubber from ELTs and REOBs). The second subsection defines and describes a scientific approach adopted to evaluate the optimum mass proportion of the recycled materials. Moreover, the experimental results were reported. The last subsection contains the rheological and chemical investigation of different possible extenders produced at different mixing temperatures. Part of this chapter contains published materials from the articles *'A study of rubber-REOB extender to produce sustainable modified bitumens'* authored by Giulia Tarsi, Paolino Caputo, Michele Porto and Cesare Sangiorgi (http://dx.doi.org/10.3390/app10041204) and *'Rubber-oil distillation bottoms blends as a new recycling solution for bitumen extension'* authored by Giulia Tarsi, Cesare Sangiorgi, Aikaterini Varveri and Cesare Oliviero Rossi (http://dx.doi.org/10.1007/978-3-030-48679-2_32).

Chapter 3 presents the definition and the considerable characterization of eight extended bitumens obtained from those extenders that have exhibited the best performances. This chapter consists of two subsections. The first one includes the rheological and chemical analysis of extended bitumens in fresh conditions (no condition has been applied). This subsection includes the storage stability investigations of the extended bitumens. The second subsection evaluates the rheo-chemical properties of the extended bitumens after being subjected to short- and long-term ageing protocols. Part of this chapter contains published materials from articles *'Effects of different aging methods on chemical and rheological properties of bitumen'* authored by Giulia Tarsi, Aikaterini Varveri, Claudio Lantieri, Athanasios Scarpas and Cesare Sangiorgi (https://doi.org/10.1061/(ASCE)MT.1943-5533.0002206).

Chapter 4 concerns the application of a homogenized micromechanical model on the extended bitumens. In particular, the self-consistent (SC) model has been applied to the investigated innovative bituminous binders. The model allows the prediction of the rheological behaviour of composite materials (i.e. extended bitumen) thanks to the rheological response of constituent products (i.e. extender and neat bitumen).

Chapter 5 presents the results of the volumetric and mechanical analysis on asphalt mixtures with high content of recycled products, which were manufactured with the eight developed extended bitumens and secondary raw aggregates. Moreover, the environmental impact of the innovative asphalt mixes has been carried out and presented. The mechanical characterization includes the determination of the stiffness modulus and the indirect tensile strength of the materials in fresh conditions and the evaluation of their water susceptibility. The leaching test has been performed according to the European standard to assess the environmental impact of the asphalt concrete. Part of this chapter contains published materials from the article *'The challenges of using reclaimed asphalt pavement for new asphalt mixtures: A review'* authored by Giulia Tarsi, Piergiorgio Tataranni and Cesare Sangiorgi (http://dx.doi.org/10.3390/ma13184052).

Chapter 6 presents a brief summary of the obtained results providing the conclusions, recommendations and suggestions for further developments.

2

Development of bitumen extenders

2.1 Introduction

The present chapter focuses on the investigation of R-REOBs interactions that occur during production of bitumen extenders. The experimental analysis that has been carried out will allow the author to define and, then, to characterize the resulting extenders in order to better comprehend the behaviour of these materials that will be used to partially replace standard bitumen. The experimental analysis was divided into two steps in order to seek two objectives:

- to establish the optimum mass proportion of the recycled materials (optimum R-REOB ratio) to further produce the extenders;
- to evaluate the effect of the production temperature on the chemo-rheological response of the R-REOB blends to define the proper production procedure of extenders.

The description and characterization of the recycled materials that have been used throughout the study are reported. Then, the explanation of adopted experimental programs and the discussion of results of both objectives are provided later on in this chapter.

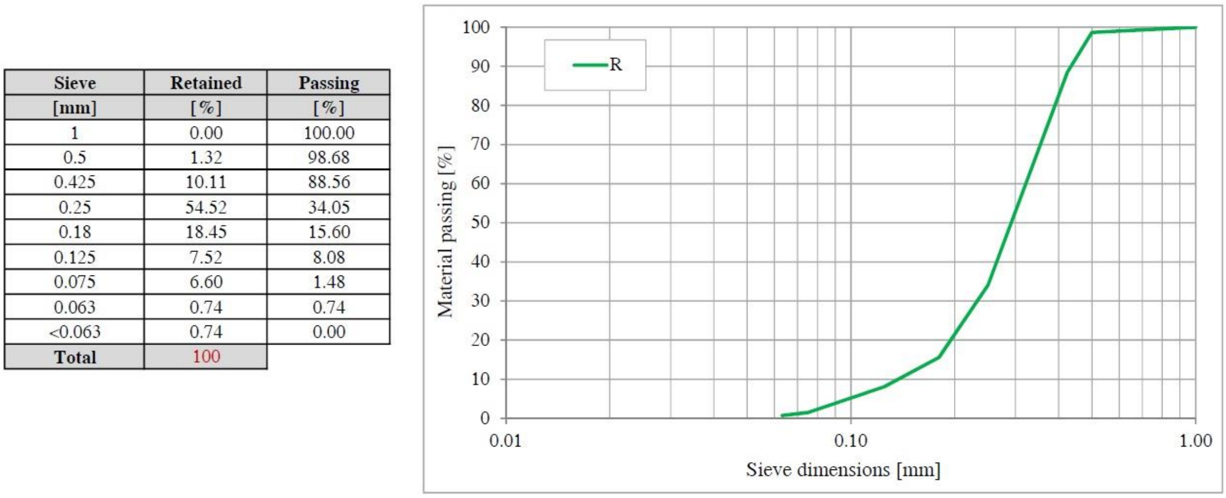
2.2 Experimental characterization of the constituents of extenders

2.2.1 Geometrical and chemical characterization of rubber

The rubber used in the present study has been provided by the Italian consortium for promoting the recycle and the reuse of waste tyres, Ecopneus Scpa. Among the 21 companies of the consortium that treats the ELTs for granular recovery, Albatros Ecologia Ambiente Sicurezza Soc. Cons. a r.l. supplied the material for logistic reason since it is located in the region of Emilia Romagna. The recycling process of ELTs for material recovery allows the reduction of tyres from trucks and passenger cars in particles with small dimensions according to the following steps (Ecopneus Scpa 2020b). The first mechanical phase consists of fragmented, ripped or torn ELTs into irregular pieces sized between 50 and 400 mm, which are called shreds. The particles of these dimensions can undergo further trituration process or, alternatively, they can be sent for energy recovery. The second shredding process reduces the tyre particles into smaller pieces until it is possible to separate rubber from steel and textile fibres. Lastly, the rubber destined for material recovery is further treated to obtain particles of different dimensions according to the intended typology of use (Ecopneus Scpa 2020b). The final treatment process obtains rubber particles that can be divided into three size categories according to the standard in force (EN 14243-1 2019):

- rubber chips with dimensions in the range of 10-50 mm;
- rubber granulate with dimensions in the range of 0.8-20 mm;
- rubber powder with dimensions typically less than 0.8 mm.

A powdered rubber from truck tyres with maximum particles' dimension equal to 0.42 mm has been employed for the production of bitumen extenders throughout this dissertation, and it is shortly referred hereafter as R. The particle size distribution of R has been evaluated following the latest legislation that has been released in the field of ELTs products, i.e. the standard EN 14243-2 (2019). Due to the maximum dimension of R, the grading curve of the material has been evaluated by means of sieves with nominal size apertures lower than 1 mm. The sieving analysis considered all available sieves that the laboratory is equipped with. The resulting data and the representation of R grading curve are reported in Fig. 2.1.



Sieve [mm]	Retained [%]	Passing [%]
1	0.00	100.00
0.5	1.32	98.68
0.425	10.11	88.56
0.25	54.52	34.05
0.18	18.45	15.60
0.125	7.52	8.08
0.075	6.60	1.48
0.063	0.74	0.74
<0.063	0.74	0.00
Total	100	

Fig. 2.1. Particle size distribution of R.

As reported in the safety and technical data sheets provided by the supplier, R particles are made of vulcanized rubber polymer and they have a mean density equal to 1.02 g/cm^3 (refer to Annexes section for further information). The chemical composition of tyres consists of four main ingredients, i.e. rubber polymer, carbon black, metals and textiles, plus additives, which are derived from the vulcanization process of natural rubber (Sibeko et al. 2020). Indeed, as previously mentioned in Chapter 1, natural rubber alone cannot withstand the conditions that the tyres are used for. The chemical formula of tyres depends on size and use of the final product, and differs from manufacturer to manufacturer (Rahman 2004). Among all constituents, natural and synthetic rubber are introduced in the recipe with a specific mass proportion, and truck tyres usually contain larger amount of natural rubber compared to that from car tyres (Lo Presti 2013). A detailed list of major chemical constituents and their related quantity of passenger car tyres has been reported by Wik and Dave (2005). Albeit the focus is on tyres for cars, an adapted version of the list is reported in Table 2.1 for providing information about type and order of magnitude of chemicals that can be commonly found in tyre products.

Table 2.1. Main constituents, ingredients and percentage of tyres for cars

Constituents	Ingredients	Percentage
Rubber polymer	Natural rubber Isoprene rubber Styrene-butadiene rubber Butadiene rubber Chlorobutyl rubber	40-60%
Reinforcement aids	Carbon black (mainly)	23-35%
Softener	Highly Aromatic (HA) oils Other oils	15-20%
Vulcanization agents	Sulphur (mainly)	1-2%
Accelerators	Chemical compounds	0.5-2%
Activators	Zinc oxide and fatty acid or Zinc stearate	2-5%
Antidegradants	Antioxidants and antiozonants	1-2%

The safety data sheet of the used R confirms the quantity of the carbon black (23-28%), zinc oxide (1.5-2%) and extenders oils (<20%) such as treated distillate aromatic extracted (TDAE) oil, low viscosity oil and naphthenic oil (refer to Annexes section for further information). The natural rubber provides elasticity to the final rubberised compound, while synthetic rubber imparts the thermal stability properties (Nivitha et al. 2016). The carbon black is mainly used to enhance rigidity in tyres (Rahman 2004). Lastly, the remaining ancillary products are necessary for helping the process of vulcanization and are introduced to gain specific effects. The TDAE is used with a dual purpose, as a softening agent in the vulcanization of natural rubber and as a component of rubber compounds to reduce the heat build-up and friction during the usage of tyres (ATDM - Avizheh Technology and Development of Middle East 2020). While, naphthenic oil is a dispersion agent of insoluble sulphur that is the most common agent used for vulcanisation process; hence, the naphthenic oil ensures a good cross-linking density (Nynas AB - Eriksson 2020). The R is not classified as hazardous nor to human health neither to aquatic environment. However, it contains heavy metal such as zinc and organic constituents that consists of polycyclic aromatic hydrocarbons (PAHs) (Sibeko et al. 2020). The presence of these materials have discouraged the use of this high-valuable recycled material.

In order to investigate and to evaluate the chemical functional groups of the used R the Fourier transform infrared (FTIR) spectroscopic analysis has been performed on a representative sample of the recycled material. The spectroscopic technique gains information on the absorption of an infrared radiation at a certain wavelength (Hofko et al. 2017). A beam light is projected to the sample, which absorbs the radiation at specific wavenumbers exciting vibrations of molecules (Hofko et al. 2017). Those vibrations are prone for infrared absorption as the dipole moment is changing due to the atomic movement (Hofko et al. 2017) and a unique spectrum is released allowing the detection of different chemical functional groups. A Perkin Elmer Spectrum 100 FTIR spectrometer (PerkinElmer, Wellesley, Massachusetts) was used in the attenuated total reflectance (ATR) mode to characterize this and further materials to be tested. Using the ATR technique, sample preparation was simple. A small amount of R particles was taken using a spatula and placed under the FTIR anvil. The R particles were manually mixed before a sample was collected from the can. The FTIR spectrum was obtained in the spectral range between 4000 and 600 cm^{-1} with a scanning resolution of 4 cm^{-1} averaging twenty scans for each measurement in order to increase the signal-to-noise ratio of the measurements. The obtained spectra of three distinct samples of R are reported in Fig. 2.2. No normalization process of the spectrum has been applied.

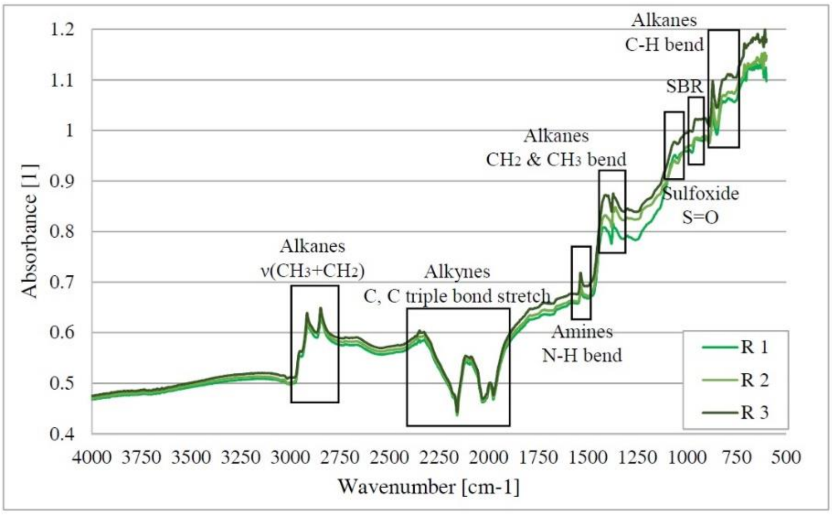


Fig. 2.2. FTIR spectra of R samples with highlights of the main functional groups.

A previous study found strong sharp peaks of rubber material in the region between 3000 and 3500 cm^{-1}, which were ascribed to the N-H stretch vibration of amines and amides (Nivitha et al. 2016). Alternatively, one large peak in the same, but enlarged band, 3000-3800 cm^{-1}, was found to be related to the absorption of OH molecular vibrations (Vasconcelos et al. 2011) (Varveri et al. 2019). The used R exhibited a weak peak at wavenumbers in the range of 3000-3500 cm^{-1} that allowed the conclusion that this material does not contain neither N-H molecules nor OH molecules. In fact, being a dry material, the presence of OH molecules was excluded *a priori*. Nitrogen compounds were detected at different wavenumbers around 1530 cm^{-1}, which are related to the presence of N-H bend vibration of amines (Delft University of Technology 2020). At wavenumbers in the range of 3000-2800 cm^{-1}, three distinct and evident peaks can be distinguished that are ascribed to the presence of aliphatic structures (alkenes). Among these three peaks, two of them correspond to the asymmetric and symmetric stretching vibration of methylene ($\nu(CH_3+CH_2)$) at around 2925 cm^{-1} and 2850 cm^{-1} wavelengths, respectively (Borrego et al. 1996) (DeDene and You 2014) (Li et al. 2019). These vibrations of aliphatic hydrocarbons are commonly found in bituminous materials, where the peak at around 2925 cm^{-1} is used as a reference for normalization of the spectra due to its slow evolution in time, i.e. during the years of use, compared to other functional groups (Lamontagne et al. 2001) (Hofko et al. 2017). Other alkenes functional groups are detected at wavenumbers around 1460 cm^{-1} and 1370 cm^{-1}, which derive from the asymmetric (CH_2) and symmetric (CH_3) bending vibration of methyl (Borrego et al. 1996) (Hofko et al. 2017). Between 2350 cm^{-1} and 1950 cm^{-1}, other three peaks can be distinguished. However, limited information are available in the definition of functional groups within these wavenumbers in the field of bituminous materials, as neat bitumen does not present significant peaks in this band. Only the vibration peak at about 2150 cm^{-1} can be identified and it corresponds to the presence of alkyl groups due to the C, C triple bond stretch (Delft University of Technology 2020) The presence of sulfoxide structures (S=O) was also detected by FTIR device. This functional groups exhibited a small peak at wavenumbers close to 1060 (Li et al. 2019). The effect of styrene-butadiene rubber (SBR) polymer is visible at wavenumbers around 965 cm^{-1} (Nivitha et al. 2016) (Zhang et al. 2017). However, a peak was not detected at 965 cm^{-1}, but absorbance values increased from wavenumber equal to 970 cm^{-1}. This indicates the C-H out-of-plane bend of butadiene (Nivitha et al. 2016). In the range of 900-700 cm^{-1} the functional groups of alkenes related to the presence of C-H vibration peak on benzene rings, which are present in R can be detected. The spectra of all samples exhibited a peak around 870 cm^{-1} and another peak around 720 cm^{-1}. The first one corresponds to the out-of-plane deformation vibration of one isolated aromatic C-H bond, while the second corresponds to band assigned to the skeletal vibration of more than four methylene groups (Borrego et al. 1996). Lastly, the presence of sulphur can be detected in the spectra at wavenumber lower than 700 cm^{-1} and some weak peaks can be observed as reported by Nivitha et al. (2016).

2.2.2 Physico-chemical characterization of REOBs

Two different REOBs supplied by Itelyum Regeneration Srl have been evaluated and compared in the present study. This company belongs to the Italian consortium in the field of waste oils management, CONOU. As previously mentioned, REOB is the by-product of the re-refining process of waste lubricating oils, which consists of three consecutive phases, and REOB represents the non-distillable fraction of the second one. In detail, during the first processing step, called preflash, the waste oil is heated up to 140 °C and undergoes through a distillation tower with a low vacuum grade to remove water and to recover any light hydrocarbons. Then, the dehydrated product is subjected to a vacuum distillation tower, which allows the recovering of three materials with higher boiling point that is three lube cuts with different viscosities. In this second phase called thermal de-asphalting, the three distillates are separated from the non-distillable fraction that is REOB. The last step involves the further processing of lube cuts for producing different grades of regenerated lubricants, which is called hydrofinishing (Itelyum Regeneration Srl 2020). A schematic overview of the recycling process of waste oils is illustrated in Fig. 2.3.

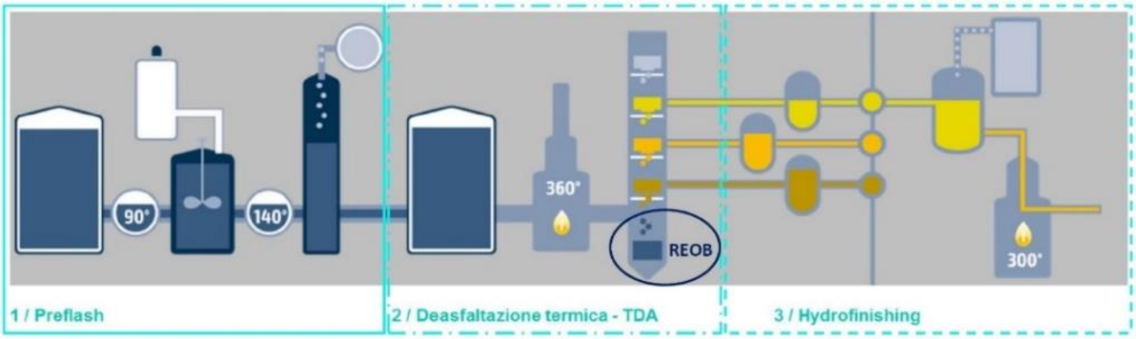


Fig. 2.3. Re-refining process of waste lubricating oils (Adapted from Itelyum Regeneration Srl 2020).

The two available REOBs come from two distinct refinery plants of the same company; one plant is located in the north of Italy (Pieve Fissiraga - Lodi), while the second one is located in the south of the country (Ceccano - Frosinone). Despite the fact that similar technologies have been employed in the refinery plants construction, the plants do not have of identical apparatus. Hence, the by-products of the refinery plants differ from each other and they are marketed with different trade names. The two materials will be referred as V1 and V2, throughout this dissertation, which are related to the REOBs coming from the plant located in the north and in the south of Italy, respectively. When either both REOBs supplied for this study or one of them were considered alternatively, they will be referred as Vx.

The two available REOBs (Vx) have similar density, which is approximately equal to 1.00 g/cm^3 (refer to Annexes section for further information). Even though the density is similar, a first visual observation reveals a different viscosity of the products as V1 seems less viscous than V2. In order to better evaluate the constituents and to determine the exact characteristics of the supplied batches of REOBs, their dynamic viscosity have been measured by the use of dynamic shear rheometer (DSR, Anton Paar, MCR 302, Austria) according to the standard EN 13702 (2018). The dynamic viscosity has been established using the cone and plate (CP) configuration with diameter equal to 50 mm applying a constant rotational load at a shear rate equal to 0.05 s^{-1}. A drop of each material has been poured on bottom plate of the DSR after stirring the Vx. The liquid-viscous state of REOBs did not request any pre-heating for preparing the testing samples. The test was performed at three temperatures, namely 60, 100 and 150 °C using a new sample for each measure. The average values of two replicates of V1 and V2 are reported in Fig. 2.4. In addition, the Fig. 2.4 represents the dynamic viscosity of a standard 50/70 penetration grade bitumen (Pen 50/70) and reference mixing value requests to any bituminous binder for handling and covering aggregates. The same Pen 50/70 from one unique batch was used throughout the present study including next studies at the binder and asphalt mixture levels. The dynamic viscosity of Pen 50/70 was evaluated using the same test configuration and conditions, but the sample preparation needed a preliminary warming period to pour the material. The obtained data confirmed the visual inspection. In detail, the viscosity of V1 halved (-54%) increasing the test temperature from 60 °C to 100 °C, while the temperature raising to 150 °C led to a reduction of dynamic viscosity of about 84% from the initial value at the lowest test temperature. A different trend can be observed for V2 specimens. This REOB exhibited an initial reduction of the dynamic viscosity passing from 60 °C to 100 °C, then close, but higher, value has been recorded increasing the test temperature from 100 °C to 150 °C. From the lowest test temperature, the dynamic viscosity of V2 reduced of about 32% at 100 °C and 26% at 150 °C. The two available REOBs had a lower temperature susceptibility compared to Pen 50/70 since the values of the dynamic viscosity experienced a higher variability at the considered range of temperature. All materials had dynamic viscosity higher than the reference value for mixing. This imply that the production temperature has to exceed the 150 °C in order to allow the correct handling of materials.

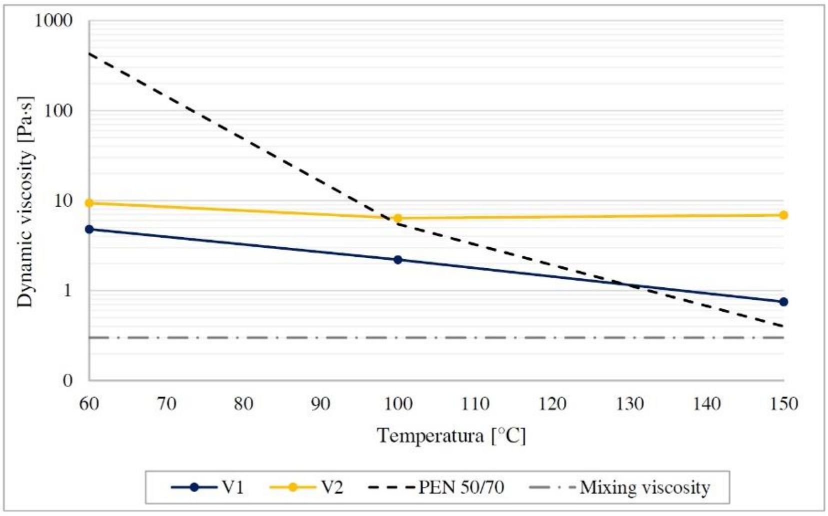


Fig. 2.4. Dynamic viscosity of V1, V2 and Pen 50/70 compared to the reference value of bitumen for mixing.

Being by-products, the molecular formula and the accurate molecular weight of both materials are not available. As a matter of fact, REOBs are classified as UVCB substances that stand for unknown or variable composition, complex reaction products or of biological materials (ECHA - European Chemicals Agency 2021). The REOBs mainly consist of hydrocarbons with low amount of metals, such as nickel, iron and vanadium as reported in the safety data sheets of V1 and V2 (refer to Annexes section for further information; the safety data sheet of V1 is reported only because the REOBs are similar, thus the safety data concerning warnings and precautions are similar). Thus, the chemical composition of REOBs is similar to that of a standard bitumen. The materials can be separated in the so-called SARA fractions and both safety data sheets of used REOBs declare that the materials approximately contain 35.7% of saturates, 61.6% of aromatics and 2.6% of the main polar fractions that is resins (refer to Annexes section for further information). Since REOB is highly dependent of the waste oils that undergo refining and the production batches may differ from each other, the exact content of asphaltenes has been determined by the Department of Chemistry and Chemical Technologies (CTC) of the University of Calabria. Each Vx was carefully dissolved in $CHCl_3$ using the same mass proportion of the materials. Then, a volume of n-pentane forty times the $CHCl_3$ volume was added to the solution, which was left in dark for two hours, mixing occasionally. Lastly, the precipitated asphaltenes were filtered in a funnel with paper filter by vacuum. The residue was washed several times with n-pentane until solvent became colourless. The filter paper was dried in oven at 80 °C for three hours and successively the residue of the solvent was removed in vacuum for two hours. The filtrate that contained maltene portion was evaporated to dryness with a rotary evaporator under reduced pressure and the residual solvent removed under vacuum pump. The results showed that V1 has a higher asphaltenes content than V2, which are equal to 6.33% and 4.41%, respectively. The asphaltene fractions of REOBs are low, but the quantities are included in the interval usually found in a standard bitumen that ranges between 5% and 20% (Lesueur 2009). The asphaltene fractions corresponded to the lower limit of the range. Conversely than a standard bitumen that mostly contains aromatics and resins (Lesueur 2009), the available and used REOBs mainly consist of saturates and aromatics. Regarding the asphaltenes content, it is well known that this fraction has a viscosity-building role (Lesueur 2009). The two REOBs have similar asphaltenes content and dynamic viscosity, which do not much vary to each other. The difference among the accurate values of asphaltenes contents' was not enough to exhibit the viscosity-building role of asphaltenes considering the exact data of dynamic viscosity of materials.

In order to further investigate and to evaluate the chemical composition of the used REOBs the Fourier transform infrared (FTIR) spectroscopic and nuclear magnetic resonance (NMR) analysis have been carried out. The spectroscopic analysis by the use of FTIR has been conducted in the same boundary conditions previously explained in section 2.2.1 for R particles. A small amount (a drop) of each REOB has been collected after stirring the material, and it was placed under the FTIR anvil for further test. The stirring phase has been carried out to minimize the possible sedimentation of heavy molecules during the storage of material. The spectra of three samples per each available REOB are shown in Fig. 2.5. No normalization process of each spectrum has been applied during the post-processing of the reported data.

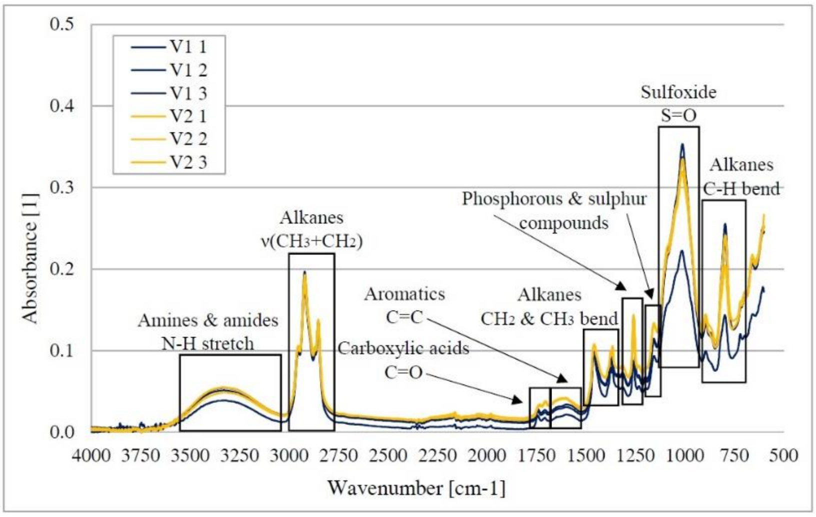


Fig. 2.5. FTIR spectra of V1 and V2 samples with highlights of the main functional groups.

Previous studies have demonstrated that the spectrum of a REOB is very similar to that of a neat bitumen with the strongest peaks at the stretching aliphatic band (alkenes) (Fernandes et al. 2018) (Li et al. 2019). Both V1 and V2 presented distinct and evident peaks at wavenumbers in the range of 3000-2800 cm^{-1}, but these peaks did not exhibit the highest absorbance. Conversely than the results found in literature, the highest absorbance of FTIR spectra of V1 and V2 were found at wavenumbers in the range of 910-1140 cm^{-1}, which are related to the presence of sulfoxide (S=O) functional group (Hofko et al. 2017) (Li et al. 2019). Further peaks can be observed at very low wavenumbers, between 900 and 700 cm^{-1} that can be ascribed to the C-H vibration peak on benzene rings (Borrego et al. 1996) (Li et al. 2019). Phosphorous compounds are detected at wavenumbers around 1250 cm^{-1} as previously found by the study of Li et al. (2019). Moreover, the V1 and V2 presented sulphur compounds around the wavenumber 1150 cm^{-1} albeit the quantity is lower than that observed for phosphorous molecules (Li et al. 2019). Other alkenes functional groups are detected at wavenumber around 1460 cm^{-1} and 1370 cm^{-1}, which derive from the asymmetric (CH_2) and symmetric (CH_3) bending vibration of methyl (Borrego et al. 1996) (Hofko et al. 2017). Small absorbance peaks have been collected in the wavenumbers around 1600 cm^{-1} and 1700 cm^{-1} related to the bond established between a carbon atom and another atom of carbon or oxygen, respectively. In detail, at about 1600 cm^{-1}, aromatics group due to the C=C stretch vibration were present; while carboxylic acids or carbonyl functional groups (C=O) were detected at about 1700 cm^{-1} (Delft University of Technology 2020). Lastly, a peak in the range of 3000 and 3500 cm^{-1} is present, which can be ascribed to the N-H stretch vibration of amines and amides (Nivitha et al. 2016). The presence of OH molecular vibration were excluded *a priori* due to the refinery process that REOBs have been subjected and the consequent removal of water and/or humidity.

The FTIR spectra of V1 and V2 are similar, even though V1 exhibited higher variability. Comparing the spectra of the two available REOBs, the V1 shows greater values of absorbance at the wavenumbers related to sulfoxide and alkanes structures. The device detected higher absorbance values of carbonyl, aromatics and some alkenes groups of V1. In general, carbonyl and sulfoxides groups are of most interest when dealing with hydrocarbons ageing, thus on the evaluation of bituminous binders ageing (DeDene and You 2014) (Hofko et al. 2017). Since REOB comes from waste oils, hence aged oils, previous studies have payed attention to the ageing susceptibility of REOB-modified bitumens (Rubab et al. 2011) (Li et al. 2019) (Karki and Zhou 2019). FTIR analysis on REOB for oil modification of neat bitumen highlighted the presence of a strong peak at wavenumbers around 1710 cm^{-1} and 1744 cm^{-1} (Li et al. 2019). The obtained results of V1 and V2 revealed a small amount of carbonyl groups, but a considerable quantity of sulfoxide groups, which may lead pavements to be more prone to ageing. Taking into account the aim of the research and the FTIR data, a further investigation on the ageing susceptibility of the bituminous materials will be necessary.

In addition, both available REOBs underwent nuclear magnetic resonance (NMR) analysis thanks to the collaboration with the CTC Department of the University of Calabria. The spectroscopic analysis was carried out by a high resolution NMR (Bruker Avance spectrometer, Germany), which operates at proton frequency equal to 300 MHz. The device evaluates the nuclei behaviour of materials that are subjected to an external magnetic field allowing the characterization of complex materials by the use of protons groups (^{1}H-NMR). The tests have been performed at ambient temperatures on samples pre-treated with CCl_4. This solvent prevents any overlapping of protonic signal. The ^{1}H-NMR spectra of V1 (blue curve) and V2 (red) are reported in Fig. 2.6. The ^{1}H-NMR spectra of both REOBs are mainly characterize by aliphatic protons, which are detected at around 1 ppm. The presence of three distinct peaks means that different aliphatic protons (alkyl) have been detected. In detail, the methyl protons in γ-position or farther from the aromatic ring are found between 0.5 ppm and 1 ppm, and the methylene protons in β-position or farther from the aromatic ring correspond to the range of 1-2 ppm (Oliviero Rossi et al. 2018). At higher frequency, from 2 to 6 ppm, small peaks of double bond molecules were visible that correspond to alpha-alkyl protons (2-4 ppm) and olefin protons (4-6 ppm) (Oliviero Rossi et al. 2018). Only the sample V2 exhibited a peak around 7 ppm, which is ascribed to aromatic protons (Oliviero Rossi et al. 2018). Thus, the spectroscopic analysis by the use of NMR confirmed the results of FTIR data and the fractional composition of bitumen reported in the safety data sheet.

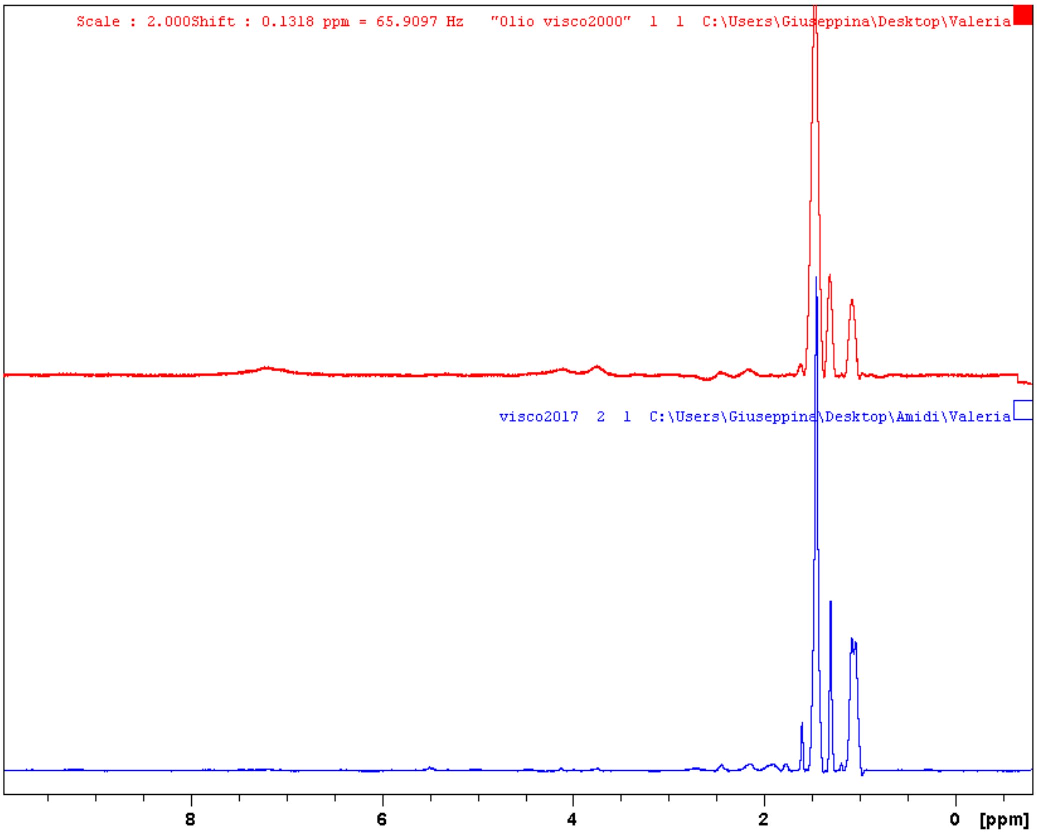


Fig. 2.6. ^{1}H-NMR spectra of V1 (blue curve) and V2 (red curve) samples.

2.3 Optimization of the constituents mass proportion of extenders

The first analysis focused on the definition of proper mass proportions of R and REOBs that will be used for the production and characterization of bitumen extenders in the further studies. With the aim to maximize the use of both recycled materials, the chemical and physical interactions that occur between R particles and V1 and, alternatively, R and V2 have been investigated.

There are no previous studies on the characterization of rubber-REOB blends in literature. Thus, a characterization protocol has been developed to define the optimum mass proportions of R and REOBs or, in other words, the optimum R-REOB ratios. The protocol was inspired by the interactions that occur between neat bitumen and rubber particles. Considerable studies are available about this topic, even though the reactions that occur between bitumen and rubber are not fully understood yet. The interactions between rubber and bitumen during wet process to produce rubberized binders are reported as a diffusion phenomenon of components of bitumen into the rubber (Airey et al. 2003). Thus, physical interactions are reported predominantly, although the possibility of chemical interactions is not ignored (Nivitha et al. 2016). It is recognized that rubber-bitumen interactions are made up of two simultaneous processes: absorption of aromatic oils available in the bitumen within the polymeric chains (i.e. rubber swelling) and partial digestion of rubber into bitumen (Lo Presti 2013). In general, rubber reacts in a time-temperature dependent manner and the physical absorption is mainly controlled by the shape and size of rubber particles that causes the rubber to swell and soften (Lo Presti 2013) (Zanetti et al. 2015). During rubber-bitumen interactions there is a contemporaneous reduction in the oily fraction of bitumen and an increase of rubber particles sizes with a consequent reduction of the inter-particle distance (Lo Presti 2013). This behaviour leads to change the R-bitumen compound to a gel like material (Way et al. 2011). In this form, the particles of rubber are still visible (granular-like appearance) in the composite binder, even if the distance between the particles themselves decreases (Zanetti et al. 2015). If curing is carried out at an excessive temperature and/or for a too long period, the degradation phenomenon becomes prevalent and the rubber particles are totally digested in the bitumen (Zanetti et al. 2015). Since REOBs used are petroleum-based products that mainly consist of light hydrocarbons such as aliphatic and aromatics molecules, it was assumed that R particles might absorb the light fractions of REOB as they absorb the light fractions of bitumen. This assumption has been used to define the optimum R-REOB ratios to produce the extenders, which correspond to the saturation of R. When R is saturated, these particles are not able to absorb REOB anymore and it can be considered that the maximum amount of both materials, REOB and R, have been used.

In order to evaluate the interactions between R and REOBs an experimental protocol has been proposed. The method combines spectroscopic techniques and microscopic analysis to define meaningful R-REOB ratios that can be considered as optimum mass proportions for both oils, V1 and V2. In detail, the nuclear magnetic resonance (NMR) spectrometer and scanning electron microscope (SEM) devices have been involved in the determination of extenders properties. In order to establish the particles mobility and the microstructures of extenders, the suggested protocol aims to determine the self-diffusion coefficient of each REOB into and onto R particles, since this parameter provides information on the molecular dynamics and the spatial dimensions of particles and cavities (Caputo et al. 2019). And, the self-diffusion coefficient is reasonably considered dependent on the mass proportion of the recycled materials. In addition, the spin-spin relaxation time (T_2) of the R-REOB blend can provide useful information about the intra-molecular interactions of materials. Lastly, the evaluation of the morphological structure of R-REOB blends has been employed to significantly contribute and support the definition of the optimum mass proportion of the recycled materials. Many R-REOB compounds made with different mass proportions of recycled materials were analysed including samples with higher amount of R than REOB or, alternatively, greater quantity of REOB than R. The details of the experimental program are described in the next section.

This study has been performed at the University of Calabria thanks to the collaboration with the Chemistry and Chemical Technologies (CTC) Department.

2.3.3 Experimental program

2.3.3.1 Preparation of extenders with different R-REOB ratios

Different compounds of the two recycled materials have been analysed to define the optimum R-REOB ratios for production of extenders. Five mixes per each REOB were prepared varying the mass of both constituent materials:

- R:Vx = 3:1;
- R:Vx = 2:1;
- R:Vx = 1:1;
- R:Vx = 1:2;
- R:Vx = 1:3.

The extenders have been prepared by thoroughly mixing the pre-heated R and REOB. The first step consisted in warming up both materials at 130 °C in oven; REOBs for at least 1 h 30’, while R for 15’. Then, a specific amount of each REOB was added to the corresponding R portion and the recycled materials were mixed by the use of a propeller mixer at a rate of about 600÷650 rpm for 15’. The mixing phase has been performed at a temperature equal to 130 °C. In order to keep the blend at a constant temperature during the mixing process, all containers were immersed in a glycerine bath, which was continuously warmed up by a heating plate. The ten R-REOB blends that have been manufactured together with the mass of R and each REOB are illustrated in Fig. 2.7.

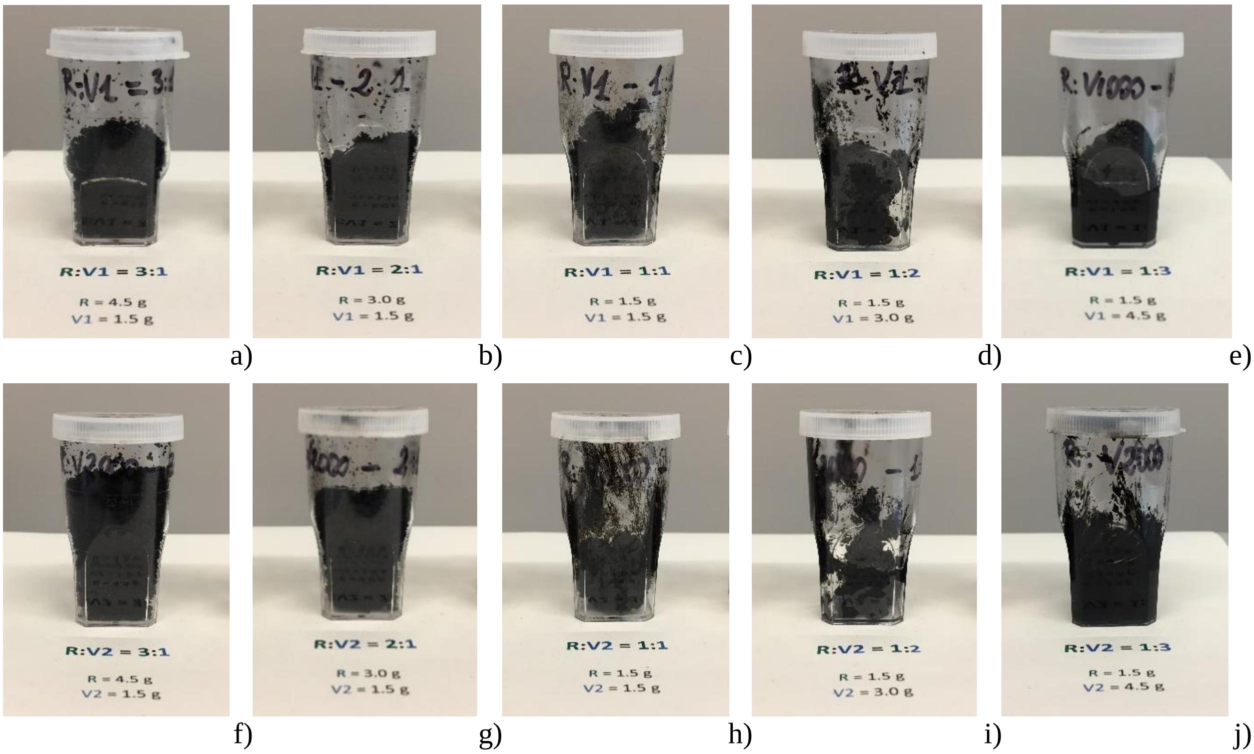


Fig. 2.7. Samples of R-REOB blends with different mass proportion: a) R:V1=3:1, b) R:V1=2:1, c) R:V1=1:1, d) R:V1=1:2, e) R:V1=1:3, f) R:V2=3:1, g) R:V2=2:1, h) R:V2=1:1, i) R:V2=1:2, j) R:V2=1:3.

2.3.3.2 Test methods

The resulting blends underwent NMR and SEM analysis. The spectroscopic analysis was performed by two NMR instruments that operate at two different proton frequencies: a high-resolution NMR (Bruker Avance spectrometer, Germany) at 300 MHz, and a low-resolution NMR (homemade) at 15 MHz. The high-resolution NMR was used to determine the self-diffusion coefficient (D) of all samples as a measure of molecular mobility. This parameter has been evaluated at the same production temperature of extenders that is 130 °C. The NMR spectra were obtained from Free Induction Decay by means of the Fourier transform. The path width equal to $\pi/2$ and 16 scans have been used to perform all these NMR tests. The self-diffusion coefficient (D) has been determined directly using a Diff30 NMR probe. The sequence that has been used is a standard pulsed gradient stimulated echo (PGStE) with a mono-exponential fitting (Calandra et al. 2013). The low-resolution NMR is a homemade instrument, which was used to carry out relaxation experiments at ambient temperature. The obtained signals were acquired by means of a Carr-Purchell-Meilboom-Gill (MCPG) spin-echo pulse sequence, which consisted of 400 echoes. Thanks to 'Mathematica' software, the collected data were post-processed and the spin-spin relaxation time (T_2) of all extenders have been determined by fitting with an exponential equation. This relaxation time concerns with the exchange of energy among spins without being affected by the surrounding environment (Oliviero Rossi et al. 2015). The same sample of the ten R-REOB blends were tested by means of both NMR apparatus. The five samples of each Vx do not need specific treatment or conditioning before performing the tests. A small portion of every R-REOB blend was introduced into a small and thin tube for testing, which is used for performing the test n both NMR instruments. A sample of each R-REOB compound was introduced into the tube by the use of a long tool with a tip at one extremity. Due to the granular aspect of samples, it was difficult to push a sufficient quantity of the material at the bottom of the tube. To overcome the difficulties, the material inserted in the tube was pushed to its bottom using a layer of PTFE (Teflon) that represented a wider surface able to be pushed by the steel tool. The Teflon has been chosen because it did not contaminate the results.

The SEM (JEOL JXA-8230, Japan) device allowed the investigation of R-REOB blends morphological structure. The tests run in a vacuum mode on pre-conditioned samples, which were sputter coated with a thin film of graphite. Various magnifications were considered to collect the images of all specimens.

2.3.4 Results of NMR spectroscopic analysis

The NMR devices exploit the presence of some atomic nuclei with a magnetic dipole that can precess or 'resonate' in an applied static magnetic field (Jones and Taylor 2015). The spectroscopic analysis evaluates the nuclei behaviour that underwent to an inhomogeneous external field, which perturbs the equilibrium in a steady uniform magnetic field. In fact, at equilibrium, nuclei are distributed among the energy levels according to the Boltzmann distribution with a specific net magnetization vector, but this state can be disrupted by the absorption of radio-frequency energy, as caused by a NMR instrument (Oliviero Rossi et al. 2015) (Leggio et al. 2016). After the removal of the disruption field, the nuclear spin system returns to its equilibrium state and the transverse component of the magnetisation vector exponentially decays. The time constant T_2 characterizes the signal decay, which is called spin-spin relaxation time because it is related to the exchange of energy between spins via flip-flop mechanisms (Filippelli et al. 2015). Usually, the collected signal decay is an envelope of multi-exponential attenuation since the relaxation time varies in the sample due to the heterogeneity or surface relaxation differences (Carr and Purcell 1954). Hence, the NMR instruments allow the implementation of relaxation experiments determining the relaxation time of materials, but it is also able to perform diffusometry analysis. Flow and diffusion properties of a material are commonly determined by applying the pulsed field gradient (PFG) method (Jones and Taylor 2015). By the use of this method, a sequence of pulses is applied to the material resulting in a movement of the magnetization vector, which induce a position dependent phase shift of the spin (Jones and Taylor 2015).

The diffusometry analysis by the use of the high-resolution NMR allow the evaluation of the self-diffusion coefficient (D) of REOB into extenders. As previously described, the present measurements provide information on molecular mobility and the microstructures of samples (Caputo et al. 2019). Hence, the D values represent an indicator of the mobility of REOB molecules. The self-diffusion coefficient can be ascribed to the average diffusion phenomena of each REOB onto (external) and into (internal) R particles and the results are shown in Fig. 2.8. In theory, the self-diffusion coefficients should decrease with the addition of R because it reduces the mobility of REOB particles and the extenders confirmed the expected results. In detail, considering the samples with equal quantity of recycled products (ratio 1:1) and higher amount of R than REOB (ratios 2:1 and 3:1), the values of D decreased for both Vx. This means that R particles can absorb the light fractions of REOBs reducing the average values of the self-diffusion coefficient. For what concern the measurements of D for V2-extenders, an error can be observed for sample R:V2=2:1 that exhibited a lower self-diffusion than R:V2=3:1. The error can be ascribed to the lower diffusion values of these materials, which were close to the sensitivity of the instrument. The self-diffusion coefficient of R-REOB blends jumps at the ratio equal to 1:1. In those samples that contain the same quantity of both recycled materials, the coefficient D reached the highest values, which remained almost constant increasing the amount of Vx into the extenders. In fact, the self-diffusion coefficients did not enhanced diminishing the quantity of R particles at lower values than 50% by the total weight. An additional phenomenon has to be taken into account to interpret this trend of data as the presence of granulate particles physically hindered (obstructed) the motion of REOB molecules regardless of the amount of R that has been introduced into the blend. It can be concluded that the R-REOB ratio equal to 1:1 permits to achieve the maximum mobility of REOB molecules while granulate particles are introduced in the matrix; this high mobility can be related to the maximum absorption of REOB by R. This ratio may balance the reduction of the mobility of REOB molecules due to their absorption by R particles and, with a lesser extent, to the physical obstruction without drastically reduce the diffusion of REOB into and onto the R.

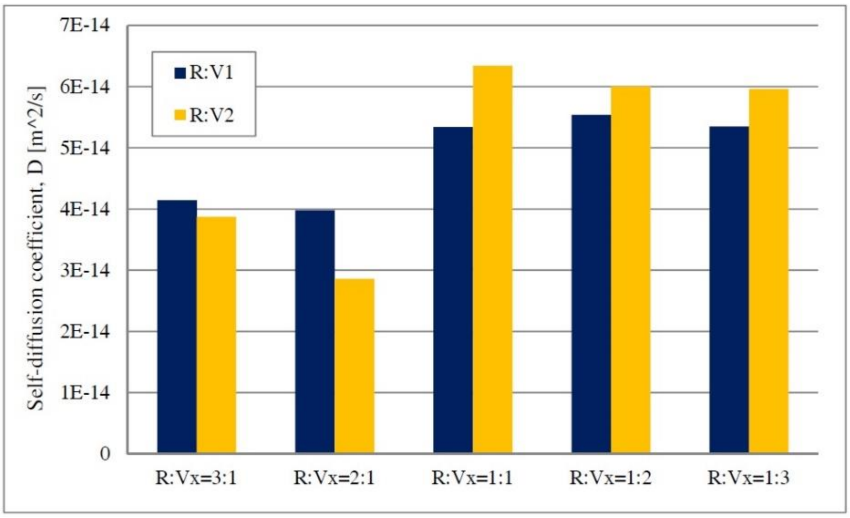


Fig. 2.8. Self-diffusion coefficients (D) of extenders.

The relaxation time T_2 of pure REOBs and extenders was evaluated by the use of low-resolution NMR device. Thanks to the instrument, it was possible to define the trend of the spin-spin relaxation times directly, and then the curves were normalized considering the highest value of time in order to better compare the results. Successively, the relaxation time T_2 have been determined by the use of

‘Mathematica’ software as previously mentioned. The trend of spin-spin relaxation time and the resulting T_2 values of both REOBs and extenders are reported in Table 2.2 and Fig. 2.9, respectively.

Table 2.2. Spin-spin relaxation time, T_2, of V1, V2 and extenders.

Samples	**Relaxation time, T_2 [s]**	
	V1	**V2**
Vx	$5.39 \cdot 10^{-3}$	$6.49 \cdot 10^{-3}$
R:Vx = 3:1	$2.71 \cdot 10^{-3}$	$3.59 \cdot 10^{-3}$
R:Vx = 2:1	$3.00 \cdot 10^{-3}$	$3.69 \cdot 10^{-3}$
R:Vx = 1:1	$4.22 \cdot 10^{-3}$	$4.90 \cdot 10^{-3}$
R:Vx = 1:2	$4.21 \cdot 10^{-3}$	$6.33 \cdot 10^{-3}$
R:Vx = 1:3	$4.07 \cdot 10^{-3}$	$6.38 \cdot 10^{-3}$

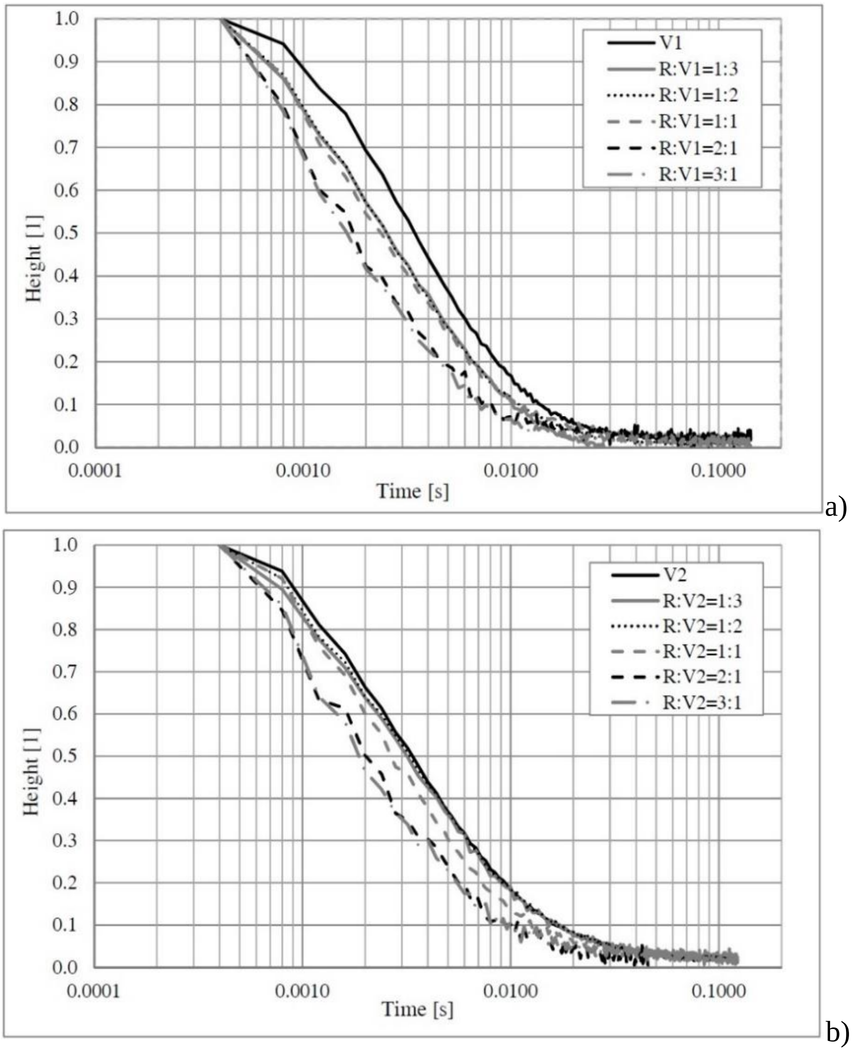


Fig. 2.9. Comparisons of the trend of spin-spin relaxation time, T_2, of REOBs and extenders based on type of REOB: a) V1 and V1-R blends; b) V2 and V2-R blends.

In general, a short T_2 time corresponds to more rigid supra-molecular particles; while, higher T_2 times refer to low intra-molecular interactions (Filippelli et al. 2013). The pure REOB showed the highest relaxation times over the corresponding Vx-extenders made with themselves, which means lower intra-molecular interactions. The introduction of R particles into V1 or V2 led to decrease the T_2 values. The REOB absorption by R limited the mobility of the oil’s molecules, therefore the T_2

relaxation times decreased in R-REOB compounds. This phenomenon reflects a more rapid relaxation decay. This trend is more evident in the extenders made with V1. The relaxation time of V1-extenders has been reduced from $5.39 \cdot 10^{-3}$ s of pure V1 to about $4 \cdot 10^{-3}$ s for those extenders with R content up to 50% by the total weight. Then, more changes in T_2 values can be observed in samples with higher quantity of V1 than R. In fact, their curves almost overlap each other. Concerning the V2-blends, the specimens R:V2 = 1:3 and R:V2 = 1:2 and pure V2 have similar T_2, which is confirmed by curves overlapping as shown in Fig. 2.9. The amount of R in these two extenders seems to do not affect their relaxation time than the reference one (V2). From the quantity of R equal to 50% and higher, it can be observed a reduction of T_2. Based on collected data, the R-REOB ratios 1:1 and 1:2 represent the latest ratios after which some changes occurred in the relaxation time values confirming the results of the diffusion measurements. Therefore, these two R-REOB ratios were defined as the optimal.

Both diffusion and relaxation measurements may be related to the affinity between R and REOB. A marked difference in the values of the self-diffusion coefficient and relaxation time may be ascribed to a higher compatibility between the recycled materials, because a higher absorption of REOB into R may lead to more pronounced changes in the values of parameters. However, the results of the self-diffusion coefficient and the relaxation time showed opposite trends. On one hand, the V2-extenders exhibited a greater reduction of the D values passing from ratio 1:1 to 3:1 than the corresponding V1-blends. On the other hand, the differences among the T_2 values were more evident in V1-extenders. The absorption phenomenon and, consequently, the D and T_2 values, depend on the molecular weight of the molecules present in REOBs and the available Vx very likely have different molecules with diverse molecular weights. In addition, it is not negligible that different batches of REOBs can be fluxed with diverse percentage of low molecular weight additive to facilitate the material handling. These lighter fractions can have a more marked affinity to R than to V2 itself. Considering all variables and the fact that the results of the diffusometry analysis were close to the instrument sensitivity, it might be deduced that the relaxation time results are more reliable, and, therefore, V1 could have higher affinity to R. However, the results are not unambiguous to identify consistent affinity between R and REOB products. Hence, further analysis are needed to determine the affinity between the materials, which may include the evaluation of the molecular weight of the constituent materials of extenders.

2.3.5 Results of microscopic analysis

The R particles and all extenders were tested using SEM to evaluate their morphological structures. The images of samples with a magnification of about 150x are shown in Fig. 2.10. The increasing amount of Vx in the specimens is clearly visible moving from the Fig. 3(a) that is rubber particles without any REOB, to Fig. 2.10(j) for extenders with V1 and Fig. 2.10(k) for those with V2, which contain a triple quantity of REOB than R. The morphological aspect of R-REOB extenders changes throughout the sequence of images due to the mass proportion of constituent materials. When the R-Vx blends have ratios equal to 3:1 and 2:1, the particles of R and their shape were distinguishable. Instead, the extenders with the highest amount of Vx (ratio 1:3) were consisted of a viscus matrix only, and the presence of R particles was almost not recognisable by the SEM images. It seems that R may firstly absorb the added REOB, when its quantity is limited; then, increasing the amount of REOB the R were covered. The coating of R particles may start when they are saturated. Since the optimum R-REOB ratio is the maximum amount of REOB that can be absorbed by R, the ratios 1:1 and 1:2 can be identified as the optimal two. The visual investigation of morphological structures of samples confirmed the results that have been obtained from NMR measurements.

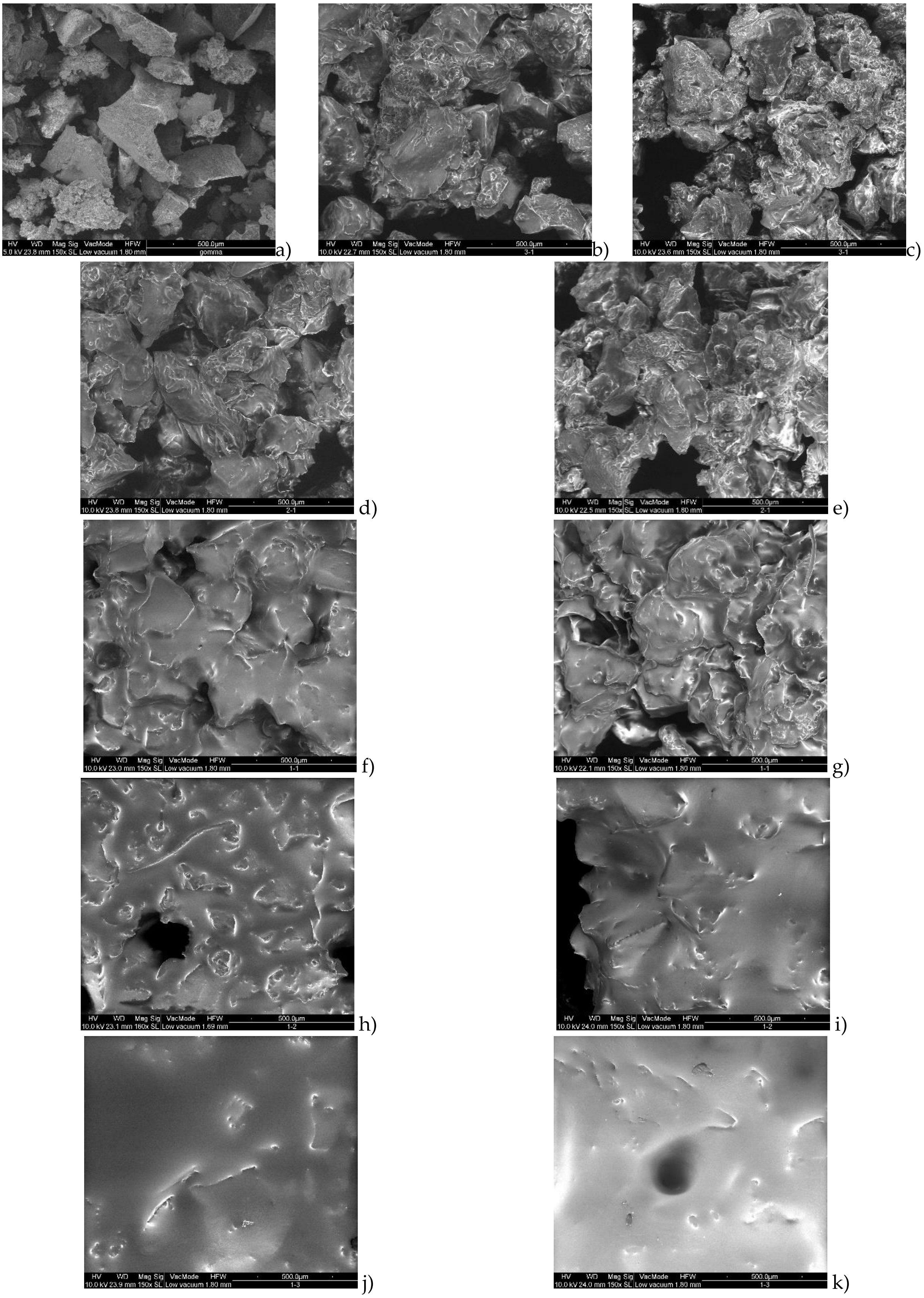


Fig. 2.10. Images of R and extenders acquired by SEM: a) R; b) R:V1=3:1; c) R:V2=3:1; d) R:V1=2:1; e) R:V2=2:1; f) R:V1=1:1; g) R:V2=1:1; h) R:V1=1:2; i) R:V2=1:2; j) R:V1=1:3; k) R:V2=1:3.

2.4 Effect of production temperature on the properties of the extenders

The second experimental phase of the extenders characterization aimed to evaluate the effects of production temperature on the final properties of the R-REOB blends. In particular, a set of samples that takes into account the two available REOBs, V1 and V2, and the two defined optimum R-REOB ratios, 1:1 and 1:2, were produced at three different production temperatures and underwent rheological and chemical investigations. As a result, the effect of production temperature on extenders made with different R content and type of REOB has been investigated; hence, three variables were considered.

The effects of rubber and/or oil modifications are strictly dependent on the constituent materials such as chemical composition, dimension and shape of particles as detailed in previous chapter. In addition, the processing conditions, such as temperature, time and device, strongly affect the final properties of the blend. This is well known for R-modified bitumen (Lo Presti and Airey 2013), but can be reasonably considered for R-REOB blends also due to the behaviour of R particles. Acting as a sponge with both materials, bitumen and REOB, the diffusion of REOB into R is affected by the production conditions. During the reactions between rubber and a petroleum-based material, rubber absorbs the light oily fraction, while increasing in particles dimension (volume increase). This absorption phase is a time-temperature dependent process (Lo Presti 2013) (Zanetti et al. 2015). Moreover, the mixing device influences the resulting blend and its physico-chemical response. Among possible mixers, the high-shear mixer provides the energy to break particle-particle bonds and this helps in reducing the agglomerations of rubber particles. All processing conditions affect the final properties of the materials, but the mixing device (in terms of applied shear stress and pressure) is secondary to the processing temperature (Lo Presti and Airey 2013). In fact, when the R-bitumen blend is subjected to prolonged high temperature the absorption phenomenon is replaced by de-polymerisation/de-vulcanization process regardless the type of device and the applied shear rate (Lo Presti and Airey 2013). Bearing in mind these considerations, processing temperature and mixing equipment (i.e. standard and high shear mixers) have been considered for further investigation at the early stage of planning experimental program. However, the first attempt revealed the difficulty to mix the R-REOB blends with the high-shear mixer, which could not guarantee a constant rotational speed and the incorporation of all constituents. As a matter of fact, only a reduced amount of material under the rotating mixer head were mixed, while the most part of the R particles and REOB remained attached to the containers walls. This was probably caused by the high quantity of R particles into the blends as they consist of 50% or 33.3% of rubber by the total weight of the blend, compared to the quantities usually incorporated in R-modified bitumen (Lo Presti and Airey 2013). Hence, a standard propeller mixer was used for blending the two recycled materials at 800 rpm. Moreover, the processing time has been considered constant and equal to 1 h. The mixing rate and time were chosen following the guidelines of rubberized bitumen adopting the same process of R-bitumen interaction for R-REOB extenders (Signus Ecovalor; Ecopneus Scpa 2014). The used production process aimed to simulate the wet process designed by McDonald, where rubber and bitumen are mixed at a low-shear rate for 45-60’ typically. Hence, the processing time equal to 60’ was considered adequate since the compound would be mixed at a relative low rotations per minute (i.e. 800 rpm).

Among processing conditions, the production temperature of R-REOB blends was considered for further studies only. Three processing temperatures were considered: 130, 160 and 180 °C. The highest temperature corresponds to the production temperature of REOBs once collected from refinery plants. The lowest temperature corresponds to that temperature used for the evaluation of R-REOB optimum ratio. In addition, an intermediate temperature has been analysed, i.e. 160 °C.

2.4.1 Experimental program

2.4.1.1 Preparation of extenders at different production temperatures

A set of extenders have been produced at three processing temperatures. Considering the two available REOBs and the two optimum R-REOB ratios that were defined in the previous study, six extenders were prepared for each type of REOB. The resulting blends with their acronyms are listed in Table 2.3. All R-REOB blends were prepared by means of a propeller mixer at three production temperatures, namely 130, 160 and 180 °C. These three values were the nominal temperatures used. The pre-heated materials were mixed at a rate of 800 rpm for 1 h (Signus Ecovalor; Ecopneus Scpa 2014). The REOBs were warmed up in a forced-air oven at the established temperature for more than 1 h 30', while R for 15'. Then, the R has been introduced in the REOB forming a homogenous compound. This incorporation phase lasted about 10' for all samples, which was not count as mixing time. During mixing phase, all compounds were continuously heated at the defined production temperature using a heating plate; however, the temperature was not constant as it dropped of about 55-65 °C from the nominal processing temperature when the R particles have been incorporated into V1 or V2. The temperature was measured at the beginning and every 15' of the mixing phase by the use of an immersion thermometer.

Table 2.3. Matrix of considered extenders and nominal production temperatures.

Temperature	**V1**		**V2**	
	R:V1 = 1:1	**R:V1 = 1:2**	**R:V2 = 1:1**	**R:V2 = 1:2**
130 °C	V1_1:1_130	V1_1:2_130	V2_1:1_130	V2_1:2_130
160 °C	V1_1:1_160	V1_1:2_160	V2_1:1_160	V2_1:2_160
180 °C	V1_1:1_180	V1_1:2_180	V2_1:1_180	V2_1:2_180

A 50/70 penetration grade bitumen (Pen 50/70) was chosen as the reference material, which was used throughout the present study including next studies at the binder and asphalt mixture levels. Taking into account the different nature of extenders and bitumen, the reference material was also investigated. This information may help to understand the behaviour of the R-REOB blends, which will been used to made the extended bitumens.

After preparation, the extenders were stored in metal cans, which were sealed. These operations prevented the UV radiation and atmosphere oxygen to reach the samples reducing the further ageing of R-REOB blends.

2.4.1.2 Test methods

The rheological and chemical analysis have been performed on unaged R-REOB compounds in order to evaluate the viscoelastic properties and chemical characteristics of the innovative and possible extenders of neat bitumen. The physico-chemical interactions occurring between the constituents affect the functional groups of the final materials, which correspond to different rheological responses.

The rheological behaviour of all R-REOB blends was evaluated using a dynamic shear rheometer (DSR) - Anton Paar MCR 302. The device was used to analyse the rheological parameters of the materials over a wide range of frequencies and/or temperatures performing the amplitude sweep (AS) test, frequency sweep (FS) test, viscosity test and multiple stress creep and recovery (MSCR) test. Each test has been replicated to guarantee the reliability of obtained data.

The first analysis (AS test) allows the definition of the linear viscoelastic range (LVE range) of materials, i.e. the maximum applicable strain to avoid irreversible structural changes in samples or, in other words, a region in which the dynamic shear modulus is neither stress-dependent nor strain-dependent (EN 14770 2012). To obtain the LVE range, a harmonic sinusoidal oscillation has been applied to the material changing the strain from 0.01% up to 15% with a logarithmic ramp, while the frequency was constant and equal to 1.59 Hz. In order to evaluate the most restrictive LVE limit of each sample, the rheological response at the lowest, intermediate and the highest test temperature was investigated. Thus, the test was performed at 10, 30 and 60 °C, which are linked to the temperature range covered by the frequency sweep test.

The FS tests were carried out in at a strain-controlled mode. The samples underwent a harmonic sinusoidal oscillation increasing the frequency from 0.1 Hz up to 10 Hz with a logarithmic ramp. The tests were performed at six temperatures starting from 10 to 60 °C with an increment of 10 °C. These two tests followed the standard EN 14770 using a plate-plate configuration with 8 mm of diameter (PP08) and considering the gap among the plates equal to 2 mm. A reduced area of the plates and a larger gap between them have been chosen to perform the AS and FS tests. This configuration can increase the thickness of the tested sample with the final goal of reducing the friction between R particles and the measurement system.

The elastic response of R-REOB compounds were measured by performing the MSCR test at 60 °C. The samples underwent shear creep loading and recovery at two stress levels; 20 creep and recovery cycles were run at 0.1 kPa shear creep stress followed by 10 cycles with an applied stress equal to 1.0 kPa. At each loading cycle, the sample is subjected to a constant load for 1 s then allowed to recover at zero load for 9 s. This test has been carried out following the standard ASTM D7405-15 (2015), when possible. Despite the shear stress requirements, the second and, higher, stress was reduced from 3.2 kPa to 1.0 kPa because it was not possible to perform the test on samples with R-REOB ratio equal to 1:2. The REOB that covered the R particles caused the samples to slip away. Consequently, the shear stress The parallel plate configuration with a dimension equal to 25 mm (PP25) and the gap equal to 1 mm were adopted according to the standard in force.

The dynamic viscosity, that is the ratio between the applied shear stress and the shear rate, of extenders were evaluated over a range of temperatures, as suggested by the standard EN 13702 (2018). According to the standard, the test was carried out at three different temperatures, namely 60, 100 and 150 °C. However, it was not possible to perform the test in the cone-plate (CP) configuration due to the dimension of R particles. Indeed, the maximum particle size is larger than the pre-fixed gap of the CP measurement system. In order to obtain representative results reducing the friction between sample and measurement system, the dynamic viscosity of materials was determined with PP08 configuration and 2 mm of gap.

The chemical functional groups of the eight extenders produced at intermediate and high processing temperatures were evaluated by means of the Fourier transform infrared (FTIR) spectrometry. To perform spectroscopic tests, a Perkin Elmer Spectrum 100 FTIR spectrometer (PerkinElmer, Wellesley, Massachusetts) was used in the attenuated total reflectance (ATR) mode. The FTIR spectrum of all extenders was obtained in the same conditions described in section 2.2. The spectral range between 4000 and 600 cm^{-1} has been considered with a scanning resolution of 4 cm^{-1} averaging twenty scans for each measurement. Four replicates have been considered and compared. As previously explained a small, but representative, amount of each R-REOB blend was taken from each sample using a spatula and was placed under the FTIR anvil for being tested after the .

The chemical investigations were performed at Pavement Engineering section of the Faculty of Civil Engineering and Geoscience at the Delft University of Technology.

2.4.2 Rheological investigation on extenders

The AS test represents the first binder characterisation that identifies the LVE range of a material. Unlike for standard bitumen, the LVE domain for the R-REOB blends decreases when the test temperature increases as can be observed in Table 2.4, where the average LVE limits of extenders and neat bitumen (Pen 50/70) are listed. Hence, the LVE range of the R-REOB mixes that have been considered for further studies are those obtained at 60 °C as the corresponding value to the 95% of the initial storage modulus (G'). In detail, the average of the first three G' values has been considered for determining the modulus reduction of 5%. The strain values obtained from the G' modulus were considered as LVE limits since they represent the minimum LVE range when compared to that obtained from the complex shear modulus or the loss modulus.

Table 2.4. Linear viscoelastic (γ_{LVE}) range of extenders and Pen 50/70 at 10, 30 and 60°C.

Type of REOB	Sample	γLVE @ 10°C	γLVE @ 30°C	γLVE @ 60°C
V1	V1_1:1_130	0.344	0.271	0.228
	V1_1:1_160	0.435	0.344	0.271
	V1_1:1_180	0.551	0.435	0.344
	V1_1:2_130	0.271	0.271	0.203
	V1_1:2_160	0.551	0.344	0.308
	V1_1:2_180	/	/	0.228
V2	V2_1:1_130	1.410	0.697	0.390
	V2_1:1_160	1.120	1.120	0.624
	V2_1:1_180	0.624	0.390	0.353
	V2_1:2_130	0.697	0.308	0.136
	V2_1:2_160	1.002	0.624	0.624
	V2_1:2_180	1.410	0.435	0.221
/	Pen 50/70	1605	4.600	9.340

In general, due to the higher amount of R both samples of V1 and V2 had wider LVE domains; it means that they can withstand larger deformations before irreversible structural changes occur. However, some exception were recorded as samples V1_1:2_160 and V2_1:2_180 did not exhibit this trend compared to the corresponding samples made with R-REOB ratio equal to 1:1. Regarding the type of REOB, the specimens produced with V1 show reduced LVE ranges than those made with V2 except for limited measurements at different test temperatures. The increase of processing temperature led to enlarge the LVE limit of about all extenders passing from 130 °C to 160 °C. However, the highest production temperature did not always exhibit the largest LVE range. Hence, the effect of processing temperature is not well defined.

In Fig. 2.11, the storage (G') and loss (G'') moduli curves of extenders produced at the three production temperatures have been reported. These two components of the complex shear modulus (G*) represent the amount of energy that is stored and released elastically and the out of phase component of the imaginary part of G*, respectively (Nur Izzi 2012). As a consequence, G' and G'' are also known as the elastic and viscous component of the complex shear modulus of a material. The results of AS test performed at 60 °C have been plotted only. The effect of processing temperature is not clear as the elastic and viscous components of complex shear modulus are close to each other. While, the influence of R content and type of REOB are significant. The elastic behaviour dominated the viscous one as the storage modulus (G') was higher than loss modulus (G'') in all R-REOB blends. This response can be ascribed to the high amount of R in the extenders. In addition, the higher R content turn into more stiff

R-REOB compounds as the G’ and G’’ values of extenders with 1:1 ratio were greater than those extenders with 1:2 ratio. The type of REOB affected the stiffness of R-REOB blends differently. The V2-blends exhibited higher G’ values when the R-REOB ratio is equal to 1:1. While, a double amount of V2 into the extenders has softened these blends more than the corresponding V1-extenders and they showed the lowest G' values. Furthermore, the G’’ values of V2-samples were higher compared to those specimens produced with V1 exhibiting a marked viscous-like behaviour. This response can be related to the type of REOB. The considerable softening effect of V2 on R-REOB blends with ratio 1:2 may confirm the supposed lower affinity among this material and R particles as hypothesized in previous studies (refer to section 2.3.2 for additional information).

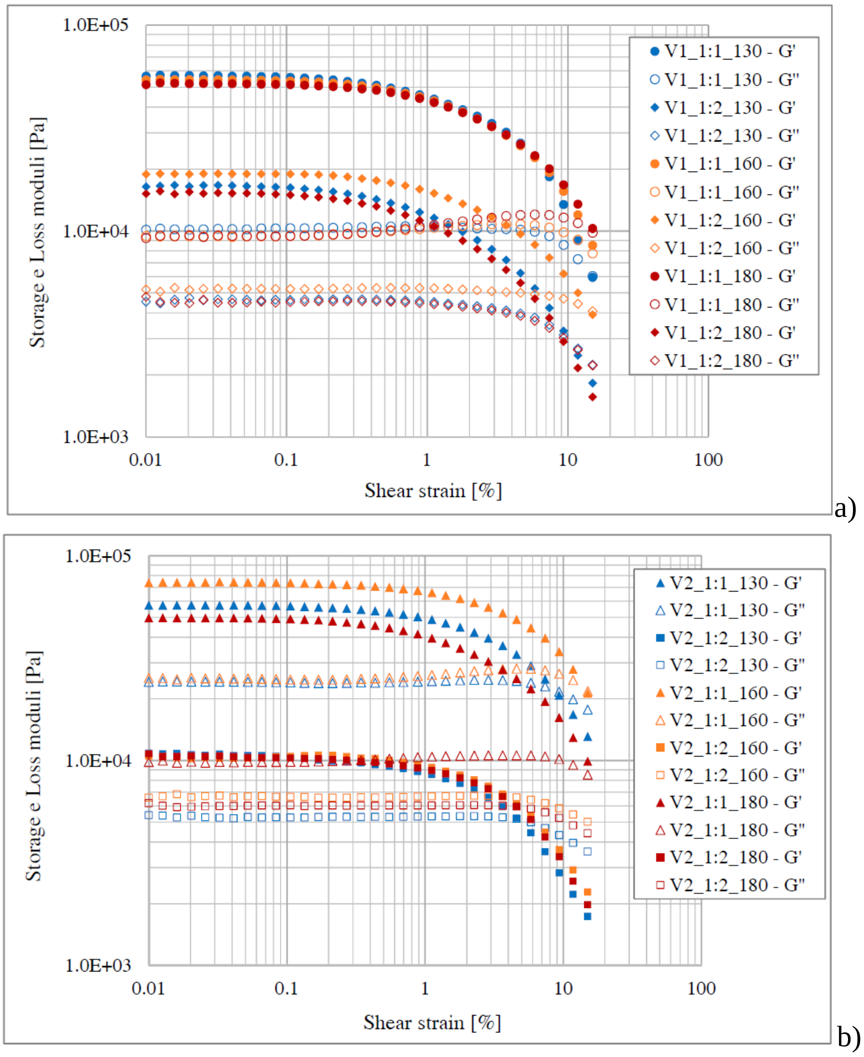


Fig. 2.11. Comparison of G’ and G’’ values of extenders produced at different production temperatures based on type of REOB: a) V1-R blends; b) V2-R blends.

As far as the frequency sweep tests are concerned, the data did not show a thermo-rheological simple behaviour, as indicated by the Black diagrams reported in Fig. 2.12 (Airey 2002). Thus, the time-temperature superposition principle (TTSP) is not valid and the master curve of the rheological properties cannot be determined as done for common bituminous binders. Nevertheless, the Black diagrams were also found to be sensitive to constituents’ proportions, type of REOB and mixing temperature. In general, the six curves that made up the representation of each extender were not aligned and elongated. This trend may be ascribed to the less temperature-susceptibility of both constituents, R and REOB. The role of R particles is crucial on the rheological response of the R-REOB compound. Increasing the amount of R, the extenders behave more elastically as the phase angle (δ) decreases and the G* modulus broadens, which may reflect the polymer network of R. Moreover, the inverse S-curve found in Black space is typical for rubberized binders as has been obtained in previous studies (Celauro et al. 2012) (Lo Presti and Airey 2013) (Wang et al. 2018). The G*-δ curves were influenced by the type of REOB, and the V1-samples showed a more elastic-like behaviour generally. The effect of processing temperature is not clear especially in those extenders made with a double amount of REOB than R.

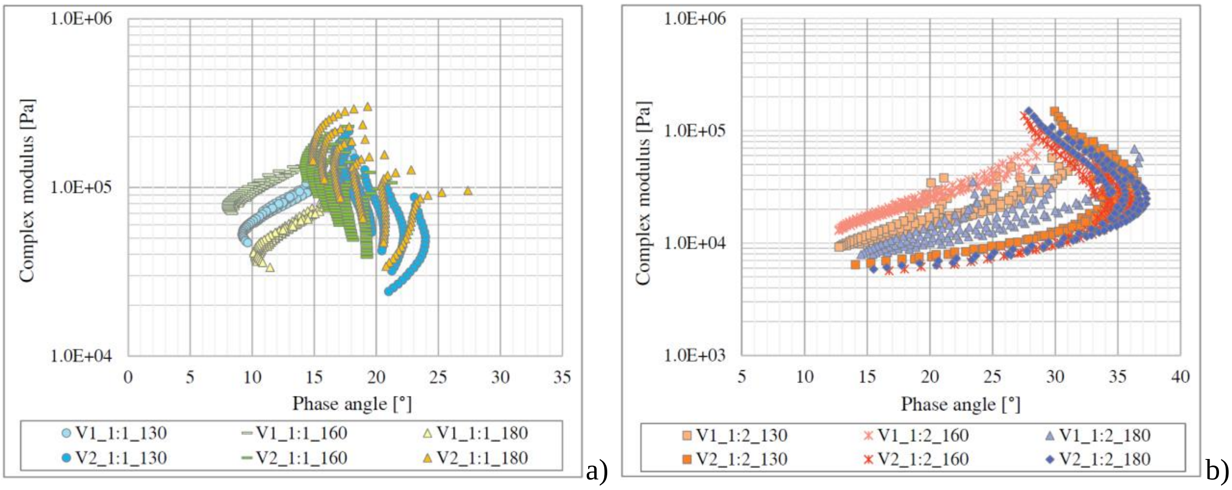


Fig. 2.12. Black diagrams of extenders based on R-REOB ratio: a) R:Vx = 1:1; b) R:Vx = 1:2.

In addition, the MSCR test allowed the investigation of the elastic response of R-REOB mixes. This test permits the evaluation of two parameters, i.e. the percent recovery (%R) and the non-recoverable creep compliance (J_{nr}), which were determined considering the latest 10 creep cycles performed at 0.1 kPa and the 10 cycles at the higher shear creep stress. The MSCR parameters for all blends including the results of the Pen 50/70 are listed in Table 2.5. The extenders and bitumen behave differently as the MSCR results have a diverse order of magnitude. The presence of a polymer, albeit recycled, heavily affects the elastic response of materials. The samples with R-REOB ratio equal to 1:1 show greater percent recovery (%R) and lesser non-recoverable deformation (J_{nr}) than those specimens with 1:2 ratio; moreover, the differences are amplified when applying the high shear creep stress (1.0 kPa). Hence, the elastic response of extenders is stress-dependent. In general, the V1-samples showed a greater %R and minor J_{nr} values than V2-specimens when produced at R-REOB ratio equal to 1:1. While, V2-extenders performed better increasing the amount of REOB into the samples themselves. A greater elastic behaviour turns into better rutting resistance. Hence, the V1-blends can better resist against permanent deformation when R and REOB are added in the same proportion; while, V2-extenders better withstand rutting when produced with higher quantity of REOB than R. This response may be ascribed to a higher elasticity of V2-extenders with R-REOB ratio equal to 1:2 increasing the test temperature as exhibited during the FS test. Despite the higher δ values of V2- blends than V1-extenders, in general, as shown in Fig.2.12, the data collected at 60 °C for V2-samples produced with ratio 1:2 exhibited higher elastic response than the corresponding V2-extenders produced with ratio 1:1. The V1-samples did not show the same behaviour. In fact, the δ values of samples with higher amount of R were lower than those extenders with ratio 1:2. Hence, the type of REOB affect the final behaviour of the extender at high temperature. The effect of higher production temperature on the elastic behaviour of R-REOB mixes is variable and the trend is not clear.

Table 2.5. Percent recovery and J_{nr} of extenders and Pen 50/70 at two stress levels (0.1 kPa and 1.0 kPa).

Type of REOB	**Sample**	**Percent recovery [%]**		**Jnr [kPa^{-1}]**	
		Stress=0.1 kPa	**Stress=1.0 kPa**	**Stress=0.1 kPa**	**Stress=1.0 kPa**
V1	V1_1:1_130	107.37	99.92	0.0000	0.0000
	V1_1:1_160	95.97	93.56	0.0006	0.0013
	V1_1:1_180	101.91	96.05	-0.0003	0.0009
	V1_1:2_130	97.16	7.72	0.0019	1.5865
	V1_1:2_160	99.72	3.82	0.0002	2.9199
	V1_1:2_180	98.61	6.96	0.0010	1.9182
V2	V2_1:1_130	104.37	99.69	0.0000	0.0000
	V2_1:1_160	95.58	92.97	0.0007	0.0014
	V2_1:1_180	98.42	97.18	0.0003	0.0006
	V2_1:2_130	99.31	14.73	0.0008	1.0296
	V2_1:2_160	99.43	20.41	0.0007	0.7017
	V2_1:2_180	99.05	19.48	0.0011	0.6818
/	Pen 50/70	1.67	0.00	2.9200	3.0400

The average dynamic viscosity (η) of all samples is reported in Table 2.6, including the value of Pen 50/70, V1 and V2. This property is fundamental for the workability of materials.

Table 2.6. Average dynamic viscosity of extenders, REOBs and Pen 50/70 at different test temperatures.

Type of REOB	**Sample**	**η @ 60°C**	**η @ 100°C**	**η @ 150°C**
V1	V1	4.81	2.21	0.75
	V1_1:1_130	11038.15	8610.59	6034.14
	V1_1:1_160	13010.97	5182.40	6817.37
	V1_1:1_180	19479.76	13527.30	6043.24
	V1_1:2_130	7344.05	4781.39	2945.21
	V1_1:2_160	12613.58	5736.83	3706.04
	V1_1:2_180	7353.41	4324.71	2871.25
V2	V2	9.39	6.38	6.89
	V2_1:1_130	8287.13	3115.70	4225.25
	V2_1:1_160	15529.46	3971.20	4834.35
	V2_1:1_180	12851.21	5850.41	6438.31
	V2_1:2_130	5864.40	2395.74	1480.34
	V2_1:2_160	8795.13	3300.41	1975.67
	V2_1:2_180	7135.15	3573.24	2606.79
/	Pen 50/70	425.31	5.47	0.40

The viscosity of extenders has magnitude considerable higher than that of REOBs and neat bitumen. The values were influenced by both R-REOB ratio and type of REOB. However, the effect of production temperature did not show a clear trend. In detail, a larger amount of R leads to increase the dynamic viscosity for the most of specimens over the range of test temperatures. This finding is ascribed to the higher quantity of solid particles present in the blends, which reduce the mobility of REOBs molecules. As previously found in section 2.3.4, the incorporation of R particles into the oily fraction of

REOB led to a decrease in the self-diffusion coefficient of the REOB molecules due to the absorption and obstruction phenomena occurring during the interactions between R and REOB. With regard to the type of REOB, V1-extenders exhibited higher dynamic viscosity than blends produced with V2. This may reflect a potential higher affinity between V1 and R. This REOB may absorb larger amount of R, which increase in size and decrease their reciprocal distance, turning into lower viscosity of the resulting R-REOB compound. The higher processing temperature did not lead to a reduction of the dynamic viscosity of the final blends. Conversely, some extenders showed higher viscosity when produced at higher temperature. In particular, all V2-blends exhibited this trend. This result may linked to the previous statement as higher temperature can accelerate the diffusion of REOB into R particles. This means a lower viscosity of the final extenders. In addition, the pure V2 has higher viscosity than V1, which can influence the final viscosity as well. Changing the test temperature from 60 to 100 °C, the values of viscosity decrease, on the other hand a viscosity increment can be observed when the test temperature was raised from 100 to 150 °C in some specimens. In detail, this response is more evident in V2 samples with R-REOB ratio equal to 1:1, and it reflects the viscosity values of V2.

In general, the rheological behaviour of extenders did not show clear changes due to production temperature. Conversely, the quantity of rubber (i.e. R-REOB ratios) and the type of REOB cause more marked reactions on the final R-REOB blends. Regardless of the mass proportion of constituents, in all extenders the elastic response dominates the viscous one, as the storage modulus (G’) is always higher than the loss modulus (G’’). Nevertheless, the higher amount of R improved the elastic response of extenders. This better elastic behaviour that has been determined at high test temperature (60 °C) turns into enhanced resistance against permanent deformation; hence, the R-REOB blends with ratio 1:1 can withstand grater deformation before structural changes will occur. The presence of V2 instead of V1 increases the stiffness of the corresponding extenders. Due to the lower influence of processing temperature, further studies will be performed on R-REOB blends produced at 160 °C and 180 °C only. These two temperatures were chosen because polymer modified bitumen is usually produced at temperatures equal or higher 160 °C (Ma et al. 2017) and high temperature may speed up the diffusion of REOB into R particles. In addition, the highest temperature corresponds to the production temperature of Vx, as previously described. Thus, this may simplify the manufacturing of R-REOB compound for a possible industrial production.

2.4.3 FTIR spectroscopic analysis on extenders

The extenders produced at 160 °C and 180 °C underwent to chemical investigation by means of FTIR spectrometer. The main chemical functional groups have been evaluated and the average results are reported in the present paragraph. In fact, four replicates per each blend have been performed. In order to better compare the obtained results, the raw data were normalized considering the reference band of asymmetric stretching vibration of the aliphatic structures. The highest peak in the range of 2800-3000 cm^{-1} (approximately at 2923 cm^{-1}) is usually considered as the reference band for normalizing the spectra of bituminous materials that do or do not contain REOB (Hofko et al. 2017) (DeDene and You 2014). This band has been chosen as a reference for normalization because it was found that the rate of aliphatic structures slowly change during ageing (Lamontagne et al. 2001). Due to the low variability of this functional group of bituminous materials in time (Lamontagne et al. 2001) together with the recommendation of normalizing the spectra to improve the repeatability and sensitivity of results (Hofko et al. 2017), the positive absorbance values of R-REOB blends have been normalized before further analyse the data. Moreover, the normalization of extenders data has been performed to allow following comparison of these results with those of extended bitumen even if the R-REOB blends do not contain bitumen. Thus, the highest absorbance value of the asymmetric stretching vibration at about 2923 cm^{-1} was taken as the basis for normalization. The normalized spectra of all extenders presented high variability especially for wavenumbers lower than 2800 cm^{-1}. Major changes were found in R-REOB blends with respect to their constituent materials. Generally, the R-REOB blends with 1:2 ratio exhibited higher variability regardless the type of REOB used. The higher quantity of REOB may allow the R particles to move more easily resulting in a less homogeneous specimen of the tested extender. The normalized spectra of two extenders, namely V1_1:1_180 and V2_1:2_180 and both constituents are reported in Fig. 2.13 since their curves present the highest variability.

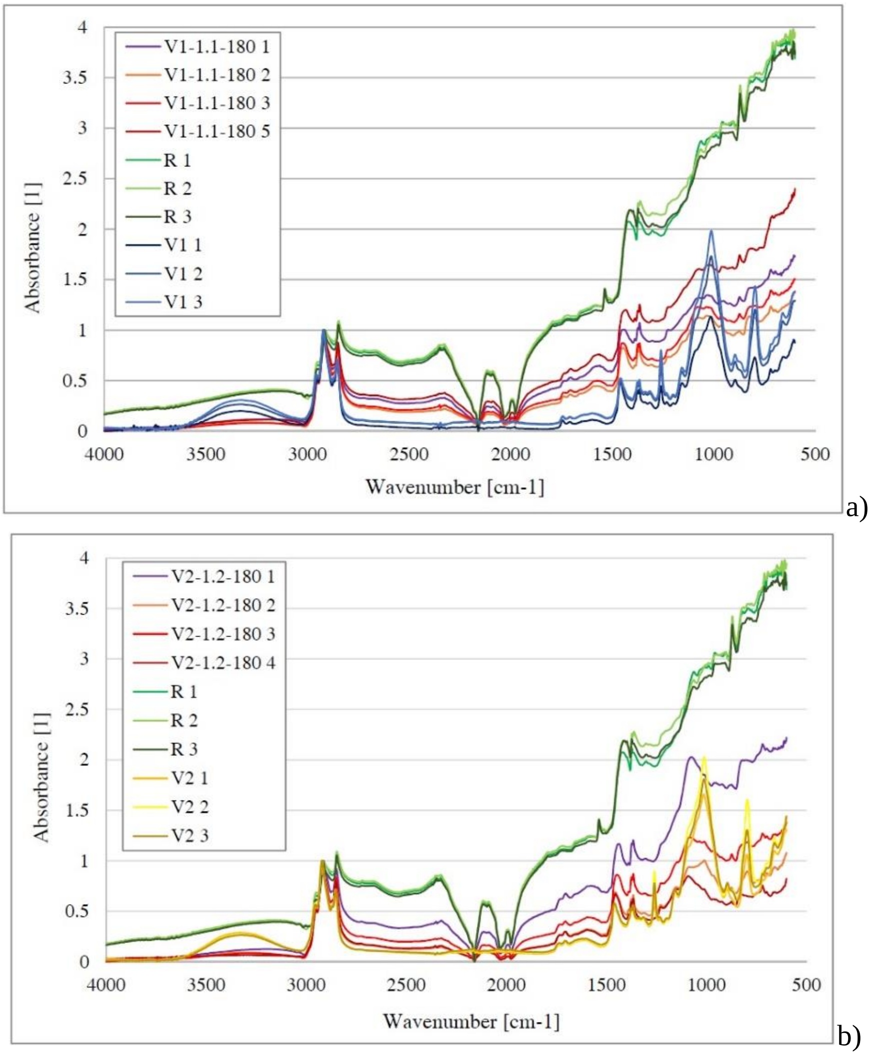


Fig. 2.13. Comparison of FTIR spectra of extenders: a) V1_1:1_180; b) V2_1:2_180.

The post-processing of data basis on the integration area under peaks of the FTIR spectra. The area under peaks of absorbance-wavenumber curve has been evaluated considering an absolute baseline at an absorbance value of zero. This evaluation together with the normalization of spectra allows the improvement of repeatability and sensitivity of results as found by Hofko et al. (2017) for neat and SBS-modified bitumens. As a result, the normalized integrated area under specific peaks wre evaluated to investigate and compare the chemical composition of different extenders. In detail, six different functional groups have been considered:

- Butadiene structures of SBR: 955-970 cm^{-1};
- Sulfoxides structure (S=O): 984-1066 cm^{-1};
- Aliphatic structures (CH_3+CH_2): 1319-1520 cm^{-1};
- Aromatic structures (C=C): 1535-1666 cm^{-1};
- Carboxylic or carbonyl structures (C=O): 1666-1746 cm^{-1};
- Amines and amides structures (N-H): 3050-3650 cm^{-1}.

The proposed wavenumber intervals have been established thanks to the chemical functional groups typically found in constituents or as traditionally meaningful for analysing bituminous materials. In detail, the butadiene peak is generated by the presence of rubber, while Vx mainly produces amines and amides, even though these structures were found in rubber as well. The wavenumber limits has been defined adjusting the band found in literature based on the peaks of the collected FTIR spectra (Nivitha et al. 2016) (Li et al. 2019). Aliphatic, carbonyl and sulfoxide groups are usually evaluated for studying bituminous binder ageing (Hofko et al. 2017). In fact, carbonyl and sulfoxide are associated to the uptake of oxygen molecules; while aliphatic molecules are stable and not affected by oxidative ageing (Hofko et al. 2017). In addition, the vibration of C=C stretching in aromatic ring were evaluated since these structures are commonly present in bitumen and were found in REOB by the NMR analysis (refer to Fig. 2.6). The aromatic molecules are spread between 4000 and 600 cm^{-1}, but the band at 1600 cm^{-1} was found to be a good wavenumbers for the appearance of aromatics (Van den bergh 2011). The band limits proposed by Van den bergh (2011) were adapted based on the collected spectra of R-REOB materials. Also the index of sulfoxide structures were adjusted to prevent the impact of the butadiene band as suggested by Hofko et al. (2017). Moreover, high absorbance values of sulfoxides groups in Vx were detected by the FTIR spectrometer, which lead to investigate the ageing-related functional groups even at this preliminary stage of the research.

The mean value (MV) of the integrated area at the six specific wavenumber limits, also called chemical indices, have been determined averaging the integrated area of all replicates executed for extenders and constituents. In addition, standard deviation (SD) and coefficient of variation (CV) of the evaluated indices were calculated. The SD represents the scatter of a single measured data with respect to the mean value, while, the CV corresponds to the scatter of results to the mean value. Thus, the CV correlates with the repeatability of measurements (Hofko et al. 2017). The results of the eight considered R-REOB blends are reported in Table 2.7.

Table 2.7. MV, SD and CV values of the eight extenders, R, V1 and V2.

Group	Parameter	R	V1	V1_1:1_160	V1_1:1_180	V1_1:2_160	V1_1:2_180
Aliphatic structures	MV [1]	369.84	64.45	163.25	163.35	120.45	111.07
	SD [1]	8.61	6.96	6.03	30.77	32.87	40.44
	CV [%]	2.33	10.79	3.69	18.84	27.29	36.41
Sulfoxide structures	MV [1]	235.89	117.47	107.83	108.98	78.96	75.58
	SD [1]	4.26	24.35	12.16	15.83	17.17	20.91
	CV [%]	1.80	20.73	11.27	14.53	21.75	27.67
Carbonyl structures	MV [1]	90.28	9.22	38.74	37.21	27.25	24.92
	SD [1]	1.48	1.92	2.17	7.89	9.26	12.11
	CV [%]	1.63	20.81	5.60	21.19	33.99	48.61
Butadiene structures	MV [1]	47.83	16.14	19.90	20.25	14.12	13.40
	SD [1]	0.75	2.95	1.97	3.54	3.98	4.90
	CV [%]	1.58	18.31	9.91	17.48	28.17	36.56
N-H structures	MV [1]	210.40	100.99	63.66	47.18	62.97	53.27
	SD [1]	4.67	18.56	22.87	8.65	9.26	12.02
	CV [%]	2.22	18.37	35.92	18.33	14.70	22.56
Aromatic structures	MV [1]	158.89	18.17	72.60	71.17	49.65	45.69
	SD [1]	2.56	3.82	4.11	14.84	17.45	22.00
	CV [%]	1.61	21.00	5.66	20.85	35.16	48.16

a)

Group	Parameter	V2	V2_1:1_160	V2_1:1_180	V2_1:2_160	V2_1:2_180
Aliphatic structures	MV [1]	78.43	208.68	172.19	116.02	130.74
	SD [1]	1.44	28.37	27.62	22.28	40.69
	CV [%]	1.84	13.59	16.04	19.21	31.12
Sulfoxide structures	MV [1]	133.47	139.50	112.71	79.76	98.49
	SD [1]	8.76	14.35	26.72	9.23	36.01
	CV [%]	6.56	10.28	23.71	11.57	36.57
Carbonyl structures	MV [1]	14.56	51.47	41.21	27.51	31.21
	SD [1]	0.51	11.42	9.05	6.29	12.23
	CV [%]	3.51	22.19	21.95	22.85	39.19
Butadiene structures	MV [1]	18.42	26.24	20.97	13.89	17.27
	SD [1]	0.58	3.48	5.23	2.44	6.89
	CV [%]	3.14	13.25	25.31	17.54	39.89
N-H structures	MV [1]	107.64	71.27	54.17	59.02	43.10
	SD [1]	3.95	7.98	12.81	9.59	9.19
	CV [%]	3.67	11.20	23.65	16.25	21.33
Aromatic structures	MV [1]	26.32	94.15	75.52	48.61	56.43
	SD [1]	0.85	21.31	17.27	11.13	22.69
	CV [%]	3.23	22.63	22.87	22.90	40.20

b)

The resulted MVs showed higher values of R than Vx at all chemical functional groups. This is caused by greater absorbance values of R spectra compared to those of REOBs and extenders among all wavenumbers. Comparing the chemical composition of V1 and V2, it can be observed that V2 presented higher values of all indices. This means that the original V2 is more rich in aliphatic, aromatic and sulfoxide molecules than the second available REOB, i.e. V1. Both SD and CV of the analysed data of extenders are much higher than the values obtained for standard bitumen or polymer modified bitumen as it was found by Hofko et al. (2017). Comparing the results obtained from the same post-processing of spectroscopic data that considers the integrated area under the normalized FTIR spectrum and an absolute baseline, the maximum SD and CV values determined by Hofko et al. (2017) are:

- SD (C=O) = 0.95 for long-term aged bitumen;
- SD (S=O) = 1.85 for long-term aged bitumen;
- CV (C=O) = 7.3% for long-term aged bitumen;
- CV (S=O) = 5.0% for unaged bitumen.

The results that were obtained in the present study showed a high variability for the calculated values, especially for the R-REOB blends. While, the constituents materials (i.e. R, V1 and V2) exhibited lower variability in terms of SD and CV values. The variability of data can be related to a lower homogeneity of the samples compared to their constituents or to standard bitumens since the area subjected to the scan is very small. However, to interpret the data it should be considered that the number of samples is not too large. In fact, only three or four replicates were compared.

In order to evaluate the changes in the resulting R-REOB blends due to the interaction of constituents, the ratios of the integrated normalized areas of each extender and the corresponding REOB were calculated at the six considered chemical indices. The mean of the area ratios of each material

(A_{ratio}) was determined averaging the four ratios that correspond to the replicates of the spectra measurements according to Equation 1:

$$A_{ratio} = \frac{A_{VxR}}{A_{Vx}} \tag{1}$$

, where A_{VxR} and A_{Vx} are the integrated normalized area at each index of a specific VxR sample and the considered Vx, respectively. These ratios allow the evaluation of the trend of the six functional groups based on R content as the noise caused by REOB is removed. Hence, considering the A_{ratio} of the pure REOBs, the results correspond to a unit. The obtained ratios are plotted in Fig. 2.14 versus the percentage of R with the corresponding error bars that represent the 95% confidence interval (CI).

The characteristic bands of R and Vx related to butadiene, amines and amides functional groups, respectively, have different trends with respect to the R content. The amines and amides index diminished from the reference unit value of the A_{ratio} of the pure Vx in all extenders with R-REOB ratio equal to 1:2 (i.e. 33%wt. of R); thus, the presence of the other constituent (R) can mitigate the quantity of functional group found within these wavenumbers limit, 3050-3650 cm^{-1}. Increasing the R content up to 50% (i.e. R-REOB ratio equal to 1:1), the A_{ratio} of all extenders experienced a slight increment. Thus, R particles do not contribute to significantly increase the quantity of amines and amides structures. Furthermore, the V2-extenders showed lower amount of amines and amides functional groups. The extenders produced at the lowest production temperature exhibited a higher amount of N-H bonds than the corresponding R-REOB blends manufactured at 180°C. Concerning the butadiene structures, this functional group is generated by the presence of R. Since Fig. 2.14a plots the area ratio between extenders and Vx versus the R content, the R-REOB compounds with 33%wt. of R did not show an increased amount of butadiene structures from the reference unit value of the A_{ratio} of pure Vx. It was necessary to increase the quantity of R up to 50%wt. in order to recognize the presence of these structures with respect to Vx. The effects of processing temperature and type of REOB is not very clearly identified.

Regarding the functional groups related to oxidative ageing, a significant increment of carbonyl structures were detected, which was almost directly proportional to R content. In general, the higher production temperature did not lead to accelerate the ageing rate as the samples produced at 160 °C showed higher carbonyl content than those manufactured at 180 °C. Moreover, V1-extenders were more prone to age than V2-blends regardless to the R content. On the other hand, the A_{ratio} related to the sulfoxide index did not exhibit notable variations in all extenders. The R-REOB blends with 33%wt. of R showed A_{ratio} a bit lower than unit; while increasing the amount of R up to 50%wt. the A_{ratio} of all R-REOB compounds was approximately equal to 1. This behaviour reflects the amount of sulfoxide structures in the constituent materials of the extenders. Although this chemical index is mainly brought by REOBs, as the FTIR spectra of both Vx showed pronounced peaks within 984-1066 cm^{-1} wavenumbers, decreasing the amount of R particles the A_{ratios} did not show reduced values. This trend is ascribed to the higher absorbance values of the R spectra over the considered wavenumbers. The production temperature and type of REOB did not show an unambiguous trend. The results of aliphatic groups are plotted in Fig. 2.14e. The A_{ratio} of the aliphatic index between extenders and REOB increased according to the increment of R content. Incorporating 50%wt. of R particles into Vx the presence of aliphatic structures almost doubled with respect to the values of extenders with ratio 1:2. The V1-extendres presented a higher amount of this chemical functional group in the resulting R-REOB blends. Conversely, no significant effect was caused by the processing temperature of the extenders. Lastly, the A_{ratios} that correspond to the aromatic structures were represented in Fig. 2.14f. The ratios of this index exhibited the same trend and magnitude of those related to the carbonyl structures for all extenders. Increasing the percentage of R into R-REOB blends, the aromatic functional group increased proportionally. Hence, the higher A_{ratios} between the aromatic structures of extenders and Vx can be ascribed to the presence of R even though both REOBs contain aromatic molecules. As for the evaluation of the A_{ratio} of the carbonyl index, the V1-extenders showed higher amount of these chemical functional groups than the corresponding R-V2 blends. Again, the effect of production temperature was not clearly demonstrated.

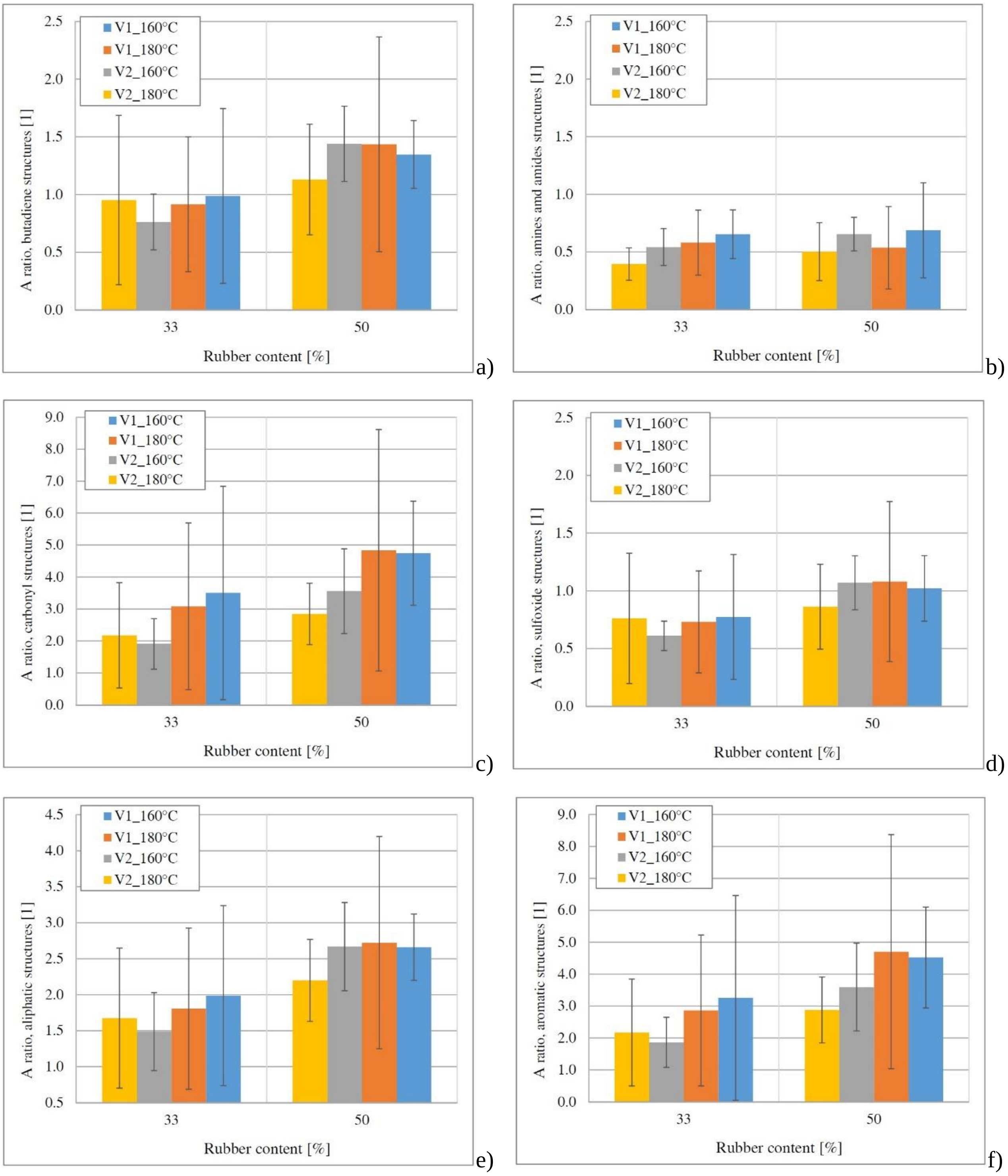


Fig. 2.14. Calculated area ratio between each Vx-extender and its Vx at six wavenumber bands: a) Butadiene structures; b) amines and amides structures; c) carbonyl structures; d) sulfoxide structures; e) aliphatic structures; f) aromatic structures.

As a general remark, the R-REOB blends that contain V1 exhibited higher values of the calculated A_{ratio} than the corresponding V2-extenders. This trend reflects the greater MV values of the pure V2.

The growth of butadiene, carbonyl, aliphatic and aromatic functional groups were found to be directly proportional to the R content. On the other hand, the N-H and S=O bonds were not directly related to the amount of R particles, as expected. The CI values highlighted the high variability of the spectroscopic data, confirming the obtained results of the SD and CV values.

2.5 Summary

The characterization of R-REOB blends and the investigations of interactions among recycled aggregates represent a crucial aspect to properly design possible bitumen extenders. The material characterization is of a worth importance especially for recycled and non-standardized materials.

Thanks to the obtained results about the optimization of R-REOB ratio, it can be concluded that the developed characterization protocol is suitable for the definition of the mass proportion of recycled materials, which is used for designing the bitumen extenders. In the present dissertation, the R-REOB ratios equal to 1:1 and 1:2 are considered as optimal for maximizing the content of both recycled materials. As a result, further studies have focused on the characterization of extenders produced with the abovementioned mass proportions and the available recycled raw materials detailed as V1 and V2. The characterization protocol should be improved in order to better evaluate the affinity between the recycled materials. This additional information is meaningful to evaluate and chose the best combination of materials among several recycled materials and or-by-products.

The investigations on the effects of processing temperature on extenders properties reveal the low temperature susceptibility of R-REOB blends. This response confirms the results gained from the characterization of constituents, especially those related to Vx. The rheological behaviour of extenders are mainly affected by the mass proportion of recycled materials and its composition instead of production temperature. Consequently, the extenders produced at 160 and 180 °C are used for further analysis at the binder and asphalt mixture levels. While, the extenders produced at the lowest processing temperature (i.e. 130°C) were neglected later on. In general, the rheological characterization highlights the great elastic response of extenders due to presence of R particles and the softening effects caused by REOB.

By means of chemical investigations on raw materials, it can be observed that both recycled materials contain particular functional groups such as N-H and butadiene structures, which are related to REOB and R, respectively. Moreover, specific functional groups related to the uptake of oxygen molecules, thus associated to ageing, are detected also at unconditioned states of the R-REOB blends and their constituents. As a result, the ageing tendency of extenders and bituminous binders modified by extenders themselves has to be taken into account.

3

Chemo-rheological characterization of extended bitumens

3.1 Introduction

The present chapter focuses on the characterization of various bituminous binders that have been produced replacing 25%wt. of a 50/70 penetration grade bitumen (Pen 50/70) with different R-REOB compounds. Among the extenders analysed in the second chapter, those manufactured at 160 °C and 180 °C were chosen for producing and evaluating eight extended bitumens. The Pen 50/70 was used as base constituent of the R-REOB-modified bitumens and as a reference material because this bituminous binder is widely used in Italy for the production of asphalt mixture.

The rheological and chemical properties of the eight extended bitumens have been determined by means of DSR and FTIR instruments. The rheological characterization included the storage stability of the innovative binders since it is well recognized that the solid particles of the added polymer tend to settle in time resulting in a poorer storage stability of polymer-modified bitumens.

The durability of extended bitumens represents a crucial aspect to assess their feasible use as road construction materials and promote their dissemination. As a result, the effects of oxidative ageing on the properties of R-REOB-modified bitumens were investigated. The eight extended bitumens underwent to an ageing protocol to simulate the ageing phenomenon experienced by asphalt pavements at the end of their service life. Then, the rheological and chemical investigations have been replicated to evaluate if and how much the innovative binders deteriorate.

The explanation of the adopted experimental program and the discussion of results of unconditioned and aged samples are provided later on in this chapter.

3.2 Experimental program

The second stage of this research addressed to road construction materials at the binder level. In detail, the present part of the dissertation focused on the production and characterization of extended bitumens thanks to the partial replacement of standard bitumen with recycled products, i.e. extenders.

3.2.1 Preparation of extended bitumens

The amount of standard petroleum bitumen in innovative modified binders was lowered from 100% to 75% by the total weight of a bituminous binder allowing the manufacturing of extended bitumens. The rheological properties of R-REOB compounds were strongly affected by the mass proportion of the constituents and the type of REOB, while the temperature as processing parameter showed less and variable impacts on the response of extenders as documented in Chapter 2. Thus, the four extenders manufactured at 160 °C together with those produced at 180 °C were chosen and used to substitute the 25%wt. of Pen 50/70. The extenders produced at the lowest processing temperature were not considered for manufacturing bituminous binders. The eight R-REOB-modified binders that have been prepared and tested with their acronyms are listed in Table 3.1.

Table 3.1. Matrix of considered extended bitumens.

Production temperature	**V1**		**V2**	
	R:V1 = 1:1	**R:V1 = 1:2**	**R:V2 = 1:1**	**R:V2 = 1:2**
160 °C	BV1R 160	BV1R2 160	BV2R 160	BV2R2 160
180 °C	BV1R 180	BV1R2 180	BV2R 180	BV2R2 180

Thanks to the previous experience in extenders' production and the collected rheological data that confirm the low temperature susceptibility of R and REOB, the production process of extended bitumens has been adapted. Two tips on limiting the drops of temperature while R-REOB compound is incorporated to bitumen have been applied for the production of the innovative R-REOB-modified binders:

- Additional warming period of the extended bitumens constituents' after their combination equal to 15';
- Using the maximum possible temperature of the heating plate during the mixing phase of binders.

Consequently, the preparation of extended bitumens followed the steps described below. Both constituents, Pen 50/70 and extenders, were pre-heated in a forced-air oven at the same processing temperature of the used extender, namely 160 °C or 180 °C. After the preliminary warming period, which lasted more than 1 h 30' for bitumen and 15' for extenders, the specific R-REOB compound was incorporated into Pen 50/70 and the constituents of the final extended bitumen were heated again for 15' in the oven. Then, every extender-bitumen compound was mixed by using the propeller mixer at a rate of 800 rpm for 1 h following the instruction of rubberized binder production (Signus Ecovalor; Ecopneus Scpa 2014). During mixing phase, all binders were continuously warmed up by means of a heating plate at its maximum temperature. As done for extenders, the production temperature of each extended bitumens was monitored every 15' during mixing phase by the use of an immersion thermometer. The mean value of the real processing temperature was about 140 °C for both groups of extended bitumens, those produced at 160 °C and the others prepared at 180 °C, which represent the nominal production temperatures. On one hand, the low temperature susceptibility of R-REOB blends seemed to nullify the different preliminary heating temperature of neat bitumen and extenders themselves. The difference of 20 °C was not enough to be observed during mixing. On the other hand, the two tips that were considered and the higher temperature susceptibility of Pen 50/70 than the recycled materials help to reduce the drops of temperature caused by the introduction of extender in the standard bitumen.

As previously mentioned, the Pen 50/70 is the reference material, which was also investigated. The behaviour of this bituminous binder together with the response of extenders previously studied allows the author to evaluate the contribution offered by each constituent material to the resulting extended bitumen.

After preparation, the extended bitumens were immediately poured on a silicone paper to realize the samples for next testing. A sufficient number of samples (drops) of each extended bitumens and Pen 50/70 were prepared that allowed the performing of all planned tests without heating the materials in a second time. Then, all metal containers of each extended bitumen were sealed. These operations prevented the UV radiation and atmosphere oxygen to reach the samples reducing the further ageing of the innovative bituminous binders.

3.2.2 Test methods

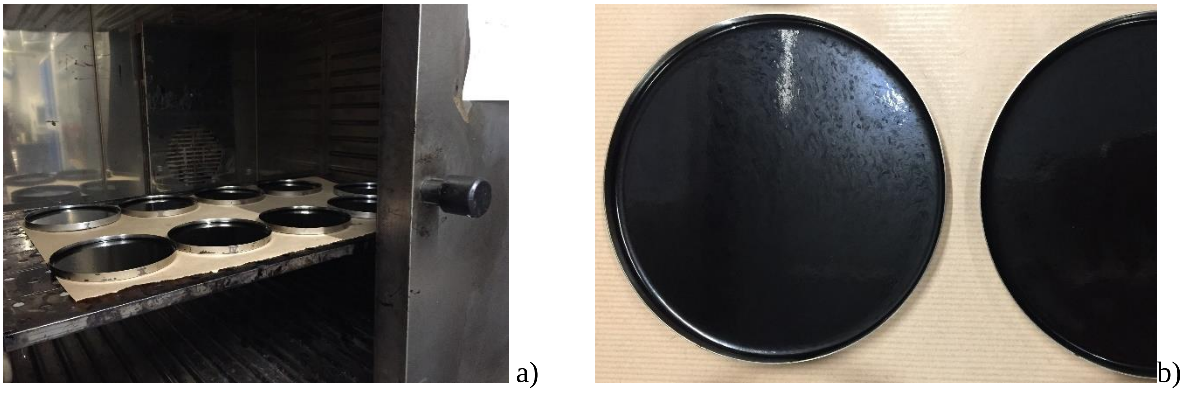
The rheological performances of neat and extended bitumens were evaluated using dynamic shear rheometers (DSR). The rheometers have been used to analyse the binders' response over a wide range of frequencies and/or temperatures performing the amplitude sweep (AS) test, frequency sweep (FS) test and multiple stress creep and recovery (MSCR) test. All tests were performed with the same settings and configurations used for the characterization of extenders as described in section 2.4.1. With respect to MSCR test, this type of test was carried out using an additional combination of loads. Thus, two different stress conditions were considered: 0.1-1.0 kPa and 0.1-3.2 kPa. The first combination is equal to the one used for extenders; while the second one represents the standardized shear stress according to the American standard ASTM D7405-15 (2015). Thanks to preliminary tests on extended bitumens, the low variability of their rheological parameters and, consequently, the high repeatability of results have been assessed. Thus, for all samples no replicate of each rheological test was performed except for AS and MSCR tests on unconditioned samples that were carried out twice at 10 °C and 60°C, respectively.

The chemical functional groups of the eight extended bitumens and Pen 50/70 were evaluated by means of the Fourier transform infrared (FTIR) spectrometry. The spectrometer was used in the attenuated total reflectance (ATR) mode obtaining the FTIR spectrum of all materials in the same conditions described in section 2.2. Four replicates of each bituminous binder have been considered and compared.

3.2.2.1 Applied conditioning on neat and extended bitumens

Both rheological and chemical analysis have been performed on neat and extended bitumens before and after the application of an ageing protocol, i.e. at fresh and aged conditions. The chosen protocol aimed to simulate the ageing phenomenon that asphalt concretes and, consequently, bituminous binders experienced at the end of their entire life while serving as pavement infrastructures. The ageing protocol considered two consecutive methods that can simulate in laboratory the short-term ageing that occurs during asphalt concrete production and paving and the long-term ageing that happens during their in-service life.

The short-term ageing was simulated using a method inspired to the Thin-Film-Oven-Test (TFOT) as detailed in the regulation EN 12607-2 (2014). Since the laboratory was not equipped with the standardized device, the ageing method was performed with a traditional forced-air oven, but applying the procedure described in the regulation. Each extended bitumen was poured in standardized tray thanks to a pre-warming period of time that allowed the material to become liquid. Then, all samples were left in oven at 163 °C for 5 h. For each binder, 50 ± 0.5 grams of material were poured in a tray with a circular shape and diameter equal to 140 mm. This amount of binder ensures the formation of a bituminous film 3.2 mm thickness. Being modified bituminous binders, the ageing temperature was raised to 163 °C following the suggestion of the standard in force for harder paving grade bitumens. The long-term ageing was simulated by the Pressure Ageing Vessel (PAV) device according to the standard EN 14769 (2005). Thus, the materials underwent ageing in PAV at 100 °C and 2.1 MPa for 20 h. The same amount of bituminous binder and the same tray are necessary for running PAV tests, this allowed saving materials. Moreover, a method similar to the TFOT instead of the common Rolling Thin Film Oven Test (RTFOT) was preferred due to the high amount of R present in extended bitumens, which could prevent the flow of binders and the formation of a moving film. In the PAV aged samples, some bubbles may be entrapped in the surface of bituminous binders due to the applied high pressure. In order to remove air and to ensure the uniformity of sample for further tests, the aged materials were stirred before been poured on a silicon paper. The devices used for ageing and aged samples are visible in Fig. 3.1. The short- and long-term ageing methods changed the materials' surface. After short-term ageing, some stripes were visible on the surface of extended bitumens as shown in Fig. 3.1b, which were not present in short-aged Pen 50/70. These changes may be ascribed to the presence of REOB since it represents an additional liquid phase or the modification of bitumen. On the other hand, all bituminous binders showed air bubbles after long-term ageing (Fig. 3.1d).


a)
b)

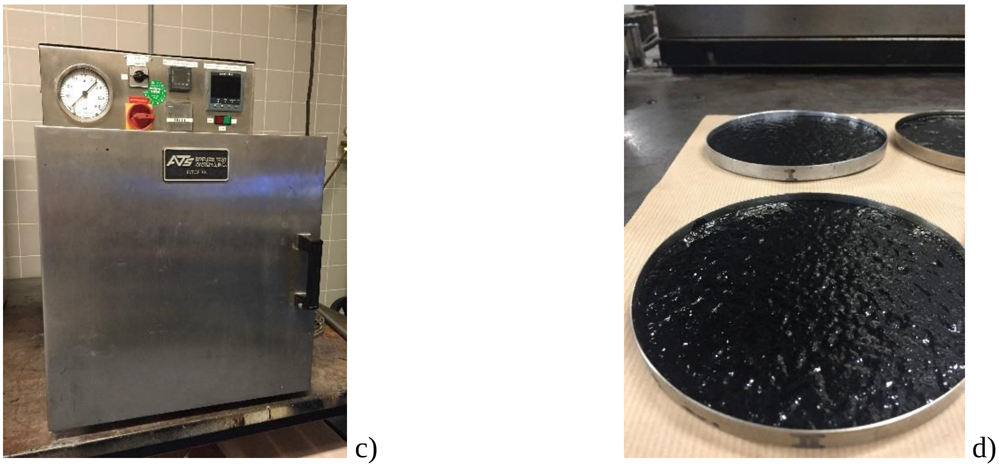


Fig. 3.1. Ageing devices and samples: a) forced-air oven with samples; b) example of short-term aged samples; c) PAV instrument; d) example of long-term aged samples.

Moreover, the fresh extended bitumens underwent to a specific conditioning to further determine their storage stability at high temperatures. This evaluation did not consider the Pen 50/70 bitumen as it is recognised that polymer-modified binders usually exhibited a poorer storage stability due to the sedimentation of the solid particles added for the modification of bitumen.

The storage stability of the eight bitumens has been evaluated according to the EN 13399 (2017). This standard reports the accelerated conditioning to perform a separation test, also known as *Tuben test*. The standardized procedure aims to simulate the conditions that the modified bituminous binders experience in storage silos. All samples have been maintained in a vertical vessel/tube at 180 °C for three days. The height of aluminium vessel has to be higher than 160 mm and their diameter has to be ranged between 25-40 mm. The eight tubes have been filled with extended bitumens at solid state without the undergoing a heating time to avoid the further ageing of the materials. Each specific mass of the two type of extended bitumens that differed in the mass proportion of the recycled materials have been calculated based on tube dimensions and the density of extended bitumens with ratio 1:1 and 1:2. The determined quantities allowed the evaluation of the correct amount of materials, leaving the necessary space to seal the aluminium containers. Then, the filled eight tubes were tightly closed and placed in a pre-heated forced-air oven for conditioning. A sealed tube prevents air reaching the bituminous samples, thus limiting further oxidative ageing of materials. The vertical position of tubes during conditioning period was maintained as much as possible by the use of supports (natural aggregates). After conditioning, each tube filled with a sample was cooled down, firstly at room temperature for about 20', following by a cooling period of 40' at about 5 °C using a refrigerator; then, the tubes were cut into three equal parts. This significant cooling phase facilitated the cutting procedure of the tubes. Among the three parts of the tubes, the top and bottom parts were used for further testing, while the middle one was discarded. Thus, the two parts, i.e. top and bottom, were heated again for 10’ in oven at 180 °C to remove samples from the vessel. These parts of the conditioned samples exhibited different textures showing the sedimentation of the R particles toward the bottom part of the tube. The pictures of one extended bitumen is reported in Fig. 3.2 as example, together with the used tubes and some steps of the conditioning procedure.

The author decided to rheologically analyse the two parts of conditioned extended bitumens with the MSCR test in accordance to the standard ASTM D7405-15 (2015) as done for fresh materials. Thanks to the collected data from fresh extended bitumens and Pen 50/70, it was possible to compare the elastic responses of samples at different conditioning states. Moreover, this kind of test is not time-consuming.

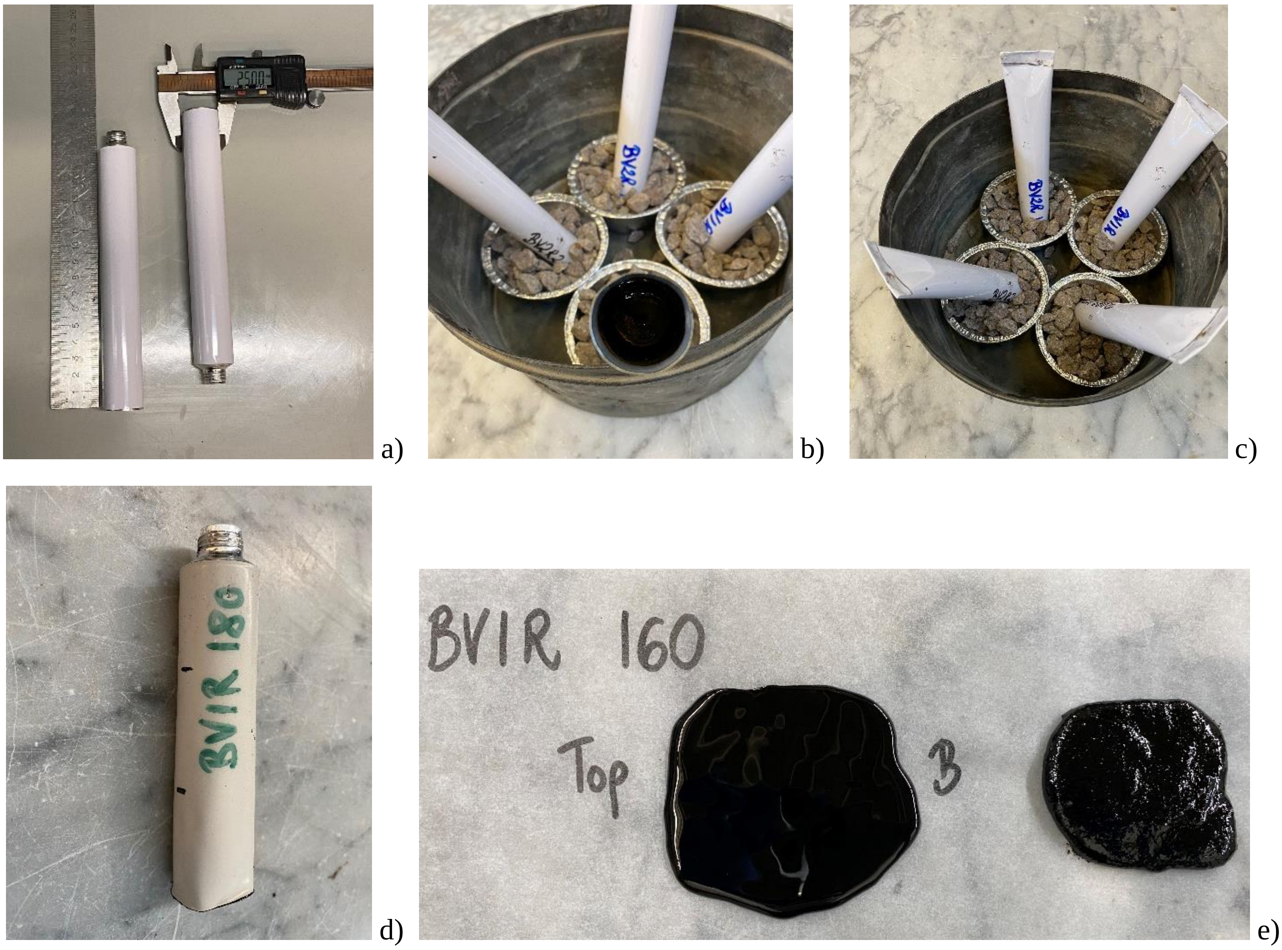


Fig. 3.2. Tools and procedure's steps to evaluate the storage stability of modified bitumens: a) tubes; b) tubes filled with extended bitumens; c) closing of the tubes; d) cutting phase after conditioning; e) example of conditioned samples.

The rheological tests were performed between the road pavement laboratories of the University of Bologna (DICAM Department) and the Delft University of Technology (Department of Engineering Structures). Thus, three different Anton Paar rheometers were used for the rheological characterization of bituminous materials: MCR 302 (Bologna), MCR 502 and EC-Twist 502 (Delft). The chemical investigations and all ageing procedures were carried out at the Delft University of Technology. The laboratory is equipped with a Perkin Elmer Spectrum 100 FTIR spectrometer. While, the separation test for the evaluation of storage stability was done at the University of Bologna.

3.3 Investigation of rheological and chemical properties of extended bitumens

3.3.1 Rheological characterization of extended bitumens

The extended and neat bitumens underwent AS test at first. By using this analysis, the LVE range of materials as the corresponding deformation of the 95% of the initial storage modulus (G') was identified. In detail, the average of the first three G' values collected during the AS test has been considered for determining the modulus reduction of 5%. The LVE domain of extended bitumens decreased as the test temperature was reduced from 60 °C to 10 °C via 30 °C. This trend is similar to those of bituminous binders typically used for paving application and reflects the high percentage of Pen 50/70 into the extended bitumens. The maximum applicable strains to avoid irreversible structural changes of all extended bitumens are listed in Table 3.2. This table shows the average results of the AS tests performed at 10 °C, which were used as input parameters for the following FS tests. Each extended bitumen exhibited an intermediate LVE range between those of its constituents, that is extender and standard bitumen (refer to Table 2.4 for comparison). This response emphasizes the importance of knowing and comprehending the composition of the products since each constituent material contributes to the final behaviour of the compound. Moreover, it is important to highlight and remember that the limit LVE strain of neat and extended bitumens was obtained at the lowest test temperature, while the most restrictive LVE range of extenders was found at the highest test temperature. The LVE domains of extended bitumens showed lower variability than that of extenders (refer to Table 2.4 for comparison). In particular, the results of R-V1-modified binders were all close to unity. The higher amount of R into the extender and, consequently, into the bituminous binder, the lower production temperature and the presence of V1 extended the LVE domain of the corresponding materials.

In Fig. 3.3, the storage (G’) and loss (G’’) moduli of neat and extended bitumens have been reported. The representation of Fig. 3.3 shows the results of the AS test performed at 10 °C, which were collected during the first replicate done per each binder. The elastic behaviour dominated the viscous one in all extended bitumens, while Pen 50/70 mainly behaved as viscous material. This response can be ascribed to the presence of R particles since all extenders exhibited it as shown in Fig. 2.11. The neat bitumen is stiffer than all extended bitumens. It means that the extender softened the resulting bituminous binder. Among the extended bitumens, those containing R and REOB with mass proportion equal to 1:1 showed greater values of both storage and loss moduli. The higher content of REOB than R (1:2 ratio) in the added extenders led to soften the final R-REOB-modified bitumen. The type of REOB affected the results as the use of V2 stiffened the materials, but it did not turn into wider LVE range. The effect of production temperature was not clear concerning the binder stiffness.

Table 3.2. Linear viscoelastic (γ_{LVE}) range of fresh extended bitumens at 10°C.

Type of REOB	Sample	γ_{LVE} @ 10°C
V1	BV1R 160	1.010
	BV1R 180	0.943
	BV1R2 160	1.002
	BV1R2 180	1.002
V2	BV2R 160	0.909
	BV2R 180	0.791
	BV2R2 160	0.909
	BV2R2 180	0.718

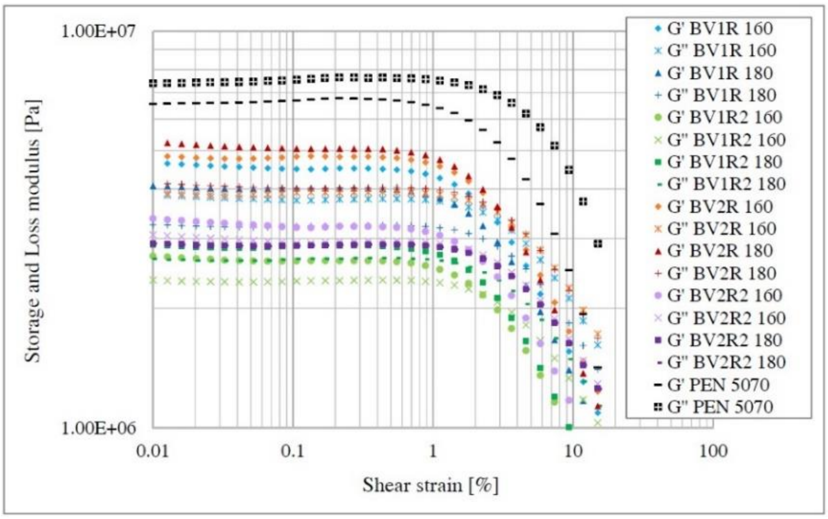


Fig. 3.3. Comparison of G’ and G’’ values of fresh extended bitumens and Pen 50/70.

The results of the FS tests carried out on all bituminous binders are plotted in the Black space showed in Fig. 3.4. This representation plots the complex shear modulus (G*) versus the phase angle (δ) and it is useful to interpret the raw data without applying any manipulation. As visible in Fig. 3.4, the partial substitution of Pen 50/70 with extenders resulted in a shifting of the rheological data towards lower δ values. Hence, the resulting bituminous binders are more elastic than the traditional bitumen. The introduction of extenders into Pen 50/70 implied different responses of the R-REOB-modified bitumen, which were influenced by the test temperature. The data of extended bitumens collected at low test temperatures (10-20 °C) resulted in lower values of the complex modulus and phase angle. Increasing the test temperatures, the G*-δ curves of R-REOB modified bitumens were less elongated than those of standard bitumen resulting in higher G* values at high test temperatures (50-60 °C). These general responses may be related to the combining effect of R-REOB blend, as the polymer network of R turns into a more elastic and stiff material; while, REOB softens the binders due to the addition of a liquid and less viscous material than Pen 50/70. Hence, the presence of R particles seems to prevent the R-REOB-modified bitumens to have a poor resistance against permanent deformation at high temperatures; while, the introduction of REOB enhances the thermal cracking resistance at low temperatures. The effect of REOB does not seem to greatly affect the rutting resistance of the final binder. Keeping in mind the FS results of extenders (refer to Fig. 2.12), the contribution of R-REOB compound can be clearly understood. Moreover, due to the polymer network defined by R particles the G*-δ curves of extended bitumens acquired the typical inverse S-shape (Celauro et al. 2012) (Wang et al. 2018).

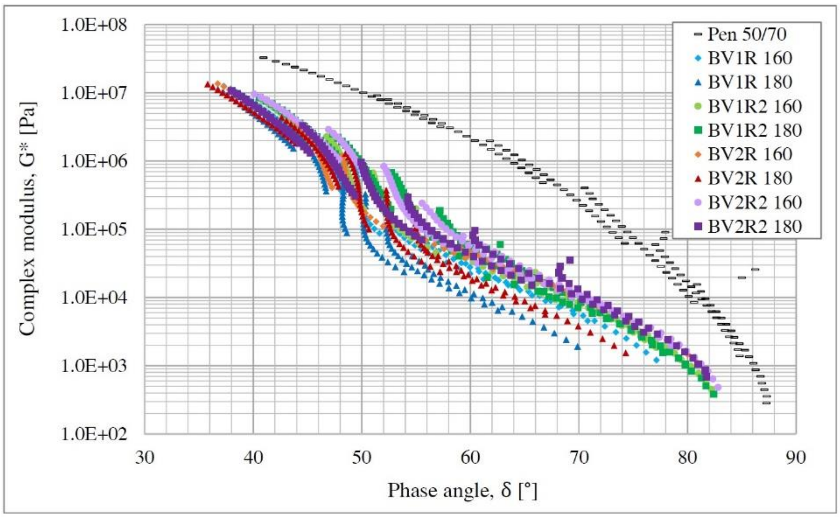


Fig. 3.4. Black diagram of fresh extended bitumens and Pen 50/70.

From the Black diagram representation (Airey 2002), it is possible to conclude that extended bitumens similarly behaved as a thermo-rheological simple material even though the collected curves at the six different temperatures of the FS test are not completely smooth. As a result, the master curves of the two rheological parameters, G* and δ, were determined using the time-temperature superposition (TTPS) principle. This principle exploits the interrelationship between frequency and temperature to produce the complex shear modulus and phase angle curves at a reduced frequency (Airey 2002).

The master curves were constructed by the use of the modified Christensen-Anderson-Marasteanu (CAM) model and the William-Landel-Ferry (WLF) equation, the latter for shift factors fitting (Bahia et al. 2001) (Williams et al. 1955). The chosen reference temperature corresponded to the intermediate temperature used for performing the FS test, i.e. 30 °C. A spreadsheet program has been developed for determining the G* and δ master curves. In detail, the temperature-shift factors at different test temperatures were defined at first. The WLF formulation that has been used is expressed in Equation 2:

$$log\frac{a_T(T)}{a_T(T_0)} = -\frac{c_1(T - T_0)}{c_2 + (T - T_0)} \tag{2}$$

, where a_T is the temperature-shift factor, T_0 is the reference temperature (30 °C) and c_1 and c_2 are two constants, which were considered equal to 8.86 and 101.6, respectively (Williams et al. 1955) (Bahia et al. 2001) (Nur Izzi 2012). The shift-factors of each test temperature were multiplied by the frequencies applied during the test allowing the definition of reduced frequency (f_r). Then, the equations proposed by Bahia et al. (2001) were applied for calculating the G* and δ master curves. The formulations of G* and δ are expressed in Equations 3 and 4, respectively.

$$G^* = G_e^* + \frac{G_g^* - G_e^*}{\left[1+\left(\frac{f_c}{f_r}\right)^k\right]^{m_e/k}} \tag{3}$$

$$\delta = 90I - (90I - \delta_m)\left\{1+\left[\frac{log(f_d/f_r)}{R_d}\right]^2\right\}^{-m_d/2} \tag{4}$$

, where G_e^* is the complex modulus at the lowest frequency (f→0), G_g^* is the glass complex modulus at the highest frequency (f→∞), f_c is the crossover frequency (f→G'≈G'') and f_d at the inflexion of δ master curve, δ_m is the phase-angle constant at f_d, f_r is the reduced frequency, and k, m_e, R_d, m_d and I are shape parameters. The detailed information on parameters can be found in the NCHRP report no. 459 (Bahia et al. 2001) and in related literature (Nur Izzi 2012) (Asgharzadeh et al. 2015). Since the parameters of Equation 3 are independent from those of Equation 4 (Bahia et al. 2001), two separate optimization processes have been performed to define the G* and δ values based on the modified CAM model. The process of optimization used the deterministic method for constrained non-linear problem supplied in Excel program, the generalized reduced gradient (GRG) method (Yeniay 2005). In particular, the method find a local optimum solution to the problem defined as Equation 5 for G* and δ values. The method minimized the relative errors between the modelled data and the experimental results using the non-linear least squares equation as detailed in Equation 5 (Harris 1998) (Kemmer and Keller 2010). The relative errors have been preferred to the absolute errors as suggested by Asgharzadeh et al. (2015).

$$\min f\left(G_g, f_c, m_e, k\right) = \sum_{i=1}^{n}\left(\frac{G^*_{experimental} - G^*_{modelled}}{G^*_{experimental}}\right)^2 \tag{5a}$$

$$\min f(\delta_m, f_d, m_d, R_d) = \sum_{i=1}^{n}\left(\frac{\delta^*_{experimental} - \delta^*_{modelled}}{\delta^*_{experimental}}\right)^2 \tag{5b}$$

The resulting master curves of the neat and extended bitumens are showed in Fig. 3.5. The master curves of complex shear modulus are displayed from bottom-left to top-right of the plot, while the curves from top-left to bottom-right are those of phase angle. With respect to G*-f_r curves, all extended bitumens exhibited lower stiffness at high frequency and/or low temperature than Pen 50/70. This means that the incorporation of any R-REOB compound can improve the thermal cracking resistance of the resulting extended bitumens. The differences between G* master curves of neat bitumen and those of R-REOB-modified bitumens decreased proceeding towards lower frequency and/or higher temperature as long as they overlapped at intermediate temperature. At opposite boundary conditions, the Pen 50/70 showed a softer behaviour than all innovative binders. This response turns into a greater resistance of extended bitumens against permanent deformation, hence rutting phenomenon. The type of extender used for bitumen modification influenced the rheological properties of the final bituminous binder differently. Noticeable differences were detected at low frequency and/or high temperature; while, almost negligible differences were exhibited at opposite boundary conditions. In general, higher amount of R into extenders led to increase the binder stiffness. Similar effect was obtained increasing the processing temperature of extenders and binders. The type of REOB showed less influence on binder behaviour than previous parameters. The use of V2 stiffened the bituminous binders when R and REOB were introduced with a mass proportion equal to 1:2. On the other hand, the stiffening effect of V2 on extended bitumens with the same proportion of recycled products were visible at high frequency only. This trend did not confirm the results of extenders as shown in Fig. 2.12, where the V1-extenders had shown to be stiffer than the corresponding V2-blends at high test temperature.

The δ-f_r curves confirmed the modelled results of G* values. In addition, the type of REOB showed a more marked influence on the rheological response of extended bitumens and the use of V1 turned into a more pronounced elastic behaviour of binders. The presence of R-REOB compound heavily affected the phase angle values of innovative binders, which showed a greater elastic-like behaviour than Pen 50/70. The phase angle of innovative binders exhibited a plateau zone due to the polymer network established by R particles. In fact, the flat region in the phase angle master curve of a rubberized binder is ascribed to the entanglements among the polymer and bitumen molecules (Asgharzadeh et al. 2015). Comparing the effect of extenders' constituents on the final behaviour of extended bitumens, the percentage of incorporated R heavily affected the responses of final binders, especially at low frequency and/or high temperature. On the other hand, the addition of REOB lowered the stiffness of extended bitumens at all boundary conditions. However, the phase angle master curves of the innovative binders mainly differed at intermediate and high frequencies due to the quantity and type of REOB. Consequently, the rheological parameters confirmed that R particles could improve the rutting resistance of the resulting binders, while REOB enhanced their cracking resistance at low temperatures.

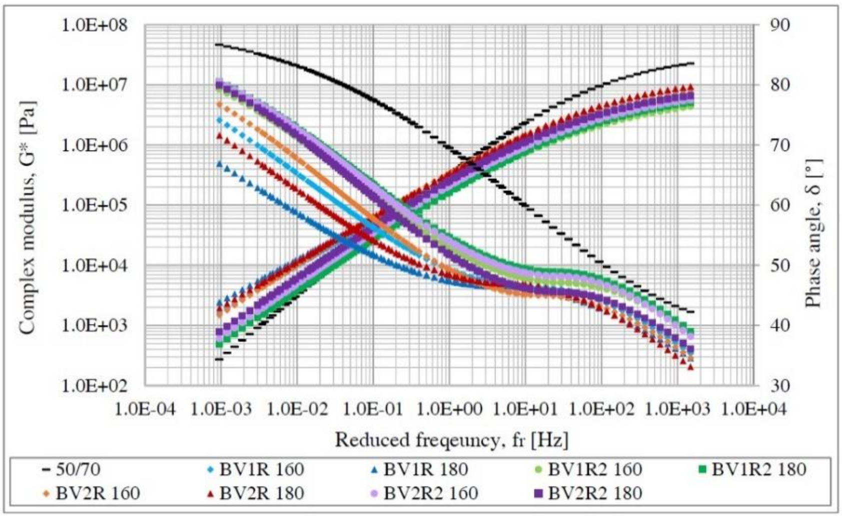


Fig. 3.5. G* and δ master curves of fresh extended bitumens and Pen 50/70.

Among the parameters that has been evaluated during the construction process of the master curves, the crossover frequency (f_c) is used to characterize the properties of the viscoelastic materials since it represents the transitory behaviour from fluid to solid state. Indeed, the crossover frequency is the frequency at which the storage and loss moduli are approximately equal. This parameter is binder specific and it indicates the general consistency of a given bituminous binder (Nur Izzi 2012). A higher value of f_c means a higher phase angle and, consequently, a greater overall viscous component in the behaviour (Bahia et al. 2001). In other words, higher f_c value suggests that bituminous materials have lower molecular mass and softening point and reduced relaxation time (Jing 2019). The calculated f_c values of the R-REOB-modified bitumens are reported in Fig. 3.6 based on the R content; the trend of this parameter is evaluated from the reference value of the Pen 50/70 that is equal to 67.58 Hz. The Pen 50/70 has an intermediate f_c value between the extended bitumens that incorporated extenders with R-REOB ratio equal to 1:2 (i.e. 8.3%wt. of R) and those with R-REOB ratio equal to 1:1 (i.e. 12.5% of R). The f_c values increased increasing the amount of R particles in all extended bitumens. Alternatively, higher content of REOB reduced the f_c values of the final extended bitumens. This trend may be related to the chemical composition of extenders and their constituents and may reflect the addition of already aged by-products such as REOBs. As a matter of fact, it has been found that the ageing phenomenon reduces the f_c values of bituminous binders (Jing 2019). Furthermore, the processing temperature of extenders and R-REOB-modified bitumens and the type of REOB influenced the response of the material. Thus, the constituent materials of the extender exhibited a crucial role on the transitory behaviour of the extended bitumens. In particular, the use of V1 and the production temperature equal to 180 °C helped to improve the behaviour of the materials concerning this parameter. Being susceptible to ageing phenomenon, the lower f_c values of V1-extended bitumens may reflect the lower amount of functional groups directly related to oxidative ageing (i.e. carbonyl and sulfoxide groups) in V1 than those in V2 as shown in Table 2.7. Surprisingly, a higher production temperature did not lead to reduce the crossover frequency of the corresponding extended bitumens. The more detrimental ageing phenomenon that can occur increasing the processing temperature may be hid from the facilitated interactions between R particles and REOB, thus from the lower quantity of free REOB.

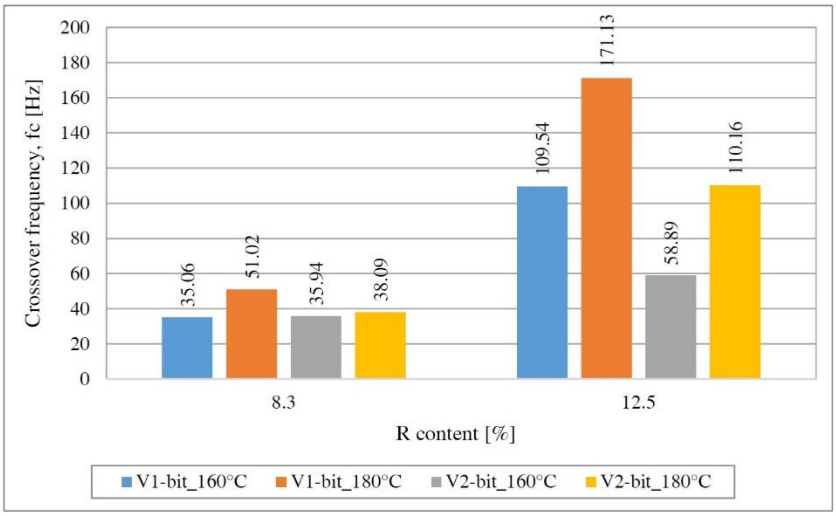


Fig. 3.6. Crossover frequency (f_c) of extended bitumens based on R content.

The measured linear viscoelastic data collected by performing the FS test can be also used to determine the material's resistance to flow. In detail, the complex viscosity and the flow activation energy have been evaluated in order to gain information and differentiate the bituminous binders based on their thermal susceptibility. The temperature dependence of the viscosity of binders can be described by Equation 6, that is an Arrhenius equation (Wang et al. 2018):

$$\eta^* = Ae^{E_a/RT} \tag{6}$$

, where A is the pre-exponential parameter, R is the universal gas constant (8.314 [J/mol·K]), E_a is the activation energy [KJ/mol], T is the temperature [K] and η* is the complex viscosity at zero or low shear rate [Pa·s]. Thanks to the FS raw data acquired during the application of an oscillatory shear stress, the complex viscosity of a bituminous binder can be directly obtained dividing the value of the complex shear modulus by the corresponding angular frequency (ω) in s^{-1}. Therefore, knowing the η* and using the inverse formula of Equation 6, the activation energy of extended bitumens has been established. The calculation of activation energy considered the complex viscosity at the lowest frequency applied during the FS tests that is equal to 0.10 Hz or, alternatively, 0.63 s^{-1}. The representation of complex viscosities at the lowest angular frequency in ln-scale versus the reciprocal value of test temperatures allowed the determination of the pre-exponential parameter (A) as the slope of the curve. The results of complex viscosity showed a temperature- and shear rate-dependent behaviour of all binders. In detail, this rheological parameter decreased as the temperature and/or frequency increased, confirming previous study (Wang et al. 2018). Furthermore, the η*-ω curve of Pen 50/70 differed from the curves of extended bitumens at different test temperatures. Fig. 3.7 shows viscosities at the lowest (10 °C), intermediate (30 °C) and the highest (60 °C) test temperatures used in FS tests. The traditional bitumen exhibited the highest complex viscosity values at 10 °C, while it had the lowest values at 60 °C. This bituminous binder achieved the behaviour of a Newtonian fluid more rapidly compared to R-REOB-modified bitumens; in fact, at test temperature equal to 60 °C, the complex viscosity of Pen 50/70 was almost independent of shear rate as per Newtonian fluids. Increasing R content, processing temperature of extenders and binders, and using V2, the resulting extended bitumens showed higher complex viscosity. The different response of neat and extended bitumens can explain the improved permanent deformation resistance of innovative binders compared to that of Pen 50/70 as extenders stiffened the resulting binders. The complex viscosity of binders confirms and reflects the results in terms of G* and δ master curves.

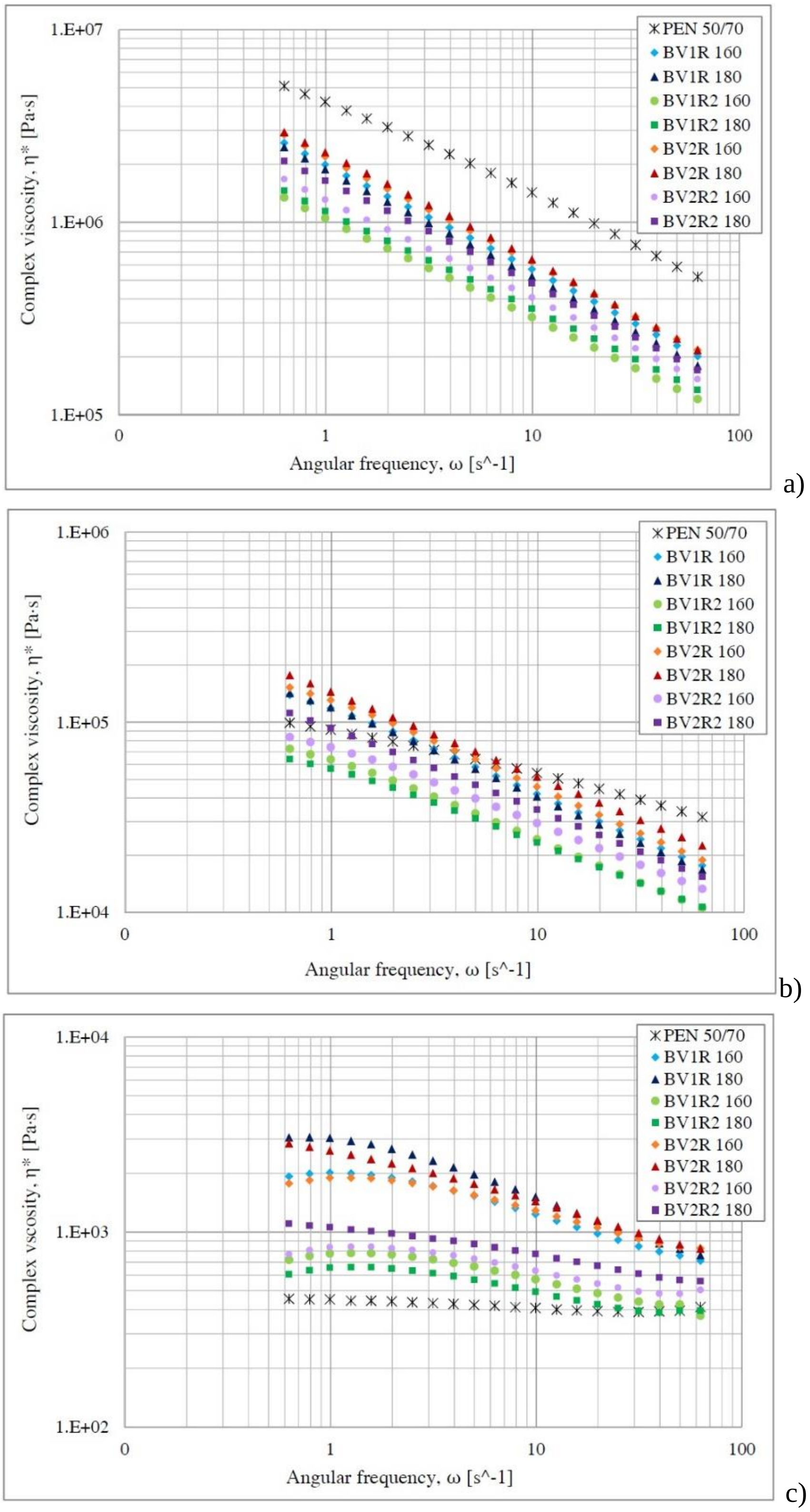


Fig. 3.7. Complex viscosity versus angular frequency of fresh extended bitumens and Pen 50/70 at different test temperatures: a) 10 °C; b) 30 °C; c) 60 °C.

The activation energy (E_a) for flow were evaluated for all bituminous binders as previously described and the results are listed in Table 3.3. The bituminous binders with low activation energy were found to be less sensitive to temperature changes (Salomon and Zhai 2002). Hence, extended bitumens showed less temperature susceptibility than Pen 50/70. This response can be ascribed to the extenders since their constituents, R and REOB, and extenders themselves demonstrated lower temperature susceptibility than neat bitumen in all rheological tests. The incorporation of higher amount of R, the higher processing temperature and the use of V1 resulted in binders with lower E_a values.

Table 3.3. Activation energy for flow of fresh extended bitumens and Pen 50/70.

Sample	**E_a [KJ/mol]**
BV1R 160	113.60
BV1R 180	104.89
BV1R2 160	118.91
BV1R2 180	123.12
BV2R 160	116.11
BV2R 180	111.39
BV2R2 160	121.52
BV2R2 180	118.53
Pen 50/70	148.21

In general, binders with higher complex viscosity and lower activation energy are less vulnerable to temperature change. Consequently, the extended bitumens manufactured at 180 °C and containing R and REOB in equal mass proportion (R-REOB ratio equal to 1:1) are preferable in terms of temperature susceptibility. Regarding the type of REOB used, this parameter had opposite effects on complex viscosity and activation energy for flow. Since R-modified binders usually have viscosity concerns, the use of V1 for producing modified binders can be promoted as it reduces the activation energy of final products exhibiting lower η^* values.

The elastic response and the rut resistance of bituminous binders was analysed with MSCR test and two parameters were evaluated, i.e. percent recovery (%R) and non-recoverable creep compliance (J_{nr}). In particular, the %R measures the elastomeric response of the polymer in a bituminous binders; while, the J_{nr} is a good indicator of the rutting resistance of the material thanks to the assessment of the nonlinearity response of bituminous materials (D'Angelo et al. 2010). As detailed in section 3.2.2, the test was carried out by applying a different load during the second phase of the test itself, which were 1.0 kPa and 3.2 kPa. While, the first phase of the MSCR test was always performed at 0.1 kPa. The results of unaged materials at three shear creep loads that have been considered are reported in Tables 3.4 and 3.5 for the parameters %R and J_{nr}, respectively. The results of deformation averaged the data of all replicates (i.e. 4 replicates for 0.1 kPa, 2 replicates for 1.0 kPa and the other 2 for 3.2 kPa). The data listed in Tables 3.4 and 3.5 were determined considering the latest 10 creep cycles performed at 0.1 kPa and the 10 cycles at the higher shear stress. Furthermore, the parameter, $J_{nr,diff}$ has been evaluated since it represents an indicator of stress sensitivity of the R-REOB-modified bitumens. This parameter was evaluated according to Equation 7:

$$J_{nr,diff} = \frac{J_{nr,3.2} - J_{nr,0.1}}{J_{nr,0.1}} \cdot 100 \tag{7}$$

, where $J_{nr,3.2}$ and $J_{nr,0.1}$ are the average non-recoverable creep compliance at 3.2 kPa and 0.1 kPa, respectively. This parameter should provide insights into the relationship between laboratory-measured changes in J_{nr} across the range of applied stress to changes in field performance of the asphalt mixes. The original intent was to define an upper limit of the $J_{nr,diff}$ parameter equal to 75%. This parameter was evaluated considering the standardized shear creep stress according to the ASTM D7405-15 (2015) standard.

Table3.4. %R of fresh extended bitumens and Pen 50/70 at three stress levels (0.1, 1.0 and 3.2 kPa).

Sample	**Percent recovery [%]**		
	Stress=0.1 kPa	**Stress=1.0 kPa**	**Stress=3.2 kPa**
BV1R 160	50.87	26.81	9.16
BV1R 180	67.56	42.11	22.77
BV1R2 160	33.10	10.27	1.90
BV1R2 180	25.13	7.25	1.65
BV2R 160	40.48	20.02	8.33
BV2R 180	54.89	35.36	17.45
BV2R2 160	24.50	7.84	1.85
BV2R2 180	27.99	11.98	3.46
Pen 50/70	1.34	0.00	0.00

Table3.5. J_{nr} and $J_{nr,diff}$ of fresh extended bitumens and Pen 50/70 at three stress levels (0.1, 1.0 and 3.2 kPa).

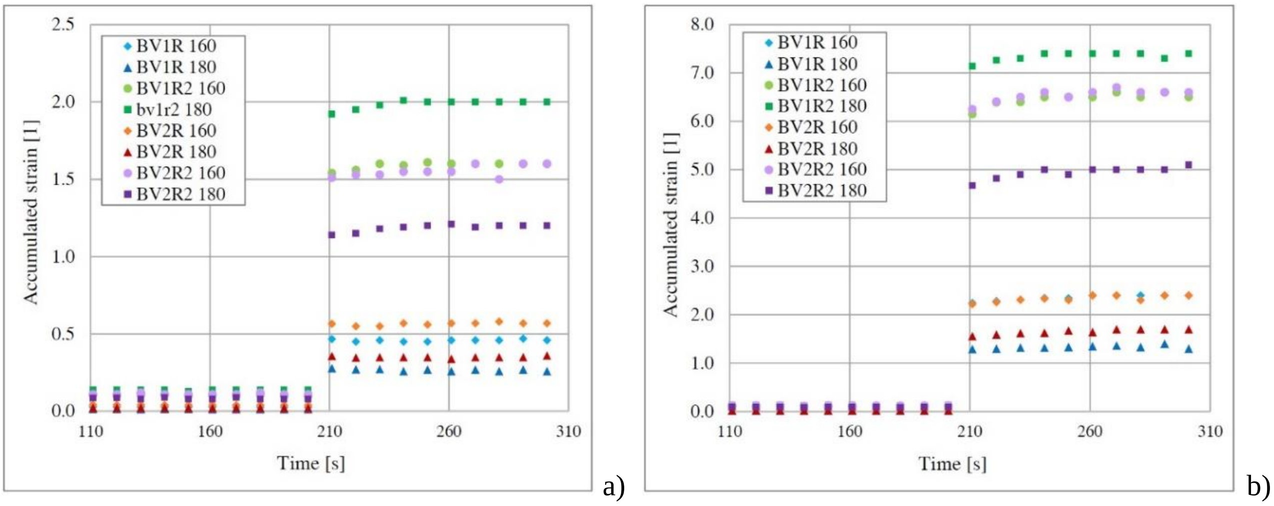
Sample	**Jnr [kPa^{-1}]**			**Jnr,diff [%]**
	Stress=0.1 kPa	**Stress=1.0 kPa**	**Stress=3.2 kPa**	**/**
BV1R 160	0.2965	0.4588	2.3525	646.83
BV1R 180	0.1405	0.2730	1.3300	870.80
BV1R2 160	0.9675	1.5575	6.4640	602.61
BV1R2 180	1.3250	1.9860	7.3400	482.54
BV2R 160	0.3760	0.5535	2.3319	538.88
BV2R 180	0.2280	0.3505	1.6506	611.47
BV2R2 160	1.1550	1.5520	6.5360	449.24
BV2R2 180	0.8590	1.1860	4.9390	458.71
Pen 50/70	2.9050	3.0400	10.2240	253.77

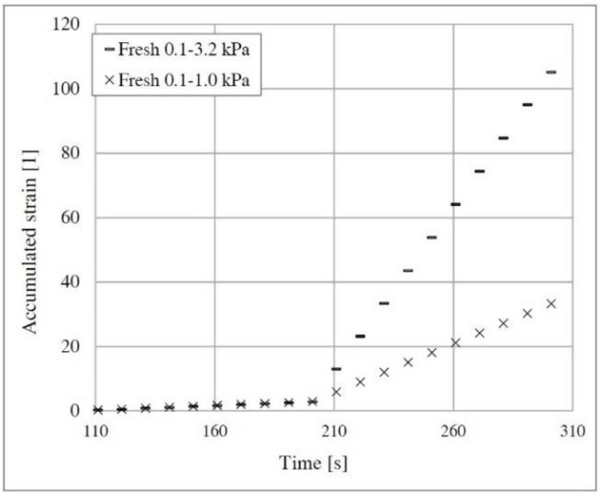
The neat and extended bitumens behaved differently and the R-REOB-modified binders showed better elastic responses than Pen 50/70 as shown in Table 3.4. The percent recovery (%R) values of extended bitumens exhibited one order of magnitude, at least, greater than traditional bitumen at all shear stresses. As suggested in a previous study of D'Angelo et al. (2010), the increased values of %R of the extended bitumens is directly related to the amount of the elastomeric polymer (that is R content in the present research) in the mix and the extent of networking of the polymer in the binder. In fact, the extended bitumens containing R-REOB extenders with ratio equal to 1:1 showed higher %R values. Hence, the positive contribution of R particles detected at the extender level has been confirmed at the binder level. The elastic behaviour of extended bitumens reflected the response of the extender that has been incorporated into neat bitumen with respect to the three variables considered for producing R-REOB compounds. The processing temperature equal to 180 °C and the equal mass proportion of recycled materials improved the elastic responses of the resulting binders. About the type of REOB, the extended bitumens with V1 exhibited a more pronounced elastic response when R and REOB were added in the same proportion; while, those with V2 behaved better when produced with higher quantity of REOB than R. This response reflects the higher elasticity of V2-extenders than V1-blends at high test temperature when was carried out the FS test on extenders (refer to Fig. 2.12).

The non-recovered deformations listed in Table 3.5 showed lower variability than the values of percent recovery; however, the better response of innovative bituminous binders than Pen 50/70 was confirmed regardless the applied shear stress. Regarding the effects of the constituent materials and processing conditions, the J_{nr} values reflect the trend of the previous parameter, i.e. %R. Thus, higher R content and production temperature led to reduce the total non-recoverable deformation; while, the type of REOB has a different influence on extended bitumens based on the amount of R particles. The J_{nr} parameter has been proven to distinguish the difference in rutting potential between various binders; in detail, it has been shown a good correlation between the non-recoverable creep compliance (J_{nr}) and the rutting resistance of asphalt mixtures (D'Angelo et al. 2010). As a consequence, the incorporation of extenders with R-REOB ratio equal to 1:1, produced at 180 °C may improve the rut resistance of the final extended bitumens and, consequently, of the asphalt mixture.

In terms of stress-sensitivity, all bituminous binders, including Pen 50/70, exceeded the maximum limit of $J_{nr,diff}$. This means that all materials have a high sensitivity when tested at 60 °C. The results are not unexpected as the compliance with this limit was found to be challenging in previous studies as claimed by Stempihar et al. (2018). The problem is amplified when bituminous materials with very low J_{nr} values are considered. As a matter of fact, the extended bitumens with higher content of R exhibited higher values of this parameter as it reduced both J_{nr} values, $J_{nr,3.2}$ and $J_{nr,0.1}$. Also, higher processing temperature led to increase the $J_{nr,diff}$ results of the corresponding extended bitumens and the use of V1 for extended bitumens containing R-REOB with ratio 1:1 and those containing V2 with R-REOB ratio equal to 1:2 followed the same trend. Among all tested bituminous binders, the Pen 50/70 showed the lowest value of this parameter. The previous study of D'Angelo et al. (2010) ascribed this difference to the non-cross linking of the polymer since the addition of R did not reduce the stress sensitivity of the binders (D'Angelo et al. 2010). However, this consideration is in contrast to the obtained results of %R parameter, as higher values of percent recovery can be related to an extended polymer network.

The elastic response of all binders are stress-dependent. The different behaviour of extended bitumens compared to Pen 50/70 is also visible in terms of accumulated strain. Fig. 3.8 shows this parameter evaluated for all bituminous binders at the two setting conditions of MSCR test. The accumulated strain of Pen 50/70 increased linearly with time regardless the shear creep stress applied. This means that the neat bitumen behaved like a viscous liquid material at high temperature (60 °C) (Zhang et al. 2016). Conversely, the R-REOB-modified binders did not exhibit the same trend. The accumulated strain of extended bitumens increased non-linearly with time. A previous study of Zhang et al. (2016) on R-modified bitumen ascribed this response to the viscoelastic fluid properties of rubberized binders. Furthermore, the increasing rate is much lower than that of Pen 50/70. The results of MSCR test confirmed those of FS tests; at high temperature, i.e. 60 °C, the Pen 50/70 behaves as a Newtonian fluid, while the extender incorporated into neat bitumen prevents extended bitumens from showing the same behaviour.





c)

Fig. 3.8. Accumulated strain versus time of all bituminous binders at different setting conditions of MSCR test: a) extended bitumens at 0.1-1.0 kPa; b) extended bitumens at 0.1-3.2 kPa; c) Pen 50/70 at 0.1-1.0 kPa and 0.1-3.2 kPa.

The rheological response of the eight extended bitumens were investigated. Being constituted of eight extenders that differs in R-REOB ratio, type of REOB and temperature of production, the resulting innovative bituminous binders were compared considering the same variables. All extended bitumens exhibited a more elastic behaviour than traditional Pen 50/70 at all frequencies and/or temperatures analysed. This response can be mainly ascribed to the presence of R particles, as it is proportional to the R content. Moreover, the higher processing temperature and the use of V1 in extended bituemns with R-REOB ratio equal to 1:1 enhance the elastic response of the corresponding binders. Regarding the stiffness of the final product, the partial replacement of standard bitumen with a R-REOB extender softens the bituminous binder at high frequency and/ or low temperature, but leads to stiff the resulting binder at the opposite conditions. The REOBs can be mainly accounted for softening effect on binders. The type and amount of REOB soften, but do not over soften the final bituminous binder at high temperatures probably due to the incorporation of R, which may mitigate the softening effect at this boundary condition. The content of rubber and production temperature strongly affect the G*, G’ and G’’ values. While these rheological parameters were found to be less dependent on the type of REOB even though V2 usually increases the resulting complex modulus of the extended bitumens and leads to a more viscous-like material. These behaviours turn into improved rutting resistance and enhanced thermal cracking resistance of R-REOB-modified bitumens. Furthermore, the innovative bituminous binders experienced a lower temperature susceptibility, which explains why extended bitumens may withstand greater permanent deformations.

3.3.2 FTIR spectroscopic analysis on extended bitumens

The chemical analysis on extended bitumens have been performed by the FTIR spectrometer. In the present chapter, the results of normalized spectra based on the highest absorbance peak at around 2923 cm^{-1} are reported (Lamontagne et al. 2001) (Hofko et al. 2017). Then, the integrated area under six specific and relevant peaks of normalized spectra have been calculated considering the absolute baseline at an absorbance value of zero (Hofko et al. 2017). The same functional groups investigated for extenders were analysed for R-REOB-modified binders and Pen 50/70. The average area (MV) of four measurements per each binder was also used to determine the SD and CV values.

Thanks to a visual investigation of normalized spectra, the effects of R-REOB compounds can be detected highlighting some typical trends of the chosen functional bands of extended bitumens with respect to Pen 50/70. In general, the extended bitumens presented higher absorbance values related to C=C and C=O stretching vibrations. These increments are related to the introduction of both recycled products as the FTIR spectra of all innovative bituminous binders was shifted towards the top part of the plot regardless the type and amount of extenders' constituents or processing conditions. More variability has been found in the replicates of binders that contain R and REOB in the same mass proportion (1:1 R-REOB ratio). Furthermore, two distinct peaks of C=O stretching vibrations were collected at about 1700 cm^{-1}. The first peak has been found between 1680-1720 cm^{-1}, while the second had wavenumber range of 1720-1750 cm^{-1}. The two band limits can be ascribed to the following specific functional groups, respectively (Van den bergh 2011):

- Aromatic ketone, aromatic aldehyde, aromatic ester, aliphatic ketone and carboxylic acid;
- Aliphatic ester and aliphatic aldehyde.

In Fig. 3.9, the spectra of Pen 50/70 and two extended bitumens considering two extenders with R-REOB ratio equal to 1:1 and 1:2 as example are reported.

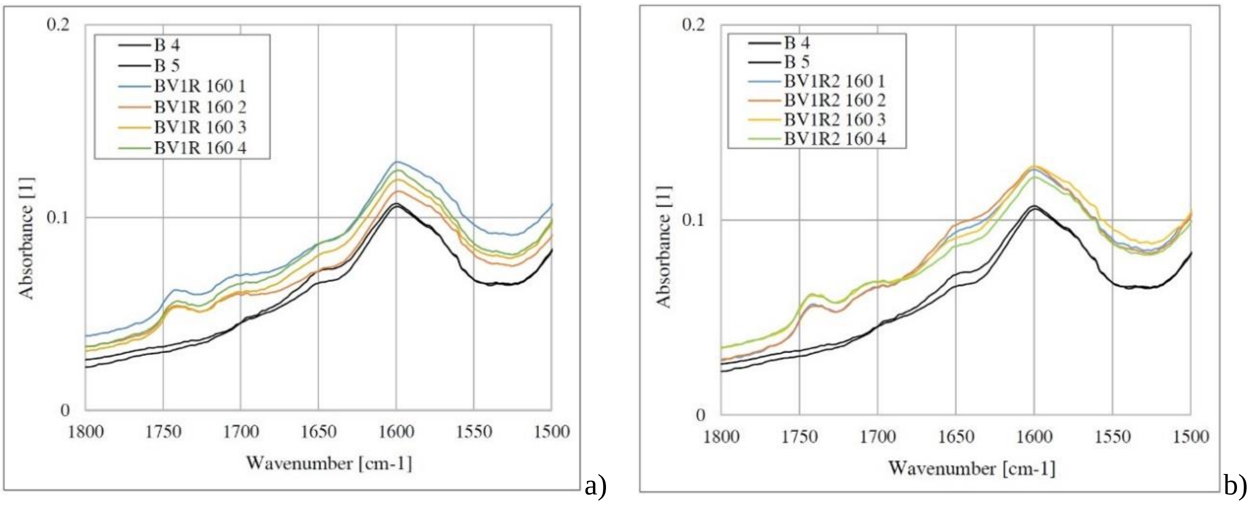


Fig. 3.9. Highlights of carbonyl and aromatics bands of FTIR normalized spectra of Pen 50/70 and two extended bitumen: a) BV1R 160; b) BV1R2 160.

Concerning the S=O and N-H bonds, the normalized spectra of extended bitumens differed from the curves of Pen 50/70 depending on the amount of REOB in the added extenders. The four innovative binders made with R-REOB ratio equal to 1:2 exhibited higher absorbance values than that measured for standard bitumen. The curves of R-REOB-modified bitumens with recycled products ratio equal to 1:1 had similar trend of those of standard bitumen as they were usually displayed within or above the replicates of Pen 50/70. A comparison between two extended bitumens and the reference material in the wavenumbers range of 950-1100 cm^{-1} and 3600-3050 cm^{-1} are reported in Fig 3.10 as example. The enhancement of sulfoxide and nitrogen peaks were caused by the introduction of Vx since they are enrich of sulfoxide, amines and amides molecules. The similar chemical compositions of neat Vx with respect of sulfoxide band (refer to Fig. 2.5) has been reflected in the absorbance values of extended bitumens, which were about 0.6-0.7 for almost all R-REOB-modified binders. Only sample BV1R2 160 showed absorbance values close to unit in two replicates. Less, but still visible, differences in the absorbance values of the four replicates of BV1R2 160 were registered by FTIR spectrum at high wavenumbers.

The amount of aliphatic molecules of extended bitumens in the interval of 1520-1319 cm^{-1} were higher than the quantity measured for Pen 50/70. As previously discussed in section 2.2, the alkanes structures were detected in both recycled materials. Therefore, it is reasonable to find higher absorbance values in the spectra of R-REOB-modified bitumens. Among V2-modified binders only, major absorbance values in aliphatic region were obtained for bitumens with R-REOB ratio equal to 1:1. The trend of the FTIR curves is reported in Fig. 3.11 for two extended bitumens as example and those of neat bitumen. Regarding the presence of butadiene structures, FTIR spectrometer did not detect a clear peak at wavenumbers in the range of 955-970 cm^{-1}. Hence, no representation are reported in this dissertation.

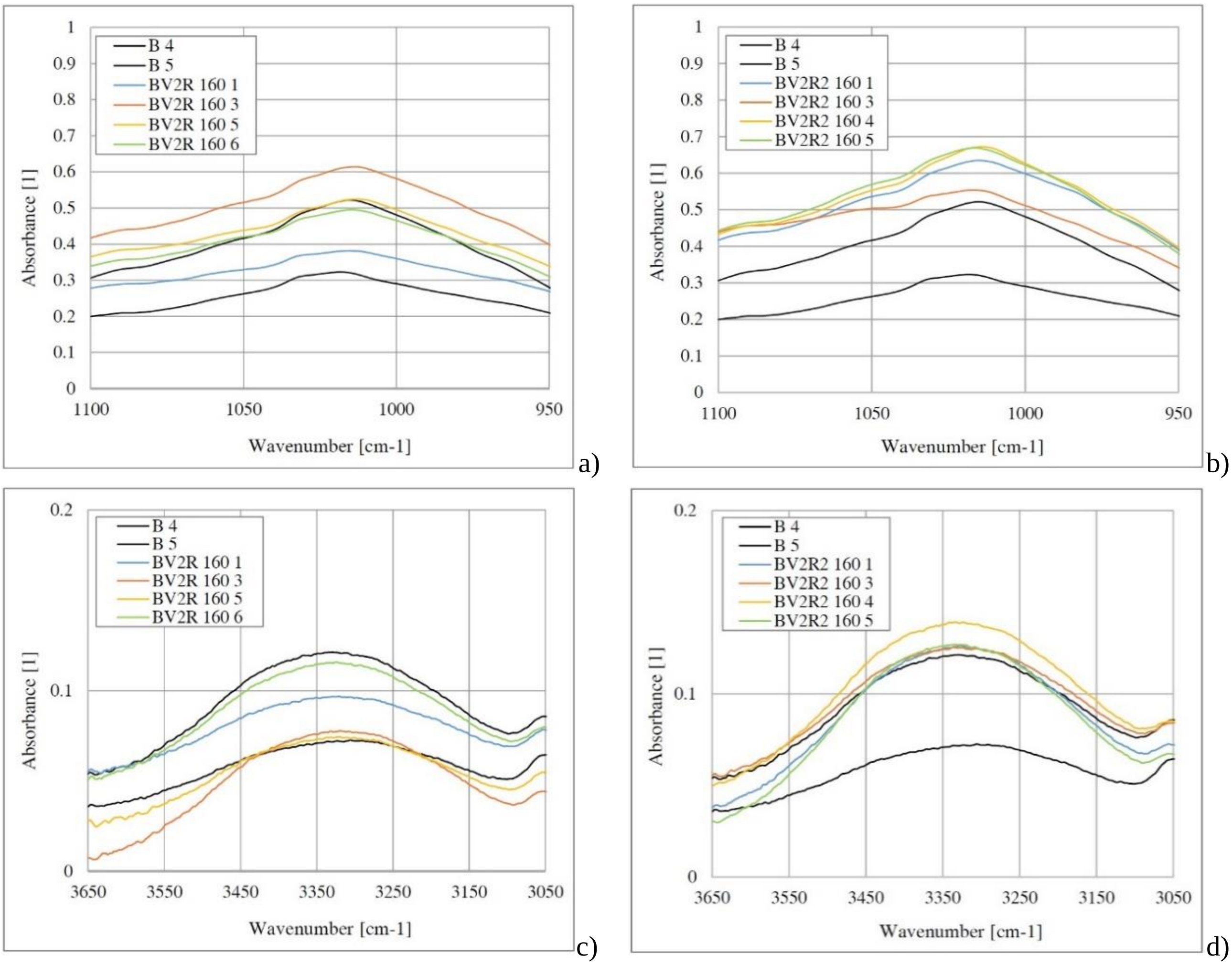


Fig. 3.10. Highlights of sulfoxide and nitrogen bands of FTIR normalized spectra of Pen 50/70 and two extended bitumen: a) S=O structures considering BV2R 160; b) S=O structures considering BV2R2 160; c) N-H structures considering BV2R 160; d) N-H structures considering BV2R2 160.

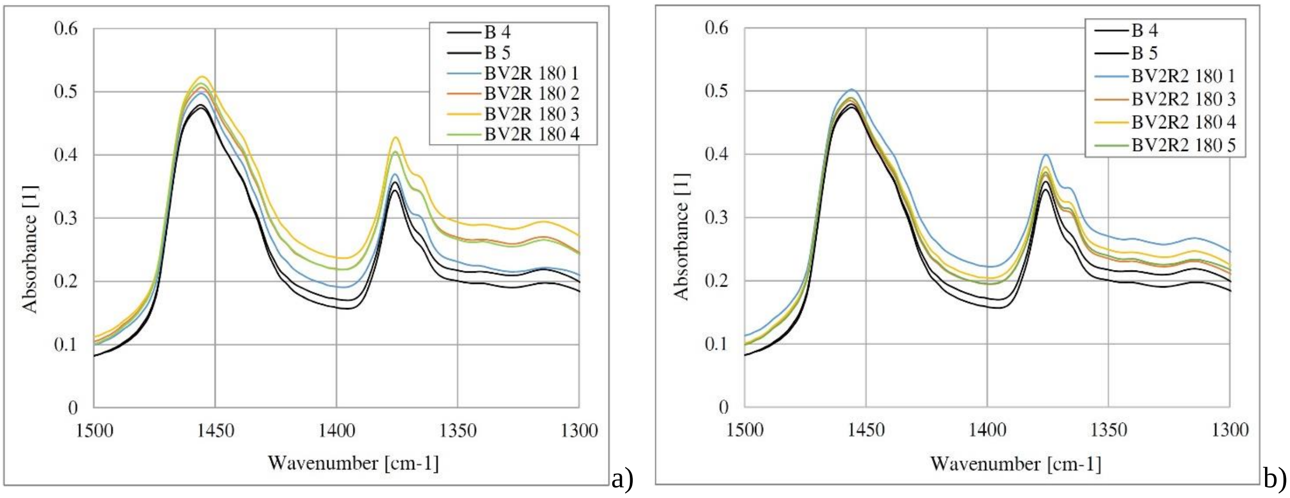


Fig. 3.11. Highlights of aliphatic band of FTIR normalized spectra of Pen 50/70 and two extended bitumen: a) BV2R 180; b) BV2R 180.

After the evaluation of the integrated area under the spectra, the mean value (MV) of the four measurements done per each R-REOB-modified bitumen was calculated for the six wavenumber limits. Moreover, the SD and CV were determined. The results of MV, SD and CV of extended bitumens and the reference material (Pen 50/70) are listed in Table 3.6.

Table 3.6. MV, SD and CV of fresh extended bitumens and Pen 50/70: a) V1-samples; b) V2-samples.

Group	Parameter	Pen 50/70	BV1R 160	BV1R 180	BV1R2 160	BV1R2 180
Aliphatic structures	MV [1]	45.49	49.58	55.61	54.13	51.59
	SD [1]	0.88	2.51	5.98	2.97	1.83
	CV [%]	1.94	5.07	10.75	5.49	3.56
Sulfoxide structures	MV [1]	30.92	32.73	42.27	59.97	50.35
	SD [1]	7.20	8.39	11.06	12.31	4.82
	CV [%]	23.28	25.64	26.15	20.52	9.57
Carbonyl structures	MV [1]	3.54	5.01	5.81	5.26	5.10
	SD [1]	0.07	0.31	0.61	0.09	0.25
	CV [%]	2.09	6.16	10.55	1.80	5.00
Butadiene structures	MV [1]	4.54	4.97	6.68	8.46	7.33
	SD [1]	0.82	1.04	1.61	1.65	0.71
	CV [%]	18.07	20.92	24.16	19.46	9.68
N-H structures	MV [1]	45.42	44.86	46.65	55.62	57.07
	SD [1]	10.55	12.58	4.95	13.80	3.65
	CV [%]	23.22	28.04	10.61	24.80	6.40
Aromatic structures	MV [1]	10.71	12.76	14.34	13.55	12.82
	SD [1]	0.17	0.71	1.40	0.31	0.24
	CV [%]	1.60	5.59	9.74	2.30	1.86

a)

Group	Parameter	BV2R 160	BV2R 180	BV2R2 160	BV2R2 180
Aliphatic structures	MV [1]	53.10	54.51	51.63	51.81
	SD [1]	2.64	2.98	1.19	2.07
	CV [%]	4.97	5.47	2.30	4.00
Sulfoxide structures	MV [1]	38.01	42.78	47.64	40.26
	SD [1]	6.10	10.54	3.00	2.72
	CV [%]	16.04	24.65	6.30	6.76
Carbonyl structures	MV [1]	5.89	5.72	5.70	6.24
	SD [1]	0.27	0.40	0.22	0.44
	CV [%]	4.52	6.97	3.81	7.10
Butadiene structures	MV [1]	5.91	6.57	7.00	6.22
	SD [1]	0.89	1.47	0.45	0.46
	CV [%]	15.00	22.38	6.47	7.38
N-H structures	MV [1]	41.08	45.89	56.67	57.60
	SD [1]	9.72	8.72	3.64	3.86
	CV [%]	23.66	19.00	6.42	6.70
Aromatic structures	MV [1]	14.32	14.16	13.52	14.18
	SD [1]	0.59	0.88	0.21	0.93
	CV [%]	4.14	6.19	1.54	6.57

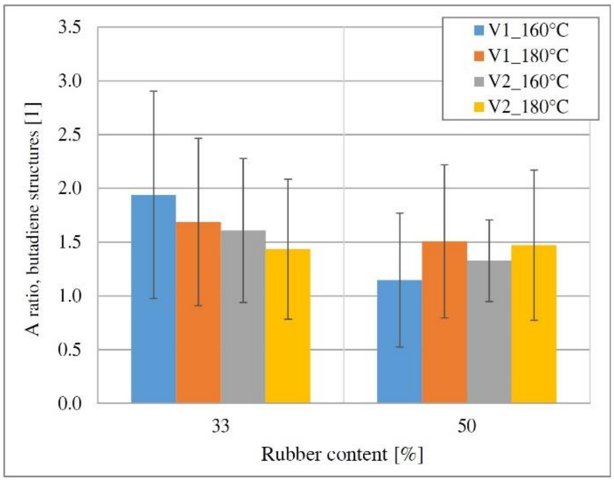
b)

The MV results of all bituminous binders had the same order of magnitude and the obtained values are less variable than extenders. In fact, the SD and CV values of neat and extended bitumens are lower than those of corresponding extenders. This means that the data measured for one replicate of a material does not differ much from the average results of all replicates (SD) or the scatter between MV and SD are not relevant (CV). The highest variability has been found among the measurement of S=O and N-H bonds.

In order to better understand the effects of extenders on neat bitumen, the area of each bituminous binder calculated at the six considered chemical indices was divided by the corresponding area of the reference bitumen. Hence, these ratios eliminate the noise caused by the base bitumen (Pen 50/70) highlighting the effect of bitumen modification. Indeed, considering the Pen 50/70 the corresponding ratios of the six areas are equal to 1. The ratio of areas was determined applying Equation 8, which represents a modification index:

$$\frac{A_{BVxRx}}{A_{Pen\ 50/70}} \tag{8}$$

, where A_{BVxRx} and $A_{Pen\ 50/70}$ are the integrated normalized area at each index of a specific innovative bituminous binders and Pen 50/70, respectively. The results of area ratios (modification index) and the error bars that represent the 95% confidence interval (CI) at the six wavenumber limits are shown in Fig. 3.12. These representations allow evaluating and comparing the influence of processing conditions, type and amount of recycled products on the final bituminous binders.



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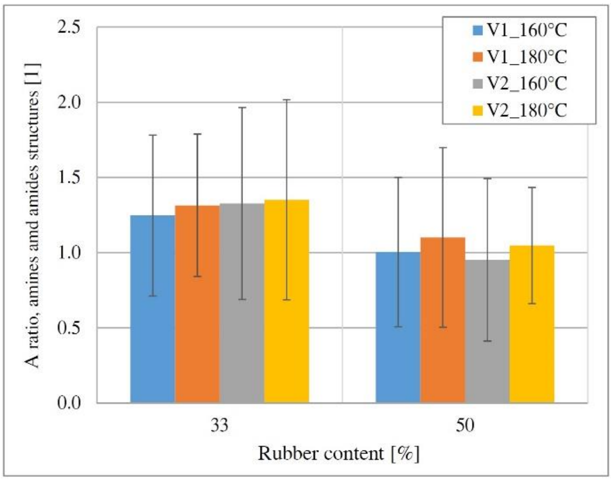

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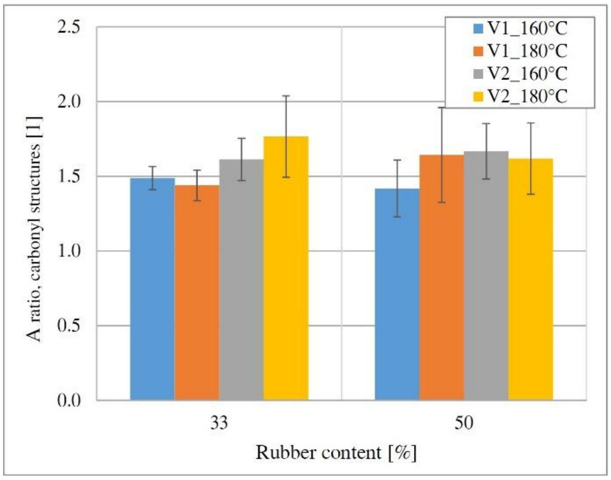

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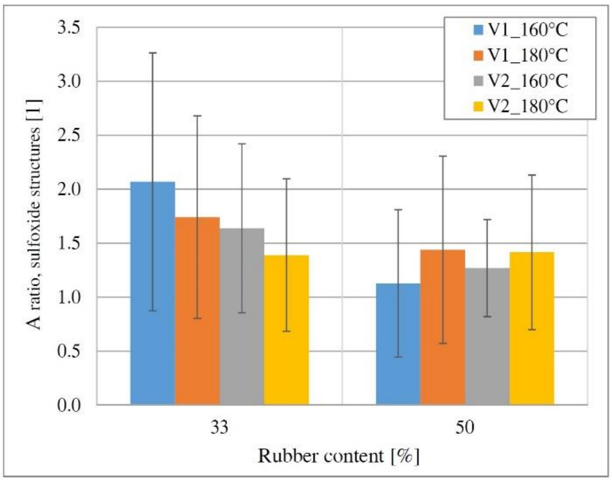

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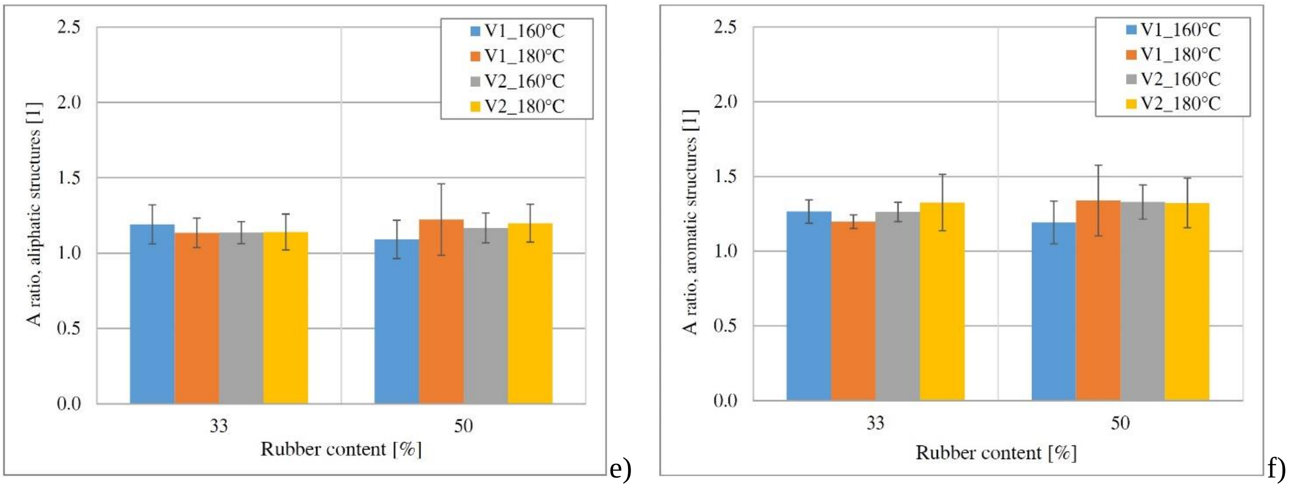


Fig. 3.12. Calculated area ratio between each fresh extended bitumen and Pen 50/70 at six wavenumber bands: a) Butadiene structures; b) amines and amides structures; c) carbonyl structures; d) sulfoxide structures; e) aliphatic structures; f) aromatic structures.

Fig. 3.12b and Fig. 3.12d confirm the effect of REOBs on sulfoxides, amines and amides molecules. Increasing the R content from 33% to 50%, the results of the modification index at these two wavenumber limits decreased for all extended bitumens; hence, in accordance to the amount of REOB. Regarding the formation of N-H bonds, no significant effects were caused by changing the processing temperature and type of REOB, as the results were almost the same for all R-REOB-modified bitumens. Albeit minimal changes, the extended bitumens that incorporated V2 showed higher values of modification index compared to R-V1-modified bitumens, which reflect the chemical composition of Vx as shown in Table 2.7. The amount of N-H structures in extended bitumens increased from the unit values of Pen 50/70 when the materials included extenders with R-REOB ratio equal to 1:2. Then, the ratios decreased to the reference value (1) when the quantity of R and REOB were the same. The effect of REOB quantity was more evident concerning the presence of sulfoxide functional group. Increasing the amount of R particles, the formation of S=O bonds in extended bitumens exhibited opposite trends in terms of production temperature and type of REOB.

The incorporation of R particles is expected to increase the integrated area between 955-970 cm^{-1} that corresponds to the vibration of butadiene molecules. Despite no evident peak was detected by the device, the FTIR spectra of R-REOB-modified bitumens were higher than that of Pen 50/70 and, consequently, the modification index exhibited values greater than unit as shown in Fig. 3.12a. Nevertheless, the butadiene molecules increased as soon as R was added to the neat bitumen, but their growth is not directly related to R quantity. Considering all modified bitumens at R content equal to 33%, it can be highlighted that R-V1-modified bitumens helped the formation of butadiene structures. This may be related to higher compatibility between V1-R extenders and Pen 50/70. As well, the production temperature equal to 160 °C seems to positively enhance the interaction between the recycled polymer and neat bitumen when extenders with R-REOB ratio equal to 1:2 are incorporated.

In general, the responses of extended bitumens at the wavenumeber limits that correspond to the SBR and S=O bonds were similar. The use of V1-extenders produced at 160 °C led to increase the formation of these two functional groups when the recycled materials were introduced with R-REOB ratio equal to 1:2. Conversely, the addition of R and REOB in the same quantity helped to increase the modification indices of extended bitumens that contain V2 and produced at 180 °C.

Taking into consideration the rheological results of extended bitumens discussed in section 3.3.1, the changes ascribed to R particles such as the improvement of elastic responses were found to increase in extended bitumen produced at higher temperature (i.e. 180 °C). This may be in contrast with the chemical investigations of extended bitumens that contain an higher amount of REOB than R. Considering both results, it may be concluded that high temperature facilitate the interactions between Pen 50/70 and extender and R particles can start to be "digested" by the liquid phase. The release of R chemicals into neat bitumen can explain the enhanced rheological results and the lower amount of chemical functional groups related to R.

The partial substitution of Pen 50/70 for extenders led to increase the aliphatic, aromatic and carbonyl structures. These results confirm the trend exhibited by R-REOB compounds (refer to section 2.4.3 for comparison). Although the area ratios of extenders were calculated removing the noise of the adopted Vx, the presence of R together with Vx clearly increased the aliphatic, aromatic and carbonyl functional groups as shown by the MVs value of the ratios in Table 2.7. The growth of carbonyl functional group was more evident than the formation of aliphatic and aromatic molecules regardless the R content. The carbonyl molecules showed a rapid increase due to the introduction of extender with R-REOB ratio equal to 1:2, then a more gradual enhancement was detected in all bituminous binder that contain the same percentage of R and REOB. In general, aliphatic, aromatic and carbonyl functional groups were less dependent to the quantity of R than the other considered groups like sulfoxide, SBR and N-H structures. Among these three functional groups, the modification indices of aliphatic and aromatic structures exhibited a low variability of results based on type of REOB and production temperature. The use of V2 and higher processing temperature tended to increase the values of the modification indices at these three wavenumber limits; however, the tendency is not unambiguous for all tested samples.

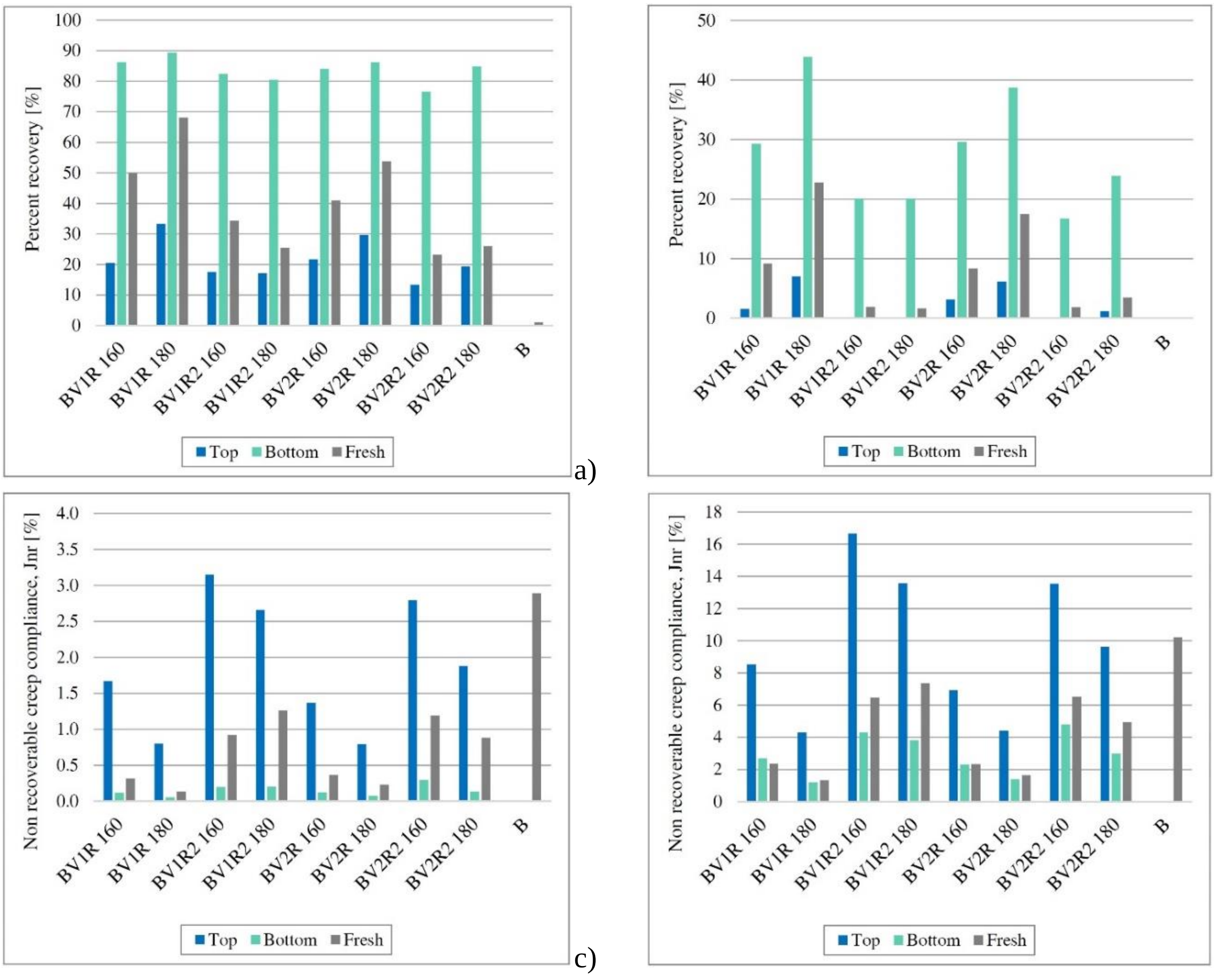
Among all, carbonyl and sulfoxide structures can be related to the ageing of bituminous materials, hence the use of extended bitumens may be disadvantageous in terms of ageing resistance. Hence, it is recommended to further investigate the ageing rate of extended bitumens. This confirms the importance to evaluate the effects of ageing phenomena, which were investigated in the present dissertation and the results are presented later on.

3.3.3 Assessment of storage stability of R-REOB-modified bitumens

Despite the positive contribution of rubber modification on bituminous binders, which has been also assessed in the present research, the rubber-modified bitumens generally show poor storage stability (Szerb et al. 2017) (Ragab and Abdelrahman 2018). The tendency of rubber particles to settle was ascribed to the resulting non-homogeneous mixture of R-bitumen blend due to shape of particles (Ragab and Abdelrahman 2018). However, the interactions between bitumen and rubber or polymers, in general, depends on several variables as explained before in section 2.3. The compatibility of polymer with bitumen and the processing conditions of modified binder affect the interaction between constituent materials. Moreover, depending on variables the interactions can change from a diffusion phenomenon toward a de-polymerisation/de-vulcanization process (Lo Presti 2013) (Lo Presti and Airey 2013) (Zanetti et al. 2015). To limit or better prevent the sedimentation of solid particles, some researchers have deeply investigated the processing conditions in order to optimize the process (Ragab and Abdelrahman 2018), while others focused on additives that can act as surfactant (Szerb et al. 2018). For the development of feasible extended bitumens, the assessment of their storage stability represents a crucial aspect since they contain a high percentage of rubber. To determine the tendency of R particles to separate from Pen 50/70 during static storage at high controlled temperature all extended bitumens underwent a specific conditioning following the standard EN 13399 (2017). The information about the adopted conditioning are detailed in section 3.2.2.

After conditioning, two parts of the same sample, distinguished as top and bottom, have been subjected to MSCR test according to the standard ASTM D7405-15 (2015). The top and bottom parts correspond to the upper and lower parts, respectively, of a tube where each sample was conditioned. Detailed information can be found in section 3.2.2.1. The results gained from both parts are reported in Fig. 3.13 in terms of percent recovery (%R) and non-recoverable creep compliance (J_{nr}) parameters. The representations in Fig. 3.13 includes results of the neat and extended bitumens in fresh conditions.

Each extended bitumen in fresh conditions exhibited an intermediate behaviour between those collected from the corresponding top and bottom parts with regard to %R and J_{nr} values. This means that the storage at high temperature detrimentally affected the elastic response and the rutting resistance of R-REOB-modified bitumens, since the two parameters correlate with the elastomeric response of polymer in bituminous binders and the rut resistance of the final product, respectively (D'Angelo et al. 2010). In general, at the lower shear stress, the extended bitumens showed improved elastic responses and rutting resistance than Pen 50/70 regardless the application of the separation conditioning. Applying the shear load equal to 3.2 kPa a higher variability among the results of %R and J_{nr} were registered. All innovative bituminous binders that contain R and REOB in the same percentage showed greater recoverable strains (%R) and lower non-recoverable deformations (J_{nr}) of both parts (top and bottom) than neat bitumen. The R particles seem to release components when interacting with Pen 50/70 allowing the top part of conditioned extended bitumen to behave more elastically and to withstand greater permanent deformations than base bitumen. Hence, it may be concluded that R-bitumen interactions combine physical and chemical phenomena. The top parts of extended bitumens that incorporate extenders with R-REOB ratio equal to 1:2 exhibited similar or lower elastic behaviour than unmodified bitumen. Thus, the use of extenders with 33% R content was not always sufficient to form a polymer network that can improve the elastic responses of the final binders after sedimentation. In particular, the applied conditioning reduced the elastic response and the resistance against permanent deformation of the top parts of samples BV1R2 160 and BV1R2 180, which showed lower %R and higher J_{nr} than Pen 50/70. The extenders and extended bitumens manufacturing at 180 °C improved the behaviour of the final products of both top and bottom parts of the same sample. The higher temperatures can facilitate the entanglement of polymer molecules with neat bitumen. The influence of Vx type was ambiguous.



a) b) c) d)

Fig. 3.13. Percent recovery and J_{nr} comparison of extended bitumens and Pen 50/70 at Top, Bottom and fresh conditions applying two stress levels: a) %R at 0.1 kPa; b) %R at 3.2 kPa; c) Jnr at 0.1 kPa; d) Jnr at 3.2 kPa.

3.4 Impact of ageing on extended bitumens rheology and chemistry

Bitumen as organic materials are prone to ageing mainly by oxidation (Hofko et al. 2017) as the atoms present in the material react with the atmospheric oxygen. These reactions occur due to the photo-oxidation and thermal reactions which lead to the diffusion-driven phenomenon of oxygen into bitumen (Lu et al. 2008). In general, the diffusion phenomenon is driven by the internal heat energy and is influenced by several parameters. The average radius of the diffusing molecules and the viscosity of the diffusion medium affect the rate of oxygen diffusion. Furthermore, intermolecular interactions, polarity and temperature influence indirectly this phenomenon (Karlsson and Isacsson 2003) (Herrington 2012). Also, temporal changes in the concentrations of oxygen and reactive bitumen species during the ageing reaction can affect the reaction itself (Herrington 2012).

The oxidation of bitumen fractions generates a number of chemical functional groups such as ketones, sulfoxides, carboxylic acids and dicarboxylic anhydrides. Ketones are formed from specific aromatic molecules that have two adjacent benzylic carbon moieties. When those molecules are oxidized, first, they result in the formation of dicarboxylic anhydrides and then, ketones are made by condensation. Carboxylic acids are produced in small amounts. On the other hand, sulfoxides are the result of organic sulphides oxidation, which represent functional moieties of many types of bitumen (Petersen 2009). The type of oxidation products are consistently the same for bitumen from different sources, but their amount may differ especially between unmodified and polymer-modified bitumen (Lu et al. 2008). In fact, Lu et al. (2008) found that sulfoxides have grown more in the neat bitumen, while a greater presence of carbonyl were detected in SBS-modified bitumen under the same ageing conditioning. For this reason, it is crucial to evaluate the ageing tendency of the R-REOB-modified bitumens that have been developed in the present research.

The rheological and physical characteristics of bituminous binders and asphalt mixtures are strongly related to the chemical ones. Ageing changes the viscoelastic behaviour of the material over time towards higher stiffness and brittleness (Hofko et al. 2017). Oxidative ageing increases binder viscosity, which depends on the type and strength of molecular interactions (Petersen 2009). Moreover, ageing causes an increased stiffness (higher G* values) and elasticity (lower δ values) of unmodified and modified bituminous binders (Lu et al. 2008) (Molenaar et al. 2010) (Tarsi et al. 2018). The more brittle bituminous binders due to the ageing processes that asphalt pavements experienced during the service life lead to asphalt mixtures prone to ravelling and cracking (Molenaar et al. 2010).

3.4.1 Rheological analysis on aged extended bitumens

Two samples of each aged bituminous binder underwent AS test at 10 °C. Since the extended bituminous binders behaved as traditional bitumens (refer to section 3.3.1), the determination of the LVE range at the intermediate (30 °C) and at the highest temperature (60 °C) of the FS test was omitted. The maximum applicable strain so as to be in the selected LVE range of all aged bituminous binders listed in Table 3.7 was used. In order to compare the results of bituminous binders before and after ageing the LVE intervals in fresh conditions have been also reported in Table 3.7. The oxidative ageing reduced the maximum applicable strain to avoid irreversible structural changes of Pen 50/70 and V1-R-modified bitumens. Conversely, the aged extended bitumens with V2 exhibited higher LVE range than the corresponding values in fresh conditions. Moreover, the use of V2 allowed the increment of LVE intervals than those of extended bitumens produced with V1 in aged conditions. The higher content of R incorporated into extended bitumens and the production of extenders at 160 °C affected the maximum strain negatively as the LVE range diminished. This first characterization of binders showed higher ageing susceptibility of extended bitumens manufactured with V1 and equal mass proportion of recycled materials at the lower processing temperature (160 °C).

The aged extended bitumens behaved as more elastic-like materials since the storage modulus (G’) was always higher than the loss modulus (G’’). These responses agreed with the results of fresh extended bitumens (refer to Fig. 3.3). Moreover, the values of G’ and G’’ of each aged innovative binder were increased compared to the data collected on unconditioned samples; also, their differences were more evident. These trends reflect the stiffening effect of ageing processes as commonly found in literature. In order to evaluate the increment of stiffness in R-REOB-modified bitumens, the results of AS tests were represented in terms of complex modulus versus strain, which are plotted in Fig. 3.14. The graph showed that the aged extended bitumens were less or as stiff as the reference bitumen in fresh conditions. The incorporation of R-REOB blends resulted in a softer binder than Pen 50/70 after ageing also. Comparing the results of aged innovative bituminous binders, the production of extenders and extended bitumens at higher temperature (180 °C), the use of V1 and the higher percentage of R allowed the reduction of G* values after ageing. Consequently, it may be concluded that these conditions (i.e. 180 °C processing temperature, 1:1 R-REOB ratio, V1-extenders) may reduce the ageing susceptibility of the extended bitumens. The R content exhibited an opposite influence on the stiffness of the aged binders with respect to fresh extended bitumens.

Table 3.7. Linear viscoelastic (γ_{LVE}) range of fresh and aged extended bitumens and Pen 50/70 at 10°C.

Type of REOB	Sample	γ_{LVE} @ 10°C	
		FRESH	AGED
V1	BV1R 160	1.010	0.790
	BV1R 180	0.943	0.883
	BV1R2 160	1.002	0.883
	BV1R2 180	1.002	1.002
V2	BV2R 160	0.909	0.943
	BV2R 180	0.791	0.943
	BV2R2 160	0.909	0.883
	BV2R2 180	0.718	1.002
/	Pen 50/70	1.605	1.420

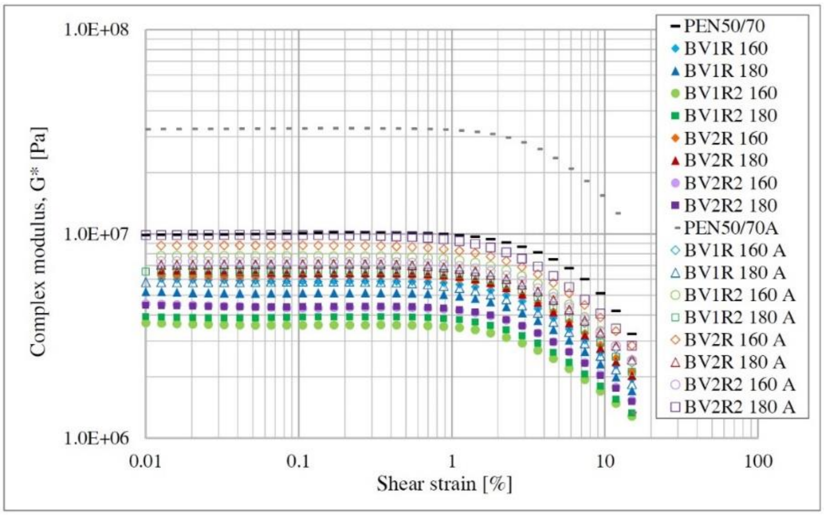


Fig. 3.14. Comparison of G* values of fresh and aged extended bitumens and Pen 50/70 from the AS test at 10 °C.

The results of FS test performed on fresh and aged bituminous binders are plotted in Black spaces for comparison and their representation are shown in Fig. 3.15.

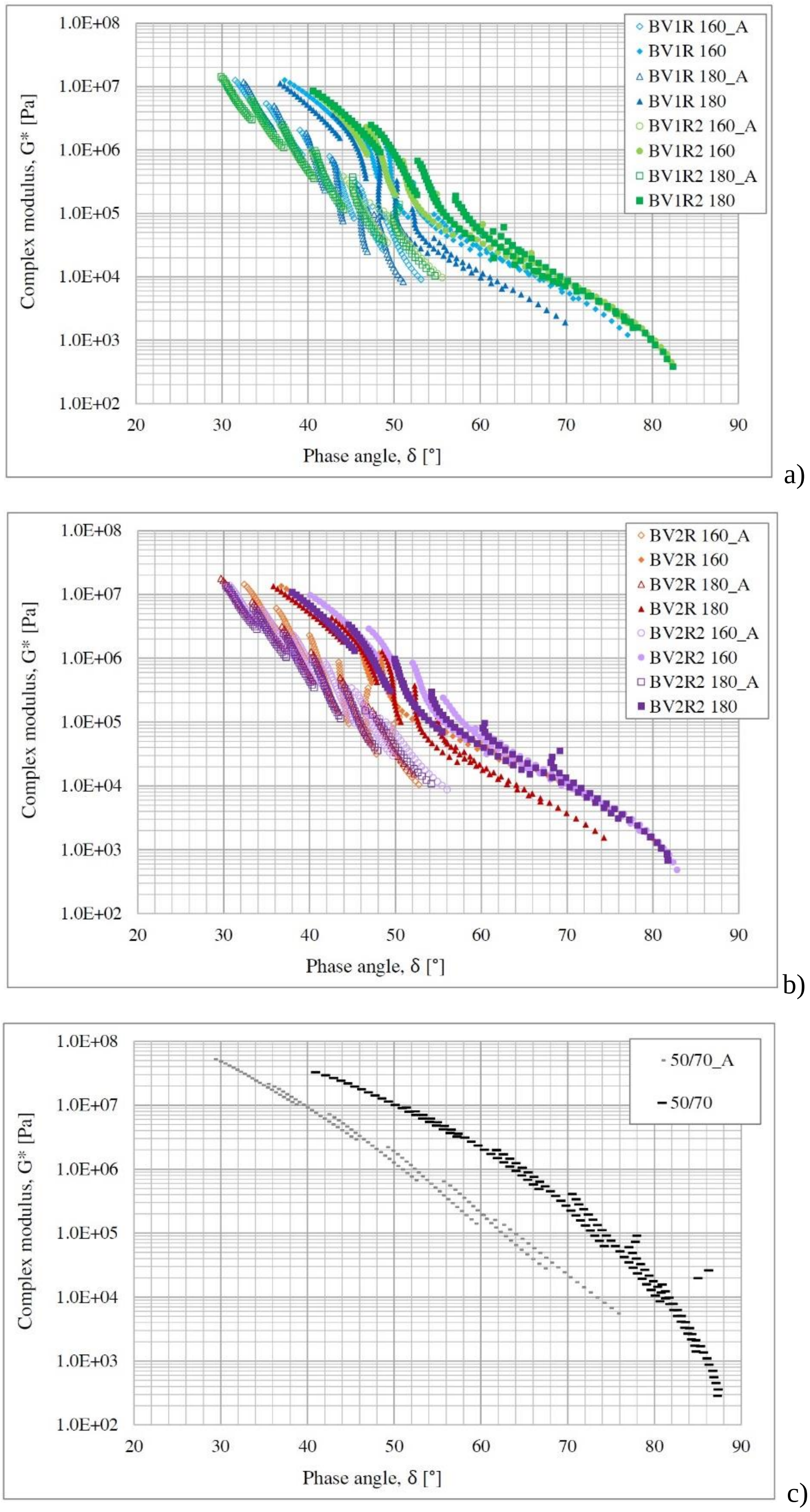


Fig. 3.15. Black diagrams representation for comparison of fresh and aged conditions of: a V1-R-modified bitumens; b) V2-R-modified bitumens; c) Pen 50/70.

The plots clearly showed the stiffening effect of oxidative ageing and the enhanced elasticity of the final products after the application of the ageing protocol. In fact, all G*-δ curves shifted towards higher values of complex shear modulus and lower values of phase angle, respectively. However, it is important to avoid that bituminous materials become too brittle in time leading to asphalt mixtures more prone to ravelling and cracking. Comparing the behaviour of extended bitumens and reference bitumen after ageing, the R-REOB-modified binders exhibited lower phase angles; the maximum δ value of Pen 50/70 was about 20° higher than those of the innovative binders containing recycled products (≈ 56°). The G* values of aged extended bitumens increased, but their maximum values were still lower than that of fresh standard bitumen. In general, the ageing processes decreased the variability of G*-δ curves of extended bitumens, which were less elongated than the corresponding curves of unconditioned samples. It may be concluded that the interactions between bitumen molecules and oxygen reduced the susceptibility of R-REOB-modified binders under frequency and temperature changes. The reference material did not exhibit the same changes. The influence of extender type, manufacturing conditions and compositions was not clear as all curves overlapped each other.

The master curves of aged bituminous binders have been modelled applying the modified Christensen-Anderson-Marasteanu (CAM) model and the William-Landel-Ferry (WLF) equation for shift factors fitting as previously described in section 3.3.1 (Bahia et al. 2001) (Williams et al. 1955). The master curves of the eight extended bitumens at fresh and aged conditions based on the reference temperature equal to 30 °C are reported in Fig. 3.16. The modelled master curves reflect the FS data representation by using the Black space, but they allow interpreting the results over a wide frequency and temperature range. Oxidative ageing stiffened the bituminous binders among all frequency/temperature considered. Nevertheless, the oxygen diffusion phenomenon related to ageing mainly affected the G* values at low frequency and/or high temperature. This may turn into increased rutting resistance of R-REOB-modified bitumen after ageing, which may withstand greater permanent deformations. At opposite boundary conditions that is high frequency and/or low temperature, the stiffening effect did not heavily affect the G* values. Hence, it seems that cracking resistance of R-REOB-modified bitumens did not experience a substantial decrease. In general, the complex modulus master curves of aged extended bitumens behaved similarly. The ageing processes minimized the differences due to the influence of R content, temperature of extender production and type of REOB as the curves almost overlap each other. Regarding the representation of δ values versus reduced frequency (f_r), the phase angle was reduced due to ageing over all frequency/temperature range. In particular, the main differences between fresh and aged results have been found at low frequency and/or high temperature where the δ values dropped from a range of 65 ÷ 80° to 50 ÷ 55°. The ageing processes seem to reduce the elastic effect given by R particles, as the phase angle master curves are almost smooth over all reduced frequencies. As found for G* values of aged material, the δ-f_r curves overlapped each other.

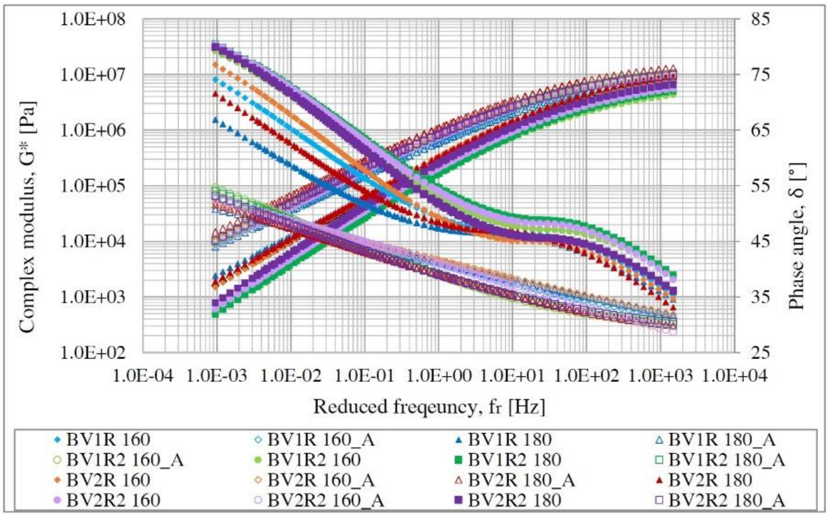


Fig. 3.16. Comparison of G* and δ master curves of extended bitumens at fresh and aged conditions.

To compare the responses of aged extended bitumens with that of aged Pen 50/70, the G* and δ master curves of all aged bituminous binders are reported in Fig 3.17. The complex modulus values of the aged extended bitumens were significantly lower than that of aged neat bitumen at high frequency and/or low temperature. It means that the innovative bituminous binders can better withstand thermal cracking than Pen 50/70 after undergoing ageing. At opposite boundary conditions (i.e. low frequency and/or high temperature), the eight R-REOB-modified bitumens were slightly stiffer than the reference bitumen after ageing. It results in improved rutting resistance, even moderate, compared to that of Pen 50/70 after ageing. These results reflect the trend of unconditioned bituminous binders. The overlapping of G*-f_r curves of reference material and innovative binders appeared at lower frequency and/or higher temperature than that previously found. The curves overlapped at 40-50 °C approximately; thus, in this condition all bitumens behave similarly. Concerning the phase angle master curves, the behaviour of innovative binders considerably differs with respect to Pen 50/70 in aged conditions. At low frequency and/or high temperature, the extended bitumens experienced a significant reduction of δ values than that of neat bitumen. The values of phase angle differed of about 20°, confirming the interpretation of data without any manipulation (refer to Fig. 3.15 for comparison). Nevertheless, the differences are less with increasing the frequency. At very high frequency and/or low temperature, all bituminous binders showed similar responses after the application of ageing. Therefore, all binders had the same elasticity at this boundary condition.

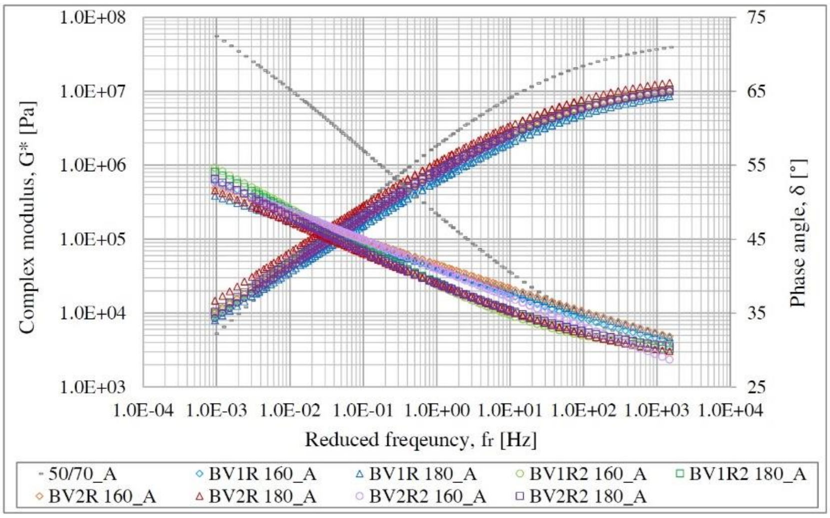


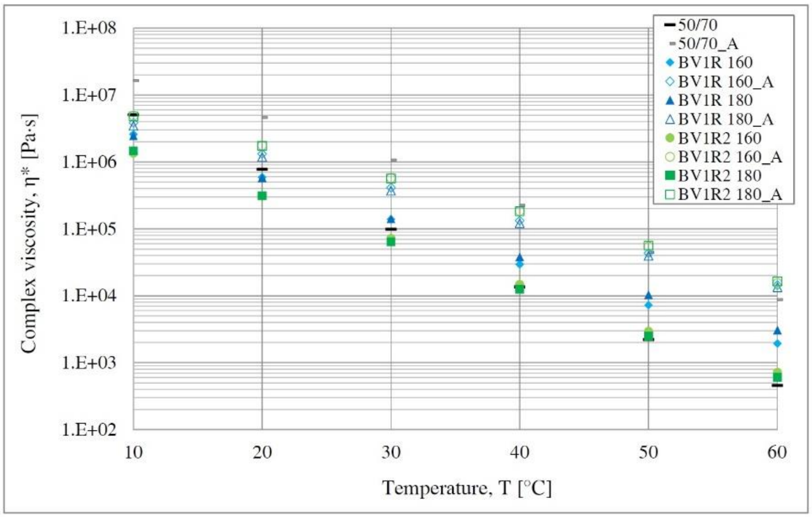
Fig. 3.17. Comparison of G* and δ master curves of extended bitumens and Pen 50/70 in aged conditions.

The crossover frequency of neat ad extended bitumens before and after the application of the ageing protocol are reported in Table 3.8. The data listed in Table 3.8 includes the difference among the values at these two conditioning stage, named as Δf_c. The values of the crossover frequency are expected to decrease due to ageing as lower f_c values suggest that bituminous materials have higher molecular mass and softening point and increased relaxation time (Jing 2019). The Pen 50/70 and R-V1-modified bitumens confirmed this trend. While, the extended bitumens containing V2 did not show the same behaviour. Based on the obtained results, it seems that the innovative binders with V1 are more prone to ageing compared to the corresponding binders with V2 since the Δf_c values are considerable. Concerning the processing temperature and the amount of R, these two variables affected the responses of the final products. In detail, higher temperature of production and greater R content had a negative influence on the difference among the f_c values before and after ageing. Although, the extended bitumens that incorporated the extenders with 1:1 R-REOB ratio were more susceptible to ageing, their f_c values after ageing were higher than those values of aged binders with ratio 1:2. The same trend was show by the extended bitumens produced at 180 °C compared to those manufactured at 160 °C. It should be pointed out that the listed f_c values were obtained from the application of the modified CAM model on the raw data of one replicate of the FS test. Hence, it is recommended to replicate the test and apply other models or analytical methods for further investigate the results. However, the results exhibited the improved behaviour of the innovative bituminous binders that incorporate extenders with the same amount of R and REOB. These R-REOB-modified bitumens showed better performances than standard Pen 50/70, generally.

Table 3.8. Crossover frequency (f_c) of extended bitumens and Pen 50/70 at fresh and aged conditions.

Type of REOB	**Sample**	**Crossover frequency, f_c [Hz]**		**$\Delta f_c = f_{c,fresh} - f_{c,aged}$ [Hz]**
		FRESH	**AGED**	
V1	BV1R 160	109.54	62.55	46.99
	BV1R 180	171.13	76.65	94.49
	BV1R2 160	35.06	35.01	0.05
	BV1R2 180	51.02	42.11	8.91
V2	BV2R 160	58.89	75.16	-16.26
	BV2R 180	110.16	47.80	62.35
	BV2R2 160	35.94	46.67	-10.73
	BV2R2 180	38.09	40.60	-2.52
/	Pen 50/70	67.58	24.92	42.66

The effect of oxidative ageing on complex viscosity and the flow activation energy have been evaluated for all aged bituminous binders as detailed in section 3.3.1. The complex viscosity of neat and extended bitumens before and after ageing are reported in Fig. 3.18. The graphs in Fig. 3.18 show the complex viscosity determined at six test temperatures considering the lowest frequency applied performing the FS test, i.e. 0.10 Hz. The results of complex viscosity showed a temperature-dependent behaviour of all binders as the viscosity decreased when the test temperature increased regardless the application of the ageing protocol. The η* values before and after ageing exhibited higher differences as test temperature increased. As observed in Fig. 3.7, the complex viscosity of fresh extended bitumens were influenced by the R content, the type of REOB and the production temperature of extenders and extended bitumens. On the other hand, aged materials exhibited minor changes due to these variables. In general, the use of V2 and higher temperature during production of extenders and extended bitumens led to greater η* values among all test temperatures. However, this effect can be observed to innovative binders with equal percentage of R and REOB only. The introduction of extenders with R-REOB ratio equal to 1:2 nullified this effect and the complex viscosity of all aged extended bitumens were similar. The type of REOB did not significantly affect the values of complex viscosity as all R-REOB-modified binder exhibited η* values with the same order of magnitude.



a)

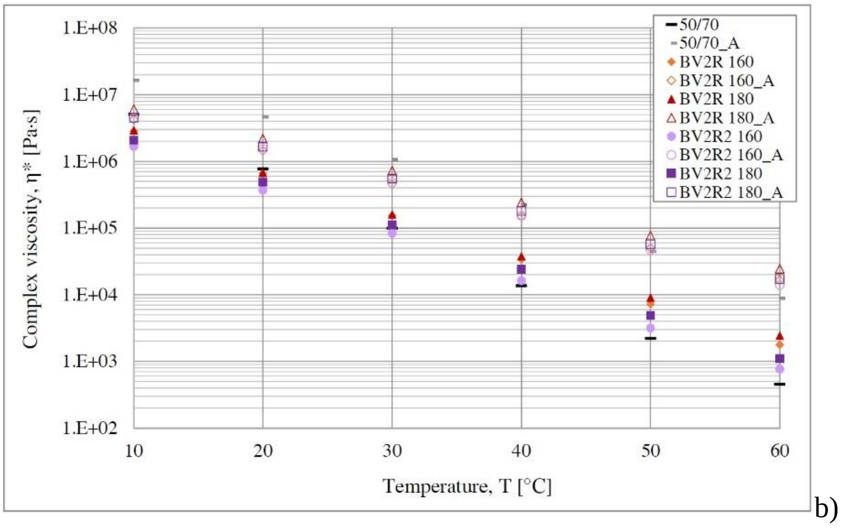


Fig. 3.18. Complex viscosity versus test temperature of extended bitumens and Pen 50/70 before and after ageing by the type of REOB: a) V1; b) V2.

The ageing reduced the flow activation energy of all bituminous binders. The lowered E_a values together with the enhanced η^* values led to decrease the thermal susceptibility of all bituminous products regardless the modification that has been done. However, the ageing that have been experienced by bituminous binders can vary and turns into different decreasing rate of E_a of various binders. The reduction percentage of E_a caused by ageing is reported in Table 3.9. Among all binders, the neat bitumen showed the lowest ageing influence as the reduction was equal to 20%. The decrease rate of sample BV1R 180 can be neglected since it disagrees with the behaviour of all other extended bitumens. In general, the modified binders that contain V1 experienced lower changes compared to V2 samples. Also, the use of higher R content decrease the influence of ageing on E_a values. The effect of temperature production on activation energy was not clear.

Table 3.9. Decrease rate of activation flow energy of extended bitumens and Pen 50/70 due to ageing.

Sample	Decrease rate of E_a [%]
BV1R 160	22.67
BV1R 180	16.00
BV1R2 160	24.38
BV1R2 180	27.83
BV2R 160	25.02
BV2R 180	22.37
BV2R2 160	25.75
BV2R2 180	26.32
Pen 50/70	20.01

The percent recovery (%R) and non-recoverable creep compliance (J_{nr}) were evaluated by means of MSCR test on aged bituminous binders after the application of the TFOT and PAV tests. As detailed in section 3.2, the test was carried out by applying a different load during the second phase of the test itself, which were 1.0 kPa and 3.2 kPa. While, the first phase of the MSCR test was always performed at 0.1 kPa. Consequently, all MSCR replicates at the first shear load (0.1 kPa) obtained similar elastic parameters. Furthermore, the parameter $J_{nr,diff}$ that represents an indicator of stress sensitivity of the bituminous materials was evaluated according to Equation 7, which considers the results of MSCR test at 0.1 kPa and 3.2 kPa only. As previously detailed, the $J_{nr,diff}$ should provide insights into the relationship between laboratory-measured changes in J_{nr} across the range of applied stress, to changes in field performance of the asphalt mixes, and the original intent was to define an upper limit of the $J_{nr,diff}$ parameter equal to 75%. The results at three shear creep loads that have been considered are reported in Table 3.10 for %R data and Table 3.11 for J_{nr} data, where the deformation values averaged the data of all replicates. The results were determined considering the last 10 creep cycles performed at 0.1 kPa and the 10 cycles at the higher shear stress.

Both parameters, i.e. %R and J_{nr}, were stress-dependent as in fresh conditions. In general, all aged bituminous binders showed improved elastic responses and higher rutting resistance compared to those found in fresh conditions (refer to Tables 3.4 and 3.5 for comparison). This behaviour at 60 °C reflected the increased stiffness and the more evident elasticity caused by ageing processes. In fact, the oxygen uptake led to decrease the δ values of all binders at all test conditions. As a result, the MSCR test confirmed the results of FS tests, which were observed above. In addition, the aged R-REOB-modified bitumens showed improved performances than Pen 50/70 overall the shear creep loads that have been applied. This response reflected the results of fresh bituminous binders; hence, the ageing did not annul the more elastic behaviour of extended bitumens.

With respect to the three variables considered for producing R-REOB compounds, the higher R content and processing temperature improved the recoverable elastic strains and reduced the non-recoverable deformations of extended bitumens after ageing, confirming the results of fresh materials. Conversely, the type of REOB affected the MSCR results to a lesser extent. The positive contribution of R particles persisted after ageing and, also, it represented the main contribution to the elasticity of bituminous binders at high temperatures in terms of %R and J_{nr}. This trend confirms the assumption that %R values are directly related to the amount of the elastomeric polymer in the mix and the extent of networking of the polymer in the binder (D’Angelo et al. 2010). The extended bitumens with higher R content that showed low J_{nr} values may reflect a better rutting resistance at the binder and the mixture levels (D’Angelo et al. 2010). The type of REOB influenced the %R and J_{nr} parameter differently. The effects are ambiguous in terms of recoverable deformations, i.e. %R; while, the use of V2 led to increase the rutting resistance of the resulting innovative bituminous binders as the J_{nr} values decreased. The incorporation of R-REOB compound increased the resistance of Pen 50/70 against permanent deformations before and after ageing.

In terms of stress-sensitivity, all aged bituminous binders, including Pen 50/70, exceeded the maximum limit of $J_{nr,diff}$ that is fixed at 75%. As in fresh conditions, all materials exhibit a high sensitivity when tested at 60 °C (refer to Table 3.5 for comparison). The results are not unexpected as the compliance with this limit was found to be challenging in previous research (Stempihar et al. 2018), and very elastic bituminous materials amplified this issue. Conversely than $J_{nr,diff}$ values in fresh conditions, the extended bitumens with lower content of R (R-REOB ratio equal to 1:2) showed higher values of this parameter after undergoing the ageing protocol. On the other hand, the processing temperature equal to 180 °C and the incorporation of V1 led to increase the $J_{nr,diff}$ results of the corresponding extended bitumens, confirming the results obtained in fresh conditions. Pen 50/70 showed the lowest value of this parameter compared to the innovative bituminous binders. Hence, the addition of R did not reduce the stress sensitivity of the binders also after ageing. The previous study of D’Angelo et al. (2010) ascribed this difference to the non-cross linking of the polymer. Comparing the results of all bituminous binders at fresh and aged conditions, it can be observed a reduction of the stress-sensitivity of all bituminous binders after the application of the ageing protocol. The standard bitumen showed the lowest difference among the $J_{nr,diff}$ values before and after ageing. While, among the R-REOB-modified bitumens, those containing R and Vx in the same quantity exhibited greater differences.

Table3.10. %R of aged extended bitumens and Pen 50/70 at three stress levels (0.1, 1.0 and 3.2 kPa).

Sample	**Percent recovery [%]**		
	Stress=0.1 kPa	**Stress=1.0 kPa**	**Stress=3.2 kPa**
BV1R 160	85.75	82.97	78.31
BV1R 180	87.02	84.04	78.85
BV1R2 160	83.71	79.77	69.64
BV1R2 180	84.65	77.15	71.25
BV2R 160	85.72	82.54	79.05
BV2R 180	86.95	84.16	80.47
BV2R2 160	80.48	77.50	69.60
BV2R2 180	84.95	78.70	73.66
Pen 50/70	38.91	34.82	33.03

Table3.11. J_{nr} and $J_{nr,diff}$ of aged extended bitumens and Pen 50/70 at three stress levels (0.1, 1.0 and 3.2 kPa).

Sample	**Jnr [kPa^{-1}]**			**Jnr,diff [%]**
	Stress=0.1 kPa	**Stress=1.0 kPa**	**Stress=3.2 kPa**	/
BV1R 160	0.0167	0.0198	0.0880	399.94
BV1R 180	0.0138	0.0174	0.0740	420.85
BV1R2 160	0.0200	0.0251	0.1297	545.17
BV1R2 180	0.0195	0.0274	0.1267	539.85
BV2R 160	0.0141	0.0207	0.0606	392.60
BV2R 180	0.0111	0.0147	0.0537	402.15
BV2R2 160	0.0233	0.0263	0.1370	439.45
BV2R2 180	0.0160	0.0210	0.0898	502.82
Pen 50/70	0.0963	0.1069	0.3073	251.20

As mentioned above, the stress-sensitivity of polymer-modified bitumens can be correlated to the development of a polymer network and the related cross-linking of the added polymer. The higher stress-sensitivity of R-REOB-modified bitumens than Pen 50/70 that has been previously detected may be ascribed to the behaviour of R particles that act as a filler (no cross-linking of polymer occurred). In order to deeper investigate the presence and the effect of R, the results of the two parameters of the MSCR test were plotted in the same graph, reporting the percent recovery versus the non-recoverable creep compliance at 3.2 kPa. The results of fresh and aged extended bitumens are illustrated in Fig. 3.19 together with a reference curve represented by Equation 9:

$$R_{3.2} = 29.731 \cdot {J_{nr,3.2}}^{-0.2633} \tag{9}$$

, where $R_{3.2}$ and $J_{nr,3.2}$ represent the average percent recovery and non-recoverable creep compliance obtained applying a shear load equal to 3.2 kPa. According to the standard AASHTO R92-18, this curve can be used to identify the presence of an elastomeric polymer (Liu et al. 2021). Specifically, when $R_{3.2}$-$J_{nr,3.2}$ data points fall on or above the curve can be concluded that the bituminous binders are modified with an acceptable elastomeric polymer. Moreover, it is important to underline that $J_{nr,3.2}$ values less than 0.1 kPa^{-1} should have a minimum $R_{3.2}$ value of 55%, and $J_{nr,3.2}$ values larger than 2 kPa^{-1} are not required to have any minimum (Liu et al. 2021). The AASHTO standard is primarily intended to be used with the residue of the rolling-thin-film-oven-test (RTFOT), but it may also be run on residue from the PAV test. In Fig. 3.19 the results on the residue of the PAV test are presented. The $R_{3.2}$ versus $J_{nr,3.2}$ data points of all aged R-REOB-modified bitumens were above the limiting curve as shown in Fig. 3.19. Thus, it is confirmed that an elastomeric polymer modified all innovative binders. However, taking into account the previous data on $J_{nr,diff}$, the added R particles may not have formed an adequate polymer network able to reduce the stress-sensitivity of the final product.

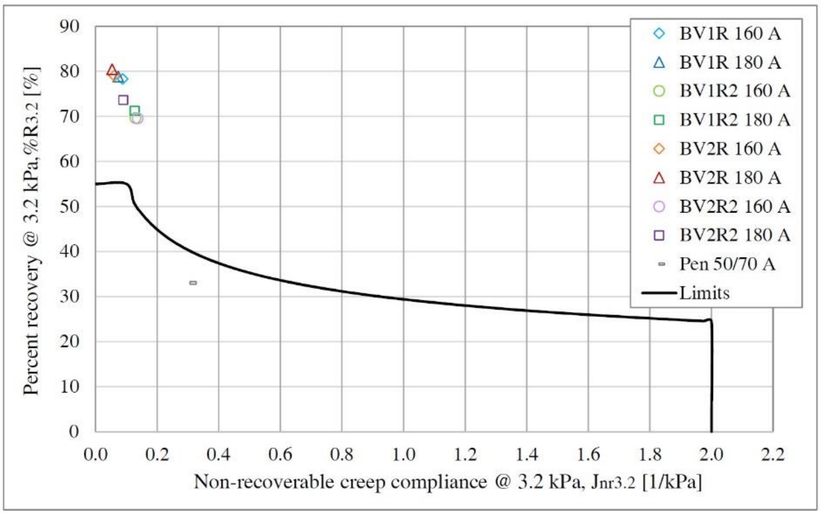


Fig. 3.19. Results of MSCR test, $R_{3.2}$ versus $J_{nr,3.2}$ values of aged extended bitumens and Pen 50/70.

The rheological analysis of bituminous binders after ageing confirmed the improved elastic response of extended bitumens due to the incorporation of R-REOB blends. And, the presence of R particles has the major contribution to binders' elasticity. In general, the oxygen uptake during ageing processes stiffened the final bituminous products. Nevertheless, the reference material was stiffer than all extended bitumens after undergoing ageing conditioning. With respect to constituent materials and processing conditions of extenders and extended bitumens, higher production temperature and R percentage, and the use of V1 resulted in reduced stiffness of innovative bituminous binders than the corresponding R-REOB-modified bitumens; however, V2-R-modified bitumens exhibited wider LVE ranges. In general, the influence of R content, type of REOB and processing temperature of R-REOB blends and extended bitumens affected the results of aged innovative binders at a lesser extent compared to those in fresh conditions. Samples that underwent ageing exhibited a lower variability of all rheological parameters turning into similar behaviour of all aged extended bitumens. Both, thermal- and stress-sensitivity were found to be reduced due to ageing. The stiffening effect of ageing was more evident at low frequency and/or high temperature, which can result in bituminous binders less prone to rutting. The enhanced performances at high temperature were confirmed by the results of the MSCR test. At opposite conditions, the eight innovative binders showed increased G* values. This means that R-REOB-modified bitumens can experience lower thermal cracking than an asphalt mixture that has been made with standard Pen 50/70.

3.4.2 FTIR spectroscopic analysis on aged extended bitumens

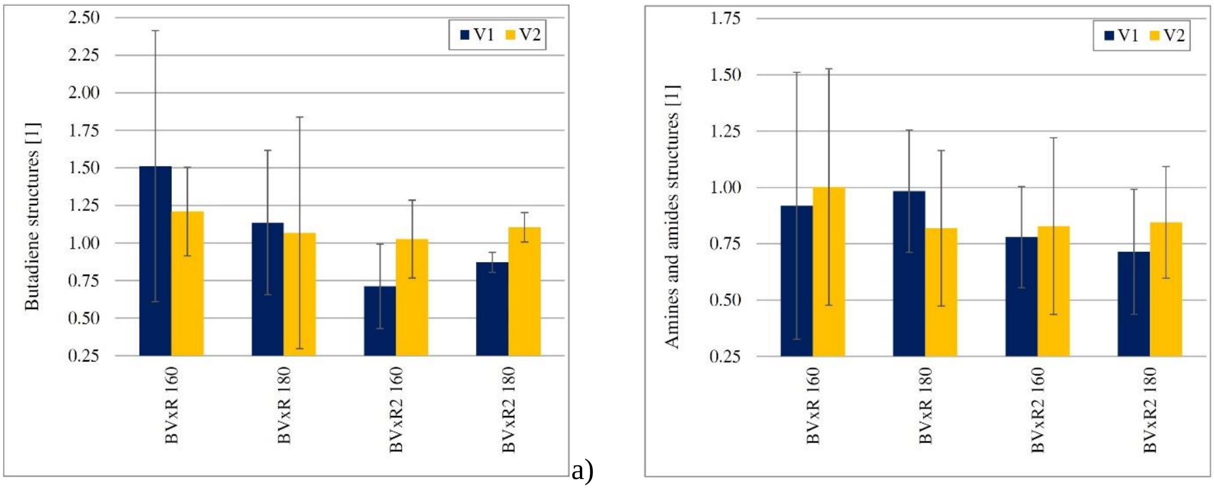
The chemical investigation by means of FTIR spectrometer is commonly used to detect and monitor the changes in the chemical composition of bituminous binders after ageing (Nivitha et al. 2016). In fact, the oxidative ageing reactions that cause enhanced stiffness and brittleness of bituminous materials can be related to the increasing association among polar components of binder itself (Hofko et al. 2017). Hence, changes in rheological properties can be correlated to changes in chemical composition of the bituminous binder. The effect of ageing on bituminous products using spectra analysis has been evaluated tracking specific molecular bonds. The aliphatic, aromatic, carbonyl, sulfoxide and long chains structures were evaluated in several studies (Lamontagne et al. 2001) (Van den bergh 2011) (Tarsi et al. 2018). Among all, carbonyl and sulfoxide bands were found to be more affected by ageing, which increase the formation of these molecules (Nivitha et al. 2016) (Hofko et al. 2017) (Li et al. 2019). In the present study, the tendency of bituminous materials to age has been analysed comparing the integrated area of normalized FTIR spectra of the bituminous binders at the six wavenumber limits in fresh and aged conditions. In detail, Equation 10 has been applied to define the ageing index as:

$$\frac{A_{binder,AGED}}{A_{binder,FRESH}} \tag{10}$$

, where $A_{binder,\ FRESH}$ and $A_{binder,\ AGED}$ represent the integrated area of the normalized spectra of a bituminous binder at each specific wavenumber limit considering the fresh and aged conditions of the material itself, respectively. Larger values of each area ratio means higher content of a functional group after ageing compared to that detected on the same material in the unconditioned state (fresh) since the FTIR spectra have higher absorbance values for those molecules' vibrations. The area ratio involves the integrated areas of one replicate measurement of the FTIR analysis on neat and extended bitumens. The FTIR analysis were replicated four times per each bituminous binder and state conditions that is fresh and aged; hence, four ratios at each specific wavenumber limits have been considered. The average area ratios at the six indices for the reference Pen 50/70 are reported in Table 3.12, while, the results of the extended bitumens are represented in Fig. 3.20. Both representations of data report the 95% confidence interval (CI) either listed or illustrated as error bars.

Table 3.12. Average area ratios of Pen 50/70 at fresh and aged conditions at the six indices.

Functional groups	$\frac{A_{Pen\ 50/70,AGED}}{A_{Pen\ 50/70,FRESH}}$	**CI [%]**
Butadiene	0.692	0.182
Amines and amides	0.572	0.382
Carbonyl	1.220	0.158
Sulfoxide	0.661	0.239
Aliphatic	0.991	0.041
Aromatic	1.239	0.486



a) b)

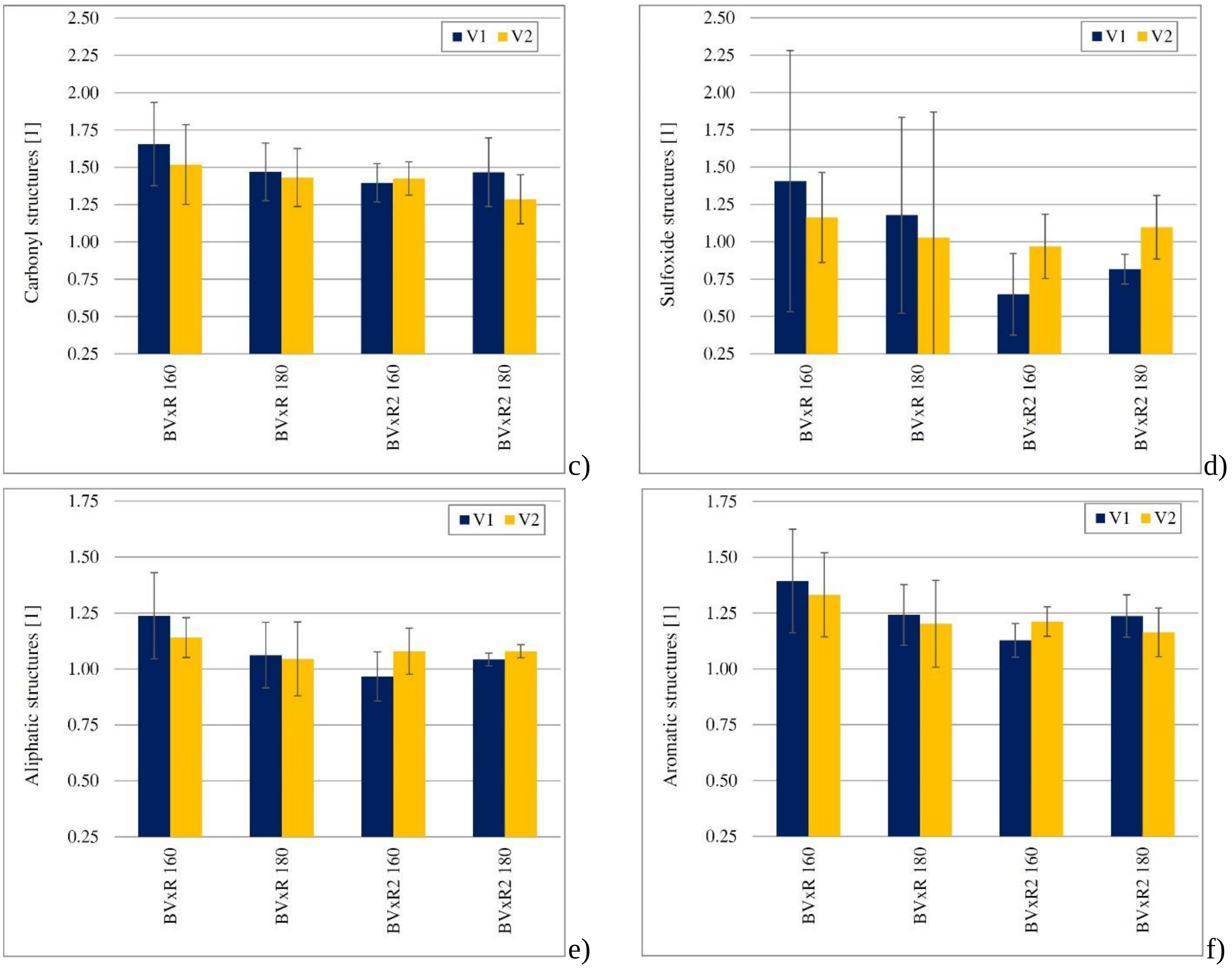


Fig. 3.20. Calculated area ratio between each extended bitumen at aged and fresh conditions at six wavenumber bands: a) Butadiene structures; b) amines and amides structures; c) carbonyl structures; d) sulfoxide structures; e) aliphatic structures; f) aromatic structures.

The characteristic peak ascribed to the presence of R and REOB, i.e. butadiene, amines and amides structures, showed different behaviours after ageing. The amount of butadiene molecules varied among the innovative bituminous binders after ageing; the extended bitumens with R-REOB ratio equal to 1:1 exhibited higher amounts of this functional group than those of extended bitumens with 1:2 R-REOB ratio as expected. The extenders and extended bitumen processing temperature showed an opposite trend between the V1-extended bitumens and V2-extended bitumens; the production of bituminous materials at 180 °C improved the growth of SBR functional group in those materials with higher quantity of Vx than R. As well, the type of REOB influenced the butadiene functional group differently. In terms of N-H bonds, the ageing diminished the presence of this functional group, as the ratio of areas is lower than unity for all R-REOB-modified bitumens. In general, the V2-extended bitumens showed greater amount of amines and amides structures reflecting the chemical composition of Vx. The influence of processing temperature was not clear.

With regard to the two functional groups commonly monitored for evaluating ageing (i.e. carbonyl and sulfoxide groups), the uptake of oxygen was clear leading to increase the C=O bonds in all extended bitumens as the area ratios were higher than 1.25 for all extended bitumens. The binders with higher content of R were more sensitive to ageing, while the use of V2 and lower processing temperature seemed to prevent the growth of carbonyl structures. On the other hand, the S=O bonds did not show a clear trend. Moreover, the sulfoxide structures decreased after ageing in the four extended bitumens with R-REOB ratio equal to 1:2 with no clear trend. As for the carbonyl index, the extended bitumens that contain the same amount of recycled materials were more prone to age. The processing temperature and type of REOB exhibited opposite trends in the innovative bituminous binders with different mass proportion of the R and REOB.

The area ratio at aliphatic and aromatic wavenumber limits experienced an increase due to the ageing. The use of V1 seemed to decrease the growth of these functional groups with a more evident effect on aromatic structures. In general, the introduction of R-REOB blend with an equal mass proportion increased the ageing tendency of the final product. This confirmed the results of unconditioned binders.

In general, the use of V2 can be preferred instead of V1 as it decreases the ageing index in terms of carbonyl and aromatic structures. The reduction of S=O bonds is unexpected as both REOB were rich in sulfoxide molecules.

The comparison between the innovative bituminous binders and the reference bitumen showed that Pen 50/70 is less prone to ageing due to the lower ageing index at carbonyl wavenumber band. While, the extended bitumens perform better concerning the formation of aromatic molecules. The presence of aliphatic molecules can be considered unchanged after ageing as the ageing index is close to unit for both neat and extended bitumen. Also, the values of these functional groups were lower than those of extended bitumens generally. The sulfoxide structures in Pen 50/70 exhibited the same trend as found in the R-REOB-modified binders, hence the S=O bonds decreased after ageing. From chemical investigations on the ageing tendency of bituminous binders, it can be observed a negative effect due to the introduction of recycled materials. However, it should not be neglected that both R and REOBs contain higher amount of aliphatic, aromatic, sulfoxide and, especially, carbonyl molecules. Hence, the ageing tendency of innovative bituminous binders should be investigated deeper analysing the ageing rate of the bituminous product, which may be reduced thanks to the presence of extenders.

3.5 Summary

The replacement of 25%wt. of an extender for standard petroleum bitumen heavily affect the behaviour and chemical composition of the resulting extended bitumen. The innovative bituminous products balance the influence of the main constituents, R-REOB blend and Pen 50/70.

The rheological characterization of extended bitumens highlights the positive effects of R and REOB. The R particles can interact with the bituminous matrix forming a polymer network that enhances the elasticity of bituminous binders. The influence of R is mainly visible at high temperatures, where the recycled polymers improve the rutting resistance of all extended bitumens. The addition of REOB reduces the stiffness of the R-REOB-modified bitumen. The softening effect is marked at low test temperature that results in higher thermal cracking resistance.

In general, the incorporation of a R-REOB blend reduces the thermal susceptibility of the final extended bitumen. On the other hand, they were sensitive to ageing phenomenon. The ageing conditioning stiffens and increases the elasticity of all innovative bituminous binders. The rheological response of R-REOB-modified bitumens was less variable than those of standard bitumen. Albeit aged, the extended bitumens were more elastic and less stiff than Pen 50/70.

The FTIR chemical investigations confirm the contribution of constituents on the final composition of R-REOB-modified bitumens. However, all innovative binders contain higher quantity of typical functional groups related to oxidative ageing at fresh condition already, which are ascribed to the recycled products. Even though the rheological data of extended bitumens were promising, the materials seem more prone to age. This aspect needs additional investigations for evaluating the ageing rate of the material.

From the rheological results of storage stability can be concluded that the interactions between R-REOB blend and neat bitumen combine physical and chemical phenomena. Despite the observed interactions, the R particles settle in time. Hence, the storage stability of the extended bitumens has to be improved.

The type and amount of recycled materials and the processing temperature affect the chemo-rheological response of the extended bitumens. The R-REOB-modified bitumens with high percentage of R and produced at high temperature (180 °C) have improved elastic behaviour and rutting resistance, and they are less vulnerable to temperature changes in fresh conditions. However, the higher amount of R results in high amount of carbonyl structures. Regarding the type of REOB, the introduction of V1 in Pen 50/70 softens the resulting material, but it enhances their elastic response. However, the use of V1 is disadvantageous concerning the ageing tendency of the final bituminous binder.

All R-REOB-modified bitumens are used for further analysis at asphalt mixture level. In fact, the considered variables, i.e. type and quantity of constituent materials and processing temperature, affect the behaviour of the R extended bitumens with similar extent, and all of them exhibit promising results. As a result, it is worth to evaluate their response when combined with aggregates.

4

Micromechanical modelling of extended bitumens

4.1 Introduction

The behaviour of a composite material can be modelled by means of analytical methods, which predict the response of final products based on individual constituents' physical properties and their microstructural aspects. These methods allow determining the effects caused by the introduction of discrete and rigid inclusions into a continuous and less rigid matrix based on homogenization theory. The inclusions disturb the uniformity of the continuous matrix and affect the responses of the final composite system. At first, micromechanical models have been developed to solve this problem and to evaluate the resulting properties of elastic composite materials (Eshelby 1957) (Eshelby 1959). Some of the most common micromechanical models that base on homogenization theory are:

- Dilute model (Eshelby 1957);
- Mori-Tanaka model (Mori and Tanaka 1973);
- Self-consistent model (Hill 1965);
- Generalized self-consistent model (Christensen and Lo 1979);

The models differ for particular simplifications and assumptions made, hence some of them have advantages for specific composites. Then, the application of these models has been extended to viscoelastic mixes thanks to the elastic-viscoelastic correspondence principle (Hashin 1970). Considering the bituminous materials as composite systems, several studies have used the micromechanics theory and the related models, sometimes improving them, to predict the behaviour of polymer-modified bitumens (Wang et al. 2020), bituminous mastics (Buttlar et al. 1999) (Yin et al. 2008), and asphalt mixtures (Luo and Lytton 2011) (Zhang et al. 2018).

The introduction of rigid inclusions such as fillers and granulate additives into a less rigid bituminous matrix stiffs the final blend resulting in a volume-filling reinforcement, which can be adequately described by some of the abovementioned models (Buttlar et al. 1999). However, there are other reinforcement mechanisms to take into account. In fact, the stiffening effect can be also caused by interfacial interations between bitumen and solid particles (i.e. absorption, adsorption and selective sorption) and the interaction among solid particles, which are usually referred as physiochemical and particle-interaction reinforcements, respectively (Buttlar et al. 1999). The complex microstructure of bituminous materials is difficult to model and not all reinforcement mechanisms are considered properly. This may account for inaccurate prediction of rheological parameters especially for high volume concentration of inclusions, which are usually underestimated (Buttlar et al. 1999) (Yin et al. 2008) (Underwood and Kim 2014).

In literature it has been found that the self-consistent model yield accurate predictions of bituminous mastics behaviour (Yin et al. 2008). Concerning the modelling of rubber-modified binders, previous research have found similar and good predictions by Mori-Tanaka model, self-consistent and generalized self-consistent models, especially at high frequencies (Wang et al. 2020). The differences between experimental and modelled data were higher at low frequencies and became greater as the percentage of R increased (Wang et al. 2020). The composite system that includes rubber is a complicated material to model since the volume fractions change in time because of particles swelling and, eventually, digestion. Hence, the reinforcement mechanisms behind volume-filling are more marked. The rubber particles interact with bitumen differently than inert fillers and it has to be considered during modelling and the following interpretation of data.

In the present dissertation, the self-consistent (SC) model has been used to predict the complex shear modulus (G*) of the developed extended bitumens. In case a good prediction of rheological parameters will be observed, the chosen model can be used as a fundamental baseline to preliminary determine the response of R-REOB-modified bitumens with different recipes. Successively, only the combinations that will have met the requirements can undergo characterization. This can allow saving time for producing and testing new bituminous materials.

This chapter describes the homogenization theory and the SC model that were used before showing and discussing the modelled data. The notation used later on is:

- $s, S, \sigma, \boldsymbol{s}$ - letters and boldfaced lower case Latin letters denote scalars and vectors;
- $\boldsymbol{\sigma}, \boldsymbol{\Sigma}$ - boldfaced Greek letters and boldfaced upper case Latin letters denote second and fourth order tensors;
- : - it denotes the contraction between a tensor of order 2 and a 3-vector, $\left[\widetilde{\boldsymbol{C}}{:}\,n\right]_i = C_{ij}n_j$;
- $\langle\cdot\rangle$ or $\langle\cdot\rangle_i$ – they denote an average over the volume.

4.2 Homogenization theory

The purpose of homogenization theory and the related models is to derive the relationship between stress and strain of a composite material (Σ, E), and its constituents (σ, ε), which are related to the macroscopic and microscopic scale, respectively (Ghossein 2014). More specifically, the theory defines the overall response of an inhomogeneous composite material from the behaviour of its constituents and from the geometrical arrangement of more rigid inclusions (Bohm 2020). The homogenization may be interpreted as describing the behaviour of a material that is inhomogeneous at microscopic scale in terms of a (fictitious) homogeneous reference material, energetically equivalent, at some macroscopic scale. The fictitious homogeneous material is sometimes referred to as the homogeneous equivalent medium. The scale transition from micro- to macroscopic scale aim at achieving a marked reduction in the number of degrees of freedom describing the system (Bohm 2020).

The considered composite material is represented by a matrix that have been reinforced by randomly distributed and oriented spherical or ellipsoidal inclusions with a different phase (solid suspensions); hence, the resulting material is a two-phase inhomogeneous product (Ghossein 2014) (Bohm 2020). For this reason, this type of composite materials is usually classified by the microscopic phase topology since the matrix shows a connected topology and the constituents play distinct roles (Bohm 2020).

The homogenization theory considers a representative volume element (RVE) of the composite material, which represents the overall mechanical response of the material itself (Zhang et al. 2018). The RVE must be sufficiently large to allow a meaningful sampling of the microscopic fields and sufficiently small for the influence of the macroscopic gradients to be negligible (Bohm 2020). The RVE can be defined, on the one hand, by requiring them to be statistically representative of a given micro-geometry in terms of purely geometry-based descriptors and the resulting RVE will be independent of the physical property to be studied (Bohm 2020). On the other hand, the definition can be based on the requirement that the overall response with respect to some given physical behaviour depends neither on the actual position of the RVE nor on the boundary conditions applied to it (Hill 1965). In the considered RVE, the volume fraction of each phase sums up to unit (Zhang et al. 2018). In particular, the homogenization technique computes the effective stiffness tensor, $\boldsymbol{C}_C$, or the compliance tensor, $\boldsymbol{S}_C$, of the composite by Equation 11 (Ghossein 2014):

$$\boldsymbol{\Sigma} = \boldsymbol{C}_C : \boldsymbol{E} \tag{11a}$$

$$\mathbf{E} = \boldsymbol{S}_C : \boldsymbol{\Sigma} \tag{11b}$$

, where **E** is the strain tensor of composite material and **Σ** is the stress tensor of the composite material.

It is possible to show that the strain and stress tensors of the composite material are obtained from the average strain and stress of constituents over the volume as described by Equation 12 (Bohm 2020):

$$\boldsymbol{E} = \langle\varepsilon(x)\rangle \tag{12a}$$

$$\boldsymbol{\Sigma} = \langle\sigma(x)\rangle \tag{12b}$$

,where $\langle\cdot\rangle$ denotes an average over the volume, hence the average value of a general function, **f**(x), over the volume of the composite, V, can be described as Equation 13 (Ghossein 2014):

$$\langle \boldsymbol{f}(x)\rangle = \frac{1}{V}\int_V \boldsymbol{f}(x)dV \tag{13}$$

, and where $\langle \varepsilon(x)\rangle$ is the average strain of constituents over the volume and $\langle \sigma(x)\rangle$ is the average stress of constituents over the volume. These two parameters can be related to the average stress and strain of each *ith* phase in combination with each volume fraction as Equation 14 (Wang et al. 2020):

$$\langle \varepsilon(x)\rangle = \sum_{i=1}^{n} \mathrm{c}_i \langle \varepsilon(x)\rangle_i \tag{14a}$$

$$\langle \sigma(x)\rangle = \sum_{i=1}^{n} \mathrm{c}_i \langle \sigma(x)\rangle_i \tag{14b}$$

, where $\langle\cdot\rangle_i$ denotes the volume average over the phase *i*, and where c_i is the volume concentration of the *ith* phase, $\langle \varepsilon(x)\rangle_i$ is the average strain of constituents over the volume of phase *i*, and $\langle \varepsilon(x)\rangle_i$ is the average stress of constituents over the volume of phase *i*. Therefore, from Equations 11a and 12, the constitutive equation of the composite material at macroscopic scale can be written as (Equation 15):

$$\langle \sigma(x)\rangle = \boldsymbol{C}_C\colon \langle \varepsilon(x)\rangle \tag{15}$$

In order to enable the calculation of the effective stiffness and the compliance tensors of the composite, the strain and stress localization tensors are introduced to relate the stress and strain fields of the composite to the local stress and strain tensors in the given RVE. Hence, the strain/stress fields of macro- and microscopic scale are related by the following Equation 16 (Ghossein 2014):

$$\varepsilon(x) = \boldsymbol{A}(x)\colon \boldsymbol{E} \tag{16a}$$

$$\sigma(x) = \boldsymbol{B}(x)\colon \boldsymbol{\Sigma} \tag{16b}$$

, where **A**(x) is strain localization tensor and **B**(x) is the stress concentration tensor. In this regard, the strain and stress fields of each *ith* phase can be written as Equation 17 (Hill 1965):

$$\langle \varepsilon\rangle_i = \langle \boldsymbol{A}(x)\rangle_i\colon \boldsymbol{E} = \boldsymbol{A}_i\colon \boldsymbol{E} \tag{17a}$$

$$\langle \sigma\rangle_i = \langle \boldsymbol{B}(x)\rangle_i\colon \boldsymbol{\Sigma} = \boldsymbol{B}_i\colon \boldsymbol{\Sigma} \tag{17b}$$

, where $\mathbf{A}_i$ is the strain localization tensor within the phase *i* and $\mathbf{B}_i$ is the stress localization tensor within the phase *i*. Being a two-phase material the localization tensors of the composite can be related to the strain/stress localization tensors of each phase and its volume fraction as described by Equation 18 (Hill 1965):

$$\langle \boldsymbol{A}(x)\rangle = (1-\phi)\boldsymbol{A}_M + \phi\boldsymbol{A}_I = \boldsymbol{I} \tag{18a}$$

$$\langle \boldsymbol{B}(x)\rangle = (1-\phi)\boldsymbol{B}_M + \phi\boldsymbol{B}_I = \boldsymbol{I} \tag{18b}$$

, where ϕ is the volume fraction of inclusions, $\mathbf{A}_M$ is the strain localization tensor within the matrix, $\mathbf{A}_I$ is the strain localization tensor within the inclusions, $\mathbf{B}_M$ is the stress concentration tensor within the matrix, $\mathbf{B}_I$ is the stress concentration tensor within the inclusions and **I** is the fourth order identity tensor. The inclusions are considered fully bonded to the matrix, hence, the averaged stress and strain of the composite material contain the contributions from the two phases (Yin et al. 2008). Thanks to the combination of the previous Equations 12, 14, 15 and 17, the following Equation 19 can be obtained (Bohm 2020):

$$\begin{aligned}\boldsymbol{\Sigma} = \langle \sigma(x)\rangle = (1-\phi)\langle \sigma(x)\rangle_1 + \phi\langle \sigma(x)\rangle_2 = (1-\phi)\boldsymbol{C}_M\colon \langle \varepsilon(x)\rangle_M + \phi\boldsymbol{C}_I\colon \langle \varepsilon(x)\rangle_I \\ = [(1-\phi)\boldsymbol{C}_M\colon \boldsymbol{A}_M + \phi\boldsymbol{C}_I\colon \boldsymbol{A}_I]\colon \boldsymbol{E}\end{aligned} \tag{19a}$$

$$\begin{aligned}\mathbf{E} = \langle \varepsilon(x) \rangle = (1-\phi)\langle \varepsilon(x) \rangle_M + \phi \langle \varepsilon(x) \rangle_I = (1-\phi)\boldsymbol{S}_M : \langle \sigma(x) \rangle_M + \phi \boldsymbol{S}_I : \langle \sigma(x) \rangle_I \\ = [(1-\phi)\boldsymbol{S}_M : \boldsymbol{B}_M + \phi \boldsymbol{S}_I : \boldsymbol{B}_I] : \boldsymbol{E}\end{aligned} \tag{19b}$$

, where $\mathbf{C}_\mathrm{M}$ is the stiffness tensor of matrix, $\mathbf{C}_\mathrm{I}$ is the stiffness tensor of inclusions, $\mathbf{S}_\mathrm{M}$ is the compliance tensor of matrix, $\mathbf{S}_\mathrm{I}$ is the compliance tensor of inclusions. From Equations 11 and 19, the effective stiffness and compliance tensors can be consequently defined as Equation 20:

$$\boldsymbol{C}_C = (1-\phi)\boldsymbol{C}_M : \boldsymbol{A}_M + \phi \boldsymbol{C}_I : \boldsymbol{A}_I \tag{20a}$$

$$\boldsymbol{S}_C = (1-\phi)\boldsymbol{S}_M : \boldsymbol{B}_M + \phi \boldsymbol{S}_I : \boldsymbol{B}_I \tag{20b}$$

Applying Equation 18, Equation 20 can be written as:

$$\boldsymbol{C}_C = \boldsymbol{C}_M + \phi(\boldsymbol{C}_I - \boldsymbol{C}_M) : \boldsymbol{A}_I \tag{21a}$$

$$\boldsymbol{S}_C = \boldsymbol{S}_M + \phi(\boldsymbol{S}_I - \boldsymbol{S}_M) : \boldsymbol{B}_I \tag{21b}$$

Because the composite material contains numerous particles and the microstructure varies randomly, it is not feasible to formulate an exact local solution. Fortunately, to obtain the effective stress-strain relation, only the averages of stress and strain are needed (Yin et al. 2008).

The homogenization theory turns the computing problem of the effective stiffness and/or compliance tensors in the definition of the strain and stress localization tensors of the inclusions. Consequently, various micromechanical models have been developed to calculate the localization tensor **A**. In particular, many models base on the Eshelby's *elastic* solution for a spherical or elliptical single inclusion that is embedded in an infinite matrix (Eshelby 1957) (Eshelby 1959) (Ghossein 2014). Eshelby (1957) showed that the strain field of a constrained inclusion is uniform when the composite material is subjected to a uniform stress-free strain, and Equation 22 defines their relationship:

$$\varepsilon^c = \boldsymbol{S}^E : \varepsilon^* \tag{22}$$

, where ε^c is the strain field in the constrained inclusion, ε* is the strain stress (free field applied) and $\mathbf{S}^\mathrm{E}$ is the Eshelby's tensor. The micromechanical models derived from Eshelby's equations are traditionally based on purely elastic solutions. Due to this reason, absolute value of complex shear modulus is directly taken as elastic modulus to use the same formulae. Thus, they can only provide the absolute value of effective complex modulus of bituminous materials but cannot predict the phase angle (Yin et al. 2008). Thanks to the elastic-viscoelastic correspondence principle it is possible to extend their applications to viscoelastic materials as bituminous binders, mortars and asphalt mixtures, which relates the effective complex shear moduli of viscoelastic composite with the effective elastic moduli of composite (Hashin 1970).

The Eshelby's tensor depends on the mechanical properties of the infinite medium as well as on the geometrical properties of the inclusions (Ghossein 2014). Hence, depending on the particular simplifications and assumptions made the use of specific micromechanical models compared to others can be advantageous (Yin et al. 2008).

4.3 Self-consistent model

The self-consistent (SC) model was originally developed for polycrystals and has been extended to composites by the work of Hill (1965) (Ghossein 2014). The present model assumes that each inclusion is isolated as an infinitesimal volume element, which is embedded in an infinite homogeneous matrix whose mechanical properties are the same as the composite (Hill 1965). The strain localization tensor for the SC model is given by Equation 23.

$$\boldsymbol{A}_I^{SCM} = \left[\boldsymbol{I} + \boldsymbol{S}^E : \boldsymbol{C}_C{}^{-1} : (\boldsymbol{C}_I - \boldsymbol{C}_C)\right]^{-1} \tag{23}$$

, where the Eshelby's tensor is obtained considering the effective properties of the composite as the infinite media instead of those of the binder. It is noted that the effective stiffness tensor, $\boldsymbol{C}_C$, is implicitly given when calculating it. Therefore, it needs to be solved using a recursive method by assuming an initial value equal to that of the matrix.

In regard to viscoelastic materials as bituminous binders and mastics, the effective stiffness of the materials can be derived from the relationship between the average strain and the applied loading on the boundary similarly to elastic materials (Christensen and Lo 1979). However, the applied stress has to be uniform and sinusoidal (Yin et al. 2008). The inclusions of a bituminous binder/mastic are elastic, but the binder is viscoelastic, thus, the stiffness (relaxation modulus) is time-dependent (Yin et al. 2008). In what follows, the quantities in the frequency domain are denoted by the over-tilde in order to distinguish them from those quantities that do not depend on time. In general, the bituminous binders, rubber or filler particles are considered as isotropic materials. Therefore, the forth rank tensors $\boldsymbol{C}_I$ and $\boldsymbol{C}_M$ can be described by two independent components of complex bulk modulus and complex shear modulus, written as k_I and μ_I, and $\tilde{k}_M$ and $\tilde{\mu}_M$, respectively (Yin et al. 2008). The effective stiffness tensor can be obtained by the combination of Equation 21a and 23 and its expression is Equation 24 (Yin and Sun 2005):

$$\boldsymbol{C}_c = \boldsymbol{C}_M + \phi(\boldsymbol{C}_I - \boldsymbol{C}_M) \cdot [\boldsymbol{I} - \boldsymbol{S}^E \cdot (\boldsymbol{C}_I - \boldsymbol{C}_C)]^{-1} \tag{24}$$

Considering the materials as isotropic, the effective complex bulk and shear moduli are further written by Equation 25 (Yin et al. 2008):

$$\tilde{k}_C = \tilde{k}_M + \frac{\phi(k_I - \tilde{k}_M)(3\tilde{k}_C + 4\tilde{\mu}_C)}{3k_I + 4\tilde{\mu}_C} \tag{25a}$$

$$\tilde{\mu}_C = \tilde{\mu}_M + \frac{5\phi(\mu_I - \tilde{\mu}_M)\tilde{\mu}_C(3\tilde{k}_C + 4\tilde{\mu}_C)}{6\mu_I(\tilde{k}_C + 2\tilde{\mu}_C) + \tilde{\mu}_C(9\tilde{k}_C + 8\tilde{\mu}_C)} \tag{25b}$$

, where $\tilde{k}_C$ is the complex bulk modulus of composite material, $\tilde{\mu}_C$ is the complex shear modulus of composite materials, $\tilde{k}_M$ is the complex bulk modulus of matrix, $\tilde{\mu}_M$ is the complex shear modulus of matrix, k_I is the complex bulk modulus of inclusions and μ_I is the complex shear modulus of inclusions.

As previously mentioned, to numerically obtain the effective material properties, the effective complex bulk and shear moduli are initialized as $\tilde{k}_C = \tilde{k}_M$ and $\tilde{\mu}_C = \tilde{\mu}_M$. Substituting these values into the right side of Equation 25 updates the effective complex moduli until that they are convergent that is the results of the effective viscoelastic moduli are obtained (Yin et al. 2008).

The extended bitumens were considered as binary composite systems where each extender is embedded in the bitumen matrix. Thus, Pen 50/70 represented the less rigid continuous matrix where the rigid phase, i.e. R-REOB blend, is dispersed. Based on this consideration, the input parameters have been defined and, the SC model has been used to predict the complex shear modulus of the extended bitumens. The input parameters of the model are the rheological data of both constituents, Pen 50/70 and extenders, and the micromechanical aspect of the composite that is represented by the volumetric fractions of inclusions. The complex shear modulus of extenders and reference bitumen have been collected by performing the FS tests. The rheological data were used for characterizing the response of extenders as seen in Chapters 2 and 3. Since the extenders are not thermo-rheologically simple materials, the input data of G* has not be subjected to the modified CAM model, hence, G* were not manipulated from those collected by the DSR. While, the reduced frequency used to plot the master curves exploited the WLF equation (Equation 2) for shift factors fitting.

The corresponding complex bulk modulus of all bituminous materials and R-REOB compound have been determined using Equation 26 (Luo and Lytton 2011):

$$|\mu_i| = \frac{2 \cdot |k_i| \cdot (1 + |\nu|)}{3 \cdot (1 - 2|\nu|)} \tag{26}$$

, where k_i is the complex shear modulus of phase i and υ is the Poisson’s ratio.

The Poisson’s ratio highly depends on material itself, and boundary conditions of tests as frequency and temperature (Yin et al. 2008). In fact, viscoelastic materials like bituminous products cannot be represented by a unique value of this parameter (Aurangzeb et al. 2017). However, practical reasons, such as the absence of experimental devices, methods and multiaxial formulation for viscoelastic characterization, lead to consider two simplifications (Aurangzeb et al. 2017):

- A constant Poisson’s ratio in linear viscoelastic characterization of bituminous materials;
- Similar relaxation functions for complex bulk and shear moduli functions.

As a consequence, the υ value considered in the first attempt was equal to 0.425, that is the mean values of a standard 50/70 penetration grade bitumen found in literature (Di Benedetto et al. 2007). In a second time, the value of the Poisson’s ratio were adjusted thanks to further analysis that tried to directly measure this parameter by direct tensile test. The concerns related to the abovementioned assumptions, the technique used and the results are explained in section 4.5.

The volume fraction of extenders vary based on the R-REOB ratio that has been used for manufacturing the extenders themselves. In fact, the occupied volume by inclusions of recycled products are different albeit the density of materials do not change among all extenders. The volume fraction of each material has been determined as the sum of the weight fraction of each constituent material divided by its density. The considered volume fractions of the two considered mass proportion of the extenders are:

- Extenders with R-REOB ratio equal to 1:1, $\phi = 0.255560$;
- Extenders with R-REOB ratio equal to 1:2, $\phi = 0.255876$.

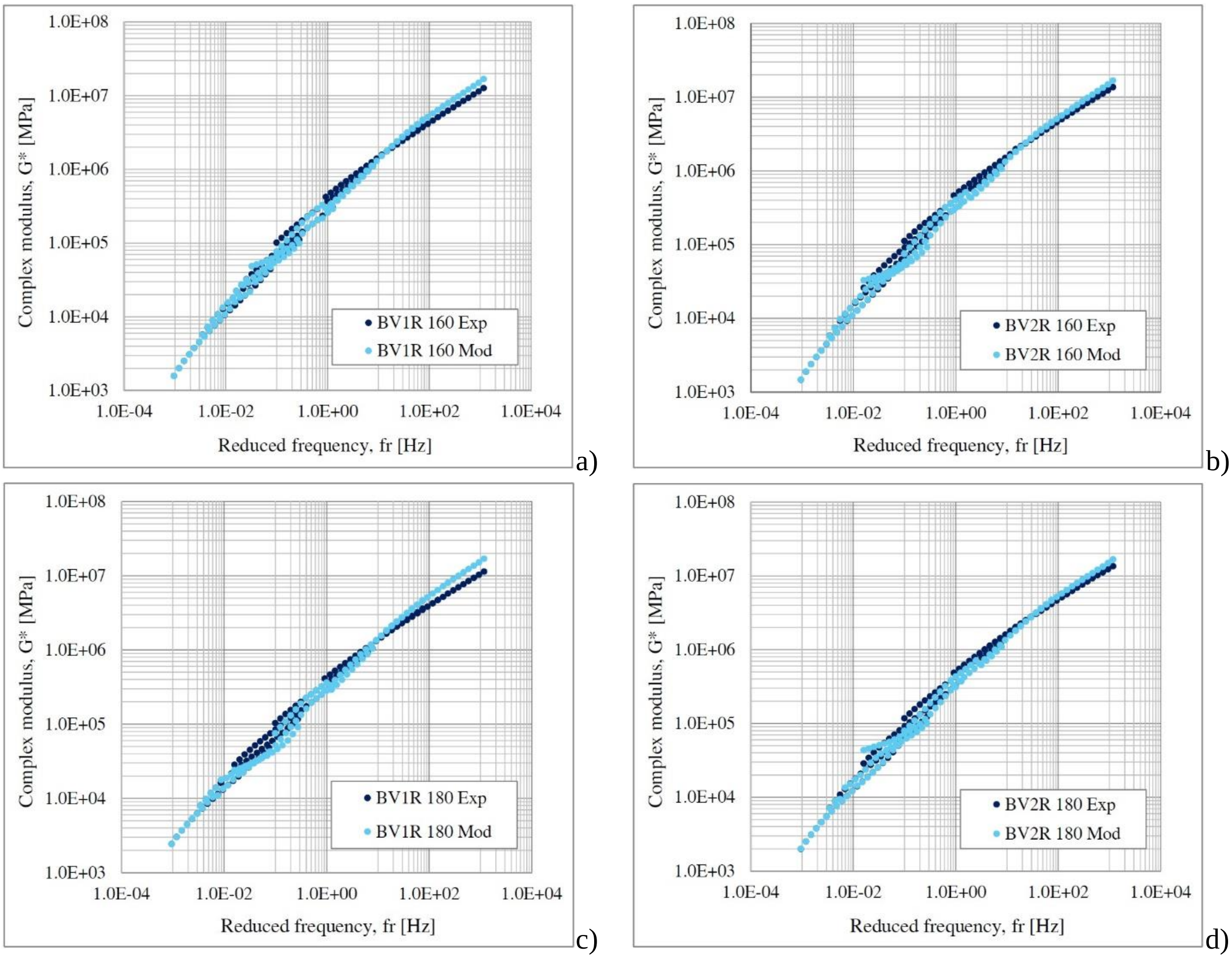
A spreadsheet program has been developed for determining the complex shear modulus, k_C (or G* of an extended bitumen), and the complex bulk modulus, μ_C, of the extended bitumens using Equation 25. Being an iterative process, the initial values were considered equal to the values of the matrix (i.e. Pen 50/70), as previously explained, then they were optimized by a minimization process. The optimization process of the modelled results of the composite has been applied on the initial values of the complex shear and bulk moduli in parallel thanks to the minimization of the sum of relative errors of each modulus. In detail, the errors of both moduli, complex shear and bulk, were evaluated using the non-linear least squares equation, which were summed as shown in Equation 27 (Harris 1998) (Kemmer and Keller 2010). Then, the deterministic optimization method for constrained non-linear problem has been applied minimizing the sum of relative errors (Yeniay 2005). The generalized reduced gradient (GRG) method was employed to find a local solution as it is already implemented in Excel program.

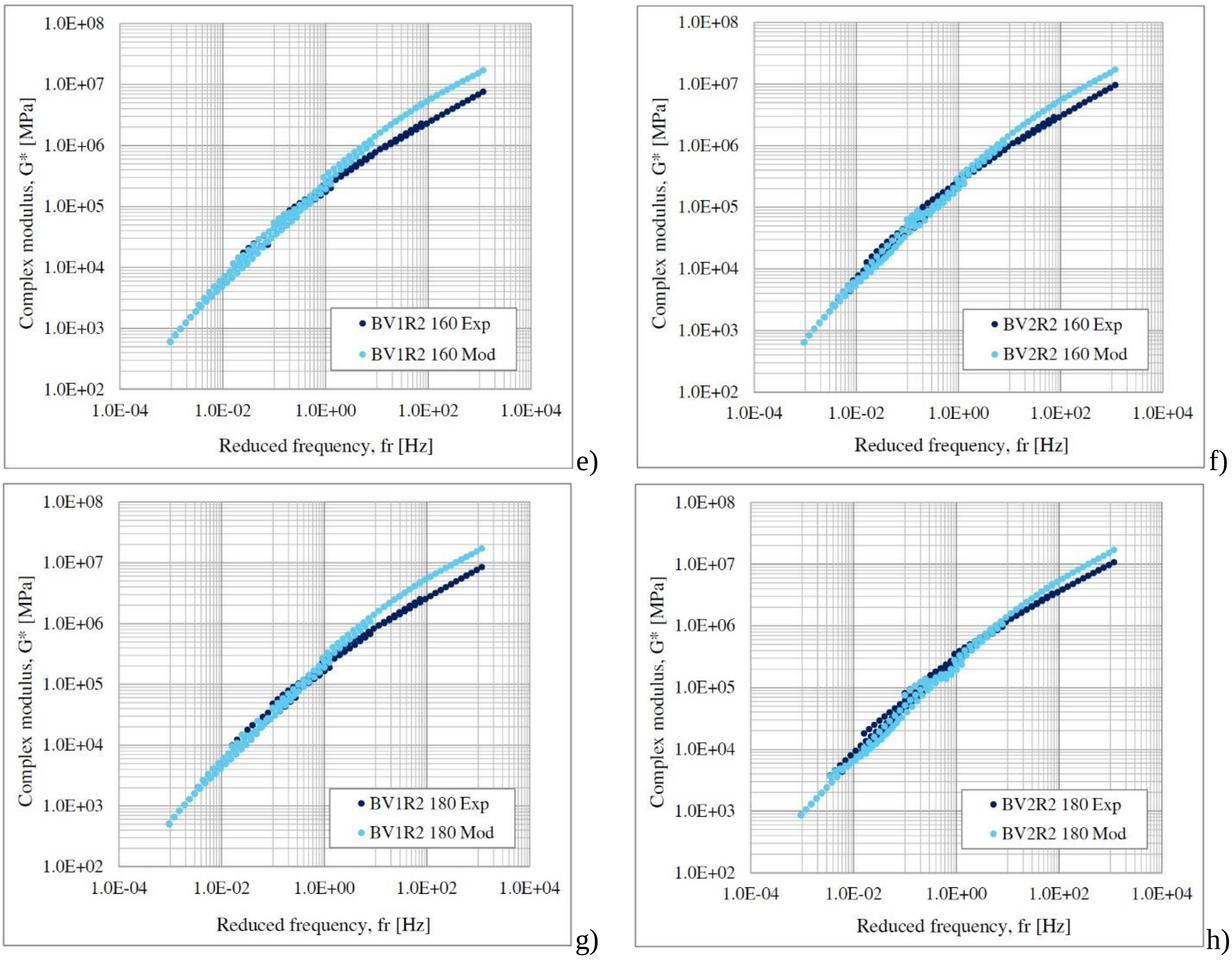
$$\begin{aligned} min\, \mu_c(\mu_M, \mu_I, k_c, \mu_c) + \min k_c(k_M, k_I, k_c, \mu_c) \\ = \sum_{\mu_c} \left(\frac{\mu_{c,experimetal} - \mu_{c,modelled}}{\mu_{c,experimetal}} \right)^2 + \sum_{k_c} \left(\frac{k_{c,experimetal} - k_{c,modelled}}{k_{c,experimetal}} \right)^2 \end{aligned} \tag{27}$$

In order to find a solution, the optimization process needed some restrictions. Consequently, it has been imposed that the complex shear and bulk moduli were positive and greater than zero, and the minimum values of k_C and μ_C was fixed equal to 10^{-4}. In Excel, the maximum number of cells that can vary during the GRG optimization method is equal to two hundreds, which includes the changing cells and those under restrictions at the same time. The total number of changing cells exceeded this limit considering the results of FS test at six test temperatures as the cells accounted those related to the variation of the initial values of the complex shear and bulk moduli and the same underwent to restrictions. Hence, the minimization process has been divided in three separate processes that consider the low test temperatures of FS tests, 10 °C and 20 °C, the intermediate test temperature, 30 °C and 40 °C, and the high test temperatures, 50 °C and 60 °C. The number of separate minimization processes was kept as low as possible because each optimization corresponds to a portion of the final G* master curve and separated processes lead to different errors, which turn into a discontinuous curve.

4.4 Application of the SC model on extended bitumens for predicting their G* values

The modelled values of complex shear modulus have been compared with the experimental data collected by the DSR. The G* master curves of experimental and modelled data were represented by using the WLF equation only for shifts factors fitting as previously explained. The comparison of experimental and modelled G* master curves are reported in Fig. 4.1.





e) f) g) h)

Fig. 4.1. Comparison of experimental and modelled G* master curves of extended bitumens: a) BV1R 160; b) BV2R 160; c) BV1R 180; d) BV2R 180; e) BV1R2 160; f) BV2R2 160; g) BV1R2 180; h) BV2R2 180.

The SC model predicted well the G* values at low frequency and/or high temperature in contrast to the previous study of Wang et al. (2020) on rubber-modified bituminous binders. Furthermore, the SC model has overestimated the predicted rheological parameter in contrast to the usual conclusions on bituminous mastics (Yin et al. 2008) (Underwood and Kim 2014) and on rubber-modified bituminous binders (Wang et al. 2020). At high frequency and/or low temperature, higher differences between the experimental data and the modelled results were observed. Moreover, the modelling of extended bitumens that contain R-REOB blends with ratio 1:2 were less precise than the prediction of the corresponding bituminous binders with the same amount of R and REOB. This response can be related to the incorporation of a compound that is not purely elastic and not completely rigid as hypothesized, and can also interact chemically. Thus, the SC model could not predict well the behaviour of inclusions that contain a high percentage of Vx due to its viscous-liquid state. The incorporation of R-REOB blend has a twofold effect on Pen 50/70 as R acts as a reinforcement, while REOB represents a softening agent. The reinforcement mechanisms were more complicated in R-REOB-modified bitumens. The G* master curves of all extended bitumens were not completely smooth at intermediate test temperature regardless the different constituents used. This discordance was more evident in R-REOB-modified bitumens with the same amount of recycled products.

In order to compare the effectiveness of using the SC model to predict the G* rheological parameter of extended bitumens, the sum of squared relative errors of G* values are listed in Table 4.1. The errors represent the quantitative distance between experimental and predicted G* values as shown by the plots of Fig. 4.1.

Table 4.1. Sum of squared relative errors between modelled and experimental G* values of extended bitumens at three temperature intervals.

Sample	Errors at 10-20 °C	Errors at 30-40 °C	Errors at 50-60 °C
BV1R 160	2.557	1.135	1.101
BV1R 180	3.548	2.965	2.572
BV1R2 160	45.838	1.750	0.026
BV1R2 180	32.119	2.042	0.042
BV2R 160	1.707	3.050	2.606
BV2R 180	1.623	2.743	1.412
BV2R2 160	16.568	1.202	0.723
BV2R2 180	5.931	3.448	2.585

Of course, the values reported in Table 4.1 confirmed the graphical representations of Fig. 4.1. Thanks to the quantification of errors, it can be observed that the highest errors were found at high frequency and/or low temperature. This behaviour may be related to the different stiffness of the inclusions (i.e. R-REOB compound) compared to that of the matrix. Conversely, the sum of the squared errors at intermediate test temperatures (i.e. 30 °C and 40 °C) were much closer to the errors at 50 °C and 60 °C. As a result, the stiffness of the matrix seemed to be more close to the stiffness of the inclusions at high test temperature in contrast to what has been observed in previous studies. At this boundary condition, the SC model may better predict the G* values since the bituminous binder that consists of matrix and inclusions may better satisfy the hypothesis of the model. The REOB presents in the inclusions, but external to the R particles, may be completely incorporated in the neat bitumen; while, the inclusions that are reduced to the R particles with the absorbed REOB may better represent the purely elastic and rigid inclusions. The portion of modelled master curves of V1-extended bitumens were predicted well at high temperatures and the errors were lower than those of the corresponded innovative binders with V2. Conversely, the G* master curves of V2-extended bitumens have been fitted better than V1-specimens at low temperatures. The amount of REOB heavily affected the modelling especially at low temperatures as previously highlighted. The production temperature of extender and extended bitumens did not show a clear influence on predicted values.

4.5 Results of the SC model with adjusted Poisson's ratio by experimental analysis

The Poisson's ratio (υ_{ji}) of linear elastic materials is commonly defined as negative ratio of two orthogonal strains when a uniaxial load is applied in direction ii (Equation 28).

$$\upsilon_{ji} = -\frac{\varepsilon_{jj}}{\varepsilon_{ii}}, i \neq j \tag{28}$$

, where ε_{ii} is the strain in axial direction and ε_{jj} is the strain in transverse direction. Homogeneous, isotropic, linear elastic materials have a constant Poisson's ratio and this parameter ranges between 0.5 and -1 (Aurangzeb et al. 2017). The Poisson's ratio is constant when a time-independent or a time-dependent load in one direction is applied as the strains in the same direction of load are constant or the material responds with the same time function, respectively (Aurangzeb et al. 2017). For viscoelastic materials, the Poisson's ratios are proven to be time and temperature dependent (Yin et al. 2008) and stress and stress history dependent (Aurangzeb et al. 2017). Therefore, the Poisson's ratio does not represent a unique property for viscoelastic materials contrary to the elastic ones (Aurangzeb et al. 2017). Being viscoelastic materials, there are difficulties to determine the value of this parameter for bituminous products. In order to overcome the difficulties these two-abovementioned simplifications, related to the use of constant Poisson's ratio and similar relaxation time for complex shear and bulk moduli, are usually considered. However, these simplifications can lead to inaccurate characterization of the viscoelastic bituminous materials.

The Poisson’s ratio of each extended bitumen is expected to change due to constituent materials; in addition, it is expected to vary under the boundary conditions of the FS test. In fact, the FS tests were performed at six temperatures and the load was applied sinusoidally changing the frequency at each test temperature. However, it is important to note that this rheological test was performed within the linear viscoelastic range. Due to the limited strains that were applied during the rheological analysis (γ_{LVE}), a constant value of the Poisson’s ratio was assumed for predicting the behaviour of the innovative bituminous binders. Nonetheless, the values of the Poisson's ratio were differentiated for each extended bitumen by experimental investigations. As a consequence, the assumptions for simplifying the materials' characterization were adopted, but specific values for each bituminous binder were determined and then used for running the SC model. The experimental tests for determining the Poisson’s ratio were performed using the equipment available at the Chemistry laboratory of DICAM Department of the University of Bologna. The testing procedure, samples definition and preparation, and the modelled results of G* values after Poisson’s ratio adjustment are reported in the next two sub-sections.

4.5.1 Experimental evaluation of Poisson’s ratio of extended bitumens

The Poisson’s ratio was determined by direct tensile (DT) test by using an Instron universal testing machine at approximately 20 °C (i.e. room temperature). The used method consists of applying a tensile stress on bituminous binder and measuring the axial and transverse strains by noncontact extensometers by using images analysis. In fact, during each DT test, a video was recorded and the deformations were computed by the use of an open-source software, Kinovea. This software was used for analysing the recorded videos, as it is able to detect small deformations; indeed, it is commonly used for sport applications. The experimental evaluation of Poisson’s ratio was performed on the four extended bitumens produced at 160 °C and the reference bitumen (i.e. Pen 50/70). The latter material was evaluated for comparison purposes as the Poisson's ratio value of traditional neat bitumen will be used as a reference value. The number of R-REOB-modified binders was reduced as the processing temperature of extenders and extended bitumens did not have a significant effect on the application of SC model. In addition, the reduced number of samples allowed saving time.

4.5.1.1 Preparation of extended bitumen samples for DT test

Five rectangular specimens have been prepared. The samples were about 85 mm length, 45 mm width and 30 mm thick, and, for their preparation, specific moulds have been constructed by cardboard covered with silicon paper. A specific quantity of every bituminous binder was warmed up and poured into the moulds. The heating time has been reduced to the minimum period in order to avoid the further ageing of the materials. The dimensions of samples differ from the usual values adopted for testing bituminous binders by DT test as requested by ASTM D6723-12 (2012) standard. Since the aim of the test is the evaluation of the Poisson’s ratio instead of the fracture properties of bituminous binders, as defined by the cited ASTM standard, it was necessary to adopt larger specimens. The dimensions of the samples have been chosen based on two considerations:

- the thickness of samples has to prevent the relaxation of bituminous materials during setting operations of the instrument;
- the width of samples has to be sufficiently large to arrange the markers for the detection and measurement of deformations and to avoid boundary disturbances during the following image analysis.

A thin bituminous sample can experience small bending deformations during setting operations before starting the test due to the relaxation of the material itself at room temperature. Moreover, the samples have to be positioned vertically with the length in the same direction of the applied tensile stress to better visualize the deformations and it increases the likelihood of the sample bending. On the other hand, a sufficiently wide surface area is crucial to determine the deformations by the use of image analysis. A set of dots has been drawn on the samples' surface as markers to detect the deformations caused by the applied tensile stress. Being drawn on the surface of the samples, the reference dots follow the strains of the materials during the DT test and allowing the visualization of the increment or reduction of their reciprocal distance in time. The tracking of the dots' displacement permit to define the deformations of the neat and the extended bitumens in time. To evaluate the deformations, thus the distances, in both axial and transverse directions, two parallel lines of white dots have been drawn on the middle part of the samples at constant distance between each other. A mask has been prepared to make the dots at the same distances in all samples. Once ready, each specimen has been glued to polymer supports that were successively clumped by the instrument. The use of polymer supports instead of directly clump the samples can reduce undesirable boundary deformations. These supports have been designed for performing the DT test specifically and they were produced by means of a 3D printer. The mask used for dots and the setting position of the Pen 50/70 samples are reported in Fig. 4.2.

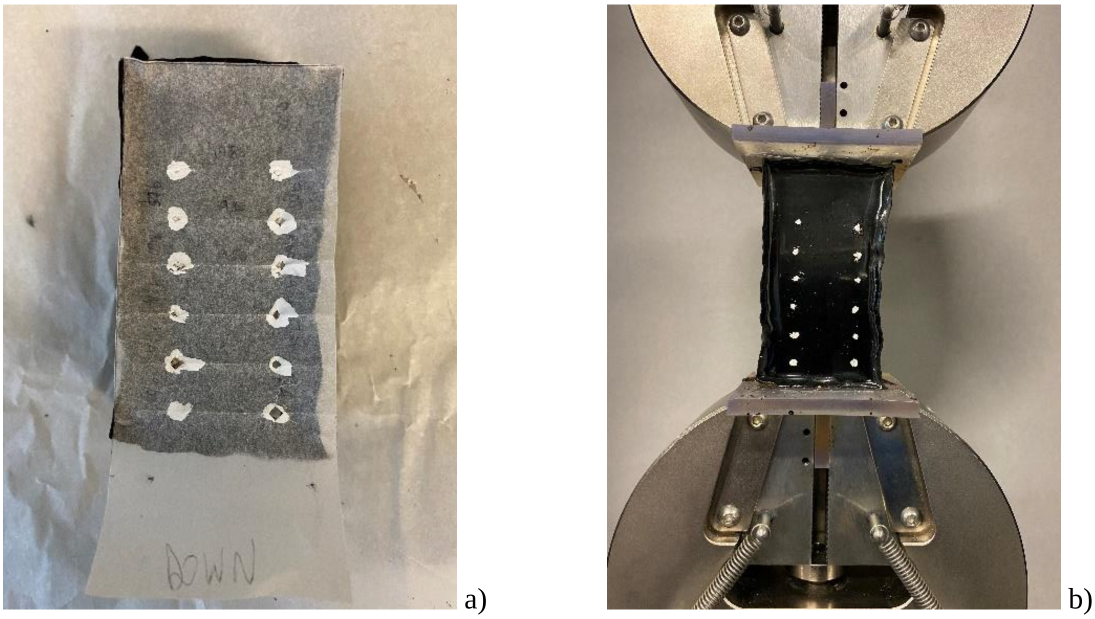


Fig. 4.2. Sample preparation and setting position of Pen 50/70 for DT test.

The Instron is not equipped with a climate chamber; hence, the DT tests have been performed at room temperature. In order to better control the test temperature all samples were stored in a climate chamber for the same period of time. The four extended bitumens and Pen 50/70 were stored at 5 °C until the test was performed. The low temperature avoided further ageing of bituminous materials and facilitated the de-moulding of specimens. When tested, the five samples were removed from the climate chamber and left at room temperature for a couple of hours. As a result, the temperature of samples during DT tests were within 18.8 °C and 20.5 °C that represented the lowest and the highest test temperatures, respectively. The temperature of every samples has been measured before running the test by a laser thermometer.

4.5.1.2 Definition of the strain-rate of the DT test

The four extended bitumens and Pen 50/70 were loaded in tension at a constant strain-rate equal to 30 mm/min. The strain-rate has been defined by preliminary tests on a standard 50/70 penetration grade bitumen. Three strain-rates, namely 25, 30 and 35 mm/min were considered and their resulting stress-strain curves are represented in Fig. 4.3.

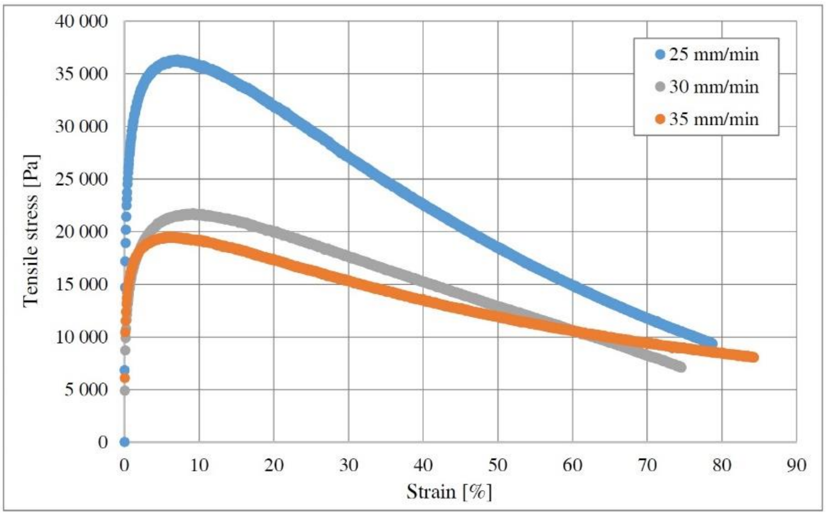


Fig. 4.3. Results of DT tests on 50/70 penetration grade bitumen at three strain-rate.

The three curves exhibited a similar trend; however, greater differences can be observed between the stress-strain data collected at 25 and 30 mm/min than those related to the tests performed at 30 and 35 mm/min. These differences can be related to the temperature of samples and the difficulties to control this parameter during the test. The bituminous specimen subjected to the strain-rate equal to 25 mm/min had the lowest temperature among the three tested samples, which reasonably increased the maximum tensile stress. The remaining two samples had surface temperature equal to 20.5 °C and 21.5 °C, respectively. The temperature of sample easily increased when the materials were removed from the climate chamber and were left at room temperature. To prevent differences among the conditions of materials, the temperature of all specimens was tried to maintain in the range of 19-20 °C. Taking into account the desired temperature of materials and the obtained stress-strain curves, the intermediate strain-rate has been considered for performing the DT tests in order to reduce the maximum stress applied by the instrument. Indeed, the maximum stress decreased as the strain-rate increased.

4.5.1.3 Post-processing of data

During post-processing of data, the white dots represented the digital markers for measuring the reciprocal distances between one point and the next one. When the bituminous material was expanded in one direction due to tensile stress, it expanded in the same direction while shrank in the perpendicular direction leading the dots to change their reciprocal distance consequently. Knowing the initial distance between the dots, the increment and/or reduction of the markers' distance can be evaluated over time.

Since the FS tests were performed within the LVE range, the Poisson's ratio were evaluated within the linear response of all bituminous binders. This can help to correlate the two testing procedures albeit the loading modes were different during FS and DT tests (i.e. oscillatory shear stress and tensile stress, respectively). Based on the raw data, the magnification of the stress-strain curves revealed that all bituminous binders behaved linearly at the beginning of the test only as shown in Fig. 4.4. The linear responses of all binders were exhibited within a strain equal to 0.10%. Thanks to this observation and considering that the data points were collected every 0.1 s, the values of the Poisson's ratio were evaluated within the three tenths of the first second from the starting time of the test.

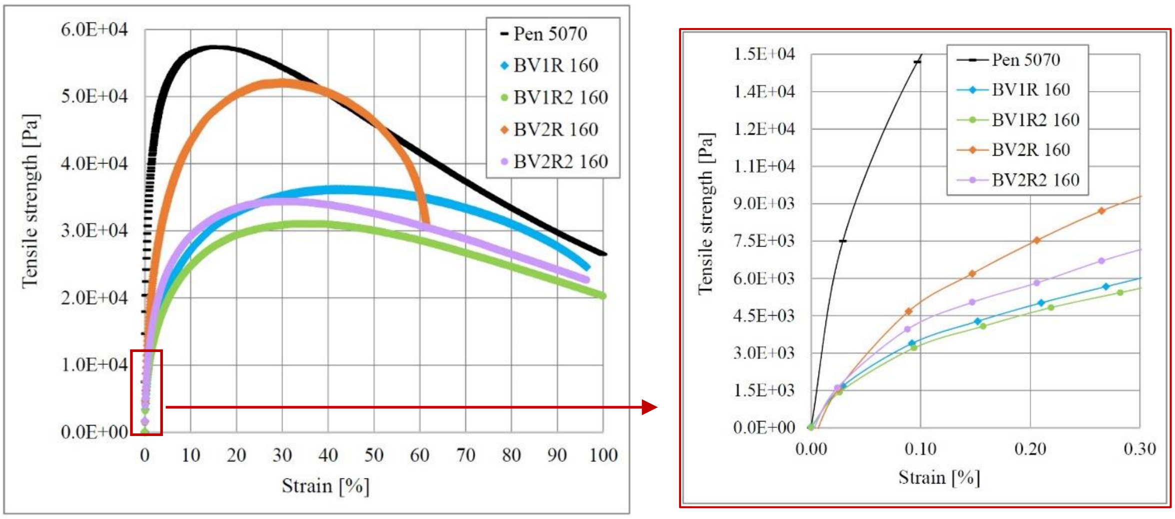


Fig. 4.4. Stress-strain curves of extended bitumens produced at 160 °C and Pen 50/70 resulting from DT test.

The frame images at the starting instant and at five consecutive instants within the three tenths of the first second of the test have been considered for evaluating the changes of dots' distances with respect to their initial reciprocal distance. In detail, the Poisson's ratio of each extended bitumen produced at 160 °C and Pen 50/70 was evaluated considering the two orthogonal strains at the beginning of the test, that represent the reference initial values, and after 0.10 s, 0.15 s, 0.20 s, 0.25 s and 0.30 s. The average of the five measurements per each orthogonal strains are represented by the difference between the strain at a specific instant and the initial strain. The mean values of the two orthogonal strains values were used to calculate the Poisson's ratio of each bituminous materials according to Equation 28.

The image analysis allowed the measurements of the reciprocal distance among the digital markers following their position in time. A descriptive image of the software during its use is reported in Fig. 4.5.

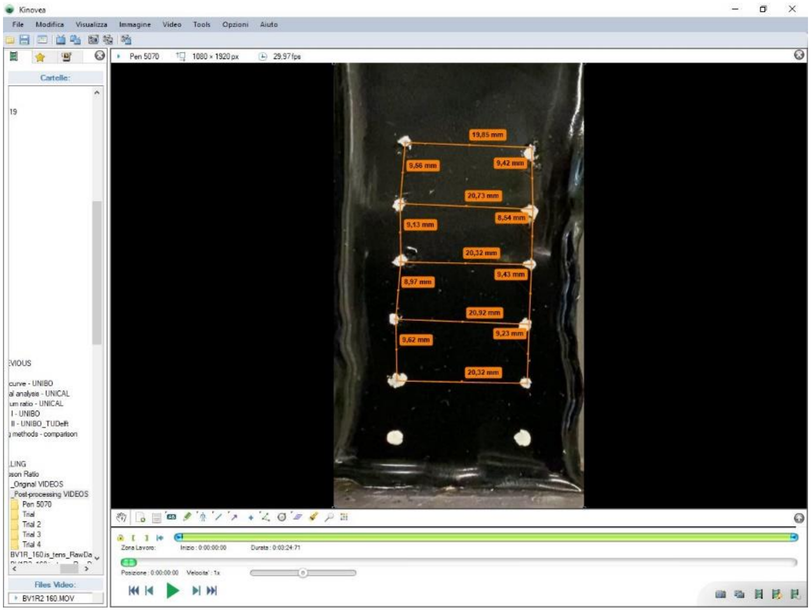


Fig. 4.5. A screen-shot of the image analysis by the use of Kinovea software.

The resulting Poisson's ratio of the neat and extended bitumens manufactured at 160 °C are listed in Table 4.2. In general, the experimental values of this parameter were found to be lower than the reference value that has been previously considered thanks to the literature review. The Poisson's ratio of the Pen 50/70 exhibited an intermediate value compared to those of extended bitumens. However, the values of the Poisson's ratio of extended bitumens did not change according neither to the R content nor to the type of REOB.

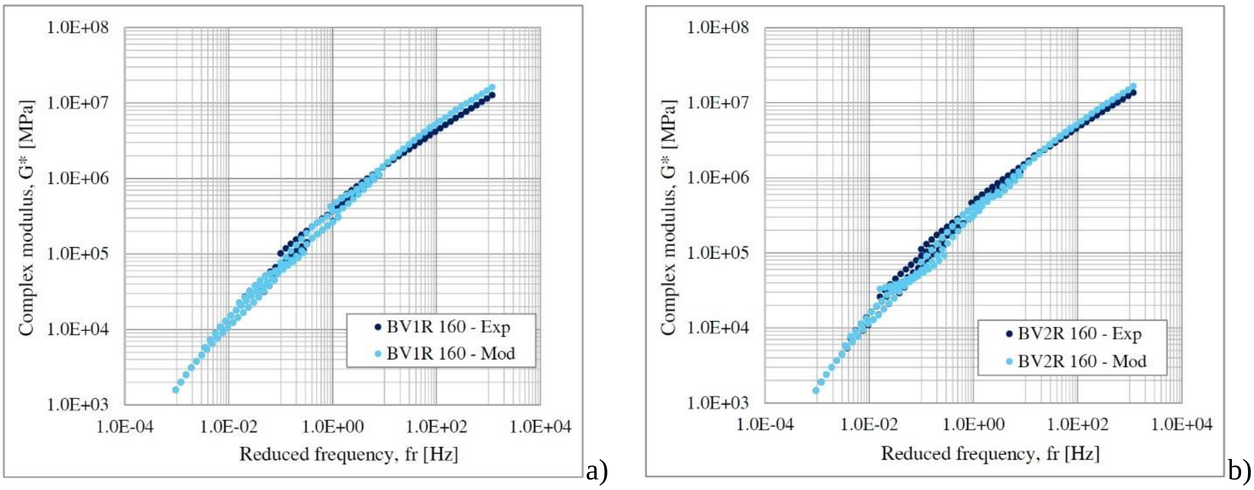
Conversely, the stress-strain curves of the DT test showed a higher stress values from samples produced with V2 and R-REOB ratio equal to 1:1. Thus, it can be observed that the stress-strain curves of extended bitumens confirmed the rheological characterization as detailed in Chapter 3; while, the Poisson's ratio did not follow the same trend. It is worth to underline the importance of the test temperature for the characterization of bituminous materials. The considered samples and the resulting data may be affected by their temperature during the DT test. Moreover, it is recommended to replicate the DT tests on each bituminous binder to better understand the trend of the Poisson's ratio based on constituent's materials and different processing conditions of the R-REOB-modified bitumens.

Table 4.2. Poisson's ratio of extended bitumens produced at 160 °C and Pen 50/70.

Sample	Poisson's ratio
BV1R 160	0.1939
BV1R2 160	0.4848
BV2R 160	0.3800
BV2R2 160	0.1616
Pen 50/70	0.3368

4.5.2 Results of modelled G* values of extended bitumens using experimental values of Poisson's ratio

The experimental values of the Poisson's ratio for the four extended bitumens manufactured at 160 °C that are listed in Table 4.2 were adopted for running the SC model on these specific innovative bituminous binders. This analysis may improve the results of the SC model as a specific property of the materials was evaluated. The modelled G* master curves, which used the experimental values of the Poisson's ratio, are illustrated in Fig. 4.6 together with the experimental G* master curves, which have been collected by the DSR. In order to quantify the errors between the experimental data and the modelled results and the contribution of the experimental values of the Poisson's ratio, the sum of squared relative errors of G* values are listed in Table 4.3.



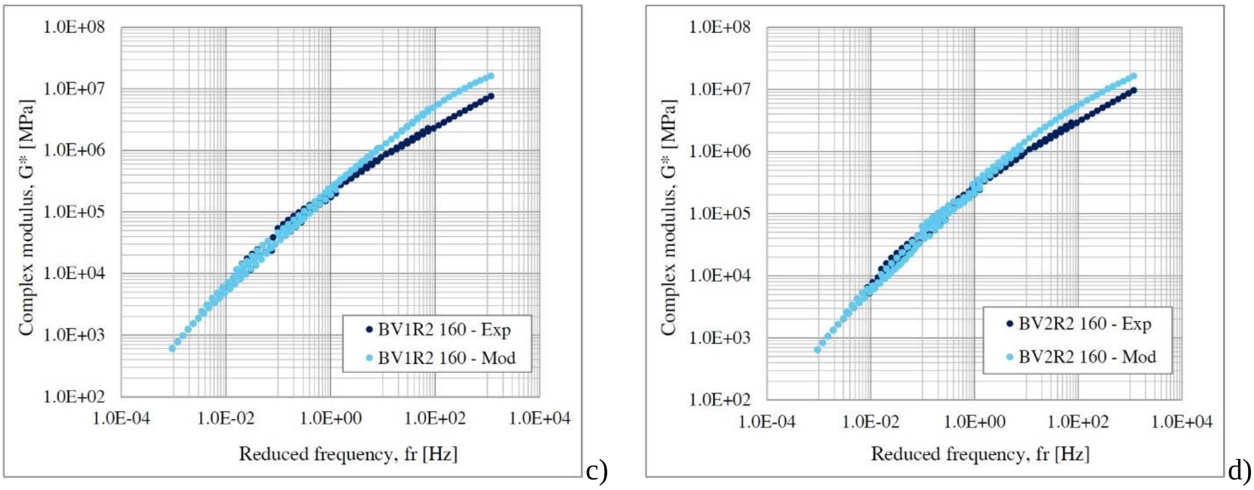


Fig. 4.6. Comparison of experimental and modelled G* master curves of extended bitumens produced at 160 °C considering the experimental value of the Poisson’s ratio: a) BV1R 160; b) BV2R 160; c) BV1R2 160; d) BV2R2 160.

Table 4.3. Sum of squared relative errors of modelled and experimental G* values of extended bitumens at three temperature intervals considering the experimental values of the Poisson’s ratio.

Sample	Errors at 10-20 °C	Errors at 30-40 °C	Errors at 50-60 °C
BV1R 160	1.840	0.786	0.050
BV1R2 160	93.417	2.159	0.233
BV2R 160	1.371	2.880	1.792
BV2R2 160	17.559	0.739	0.483

The representation of the predicted G* master curves by the use of the SC model and the sum of the squared relative errors confirmed the good fitting of the rheological data at low frequency and/or high temperature and the overestimation of the results at opposite boundary conditions regardless the different values of the Poisson's ratio. Furthermore, the SC model performed better when the extended bitumens with R-REOB ratio equal to 1:1 were involved. The type of REOB exhibited a different influence on the prediction of the G* values depending on the test temperature as previously highlighted.

The use of different and specific values of the Poisson’s ratio of each material improved the fitting of the SC model. All extended bitumens produced at 160 °C showed a reduction of the squared relative errors compared to the same material with a fixed Poisson’s value, except for specimen BV1R2 160 (refer to Table 4.1 for comparison). This extended bitumen (BV1R2 160) that exhibited the highest differences between the experimental and modelled G* data had the highest experimental value of ν among the other bituminous binders, which was greater than the reference value (i.e. 0.425).

The homogenization theory has been found to be a good and useful tool to acquire information about the possible rheological behaviour of R-REOB-modified bitumens. However, the SC model gave more approximate information at high frequency and/or low temperature than the intermediate and low range of considered frequencies. Hence, it is recommended to adjust the model in order to better evaluate the softer inclusions into the bituminous matrix due to the presence of REOB or to apply a different model that can better predict the response of the final composite bituminous binder. The use of experimental Poisson’s ratio has helped to improve the modelling. Nonetheless, the characterization that has been done represent a first step, which has to be replicated in order to assess the correct ν values of each involved material and, eventually, to assess the effectiveness of a new protocol that exploits the DT test to experimentally determine the Poisson's ratio values.

4.6 Summary

The modelled values of complex shear modulus show different accuracy depending on the used mass proportion of R-REOB blend that has been incorporated into standard bitumen. In detail, the SC model better predicts the rheological parameter of the extended bitumens with R-REOB ratio equal to 1:1. The lower precision can be related to the incorporation of a liquid-viscous phase together with rigid R particles as hypothesised by the model.

Further evaluations can help reducing the inaccuracies of the predicted data. In this regard, the experimental evaluation of the Poisson’s ratio has been performed, which were found to have a positive influence on the modelled G* values. However, further investigations of this parameter are necessary to better evaluate the contribution of this parameter and to establish a possible characterization protocol. Moreover, additional characterization of the inclusions and geometrical aspects can improve the results. Alternatively, another micromechanical model that has different, but more realistic, assumptions can be adopted.

5

Characterization of asphalt mixes with extended bitumens and recycled aggregates

5.1 Introduction

The present chapter considers the application of the developed extended bitumens in asphalt mixtures. The fourth phase of this study aims to characterize the mechanical responses and environmental impacts of eight asphalt mixes with a high percentage of recycled materials. In fact, asphalt concrete mixtures were produced with the eight innovative bituminous binders developed in the previous studies and 50% of recycled raw aggregates by the total weight of aggregates. Therefore, the recycled products were included in both, bituminous binder and aggregate skeleton, for a total amount of 48.65% by the total weight of the mix.

The considered asphalt mixtures underwent volumetric analysis and mechanical tests. The latter allowed for the determination of stiffness, tensile strength and moisture susceptibility of the eight asphalt concretes that were compared to a reference mixture. These investigations are necessary and preliminary to assess the feasibility of using R-REOB-modified bitumens as road construction materials in mixtures that contain recycled raw aggregates in the aggregate skeleton also. The use of recycled products, especially reclaimed asphalt pavement (RAP) were found to increase the stiffness and indirect tensile strength of the final mix. Moreover, the moisture absorption may be enhanced due to presence of recycled raw aggregates that may have different and higher absorption properties than virgin ones.

Furthermore, it has been planned to assess the environmental impact of the asphalt mixtures by means of leaching test. The evaluation of potential leaching of contaminants into road runoff or water infiltrating the road surface represents a crucial aspect when recycled products are used in road construction materials. In fact, the possibility to leach of recycled and recovered products is a concern related to the use of recycled raw materials.

The description of the adopted experimental program and the discussion of results are provided later on in this chapter.

5.2 Experimental program

5.2.1 Preparation of asphalt mixtures with high percentage of recycled materials

By using the extended bitumens, asphalt mixes for wearing course layer with high percentage of recycled products were produced and underwent volumetric and mechanical tests. These experimental mixes contained recycled materials at the binder level, as they used the R-REOB-modified bitumens for binders' production; in addition, they were introduced in the aggregate skeleton by using recycled raw aggregates in partial substitution of virgin ones. The asphalt concretes with high percentage of recycled products, i.e. 48.65% by the total weight of the mix, are referred hereafter as CAM mixes, which is the Italian acronym of Minimum Environmental Criteria, followed by the name of extended bitumen used. The CAM mixtures with extended bitumens were compared with a CAM mix manufactured with Pen 50/70 (namely, CAM B 50/70) and a traditional wearing course asphalt mix that mainly contains virgin materials (namely, Traditional). This last mix was also produced with the reference bitumen that is Pen 50/70 and consisted of 90% of virgin natural aggregates and 10% of reclaimed asphalt pavement (RAP) aggregates.

The mix design for wearing course samples was done in previous studies according to the Italian technical specifications. The CAM B 50/70 and Traditional mixtures were designed to obtain asphalt concrete with 4% of air voids content (V_a) approximately. Virgin and recycled raw aggregates have been used to design the CAM mixture. Different types of aggregates were introduced in diverse quantities in order to meet the required grading curve as each type of aggregates has different size dimension and distribution. The size and percentage of each type of aggregates are listed in Table 5.1. The distribution of the CAM and Traditional wearing course samples are illustrated in Fig. 5.1. The optimum binder content was selected according to 5.70% for CAM mixes and to 5.60% for the Traditional wearing course samples. Both contents of bitumen were considered by the total weight of the aggregates. The eight CAM mixes with R-REOB-modified bitumens have been produced following the mix design of CAM B 50/70.

Table 5.1. Type and percentages of aggregates used for the production of CAM mixtures.

Type of aggregates	**Dimensions [mm]**	**Percentage [%]**
Virgin	4-8	18
Virgin	2-6.3	6
Virgin	0-6.3	23
Recycled from urban waste	0-4	8
Recycled from industrial waste	4-8	22
RAP	0-10	20
Filler	0-1	3

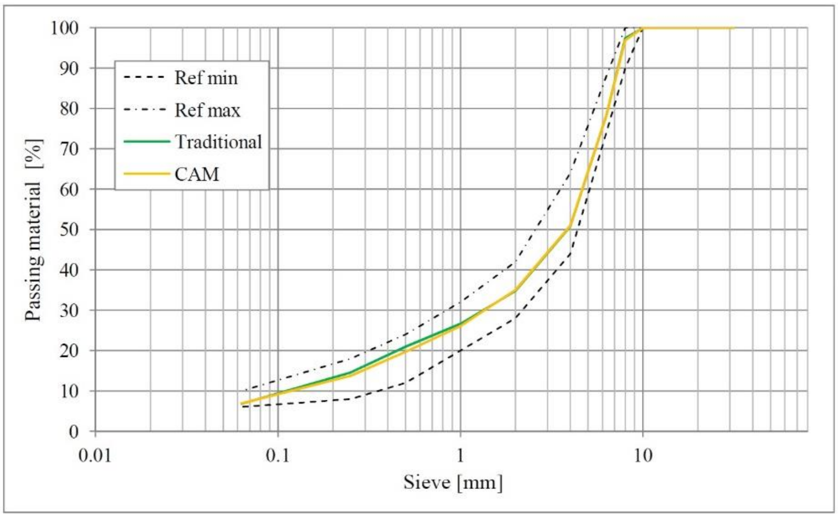


Fig. 5.1. Grading distribution of traditional and CAM mixes and the reference curves.

Four samples per each asphalt mixture were manufactured in the laboratory by using an automatic mixer and the gyratory compactor according to the EN 12697-31 (2007) standard. Both, aggregates and binders, were warmed up at 150 °C (designed compaction temperature) before mixing them; the aggregates was heated for 4 h, while bituminous binders for 1 h at least. The constituent materials of each asphalt concrete were mixed at a constant rotational rate of 49 min^{-1}. At first, one binder was incorporated into the aggregates and the materials have been mixed for 8'; then, the filler was added and all constituents have been mixed for another 8'. Before the compaction phase, each homogeneous mixture was left in a forced-air oven at 150 °C for a minimum period of 40'. All samples were manufactured singularly by applying 120 gyrations at an average compaction temperature equal to 150 °C. The cylindrical samples had diameter equal to 100 mm and were 52 mm tall on average. An example of the produced samples is illustrated in Fig. 5.2.

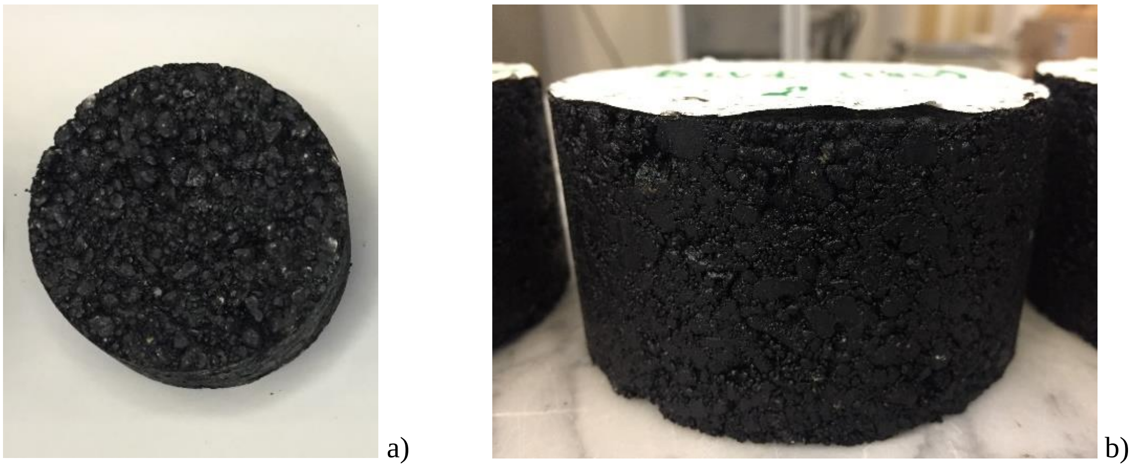


Fig. 5.2. A representative sample of one CAM asphalt mixture.

5.2.2 Test methods

The samples underwent volumetric and mechanical tests after being cured for a minimum of 24 h. The air voids content (V_a) of each specimen was evaluated following the Superpave method thanks to the collected data from the gyratory compactor, which registered the height and density of the samples after each gyration. In addition, the obtained V_a contents were compared with the results gained by using the Italian technical specification.

The mechanical analysis consisted of dynamic and static characterizations. The dynamic test was used to determine the stiffness modulus of all samples by using a servo-pneumatic testing machine. The stiffness modulus was established according to EN 12697-26 (2012) standard, in the indirect tensile configuration (IT-CY). Hence, the indirect tensile stiffness modulus (ITSM) has been determined for all asphalt concretes. A pulse loading was applied with a 124 ms rise-time to generate a horizontal deformation of 5 ± 2 μm. Being a non-destructive test, it was replicated at three different test temperatures, namely 10, 20 and 30 °C. Before being tested, all samples were kept in a climate chamber at the test temperature for at least 4 h.

Two static mechanical characterizations were used to measure the indirect tensile strength (ITS) and the indirect tensile strength ratio (ITSR) of all mixes in compliance with the EN 12697-23 (2017) and EN 12697-12 (2008) standards, respectively. The tensile strength of asphalt concretes was determined applying a compression load with a constant speed rate of 51 mm/min. The ITS test was performed at 25 °C. The last characterization, i.e. the ITSR ratio, aimed to measure the durability of the wearing course samples as it determines the effect of saturation and accelerated water conditioning. This investigation quantifies the ratio between the ITS values of an asphalt mix after water conditioning to that of dry specimen. According to the Method A of the standard, the samples were saturated and stored in a water bath at 40 °C for three days. Successively, the samples were removed, dried and conditioned at a 25 °C into a climate chamber to further underwent the loading condition of the ITS test. The two static characterizations applied a load until failure; hence, the set of four specimens per each asphalt mix have been halved to perform the ITS test on dry and wet samples, respectively. Before being tested, all samples were kept in a climate chamber at the test temperature for at least 4 h.

To complete the characterization of the innovative asphalt mixes, their environmental impact was considered and the leaching tests were planned in order to assess the possible release of dangerous substances. In detail, three wearing course samples for four asphalt mixtures containing the extended bitumens produced at 160 °C were produced following the same procedure described above in section 5.2.1. The samples were subjected to volumetric analysis and dynamic mechanical characterization at 20 °C as previously explained. This allowed verifying the reproducibility of the asphalt concrete production and their mechanical behaviour.

Successively, the specimens underwent to the horizontal dynamic surface leaching test according to the PD CEN/TS 16637-2 (2014) standard. The leaching tests are being performed at the CAWR laboratories of the Coventry University (United Kingdom) and they are on-going. Unfortunately, the evaluation of the environmental impact of the materials was influenced to the restrictions due to the COVID19 pandemic.

5.3 Assessment of the responses of asphalt mixtures with high percentages of recycled products

5.3.3 Volumetric analysis of CAM mixtures with extended bitumens

The Superpave method evaluates the V_a content by means of Equation 29:

$$V_a = \frac{G_{mm} - G_{mb}}{G_{mm}} \cdot 100 \qquad (29)$$

, where G_{mm} is the maximum specific gravity and G_{mb} is the bulk specific gravity of a compacted asphalt concrete. This method uses a numerous input data to evaluate these two parameters at each gyration of the gyratory compactor. The measured final weight and dimensions of samples together with the height of every sample after each gyration are considered. The device automatically registers the number of gyration, and the height and density of each sample during compaction. Furthermore, the maximum density of the asphalt mixtures, the apparent and saturated surface dry (SSD) density of aggregates are necessary. These values were obtained in compliance with the EN 12697-5 (2012) and EN 1097-6 (2013), respectively. Also, the bituminous binder content by the weight of the asphalt mixture and its density are needed. The percentage of innovative bituminous binders and Pen 50/70 that were incorporated in all CAM asphalt mixtures was 5.70%wt., but the content of binder in the asphalt mix should consider the quantity of aged bitumen already present in RAP aggregates. As a result, the amount of bituminous binder in all CAM mixes was equal to 6.37% by the total weight of the mix. The percentage of binder in Traditional wearing course samples corresponded to the optimum binder content determined during the mix design (5.60%wt.).

The Italian technical specification evaluates the V_a content by Equation 30:

$$V_a = 100 - \rho_{bulk} \cdot \left(\frac{P_b}{G_b} + \frac{100 - P_b}{\rho_{agg}} \right) \qquad (30)$$

, where ρ_{bulk} is the bulk density of the asphalt concrete, P_b is the percentage of bituminous binder by the weight of mix, G_b is the density of bituminous binder, and ρ_{agg} is the apparent aggregates density. The ρ_{agg} was determined as previously mentioned. As well, the percentages of bituminous binders in CAM and Traditional mixes were defined above. In all calculations of V_a content, the binder density was considered equal to 1.035 g/cm^3, which is the typical density of a traditional neat bitumen. Since R and REOB have density close to unit, the introduction of recycled materials into extended bitumens did not significantly change the final density of binders compared to that of Pen 50/70. Thus, this value has not been changed during the V_a determination.

The average V_a content of four samples per each CAM mixes produced with extended bitumens are listed in Table 5.2. The results of these asphalt mixtures were compared to the average V_a content of CAM B 50/70 and Traditional mixtures that were determined in previous studies, and their values were 3.6% and 3.8%, respectively. The V_a contents obtained from the two methods differed of about 0.6% due to the intrinsic differences of the procedures themselves. In general, the CAM mixes with extended bitumens showed lower V_a contents than the same CAM mix with Pen 50/70 (CAM B 50/70) and Traditional mixture. The presence of REOB reduced the V_a content on the resulting mixes, thus it seemed to improve the workability of the mix.

In fact, increasing the amount of Vx in the extended bitumens, the V_a values decreased. This consideration is reasonable due to the introduction of a soften agent (i.e. REOB) into extended bitumens. The results highlighted that a specific mix design should be carried out for CAM mixes that used the R-REOB-modified bitumens in order to meet the required 4% of V_a content of the final asphalt product, especially for those containing R-REOB extender with ratio equal to 1:2. Limited differences were found based on production temperature of extenders and extended bitumens and on the type of REOB used.

Table 5.2. Evaluation of air voids content by Superpave method and Italian technical specification of CAM mixtures.

Asphalt mixture	**Va – Superpave [%]**	**Va – Italian [%]**
CAM BV1R 160	2.5	3.1
CAM BV1R 180	3.1	3.7
CAM BV1R2 160	1.2	1.8
CAM BV1R2 180	1.9	2.5
CAM BV2R 160	1.9	2.5
CAM BV2R 180	2.9	3.5
CAM BV2R2 160	1.3	1.9
CAM BV2R2 180	1.1	1.7

5.3.4 Mechanical characterization of CAM mixtures with extended bitumens

The mechanical characterization by means of cyclic tests has been performed at three test temperatures, as described in section 5.2.2, on the eight CAM mixes produced using extended bitumens. Previous studies have investigated the mechanical responses of CAM B 50/70 and Traditional mixtures applying the same test methodology. The ITSM values of all asphalt concretes are reported in Fig. 5.3 for comparison.

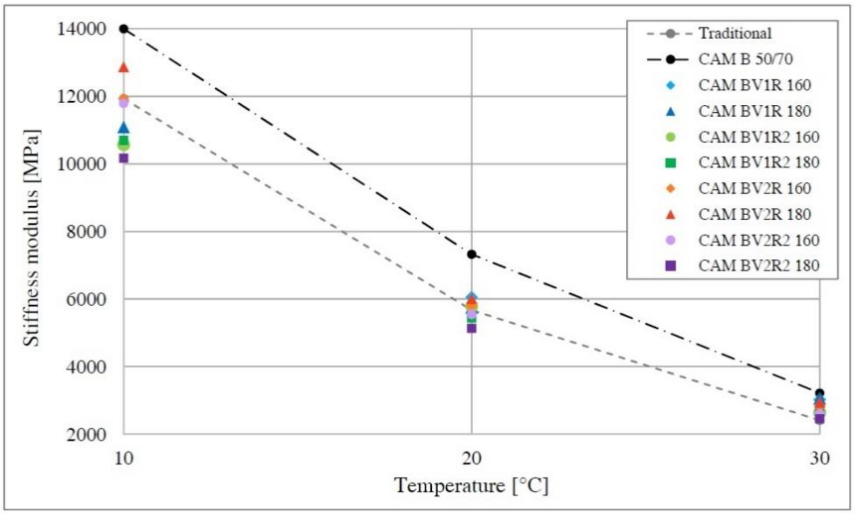
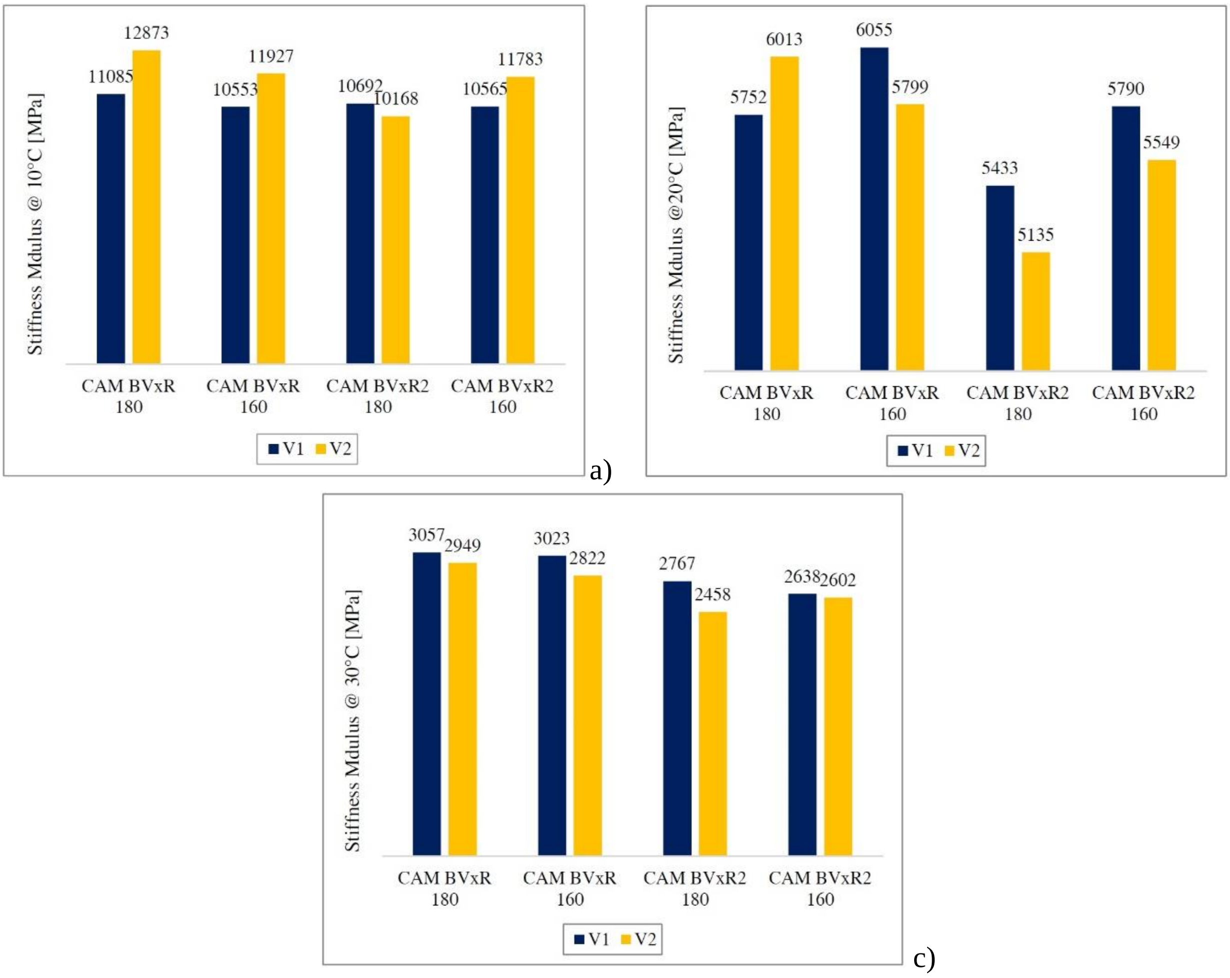


Fig. 5.3. Indirect Tensile Stiffness Modulus (ITSM) of traditional and all CAM mixes at three test temperatures.

The results showed that the CAM mixes with extended bitumens behaved similarly to the Traditional mix, especially at 20 °C. At the lowest test temperature (10 °C), the CAM mix with R-REOB-modified bitumens exhibited a similar or lower stiffness than the Traditional mix generally. This response confirmed the rheological data of bituminous binders and can be related to the softening effect caused by Vx. The Traditional asphalt concrete exhibited lower stiffness than the CAM mixes with extended bitumens at 30 °C. The presence of R stiffened the innovative bituminous binders and in turn resulted in higher stiffness for the final asphalt mixtures. Both, Traditional and CAM mixes with extended bitumens were less stiff than CAM B 50/70 at all test temperatures. The higher stiffness of the CAM mix produced with the reference Pen 50/70 than Traditional mixture can be ascribed to the presence of recycled aggregates and, especially, RAP aggregates. The RAP material substituted 20%wt. of virgin aggregates, and this quantity can turn into higher stiffness of the final asphalt product. Indeed, the threshold value that permits to neglect the quantity of RAP aggregates in a mix is usually considered to fall in the range from 10%wt. to 20%wt. depending on the stiffness of the aged binder (McDaniel et al. 2000). Being composed by aged bituminous binder, that is more stiff and brittle, the RAP material exhibits higher stiffness of the resulting asphalt concrete (McDaniel et al. 2000).

In order to investigate the differences among the CAM mixes with the extended bitumens, the results were separated based on test temperature and the only results of the eight CAM mixtures with the innovative bituminous binders are reported in Fig. 5.4. The stiffening effect of R is evident in all CAM mixes with extended bitumens, and at all test temperatures. This trend confirms the results obtained from the rheological characterization of the innovative bituminous binders. The type of REOB influenced the ITSM values in a different manner depending on the test temperature. At 10 °C, the use of V2 increased the stiffness of the final asphalt concrete. However, opposite effect has been observed at intermediate and high test temperatures. The production temperature of extenders and binders showed a not clear trend among the ITSM values at the three test temperatures.



a) b) c)

Fig. 5.4. Comparison of Indirect Tensile Stiffness Modulus (ITSM) of CAM mixes with extended bitumens based on type of REOB at: a) 10 °C; b) 20 °C; c) 30 °C.

The average results of indirect tensile strength (ITS) of the CAM and Traditional mixtures are shown in Fig. 5.5. In general, this static characterization confirms the intermediate response of CAM mixes manufactured by extended bitumens between the two reference mixtures, i.e. Traditional and CAM B 50/70. Only CAM BV1R 180 and CAM BV1R2 180 mixes exhibited lower ITS values than Traditional mixture.

Nonetheless, all mixes agreed with the Italian technical specification that requires ITS value higher than 0.7 MPa. The greater content of R in extended bitumens led to improve the tensile strength of the related CAM asphalt mixes. The processing temperature of extenders and extended bitumens, and the type of REOB affected the ITS values of the asphalt concretes. The lower production temperature (160 °C) of extenders and extended bitumen increased the final tensile resistance of the CAM mixes. Also, the use of V2 increased the ITS values.

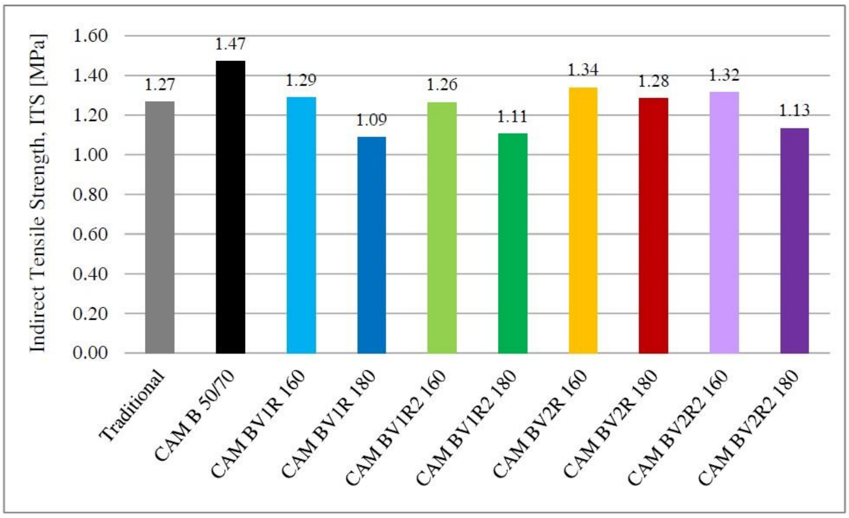


Fig. 5.5. Indirect Tensile Strength (ITS) of traditional and all CAM mixes at 25 °C.

Thanks to a comparison between the ITSM and ITS values of the CAM mixes with extended bitumens, it can be observed that the presence of R positively enhanced the stiffness and the tensile strength regardless the test conditions. In fact, stiffness and tensile resistance showed the same trend based on R content. The use of V2 at intermediate temperature (i.e. 20 °C and 25 °C for ITSM and ITS tests, respectively) allowed the increase of stiffness and tensile strength; however, this trend was not confirmed by the ITSM values when decreasing the test temperature. Also, the processing temperature did not show unambiguous results for both mechanical characterizations.

The results of the last mechanical characterization on CAM mixes produced with extended bitumens in terms of ITSR values are presented in Fig. 5.6. In addition to the average ratio values of two replicates per each conditioning (i.e. dry and wet), the Fig. 5.6 plots the error bars considering the standard deviation of the collected data in order to give additional information about the variability of the results. The data of the innovative CAM mixes were compared with those of the reference mixes.

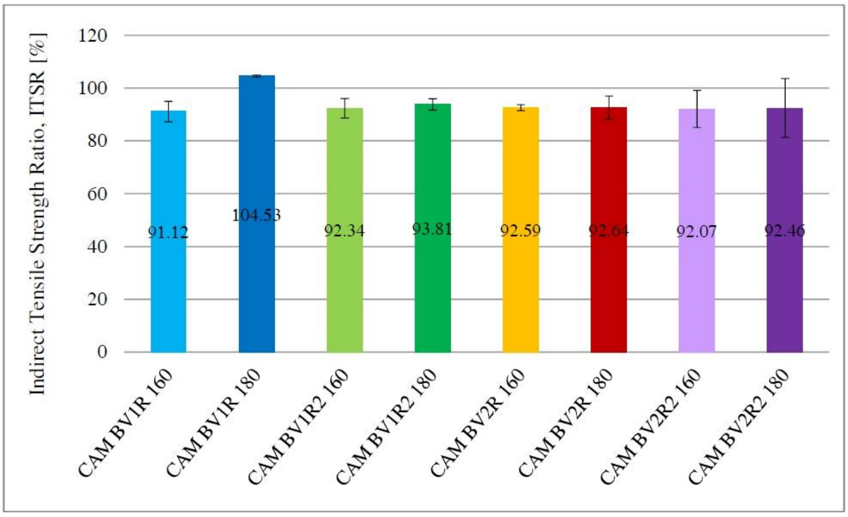


Fig. 5.6. Indirect Tensile Strength Ratio (ITSR) of CAM mixes produced with extended bitumens at 25 °C.

Both Traditional and CAM B 50/70 mixtures showed a very low water susceptibility since the ITSR values were equal to 99.7% and 101.52%, respectively. Despite all asphalt mixtures exceeded the minimum ITSR value requested by the Italian technical specification that is usually considered equal to 90%, the CAM mixtures produced with the eight extended bitumens were more sensitive to water damage compared to the two reference mixes. The ITS values of the innovative CAM mixes decreased after the storage in water bath, except for CAM BV1R 180 that showed higher ITSR value than 100%. However, this response did not follow the trend of similar asphalt mixtures and it may represent erroneous measurements. It can be recommended to further investigate the water damage of CAM mixtures considering a larger number of samples. The effects of processing conditions, type and amount of constituents were not the same among all samples. In detail, higher production temperature (180 °C) of the extended bitumens reduced the water susceptibility of the corresponding CAM mixes. This behaviour may be related to the enhanced interactions between R-REOB blend and Pen 50/70 during processing conditions, which may lead to create a more homogeneous bituminous binder that coat the aggregates. The higher R content improved the ITSR values of CAM mixes containing V2; the response of CAM mixtures with V1 were not unambiguous since the comparison between the average ITSR values of CAM BV1R 180 and BV1R2 180 may be compromised due to erroneous measurements. In general, the use of V1 improved the final values of the ITSR ratios. Nonetheless, the possible erroneous data of the samples of one CAM mixture that contain the R-V1-modified bitumens reduced the certainty of this conclusion.

5.3.5 Comparison of rheo-mechanical behaviour of extended bitumens and CAM mixtures

The comparison of dynamic mechanical characterization and the rheological data obtained by the FS test has been investigated to relate the stiffness of one extended bitumen with that of the corresponding asphalt mixture. In detail, the complex shear modulus obtained from rheological characterization of bituminous binders were compared with the elastic modulus that is the ITSM values at the same frequency. The stiffness values at about 0.33 Hz have been considered, as it is the reciprocal of the pulse repetition load of standardized ITSM test. The elastic moduli, ITSM or E values, versus complex shear moduli, G*, of neat and extended bitumens are reported in Fig. 5.7.

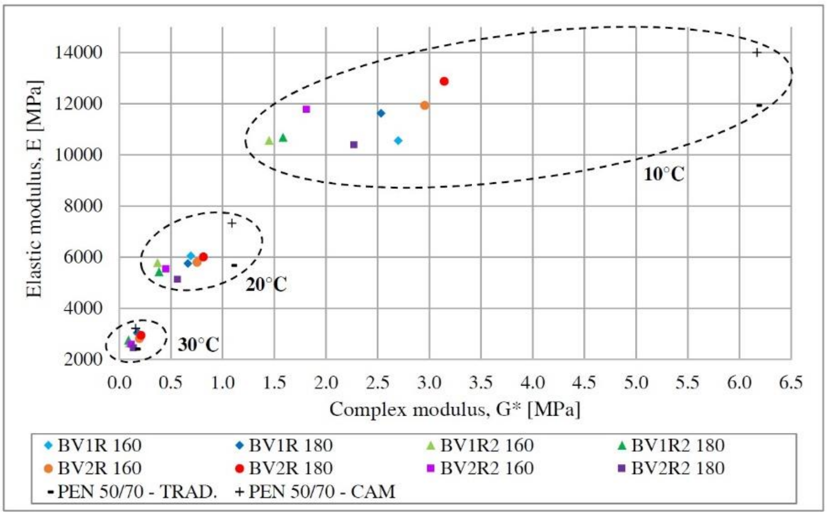


Fig. 5.7. Representation of elastic modulus, E, of asphalt mixtures versus complex modulus, G*, of the corresponding extended bitumens and Pen 50/70 at 10, 20 and 30 °C.

The graph exhibited the higher stiffness of Pen 50/70 and Traditional and CAM B 50/70 mixes than R-REOB-modified bitumens and the corresponding CAM mixes at 10 °C and 20 °C, especially in terms of complex shear modulus. This confirmed the softening effect due to the partial substitution of Pen 50/70 with a R-REOB compound regardless the constituent materials, their mass proportion and the processing conditions.

At high test temperature, namely 30 °C, the differences between all data decreased. From this trend, it can be deduced that the incorporation of R may mitigate the softening effect of REOB, confirming again the rheological results obtained in Chapter 3 and in the abovementioned mechanical characterization. In general, the behaviour of bituminous binders was reflected in those of asphalt mixtures.

In order to better evaluate the correlation between the innovative bituminous binders and the corresponding CAM asphalt mixes, the results of these materials only are reported in Fig. 5.8. The main differences can be observed at 10 °C, while increasing the test temperature the results were more close to each other. At the lowest test temperature the results obtained from ITSM and FS tests can be easily grouped based on type of REOB and R-REOB ratio. Fig. 5.8b clearly shows the strong effect of the R content on both, asphalt mixes and extended bitumens. In fact, a higher amount of R particles led to increased values of both elastic and complex moduli. Moreover, being an elastic material, R exhibited greater effects on E values than on G* values. Concerning the influence of the type of REOB, the use of V2 leads to major changes on complex modulus values instead of those of elastic modulus. At 10 °C, the V2-samples exhibits greater values of G* than the corresponding results of V1-samples; however, they do not always result in the higher elastic modulus values. All data confirmed the results previously found.

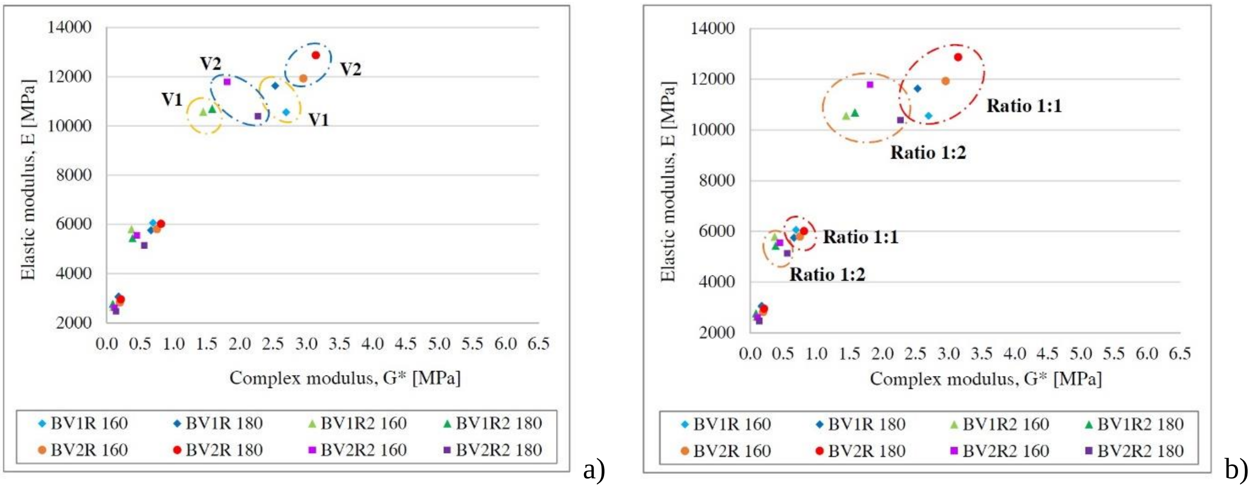


Fig. 155.8. Representation of elastic modulus, E, of asphalt mixtures versus complex modulus, G*, of the corresponding extended bitumens at 10, 20 and 30 °C grouped by: a) type of REOB; b) R-REOB ratio.

5.4 Leaching test

Due to the use of recycled materials and by-products in innovative bituminous binders and asphalt mixtures, the evaluation of the environmental impact of the extended bitumens and CAM asphalt mixes represents a crucial aspect to assess their feasible use as road construction materials. As detailed in Chapter 2 and reported in safety data sheets of materials (refer to Annex), both R and REOBs used for producing innovative bitumen extenders contain or may contain traces of metals, heavy metals and organic compounds that consists of Polycyclic Aromatic Hydrocarbons (PAHs).

As detailed above, the environmental impact of the bituminous products that contain recycled materials at the binder and the asphalt mixture levels will be performed on the CAM mixes with extended bitumens produced at 160 °C, that is CAM BV1R 160, CAM BV1R2 160, CAM BV2R 160 and CAM BV2R2 160. Three specimens for each asphalt concrete mixture were manufactured and underwent to preliminary volumetric and dynamic mechanical characterizations. Then, the same samples are subjecting to the horizontal dynamic surface leaching test.

The leaching test are on-going at the CAWR laboratories of the Coventry University. Unfortunately, the completion of the planned tests has influenced and, consequently slowed down, to the restrictions due to the COVID19 pandemic. The results are not available at the deadline of thesis submission.

5.4.1 Preliminary volumetric and dynamic mechanical characterizations of samples

The air voids content of the considered CAM mixtures was determined by the use of Superpave method only, since this method and the one that exploits the Italian technical specification were found to gain similar V_a results that always differ in 0.6%. The resulting V_a values of the CAM mixtures manufactured for environmental (last) characterization are listed in Table 5.3. For comparison, Table 5.3 reports the previous V_a data that was obtained from the samples produced for volumetric and mechanical (previous) analysis. Indeed, the samples of CAM mixtures with extended bitumens produced at 160 °C that were used for volumetric and mechanical characterizations in section 5.3 and those produced for assessing the environmental impact of the final products were manufactured in two distinct times.

Table 5.3. Comparison of air voids contents of CAM mixtures with extended bitumens produced at 160 °C for volumetric and mechanical (previous), and environmental (last) characterizations.

Asphalt mixture	**Previous**	**Last**
	Va – Superpave [%]	**Va – Superpave [%]**
CAM BV1R 160	2.5	3.5
CAM BV1R2 160	1.2	1.5
CAM BV2R 160	1.9	3.3
CAM BV2R2 160	1.3	1.7

The average V_a content of three samples per each of the CAM mixes produced for environmental (last) analysis confirmed the lower porosity of the innovative asphalt mixtures that contain a higher amount of REOB than R compared to the reference mixes (i.e. Traditional and CAM B 50/70). The last CAM mixtures produced with extended bitumens with equal mass proportion of R and REOB showed lower, but closer, V_a contents than both reference mixes, which were higher than the V_a values of the previous CAM mixtures used for volumetric and mechanical characterizations. The type of REOB did not influence the volumetric analysis. As a general remark, the results confirmed the necessity of adjusting the mix design for CAM mixes that used the R-REOB-modified bitumens in order to meet the required 4% of V_a content of the final asphalt product. Few and limited adjustments may be sufficient to satisfy the requirements for the CAM mixture with contain the same quantity of R and REOB. Nonetheless, it seems that the production methodology and precision of testing affected the final volumetric characteristics of the asphalt products due to the differences between the samples that were produced in different times.

The mechanical characterization by means of cyclic tests has been performed at the intermediate test temperature only, as described in section 5.2.2. The resulted stiffness moduli at 20 °C of the CAM mixtures with extended bitumens produced at 160 °C for mechanical (previous) and environmental (last) characterizations are plotted in Fig. 5.9. The results showed a reduction of the average ITSM values of every CAM mixture produced for the environmental characterization compared to those considered for mechanical characterization. In addition, based on type of REOB, the stiffness of the last CAM mixtures reduced when the V1 was used for the production of the asphalt products according to previous ITSM values at 10 °C. The opposite trend was found in the samples used for the volumetric and mechanical (previous) characterization. Moreover, the stiffness of the last set of samples exhibited a lower variability with respect to the quantities of recycled materials.

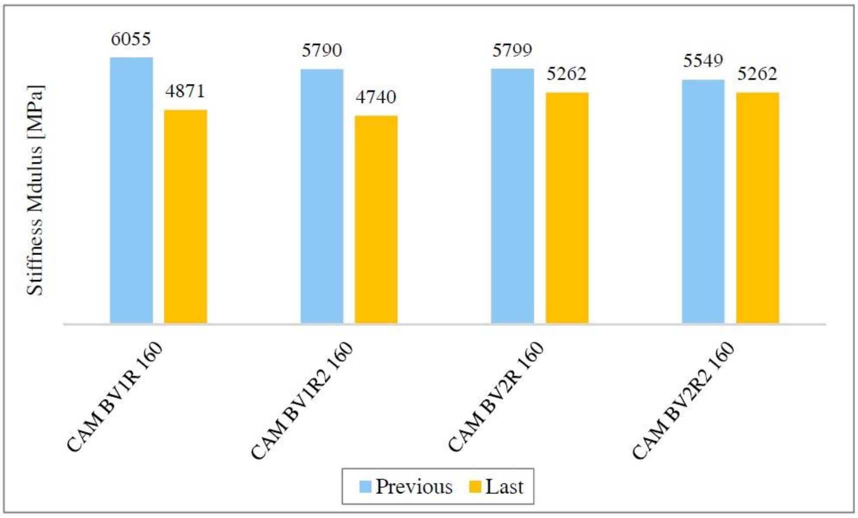


Fig. 5.9. Comparison of Indirect Tensile Stiffness Modulus (ITSM) at 20 °C of CAM mixtures with extended bitumens produced at 160 °C for volumetric and mechanical (previous), and environmental (last) characterizations.

5.4.2 Planned methodology to assess the potential release of dangerous substances

The potential release of dangerous substances from construction products into soil, surface water and ground water was planned to be assessed according to the PD CEN/TS 16637-2 (2014) standard using monolithic construction products. In fact, all samples with minimum dimensions of 40 mm in all directions can be considered as monolithic test pieces according to the considered standard. The requested dimensions allowed the author to produce the necessary specimens using the same production process of a standard bituminous material, thus the same adopted for producing specimens for volumetric and mechanical characterizations. Being standardized specimens for asphalt mixture characterization, the considered CAM mixtures for environmental analysis were subjected to volumetric and mechanical characterization as described above in section 5.4.3.

The horizontal dynamic surface leaching test consists of submerging the exposed surface of a sample in a leachant that is usually demineralized water or deionized water or water of equivalent purity with a specific conductivity. The leachant is introduced in the leaching vessel up to a given volume of liquid to surface area ratio (L/A ratio) at a given temperature and time intervals. In particular, the temperature of the leachant should be in the range of 19-25 °C and eight time intervals should be considered according to the standard such as:

- 6 h ± 15';
- 18 h ± 15';
- 30 h ± 45';
- 42 h ± 75';
- 120 h ± 75';
- 168 h ± 75';
- 480 h ± 7h;
- 672 h ± 12'.

During conditioning the investigated materials may leach some substances through diffusion and initial surface wash-off mechanisms and other processes such as solubility control, changes in speciation or depletion. After each conditioning time interval, the solution, i.e. the eluate, will be recovered from the leaching vessel without removing small parts of material that may be have fallen off the test sample. And, every eluate shall subsequently be characterized by physical, chemical and ecotoxicological methods according to current existing methods. The PD CEN/TS 16637-2 (2014) standard requests for the evaluation of pH and conductivity values of each eluate in accordance with EN 16192 and EN 16192 standards, respectively. The analysis of the eluates provides the value of the concentration of the substances in the solution of each individual time interval. In addition to the standard procedure, the total dissolved solids (TDS), the analysis for organic and inorganic compounds and FTIR analysis for microplastics will be investigated after each time interval.

5.5 Summary

The dynamic mechanical characterization of asphalt mixtures with high percentage of recycled materials confirm the rheological analysis performed on bituminous binders. In detail, the stiffening effect of R particles is evident, especially at high test temperature; while REOB softens the resulting asphalt mix and its influence is more marked at low test temperature.

The CAM mixes with extended bitumens have an intermediate behaviour between the reference mixes in terms of stiffness and tensile resistance. This means that the use of R-REOB-modified bitumens can mitigate the increased stiffness caused by the use of recycled raw aggregates. Higher R content on the incorporated extenders increases the ITSM and ITS values. The higher processing temperature of extenders and extended bitumens shows different influence on the stiffness and the indirect tensile strength of CAM mixes; it generally increases the ITSM values, while reduces the ITS values. Concerning the type of REOB, the introduction of V2 improves the indirect tensile strength of the asphalt concretes and, softens the resulting mixtures at intermediate and high test temperature.

The water conditioning has a negative effect on CAM asphalt mixtures. Albeit all mixes meet the Italian technical specification, the use of recycled materials seems to increase the water susceptibility of the final asphalt materials.

The results of volumetric analysis highlight the necessary of specific mix design for CAM asphalt mixture with extended bitumens as the V_a content is lower than the desired value. The higher quantity of REOB improves the handling of the asphalt concrete, which turns into less air voids content.

6

Conclusions and recommendations

The concepts of circular economy and sustainability are the basis of the reported research activities. The dissertation mainly focuses on the development and the chemo-mechanical characterization of bitumen extenders containing R and REOB for the production of innovative and eco-friendly bituminous binders and asphalt mixtures. In order to create a more sustainable asphalt concrete, also recycled aggregates are used for partial replacement of virgin natural aggregates in the aggregate skeleton. The experimental program encompassed five successive steps: (i) the evaluation of physicochemical properties of R and REOB, (ii) the definition of the optimal extenders by the development of a new protocol and their characterizations, (iii) the realization and investigation of the chemo-rheological behaviours of the extended bitumens at different boundary conditions, (iv) the assessment of the effectiveness of analytical method to predict the rheological parameters of extended bitumens and, finally, (v) the analysis of the mechanical performances of the corresponding asphalt mixtures. A standard 50/70 penetration grade bitumen (Pen 50/70) was tested for its chemo-rheological characterization as it represents the reference material and the main constituent of the innovative R-REOB-modified bitumens and CAM asphalt mixes. Based on the experimental research activities, the following conclusions and recommendations for further studies can be drawn:

- The laboratory analysis on the recycled products, R and REOB, and the corresponding extenders highlight the importance of material characterization in order to understand their chemo-rheological impact on the final extended bitumens. The recycled materials have intrinsic high variability since the final products vary due to the chemical composition of their virgin constituent materials and their production/refinery process. Moreover, the chemical composition of final recycled products is influenced by the changes due to ageing phenomena experienced by virgin tyre's rubber or lubricants during the in-service period, which can lead to deteriorate the materials in time. The differences were found especially for REOBs as V1 and V2 differ in terms of molecular components, which turn into different viscosity values and rheological responses. All these aspects affect the interactions between R and REOB.

- The developed characterization protocol can be successfully used to determine the optimum mass proportion of the recycled materials to produce bitumen extenders. The spectroscopic and morphologic analysis can define the maximum quantity of REOB that can be absorbed by R particles. However, the affinity between Vx and R is not well defined. Thus, it is suggested to improve the protocol with additional assessments in order to gain further insights into the affinity between R and REOBs.

- The incorporation of a R-REOB blend into Pen 50/70 improves the performances of the final bituminous binder at both high and low temperatures, which can be mainly ascribed to R particles and Vx, respectively. The investigations reveal that the type and quantity of extender's constituents considerably influence the rheological properties of R-REOB blends and final extended bitumens. The presence of R and, consequently, the formation of a polymer network within the matrix consistently improve the elasticity of the final products. Moreover, the higher R content enhances the rutting resistance and the maximum deformation that the materials can withstand before structural changes occur, while reduces the thermal susceptibility of the resulting products. On the other hand, higher R content increases the stiffness and the dynamic viscosity of the final products. Further investigations are recommended in order to reduce the final viscosity of the products without compromise the positive effect caused by the presence of polymers, albeit recycled. The use of V2 generally results in a more viscous-like behaviour of the extenders and extended bitumens. The addition of V1 is preferable in terms of rutting resistance, when the R-REOB ratio is equal to 1:1, and of thermal susceptibility. Regardless the type of REOB, the incorporation of this soften agent leads to increase the performances of materials at low temperatures.

- The processing conditions influence the chemical interactions between the constituents and the resulting rheological behaviour of final products; however, the effect of production temperature is more evident in the novel extended bituminous binders rather than in the extenders. This characteristic reflects the low temperature susceptibility of the considered recycled materials. The higher temperature production of R-REOB-modified bitumens improves the rutting resistance and the susceptibility to temperature changes. In addition, it stiffens the resulting binders. The higher processing temperature seems to reactivate the interactions with polymers, in this case between neat bitumen and extenders.

The separation conditioning affect the rheological responses of the extended bitumens. The storage of R-REOB-modified bitumens at high temperatures has detrimental effects on the binders' rheology. During storage, the solid particles of recycled polymer settle in time resulting in bottom parts of samples being rich in R particles. Despite the settlement of polymer particles, the formation of a polymer network within the neat bitumen matrix and its residual effects are still visible after the separation due to conditioning. Hence, the interactions between Pen 50/70 and R-REOB blends combine physical and chemical phenomena. Nonetheless, the higher R content leads to improves the elastic response of the corresponding innovative bituminous binder compared to that of Pen 50/70 even after an experienced sedimentation of polymer particles. Moreover, the higher temperatures facilitate the entanglement of R molecules with the Pen 50/70. The influence of Vx type was not unambiguously clear.

- The ageing phenomenon results in more stiff and elastic bituminous binders, which are less sensitive to frequency and temperature changes. The combination of R and REOB allows the extended bitumens to be less rigid and more elastic than the aged Pen 50/70. However, the response of the extended bitumens has a low variability than the neat bitumen through the testing frequencies and temperatures. Conversely to the results of fresh R-REOB-modified bitumens, higher amount of R and higher processing temperature show lower stiffness values. The use of V1 decreases the LVE range, while V2-samples can withstand greater deformations than those of unconditioned samples. This can mean that extended bitumens produced with V2 are less vulnerable to ageing than those containing V1.
- On the basis of the chemical investigations, the different composition of recycled materials and extenders from that of bituminous binders are observed. Specific functional groups associated to the constituents of recycled materials are detected. In detail, aliphatic, sulfoxide, carbonyl and aromatic groups are present in both, R and Vx. While, N-H stretch vibration and the butadiene bending vibration molecules are related only to REOB and R, respectively. Among specific functional groups of recycled materials, there are molecules typically associated to oxidative ageing such as carbonyl and sulfoxide structures. Consequently, the use of recycled material may be disadvantaged in terms of ageing resistance of the final extended bitumens as they bring additional S=O, C=O and C=C structures. The reference Pen 50/70 seems less prone to age as it counts lower quantity of sulfoxide and carbonyl structures than extended bitumens. Lower R content and production temperature and the use of V2 instead of V1 permits to reduce the increment of C=O bonds. The S=O bonds was found to be related to quantity of R particles mainly, hence higher R content increases the formation of sulfoxide structures. However, it should be considered that the FTIR spectra of R has higher absorbance values at low wavenumbers compared to that of petroleum-based materials, which may enhance the final value of C=O and S=O structures. It can be concluded that V1 is more susceptible to ageing than V2 and this result confirms what was obtained by the rheological analysis. However, it is recommended to further investigate the ageing rate of extended bitumens. In fact, albeit the recycled materials contain higher functional groups related to oxidative ageing, they may age less rapidly than Pen 50/70.
- The use of the SC model for predicting the complex shear modulus of extended bitumens starting from constituents' physical properties and geometrical aspect was found to be suitable for R-REOB-modified bitumens with equal mass proportion of recycled material. Higher differences between experimental and modelled data are obtained for extended bitumens with higher percentage of Vx than R. The lower precision are ascribed to the incorporation of a liquid-viscous phase together with R particles because it is not a rigid inclusion as hypothesised by the model. To overcome the inaccuracies it is helpful to further investigate the input parameters of the model by deeper experimental analysis on materials as proved by the evaluation of the specific Poisson's ratio. Moreover, the model can be specifically adjusted to

consider the introduction of a soften agent or, alternatively, other micromechanical models based on the homogenization theory can be taken into consideration for comparison and for verifying the suitable use of the theory. The models differ from the initial assumptions and simplifications, but also in terms of procedure; hence, a deeper investigation or a rearrangement of the model can help to better simulate the behaviour of the innovative binders.

- The volumetric analysis of asphalt mixtures manufactured with the eight extended bitumens reveals that a specific mix design should be performed and, then, used for producing the CAM mixtures. In detail, the higher quantity of REOB added into the bitumen's extenders acts as a softening agent that facilitates the handling and compaction of the materials.
- The mechanical performances of CAM mixtures with R-REOB-modified bitumens are intermediate to that of Traditional and CAM B 50/70 at about 20-25 °C. In general, the CAM mixtures with R-REOB-modified bitumens are stiffer than those with the Traditional bitumen at high test temperatures and less rigid at low test temperatures. The presence of a R-REOB blend can improve the rutting and thermal cracking resistances of the final asphalt mixtures confirming the results at the binder level. The incorporation of R has positive effects on stiffness and tensile resistance at the asphalt mix level, while the changes caused by type of REOB and processing temperature are not well identified. The water conditioning has a negative effect on CAM mixtures made with extended bitumens, even though the recorded values meet the Italian technical specification. Since the use of recycled materials may reduce the durability of the final asphalt concrete, it is recommended to further investigate the behaviour of CAM mixes under different damaging conditions.

Bibliography

Airey, G. (2017). 'Rheological and fracture characterisation of sustainable bio-binders and rejuvenators for virgin and recycled asphalt mixtures'. *Proceeding of the 1st Winter School 'Advances in Sustainable Asphalt Pavements'*, Moena - Italy.

Airey, G. D. (2002). 'Use of Black Diagrams to Identify Inconsistencies in Rheological Data'. *Road Materials and Pavement Design*, 3(4), 403–424.

Airey, G. D., Rahman, M. M., and Collop, A. C. (2003). 'Absorption of Bitumen into Crumb Rubber Using the Basket Drainage Method'. *International Journal of Pavement Engineering*, 4(2), 105–119.

Al-Qadi, I. L., Elseifi, M., and Carpenter, S. H. (2007). *Reclaimed asphalt pavement - A literature review - Report No. FHWA-ICT-07-001. Federal Highway Administration (FHWA)*, Urbana, Illinois - USA.

Amini, A., and Imaninasab, R. (2018). 'Investigating the effectiveness of Vacuum Tower Bottoms for Asphalt Rubber Binder based on performance properties and statistical analysis'. *Journal of Cleaner Production*, Elsevier Ltd, 171, 1101–1110.

Andersen, M. S. (2007). 'An introductory note on the environmental economics of the circular economy'. *Sustainability Science*, 2, 133–140.

Asgharzadeh, S. M., Tabatabaee, N., Naderi, K., and Partl, M. N. (2015). 'Evaluation of rheological master curve models for bituminous binders'. *Materials and Structures/Materiaux et Constructions*, 48, 393–406.

Asphalt Institute. (2016). *State of the knowledge - The use of REOB/VTAE in asphalt - IS-235*. (Asphalt Institute, ed.), USA.

ASTM D6723-12. (2012). *Standard Test Method for Determining the Fracture Properties of Asphalt Binder in Direct Tension (DT)*. U.S.A., 1–13.

ASTM D7405-15. (2015). *Standard Test Method for Multiple Stress Creep and Recovery (MSCR) of Asphalt Binder Using a Dynamic Shear Rheometer 1 , 2*. U.S.A., 10–13.

ATDM - Avizheh Technology and Development of Middle East. (2020). 'treated distillate aromatic extracted (TDAE)'.

Aurangzeb, Q., Ozer, H., Al-Qadi, I. L., and Hilton, H. H. (2017). 'Viscoelastic and Poisson's ratio characterization of asphalt materials: critical review and numerical simulations'. *Materials and Structures*, Springer Netherlands, 50(49), 1–12.

Australian Asphalt Pavement Association - AAPA. (2018). *Reclaimed Asphalt Pavement (RAP) Management Plan. National Technology & Leadership Committee*, Port Melbourne, Victoria - Australia.

Aziz, Md M.A., Rahman, Md T., Hainin, M.R. and Bakar, W. A. W. A. (2015). 'Alternative binders for flexible pavement'. *Construction and Building Materials*, Elsevier Ltd, 84, 315–319.

Bahia, H. U., Hanson, D. I., Zeng, M., Zhai, H., Khatri, M. A., and Anderson, R. M. (2001). *Caracterization of Modified Asphalt Binders in Superpave Mix Design - NCHRP Report 459. National Cooperative Highway Research Program (NCHRP)*, National Academies Press, Washington DC, Columbia - USA.

Becker, Y., Méndez, M. P., and Rodríguez, Y. (2001). 'Polymer modified asphalt'. *Vision Tecnologica*, 9(1), 39–50.

Di Benedetto, H., Delaporte, B., and Sauzéat, C. (2007). 'Three-Dimensional Linear Behavior of Bituminous Materials: Experiments and Modeling'. *International Journal of Geomechanics*, 7(2), 149–157.

Van den bergh, W. (2011). 'The Effect of Ageing on the Fatigue and Healing Properties of Bituminous Mortars'. PhD thesis - Delft University of Technology.

Bohm, H. J. (2020). *ILSB Report / ILSB-Arbeitsbericht 206: A Short Introduction to Basic Aspects of Continuum Micromechanics. Institute of Lightweight Design and Structural Biomechanics (ILSB) Vienna University of Technology*.

Borrego, A. G., Blanco, C. G., Prado, J. G., Díaz, C., and Guillén, M. D. (1996). '1H NMR and FTIR Spectroscopic Studies of Bitumen and Shale Oil from Selected Spanish Oil Shales'. *Energy & Fuels*, 10, 77–84.

Brock, J. D., and Richmond, L. J. (2006). *Milling and Recycling - Technical paper T-127. ASTEC 2006*.

Buttlar, W. G., Bozkurt, D., Al-Khateeb, G. G., and Waldhoff, A. S. (1999). 'Understanding asphalt mastic behavior through micromechanics'. *Transportation Research Record*, (1681), 157–169.

Calandra, P., Nicotera, I., Oliviero Rossi, C., and Turco Liveri, V. (2013). 'Dynamical properties of self-assembled surfactant-based mixtures: Triggering of one-dimensional anomalous diffusion in Bis(2-ethylhexyl)phosphoric acid/ n -octylamine systems'. *Langmuir*, 29(48), 14848–14854.

Caputo, P., Porto, M., Loise, V., Teltayev, B., and Rossi, C. O. (2019). 'Analysis of mechanical performance of bitumen modified with waste plastic and rubber (SBR) additives by rheology and PGSE NMR experiments'. *Eurasian Chemico-Technological Journal*, 21(3), 235–239.

Carr, H. Y., and Purcell, E. M. (1954). 'Effects of diffusion on free precession in nuclear magnetic resonance experiments'. *Physical Review*, 94(3), 630–638.

Celauro, B., Celauro, C., Lo Presti, D., and Bevilacqua, A. (2012). 'Definition of a laboratory optimization protocol for road bitumen improved with recycled tire rubber'. *Construction and Building Materials*, Elsevier Ltd, 37, 562–572.

Christensen, R. M., and Lo, K. H. (1979). 'Solution for effective shear proprties in three phase sphere and cylinder models'. *Journal of the Mechanics and Physics of Solids*, 27(4), 315–330.

CONOU. (2019). *Rapporto di Sostenibilità 2018*. Roma - Italy.

Copeland, A. (2011). *Reclaimed Asphalt Pavement in Asphalt Mixtures: State of the Practice - Report No. FHWA-HRT-11-021. Federal Highway Administration (FHWA)*, McLean, Virginia - USA.

Council of European Union. (1999). *Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste*. *Official Journal of the European Communities*.

D'Angelo, J., Reinke, G., Bahia, H., Wen, H., Johnson, C. M., and Marasteanu, M. (2010). *Development in Asphalt Binder Specifications*. *Transportation Research Circular E-C147: Development in asphalt binder specifications*, Washington DC - U.S.A.

DeDene, C. D., and You, Z. (2014). 'The performance of aged asphalt materials rejuvenated with waste engine oil'. *International Journal of Pavement Research and Technology*, 7(2), 145–152.

Delft University of Technology. (2020). 'List of functional groups and related wavenumber (cm-1) - Available and free information for students'.

Ding, X., Ma, T., Zhang, W., and Zhang, D. (2017). 'Experimental study of stable crumb rubber asphalt and asphalt mixture'. *Construction and Building Materials*, Elsevier Ltd, 157, 975–981.

Dondi, G., Tataranni, P., Pettinari, M., Sangiorgi, C., Simone, A., and Vignali, V. (2014). 'Crumb Rubber in cold recycled bituminous mixes: Comparison between Traditional Crumb Rubber and Cryogenic Crumb Rubber'. *Construction and Building Materials*, Elsevier Ltd, 68, 370–375.

ECHA - European Chemicals Agency. (2021). 'Che cos'è una sostanza'. <https://echa.europa.eu/it/support/substance-identification/what-is-a-substance#:~:text=UVCB stands for unknown or,products or of biological materials.> (Mar. 22, 2021).

Ecopneus Scpa. (2020a). *Il circolo vizioso che fa crescere il Paese - Report 2019*. Milano (MI) - Italy.

Ecopneus Scpa. (2020b). 'Recycling and recovery of ELTs'.

EN 1097-6. (2013). *BSI Standards Publication - Tests for mechanical and physical properties of aggregates, Part 6 : Determination of particle density and water absorption*. United Kingdom.

EN 12607-2. (2014). *Nederlandse norm - Bitumen and bituminous binders - Determination of the resistance to hardening under influene of heat and air, Part 2: TFOT method*. Nederland.

EN 12697-12. (2008). *BSI Standards Publication - Bituminous mixtures - Test methods for hot mix asphalt, Part 12: Determination of the water sensitivity of bituminous specimens*. United Kingdom.

EN 12697-23. (2017). *BSI Standards Publication - Bituminous mixtures — Test methods, Part 23: Determination of the indirect tensile strength of bituminous specimens*. United Kingdom.

EN 12697-26. (2012). *BSI Standards Publication - Bituminous mixtures - Test methods for hot mix asphalt, Part 26: Stiffness*. United Kingdom.

EN 12697-31. (2007). *BSI Standards Publication - Bituminous mixtures - Test methods for hot mix asphalt, Part 31: Specimen preparation by gyratory compactor*. United Kingdom.

EN 12697-5. (2012). *BSI Standards Publication - Bituminous mixtures - Test methods for hot mix asphalt, pART 5: Determination of the maximum density*. United Kingdom.

EN 13399. (2017). *BSI Standards Publication Bitumen and bituminous binders - Determination of storage stability of modified bitumen*. United Kingdom.

EN 13702. (2018). *BSI Standards Publication - Bitumen and bituminous binders - Determination of dynamic viscosity of bitumen and bituminous binders by the cone and plate method*. United Kingdom.

EN 14243-1. (2019). *BSI Standards Publication - Materials obtained from end of life tyres - Part 1: General definitions related to the methods for determining their dimension(s) and impurities*. United Kingdom.

EN 14243-2. (2019). *BSI Standards Publication - Materials obtained from end of life tyres - Part 2: Granulates and powders- Meyhods for determining the particle size disttribution and impurities, including free steel and free textile content*. United Kingdom.

EN 14769. (2005). *Nederlandse norm - Bitumen and bituminous binders - Accelerated long-term ageing conditioning by a Pressure Ageing Vessel (PAV)*. Nederland.

EN 14770. (2012). *BSI Standards Publication - Bitumen and bituminous binders - Determination of complex shear modulus and phase angle - Dynamic Shear Rheometer (DSR)*. United Kingdom.

Eshelby, J. D. (1957). 'The determination of the elastic field of an ellipsoidal inclusion, and related probems'. *Proceeding of the Royal Society of London - Series A*, 376–396.

Eshelby, J. D. (1959). 'The elastic field outside an ellipsoidal inclusion'. *Proceeding of the Royal Society of London - Series A*, 561–569.

ETRma. (2019). *Europe - 92 % of all End of Life Tyres collected and treated in 2017*. Brussels - Belgium.

European Commission. (2020). *A new Circular Economy Action Plan for a cleaner and more competitive Europe, COM(2020) 98 Final*. Brussels - Belgium.

European Parliament and Council. (2008). *Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain directives*. *Official Journal of the European Union*, 3–30.

European Tyre & Rubber manufacturers' association. (2019). *Press release Europe - 92 % of all End of Life Tyres collected and treated in 2017*.

Eurostat - EU Commission. (2020a). 'Circular economy - Overview'. <https://ec.europa.eu/eurostat/web/circular-economy> (Oct. 20, 2020).

Eurostat - EU Commission. (2020b). 'Generation of waste by economic activity'. <https://ec.europa.eu/eurostat/web/waste/data/main-tables> (Oct. 20, 2020).

Fernandes, S. R. M., Silva, H. M. R. D., and Oliveira, J. R. M. (2018). 'Developing enhanced modified bitumens with waste engine oil products combined with polymers'. *Construction and Building Materials*, Elsevier Ltd, 160, 714–724.

Filippelli, L., Oliviero Rossi, C., Carini, M., Chiaravallotti, F., and Gentile, L. (2013). 'Structural characterization of bitumen system by Prony-like method applied to NMR and rheological relaxation data'. *Molecular Crystal and Liquid Crystal*, 572(1), 50–58.

Filippelli, L., De Santo, M. P., Gentile, L., and Oliviero Rossi, C. (2015). 'Quantitative evaluation of the restructuring effect of a warm mix additive on bitumen recycling production'. *Road Materials and Pavement Design*, 16(3), 741–749.

Fini, E. H., Hosseinnezhad, S., Oldham, D., Mclaughlin, Z., Alavi, Z., and Harvey, J. (2019). 'Bio-modification of rubberised asphalt binder to enhance its performance'. *International Journal of Pavement Engineering*, Taylor & Francis, 20(10), 1216–1225.

GEIR. (2008). *'Clean , Clever and Competitive' - Why the Recycling of Waste Oils Must Remain an EU Policy Priority*. Brussels - Belgium.

GEIR. (2016). *Waste Framework Directive revision: European waste oil re-refining industry position*. Brussels - Belgium.

Ghossein, E. (2014). 'Numerical validation of analytical homogenization models for the case of randomly distributed and oriented ellipsoidal fibers reinforced composites'. Ecole Polytechnique de Montréal.

Golalipour, A., and Bahia, H. (2014). 'Evaluation of Oil Modification Effect on Asphalt Binder Thermal Cracking and Aging Properties'. *Proceedings of the 59th Annual Conference of the Canadian Technical Asphalt Association,* Victoria BC.

Harris, D. C. (1998). ‘Nonlinear least-squares curve fitting with microsoft excel solver’. *Journal of Chemical Education*, 75(1), 119–121.

Hashin, Z. (1970). ‘Complex moduli of viscoelastic composites-I. General theory and application to particulate composites’. *International Journal of Solids and Structures*, 6, 539–552.

Herrington, P. R. (1992). ‘Use of rerefined oil distillation bottoms as extenders for roading bitumens’. *Journal of Materials Science*, 27(24), 6615–6626.

Herrington, P. R. (2012). ‘Diffusion and reaction of oxygen in bitumen films’. *Fuel*, Elsevier Ltd, 94, 86–92.

Hill, R. R. (1965). ‘A Self-Consistent mechanics of composite materials’. *Journal of Machanics and Physics of Solids*, 13, 213–222.

Hofko, B., Alavi, M. Z., Grothe, H., Jones, D., and Harvey, J. (2017). ‘Repeatability and sensitivity of FTIR ATR spectral analysis methods for bituminous binders’. *Materials and Structures/Materiaux et Constructions*, Springer Netherlands, 50(187).

Hossain, M. U., Poon, C. S., Lo, I. M. C., and Cheng, J. C. P. (2016). ‘Comparative environmental evaluation of aggregate production from recycled waste materials and virgin sources by LCA’. *Resources, Conservation and Recycling*, Elsevier B.V., 109, 67–77.

Huang, S.-C. (2008). ‘Rubber concentrations on rheology of aged asphalt binders’. *Journal of Materials in Civil Engineering*, 20(3), 221–229.

Huang, Y., Bird, R. N., and Heidrich, O. (2007). ‘A review of the use of recycled solid waste materials in asphalt pavements’. *Resources, Conservation and Recycling*, 52, 58–73.

Ingrassia, L. P., Lu, X., Ferrotti, G., and Canestrari, F. (2020a). ‘Chemical, morphological and rheological characterization of bitumen partially replaced with wood bio-oil: Towards more sustainable materials in road pavements’. *Journal of Traffic and Transportation Engineering (English Edition)*, Elsevier Ltd, 7(2), 192–204.

Ingrassia, L. P., Lu, X., Ferrotti, G., Conti, C., and Canestrari, F. (2020b). ‘Investigating the “circular propensity” of road bio-binders: Effectiveness in hot recycling of reclaimed asphalt and recyclability potential’. *Journal of Cleaner Production*, Elsevier Ltd, 255, 120193.

Itelyum Regeneration Srl. (2020). ‘Processo tecnologico’. <https://www.itelyum-regeneration.com/it/tecnologia/processo-tecnologico/> (Nov. 22, 2020).

Jing, R. (2019). ‘Ageing of bituminous materials - Experimental and numerical characterization’. PhD Thesis - Delft University of Technology.

Jones, M., and Taylor, S. E. (2015). ‘NMR relaxometry and diffusometry in characterizing structural, interfacial and colloidal properties of heavy oils and oil sands’. *Advances in Colloid and Interface Science*, Elsevier B.V., 224, 33–45.

Kalantar, Z. N., Karim, M. R., and Mahrez, A. (2012). ‘A review of using waste and virgin polymer in pavement’. *Construction and Building Materials*, Elsevier Ltd, 33, 55–62.

Kandhal, P. S., and Mallick, R. B. (1997). *Pavement Recycling Guidelines for State and Local Governments - Report No. FHWA-SA-98-042. Federal Highway Administration (FHWA)*, Auburn, Alabama - USA.

Karki, P., and Zhou, F. (2019). ‘Impact of Re-Refined Engine Oil Bottoms on Asphalt Binder Properties’. *Journal of Transportation Engineering, Part B: Pavements*, 145(4).

Karlsson, R., and Isacsson, U. (2003). ‘Diffusion and reaction of oxygen in bitumen films’. *Journal of Materials in Civil Engineering*, Elsevier Ltd, 38, 2835–2844.

Karlsson, R., and Isacsson, U. (2006). ‘Material-Related Aspects of Asphalt Recycling—State-of-the-Art’. *Journal of Materials in Civil Engineering*, 18(1), 81–92.

Kemmer, G., and Keller, S. (2010). ‘Nonlinear least-squares data fitting in Excel spreadsheets’. *Nature Protocols*, Nature Publishing Group, 5(2), 267–281.

Kluttz, R. (2012). ‘Considerations for Use of Alternative Binders in Asphalt Pavements - Material Characteristics’. *Transportation Research Circular E-C165: Alternative Binders for Sustainable Asphalt Pavements*, Transportation Research Board (TRB), Wasghington DC, Columbia - USA.

Kök, B. V., and Çolak, H. (2011). ‘Laboratory comparison of the crumb-rubber and SBS modified bitumen and hot mix asphalt’. *Construction and Building Materials*, Elsevier Ltd, 25(8), 3204–3212.

Kuhlman, T., and Farrington, J. (2010). 'What is sustainability?' *Sustainability*, 2(11), 3436–3448.

Lamontagne, J., Dumas, P., Mouillet, V., and Kister, J. (2001). 'Comparison by Fourier transform infrared (FTIR) spectroscopy of different ageing techniques: Application to road bitumens'. *Fuel*, 80, 483–488.

Leggio, A., Belsito, E. L., De Luca, G., Di Gioia, M. L., Leotta, V., Romio, E., Siciliano, C., and Liguori, A. (2016). 'One-pot synthesis of amides from carboxylic acids activated using thionyl chloride'. *RSC Advances*, Royal Society of Chemistry, 6(41), 34468–34475.

Lei, Z., Bahia, H., Yi-qiu, T., and Ling, C. (2017). 'Effects of refined waste and bio-based oil modifiers on rheological properties of asphalt binders'. *Construction and Building Materials*, Elsevier Ltd, 148, 504–511.

Lesueur, D. (2009). 'The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification'. *Advances in Colloid and Interface Science*, 145, 42–82.

Li, J., Yu, M., Cui, X., and Wang, W. (2019). 'Properties and components of recycled engine oil bottom rejuvenated asphalt and its grey relationship analysis'. *Advances in Materials Science and Engineering*, 2019, 70–80.

Li, X., Gibson, N., Andriescu, A., and S. Arnold, T. (2017). 'Performance evaluation of REOB-modified asphalt binders and mixtures'. *Road Materials and Pavement Design*, 18, 128–153.

Liu, H., Zeiada, W., Al-Khateeb, G. G., Shanableh, A., and Samarai, M. (2021). 'Use of the multiple stress creep recovery (MSCR) test to characterize the rutting potential of asphalt binders: A literature review'. *Construction and Building Materials*, 269.

Lu, X., Talon, Y., and Redelius, P. (2008). 'Aging of bituminous binders – laboratory tests and field data'. *The 4th eurasphalt & eurobitume congress*, 1–12.

Luo, R., and Lytton, R. L. (2011). 'Self-Consistent Micromechanics Models of an Asphalt Mixture'. *Journal of Materials in Civil Engineering*, 23(1), 49–55.

Ma, F., Sha, A., Lin, R., Huang, Y., and Wang, C. (2016). 'Greenhouse gas emissions from asphalt pavement construction: A case study in China'. *International Journal of Environmental Research and Public Health*, 13(3).

Ma, T., Wang, H., He, L., Zhao, Y., Huang, X., and Chen, J. (2017). 'Property Characterization of Asphalt Binders and Mixtures Modified by Different Crumb Rubbers'. *Journal of Materials in Civil Engineering*, 29(7), 04017036.

Martinho, F. C. G., Picado-Santos, L. G., and Capitão, S. D. (2018). 'Feasibility assessment of the use of recycled aggregates for asphalt mixtures'. *Sustainability*, 10(1737).

McDaniel, R. S., Soleymani, H., Anderson, R. M., Turner, P., and Peterson, R. (2000). *Recommended Use of Reclaimed Asphalt Pavement in the Superpave Mix Design Method - NCHRP Web Document 30*. *NCHRP Web Document 30 - Project D9-12: Contractor's Final Report*, Wasghington DC, Columbia - USA.

Mills-Beale, J., and You, Z. (2010). 'The mechanical properties of asphalt mixtures with Recycled Concrete Aggregates'. *Construction and Building Materials*, Elsevier Ltd, 24(3), 230–235.

Mogawer, W. S., Austerman, A., Al-Qadi, I. L., Buttlar, W., Ozer, H., and Hill, B. (2017). 'Using binder and mixture space diagrams to evaluate the effect of re-refined engine oil bottoms on binders and mixtures after ageing'. *Road Materials and Pavement Design*, 18(1), 154–182.

Molenaar, A. A. A., Hagos, E. T., and van de Ven, M. F. C. (2010). 'Effects of Aging on the Mechanical Characteristics of Bituminous Binders in PAC'. *Journal of Materials in Civil Engineering*.

Mori, T., and Tanaka, K. (1973). 'Average stress in matrix and average elastic energy of materials with misfitting inclusions'. *Acta Metallurgica*, 21, 571–574.

Mturi, G. A. J., O'Connell, J., Zoorob, S. E., and De Beer, M. (2014). 'A study of crumb rubber modified bitumen used in South Africa'. *Road Materials and Pavement Design*, 15(4), 774–790.

Murray, A., Skene, K., and Haynes, K. (2017). 'The Circular Economy: An Interdisciplinary Exploration of the Concept and Application in a Global Context'. *Journal of Business Ethics*, Springer Netherlands, 140(3), 369–380.

Newcomb, D. E., Ray Brown, E., and Epps, J. A. (2007). *Designing HMA mixtures with High RAP content: A practical guide - NAPA, Quality Improvement Series 124*. *National Asphalt Pavement Association (NAPA)*, Lanham, Maryland - USA.

Nivitha, M. R., Prasad, E., and Krishnan, J. M. (2016). 'Ageing in modified bitumen using FTIR spectroscopy'. *International Journal of Pavement Engineering*, Taylor & Francis, 17(7), 565–577.

Nur Izzi, M. Y. (2012). 'Modelling the linear viscoelastic rheological properties of bituminous binders'. PhD thesis - University of Nottingham.

Nynas AB - Eriksson, A. (2020). 'Knowledge tank - Assisting an agent'. <https://www.nynas.com/en/product-areas/tyre-rubber-oils/knowledge-tank/assisting-an-agent/> (Nov. 23, 2020).

Oliviero Rossi, C., Caputo, P., De Luca, G., Maiuolo, L., Eskandarsefat, S., and Sangiorgi, C. (2018). '1H-NMR spectroscopy: A possible approach to advanced bitumen characterization for industrial and paving applications'. *Applied Sciences*, 8, 229.

Oliviero Rossi, C., Spadafora, A., Teltayev, B., Izmailova, G., Amerbayev, Y., and Bortolotti, V. (2015). 'Polymer modified bitumen: Rheological properties and structural characterization'. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 480, 390–397.

Ossa, A., García, J. L., and Botero, E. (2016). 'Use of recycled construction and demolition waste (CDW) aggregates: A sustainable alternative for the pavement construction industry'. *Journal of Cleaner Production*, Elsevier Ltd, 135, 379–386.

Paliukaite, M., Assuras, M., and Hesp, S. A. M. (2016). 'Effect of recycled engine oil bottoms on the ductile failure properties of straight and polymer-modified asphalt cements'. *Construction and Building Materials*, Elsevier Ltd, 126, 190–196.

Paranavithana, S., and Mohajerani, A. (2006). 'Effects of recycled concrete aggregates on properties of asphalt concrete'. *Resources, Conservation and Recycling*, 48, 1–12.

Pasandín, A. R., and Pérez, I. (2015). 'Overview of bituminous mixtures made with recycled concrete aggregates'. *Construction and Building Materials*, 74, 151–161.

PD CEN/TS 16637-2. (2014). *BSI Standards Publication - Construction products - Assessment of release of dangerous substances, Part 2: Horizonalt dynamic surface leaching test*. United Kingdom.

Pérez, I., Pasandín, A. R., and Gallego, J. (2012). 'Stripping in hot mix asphalt produced by aggregates from construction and demolition waste'. *Waste Management and Research*, 30(1), 3–11.

Petersen, J. C. (2009). *A review of the fundamentals of asphalt oxidation*. *Transportation Research Circular E-C140: A review of the fundamentals of asphalt oxidation*, Washington DC - U.S.A.

Lo Presti, D. (2013). 'Recycled Tyre Rubber Modified Bitumens for road asphalt mixtures: A literature review'. *Construction and Building Materials*, Elsevier Ltd, 49, 863–881.

Lo Presti, D., and Airey, G. (2013). 'Tyre rubber-modified bitumens development: the effect of varying processing conditions'. *Road Materials and Pavement Design*, 14(4), 888–900.

Lo Presti, D., Vasconcelos, K., Orešković, M., Pires, G. M., and Bressi, S. (2019). *On the degree of binder activity of reclaimed asphalt and degree of blending with recycling agents*. *Road Materials and Pavement Design*.

Ragab, M., and Abdelrahman, M. (2018). 'Enhancing the crumb rubber modified asphalt's storage stability through the control of its internal network structure'. *International Journal of Pavement Research and Technology*, Chinese Society of Pavement Engineering, 11, 13–27.

Rahman, M. (2004). 'Characterization of Dry Process Crumb Rubber Modified Asphalt Mixtures'. *University of Nottingham*, PhD Thesis - University of Nottingham, School of Civil Engineering.

Rubab, S., Burke, K., Wright, L., Hesp, S. A. M., Marks, P., and Raymond, C. (2011). 'Effects of engine oil residues on asphalt cement quality'. *Proceesings of the 56th Annual Conference of the Canadian Technical Asphalt Association, Quebec City (Canada)*, Victoria BC.

Salomon, D., and Zhai, H. (2002). 'Ranking asphalt binders by activation energy for flow'. *Journal of Applied Asphalt Binder Technology*, 2(2), 52–60.

Sangiorgi, C., Eskandarsefat, S., Tataranni, P., Simone, A., Vignali, V., Lantieri, C., and Dondi, G. (2017). 'A complete laboratory assessment of crumb rubber porous asphalt'. *Construction and Building Materials*, Elsevier Ltd, 132, 500–507.

Sibeko, M. A., Adeniji, A. O., Okoh, O. O., and Hlangothi, S. P. (2020). 'Trends in the management of waste tyres and recent experimental approaches in the analysis of polycyclic aromatic hydrocarbons (PAHs) from rubber crumbs'. *Environmental Science and Pollution Research*, Environmental Science and Pollution Research, 27, 43553–43568.

Signus Ecovalor; Ecopneus Scpa. (2014). *Guida per la produzione di bitumi con polverino di gomma da Pneumatico Fuori Uso*.

Southern African Bitumen Association - SABITA. (2019). *Use of reclaimed asphalt in the production of asphalt - MANUAL 36/TRH 21*. Cape Town - South Africa.

Stempihar, J., Gundla, A., and Underwood, B. S. (2018). 'Interpreting Stress Sensitivity in the Multiple Stress Creep and

Recovery Test'. *Journal of Materials in Civil Engineering*, 30(2).

Szerb, E. I., Nicotera, I., Teltayev, B., Vaiana, R., and Oliviero Rossi, C. (2017). 'Highly stable surfactant-crumb rubber-modified bitumen: NMR and rheological investigation'. *Road Materials and Pavement Design*, Taylor & Francis, 19.

Szerb, E. I., Nicotera, I., Teltayev, B., Vaiana, R., and Oliviero Rossi, C. (2018). 'Highly stable surfactant-crumb rubber-modified bitumen: NMR and rheological investigation'. *Road Materials and Pavement Design*, 19(5), 1192–1202.

Tarsi, G., Tataranni, P., and Sangiorgi, C. (2020). 'The challenges of using reclaimed asphalt pavement for new asphalt mixtures: A review'. *Materials*, 13, 4052.

Tarsi, G., Varveri, A., Lantieri, C., Scarpas, A., and Sangiorgi, C. (2018). 'Effects of different aging methods on chemical and rheological properties of bitumen'. *Journal of Materials in Civil Engineering*, 30(3).

Thompson, D. C., and Hoiberg, A. J. (1979). *Bituminous materials: Asphalt tars and pitches*. (D. C. Thompson and A. J. Hoiberg, eds.), Krieger Publishing Co., New York, New York - USA.

Underwood, B. S., and Kim, Y. R. (2014). 'A four phase micro-mechanical model for asphalt mastic modulus'. *Mechanics of Materials*, Elsevier Ltd, 75, 13–33.

United Nations Environmental Programme. (2006). *PRODEV: Supporting the circular economy development of Guiyang*.

Varveri, A., Mocetti, F., Scarpas, A., Lantieri, C., and Sangiorgi, C. (2019). 'An evaluation of water effects on bitumen'. *98th Transportation Research Board Annual Meeting Compendium of Papers*.

Vasconcelos, K. L., Bhasin, A., and Little, D. N. (2011). 'History dependence of water diffusion in asphalt binders'. *International Journal of Pavement Engineering*, 12(5), 497–506.

Wang, H., Dang, Z., Li, L., and You, Z. (2013). 'Analysis on fatigue crack growth laws for crumb rubber modified (CRM) asphalt mixture'. *Construction and Building Materials*, Elsevier Ltd, 47, 1342–1349.

Wang, H., Liu, X., Apostolidis, P., and Scarpas, T. (2018). 'Rheological behavior and its chemical interpretation of crumb rubber modified asphalt containing warm-mix additives'. *Journal of TRansportation Research Board*, 2672(28), 337–348.

Wang, H., Liu, X., Zhang, H., Apostolidis, P., Erkens, S., and Skarpas, A. (2020). 'Micromechanical modelling of complex shear modulus of crumb rubber modified bitumen'. *Materials and Design*, The Author(s), 188, 1–12.

Way, G. B., Kaloush, K. E., and Biligiri, K. P. (2011). 'Asphalt Rubber Standard Practice Guide'.

Wielinski, J., Kriech, A., Huber, G., Horton, A., and Osborn, L. (2015). 'Analysis of vacuum tower asphalt extender and effect on bitumen and asphalt properties'. *Road Materials and Pavement Design*, 16, 90–110.

Wik, A., and Dave, G. (2005). 'Environmental labeling of car tires-toxicity to Daphnia magna can be used as a screening method'. *Chemosphere*, 58, 645–651.

Williams, E. (2019). *Achieving Climate Goals by Closing the Loop in a Circular Carbon Economy - Report KS--2019-II10. King Abdullah Petroleum Studies and Research Center*, Riyadh, Saudi Arabia.

Williams, M. L., Landel, R. F., and Ferry, J. D. (1955). 'The Temperature Dependence of Relaxation Mechanisms in Amorphous Polymers and Other Glass-forming Liquids'. *Journal of the American Chemical Society*, 77, 3701–3707.

Willis, J. R., Turner, P., Julian, G., Taylor, A. J., Tran, N., and Padula, F. de G. (2012). *Effects of Changing Virgin Binder Grade and Content on Rap Mixture Properties - NCAT Report 12-03. National Center for Ashalt Technology*, Auburn, Alabama - USA.

World Commission on Environment and Development. (1987). *Our Common Future. Oxford University Press*, New York, New York - USA.

Yeniay, O. (2005). 'A comparative study on optimization methods for the constrained nonlinear programming problems'. *Mathematical Problems in Engineering*, 2005(2), 165–173.

Yildirim, Y. (2007). 'Polymer modified asphalt binders'. *Construction and Building Materials*, 21, 66–72.

Yin, H. M., Buttlar, W. G., Paulino, G. H., and Benedetto, H. Di. (2008). 'Assessment of Existing Micro-mechanical Models for Asphalt Mastics Considering Viscoelastic Effects'. *Road Materials and Pavement Design*, 9(1), 31–57.

Yin, H. M., and Sun, L. Z. (2005). 'Elastic modelling of periodic composites with particle interactions'. *Philosophical Magazine Letters*, 85(4), 163–173.

Zanetti, M. C., Fiore, S., Ruffino, B., Santagata, E., Dalmazzo, D., and Lanotte, M. (2015). 'Characterization of crumb rubber from end-of-life tyres for paving applications'. *Waste Management*, Elsevier Ltd, 45, 161–170.

Zaumanis, M., and Mallick, R. B. (2015). 'Review of very high-content reclaimed asphalt use in plant-produced pavements: State of the art'. *International Journal of Pavement Engineering*, 16(1), 39–55.

Zhang, H., Anupam, K., Scarpas, A., and Kasbergen, C. (2018). 'Comparison of different micromechanical models for predicting the effective properties of open graded mixes'. *Transportation Research Record*, 2672(28), 404–415.

Zhang, H., Chen, Z., and Li, L. (2017). 'Effect of Nanozinc Oxide and Organic Expanded Vermiculite Compound on Antiaging Properties of SBR Modified Bitumen'. *Journal of Materials in Civil Engineering*, 29(11), 04017204.

Zhang, L., Xing, C., Gao, F., Li, T., and Tan, Y. (2016). 'Using DSR and MSCR tests to characterize high temperature performance of different rubber modified asphalt'. *Construction and Building Materials*, Elsevier Ltd, 127, 466–474.

Zhou, F., Hu, S., Das, G., and Scullion, T. (2011). *High RAP mixes design methodology with balanced performance - Report No. FHWA/TX-11/0-6092-2. Federal Highway Administration (FHWA)*, College Station, Texas - USA.

Zhu, J., Wu, S., Zhong, J., and Wang, D. (2012). 'Investigation of asphalt mixture containing demolition waste obtained from earthquake-damaged buildings'. *Construction and Building Materials*, Elsevier Ltd, 29, 466–475.

Ziari, H., Goli, A., and Amini, A. (2016). 'Effect of crumb rubber modifier on the performance properties of rubberized binders'. *Journal of Materials in Civil Engineering*, 28(12).

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Giulia Tarsi

Bologna, 31/12/2020

Annexes

SCHEDA TECNICA DI PRODOTTO

POLVERINO DI GOMMA B.0/0.42

Revisione 06.2016

PRODUTTORE:	Albatros Ecologia Ambiente Sicurezza Soc. Cons. a r.l.
IMPIANTO:	Via Argine San Paolo n. 18/A, 48024 Massa Lombarda (RA), Italia Tel. +39(0)545.97.12.11 e-mail: rubber@albatros.ra.it

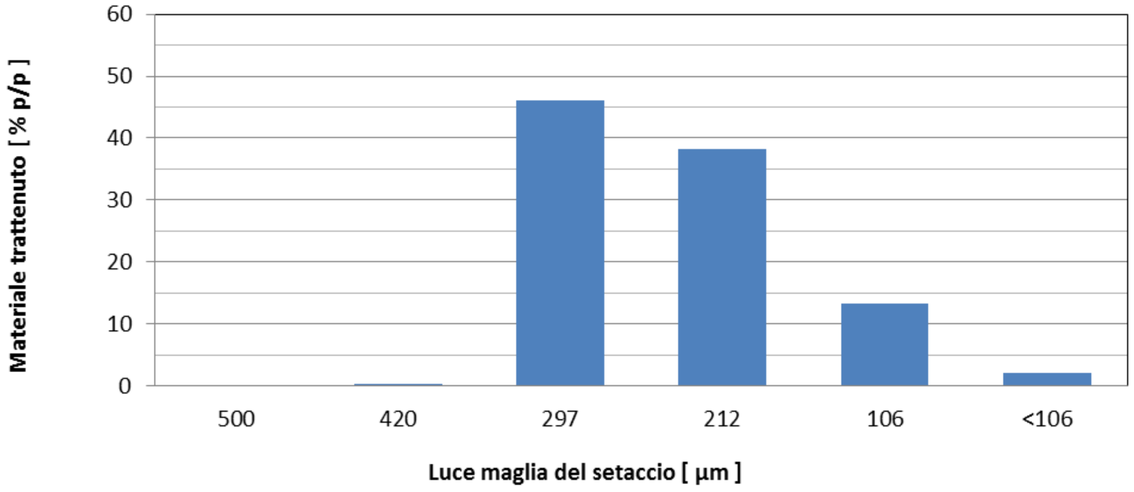
Polverino di gomma ottenuto dalla lavorazione degli pneumatici fuori uso di tipo autocarro.
Usi comuni: ingrediente per la produzione di mescole elastomeriche e plastomeriche; additivo per asfalti stradali; componente per la preparazione di resine, di pavimenti per interni ed esterni; prodotti per l'edilizia; infrastrutture varie, tramviarie e portuali; prodotti per l'ingegneria civile; componente di pannelli per isolamento acustico. Di seguito si riportano i valori statistici delle proprietà chimico-fisiche e granulometriche.

Proprietà Chimico - Fisiche

Parametro	U.M.	Valore	Metodo analitico
Apparenza	-	Solido in polvere di colore nero	-
Estratto acetonico	%	5,22	ASTM D 297
Ceneri	%	8,56	Interno parzialmente in accordo con il metodo ISO 9924-1
Carbonato di calcio	%	4,95	
Carbon black	%	25,62	
Carbonio organico totale	%	62,11	
Peso specifico apparente	kg/L	0,51	Interno
Peso specifico reale	kg/L	1,02	Interno
Contenuto di tessile residuo	%	< 0,01	UNI CEN TS 14243
Contenuto di acciaio residuo	%	< 0,01	UNI CEN TS 14243

Curva Granulometrica

Serie setaccio	MESH	µm	% trattenuto	Metodo analitico
ASTM	40	420	0,35	UNI CEN TS 14243
ASTM	50	297	46,12	
ASTM	70	212	38,29	
ASTM	140	106	13,20	
ASTM	< 140	< 106	2,04	



Section 1: IDENTIFICATION OF THE SUBSTANCE/MIXTURE AND OF THE COMPANY/UNDERTAKING

1.1 Product indentifier

Commercial name:	Rubber Powder B.0/0.42
Mixture name:	Rubber powder made of vulcanized rubber polimer, containing Carbon Black (CAS 215-609-9), zinc oxide (CAS 215-222-5), magnesium silicate (CAS 238-877-9), aluminium silicate (CAS 310-194-1), extender oils (CAS 64741-88-4, CAS 64742-65-0, CAS 64742-52-5, CAS 68783-04-0).
CAS Number	n.a.
EC Number	n.a.
Index Number	n.a.
Registration number	n.a.
Chemical Formula	n.a. (vulcanized rubber polymer)
Molecular weight	n.a. (vulcanized rubber polymer)

1.2 Relevant identified uses of the substance or mixture and uses advised against

Description of common uses:
Used to produce elastomeric and plastomeric compounds; additive in road asphalt mixtures; component for the preparation of resins, component in flooring for indoor and outdoor; component in building products; transportation or port infrastructures and civil engineering, panels for acoustic insulation.

Main User Group:
SU3: Industrial uses: Uses of substances as such or in preparations at industrial sites
SU22: Professional uses: Public domain (administration, education, entertainment, services, craftsmen)

Sector of Use:
SU11: Manufacture of rubber product;
SU12: Manufacture of plastics products, including compounding and conversion
SU13: Manufacture of other non metallic mineral products, e.g. plasters, cement
SU19: Building and construction work.

Process Categories:
PROC21: Low energy manipulation and handling of substances bound in/on materials or articles
PROC23: Open processing and transfer operations at substantially elevated temperature

Environmental Release Categories.
ERC5: Use at industrial site leading to inclusion into/onto article

Disadvised uses: Uses implying either the direct and prolonged or the indirect and repeated contact with the skin or the oral cavity should be avoided.
The use at temperatures greater than 170 °C can lead to the issuance of noxious odor due to the release of sulfurate substances.

1.3 Details of the supplier of the safety data sheet

Company name	Albatros Ecologia Ambiente Sicurezza Soc. Cons. a r. l.
Plant address	Via Argine San Paolo n. 18/A, 48024 Massa Lombarda (RA), Italia
Contact person	Technical office
Phone number	+39.(0)545.971211 (office hours)
Fax	+39.(0)545.985350
e-mail	rubber@albatros.ra.it

1.4 Emergency telephone number

If exposed to combustion fumes, consult your nearest Poison Control Center, which will provide information service in the event of poisoning or ingestion of toxic or caustic substances.
Milan area: MAJOR HOSPITAL CA' GRANDA NIGUARDA, Piazza Ospedale Maggiore, 3-20162 MILAN, Telephone Reference: 02-66101029 - AVAILABILITY H 24.

Section 2: HAZARD IDENTIFICATION

Physical-chemical hazards:	In case of combustion may generate toxic fumes.
Hazards to health:	Not classified as hazardous to human health according to the criteria established by Regulation EC 1272/2008. The fine granulate or powder may cause a slight and temporary foreign-body eye irritation. Rubber powder or granulate do not contain carcinogenic substances in concentrations greather than 0.1% and do not contain B(a)P in concentrations greather than 0.05%. Notwithstanding the above, as the concentration of PAHS may exceed the limit of 1 ppm, the Regulation 1272/2013 requires that uses leading to direct and prolonged or repeated short-term contact with the skin or the oral cavity are avoided.
Hazards for the environment:	Based on leaching test carried out by the producers, demonstrating a bioavailable concentration of Zn lower than 0.003%, the mixture is not classifiable as hazardous for the aquatic ecosystem. Rubber powder and granulate do hot have acute toxicity properties for the aquatic environment, based on aquatic toxicity tests performed in accordance with Regulation EC 1907/2006 and Regulation 440/2008.
Others hazards:	Rubber powder with average particle size equal to or less than 200 µm is classified as weakly explosive (Category ST1 according to method UNI EN 14034-2: 2011). The rubber powder is not a flammable solid under the CLP Regulation. The auto-ignition temperature, based on method CEI-EN 50528-1-2-1 (Method B) 1999, is 430°C.

2.1 Classification of the mixture

Not classifiable as a dangerous mixture.

Section 3: COMPOSITION / INFORMATION ON INGREDIENTS

3.2.2. In compliance with Regulation 1907/2006, the following substances present in the mixture with a concentration greater than 1%, which may bring hazard for the health or the environment or for which exposure limits in the workplace have been set.
Rubber powder does not contain substances with a concentration greater than 0.1% by weight classified as persistent, bioaccumulative and toxic in accordance with the criteria set out in Annex XIII, and very persistent, very bioaccumulative in accordance with the criteria set out in Annex XIII, or which are included in the list established pursuant to Article 59, paragraph 1, for reasons other than the hazards referred to in point a).

Substance	CAS	EC	% w/w
Carbon black	1333-86-4	215-609-9	23 - 28 %

Silicates: Magnesium silicate Aluminium silicate	 14807-96-6 1332-58-7	 238-877-9 310-194-1	6 - 7 %
Zinc oxide *	1314-13-2	215-222-5	1.5 – 2% (bioavailable < 0.003%)
TDAE oil **	64741-88-4	265-090-8	<20%
Low viscosity oil **	64742-65-0	265-169-7	<20%
Naphthenic oil **	CAS 64742-52-5	265-155-0	<20%
TDAE oil **	CAS 68783-04-0	272-180-0	<20%

* Concerning Zn, based on the leaching tests carried out (method DIN 18035-7) the bioavailable concentration of Zinc Oxide is in the worst case lower than 0.003%. Article 12 of regulation CE 1278/2008 “CLP” therefore applies, establishing that “conclusive scientific experimental data show that the substance or mixture is not biologically available and those data have been ascertained to be adequate and reliable”.

** Based on the SDS of the manufacturer of extender oils, for all the oils used in tyre production, note L from the annex VI of the regulation CE/1272/2008 shall apply, saying that “*The classification as a carcinogen need not apply if it can be shown that the substance contains less than 3 % DMSO extract as measured by IP 346 «Determination of polycyclic aromatics in unused lubricating base oils and asphaltene free petroleum fractions — Dimethyl sulphoxide extraction refractive index method», Institute of Petroleum, London. This note is applied only to certain compound substances derived from petroleum and present in the part 3.*”

Section 4: FIRST AID MEASURES

4.1 Description of first aid measures

Eye contact:	Wash thoroughly with water and do not rub. Remove contact lenses, if present.
Skin contact:	In case of direct and prolonged contact with skin, wash thoroughly with water and detergens suitable for skin cleansing.
Ingestion:	Do not induce vomiting Rinse mouth with water. In case of Unwellness, call a doctor.
Inhalation:	Ventilate the room. Bring the person to a well ventilated, uncontaminated area. In case of illnes or difficulty of breathing, seek medical advice. The exposure to high concentrations of powders may cause difficulty in breathing.

4.2 Most important symptoms and effects, both acute and delayed

Effects after eye contact:	Foreign-body sensation in the eye, redness and tearing.
Effects after inhalation:	Unwellness and difficulty breathing at high concentrations of fine dust.

4.3 Indication of any immediate medical attention and special treatment needed

In case of prolonged exposure to high concentration of the respirable fraction of rubber dust in closed environment and with asfixia simptoms.

In case of exposure to combustion fumes.

Section 5: FIREFIGHTING MEASURES

5.1 Extinguishing media

Suitable extinguishing media:	Multi-purpose chemical extinguisher, carbon dioxide, firefighting foam.
Unsuitable extinguishing media:	Not relevant.
Firefighting instructions:	Avoid inhalation exposure to combustion fumes.
Raccomandations for firefighters:	Firefighters must use active carbon masks or breathing apparatus.
Explosion hazard:	n.a. in normal working conditions.
Fire hazard:	Rubber materials generate class A fires, namely fires of solid materials, usually of an organic nature, leading to the formations of embers. In case of fire the material will burn rapidly with emission of thick, black smoke, irritating the respiratory tract and the eyes. The combustion produces toxic fumes, carbon oxides, sulfur oxides and nitrogen.

5.2 Special hazards arising from the substance or mixture

In case of combustion toxic fumes, carbon oxides, sulfur oxides and nitrogen are generated.

5.3 Advice for firefighters

Prevent firefighting waters from contaminating surface and underground waters.

Section 6: ACCIDENTAL RELEASE MEASURES

No risk condition due to accindental dispersion is envisaged.
The following recommendations relates to the fine fraction (ELTs dust).

6.1 Personal precautions, protective equipment and emergency procedures

In case of release of dust: wear protection glass, gloves, suits and make use of protection mask (at least FFP2). Stay upwind. Remove people from the release area.

6.2 Environmental precautions

Do not release to the environment. Prevent the dispersion in the atmosphere of the fine dust. Avoid sources of ignition. Do not release the product into a water course or sewage system. Do not abandon the product on the ground. If the product has escaped into a water course, into the drainage system or has contaminated soil or vegetation, call the relevant authorities.

6.3 Methods and material for containment and cleaning up

Rapidly recover the product, wearing goggles, gloves and anti-dust filter mask class FFP2. Prevent it from entering the drainage system. Avoid production of dust. Use vacuum cleaners to remove the dust.

6.4 Reference to other sections

Make reference to sections 8 and 13 for further details.

Section 7: HANDLING AND STORAGE

7.1 Precautions for safe handling

7.1.1 Protective measures

Direct use:	The fine rubber dust normally used as an additive in asphalt mixtures should be mixed by means of closed circuit equipment, capable to prevent the dispersion into the atmosphere during the process. Whilst handling rubber powder it is necessary to adopt protective equipment such as gloves, goggles, dust masks, protective clothing to prevent continuous or repeated short-term contact with the skin.
Empting or filling of tanks and containers:	Wear the recommended personal protective equipment (see Section 8.2.2). Ensure adequate ventilation, especially in enclosed areas. Avoid creating excessive dust.

7.1.2 Hygiene measures

Use good housekeeping practices during storage, transfer and handling.
Do not eat, drink and smoke in work areas.
Wash hands after use.
Remove contaminated clothing and protective equipment before entering areas in which food is consumed.

7.2 Conditions for safe storage, including any incompatibilities

Store the product in original sealed packaging, in ventilated rooms and away from sources of ignition.
Keep in properly labeled containers. Keep containers tightly closed when not in use.
Storage areas should be equipped with adequate fire protection system.
Protect from heat.
Keep away from food and animal feeds.

7.3 Specific end uses

The recommendations described in subsections 7.1 to 7.2 relate to the use of the mixture for the uses stated in subsection 1.2. Uses other than those indicated are considered not controlled and in any case not covered by this document.

Section 8: EXPOSURE CONTROLS/PERSONAL PROTECTION

8.1 Control parameters

8.1.1 National occupational exposure limit values

8.1.1.1 National occupational exposure limit values corresponding to the EU limits

Substance name	**N. CAS**	**Limit value for a reference period of 8 hours (TLV-TWA)**	**Source**
Carbon Black	1333-86-4	3.5 mg/m^3	NIOSH e OSHA
Zinc oxide	1314-13-2	Respirable fraction/fume: 10 mg/m^3 Dust: 15 mg/m^3	OSHA
		Respirable fraction: 2 mg/m^3	ACGIH
		Dust/fume: 5 mg/m^3	NIOSH
Magnesium silicate	14807-96-6	2 mg/m^3	ACGIH e NIOSH

Aluminium silicate	1332-58-7	Respirable fraction: 5 mg/m^3	NIOSH
		Respirable fraction: 2 mg/m^3	ACGIH

8.1.1.3 National occupational exposure limit values established by other organizations not having the force of law

Inhalable dust PNOC: 10 mg/m^3	TLV, source ACGIH
Respirable dust PNOC: 3 mg/m^3	TLV, source ACGIH

8.1.1.4 National biological limit values corresponding to the EU limits

There are no statutory limit values regulating biological exposure.

8.1.1.5 Biological limit values established by other organizations not having the force of law

There are no proposed limit values of biological exposure.

8.1.2 Information on recommended procedures for monitoring exposure

Norm	Description	Source
UNI EN 481:1994	Air quality at workplace. Definition of the granulometric fraction for the measurement of particles dispersed in the atmosphere.	Technical norm for the correct conduction of exposure monitoring. (Annex XLI D.lgs 81/08 integrated by D.lgs 106/09).
UNI EN 689:1997	Air quality at workplace. Guide on the assessment of inhalation exposire for the comparison with limit values and measurement strategy.	
UNI EN 482:1998	Air quality at workplace. General performance requirements for the methodologies of chemical agents measurement.	
UNI EN 1540:2001	Air quality at workplace. Terminology.	

As far as the occupational exposure to PAH is concerned, although no increase to the occupational exposure associated to the use of rubber dust from ELTs as additive in asphalt mixtures has been demonstrated, it is recommended to make reference to the occupational limit values recommended by relevant authorities for this sector.
More specifically, in Germany a limit of 2 µg/m^3, as TRK has been set for B(a)P; OSHA has set for the total PAHs measured as fraction extractable in benzene a limit of 0.2 mg/m^3, expressed as TLV-TWA; ACGIH and NIOSH do not set a numeric limit values. Instead they recommend that the workplace exposure limit for PAHs be set at the lowest detectable concentration (which was 0.1 mg/m^3 for coal tar pitch volatile agents at the time of the recommendation).

8.1.3 Information on the generation of atmospheric pollutants as a consequences of an intentional use.

The uses of rubber dust recovered from ELT covered as from section 1.2 can lead to the generation of atmospheric pollutants.
In the case of use at temperatures higher than 170 °C, can lead to the release of unpleasant odors caused by substances containing sulfur and which can cause temporary discomfort to workers may occurr.

8.1.4 Information related to the Chemical Safety Report DNEL(S) and PNEC(S)

N.a.

8.2 Exposure controls

8.2.1 Appropriate engineering controls

Mimimize exposure to dust. Check the proper working of the aspiration/ventilation/aeration equipments.

8.2.2 Personal protective equipment

a) Eye and face protection	Prevent contact with eye using protective goggles.	Reference norm EN 166

b) Skin protection	Prevent prolonged contact with skin using protective gloves.	Reference norm UNI EN 374
c) Respiratory protection	Prevent direct exposure using proper protective mask (at least FFP2).	Reference norm EN 149:2001
d) Thermal hazard protection	n.a. in normal working conditions.	

8.2.3 Environmental exposure controls

Any manholes and exhaust ports must be provided with suitable grids to prevent rubber granules to enter the drain system or water bodies.

Section 9: PHYSICAL AND CHEMICAL PROPERTIES

PROPERTIES		METHOD
Colour	Dark gray or black	
Physical state	Solid elastomer	
Appearance	Powder	
Granulometry	Maximum size of granule: 420 µm	
Odour	Typical of rubber	
Odour threshold	n.a. in normal using conditions	
pH	7.3 – 7.9	
Melting / freezing point	n.a. in normal using conditions	
Initial boiling point	n.a. in normal using conditions	
Flash point	n.a. in normal using conditions	
Vaporisation rate	n.a. in normal using conditions	
Flammability (solids, gases)	Not highly flammable	Council Regulation (EC) No 440/2008 of 30 May 2008, Part A: Methods for the Determination of Physico-Chemical Properties: A.10 “Flammability (solids)”.
Flammability (solid)	Not a readily combustible substance of Division 4.1 of the ADR, neither a flammable solid under the CLP Regulation	United Nations Document, Recommendations on the Transport of Dangerous Goods, UN Test Reference Test N.1
Upper/lower flammability limit	60 g/m^3	UNI/EN 14034-3:2011
Upper/lower explosion limit	n.a. in normal using conditions	
Vapour pressure	n.a. in normal using conditions	
Vapour density	n.a. in normal using conditions	
Relative density	0.46 – 0.51 g/cm^3	ASTM D297/81 p.to 15
Solubility	insoluble in water; partially soluble in acetone, aromatics, ketones, chlorinated and dimethyl sulfoxide	
Partition coefficient: n-octanol/water	n.a. for the mixtures	
Auto-ignition temperature-layer (5mm)	300 °C	CEI-EN 50528-1,2,1, 1999

Auto-ignition temperature-cloud	430 °C	CEI-EN 50528-1,2,1, (Method B) 1999
Decomposition temperature	287 – 403 °C	Council Regulation (EC) No 440/2008 of 30 May 2008, Part A: Methods for the Determination of Physico-Chemical Properties: A.1 “Melting/Freezing Temperature (Capillary Method)”.
Viscosity	n.a. in normal using conditions	
Explosive properties	n.a. in normal using conditions	
Oxidising properties	n.a. in normal using conditions	
Polymer content	≥ 45 % w/w	ISO 9924-1
Acetone extract	≤ 10 % w/v	ASTM D297/81 p.to 18

Section 10: STABILITY & REACTIVITY

10.1 Reactivity

Not reactive in normal using conditions.

10.2 Chemical stability

Stable in all ordinary circumstances and under normal conditions of use.

10.3 Possibility of dangerous reactions

None in normal using conditions.

10.4 Condition to be avoided

Keep away from heat/sparkes/open flames/hot surfaces. No smoking.

10.5 Incompatible materials

None in normal using conditions.

10.6 Hazardous decomposition products

None in normal using conditions.

Section 11: TOXICOLOGICAL INFORMATION

11.1.Information on toxicological effects

Information provided in this section, unless otherwise specified, refer to the material identified as granulate of ELTs.

a) Acute toxicity

Oral-ingestion exposure:	No data available in the literature on the tests carried out on animals and humans aimed at assessing the consequences of ingestion of the substance.

Dermal exposure - absorption through skin / eyes:	No data available in the literature on the tests carried out on animals and humans aimed at assessing the consequences of skin absorption of the substance.
Inhalation exposure:	No data available in the literature on the tests carried out on animals and humans aimed at assessing the consequences of inhalation of the substance.

b) Skin corrosion/irritation

Corrosion:	No data available in the literature. No evidence of corrosion actions.
Skin irritation:	No data available in the literature.

c) Serious eye damage/irritation

Irreversible effects on eyes / serious eye damage:	No data available in the literature. There are no specific studies about.
Reversible effects on eyes / serious eye irritation:	No data available in the literature. There are no specific studies about.

d) Respiratory or skin sensitization

Respiratory sensitisation:	No data available in the literature. There are no specific studies about.
Skin sensitisation:	No data available in the literature. There are no specific studies about.

e) Germ cell mutagenicity

In vitro genotoxicity

Type of genotoxicity	**Type of study**	**Animal species**	**Result**	**Year**	**Source**
The genotoxicity was evaluated by the increase in the number of tested colonies (minimum increase of 1.5) compared to the controls, demonstrating a dose-dependent response.	Mutagenicity fluctuation Assay	*Salmonella typhimurium* TA98, TA100, TA1535 and TA1537	Absence of toxicity. No test shows an evident genotoxicity. No test performed with microsomal activation demonstrates genotoxic activity. No damage to DNA or chromosomes.	2003	A. Birkholz, K. L. Belton, T. L. Guidotti. Toxicological Evaluation for the Hazard Assessment of Tire Crumb for Use in Public Playgrounds.
	SOS chromotest				
	Mutatox				

f) Carcinogenicity

Carcinogenicity	No data available in the literature.

g) Reproductive toxicity

Adverse effects on sexual function and fertility:	No data available in the literature.
Adverse effects on developmental toxicity:	No data available in the literature.
Effects on or via lactation:	No data available in the literature.

h) Specific target organ toxicity (STOT) - single exposure

No data available in the literature.

i) Specific target organ toxicity (STOT)-repeated exposure

No data available in the literature.

j) Aspiration hazard

No data available in the literature.

Section 12: ECOLOGICAL INFORMATION

12.1 Toxicity

ELTs powder or granulate consists of substances whose spread in the air is considered minor.
More significant is the release of substances in water, sediment and soil, with particular reference to zinc.

Type of test	**Result**			**Source**
Acute toxicity test for invertebrates	**24 h EC50 (mg/l)**	**48 h EC50 (mg/l)**	**NOAEC (mg/l)**	
Daphnia Magna	>100	>100	100	Noè, Dini (2012)
Daphnia magna		26750; 53300		Gualtieri et al. (2005b)
Daphnia magna	300-32000			Wik and Dave (2005)
Daphnia magna		100-2400		Wik and Dave (2005)
Daphnia magna		60-400		Wik and Dave (2005)
Daphnia magna	1200->10000			Wik and Dave (2006)
Daphnia magna		300->10000		Wik and Dave (2006)
Daphnia magna		370-7500		Wik et al. (2008)
Ceriodaphnia dubia		550-5000		Wik et al. (2008)
D. magna (Sediment elutriate)		>10000	>10000	Britt McAtee et al. (2011)
D. magna (Leachate, 44° C)		4360 (3660–5250)	1250	Britt McAtee et al. (2011)
D. magna (Leachate, 21° C)		>10000	>10000	Britt McAtee et al. (2011)
D. magna (Leachate + sediment, 44° C)		5080 (4250–6070)	2.500	Britt McAtee et al. (2011)
D. magna (Leachate + sediment, 21° C)		>10000	>10000	Britt McAtee et al. (2011)
Chronic toxicity test for invertebrates			**NOAEC (mg/l)**	
Ceriodaphnia dubia			194	Wik et al. (2008)
Acute toxicity test for algae			**NOEC (mg/l)**	
			9.8	Noè, Dini (2015)

	72-h EC50 (mg/l)			
P. subcapitata (growth rate) Sediment elutriate	> 10000		> 10000	Britt McAtee et al. (2011)
Pseudokirchneriella subcapitata	470; 1640			Gualtieri et al. (2005b)
Pseudokirchneriella subcapitata	50-2800			Wik et al. (2008)
Acute toxicity test for fish	**48-h LC50 (mg/l)**	**96-h LC50 (mg/l)**		
Zebrafish Danio rerio	>100	>100	100	Noè, Dini (2012)
Acute toxicity test for fish		**48-h LC50 (mg/l)**		
Zebrafish eggs Danio rerio		550->10000		Wik et al. (2008)

12.2 Persistence and degradability

No specific studies on the possibility that the mixture degrade in the environment through processes such as photolysis, hydrolysis or other are available.

Photodegradation:	No data available in the literature.
Stability in water:	The mixture is not soluble in water.
Rapid degradability of organic substances:	No data available in the literature.

12.3 Bioaccumulative potential

No data available for this parameter.

Partition coefficient: n-octanol/water:	N.a. for the mixtures.
BioConcentration Factor (BCF):	N.a. for the mixtures.

12.4 Mobility in soil

No data available in the literature.

12.5 Results of PBT and vPvB assessment

Substances not present.

12.6 Other adverse effects

None

Section 13: DISPOSAL CONSIDERATIONS

13.1 Waste treatment methods

The producer of the waste is responsible of the assignment of the EWC code more relevant based on the manufacturing process which is generated them.
Disposal of waste resulting from this product must be done according to the relevant legislation in force in the country where the waste is generated and disposed. In Europe, the relevant legislation are the Directive 2008/98 (Waste Framework Directive), the Decision 2000/532 on the list of waste, and their amendments.
If possible, recover the waste or send to authorized plants.
Container disposal: Do not dispose containers into the enviroment.
Disposal must be done according local regulations.

Section 14: TRANSPORT INFORMATION

The product is not considered harmful according to the provisions in force regarding carriage of dangerous goods by road (ADR), by railway (RID), by sea (IMDG Code) and by plane (IATA).

14.1 UN number

N.a.

14.2 UN proper shipping name

N.a.

14.3 Transport hazard classes

Road/railway transport (ADR/RID)	Sea transport (IMDG Code)	Air transport (IATA DGR)
Not classified	Not classified	Not classified

14.4 Packing group

Road/railway transport (ADR/RID)	Sea transport (IMDG Code)	Air transport (IATA DGR)
n.a.	n.a.	n.a.

14.5 Environmental hazards

Road/railway transport (ADR/RID)	Sea transport (IMDG Code)	Air transport (IATA DGR)
Not dangerous for the environment under ADR regulation	n.a.	n.a.

14.6 Special precautions for users

During the phases of loading / unloading of the material should be used same precautions described in sect. 7 regarding the safe handling. Previously ensure the load compatibility in common with other goods eventually to be loaded.

14.7 Transport in bulk according to Annex II of MARPOL 73/78 and the IBC Code:

N.a.

Section 15: REGULATORY INFORMATION

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture

Regulation (EC) No. 1272/2008 on classification, labelling and packaging of substances and mixtures.

Regulation (EC) No. 790/2009 amending in view of adapting of Regulation EC 1272/2008 on classification, packaging and labelling of substances and mixtures to the scientific and technical progress.

Regulation (EC) No. 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH).

15.2 Chemical safety assessment

According to art. 2, par.7, letter b) of the Regulation (EC) No. 1907/2006 as amended, the substance is exempted from the application of the provisons of Titles II, V, VI of the Regulation.
Therefrore, the producer of the mixture is exempted from the obligation to perform the chemical safety assessment according to art. 14 of Title II of the Regulation.

Section 16: OTHER INFORMATION

It is highly advisable that the concerned workers are previously informed of the content of this safety data sheet. The information and recommendations described above are believed to be accurate and reliable, but not exhaustive. All indications are for the use of the product in the conditions described above, including as well our experience in the field: any chemical modification and/or physical modification of this product is not covered by this safety data sheet, and therefore ALBATROS Ecologia Ambiente Sicurezza does not accept any responsibility.
The user is in any case not exempt from observing all legal, administrative and regulatory procedures relating to the product, personal hygiene, and protection of human welfare and the environment in which he/she operates.

a) Indcation of changes

This is a total revision of the previous safety data sheet in accordance with the provisions of Annex II of REACH Regulation.

b) Abbreviations and acronyms

ACGIH	American Conference of Governmental Industrial Hygienists
ADR	European Agreement concerning the International Carriage of Dangerous Goods by Road
ASTM	American Section of the International Association for Testing Materials
BCF	Bioconcentration Factor
EWC	European Waste Catalogue
DNEL	Derived No Effect Level
DMEL	Derived Minimal Effect Level
EC50	Effective Concentration, 50%
IATA DGR	International Air Transport Association Dangerous Goods Regulations
IMDG Code	International Maritime Dangerous Goods Code
PAH	Polycyclic Aromatic Hydrocarbons
LC50	Lethal Concentration, 50%
n.a.	Not applicable

n.d.	Not available
NIOSH	National Institute for Occupational Safety and Health
NOAEC	No observed Adverse Effect Concentration
UN	United Nations
OSHA	Occupational Safety and Health Administration
PBT	Persistent, Bioaccumulative, Toxic
ELT	End of life tyres
PNEC	Predicted No Effect Concentration
PNOC	Particulates not otherwise classifiable
RID	Regulations concerning the International Carriage of Dangerous Goods by Rail
STOT RE	Single Target Organ Toxicity- Repeated exposure
STOT SE	Single Target Organ Toxicity- Single exposure
TLV	Threshold Limit Values
TWA	Time Weighted Average
TRK	Technische Richtkonzentration- Technical guidance concentration
UVCB	Substance of Unknown or Variable composition, Complex reaction products or Biological materials
vPvB	very Persistent, very Bioaccumulative

c) Key literature references and sources for data

Threshold Limit Value: Italian Journal of Occupational and Enviromental Hygiene - year 2010

IUCLID data set REACH Registration dossiers – European Chemicals Agency (ECHA) – year 2012

e) Relevant H- and EUH-phrases

None

1 Identificazione della sostanza/miscela e della società/impresa

1.1 Identificatore del prodotto

-	Nome della sostanza:	Bitume
-	Sinonimi:	Asphalt (Viscoflex 1000)
-	Numero CAS	8052-42-4
-	Numero CE	232-490-9
-	Numero di Registrazione	01-2119480172-44-XXXX
-	Formula chimica	La sostanza è un complesso UVCB pertanto non è possibile fornire una formula molecolare.
-	Peso Molecolare	La sostanza è un complesso UVCB pertanto non è possibile fornire un peso molecolare.

1.2 Usi identificati pertinenti della sostanza o della miscela e usi sconsigliati:

- USO COMUNE: Membrane bituminose, guaine bituminose e compounds polimerici. Produzione di bitumi ossidati industriali e bitumi modificati.
- USI IDENTIFICATI NELLA RELAZIONE SULLA SICUREZZA CHIMICA:
  - Usi industriale:
    - produzione della sostanza,
    - distribuzione della sostanza,
    - produzione e lavorazione della gomma – industriale,
    - formulazione e (re)imballaggio delle sostanze e delle miscele,
    - utilizzo come intermedio,
    - utilizzo nei rivestimenti,
    - utilizzo nelle attività di perforazione e produzione di pozzi destinati all'estrazione di petrolio e gas naturale,
    - lubrificanti.
    - Uso in fluidi per la lavorazione dei metalli: industriale
    - Uso come agente di fissaggio o rilascio: industriale
    - Uso come combustibile: industriale
    - Uso come fluido di supporto: industriale.
  - Uso professionale:
    - utilizzo nei rivestimenti;
    - utilizzo nelle attività di perforazione e produzione di pozzi destinati all'estrazione di petrolio e gas naturale;
    - applicazioni stradali ed edili;
    - lubrificanti.

- Consumatori:
    - utilizzo nei rivestimenti.

USI SCONSIGLIATI: gli usi pertinenti sono sopra elencati. Non sono raccomandati altri usi a meno che non sia stata condotta una valutazione, prima dell'inizio di detto uso, che dimostri che tale uso sarà controllato. Per ogni valutazione addizionale sono responsabili i singoli registranti.

1.3 Informazioni sul fornitore della scheda di dati di sicurezza:

Identificazione della società:	Viscolube S.r.l. Via Tavernelle, 19 26854 Pieve Fissiraga LO tel. 0371 25031 fax 0371 98030
- Stabilimento di produzione:	Viscolube S.r.l. Stabilimento di Pieve Fissiraga LO Via tavernelle 19 16854 pieve Fissiraga Lo tel. 0371 25031 fax 0371 98352 Direttore dello Stabilimento: ing. Francesco Gallo
- Responsabile della Scheda di dati di sicurezza:	f.gallo@viscolube.it

1.4. Numero telefonico di emergenza

Per informazioni urgenti rivolgersi a

Centro antiveleni (24/24h):
1.Foggia 0881/732326;
2.Pavia 0382/24444;
3.Milano 02/66101029;
4.Bergamo 800/83300;
5.Firenze 055/7947819;
6.Roma Gemelli 06/3054343;
7.Roma Umberto I 06/49978000;
8.Roma Osp. Ped. Bambino Gesù 06/68593726
9.Napoli 081/7472870

2 Identificazione dei pericoli

Pericoli fisico-chimici: nessun pericolo secondo i criteri di classificazione di cui all’allegato I alla parte 2 del Regolamento 1272/2008 e s.m.i.

Pericoli per la salute: nessun pericolo secondo i criteri di classificazione di cui all’allegato I alla parte 3 del Regolamento 1272/2008 e s.m.i.,

Pericoli per l’ambiente: nessun pericolo secondo i criteri di classificazione di cui all’allegato I alla parte 4 del Regolamento 1272/2008 e s.m.i.

2.1 Classificazione della sostanza o della miscela

Non classificata.

2.2 Elementi delletichetta

N.A.

2.3 Altri pericoli

Dato l'utilizzo a caldo del prodotto il pericolo maggiore per gli utilizzatori è la possibilità di ustioni per contatto con il prodotto fuso o i suoi fumi. Il bitume riscaldato emette fumi. Anche se si presume che tali fumi non presentino pericoli significativi per la salute, la normale prudenza consiglia di limitare al massimo l’esposizione, utilizzando procedure di lavoro corrette e assicurando una buona ventilazione degli ambienti di lavoro. L'inalazione prolungata dei fumi del prodotto caldo può causare irritazione delle vie respiratorie.

Nei fumi potrebbe essere presente solfuro d’idrogeno/idrogeno solforato (gas tossico e infiammabile), che può accumularsi fino a raggiungere concentrazioni pericolose nei serbatoi o altri contenitori di stoccaggio.

Il prodotto non soddisfa i criteri di classificazione PBT o vPvB di cui all’allegato XIII del regolamento REACH.

3 Composizione/informazione sugli ingredienti

3.1 Sostanze

La sostanza è un complesso UVCB (N. reg. 01-2119480172-44-XXXX)

Asfalto (“Combinazione complessa di idrocarburi organici ad alto peso molecolare, contenente una quantità relativamente elevata di idrocarburi con numero di atomi di carbonio prevalentemente superiore a C25 ed alti rapporti carbonio-idrogeno. Contiene anche piccole quantità di metalli quali nickel, ferro o vanadio. Si ottiene come residuo non volatile della distillazione del petrolio grezzo, o mediante separazione in forma di raffinato da un olio residuo, in un processo di deasfaltazione o decarbonizzazione”).

La composizione è complessa e variabile. Grado di purezza 100% in peso.

Idrocarburi Saturi	35,74%
Aromatici	61,64%
Idrocarburi Polari	2,62%

Questo tipo di sostanza contiene composti solforati che, in particolari circostanze, possono liberare piccole quantità di idrogeno solforato.

4 Misure di primo soccorso

4.1 Descrizione delle misure di primo soccorso

Inalazione

L' inalazione di vapori a temperature ambiente è poco probabile a causa della bassa pressione di vapore della sostanza. L' esposizione ai vapori può comunque accadere in caso la sostanza venga maneggiata a alte temperature e in condizioni di scarsa ventilazione.

In caso di sintomi da inalazione di fumi o vapori:

- In caso di respirazione difficoltosa, se le condizioni di sicurezza lo permettono, trasferire l' infortunato in un posto tranquillo e ben ventilato portare e mantenerla in una posizione comoda per la respirazione.
- Consultare un medico.
- Trasferire immediatamente l' infortunato in ospedale.

Se la vittima è incosciente e non respira:

- verificare l'assenza di ostacoli alla respirazione e praticare la respirazione artificiale da parte di personale specializzato. Se necessario, effettuare un massaggio cardiaco esterno e consultare un medico.
- Trasferire immediatamente l' infortunato in ospedale.

Se la vittima è incosciente e respira:

- Tenere sotto controllo la respirazione e il battito cardiaco.
- Mantenerla in posizione laterale di sicurezza e consultare un medico.
- Somministrare ossigeno se necessario.
- Trasferire immediatamente la vittima in ospedale. Iniziare immediatamente la respirazione artificiale se la respirazione si è arrestata.

In presenza di sospetta inalazione di H_2S (solfuro di idrogeno):

- I soccorritori devono indossare adeguati apparati respiratori, cinture e corde di sicurezza, nonché adottare le procedure di soccorso previste.
- Spostare la vittima in un posto tranquillo e ben ventilato portare e mantenerla in una posizione comoda per la respirazione.
- Trasferire immediatamente la vittima in ospedale. Iniziare immediatamente la respirazione artificiale se la respirazione si è arrestata.
- Somministrare ossigeno se necessario.

Contatto cutaneo:

Nel caso in cui il prodotto caldo entri accidentalmente in contatto con la pelle:

- Immergere immediatamente la parte lesa sotto acqua corrente fresca per almeno 10 minuti.
- Dopo il raffreddamento NON tentare di rimuovere il bitume che aderisce alla pelle presso il luogo di lavoro.
- In caso di ustioni circonferenziali con aderenza del bitume, incidere il materiale per prevenire un effetto "laccio emostatico" durante il raffreddamento.
- Chiedere immediatamente l'intervento di un medico.

Per ustioni termiche minori:

- Raffreddare la parte lesa: tenere la parte ustionata sotto acqua corrente fredda per almeno 5 minuti, o fino a quando il dolore scompare.
- Evitare comunque un'ipotermia generale.
- NON applicare ghiaccio sull'ustione.
- NON tentare di rimuovere le porzioni di indumento attaccate alla pelle bruciata ma tagliarne i contorni.
- Gli operatori di primo soccorso non devono mai utilizzare benzina, cherosene o altri solvente per pulire la pelle contaminata.

Consultare un medico in tutti i casi di ustioni senza attendere la comparsa dei sintomi.

Contatto con gli occhi:

- Rimuovere, se presenti, le lenti a contatto se la situazione consente di effettuare l'operazione con facilità.
- Continuare a risciacquare.
- Consultare immediatamente un medico nel caso in cui irritazioni, vista offuscata o rigonfiamenti persistenti si sviluppano e persistono.

Nel caso in cui il prodotto caldo entri in contatto con gli occhi:

- Sciacquare la parte lesa con acqua per dissipare il calore mediante risciacquo con acqua corrente fresca per diversi minuti.
- Non fare alcun tentativo per rimuovere il bitume.
- Chiedere immediatamente l'intervento di un medico.
- Trasportare il colpito in ospedale.

Ingestione/aspirazione:

- Non indurre il vomito.
- Consultare il medico.

In caso di vomito spontaneo:

- Mantenere la testa in basso per evitare il rischio aspirazione del vomito nei polmoni.
- Trasportare d' urgenza il colpito in ospedale.
- Aspirazione: non applicabile visto lo stato fisico del bitume.

4.2 Principali sintomi ed effetti, sia acuti che ritardati

- Nessun sintomo in caso di contatto con la pelle con il prodotto a temperatura ambiente.
- L' inalazione di fumi o vapori può causare irritazione del tratto respiratorio.
- Leggera irritazione agli occhi in caso di contatto con il prodotto a temperatura ambiente.
- Il contatto con il prodotto caldo può causare gravi ustioni termiche.
- Ingestione: pochi o nessun sintomo previsto. Eventualmente, può presentarsi leggero effetto di nausea.

4.3 Indicazione della eventuale necessità di consultare immediatamente un medico e di trattamenti speciali

- Consultare immediatamente un medico nei casi indicati al par. 4.1 in particolare nei casi in cui irritazioni, gonfiore o rossore si sviluppano e persistono.
- Consultare un medico in tutti i casi di ustioni.
- Trasferire immediatamente l' infortunato in ospedale.
- Non attendere la comparsa dei sintomi.

NOTA: in caso di eventi incidentali che avvengono nelle aree di pertinenza dello Stabilimento Viscolube di Pieve Fissiraga si faccia riferimento al Piano Di Emergenza Interna (PEI) del sito.

5 Misure antincendio

5.1 Mezzi di estinzione

Il bitume non è classificato infiammabile, ma è una sostanza combustibile, e può bruciare.

Incendi di piccole dimensioni:

- terra o sabbia, anidride carbonica, polvere chimica secca,
- schiuma (solo personale addestrato),
- acqua nebulizzata (solo personale addestrato),
- altri gas inerti (come permessi dalla normativa)

Incendi di grandi dimensioni:

- schiuma (solo personale addestrato),
- acqua nebulizzata (solo personale addestrato),
- altri gas inerti (come permessi dalla normativa)

Mezzi di estinzione non adatti:

- Non utilizzare getti d'acqua diretti sul prodotto che brucia, possono causare schizzi e diffondere l'incendio.
- Evitare l'utilizzo simultaneo di schiuma e acqua sulla stessa superficie poiché l'acqua distrugge la schiuma.
- Coprire gli eventuali spandimenti che non hanno preso fuoco con schiuma o terra.

5.2 Pericoli speciali derivanti dalla sostanza o dalla miscela

- Il contatto del prodotto caldo con acqua genera una violenta espansione poiché l'acqua si tramuta in vapore, ciò può generare schizzi di prodotto caldo, oppure danni o la perdita completa del tetto della cisterna e problemi respiratori o nausea causati dall'eccessiva esposizione dei fumi generati dal prodotto caldo.
- La combustione incompleta potrebbe generare una complessa miscela di particelle solide e liquide aerodisperse e di gas, incluso CO (monossido di carbonio), H_2S (solfuro di idrogeno), SO_x (ossidi di zolfo) o H_2SO_4 (acido solforico) e composti organici e inorganici non identificati.

5.3 Raccomandazioni per gli addetti all' estinzione degli incendi

In caso di incendio o in spazi confinati o scarsamente ventilati, indossare un indumento completo di protezione individuale ignifugo e un respiratore autonomo dotato di autorespiratore.

NOTA: in caso di eventi incidentali che avvengono nelle aree di pertinenza dello Stabilimento Viscolube di Pieve Fissiraga si faccia riferimento al Piano di Emergenza Interna (PEI) del sito.

6 Misure in caso di rilascio accidentale

Nota: Le misure raccomandate nella presente sezione si basano sugli scenari più probabili di sversamento per questo prodotto. Le condizioni locali (vento, temperatura dell'aria, direzione e velocità delle onde e delle correnti) possono, tuttavia, influire significativamente sulla scelta dell'azione da compiere.

Consultare, pertanto, esperti locali se necessario. Le normative locali possono altresì prescrivere o limitare le azioni da intraprendere.

6.1 Precauzioni personali, dispositivi di protezione e procedure in caso di emergenza

6.1.1 PER CHI NON INTERVIENE DIRETTAMENTE

- Se le condizioni di sicurezza lo consentono, arrestare o contenere la perdita alla fonte.
- Evitare il contatto diretto con il materiale rilasciato.
- Rimanere sopravvento.
- In caso di sversamenti di grande entità, avvertire i residenti delle zone sottovento.
- Allontanare il personale non coinvolto dall'area dello sversamento.
- Avvertire le squadre di emergenza.

Salvo in caso di versamenti di piccola entità, la fattibilità degli interventi deve sempre essere valutata e approvata, se possibile, da personale qualificato e competente incaricato di gestire l'emergenza. In questi casi, quando si sospetta o si accerta la presenza di quantità pericolose di H_2S nel prodotto versato/fuoriuscito, possono essere indicate delle azioni supplementari o speciali, quali la limitazione degli accessi, l'utilizzo di speciali dispositivi di protezione individuali, l'adozione di specifiche procedure e la formazione del personale.

- Eliminare tutte le fonti di accensione se le condizioni di sicurezza lo consentono (es.: elettricità, scintille, fuochi, fiaccole).

- Se richiesto, comunicare l'evento alle autorità preposte conformemente alla legislazione applicabile.

6.1.2 PER CHI INTERVIENE DIRETTAMENTE**Sversamenti di piccola entità:** I tradizionali indumenti di lavoro antistatici sono generalmente appropriati.

Sversamenti di grande entità: Indumento di protezione totale resistente agli agenti chimici e realizzato in materiale antistatico. Se necessario, resistente al calore e isolato termicamente.

Utilizzare opportuni dispositivi di protezione individuale per la bonifica del materiale sversato, riferirsi alla sezione 8 per l' idonea tipologia.

6.2 Precauzioni ambientali

Evitare che il prodotto finisca nelle fognature, nei fiumi o in altri corpi d'acqua.

Fuoriuscite di quantità limitate di prodotto, soprattutto all'aria aperta, quando i vapori vengono di solito rapidamente dispersi, sono situazioni dinamiche, che è in maniera improbabile comportano l'esposizione a concentrazioni pericolose. Una possibile eccezione può essere rappresentata dalla formazione di concentrazioni pericolose in luoghi specifici, come fossi, trincee, depressioni o spazi limitati in quanto l' H_2S ha una densità maggiore dell'aria. In tutte queste circostanze, le idonee azioni da intraprendere, devono essere valutate caso per caso.

6.3 Metodi e materiali per il contenimento e per la bonifica

- Le perdite e gli sversamenti sono formati da materiale liquefatto caldo, con il rischio di ustioni gravi.

- Il prodotto solidificato può intasare tombini e fognature.

6.3.1 Spandimenti sul suolo:

- Se necessario, arginare il prodotto con terra asciutta, sabbia o altro materiale non infiammabile.

- Lasciare che il prodotto caldo si raffreddi naturalmente. Se necessario, utilizzare con precauzione acqua nebulizzata per aiutare il raffreddamento.

- NON dirigere getti diretti di schiuma o acqua sullo sversamento di prodotto fuso per evitare schizzi. All'interno di edifici o spazi chiusi, garantire una ventilazione appropriata.

- All'interno di edifici o spazi chiusi, garantire una ventilazione appropriata.

- Raccogliere il prodotto solidificato con mezzi adeguati (es.: pale).

- Raccogliere e trasferire il prodotto recuperato e gli altri materiali in adeguati serbatoi o contenitori, per il riciclo o lo smaltimento in sicurezza.

- In caso di contaminazione del terreno, rimuovere il suolo contaminato e trattare conformemente alla legislazione locale.

- NON utilizzare solventi o disperdenti.

-

6.3.2 *Spandimenti in acqua:*

- Il prodotto si raffredda rapidamente, divenendo solido.
- Il prodotto allo stato solido è più denso dell'acqua, affonda lentamente e si adagia sul fondo, rendendo normalmente impraticabile ogni tipo di intervento.
- Se possibile, contenere il prodotto e i materiali contaminati utilizzando mezzi meccanici.
- Trasferire il prodotto e gli altri materiali contaminati raccolti in adeguati serbatoi o contenitori per il riciclo o lo smaltimento in sicurezza.

Le misure raccomandate si basano sugli scenari più probabili di sversamento per questo prodotto. Le condizioni locali (vento, temperatura dell'aria, direzione e velocità delle onde e delle correnti) possono, tuttavia, influire significativamente sulla scelta dell'azione da compiere. Consultare, pertanto, esperti locali se necessario.

6.4 Riferimento ad altre sezioni

Per maggiori informazioni in merito ai dispositivi di protezione individuale, fare riferimento alla sezione "Controllo delle esposizioni e protezione individuale" in sezione 8 e alla sezione 13.

NOTA: in caso di eventi incidentali che avvengono nelle aree di pertinenza dello Stabilimento Viscolube di Pieve Fissiraga si faccia riferimento al Piano Di Emergenza Interna (PEI) del sito.

7 Manipolazione e immagazzinamento

7.1 Precauzione per la manipolazione sicura

7.1.1 *Misure protettive*

- Assicurarsi che tutte le disposizioni in materia di strutture di gestione e stoccaggio del prodotto siano correttamente rispettate.
- Evitare il contatto del prodotto caldo con acqua.
- Rischio di schizzi generati dal materiale caldo.
- Il prodotto può rilasciare H_2S (solfuro di idrogeno): effettuare una valutazione specifica dei rischi da inalazione derivanti dalla presenza di solfuro di idrogeno negli spazi liberi delle cisterne, negli ambienti confinati, nei residui e nelle eccedenze di prodotto, nei fondami e acque reflue dei serbatoi, e in tutte le situazioni di rilascio non intenzionale, per determinare quali siano i migliori mezzi di controllo in funzione delle condizioni locali.
- La concentrazione di H_2S nello spazio di testa dei serbatoi o delle cisterne può raggiungere valori pericolosi, soprattutto in caso di stoccaggio prolungato. Questa situazione è particolarmente rilevante per quelle operazioni che comportano l'esposizione diretta ai vapori nello spazio confinato.
- NON respirare i fumi generati dal prodotto caldo. Utilizzare appropriati dispositivi di protezione individuale, se necessario.
- Assicurare la messa a terra del contenitore, dei serbatoi e delle attrezzature per la ricezione e il trasferimento.

- Tenere lontano da fonti di calore/scintille/fiamme libere/superfici calde.
- NON fumare
- Evitare il contatto con pelle e occhi.
- Non ingerire.
- Non respirare i vapori.
- Evitare il contatto con il prodotto.
- Utilizzare solo oggetti che non producono scintille.
- Prevenire il rischio di scivolamento.
- Adottare misure precauzionali contro l'elettricità statica.
- Non utilizzare aria compressa durante le operazioni di riempimento, scarico o manipolazione.

7.1.2 Indicazioni in materia di igiene del lavoro

- Assicurarsi che siano adottate adeguate misure di pulizia (housekeeping).
- Il materiale contaminato non deve accumularsi nei luoghi di lavoro e non deve mai essere conservato in tasca.
- Tenere lontano da cibi e bevande.
- Non mangiare, bere o fumare durante l'utilizzo del prodotto.
- Lavare accuratamente le mani dopo la manipolazione.
- Non riutilizzare gli indumenti contaminati. Non utilizzare solventi o altri prodotti con un effetto sgrassante sulla pelle.

7.2 Condizioni per lo stoccaggio sicuro, comprese eventuali incompatibilità

- La struttura dell'area di stoccaggio, le caratteristiche dei serbatoi, le apparecchiature e le procedure operative devono essere conformi alla legislazione pertinente in ambito europeo, nazionale o locale.
- Gli impianti di stoccaggio devono essere dotati di appositi sistemi per prevenire la contaminazione del suolo e delle acque in caso di perdite o sversamenti.
- Le attività di pulizia, ispezione e manutenzione della struttura interna dei serbatoi di stoccaggio devono essere effettuate da personale qualificato e correttamente attrezzato, così come stabilito dalla legislazione nazionale, locale, o regolamenti aziendali.
- Prima di accedere ai serbatoi di stoccaggio e avviare qualsiasi tipo di intervento in uno spazio confinato, controllare l'atmosfera e verificare il contenuto di ossigeno, la presenza di solfuro di idrogeno (H_2S) e il grado di infiammabilità.
- Conservare separato dagli agenti ossidanti.
- Conservare in un luogo ben ventilato.
- Il fenomeno dell'autoriscaldamento e successiva autoaccensione delle superfici di materiale poroso o fibroso impregnato con olio o bitume, può verificarsi a temperature anche inferiori o uguali a 100°C.

- Evitare la contaminazione con olio e bitume di materiali isolanti e l' accumulo di stracci sporchi vicino a superfici calde.
- Depositi di materiale carbonioso e di sulfuri di ferro possono svilupparsi sulle pareti interne e sui tetti dei serbatoi in caso di stoccaggio per lungo tempo. Questi depositi potrebbero diventare piroforici incendiarsi a contatto con l' aria.

Materiali raccomandati:

- Utilizzare acciaio dolce e acciaio inossidabile per contenitori e rivestimenti.
- Alcuni materiali sintetici possono non essere adatti ai contenitori o ai rivestimenti sulla base delle caratteristiche del materiale e degli usi previsti. Verificare la compatibilità presso il produttore.
- La maggior parte dei materiali sintetici non è adatta per contenitori o ai rivestimenti a causa del basso grado di resistenza al calore.
- Se il prodotto è fornito in contenitori, conservare esclusivamente nei contenitori originale o in contenitori adatti al tipo di prodotto.
- Il prodotto caldo non deve mai essere trasferito nei contenitori senza prima aver controllato che il contenitore sia completamente asciutto.
- I contenitori vuoti possono contenere residui combustibili di prodotto. Non saldare, brasare, perforare, tagliare o incenerire i contenitori vuoti a meno che essi non siano stati adeguatamente bonificati.

7.3 Usi finali particolari

Non sono necessarie informazioni aggiuntive a quelle riportate sopra.

8 Controllo dell' esposizione / Protezione individuale

8.1 Parametri di controllo

Valori limite di esposizione (sostanza) AGCH:

Asfalto (Bitume fumi)

ACGIH 2013:

TLV®-TWA: 0,5 mg/m^3

Idrogeno solforato:

ACGIH 2013:

- TLV®-TWA: 1 ppm
- TLV®-STEL: 5 ppm

OEL EU (Direttiva 2009/161/UE; Direttiva 2006/15/CE; Direttiva 2004/37/CE; Direttiva 2000/39/CE).

Valori Limite (8 ore):	5 ppm; 7 mg/m3
Valori Limite (breve termine):	10 ppm; 14 mg/m3

VLEP (DLgs N°81/2008, ALLEGATO XXXVIII)

Idrogeno solforato:

Valori Limite (8 ore):	5 ppm; 7 mg/m3
Valori Limite (breve termine):	10 ppm; 14 mg/m3

Procedure di monitoraggio.

Fare riferimento al D.Lgs. 81/2008 e s.m.i. o alle buone pratiche di igiene industriale.

DNEL (Livello Derivato di Non Effetto) e DMEL (Livello Derivato di Effetto Minimo)

DNEL / DMEL (Lavoratori)	
A lungo termine - effetti locali, inalazione	2,9 mg/m³ (DNEL, 8h) (Fumi di asfalto [bitume])
DNEL / DMEL (popolazione generale)	
A lungo termine - effetti locali, inalazione	0,6 mg/m³ (DNEL, 24h) (Fumi di asfalto [bitume])

PNEC(S)
(Concentrazione Prevista di Non Effetto)

Non derivati in quanto la sostanza non è pericolosa per l' ambiente

Valori limite biologici (sostanza):

Bitume (valori limite riferiti agli Idrocarburi Policiclici Aromatici).

8.2 Controlli dell'esposizione

8.2.1 ***Controlli tecnici idonei***

- Minimizzare l'esposizione a nebbie/vapori/aerosol.
- Durante la manipolazione del prodotto caldo in spazi confinati, garantire una ventilazione efficace.
- Prima di accedere ai serbatoi di stoccaggio e avviare qualsiasi tipo di intervento in uno spazio confinato, controllare l'atmosfera e verificare il contenuto di ossigeno la presenza di solfuro di idrogeno (H2S) e il grado di infiammabilità.

8.2.2 ***Misure di protezione individuale, quali dispositivi di protezione individuale***

(a) Protezione per occhi/ volto:

- Sono consigliabili, schermi protettivi per le operazioni che provocano schizzi.
- Elmetto con protezione della nuca.
- Indossare occhiali di protezione (UNI EN 166) o dispositivi di protezione per il viso se schizzi o contatto con gli occhi sono possibili o prevedibili.

(b) Protezione della pelle:

i) Protezione delle mani

In assenza di sistemi di contenimento e in caso di possibilità di contatto con la pelle, usare guanti con polsini alti (preferibilmente guanti a mezzo braccio) che forniscano un'adeguata resistenza agli agenti chimici, in particolare agli idrocarburi aromatici (UNI EN 374-470), felpati internamente, se necessario isolati termicamente. Materiali presumibilmente adeguati: nitrile, PVC o PVA (polivinilalcool) con indice di protezione da agenti chimici almeno pari a 5 (tempo di permeazione > di 240 minuti). I guanti realizzati in PVA (Polivinilalcool) non sono resistenti all'acqua e non sono adatti per uso di emergenza. Usare i guanti nel rispetto delle condizioni e dei limiti fissati dal produttore.

I guanti devono essere sottoposti a periodica ispezione e sostituiti in caso di usura, perforazione o contaminazione.

ii) Altro

Abiti con maniche lunghe (secondo UNI-EN 463 -465-466-467).

Sostituire e pulire le tute di protezione al termine del proprio turno di lavoro per evitare eventuali trasferimenti di prodotto agli indumenti o alla biancheria intima.

(c) Protezione respiratoria:

In caso di sversamento, a seconda dell'entità dello sversamento e del livello prevedibile di esposizione, utilizzare una semimaschera o una maschera intera dotata di filtro(i) per vapori organici e H2S (ove applicabile) o un respiratore autonomo; nel caso in cui la situazione non possa essere completamente valutata o se c'è il rischio di carenza di ossigeno, utilizzare esclusivamente un respiratore autonomo.

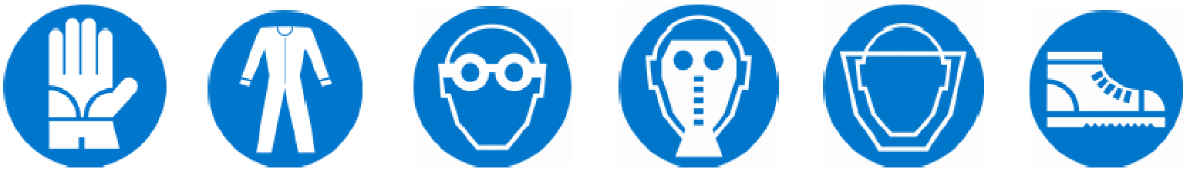
Nei luoghi in cui il solfuro di idrogeno può accumularsi, utilizzare dispositivi approvati di protezione delle vie respiratorie: maschere intere dotate di cartuccia filtro di tipo B (grigio per vapori inorganici, H_2S incluso), o respiratori autonomi (EN 529). Se non è possibile determinare o stimare con buona certezza i livelli di esposizione o se è possibile che si verifichi una carenza d'ossigeno, utilizzare esclusivamente un respiratore autonomo.

(d) Pericoli termici:

Indossare indumenti di protezione durante le operazioni che coinvolgono materiale caldo, resistenti al calore a agli agenti chimici (con pantaloni sopra gli stivali e maniche sopra il polsino dei guanti), stivali pesanti resistenti al calore e antisdrucciolo (es.: cuoio) (EN 943-13034-14605) e resistenti al calore e agli agenti chimici Si veda inoltre la precedente lettera b.

(e) Altro

- Scarpe o stivali di sicurezza antistatici e antisdrucciolo.
- Durante le operazioni di carico/scarico indossare un elmetto con visiera integrale (EN 397) .



8.2.3 Controlli dell' esposizione ambientale

Non rilasciare nell'ambiente.

Gli impianti di stoccaggio devono essere dotati di appositi sistemi per prevenire la contaminazione del suolo e delle acque in caso di perdite o sversamenti.

Non distribuire i fanghi generati dal trattamento delle acque industriali sui terreni naturali (OMS2).

I fanghi generati dal trattamento delle acque industriali devono essere inceneriti, mantenuti sotto contenimento o trattati.

9 Proprietà fisiche e chimiche

9.1 Informazioni sulle proprietà fisiche e chimiche fondamentali

			Metodo
a	Aspetto (a T di 20 °C e P di 101.3 kPa)	semisolido nerastro a temperatura ambiente	
b	Odore	caratteristico	
c	Soglia olfattiva	Informazione non disponibile	
d	pH	Non applicabile	
e	Punto di fusione	Informazione non disponibile	
f	Punto di ebollizione iniziale (°C)	> 320 °C	ASTM D 86
g	Punto di infiammabilità (COC vaso aperto), °C:	min. 250 °C	ASTM D 92
h	Velocità di evaporazione	Informazione non disponibile	
i	Infiammabilità (solidi e gas)	Informazione non disponibile	
j	Limiti inferiori/superiori di infiammabilità o di esplosività	Informazione non disponibile	
k	Tensione di vapore	Informazione non disponibile	
l	Densità di vapore	Informazione non disponibile	
m	Densità relativa a 15°C, kg/m^3:	900 – 1.250 (tipico 1.000)	ASTM D 4052
n	Solubilità	Tutti i solventi organici	
	Idrosolubilità	Non solubile	
o	Coefficiente di ripartizione :n-ottanolo/acqua	Informazione non disponibile	
p	Temperatura di autoaccensione	> 400 °C	
q	Temperatura di decomposizione	Informazione non disponibile	
r	Viscosità cinematica a 100°C, cSt:	500 – 4.000	ASTM D 445
s	Proprietà esplosive	Nessun gruppo chimico associabile alla molecola con proprietà esplosive	
t	Proprietà ossidanti	La sostanza non reagisce esotermicamente con materiali combustibili	

9.2 Altre informazioni

Contenuto di zolfo in %	valori tipicamente inferiori al 2% in peso	ASTM D1552
Softening point	Da 30 °C a + 128 °C	ASTM D36/EN
Costante di dissociazione	Non contiene gruppi funzionali soggetti a dissociazione	Costante di dissociazione
Granulometria	Non applicabile in quanto la sostanza è un solido a T ambiente	

I metodi di analisi delle caratteristiche sono quelli riconosciuti a livello nazionale ed internazionale, riportati per lo più nelle specifiche tecniche del prodotto.

10 Stabilità e reattività

10.1 Reattività

La sostanza è stabile in circostanze ordinarie e a temperature ambiente e se rilasciato nell' ambiente, non presenta pertanto ulteriori pericoli legati alla reattività rispetto a quelli riportati nei sottotitoli successivi.

10.2 Stabilità chimica

Il bitume è normalmente stoccato e manipolato a temperature superiori a 100 °C, e il contatto con l' acqua provoca una violenta espansione con pericolo di schizzi e ribollimenti.

10.3 Possibilità di reazioni pericolose

Non avvengono in tutte le circostanze ordinarie e nelle normali condizioni di utilizzo.

Una miscela con nitrati o altri ossidanti forti (quali clorati, perclorati e ossigeno liquido) può generare una massa esplosiva.

La sensibilità al calore, alla frizione e allo shock non possono essere valutate in anticipo.

10.4 Condizioni da evitare

- Tenere lontano da fonti di calore/scintille/fiamme libere/superfici calde.
- Evitare la formazione di cariche elettrostatiche.
- Un riscaldamento eccessivo a temperatura al di sopra di quella consigliata provoca alterazioni del prodotto e lo sviluppo di fumi infiammabili.

10.5 Materiali incompatibili

- Evitare il contatto del bitume caldo con acqua o altri liquidi.
- Evitare il contatto con forti ossidanti.
- Evitare la contaminazione da olio e bitume dei materiali isolanti termici e l'accumulo di residui oleosi o materiale simile in prossimità delle superfici calde e sostituire il rivestimento termico isolante, ove necessario, con un isolante non assorbente.
- Il fenomeno dell'autoriscaldamento e successiva autoaccensione delle superfici di materiale poroso o fibroso impregnato con olio o bitume può verificarsi a temperature anche inferiori o uguali a 100°C.

10.6 Prodotti di decomposizione pericolosi

Nessuno in condizioni normali e temperatura ambiente.

La combustione incompleta potrebbe generare una complessa miscela di particelle solide e liquide aerodisperse e di gas, incluso CO (monossido di carbonio), H_2S (solfuro di idrogeno), SO_x (ossidi di zolfo) o H_2SO_4 (acido solforico) e composti organici e inorganici non identificati.

Si potrebbero creare degli accumuli di solfuro d' idrogeno (H2S) in specifici luoghi quali fossi, depressioni o spazi chiusi in quanto questo ha una densità maggiore dell'aria.

11 Informazioni tossicologiche

11.1 Informazioni sugli effetti tossicologici

Sostanze complesse come il bitume non si prestano ad analisi tossico cinetiche. Comunque la tossicocinetica di alcuni singoli componenti, come alcune componenti organiche volatili specifiche e gli idrocarburi policiclici aromatici (IPA), è stata studiata in dettaglio. Per gli essere umani le principali vie di esposizione al bitume sono l'inalazione e la via cutanea.

I principali siti di assorbimento potenziale di IPA da bitume negli esseri umani sono i polmoni e l'apparato respiratorio, dopo l'esposizione per inalazione a fumi di bitume, e la pelle, a causa del contatto con il bitume o ai fumi condensati dal bitume.

In generale, i singoli costituenti del bitume e fumi da bitume subiscono il metabolismo ossidativo, che può portare a bioattivazione.

La distribuzione degli IPA in tutto il corpo è stato studiata nei roditori. Questi studi hanno dimostrato che un basso livello di IPA, può essere trovato in organi interni, soprattutto nel tessuto adiposo.

In generale, gli IPA vengono eliminati per via urinaria o biliare.

a Tossicità acuta: Non classificato

Via orale

La tossicità acuta per via orale del bitume è stata valutata in alcuni studi condotti su ratto.

Da questi studi è emersa una DL50 orale acuta superiore a 5 g/kg che non comporta la classificazione ai sensi delle normative sulle sostanze pericolose (compresa CLP).

Di seguito è riportata una sintesi degli studi maggiormente rappresentativi del Dossier di registrazione.

Metodo	Risultato	Commenti	Fonte
RATTO (Maschi/ femmine) Somministrazione: sonda gastrica OECD Guideline 401 (Acute Oral Toxicity)	DL50:>5.000 mg/kg (maschi/femmine)	Studio chiave (studio di maggiore pertinenza) CAS 64741-56-6	Studio di American Petroleum Institute (API) 1982a

Via Inalatoria

Per valutare la tossicità acuta per via inalatoria del bitume sono disponibili alcuni studi su ratto.

Da questi studi è emersa una CL50 inalatoria acuta elevata che non comporta nessuna classificazione ai sensi delle normative sulle sostanze pericolose (compresa CLP).

Di seguito è riportata una sintesi degli studi maggiormente rappresentativi del Dossier di registrazione.

Metodo	Risultato	Commenti	Fonte
RATTO (Maschi/ femmine) Vapori (naso soltanto) OECD Guideline 403 (Acute Inhalation Toxicity)	CL50: > 94,4 mg/m³ (maschi/femmine)	Studio chiave (studio di maggiore pertinenza) Read-across Aerosol of fumi condensati di bitume ossidato	Fraunhofer Institute of Toxicology and Aerosol Research (2000)

Via Cutanea

La tossicità acuta per via cutanea del bitume è stata valutata in alcuni studi condotti su conigli. Da questi studi è emersa una DL50 cutanea acuta superiori a 2 g/kg che non comporta nessuna classificazione ai sensi delle normative sulle sostanze pericolose (compresa CLP).

Di seguito è riportata una sintesi degli studi maggiormente rappresentativi del Dossier di registrazione.

Metodo	Risultato	Commenti	Fonte
CONIGLIO (maschi/femmine) Bendaggio occlusivo OECD Guideline 402 (Acute Dermal Toxicity)	DL50>2.000 mg/kg (maschi/femmine)	Studio chiave CAS 64741-56-6	Studio di American Petroleum Institute (API) 1982a

Altre vie

Non ci sono informazioni disponibili.

Informazioni sugli umani

Non sono disponibili studi specifici sulla tossicità acuta del bitume sugli umani. Comunque in uno studio effettuato su volontari esposti esposti a fumi di bitume non furono registrato effetti avversi (Knecht 2001)

b Corrosione cutanea/irritazione cutanea: Non classificato (dati conclusivi ma non sufficienti per la classificazione)

Corrosione

In questa sezione non vengono riportati specifici studi. Sulla base dei dati disponibili è prevedibile che la sostanza, in generale, non sia corrosiva.

Irritazione cutanea

Il potenziale di irritazione cutanea di bitume è stato testato in alcuni studi condotti sul coniglio. Le conclusioni di questi studi indicano assenza di irritazione cutanea.

Tali risultati non portano a nessuna classificazione nell'ambito della normativa sulle sostanze pericolose (compresa CLP).

Di seguito è riportata una sintesi degli studi maggiormente rappresentativi del Dossier di registrazione.

Metodo	Risultato	Commenti	Fonte
CONIGLIO (Bendaggio occlusivo) OECD Guideline 404 (Acute Dermal Irritation/ Corrosion)	Non irritante Punteggio medio Eritema: 0,1 di max. 4 (cute intatta) Indice Edema: 0,1 di max. 4 (cute intatta)	Studio chiave CAS 64741-56-6	Studio di American Petroleum Institute (API) 1982a

Informazioni sugli umani

In un' indagine effettuata mediante un questionario su alcuni lavoratori nel settore del bitume, emerse l' estrema difficoltà di relazionare l' irritazione della pelle mostrata da questi all' esposizione al bitume a causa dei numerosi fattori fuorvianti presenti nello studio legati alla tipologia di lavorazione stessa (Riala 1998).

c Gravi danni oculari/irritazionie oculare: Non classificato (dati conclusivi ma non sufficienti per la classificazione)

Il potenziale di irritazione degli occhi del bitume è stato testato in alcuni studi condotti sul coniglio.

Tutti gli studi hanno evidenziato assenza di irritazione degli occhi, non è pertanto necessaria classificare la sostanza (compresa CLP).

Di seguito è riportata una sintesi degli studi maggiormente rappresentativi del Dossier di registrazione.

Metodo	Risultato	Commenti	Fonte
CONIGLIO OECD Guideline 405 (Acute Eye Irritation / Corrosion)	Non irritante	Studio chiave CAS 64741-56-6	Studio di American Petroleum Institute (API) 1982a

Informazioni sugli umani

In un' indagine effettuata su alcuni lavoratori nel settore del bitume, emerse l' estrema difficoltà di relazionare l' irritazione degli occhi mostrata da questi all' esposizione al bitume a causa della contemporanea esposizione ad altre sostanze (Norseth et al 2000).

d Sensibilizzazione respiratoria o cutanea Non classificato (dati conclusivi ma non sufficienti per la classificazione)

Sensibilizzazione respiratoria

Questo endpoint non è un requisito REACH e non sono disponibili dati per questo endpoint.

Sensibilizzazione cutanea

Sono disponibili alcuni studi condotti per saggiare il potenziale di sensibilizzazione del bitume.

I risultati ottenuti da questi studi indicano l'assenza di potenziale di sensibilizzazione cutanea, non è pertanto necessaria classificare la sostanza (compreso CLP).

Di seguito è riportata una sintesi degli studi maggiormente rappresentativi del Dossier di registrazione.

Il potenziale di sensibilizzazione del bitume è stato testato in alcuni studi condotti sul porcellino d' india.

Metodo	Risultato	Commenti	Fonte
PORCELLINO D' INDIA OECD Guideline 406 (Skin Sensitisation)	Non sensibilizzante	Studio chiave CAS 64741-56-6)	Studio di American Petroleum Institute (API) 1983a

Informazioni sugli umani

Non sono disponibili informazioni.

e Mutagenicità delle cellule germinali: Non classificato

Il potenziale mutageno del bitume è stato ampiamente studiato in una serie test in vivo e in vitro. La maggior parte degli studi non hanno mostrato prove coerenti di attività mutagena, pertanto non è necessario classificare la sostanza i sensi della normativa sulle sostanze pericolose (compresa CLP).

Di seguito è riportata una sintesi degli studi maggiormente rappresentativi del Dossier di registrazione.

Studi in vitro:

Metodo	Risultato	Commenti	Fonte
Test di Ames con e senza attivazione metabolica S. typhimurium TA98, T100, YG 1041, YG 1042 Dosi: ≤ 10 μ L and 0.1 mL (OECD Guideline 471 (Bacterial Reverse Mutation Assay)	Negativo senza attivazione metabolica Positivo con attivazione metabolica	Studio chiave Condensati di fumi di bitume	De Meo, M., Genevois, C., Brandt, H, Laget, M., Bartsch, H., Castegnaro, M. (1996)

Studi in vivo:

Metodo	Risultato	Commenti	Fonte
Saggio mutagenicità transgenica in animali RATTO (maschi) Via di somministrazione: inalazione vapori Dosi: 100, mg/m3 (idrocarburi totali)	Negativo	Studio chiave CAS 8052-42-4	Bottin, M.C., Gate, L., Rihn, B., Micillino, J.C., Nathalie, M., Martin (2006)
Saggio mutagenicità transgenica in animali TOPO (C57b1/6) (Labda Liz, Big Blue) (maschi) Via di somministrazione: aerosol Dosi: 98,7±6,1 mg/m3 (concentrazione fumi 100 mg/m3)	Negativo	Studio Chiave CAS: 8052-42-4	Micillino, J.C. Coulais, C. Binet, S. Bottin, M.C, Keith, G (2002)
Saggio del micronucleo (mutazione genica) RATTO (maschi/ Femmine) Via di somministrazione: inalazione vapori Dosi: 0, 30, 100, 300 mg/m3 (idrocarburi totali) OECD Guideline 474 (Mammalian Erythrocyte Micronucleus Test)	Negativo	Studio chiave Read-acros Con condensati di fumi di asfalto ossidato (CAS 64742-93-4)	Fraunhofer (2009a) Parker et al. (2011)

Informazioni sugli umani

Sono disponibili diversi studi (es. McClean 2007) dai quali è emerso che effetti avversi sono stati notati in caso di co esposizione dei soggetti ad altre sostanze con il bitume.

f Cancerogenicità: Non classificato

Sono disponibili alcuni studi di cancerogenesi per le vie di esposizione inalatoria e cutanea.

Per la via inalatoria lo studio disponibile non ha rilevato alcune effetto cancerogeno.

Per l'esposizione cutanea, alcuni studi su animali riportano debole attività. Si precisa che la presenza di solventi utilizzati nella somministrazione del bitume aumenta chiaramente la biodisponibilità e/o assorbimento dermico.

Sulla base di una valutazione complessiva dei risultati degli studi sugli animali chiave e di supporto, e dei due studi epidemiologici chiave, si è concluso che non ci sono prove per sostenere che per via cutanea o per inalazione il bitume presenti un rischio cancerogeno in condizioni normali di utilizzo.

Di seguito sono riportati alcuni studi su animali maggiormente rappresentativi del Dossier di registrazione.

	Risultato	Commenti	Fonte

Metodo			
RATTO (maschi/ femmine) Inalazione (naso soltanto) Esposizione: 104 settimana (6 ore al giorno per 5 giorni a settimana) Dosi: 0, 4, 20, or 100 mg/m3 OECD Guideline 451 (Carcinogenicity Studies)	NOAEC (carcinogenicità): 103,9 mg/m^3 aria (analitico) (valore aggiustato per istopatologia neoplastica: 172,5 mg/m^3) NOAEC (carcinogenicità): 10,4 mg/m^3 aria (analitico) (valore aggiustato per istopatologia neoplastica: 17,2 mg/m^3) Effetti neoplastici: nessun effetto.	Studio chiave Read-across Con condensati di fumi di bitume ossidato	Fraunhofer (2006) Fuhst et al. (2007)

Metodo	**Risultato**	**Commenti**	**Fonte**
RATTO (maschi/ femmine) Inalazione (naso soltanto) Esposizione: 104 settimana (7 giorni/settimana una volata al giorno); 2 giorni/settimana – una volta ogni 3-4 giorni Dosi: 0, 7.14, in 37.5 ul di olio mineral OECD Guideline 453	LOAEL (irritazione): 7,14 mg/day	Studio chiave sperimentale Con condensati di fumi di bitume ossidato	Clark et all (2011)
Topo (C3H/HeCrlBR) maschio 37.5 ul (due volte a settimana dose totale 75 ul) Esposizione totale: 24 mesi	Incidenza dei tumori della pelle; (nessuna massa tumorale nei topi)	Studio chiave Sperimentale (CAS#8052-42-4; CAS# 64741-56-6)	Goyak, K.O. McKee, R.H. Minsavage, G. D, McGowan C, Daughtrey W.C. Freeman (2011)

Informazioni sugli umani

In due studi epidemiologici su lavoratori esposti all' asfalto non è stato possibile riscontrare un nesso causale tra l' esposizione a fumi di bitume e il rischio di cancro ai polmoni (si riporta di seguito uno dei due studi).

Metodo	Risultato	Commenti	Fonte
Lavoratori Europei impiegati nel settore dell' asfalto Determinazione della probabilità di aumento del rischio di contrarre cancro polmonare Periodo di studio dicembre 2002 – giugno 2005 (Carcinogenicity Studies)	Non è stata rilevata una sostanziale evidenza di connessione tra gli indicatori di esposizione inalatoria o dermica al bitume presi in considerazione e il rischio di cancro ai polmoni.	Studio chiave Con condensati di fumi di bitume ossidato	IAR C (2009)

g Tossicità per la riproduzione Non classificato

Non sono disponibili informazioni. Non si prevedono effetti avversi.

E' disponibile un unico studio sulla tossicità per la riproduzione (riassunto nella tabella successiva) che riguarda sia gli effetti sulla fertilità che sullo sviluppo. Tale studio non ha evidenziato alcun effetto per tale end-point da parte del bitume, pertanto la sostanza non è classificata pericolosa ai sensi delle normative europee.

Metodo	Risultato	Commenti	Fonte
RATTO (Maschi/ femmine) Studio di tossicità ripetuta combinato con tossicità per la riproduzione/sviluppo Dosi: 30, 100, o 300 mg/m3 Somministrazione per via inalatoria (naso soltanto) Esposizione: maschi: 28 giorni femmine: 50 giorni 6ore al giorno per 7 giorni a settimana OECD Guideline 422 (Combined Repeated	NOAEC (P): 30 mg/m³ aria (peso degli organi) (NOAEC (P): 300 mg/m³ aria (indice di accoppiamento, indice di fertilità, numero di siti di impianto, durata della gravidanza, indice di nascite, indice di vita del neonato, indice di gravidanza, dimensioni della nidiata, peso della nidiata, indice di sopravvivenza, caratterizzazione dello sperma) NOAEC (F1): 300 mg/m³ aria	Studio chiave Read-across Con condensati di fumi di asfalto (CAS 64742-93-)4	Fraunhofer (2009a)

Dose Toxicity Study with the Reproduction / Developmental Toxicity Screening Test)	(nominal) (tutti gli effetti)

Metodo	Risultato	Commenti	Fonte
Coniglio Esposizione: dermica – 3 giorni/settimana per 4 settimane Dosi: 0, 200, 1000, 2000 mg/kg	Nessun effetto su gli organi riproduttivi	Residuo da distillazione (API 81-13)	API 1983a
Coniglio Esposizione: dermica – 3 giorni/settimana per 4 settimane Dosi: 0, 200, 1000, 2000 mg/kg	Nessun effetto su gli organi riproduttivi	Residuo da distillazione (API 81-14)	API 1983b

Informazioni sugli umani

Non sono disponibili informazioni.

h Tossicità specifica per organi bersaglio (STOT) - esposizione singola: Non classificato

Studi su ratti dimostrano che l’ esposizione a condensati di fumi di bitume non induce infiammazione polmonare.

In uno studio su 170 lavoratori esposti a fumi di bitume (con concentrazioni fino a 1,3 mg/m^3) non è stata riscontrata un’ associazione tra gli effetti acuti sulla funzionalità polmonare, l’ irritazione respiratoria o altri sintomi e l’ esposizione ai fumi di bitume.

i Tossicità specifica per organi bersaglio (STOT) - esposizione ripetuta: Non classificato

Studi di tossicità ripetuta per via orale sul bitume non sono appropriati in quanto le principali vie di esposizione per l’ uomo sono l’ inalatoria e la cutanea. In tutti gli studi condotti per via inalatoria e dermica è stata rilevata assenza di effetti sistemici avversi anche alle dosi maggiori somministrate, pertanto il bitume non è classificato pericoloso per tale end-point ai sensi delle normative sulle sostanze pericolose.

Di seguito è riportata una sintesi degli studi maggiormente rappresentativi del Dossier di registrazione.

Metodo	**Risultato**	**Commenti**	**Fonte**
	Inalazione		
RATTO (Maschi/femmine) Studio combinato di tossicità dose ripetuta (cronica) e carcinogenicità Dosi: 4, 20, o 100 mg/m3 Esposizione: 2 anni (6 ore al giorno per 5 giorni a settimana (eccetto durante le vacanze) OECD 451	NOAEC (effetti locali): 10,4 mg/m³ aria (analitico) (Valore aggiustato sulla base dell' istopatologia 17,2 mg/m³) NOAEC (effetti sistemici): 103,9 mg/L aria (analitico) (valore aggiustato 172,5 mg/m³) LOAEC (effetti locali): 20,7 mg/m³ aria (analitico) (Valore aggiustato sulla base dell' istopatologia 34,4 mg/m³)	Studio chiave Read-across Aerosol of fumi condensati di bitume ossidato	Fraunhofer (2006)
	Cutanea		
RATTO (Maschi/femmine) Subacuto 28 giorni (3 volte a settimana per 6 ore a volta) Dosi: 200, 1000, o 2000 mg/kg/giorno OECD Guideline 410 (Repeated Dose Dermal Toxicity: 21/28-Day Study) OECD Guideline 410 (Repeated Dose Dermal Toxicity: 21/28-Day Study)	NOAEL (effetti topici): 200 mg/kg/giorno (sulla base di assenza di risultati istopatologici significativi) NOAEL (effetti sistemici): 2000 mg/kg/giorno (sulla base di dati sul peso corporeo in assenza di risultati istopatologici significativi)	Studio chiave CAS 64741-56-6	Studio di American Petroleum Institute (API) 1983a

j Pericolo in caso di aspirazione: Non classificato

Tenuto conto del valore di viscosità stimato o misurato per il bitume, la sostanza non è classificata per il pericolo di aspirazione nei polmoni anche ai sensi del Regolamento CLP.

Altre informazioni

Non sono disponibili ulteriori informazioni.

12 Informazioni ecologiche

Sulla base delle informazioni ecologiche sotto riportate ed in base ai criteri indicati dalle normative sulle sostanze pericolose, il bitume NON è classificato pericoloso per lambiente anche ai sensi del Regolamento CLP.

12.1 Tossicità

Di seguito è riportata una sintesi degli studi maggiormente rappresentativi del Dossier di registrazione.

Endpoint	Risultato	Commenti
Tossicità acquatica		
Pesce Breve termine Oncorhynchus mykiss	LL50 96/ore: >1.000 mg/l	Studio chiave Redman Et al (2010b) QSAR
Invertebrati Daphnia magna Breve termine	LL50 48/ore: >1.000 mg/l	Studio chiave Redman Et al (2010b) QSAR
Invertebrati Daphnia magna Lungo termine	NOAEL 21/giorni: >=1.000 mg/l	Studio chiave Redman Et al (2010b) QSAR Read/Across
Alghe Selenastrum capricornutum	EL50 72/ore: >=1.000 mg/l	Studio chiave Redman Et al (2010b) QSAR
Pesce Lungo termine Oncorhynchus mykiss	LL50 28 /giorni: >1.000 mg/l NOEL: 28/ giorni >= 1.000 mg/l	Studio chiave Redman Et al (2010b) QSAR

12.2 Persistenza e degradabilità

Degradabilità abiotica

Idrolisi: componenti del bitume sono resistenti all'idrolisi a causa della mancanza di un gruppo funzionale che è idroliticamente reattivo. Pertanto, questo processo di degradazione non contribuirà alla rimozione della sostanza nell'ambiente.

Fotolisi in aria: endpoint non richiesto dal REACH

Fotolisi in acqua e suolo: endpoint non richiesto dal REACH.

Degradabilità biotica:

Acqua/sedimenti/suolo: i test standard per questo endpoint non sono applicabili alla sostanze UVCB.

12.3 Potenziale di bioaccumulo

Acqua/sedimenti/suolo: I test standard per questo endpoint non sono applicabili alle sostanze UVCB.

12.4 Mobilità nel suolo

Assorbimento Koc: i test standard per questo endpoint non sono applicabili alla sostanze UVCB.

12.5 Risultati della valutazione PBT e vPvB

Comparazione con i criteri dell' allegato XIII del Regolamento REACh

Valutazione della persistenza: alcune strutture di idrocarburi contenuti in questa categoria presentano caratteristiche di P (Persistent) o Vp (very Persistent).

Valutazione del potenziale di bioaccumulo: la struttura della maggior parte degli idrocarburi contenuti in questa categoria NON presentano caratteristiche di vB (very Bioaccumulative) tuttavia alcuni componenti presentano caratteristiche di B (Bioaccumulative).

Valutazione della tossicità: per le strutture che hanno mostrato caratteristiche di P e B è stata valutata la tossicità ma nessun componente rilevante soddisfa i criteri di tossicità ad eccezione dell' antracene il quale è stato confermato un PBT. Poiché l' antracene è presente in concentrazioni < 0,1% il prodotto non è PBT/vPvB.

Volatilizzazione

Tale parametro dipende dalla costante di Henry (HC) che non è applicabile alle sostanze complesse.

Distribuzione nell' ambiente

Assorbimento/desorbimento

I test standard per questo end point non sono applicabili alla sostanze UVCB.

Distribuzione su scala regionale la distribuzione della sostanza è:

36,22% in aria

0,07% in acqua

38,79 nei sedimenti

24,91 al suolo.

In una serie di test statici e dinamici hanno rivelato che il bitume è altamente insolubile in acqua e quando usato nell' asfalto crea una matrice che blocca tutti i componenti potenzialmente tossici (es. IPA).

12.6 Altri effetti avversi

Non presenti.

13 Considerazioni sullo smaltimento

13.1 Metodi di trattamento dei rifiuti

Non scaricare sul terreno né in fognature, cunicoli o corsi d'acqua.

Per lo smaltimento dei rifiuti derivanti dal prodotto, inclusi i contenitori vuoti non bonificati, attenersi in Italia al D.Lgs. 152/06 ed s.m.i. e ai Codici del Catalogo Europeo dei Rifiuti.

Il detentore ha la responsabilità di scegliere il codice più adeguato sulla base dell' uso effettivo del prodotto, eventuali alterazioni e contaminazioni.

Il prodotto come tale non contiene composti alogenati.

Smaltimento dei contenitori: Non disperdere i contenitori nell'ambiente. Smaltire secondo le norme vigenti locali.

14 Informazioni sul trasporto

14.1 Numero ONU:

3257

Si precisa che il prodotto è classificato come merce pericolosa solo se è trasportato fuso a temperatura > 100 °C.

14.2 Nome di spedizione ONU:

LIQUIDO TRASPORTATO A CALDO, N.A.S. (bitume fuso)

14.3 Classi di pericolo connesso al trasporto:

Trasporto stradale/ferroviario (ADR/RID):

Classe 9, M9

Trasporto marittimo (IMDG):

Classe 9

Trasporto aereo (IATA):

Classe 9

Il trasporto è vietato sia su voli cargo che passeggeri

14.4 Gruppi di imballaggio:

III; Etichetta 9 + Etichetta per le materie trasportate a caldo

14.5 Pericoli per l’ ambiente:

Sostanza NON pericolosa per l’ ambiente ai sensi dei codici ADR, RID, ADN e IMDG.

14.6 Precauzioni speciali per gli utilizzatori (operazioni di trasporto):

Indossare guanti di protezione contro gli agenti chimici (conformi allo standard EN374), insieme a un corso di addestramento base.

14.7 Trasporto alla rinfusa secondo l’ allegato II di MARPOL 73/78 ed il codice IBC

Se si intende effettuare il trasporto alla rinfusa attenersi al allegato II MARPOL 73/78 e al codice IBC ove applicabili.

Altro

Codice di restrizione Tunnel (ADR): D

15 Informazioni sulla regolamentazione

15.1 Disposizioni legislative e regolamenti su salute, sicurezza ed ambiente specifiche per la sostanza o la miscela

Autorizzazione ai sensi del Regolamento REACH (Regolamento CE n. 1907/2006 ed s.m.i.): sostanza non presente nell’ elenco delle sostanze estremamente preoccupanti (SVHC) candidate all’ autorizzazione

Restrizioni all’ uso ai sensi del Regolamento REACH (Regolamento CE n. 1907/2006 ed s.m.i.): Sostanza NON soggetta a Restrizioni ai sensi del Titolo VIII (Allegato XVII, Appendice 2).

Normativa sui rischi di incidenti rilevanti : Non applicabile

15.2 Valutazione della sicurezza chimica

Il bitume non è classificato pericoloso tuttavia è stata condotta una valutazione della sicurezza chimica che ha generato il CSR.

16. Altre informazioni

Le informazioni contenute nella presente scheda si riferiscono soltanto al prodotto indicato e possono non valere se il prodotto viene usato in combinazione con altri od in lavorazione.
Non utilizzare il prodotto per usi differenti da quelli previsti.
In tal caso l’ utilizzatore potrebbe essere soggetto a rischi non preventivati. Il prodotto deve essere utilizzato secondo le norme di igiene, sicurezza e buona pratica industriale secondo le indicazioni tecniche del fornitore ed in conformità alle disposizioni di Legge.

Le informazioni sono redatte al meglio delle nostre conoscenze alla data di settembre 2015 e sostituisce la precedente versione rev. 14 del 03/02/2015 rispetto alla quale è stata effettuata una revisione generale (tutte le sezioni).

Quanto contenuto nella presente scheda è però informativo e non costituisce garanzia. L' uso del prodotto avviene sotto controllo degli utilizzatori ed è perciò loro responsabilità adeguarsi alle condizioni di corretto esercizio indicate nella scheda, nonché adeguarsi a idonee pratiche di igiene industriale. Il presente documento non sostituisce l' analisi del rischio chimico che rimane a totale carico del datore di lavoro.

La presente scheda è stata compilata seguendo le disposizioni dell' Allegato II (modificato dal reg. 830/2015) del Regolamento (CE) n. 1907/06 e s.m.i.

Glossario:

N.A.	Non applicabile
N.D.	Non disponibile

Consigli di prudenza

Non applicabile

Indicazione di pericolo H

Non applicabile

Consigli di prudenza

Non applicabile

Indicazioni sulla formazione:

Formare in maniera adeguata i lavoratori potenzialmente esposti a tale sostanza sulla base dei contenuti della presente scheda di sicurezza

Normativa di riferimento

- Dossier di Registrazione
- D. Lgs. n° 152/06 Norme in materia ambientale.
- D.M. 27/11/06 Quarto elenco riepilogativo di norme armonizzate concernente l' attuazione della direttiva n.
- 89/686/CEE, relativa ai dispositivi di protezione individuale
- D. Lgs. n° 81/08 Attuazione dell' articolo 1 della legge 3 agosto 2007, n. 123, in materia di tutela della salute e
- della sicurezza neri luoghi di lavoro.
- Reg. 440/08 e s.m.i. che istituisce dei metodi di prova ai sensi del regolamento (Ce) n. 1907/2006 del Parlamento Europeo e del Consiglio concernente la registrazione, la valutazione, l'autorizzazione e la restrizione delle sostanze chimiche (Reach).
- (CE) n° 1907/06 Regolamento concernente la registrazione, la valutazione l' autorizzazione e la restrizione delle sostanze chimiche (REACH), che istituisce un' Agenzia europea per le sostanze chimiche, che modifica la direttiva 1999/45/CE e che abroga il regolamento (CEE) n.793/93 del Consiglio e il Regolamento (CE) n. 1488/94 della Commissione, nonché la direttiva 76/769/CEE del Consiglio e le direttive della Commissione 91/155/CEE, 93/67/CEE, 93/105/CE e 200/21/CE.
- Reg.1272/08 (CLP) Relativo alla classificazione, all"etichettatura e all"imballaggio delle sostanze e delle miscele che modifica e abroga le direttive 67/548/CEE e 1999/45/CE e che reca modifica al regolamento (CE) n. 1907/2006 e s.m.i..

Legenda delle abbreviazioni e acronimi:

ACGIH = American Conference of Governmental Industrial Hygienists
CSR = Relazione sulla Sicurezza Chimica
DNEL = Livello Derivato di Non Effetto
DMEL = Livello Derivato di Effetto Minimo
EC50 = Concentrazione effettiva mediana
IC50 = Concentrazione di inibizione, 50%
LC50 = Concentrazione letale, 50%
LD50 = Dose letale media
PNEC = Concentrazione Prevista di Non Effetto
n.a. = non applicabile
n.d. = non disponibile
PBT = Sostanza Persistente, Bioaccumulabile e Tossica
STOT = Tossicità specifica per organi bersaglio
(STOT) RE = Esposizione ripetuta
(STOT) SE = Esposizione singola
TLV®TWA = Valore limite di soglia – media ponderata nel tempo
TLV®STEL = Valore limite di soglia – limite per breve tempo di esposizione
vPvB = molto Persistente e molto Bioaccumulabile
UVCB = sostanze dalla composizione sconosciuta o variabile, prodotti di reazioni complesse o materiali biologici.

Poiché il bitume non è una sostanza classificata pericolosa non è richiesta la valutazione dell’ esposizione né la caratterizzazione del rischio. Pertanto non è necessario elaborare gli scenari di esposizione.