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DESIGN AND DEVELOPMENT OF INNOVATIVE AND MORE SUSTAINABLE HIGH-PERFORMANCE PVC SYNTHETIC LEATHERS, FOR AUTOMOTIVE INTERIORS APPLICATIONS WITH INCREASED COMFORT AND SAFETY

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Table of Contents

1

Introduction

1.1. Brief history of PVC

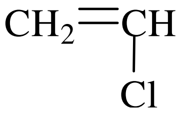
Amongst the plastic universe, composed by myriads of different polymers and co-polymers, one of the most widely spread still nowadays is certainly PVC, acronym for Poly(Vinyl Chloride). In fact, PVC is the third most used plastic material in the world, with a global consume of 39.3 million tonnes in 2013, and an expected increase of 3.2 %/year until 2021 [1]. Concerning Europe (EU–28+NO/CH), 2015 saw a total demand of 49 million tonnes of plastics, with PVC accounting for about 5 million tonnes (10.1 %), being also in Europe the third plastic material after PP and PE (LDPE/HDPE) [2].

PVC is considered the oldest synthetic plastic, followed by polystyrene and polyolefins. This polymer was accidentally discovered in the early years of the 19th century, by two scientists. The first one was, in 1838, the French physicist and chemist Henri Victor Regnault, in Justus Liebig's laboratory in Gießen, Germany. He observed the formation of a white powder inside sealed tubes containing vinyl chloride (VC) [3]. Later, in 1872, the German Eugen Baumann found a white material inside glass flasks containing gaseous VC exposed to sunlight [4]. However, it was only in 1912–13 that a German company (Chemische Fabrik Griesheim–Elektron) took the first patents, based on the work of scientist Friedrich Heinrich August Klatte, about the reaction between acetylene and hydrogen chloride to obtain vinyl chloride, and its subsequent polymerization with sunlight irradiation [5, 6]. However, only in late 1920s different scientists and companies, mainly located in the United States (i.e. DuPont, Carbon and Carbide Chemical Corp.) and Germany (i.e. I.G. Farben A.G., now BASF), disclosed patents concerning viable methods to polymerise Vinyl Chloride Monomer (VCM) and obtain PVC. In the same years, more easily processable vinyl chloride copolymers (i.e. with vinyl acetate, VAc) were introduced.

Another milestone in the diffusion of PVC was reached in the United States, when American inventor Waldo Semon was hired by B.F. Goodrich Company to find synthetic alternatives to natural rubber. Between 1927 and 1933 he discovered that the addition of plasticizing agents to PVC resulted in a processable material at low temperatures. PVC poor heat resistance, in fact, was the main issue encountered when trying to process it. Although Klatte previously proposed the use of low quantity of solvents, insufficient to create a solution, to obtain a processable mixture even without heating, the use of plasticizing agents provided materials that could be permanently flexible. Semon is therefore considered the inventor of the true "external plasticization", which opposes to "internal plasticization" obtained through co-polymerization, and of the plastisol method to produce coated fabrics. Meanwhile, in Europe suspension polymerisation were developed by ICI (England) and I.G. Farben A.G. (Germany). The commercial production of PVC polymers began in United States and Europe in late 1930s – early 1940s, just before and during World War II, using methods and equipment derived from rubber and celluloid industries. These methods were compounding, calendering, compression moulding and extrusion [7]. During World War II flexible PVC became of crucial importance in substituting rubber, which has become rare and expensive. The production and use of un–plasticized (i.e. rigid) PVC considerably increased during the 1950s and 1960s, due to the discovery and diffusion of effective heat stabilization systems and processing equipment improvements [8, 9].

1.2. VCM production

PVC is obtained through free–radical polymerization of VCM (Figure 1.1) which is a colourless gas at room temperature and atmospheric pressure. It exhibits a boiling point of -13.9 °C and explosive limits of 4–20 %vol. in air. Moreover, it is clearly harmful for human health, as pointed out in Paragraph 2.1.



$$CH_2{=}CH(Cl)$$

Figure 1.1: chemical structure of VCM.

Due to these reasons, VCM for industrial processing is kept in liquid form under pressure. This monomer could be produced following two main routes, starting from acetylene or ethylene. The acetylene route has become obsolete and, due to the use of a mercury–based catalyst, is nowadays abandoned, with the exception of China [10]. The remaining production of VCM starts from ethylene, which reacts with chlorine (direct chlorination) or with hydrogen chloride and oxygen (oxychlorination) to obtain 1,2–ethylenedichloride (EDC). The latter is then converted to VCM via thermal cracking (i.e. pyrolysis at 450–550 °C) and the resultant hydrogen chloride by–product is recycled for oxychlorination reaction. The involved reactions are shown in Scheme 1.1.

Direct Chlorination $C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$

EDC Pyrolysis $C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl$

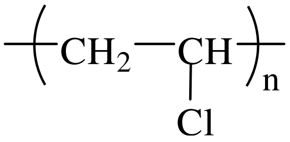
Oxychlorination $C_2H_4 + 2\,HCl + 0.5\,O_2 \rightarrow C_2H_4Cl_2 + H_2O$

Scheme 1.1: reactions of the ethylene route to VCM.

Thus, a typical VCM production plant is configured to perform both the reactions: half of the ethylene is fed to direct chlorination, while the other half is subjected to oxychlorination using hydrogen chloride recovered by the thermal cracking of EDC [11].

1.3. VCM polymerization [12]

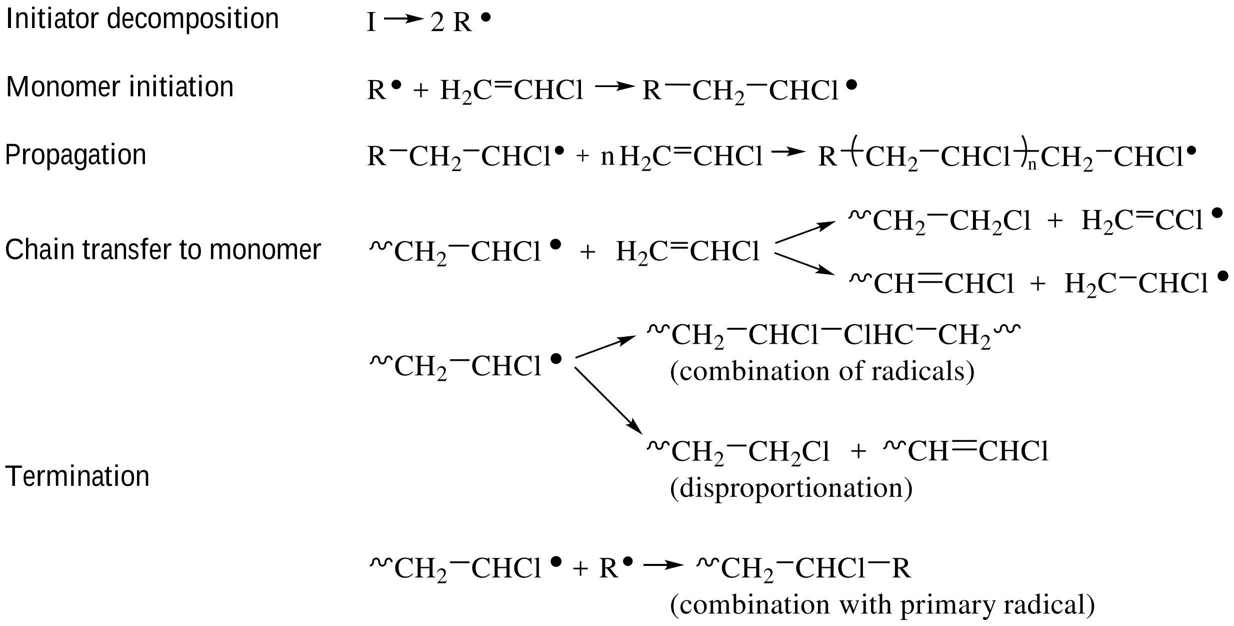
The typical chemical structure identifying PVC is reported in Figure 1.2. Observing the structure, it appears clear the reason of the uniqueness of this polymer, which is the presence of chlorine in the repeating unit: chlorine constitutes the 57 %wt. of the polymer. This fact leads to polar bonds and this is the reason behind its great ability to be compounded with a number of additives. Moreover, the presence of chlorine makes PVC almost not flammable. Normally, PVC is formed by linear chains with a head–to–tail sequence. These sequences tend to be atactic, thus resulting in completely amorphous fragments, even though syndiotactic sequences may be found. This syndiotacticity is likely to be the cause of the presence of crystalline domains which are usually present in the 5–10 % range of the whole polymer [9, 13].



$\left(CH_2-\underset{\underset{Cl}{|}}{C}H \right)_n$

Figure 1.2: chemical structure of PVC.

Free–radical polymerization of VCM, as represented in Scheme 1.2, is possible due to the high reactivity of its radical form.



Scheme 1.2: free–radical polymerization of VCM [8].

This high reactivity means, as a consequence, that the chain transfer reactions are targeted to any of the species present in the polymerization system: monomer, initiator, solvent (if present) and the polymer itself. Consequently, free–radical polymerization of VCM causes the introduction of different types of defects alongside the polymer chain, resulting in the low thermal stability issues observed and well–known since the first experiments on PVC polymerization conducted a century ago. The synthesis of PVC can be carried out with different polymerization techniques: suspension, emulsion, bulk (or mass) and solvent polymerization, in order of commercial relevance.

- *Suspension polymerization* is obtained by introducing in a pressure vessel (autoclave) liquid VCM and suspending agents into water, and applying a high–speed agitation to obtain a fine dispersion of VCM droplets (about 50–150 μm). Then, a VCM–soluble radical initiator is fed to the reactor and the monomer droplets begins to polymerize, giving a slurry of PVC particles of about the same diameter of the VCM droplets. The reactor could reach pressures up to 1.5 MPa, and temperatures of 80 °C, until the monomer reaches about 80–90 % of conversion, point at which the reaction is typically stopped and the excess of VCM stripped out from the slurry. Solid PVC is then centrifuged to separate it from water and carefully dried, giving a fine white, odourless and non–toxic powder.

- *Emulsion polymerization* is the oldest method amongst those ones known to polymerize PVC. It involves the use of liquid VCM and water, with the addiction of emulsifiers and a water–soluble free–radical initiator, such as potassium or ammonium persulphates or more complex redox systems. The solubility of the initiator is the key differences between suspension and emulsion polymerization systems. The presence of emulsifiers results in extremely dispersed emulsion, with micelles down to 0.1–1.5 μm in diameter. Due to the presence of the initiator in water, the polymerization begins at the interface between water and the VCM micelles, and propagates inside the latter. The reaction is usually stopped around 90% of conversion, and the excess of VCM stripped out from the polymer slurry, even if, in this case, the process is more difficult. It is worth noting that the emulsifiers are not completely removed after the process, and this residual process additive helps the dispersion of emulsion PVC used in plastisol applications [9].
- *Micro–suspension polymerization* is a hybrid technique which lies between suspension and emulsion polymerization. In fact, the reaction is set–up like in suspension polymerization (i.e. the initiator is VCM–soluble), but emulsifiers are added, so that the process is essentially the same of the emulsion polymerization.
- *Bulk polymerization* (also referred to as mass polymerization) is obtained using only the monomer and a free–radical initiator (e.g. an acyl peroxide or peroxycarbonate). In order to work in liquid phase, the reactor is kept under pressure and at temperatures in the range of 40–70 °C. During the process, there is the formations of PVC particles, which are insoluble in the monomer, thus originating a heterogeneous system. The uniformity in terms of dimensions and morphology of the polymer grains is ensured by high speed agitation. At low conversion (8–12 %) the polymer grains, which are

porous, absorb the liquid monomer and the system viscosity increases to a point at which mixing is no more efficient. Then, the whole reaction mass is transferred to a second reactor where the grains enhance in size and become more and more "dried" with the increasing of the monomer conversion. When a predetermined conversion is reached (e.g. 80 %), the reaction is stopped and the excess of monomer stripped by de–gassing, with the eventual aid of steam or inert gases.

- *Solvent polymerization* is very seldom performed, and usually not on a commercial scale. It involves the use of an organic solvent which solubilizes VCM and the initiator, but where PVC is insoluble. As VCM polymerizes, PVC particles precipitates and are collected as solid at the end of the process via filtration. This technique poses obvious risks for both human health and the environment due to massive use of organic solvents.

As for many other polymers, PVC properties strongly depend on its average molecular weight, which is commonly expressed as "viscosity number", also known as reduced viscosity (Equation 1.1), or as the more often used in industry "K–value" (Equation 1.2). These values are calculated from viscosity measurements of dilute polymer solutions in cyclohexanone, using equations described by international standards (e.g. ISO 1628–2).

Equation 1.1 [12] $$\frac{(\eta - \eta_0)}{\eta_0 c} \text{ equivalent to } \frac{(t - t_0)}{t_0 c}$$

Where:

η and η_0 are the viscosities of polymer solution and pure solvent;

t and t_0 are the average flow times of solution and pure solvent in specified conditions;

c is the concentration of the solution (g_{polymer} / mL_{solution}).

In particular, K–value was conceived by German industrial chemist Hans Fikentscher in late 1920s as a viscosity index for cellulosic polymers [14]. Commercial PVC resins have K–values ranging from 50 to 90, and different values are used for different applications. For example, resins with K–values of 57–58 are used for rigid applications, while values greater than 65, and up to 82, are more suitable for plasticized applications [9]. The main process parameter influencing molecular weight and, hence, K–value, is the temperature at which the polymerization is carried out: an increase in polymerization temperature leads to reduced molecular weight of the polymer, because of the higher rate of chain transfer to monomer than propagation rate (see Scheme 1.2) [15].

Equation 1.2 [16]

$$K = \frac{1.5\log\eta_r - 1 + \sqrt{1 + \left(\frac{2}{c} + 2 + 1.5\log\eta_r\right)1.5\log\eta_r}}{150 + 300c} \times 1000$$

Where:

$\eta_r = \frac{\eta}{\eta_0} = \frac{t}{t_0}$	is the ratio of the viscosities (and flow times) of polymer solution and pure solvent;
t and t_0	are the average flow times of solution and pure solvent in specified conditions;
c	is the concentration of the solution (g_{polymer} / mL_{solution}).

1.4. Applications of PVC

The research for artificial products capable to imitate and substitute natural materials, as well as mix them with the newly discovered ones, started in 19th century. These new materials had a common problem related to their reception by the audience, because of its artificial and “unnatural” origin. For example, Americans firstly refused to buy households or personal products made of Celluloid, invented in 1869, unless these products resembled “natural” materials [17]. In this context, PVC acquired crescent importance and since World War II the diffusion of products based on this polymer greatly increased worldwide. This was thanks to its versatility and the ability to be filled with a variety of different additives to obtain a huge range of materials suitable for countless applications. Based on the type of additives, in fact, it is possible to manufacture from rigid materials (uPVC), such as sewage piping, windows framing or floor tiles, to soft and flexible products like plastic toys, shower curtains and leather–like materials (pPVC), with any degree of softness in between. Moreover, these materials could be made coloured or colourless, opaque or transparent, fireproof, resistant to solvents or chemicals, scratch–resistant, UV–resistant, and so on. In particular, during the years, leather–like materials became increasingly better in imitating their natural counterpart, to a point that nowadays only expert eyes and hands could tell the differences between natural and synthetic leathers.

1.5. PVC synthetic leathers (SLs)

Amongst PVC products, SLs are certainly a class of material that is born to simulate the aspect and feel of "real", or "hide" leather. Through the years, many attempts and many different materials have been developed to reach this goal. Early in 20th century, for example, DuPont invented *Fabrikoid*, an imitation leather based on cotton cloth coated with nitrocellulose, which became widely diffused in the 1920s and used for luggage, dress trimming, upholstery, seat covers and rooftops in automobiles [18]. In the same years, Waldo Semon replaced natural rubber with pPVC for textile coating in a number of applications, like umbrellas, curtains, tents or other outdoor fabrics, in order to make them waterproof. This material was patented and commercialized in the 1930s under the name *Koroseal* [19].

> *"My wife had been making curtains for the living room," he said. "I brought some of the fabric into the laboratory and coated it with PVC, and lo and behold, it looked like silk and it was waterproof… I became so enthusiastic… I forgot about protocol and went directly to the vice president of sales, and he looked at it and he says, 'Hell, what do you mean, waterproof?' So I grabbed the fabric and put it on top of his incoming mail and took a decanter of water and poured it. Oh, he was really frightened, but it didn't leak… I've often wondered what would have happened to me or to PVC if it had leaked."*
>
> *Waldo Semon [20]*

After World War II, the demand for faux leather of good quality increased with the economic boom. Along the pPVC–based products, many alternatives to hide leather were based on polyurethanes (PU) polymers. Leatherette was a common term for coated fabrics, developed and rapidly diffused in the 1960s. Leatherette was much easier to keep clean, didn't creep easily and maintained colours, becoming a diffuse material in automobiles interiors. However, leatherette was quite stiff and not porous, thus not suitable for clothing or car seats which require breathability. In the mid–1960s, DuPont engineered this issue and produced and commercialized a more breathable "poromeric" (fusion of the words *poro*us and poly*meric*) faux leather under the name *Corfam*. After a marketing promotion of millions of dollars, however, the product failed and was sold to a Polish company. In fact, the improvements with respect to hide leather were not so impressive: *Corfam* lacked a good breathability and softness, and its costs were too high and unjustified for the performances.

The term "*pleather*" (for plastic leather) to indicate faux leather was adopted in the 1980s. Nowadays, synthetic leathers commonly used for upholstery, clothing and automotive industry reached very high standards of quality and comfort. In particular, SLs are widely used for automotive applications, as vehicle interiors. For example, inside of a car cockpit, SLs are used to manufacture a great number of parts, as illustrated in Figure 1.3. Even if they all look and feel different, these parts may be all made in pPVC. This is just one proof of the complexity reached by the PVC industry applied to the automotive interiors.

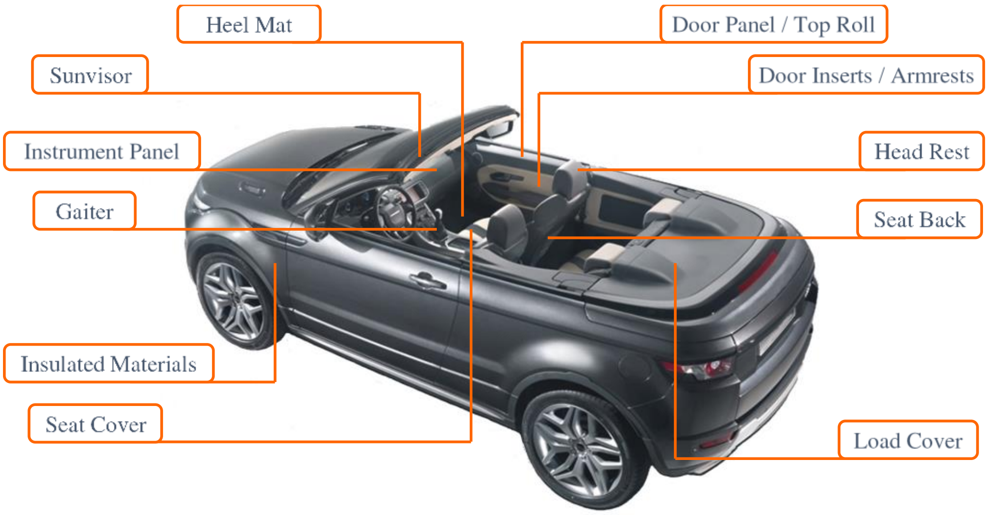


Figure 1.3: list of SLs parts used inside a car cockpit. Source: Vulcaflex S.p.A.

From a technical point of view, pPVC synthetic leathers belong to different types, manufactured with different machineries and processes. A typical pPVC SL is composed of several layers of PVC, with different formulation and aspect, a topcoat thin layer made of a polymer–based lacquer (PU or acrylic), and, in some cases, it may be supported by a backing textile (typically cotton and/or PET). A supported structure is shown in Figure 1.4.

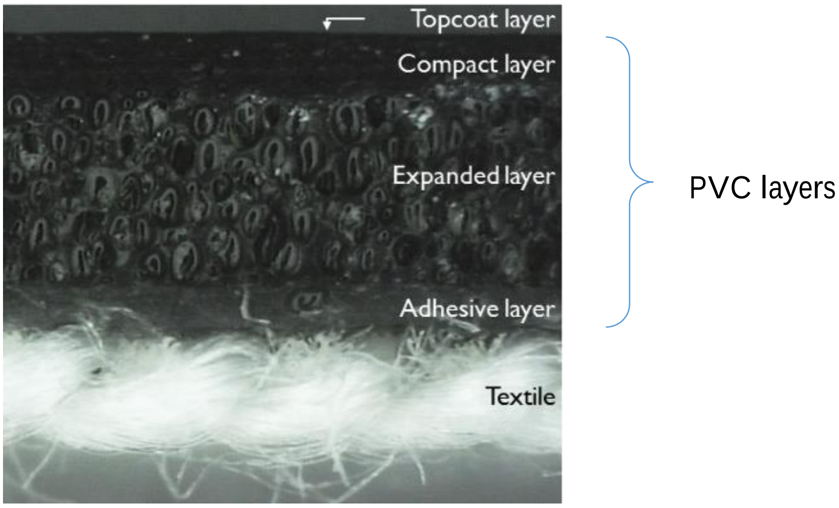


Figure 1.4: typical cross–section of a supported pPVC SL.

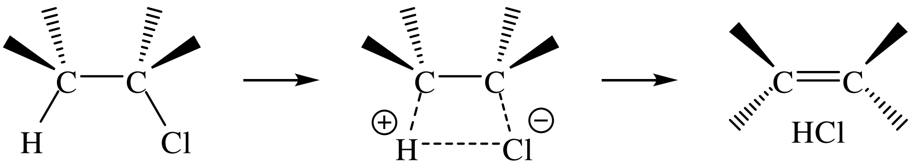
As it can be seen, the three PVC layers are different in aspect, and they impart different properties to the finite product. The upper one is a compact layer, and it is necessary to give solidity and a certain degree of stiffness to the material. Moreover, it results an even surface on top of which lacquers can be applied and engraving processes can be carried out with consistency of results. The median one is an expanded layer, a closed–cell foamy material that still preserves structure but imparts to the finite product the sought softness, the key property needed to emulate the touch and feel of hide leather. The lower and last of the PVC layers is an adhesive layer which is necessary to bond the textile backing when present. Other structures might see the absence of textile (i.e. unsupported SL), or its presence armed inside one of the PVC layers.

1.6. Typical additives for pPVC SLs

As previously mentioned, one of the unique features of PVC is its ability to be compounded with a number of different additives, to obtain virtually infinite combinations of compounds, from flexible to rigid products. These additives could be subdivided into two main categories, essentials and optional. The first ones are, basically, process additives which are fundamental for the stability and durability of the material throughout its processing and life; among these additives, there are heat stabilizers and co–stabilizers, antioxidants and UV light absorbers, with the firsts being particular important. The optional additives comprise all the other additives which are used to fine–tune the material final properties, as well as the ease of its processing: these are rheology modifiers, plasticizers and internal lubricants, blowing agents, flame retardants, colorants and pigments. Among these, the additives object of this research project, which will be discussed more in–depth in the following chapters, find place.

- *Heat stabilizers*

Heat stability was one of the major issues encountered by the first chemists and engineers which tried to process PVC. Although every plastic material undergoes thermal degradation at high temperatures, some of them, in the first degradative step, tend to eliminate small molecules at relatively mild temperatures (i.e. approx. 120 °C for PVC). These polymers include, amongst many and in addition to PVC, Chlorinated Polyethylene (CPE), Polychloroprene (Neoprene), Chlorosulphonated Polyethylene (CSPE, Hypalon®), Poly(Vinyl Acetate) (PVAc) and several fluoropolymers. However, the elimination of hydrogen chloride (HCl) from PVC could not be controlled using, as for the other polymers, reactive basic additives (e.g. magnesium or lead oxide) [9]. This could be partly due to a sufficiently regular structure which favour dehydrochlorination of PVC through "unzipping" of hydrogen chloride, which is an autocatalytic reaction resulting in the formation of a conjugated polyene. However, the origin of these degradation phenomena has to be found in structural defects of the polymer chain, the most important of which are tertiary and allylic chlorine. In particular, tertiary chlorine has been thought to be the most influential initiator of dehydrochlorination process due to its high concentration as defect in the polymer chains [21], despite the fact that chloroallyl groups show a greater constant of dehydrochlorination [22] and C–Cl bond in these groups has lower energy [23]. According to comprehensive studies on low molecular weight models, elimination of hydrogen chloride occurs via a four–centre mechanism as reported in Scheme 1.3.



Scheme 1.3: dehydrochlorination due to the presence of tertiary chlorine [22, 24, 25].

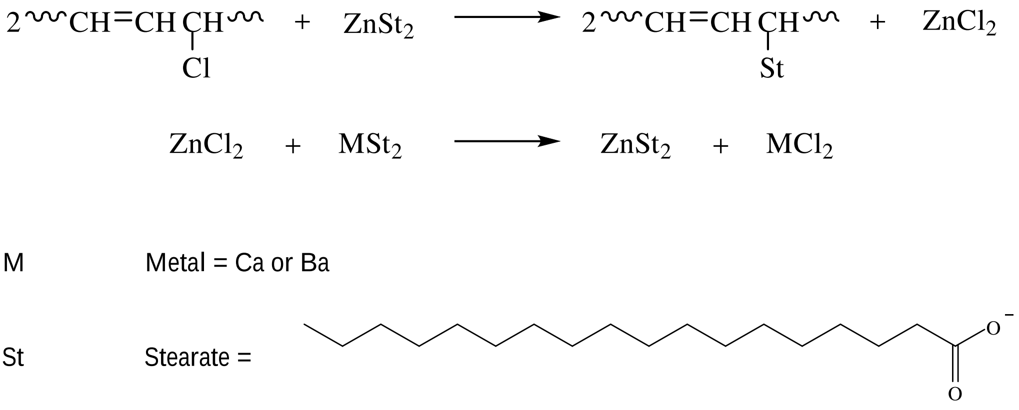
These unsaturations along the chain are then responsible for two different kind of further degradation steps. First, their presence origins chloroallyl groups and subsequent dehydrochlorination. Secondly, they are subjected to oxidative reactions which produce hydroperoxides and carbonyl groups. The sum of these degradation reactions results in the release of volatiles (mainly HCl until 200 °C, then organic compounds until 280 °C when HCl returns to increase due to HCl catalysed dehydrochlorination) and a correspondent weight loss, and terminates with char formation. During all of these stages, PVC undergoes a progressive colour change (Figure 1.5) caused by the formation of double bonds and polyene chains.

Figure 1.5: example of typical colour change in a un–stabilized PVC foil (right) compared with stabilized PVC (left).

Heat stabilizers are, thus, necessary to counteract degradation reactions occurring during processing of PVC. Many different classes of heat stabilizers may be used, but a common principle of action is the substitution of labile chlorine atoms along the polymer chains with other groups less prone to be in turn substituted. The most common and used heat stabilizers are described below.

Calcium/zinc and Barium/zinc stabilizers

These ones are metal soaps, otherwise called carboxylates, the most common of which is stearate (also called octoate). These compounds react with chloroallyl groups and substitute the labile chlorine atom with the stearate group, a definitely worst leaving group. The drawback of this reaction, shown in Scheme 1.4, is the formation of zinc chloride ($ZnCl_2$), which is known to be a catalyst for dehydrochlorination. However, its presence is also mitigated by the presence of calcium or barium cations which perform an ionic exchange reaction with it, regenerating, in part, the active zinc stearate.



$$2\sim CH{=}CH\underset{Cl}{CH}\sim \;+\; ZnSt_2 \longrightarrow 2\sim CH{=}CH\underset{St}{CH}\sim \;+\; ZnCl_2$$

$$ZnCl_2 + MSt_2 \longrightarrow ZnSt_2 + MCl_2$$

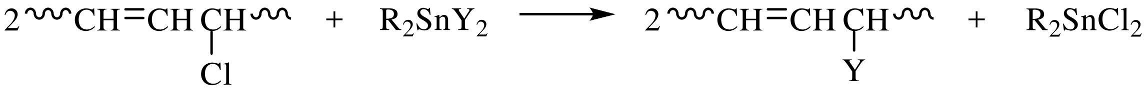
M Metal = Ca or Ba

St Stearate =

Scheme 1.4: mechanism of action of calcium (barium)/zinc stearates heat stabilizers [26].

Organotin stabilizers

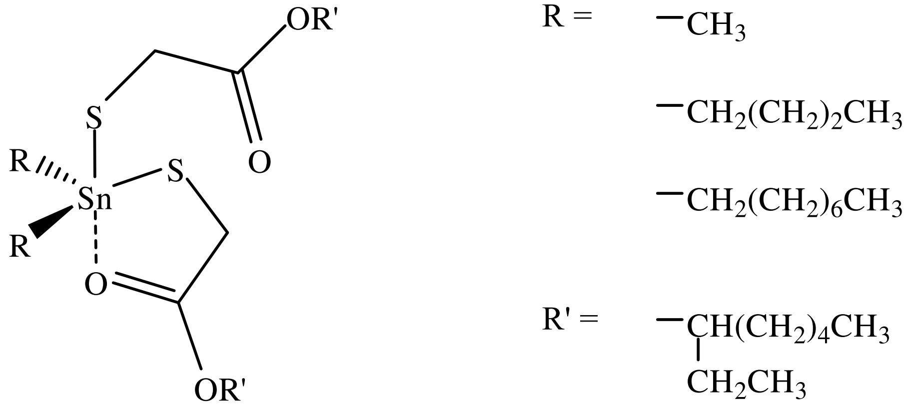
These class of heat stabilizers is based on organometallics based on tin, particularly dialkyltins (R_2SnY_2) and monoalklyltins ($RSnY_3$). Higher alkylated organotins are too generally toxic to be used without concern. Commercial stabilizers are usually a mix of mono– and dialkyltins (tin carboxylates), very often with sulphur containing groups. In fact, tin mercaptides are proven to be efficient heat stabilizers due to the presence of sulphur [26]. Unfortunately, these compounds have a limited field of application due to the residual sulphur–containing reagents, difficultly removable from the synthetized additive. This issue is of particular concern for the automotive industry, where the high standards required for comfort in the vehicle interiors excludes the use of such compounds. This was particularly true in the past, while nowadays, methods to obtain low–odour tin mercaptides (e.g. vacuum removal) have been adopted, making these additives viable for certain automotive applications. A simplified mechanism of action, analogous to that of metal soaps, is reported in Scheme 1.5.



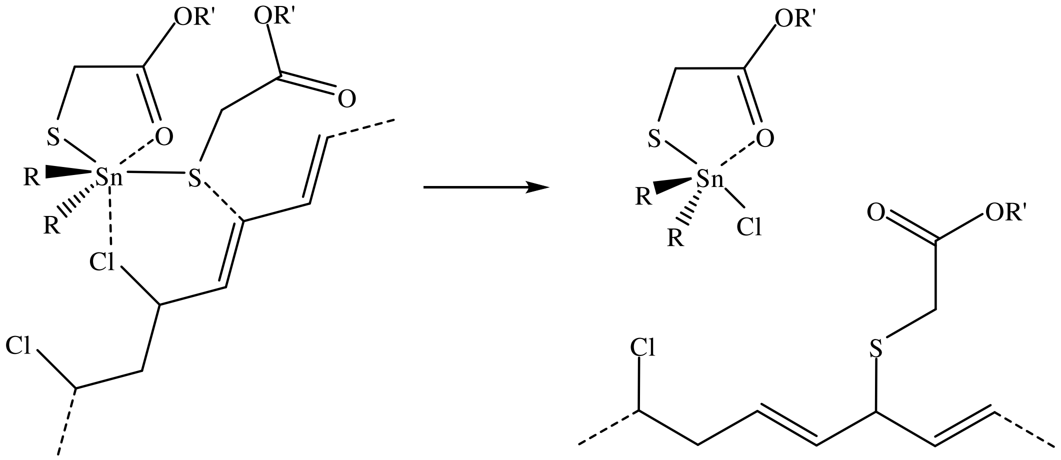
$$2\sim CH{=}CH\underset{Cl}{CH}\sim \;+\; R_2SnY_2 \longrightarrow 2\sim CH{=}CH\underset{Y}{CH}\sim \;+\; R_2SnCl_2$$

Scheme 1.5: simplified mechanism of action of organotin heat stabilizers [26].

More in detail, the structure of a general sulphur–containing organotin stabilizer, like an alkyltin thioglycollate (e.g. dialkyltin β –mercaptopropionate) is reported in Scheme 1.6, and a simplified mechanism of action is shown in Scheme 1.7.



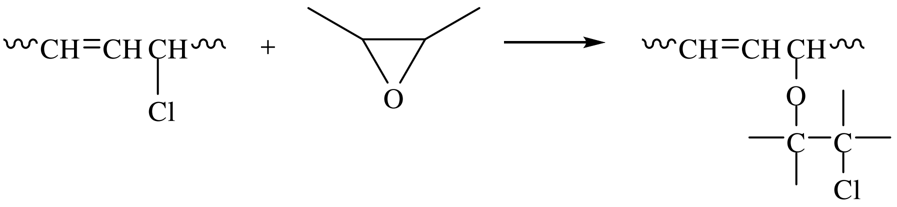
Scheme 1.6: general structure of an alkyltin thioglycolate [27].



Scheme 1.7: simplified mechanism of action of a general alkyltin thioglycolate [27].

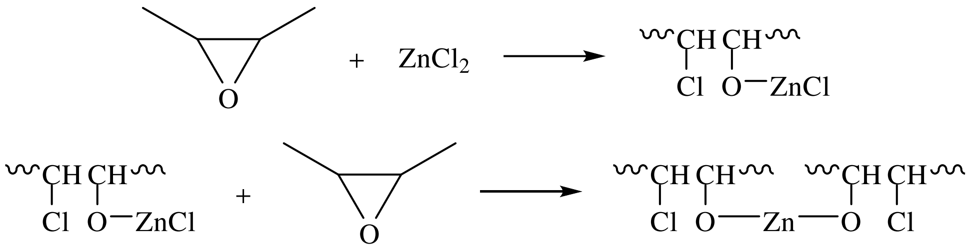
Epoxidized stabilizers and co–stabilizers

The oxirane rings present in this class of compounds makes them reactive versus labile chlorine atoms (Scheme 1.8) and free hydrogen chloride [28].



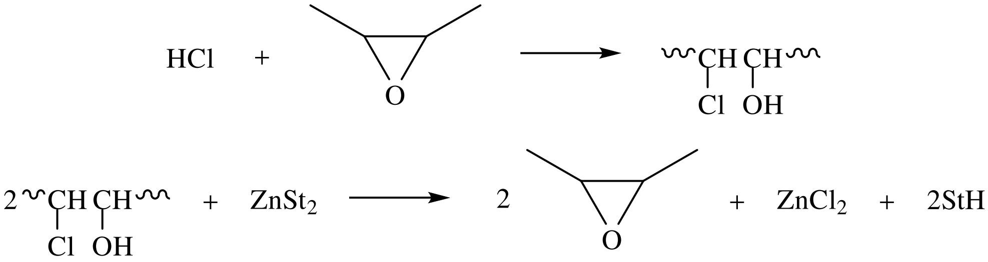
Scheme 1.8: possible mechanism of action of epoxy compounds heat stabilizers [28].

Moreover, these groups are capable to complex zinc chloride [29], which is responsible for catalytic effects on dehydrochlorination reaction (Scheme 1.9).



Scheme 1.9: proposed mechanism for ZnCl2 complexing by epoxy compounds [26].

Finally, epoxy compounds act also as hydrogen chloride scavengers, taking part in HCl transfer from polymer to metal soap stabilizers, being recovered at the end of this reaction, which is, thus, reversible. A proposed mechanism is reported in Scheme 1.10, based on experiments with an epoxy compound (i.e. octyl epoxystearate) and zinc stearate in a solution of HCl [30].



Scheme 1.10: mechanism of HCl scavenging and transferring by epoxy compounds.

It must be said, however, that epoxy compounds alone do not have any stabilizing effect on PVC: their function is explicated only in the presence of synergic and activating elements, like those granted by organic salts. Thus, epoxy compounds are frequently added as co–stabilizers with metal soaps. Amongst these epoxidized stabilizers, a particular mention should be reserved to Epoxidized Soybean Oil (ESO or ESBO, see Table 2.1 – page 38), which combines co–stabilizing and plasticizing effects.

1.7. Production techniques for pPVC SLs

Synthetic leathers are typically manufactured with two different methods, which are calendering and coating. The first one is usually used to manufacture thin single–layer foils, that can be used for the production of sunvisors or, if laminated to a semi–rigid foam (e.g. PP foams), for in–mould graining applications, while the latter one is used to obtain both supported and unsupported SLs, with expanded layers in their structure. A huge difference between the two methods resides in the compounding techniques: coating techniques are paste–based which are obtained by cold mixing compounding, while calendering uses dry blends which are melt–mixed prior to enter the calender rolls for lamination. The calender could be arranged in many configurations based on the number and position of rolls (e.g. Figure 1.6). Due to the aim of the present work, only coating techniques will be considered and, thus, more in–depth described.

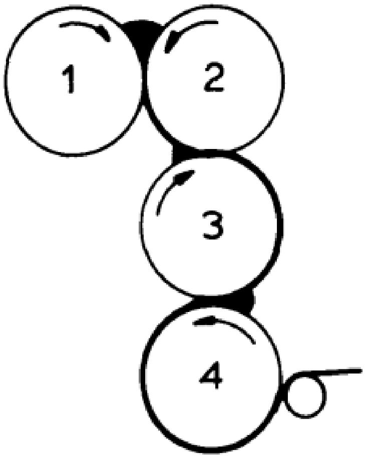


Figure 1.6: typical inverted 'L' 4-roll stack [7].

The first step of the direct/transfer coating method is the formulation and preparation of a PVC paste (so-called *plastisol*), which is a fine dispersion of vinyl resin and other additives in plasticizer. The vinyl resins used for plastisol applications are usually obtained via emulsion polymerization, with a very fine particle size (1–2 μm). However, formulations for plastisols often include also small quantities of suspension grade vinyl resin, referred to as blending resins. The addition of resins with a greater particle size has the effect to decrease the global surface area available for plasticizer, resulting in a lower and more stable viscosity of the plastisol, for both shelf–life and processing. Nevertheless, the drawback is the formation of a more inhomogeneous system, with more possibility to settle, causing reductions in mechanical properties, clarity, gloss and speed of gelation [9].

- *Plastisol preparation*

Plastisol are prepared following various steps. First, its components are mechanical mixed to obtain a paste–like compound. The mechanical mixing alone is not sufficient to obtain a homogeneous paste, so after this first step, the paste is passed through a triple–roll mill (for laboratory scale or industrial colour pastes preparation) or a dissolver (for industrial applications), which reduce the dimensions of resin (and eventually fillers) aggregates and finely disperse them into plasticizer. The resulting plastisol needs then to be degassed under vacuum, in order to remove trapped air and gases bubbles as well as humidity, which all have a negative impact during the phase of gelation in oven. Degassing may be performed during the mixing in the dissolver or in a separate operation. In industrial practice, a filtering operation is then usually performed, in order to remove any possible coarse particle still present in the plastisol. All of these operations are normally performed in batches

- *Coating*

Once the plastisol is homogeneous and degassed, it is ready to be coated. Two different coating methods exists, direct and transfer (or revers), which differ on the substrate onto which the plastisol is spread. Direct coating involves applying the plastisol directly to a continuous sheet of the substrate to be coated (i.e. textiles or non –woven fabrics, paper), while the transfer technique consists in the plastisol spreading onto a continuous sheet of a carrier substrate with an easy–release surface (i.e. silicone release papers), and the subsequent lamination of the substrate to be coated with the final removal of the material from the carrier (which may be used multiple times). Transfer coating is also called reverse due to the fact that the material is obtained in a reverse construction: the first spread layer, which acts as a base for the following, is the upper layer in the finite material. The spreading of the plastisol onto the substrate is typically made using a doctor blade knife, with different profiles as shown in Figure 1.7, and various configurations as shown in Figure 1.8.

Figure 1.7: schematic representation of some common doctor blade profiles. Substrate movement left to right. They are used for fabrics (A, D, E), heavy fabrics and paper (B, C) [12].

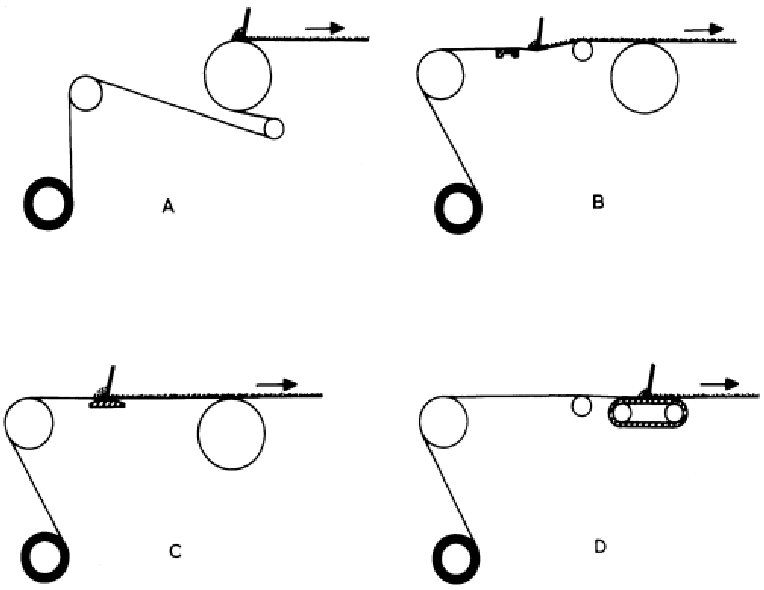


Figure 1.8: knife coating configurations. A: knife over roller; B: air knife; C: knife over plate; D: knife over blanket [7].

For laboratory scale purposes, transfer coating is carried out on silicone release paper, mounted on the mobile carriage of a Mathis “Labcoater” oven, and spread with the aid of a sliding doctor blade mounted on gauges that allow to adjust the thickness of the layers.

- *Gelation and fusion in oven*

The final step of the coating methods is the gelation and fusion of the plastisol in ovens, which ends with the obtainment of a solid, homogeneous, rubbery material. The mechanisms involved are quite complex and mostly dependent on the type of experiment carried out. A simple separation between gelation and fusion steps could be done [7]. According to this proposal, gelation is an adsorption process, due to a temperature increase or extreme ageing, after which a weak gel with poor mechanical properties is obtained. The subsequent fusion process, taking place at 150 °C or higher temperatures, sees a concurrent melting of PVC particles and plasticizer which become a homogeneous mass and, after cooling, pPVC materials are obtained. According to other works, a number of intermediate steps could be individuated. For example, one of the theories [31] identifies six steps:

1. Beginning of gelation process, with plasticizer molecules that penetrates irreversibly the porosity of PVC grains and adsorption takes place;

2. Induction period, during which plasticizer slowly solvates PVC resin;
3. Absorption of plasticizer and swelling of PVC particles, with total volume decrease;
4. Plasticizer forms clusters among polymer chains, solvating hydrogen bonding and polar groups available. This step requires high activation energies. PVC and plasticizers starts to lose their identity and the mixture becomes a melted homogeneous material;
5. Polymer and plasticizer clusters definitely disappear, if heating continues, and a homogeneous material is formed;
6. During cooling, the plasticized polymer hardens due to crystallization and creation of weak bonds between plasticizer and polymer (Van der Waals forces and hydrogen bonds).

The first two steps, and eventually the third one (depending on the plasticizer solvating power) may take place at ambient temperature after PVC–plasticizer mixing. The fourth and fifth steps need high energies and, thus, heating the sample. The sixth step may take from hours up to days.

For industrial production of SLs, different layers of plastisols need to be spread via transfer coating (Figure 1.9).

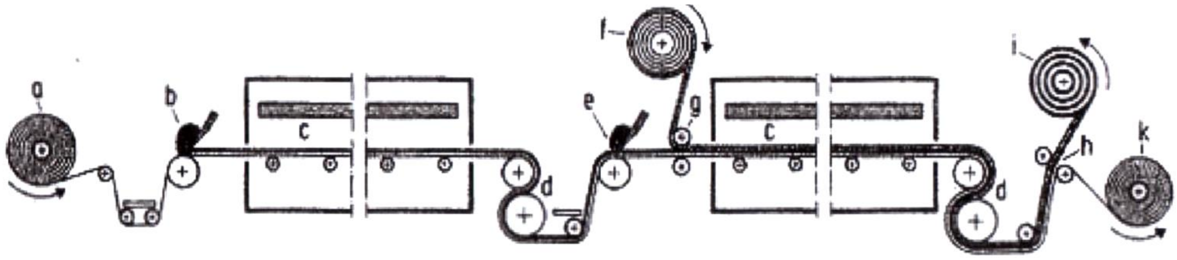


Figure 1.9: scheme of an industrial transfer coating line. a) support feeding; b) compact plastisol knife coating; c) ovens; d) cooling cylinders; e) adhesive knife coating; f) textile backing feeding; g) applicator roller; h) separating system; i) SLs winding roll; k) support winding roll.

After the application of each layer, the carrier with the plastisol spread on it passes through an oven. In a typical configuration, the first oven is used to obtain a partial gelation of the skin, onto which the plastisol containing blowing agents is spread before entering the second oven, where the simultaneous complete gelation of the skin, and the expansion of the foamed layer occur. At the exit of the second oven, the adhesive layer is spread onto the foamed one and the substrate to be coated is laminated before the passage in the last oven which completes the gelation of the adhesive. The speed and tension of the carrier, as well as the temperature of each one of the ovens, are key process parameters that control the properties of finished product.

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2

Aim of the project

2.1. Issues related to pPVC SLs

Plastic materials became commonly used starting from the 1940s, and their demand and production is since constantly increasing all over the world (Figure 2.1), causing more than a problem.

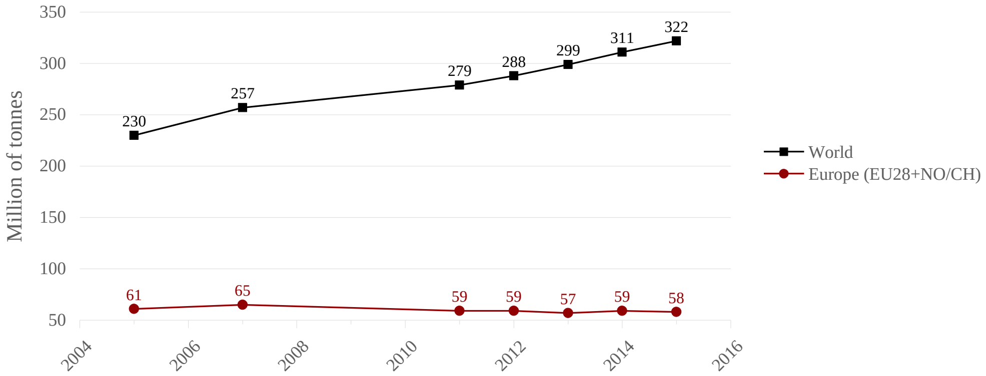


Figure 2.1: World and EU plastic production 2005-2015 [1].

This massive production of plastic goods, mainly commodity plastics, cause a great consumption of raw materials, largely derived from fossil fuels. This trend is expected to reach the 20 % of the total oil consumption used to produce plastics by 2050 [2]. The origin of the production of this enormous amount of plastic could be placed in the 1950s.

Figure 2.2: A man, woman and child toss "disposable" items into the air, 1955. © Peter Stackpole — The LIFE Picture Collection/Getty Images.

A document of this perspective and habit change that involved our society at the time is represented by a number of LIFE magazine published in august 1955. A two-page article titled "*Throwaway living – Disposable items cut down household chores*" promoted the benefits and freedom brought by the rise of disposable plastic goods (Figure 2.2). However, the disposal of plastic materials became of concern only starting from the 1970s (Figure 2.3), with the first recycling programs started in the late 1970s and 1980s.

Figure 2.3: International recycling symbol.
© Gary Anderson, 1970.

- *PVC*

Amongst the plastic materials, PVC is quite difficult to recycle and the majority of its wastes went, and still goes, into landfills. Since then, the attention of public opinion, associations, politicians, Governments and, obviously, scientific researchers from the entire world has been greatly focused on the "plastic problem", especially related to packaging materials, which have a very short life use. It has now become mandatory to move away from non-renewable feedstock for the production of polymers and additives for the plastic industry, and to push the research boundaries towards more efficient materials and designs, conceived and developed to guarantee the end-of-life recovery of most of the materials used, respecting the reduce–reuse–recycle approach.

In fact, plastic industry, like any other human activity, should follow the guidelines of sustainable development. This term was defined for the first time in the 1987 Bruntland Commission Report [3] to the United Nations (entitled "Our Common Future"). The definition at that time adopted is the following:

> *Development that meets the needs of the present generation without compromising the ability of future generations to meet their needs.*

Since then, many other definitions have been proposed, which best overcome some limitations of the Bruntland definition, like the following emerged in 1998 from a UK non-profit organization known as "Forum For The Future" [4], founded by British environmentalist and writer Jonathon Porritt:

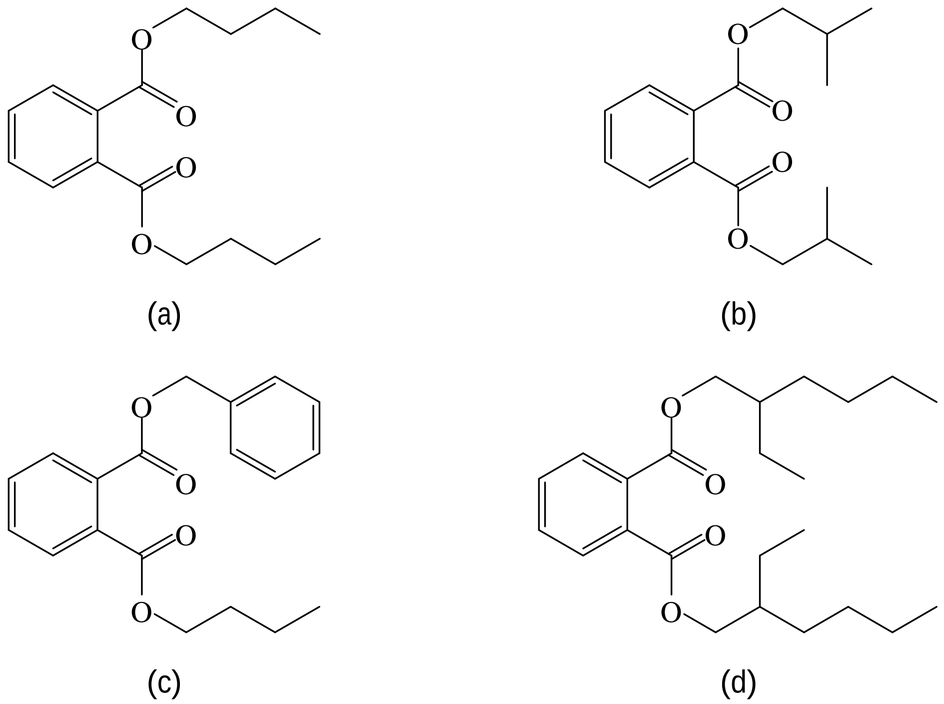
> *Sustainable development is a dynamic process which enables all people to realise their potential and to improve their quality of life in ways which simultaneously protect and enhance the Earth's life support systems.*

With the years, we assisted to a widespread adoption of sustainable development practises and behaviours, sign of a recognition of the importance of this approach. However, it is nevertheless a fact that an increasing number of indicators and aspects have been included in the list of factors which contributes to the definition of sustainable development. This possibly means that its concept has reached a level of complexity that makes this term confusing, if not almost useless, as a guidance tool for policy makers [5]. We reached a point at which studies have argued that the sustainability development concept is in danger of becoming irrelevant [6, 7].

The use of PVC has been put under the lens many times through the years, from an environmental and health point of view, leaving unresolved and debated points. These constant campaigns, led by organizations like Greenpeace [8], put in evidence some issues related to the production, use and disposal of PVC. The synthesis of its monomer (VCM) and its manipulation poses great risks for the workers and the population who resides nearby VCM production and polymerization plants. In fact, VCM is known for its hepatoxicity since the 1930s, and it has been correlated with angiosarcoma of the liver for the first time at the beginning of the 1970s [9-11]. Aside from hazards concerning its monomer, another critical point often cited talking about PVC is its chlorine content, one of the key features of this polymer. Organic chlorine is considered the main responsible of dioxin generation during combustion, as in municipal wastes incinerators or in building fires involving PVC construction materials (i.e. piping, floors, window frames), but also during VCM synthesis. Chlorine chemistry has proved to be potentially dangerous in many occasions, for example for the damage of ozone layer caused by chlorofluorocarbons (CFCs), or the persistence in the environment and the bioaccumulation of poly–chlorinated biphenyls and dioxins.

- *Phthalates (Plasticizers)*

As said, the presence of chlorine and the consequent polarity of PVC molecules is the main reason of its ability to be compounded with a great number of additives. This is particularly true for pPVC, where plasticizers represent the most significant class of additives, in terms of both importance and weight. Amongst the plasticizers, the most widely used for decades have been phthalates, which are obtained by reaction between phthalic anhydride and alcohols ranging from methanol to tridecanol [12]. Phthalates are classified into two groups, based on the length of the alcohols used: low molecular weight (LMW) are those with 3–6 carbon atoms composing the alcohol backbone, while high molecular weight (HMW) are those with 7–13 carbon atoms. The firsts are without a doubt the most critical representatives of phthalate family. Amongst these, Dibutyl Phthalate (DBP), Diisobutyl Phthalate (DIBP), Benzyl Butyl Phthalate (BBP) and, primarily, Di(2–Ethylhexyl) Phthalate (DEHP) are the plasticizers which were mostly used in the manufacturing of SLs (Figure 2.4).



(a) (b)

(c) (d)

Figure 2.4: chemical structures of (a) DBP, (b) DIBP, (c) BBP and (d) DEHP.

Other phthalates like Dimethyl Phthalate (DMP) and Diethyl Phthalate (DEP) were employed in adhesives, inks and coatings and are not considered in the LMW group due to different application areas. Nowadays, these (in)famous compounds have become ubiquitous environmental contaminants [13]. Through the years, many different studies have been performed in order to associate exposure to phthalates, in particular the LMW molecules, with health risks and diseases. For example, several epidemiologic and *in vivo* studies investigated the possible action of inhaled or ingested phthalates [14] as allergens and adjuvants in asthma and other IgE–mediated allergies [15-17]. However, their most negative impactful property on human health is due to their ability of mimic naturally occurring hormones like estrogens and androgens, interfering with the endocrine system and inducing developmental and reproductive toxicity [18-21]. For these reasons, LMW phthalate have been classified as Endocrine Disruptors Chemicals (EDCs) [22].

For all the aforementioned reasons, the use of LMW phthalates have been strongly limited in Europe by their listing in Annex XIV (“Authorisation List”) of REACH regulation and the subsequent ban for their use without authorization from the European Chemicals Agency (ECHA) since February 21st, 2015 [23]. However, the worldwide production and use of LMW phthalates, particularly DEHP, is far from being ceased, as demonstrated by data reported in Figure 2.5. In fact, DEHP alone represents more than one third of the global plasticizer market, since it is still produced and used in China, India and other areas in Middle East, Latin America and Africa [22].

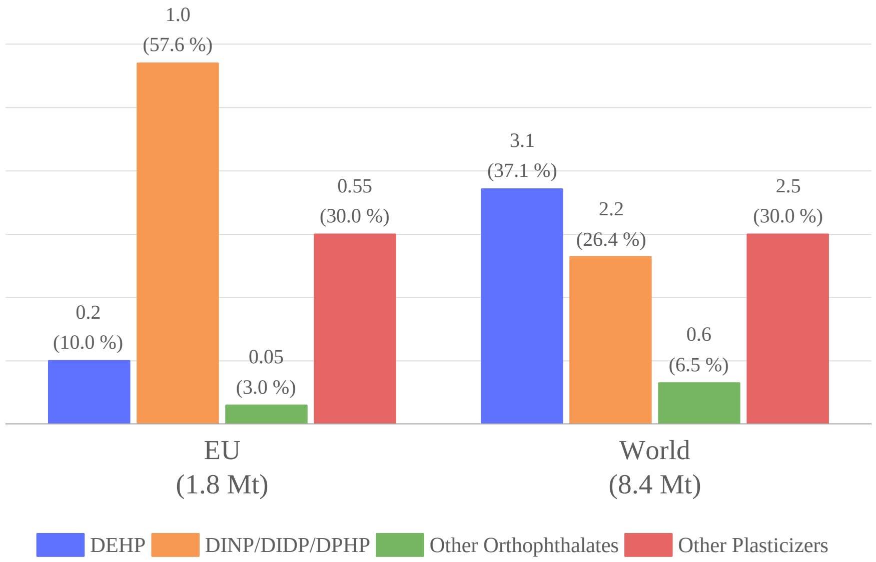


Figure 2.5: EU and World plasticizer market. Source: 2015 IHS and ECPI estimates.

The HMW phthalates have also been subjected to study, with the result that Diisononyl Phthalate (DINP) and Diisodecyl Phthalate (DIDP) were not considered EDCs [24], but their use has been limited in toys and childcare products as precautionary measure [25].

- *Antimony trioxide (Flame retardant)*

Not only plasticizers created concern about the use of pPVC. As said, PVC contains a great amount of chlorine (approx. 57 wt%) making it difficult to ignite and practically not–flammable. In fact, hydrogen chloride released during PVC decomposition interferes with the radical reactions that takes place during combustion, acting as free–radical scavenger and inhibiting propagation reactions. However, adding up to 40 wt% of plasticizers in pPVC results in a flammable material, which needs the addition of substances capable to reduce its flammability, called flame retardants (FRs). Flame resistance is a very important feature demanded to any automotive component. This is especially the case for SLs and other plastic parts, because fire retardancy is the only safety characteristic that these components could have. Amongst the compounds available, the most efficient in pPVC formulations is antimony trioxide (ATO, Sb_2O_3), an inorganic oxide which is incredibly active in presence of halogens, at very low loadings. The drawback is that antimony, both pure and in the oxidation state of the trioxide (Sb(III)) is classified as a suspected human carcinogen (Group 2B, H351) [26] with negative effects on human health when inhaled. Hence, the health risks are particularly significant for workers who extract, transport and transform antimony products, thus, an occupational hazard. In fact, several evidences of pneumoconiosis and other respiratory effects from chronic exposure to ATO, even though toxicological data comes from the time when primitive work conditions prevailed. Moreover, antimony is often mined with arsenic and lead, which possess similar geochemistry, and it is not easy to discriminate among them [27]. Finally, it is considered a persistent inorganic pollutant (PIP), with tendency to bio–accumulate and enter the food chain [28]. For these reasons, antimony trioxide is considered a Substance of Very High Concern (SVHC) and is listed in Annex XV of REACH regulation. Moreover, ATO is found in the Community Rolling Action Plan (CoRAP), so that evaluation by a Member State (i.e. Germany) will be conducted in 2018 [29]. Lastly, recent studies indicate that antimony is one of the scarcest mineral resources and suggest that global extractable resources could be exhausted before 2050 if the extraction continues to increase with the current paces [30-32].

- *Azodicarbonamide (Blowing agent)*

The last of the additives for pPVC that pose issues for human health is azodicarbonamide (AZO, $C_2H_4O_2N_4$) (Figure 2.6), a common chemical blowing agent (BA), which is also used as food additive (e.g. flour bleaching agent, dough conditioner), mainly in USA (E927 code), where it has Generally Recognized as Safe (GRAS) status. On the contrary, Europe and Australia did not authorize the use of AZO as a food additive.

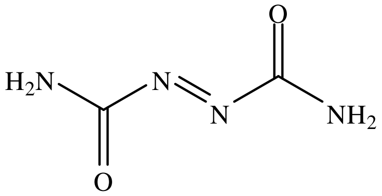


Figure 2.6: chemical structure of azodicarbonamide (AZO).

This molecule thermally decomposes releasing gases like CO, CO_2, N_2 and NH_3 at pPVC process temperatures, creating gas bubbles inside the material and thus allowing the production of foamed layers and materials. The decomposition also leaves solid residues, as urea, urazole, biuret, cyanuric acid and ammonium salts [33]. There are scientific evidences that AZO is a respiratory sensitizer, induces occupational asthma, and that prolonged exposure may result in persistent symptoms lasting for years [34, 35]. Moreover, partial decomposition of AZO could originate semicarbazide (SEM, CH_7ON_3) which has also been object of studies, though not comprehensive nor definitive, concerning its possible toxicity [36, 37]. For these reasons, AZO has been listed in Annex XV of REACH regulation as a Substance of Very High Concern (SVHC) [38].

2.2. Aim of the research

It must be pointed out that the issues previously described were overcome, to a certain extent, due to legislative limitations, partial phasing–out from some industries and huge improvements made in the whole cycle of PVC, from designing and manufacturing to disposal. A demonstration of this is also a slight fading of Greenpeace campaigns against chlorine chemistry and PVC*, also thanks to the efforts put by the organization in the past (mainly in the 1990s) to turn the spotlights on these issues. Nevertheless, the substitution of PVC in many applications is still difficult or inconvenient, as in the case of synthetic leathers. It is therefore mandatory, for the industrial researcher, to act in such a way to improve the sustainability of these PVC products, following different paths, from the monomer synthesis to the finite product disposal.

The path chosen for the present research work regards the formulation industry and, hence, the choice of more sustainable and less toxic additives rather than those used until these days. Thus, the aim of the work is the research, characterization and testing of alternative and innovative additives for the formulation of pPVC synthetic leathers. In particular, the research focused on the study of substitute alternatives for the three main additives used in pPVC previously presented, plus a novel class of nano–additives (i.e. nanoclays) never used nowadays, at our knowledge, in the manufacturing of SLs. Each of these additives will be discussed in a dedicated chapter, but here briefly described.

2.2.1. Plasticizers

More than 40 different commercial plasticizers, belonging to eight different chemical families, were characterized and a selected number of that were subjected to testing in two different formulations, according to the most common standards used by manufacturers of pPVC SLs for the automotive industry. The tests included tensile properties, hardness and cold resistance, thermal and flame properties, volatility and migration evaluation. Fossil fuel as well as renewable based plasticizers were studied and their properties compared to those of commonly used phthalates which were considered as benchmark.

Table 2.1 reports the studied plasticizers, with some basic information.

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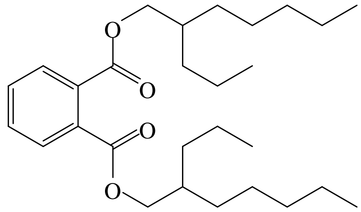
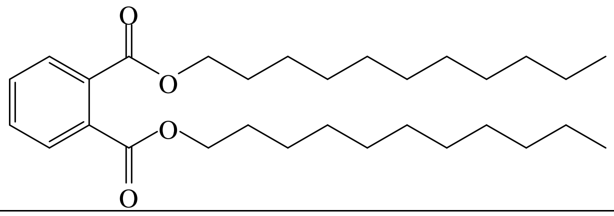
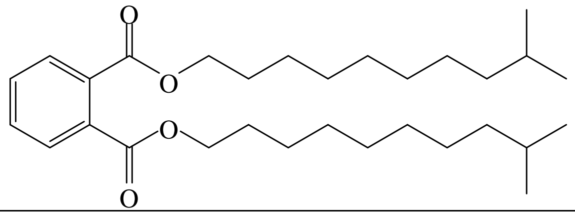
* The last detox report by Greenpeace which focused on PVC regards its use in electronic devices 2014 [39], while the class of compounds being contrasted the most nowadays is the PFCs (Perfluorinated compounds), used for example in weatherproofing fabrics like Gore–Tex® [40], with recent successes obtained by Greenpeace [41].

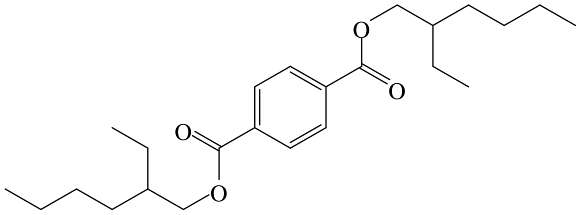
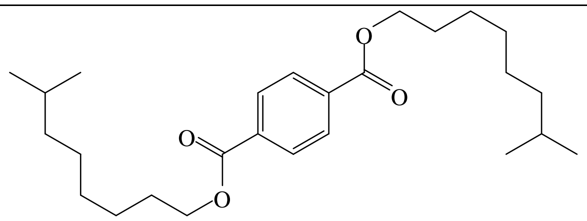
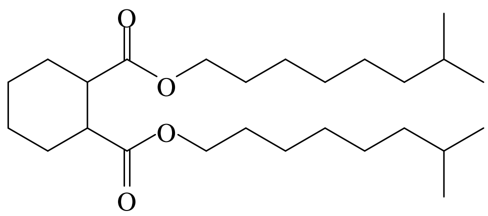
Table 2.1: list of plasticizers subjected to testing.

PHTHALATES

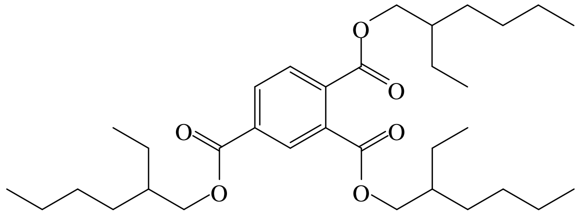
#	Name & Information	Structure
1	Di(2–Propylheptyl) Phthalate **DPHP** $C_{28}H_{46}O_4$ (MW: 446,66 Da) CAS N°: 53306–54–0	
2	Diundecyl Phthalate **DUP** $C_{30}H_{50}O_4$ (MW: 474,72 Da) CAS N°: 3648–20–2	
3	Diisoundecyl Phthalate **DIUP** $C_{30}H_{50}O_4$ (MW: 474,72 Da) CAS N°: 85507–79–5	

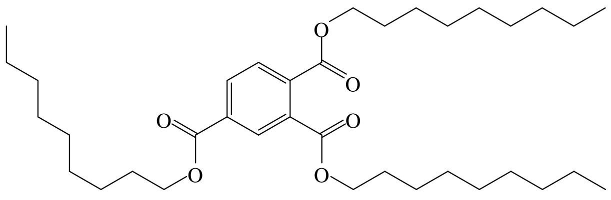
NON–PHTHALATES

PHTHALATES–LIKE

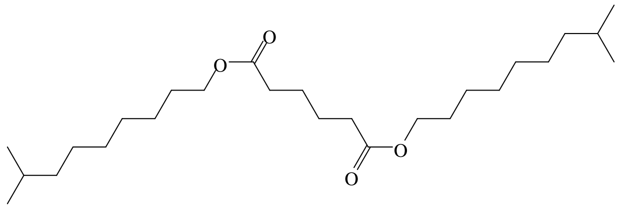
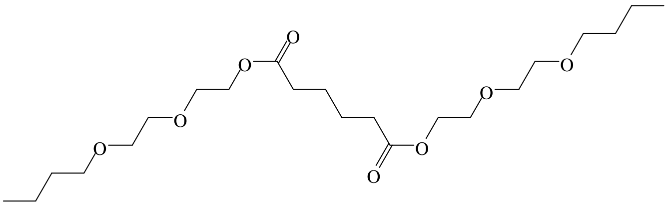
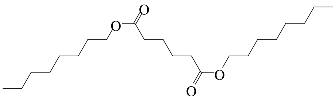
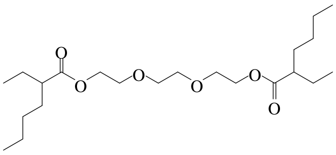
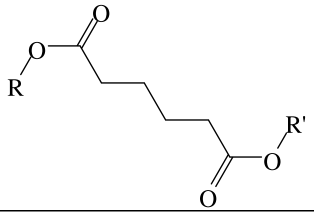
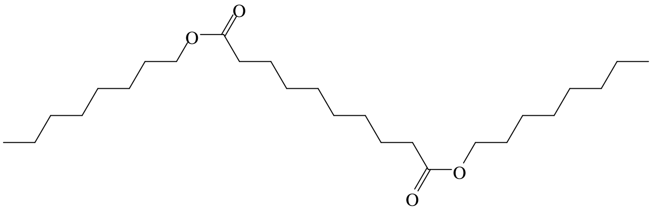
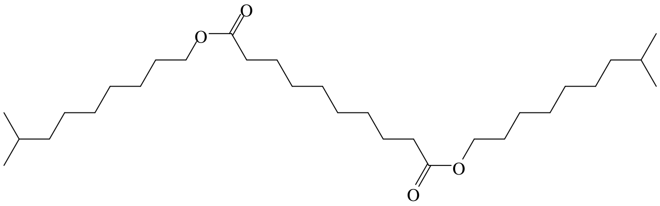
#	Name & Information	Structure
4	Dioctyl Terephthalate **DOTP** $C_{24}H_{38}O_4$ (MW: 390,56 Da) CAS N°: 6422–86–2	
5	Diisononyl Terephthalate **DINTP** $C_{26}H_{42}O_4$ (MW: 418,61 Da) CAS N°: 119–05–1	
6	Diisononyl Cyclohexane–1,2–Dicarboxylate **DINCH** $C_{26}H_{48}O_4$ (MW: 424,66 Da) CAS N°: 166412–78–8	

TRIMELLITATES

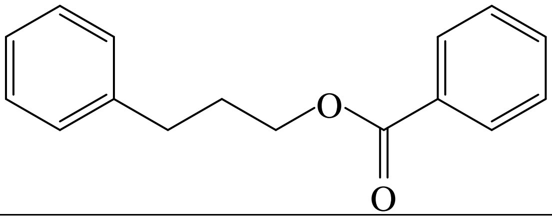
#	Name & Information	Structure
7	Trioctyl Trimellitate **TOTM** $C_{33}H_{54}O_6$ (MW: 546,79 Da) CAS N°: 3319–31–1	

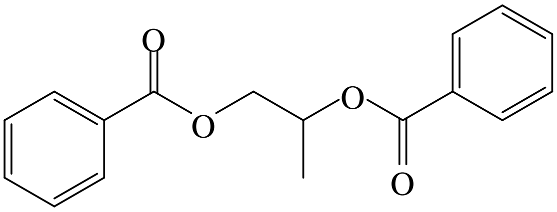
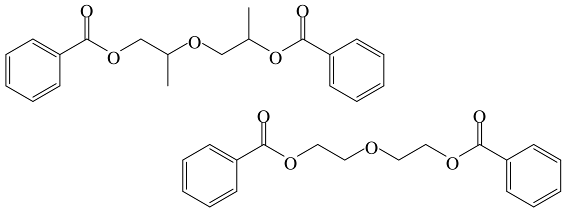
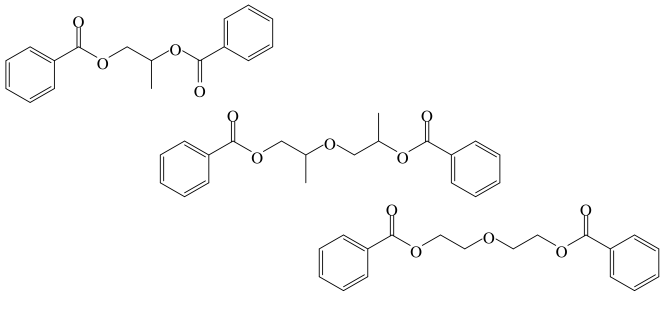
8	Trinonyl Trimellitate **TNTM** $C_{33}H_{54}O_6$ (MW: 588,87 Da) CAS N°: 3319–31–1	

DICARBOXYLIC ACIDS DIESTERS

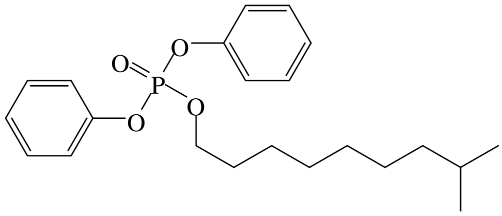
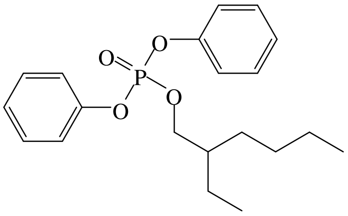
9	Diisodecyl Adipate **DIDA** $C_{26}H_{50}O_4$ (MW: 426,67 Da) CAS N°: 27178–16–1	
10	Di(2–(2–Butoxyethoxy)Ethyl) Adipate **DBEEA** $C_{22}H_{42}O_8$ (MW: 434,56 Da) CAS N°: 141–17–3	
11	Dioctyl Adipate + Triethylene Glycol Di(2–Ethylhexanoate) **DOA–TEGDEH** $C_{22}H_{42}O_6$ (MW: 402,57 Da) $C_{22}H_{42}O_4$ (MW: 370,57 Da) CAS N°: 123–79–5 CAS N°: 94–28–0	 
12	Modified ester of Adipic Acid **ModA** Unknown CAS N°: proprietary	
13	Dioctyl Sebacate **DOS** $C_{26}H_{50}O_4$ (MW: 426,67 Da) CAS N°: 122–62–3	
14	Diisodecyl Sebacate **DIDS** $C_{30}H_{58}O_4$ (MW: 482,78 Da) CAS N°: 28473–19–0	

BENZOATES

15	Phenyl Propyl Benzoate **PPB** $C_{16}H_{16}O_2$ (MW: 240,30 Da) CAS N°: 60045–26–3	

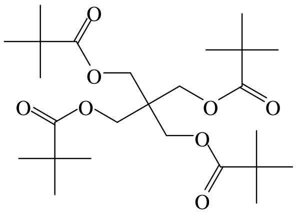
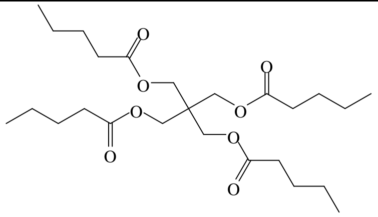
16	Propylene Glycol Dibenzoate **PGDB** $C_{17}H_{16}O_4$ (MW: 284,31 Da) CAS N°: 19224–26–1	
17	Dipropylene/Diethylene Glycol Dibenzoate **DP/DE–GDB** $C_{20}H_{22}O_5$ (MW: 342,39 Da) $C_{18}H_{18}O_5$ (MW: 314,33 Da) CAS N°: 27138–31–4 (DPGDB) CAS N°: 120–55–8 (DEGDB)	
18	Propylene/Dipropylene/Diethylene Glycol Dibenzoate **P/DP/DE–GDB** $C_{17}H_{16}O_4$ (MW: 284,31 Da) $C_{20}H_{22}O_5$ (MW: 342,39 Da) $C_{18}H_{18}O_5$ (MW: 314,33 Da) CAS N°: 19224–26–1 (PGDB) CAS N°: 27138–31–4 (DPGDB) CAS N°: 120–55–8 (DEGDB)	

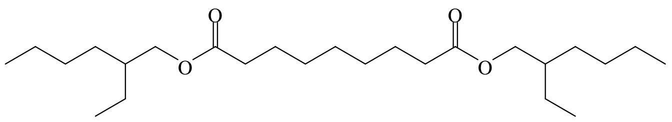
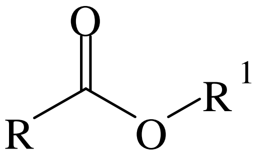
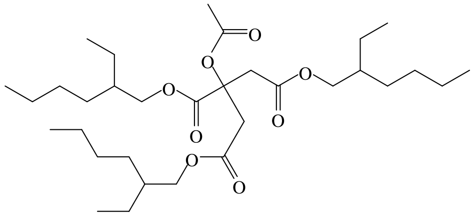
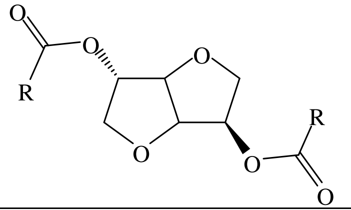
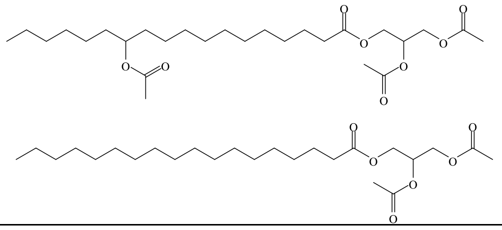
PHOSPHATES

19	Isodecyl Diphenyl Phosphate **IDDPP** $C_{22}H_{31}O_4P$ (MW: 390,46 Da) CAS N°: 29761–21–5	
20	2–Ethylhexyl Diphenyl Phosphate **EHDPP** $C_{20}H_{27}O_4P$ (MW: 362,41 Da) CAS N°: 1241–94–7	

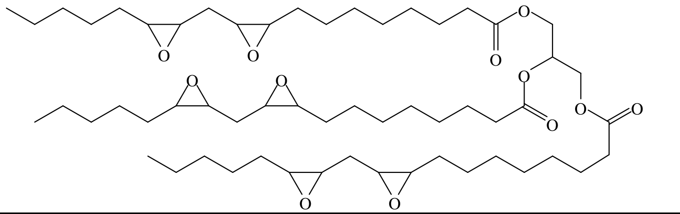
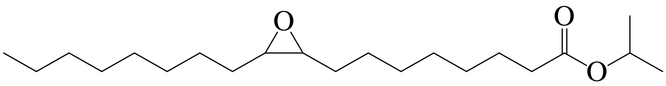
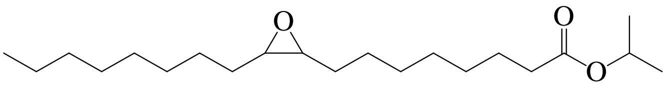
RENEWABLE BASED PLASTICIZERS

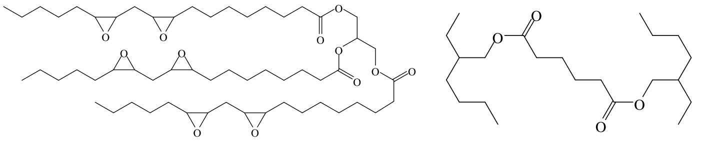
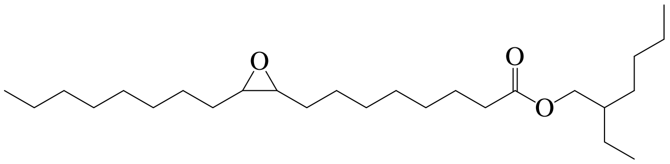
BIOBASED ALIPHATIC ESTERS

21	Pivalic acid, neopentanetetrayl ester **PIV** $C_{25}H_{44}O_8$ (MW: 472,62 Da) CAS N°: 5178–17–6	
22	Pentaerythritol Tetravalerate **PETV** $C_{25}H_{44}O_8$ (MW: 472,62 Da) CAS N°: 15834–04–5	

23	Dioctyl Azelate **DOZ** $C_{25}H_{48}O_4$ (MW: 412,66 Da) CAS N°: 103–24–2	
24	Renewable feedstock ester, 100% biodegradable **RFE** Unknown CAS N°: proprietary	
25	Acetyl Tri–2–ethylhexyl Citrate **ATEHC** $C_{32}H_{58}O_8$ (MW: 570,81 Da) CAS N°: 144–15–0	
26	Isosorbide Ester **ISE** $C_{32}H_{58}O_8$ (MW: 412,66 Da) CAS N°: 144–15–0	
27	Acetylated Glycerol Monostearates **AGM** $C_{27}H_{48}O_8$ (MW: 500,66 Da) CAS N°: 736150–63–3	

EPOXIDIZED VEGETABLE OILS

28	Epoxidized Soybean Oil **ESBO** $C_{57}H_{98}O_{12}$ (MW: 975,38 Da) CAS N°: 8013–07–8	
29	Epoxidized vegetable oils mix **ModESBO** $C_{21}H_{40}O_3$ (MW: 340,55 Da) CAS N°: n/a	
30	Epoxidized vegetable oils mix **ModESBO_1** $C_{21}H_{40}O_3$ (MW: 340,55 Da) CAS N°: n/a	

31	Epoxidized Soybean Oil + Di(2–Ethylhexyl) Adipate **ModESBO_2** $C_{57}H_{98}O_{12}$ (MW: 975,38 Da) $C_{22}H_{42}O_4$ (MW: 370,57 Da) CAS N°: 8013–07–8 CAS N°: 123–23–1	
32	2–Ethylhexyl Epoxy Soyate **ModESBO_3** $C_{26}H_{50}O_3$ (MW: 410,68 Da) CAS N°: 68082–834–8	

Entries #21 and #22 (PIV and PETV) are two different versions, respectively older and newer, of the same additive, based on slightly different molecules. For this reason, they will be compared as they were the same plasticizer.

2.2.2. Flame Retardants

For the purposes of the present work, 8 different flame retardants (FRs, Table 2.2), used in different quantities and combination were tested, obtaining almost 40 different FR systems that were evaluated compared to ATO, used as standard benchmark. These additives represent readily available alternatives from the market, that are normally used for other polymers and/or applications, but that are not usually used for SLs, particularly in the automotive interior industry. The reasons of the difficulties to overcome ATO in this area are related to the high standards requested for both performances and safety of the finished materials.

Table 2.2: list of flame retardants subjected to testing.

#	Acronym	Type	Formula
1	ATO	Antimony Trioxide	Sb_2O_3
2	ATH	Aluminium Trihydroxide	$Al(OH)_3$
3	HT	Hydrotalcite	$Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O$
4	CARB	Natural carboxylic acid salts	R–COO–R’
5	Ph1	Phosphate–based	–
6	Ph2	Phosphate–based	–
7	CHP	Calcium Hypophosphyte	$Ca(H_2PO_2)_2$
8	ZB	Zinc Borate	$2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$
9	ZHS	Zinc Hydroxystannate	$ZnSn(OH)_6$

In particular, we retained of interest to study:

- inorganic hydroxides and hydroxycarbonates FRs (ATH, HT and CARB) which are, basically non–toxic and environmentally friendly (particularly the latter);
- phosphorous–containing FRs (Ph1, Ph2 and CHP);
- zinc borate (ZB), which is a mixed tin–boron oxide, typically used as synergist;
- zinc hydroxystannate (ZHS), a zinc/tin hydroxide used both as primary FR and as synergist.

All of the additives subjected to testing are halogen–free, being the source of chlorine the polymer itself.

2.2.3. Blowing Agents

In order to find viable alternatives to the use of AZO in the manufacturing of foamed layers in pPVC materials, 4 different alternative BAs (Table 2.3) were considered and subjected to testing, including physical (P) and exothermic and endothermic chemical (C(Exo) and C(Endo) respectively) compounds.

Table 2.3: list of blowing agents subjected to testing. C = Chemical; P = Physical.

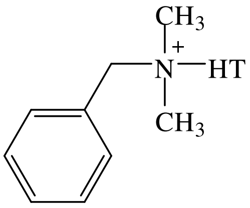
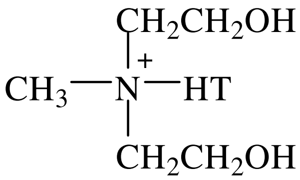
#	Acronym	Name	Type	Formula
1	AZO	Azodicarbonamide	C (Exo)	$C_2H_4O_2N_4$
2	AZO(k)	Azodicarbonamide + *kicker*	C (Exo)	$C_2H_4O_2N_4$ + Zn
3	OBSH	4,4'-Oxydibenzenesulfonyl Hydrazide	C (Exo)	$C_{12}H_{14}O_5N_4S_2$
4	OBSH(k)	4,4'-Oxydibenzenesulfonyl Hydrazide + *kicker*	C (Exo)	$C_{12}H_{14}O_5N_4S_2$ + Zn
5	BIC/CIT	Bicarbonate/Citric acid mix	C (Endo)	$NaHCO_3 + C_6H_8O_7$
6	EMS	Expandable Microspheres	P	–

Amongst the C(Exo) BAs, 4,4'-Oxydibenzenesulfonyl Hydrazide (OBSH), a quite common chemical foaming agent, and AZO were tested also in presence of a kicker; AZO and AZO combined with a kicker (AZO(k)) were used as references. The C(Endo) BA tested is a mix mainly constituted of sodium bicarbonate and citric acid. Finally, expandable microspheres (EMS), a physical BA, have been selected for testing and comparison.

2.2.4. Organic modified nanoclays

Lastly, 3 different commercial phyllosilicates, belonging to the novel class of nanoclays (NC) and including two being organically modified (OMNC), were subjected to testing and evaluated as reinforcing agents, flame retardants and anti–migration additives. The purpose of this work is the evaluation of their potential in the manufacturing of pPVC SLs, being quite an unexplored field of application for these compounds. In order to have a benchmark for the properties measured, obtained results were compared to those of a neutral foil plasticized with 75 phr of DUP and with 2 phr of antimony trioxide (ATO). Table 2.4 reports the nanoclays selected for testing.

Table 2.4: list of nanoclays subjected to testing.

#	Name & Information	Interlayer cation
1	Montmorillonite with benzyl(hydrogenated tallow alkyl)dimethyl quaternary ammonium salt **10A** $(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$ CAS N°: 71011–24–0 Particle size < 10 µm	
2	Montmorillonite with methyl dihydroxyethyl hydrogenated tallow quaternary ammonium salt **I34** $(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$ CAS N°: 341537–63–1 Particle size < 20 µm	 $\begin{array}{c} CH_2CH_2OH \\ \vert \\ CH_3-\overset{+}{N}-HT \\ \vert \\ CH_2CH_2OH \end{array}$
3	Halloysite nanoclays, unmodified **HYS** $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$ CAS N°: 1332–58–7 Nanotubes, 30–70 nm (d) x 1–3 µm (L)	Na^+

Two of the tested nanoclays, 10A and I34, are organic modified montmorillonites, belonging to the family of smectites. The two quaternary ammonium salts used to exchange sodium cations exhibits different polarity, and both contains a long alkyl saturated chain (referred to as “hydrogen tallow”, HT in the formula in Table II.4). The third nanoclay (HYS) is an unmodified halloysite, part of the kaolinites, chosen for its peculiar nanotubular form factor.

This research project, financed by Regione Emilia–Romagna with DGR n° 1146 dated 02/08/2013 within the framework "*Ricerca, Innovazione e Crescita*" approved with DGR 266/2012, was carried out in strict collaboration with Vulcaflex S.p.A., an Italian private company based in Milan but with its two production facilities located in Cotignola, near Ravenna. Vulcaflex is amongst the major companies in the World that manufacture synthetic leathers, mainly for the automotive industry. Most of the tests described in the following chapters were performed in Vulcaflex R&D laboratory, by means of the equipment and procedures commonly used by the laboratory staff during their work.

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3

Instruments, characterization and methods

3.1. Sample preparation

All the components of the plastisol were weighted and manually mixed until all the resin was completely dispersed in the plasticizer, and a paste, even if not perfectly homogeneous, was obtained. Afterwards, the paste was homogenized through a laboratory–scale three–roll mill (Figure 3.1), with the aim to disrupt eventual PVC aggregates.

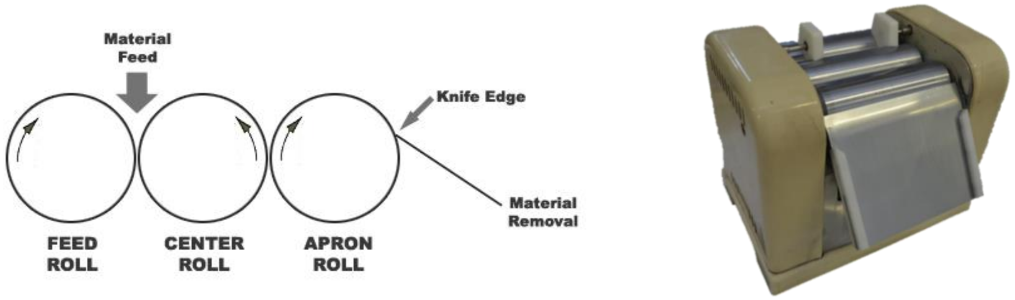

Figure 3.1: three-roll mill apparatus scheme and actual equipment.

The obtained plastisols were finally put in a laboratory–scale high speed dissolver (Figure 3.2), under vacuum, for 10 minutes at 800 rpm. The simultaneous usage of high–speed mixing and vacuum, ensures both a very fine and stable dispersion of the plastisol and the efficient removal of air bubbles (incorporated during previous mixing stages) and humidity traces. This step is usually referred to as degassing.

Figure 3.2: dispersion blade geometry and laboratory–scale vacuum dissolver.

Once the plastisol was degassed, it was ready to be gelled and fused in a Mathis oven (Figure 3.3), for 60 s at 200 °C. The plastisols were spread to obtain foils with similar grammage (i.e. mass per unit of area, expressed in grams per square meter), so the gauges of the mobile blade were individually set for each sample to obtain a final grammage of 800 g/m^2.

Figure 3.3: Mathis "Labcoater" Oven used for plastisols gelation.

3.2. Tests performed

The previously mentioned new requirements involved also some of the tests performed on pPVC samples, which has been subjected to modification between the first and second batches of tests (i.e. migration tests). Once the samples were prepared, they were stored in dark at standard laboratory atmosphere in accordance to ASTM D618 – Procedure A (i.e. 40 h at 23 °C and 50 % RH) [1] prior to testing, in order to condition the samples and allow their comparison. The tests performed on each sample are hereafter reported and briefly described.

3.2.1. Plasticizers characterization

FT–IR spectra were recorded in ATR mode, using a Perkin Elmer Frontier equipped with a diamond/KRS–5 crystal (*n* = 2,4) UATR module. Spectra were acquired in the wavenumber range 4000–650 cm^{-1}, with a resolution of 4 cm^{-1} and 4 acquisitions per sample.

Mass spectra were obtained after gas–chromatography analysis, performed with a Thermo Scientific FOCUS GC coupled with a Thermo DSQ single–quadrupole mass spectrometer and equipped with a 5MS ((5% Phenyl)–methylpolysiloxane, 30 m, 0,25 mm ID, 0,25 µm film) capillary column. For each plasticizer, a dichloromethane (DCM, Sigma Aldrich, ≥ 99 %) solution with a concentration of approx. 750 ppm was prepared and injected. The used temperature program and the other instrumental parameters are summarized in Table 3.1.

Table 3.1: instrument setup (GC) and temperature program.

Instrument setup	
T_{injector} (°C)	280
$T_{\text{transfer line}}$ (°C)	300
$T_{\text{MS source}}$ (°C)	250
Gas Carrier	Helium (He)
Split Flow (mL/min)	1.0
Split Ratio	10:1

Temperature program	
0	Solvent delay: 1 min
1	Isotherm: 80 °C, 2 min
2	Heat ramp: 10 °C/min up to 300 °C
3	Isotherm: 300 °C, 10 min
	Total time: 34 min

3.2.2. Mechanical tests

Hardness was measured by means of a Shore durometer using both Shore A and Shore D scales, with the first being the choice for softer materials, according to ISO 868 [2, 3]. Two cylindrical specimens for each sample, with minimum thickness of 4 mm, were obtained by hot pressing several layers of PVC foils. Each value was read after 15 seconds of application of the force on the material.

Ultimate tensile strength (UTS), elongation at break (EB) and tearing strength (TS) were measured by means of a MTS Synergie 400 one–column tabletop universal testing machine, equipped with a 2 kN load cell. The first two properties were measured simultaneously according to ASTM D751–06, procedure B (cut strip method) [4], properly modified following directives from OEMs and automotive industries specifications. For each sample, at least three specimens measuring 25 x 200 mm were cut out. The gauge length was of 50 mm with a test speed of 100 mm/min. A typical graph obtained by UTS test is reported in Figure 3.4. Both tensile strength and elongation were determined at rupture of the sample, and UTS was normalized taking into account the section area of the specimen subjected to testing. TS was measured according to ASTM D751–06, trapezoidal tear [4].

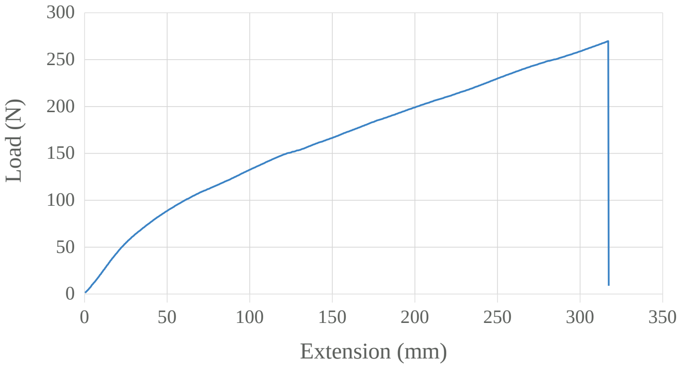

Figure 3.4: typical experimental results acquired during mechanical testing.

Bally flex tests were performed for the determination of flex resistance both in cold temperatures (cold resistance) and at room temperature (flex resistance). The first was used for the evaluation of plasticizers and the finished materials for blowing agents industrial testing, while the latter for the blowing agents only. PVC foils was evaluated by means of a Bally flexometer, in according to ISO 5402–1 [5]. The flexing machine (Figure 3.5) is configured to perform 10,000 flex cycles at a temperature of -20°C (Paragraph 4.2.2), 30,000 cycles at -10 °C (Paragraph 6.2.4) or 100,000 at room temperature (Paragraph 6.2.3). Three specimens for each sample were cut out and conditioned at -20 °C for 2h prior to test beginning.

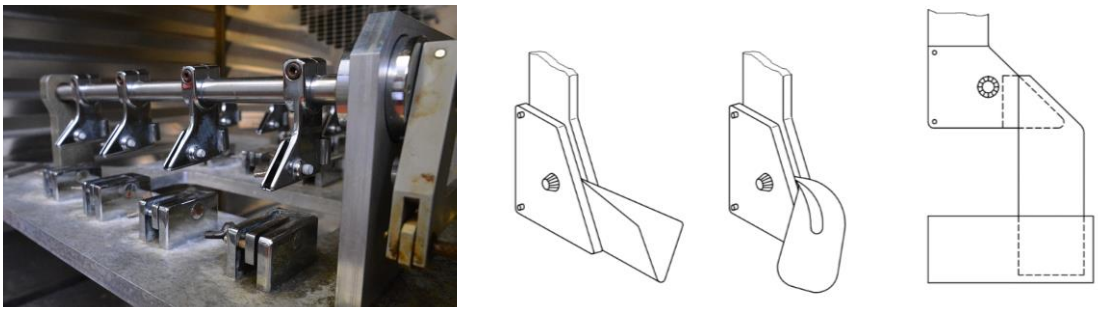

Figure 3.5: Bally flexometer (left) and configuration of the specimen mount (right).

The performance of each plasticizer was visually evaluated for cracks or fractures using a qualitative scale reported in Figure 3.6, where 0 indicates no cracks and 4 stands for complete fracture.

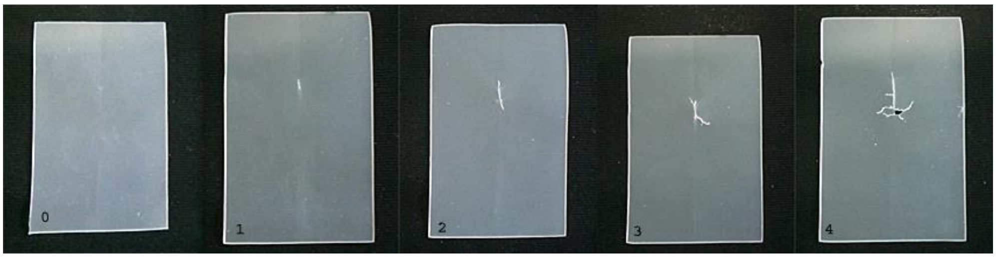

Figure 3.6: examples of the aspect of samples after Bally flex test, with evaluation from 0 to 4.

3.2.3. Thermal and flame resistance tests

Thermal stability of each sample (250 x 20 mm) at the process temperatures, i.e. 200 °C, was evaluated in a Mathis oven equipped with an accessory mobile carriage, which moves outward by 15 mm every 2 minutes until it is completely extracted from the oven. In this way, each portion of the sample is exposed to the desired temperatures, for increasing time, allowing the evaluation of the progressive degradation of the material (Figure 3.7).

Figure 3.7: samples after the thermal stability test.

The evaluation of the extent of degradation and, therefore, of the thermal stability, is performed by assessing the colour change of the material, in particular measuring the Yellowing Index (YI) and its variation (ΔYI) by means of a Datacolor 650 spectrophotometer following standard method ASTM E313 [6].

Thermal aging was evaluated by placing two specimens for each sample in a forced convection oven set at 90 °C, as per UNI 12280–1. The Yellowing Index (YI) and its variation (ΔYI) were determined after several intervals of time (namely 1, 3, 5 and 7 days) by means of a Datacolor 650 spectrophotometer, as per ASTM E313 [6].

Flame resistance of the studied formulations was evaluated by a horizontal combustibility test, mainly performed according to ISO 3795 [7]. This test is the most common one employed in the automotive industry and uses a 356 x 100 mm rectangular sample, which is clamped to a U–shaped sample holder with three marks positioned as per Figure 3.8.

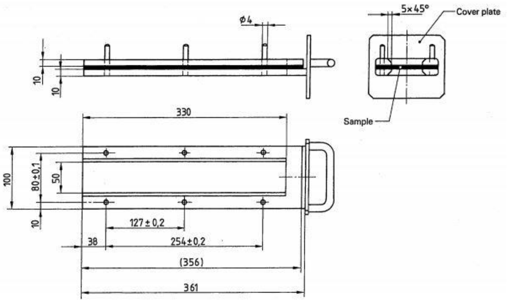

Figure 3.8: example of U–shaped sample holder according to ISO 3795 [7].

The combustion chamber (Figure 3.9), placed under an extractor hood, is equipped with a Bunsen burner at one end, while the sample holder is inserted from the opposite side. The test starts when the loose end of sample comes into contact with the flame of Bunsen burner; after 15 seconds, the flame is extinguished (closing the fuel valve) and a stopwatch is started when the flame front (indistinctly on the upper or lower side of the sample) reaches the first mark; then, the time to flameout or total burning of the sample (i.e. when the flame front reaches the third mark) is measured. Results are expressed as *burning rate*, in millimetre per minute (mm/min). The test was executed on 3 specimens for each plasticizer.

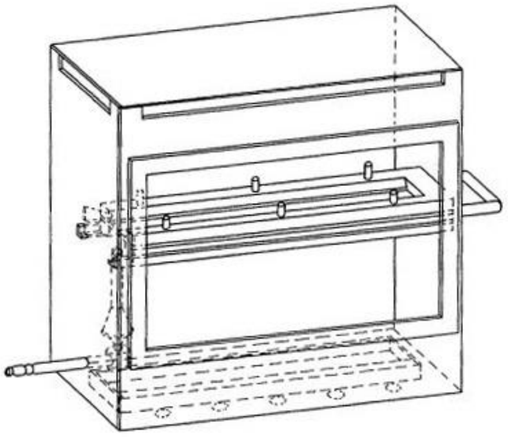

Figure 3.9: combustion chamber with sample holder placed in position [22]

Flame response of pPVC samples was also assessed by an oxygen consumption cone calorimeter as per ASTM E1354–16a (Figure 3.10) and ISO 5660–1.

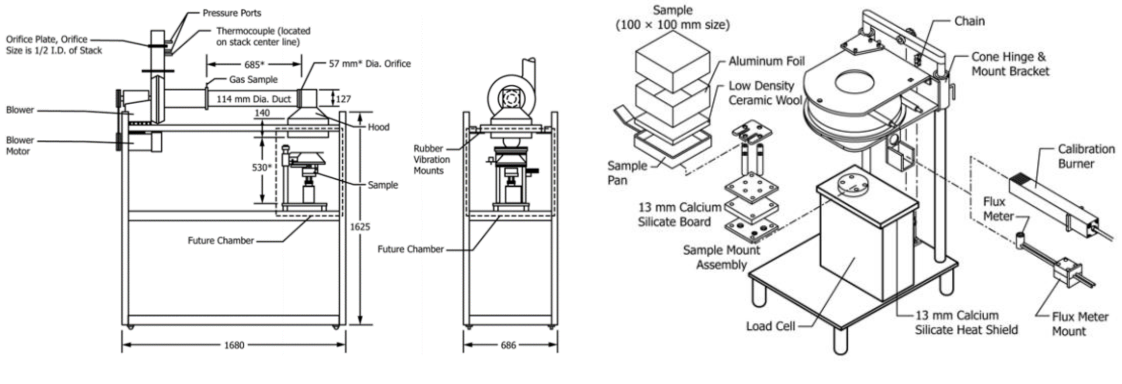

Figure 3.10: schematic representation of cone calorimeter (left) and exploded view of sample holder and test chamber (right) [8].

Tests were performed at a radiant heat flux of 25 kW/m^2, which corresponds to exposing the samples at a temperature of approx. 600 °C, in presence of a spark igniter. Specimen dimensions are 100 x100 mm, with an exposed surface area of 88.4 cm^2, placed at a distance of 25 mm from the cone heater. At least two specimens for each sample were tested. Prior to testing, specimens were weighted and their thickness measured.

3.2.4. Volatility and migration tests

Fog tests were performed according to DIN 75201 and ISO 6542 [9]. The equipment used consists of a thermostatic oil bath, maintained typically at 100 °C, and a coolant system connected to metal plates which recirculates distilled water kept at 21 °C. The aforementioned standard methods provide two different testing typologies, both used in this work, which require circular specimens, with known and precise surface. These specimens are put at the bottom of cylindrical beakers immersed in the oil bath, with the cooled metal plates on top of them. Differences between the two methods reside on the condensation surface and subsequent fogging measure. *Gravimetric fogging* (GF) uses aluminium foils, placed between the beaker and the cooling plate, to condensate the volatiles, weighting them before and after the test. This procedure demands to heat the sample for 16 h after which the aluminium foil is left for 12 h in a desiccator to cool down to room temperature before weighting. Diversely, *reflectometric fogging* (RF) uses square (10 x 10 cm), properly treated, glass slides placed on top of the beakers. The fogging value is calculated as a percentage ratio of the gloss of the glass slide after and before the test, measured by means of a Zehntner ZGM 1020 60° glossmeter, as per Equation 3.1.

Equation 3.1

$$F = \left(\frac{R_1}{R_0}\right) \times 100$$

Where:

F	are the average flow times of solution and pure solvent in specified conditions;
R_1 and R_0	are the reflectometer readings for the fogged and unfogged plate, in %;

Odour assessment is a crucial test for the automotive interiors industry. Considering that sense of smell is a very subjective matter, all the standards related to the evaluation of this characteristic requires the smelling of the sample, suitably conditioned in different ways (e.g. mild/high temperatures for long/short periods of time, presence/absence of humidity), by at least five operators, which rates individually the perceived odour intensity on a scale from 1 to 6, half–votes included, as per Table 3.2

Table 3.2: rating criteria for odour test [10].

Rating Scale	Description
1	Not perceptible
2	Perceptible, not disturbing
3	Clearly perceptible but not disturbing
4	Disturbing
5	Strongly disturbing
6	Extremely disturbing

Plasticizer migration was evaluated as weight loss percentage compared to the weight of the sample before test. All the samples were subjected to different tests as required by different automotive industries. These different internal tests are hereafter briefly outlined.

Migration into semi–rigid PVC foil (SRFM) is a test conceived to simulate the possible migration of plasticizers from the SL to other plastic materials which are typically rigid or less plasticized. Weighted counterparts of semi–rigid PVC were prepared and put in contact with the weighted samples, between two glass plates and a 5 kg weight on top. These assemblies were then placed in a forced convection oven for a certain time. The simultaneous application of prolonged heating and the mechanical action of the weight applied promotes the migration of the plasticizer, simulating and accelerating possible conditions of use. The test was conducted at different temperatures and for various amount of time, depending on the series tested:

- Recipe A: 168 h (7 d) at 70 °C. Counterparts were plasticized with 30 phr of DUP.
- Recipe B: 72 h (3 d) at 90 °C. Due to the higher temperature, which results in a more aggressive test, the counterparts were plasticized with 30 phr of TOTM[*].

Migration into extracting substances is, instead, a test based on the action of a substances that simulate possible real situations in which a substance could enter in contact with the

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[*] This choice was made based on the better results of fogging tests obtained by TOTM in recipe A formulations (see *Fogging*, page 38).

SL and favour the extraction of plasticizers shifting the equilibrium at the interface. Also in this case, two different approaches were used:

- Recipe A: weighted samples were submerged into soapy water (alkaline detergent, 10 g/L) and kept at 70°C for 24h, then removed, dried and reweighted. This test simulates and accelerates the potential action of cleaning agents.
- Recipe B: each weighted sample was spread with 5 g of butter (fat content: ≥ 82 %) and stored in dark at standard laboratory atmosphere (23 °C and 50 % RH) for 168 h (7 d), then cleaned and reweighted. This test simulates the action of food contact with SLs.

References

[1] ASTM D618, *Standard Practice for Conditioning Plastics for Testing*, ASTM International, West Conshohocken, PA, 2013.

[2] DIN 75201, *Determination of the fogging characteristics of trim materials in the interior of automobiles*, Deutsches Institut fur Normung (DIN), 2011.

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[4] ASTM D751-06, *Standard Test Methods for Coated Fabrics*, ASTM International, West Conshohocken, PA, 2011.

[5] ISO 5402-1, *Leather - Determination of flex resistance. Part 1: Flexometer method*, International Organization for Standardization, Genève, Switzerland, 2017.

[6] ASTM E313, *Standard Practice for Calculating Yellowness and Whiteness Indices from Instrumentally Measured Color Coordinates*, ASTM International, West Conshohocken, PA, 2015.

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4

Plasticizers

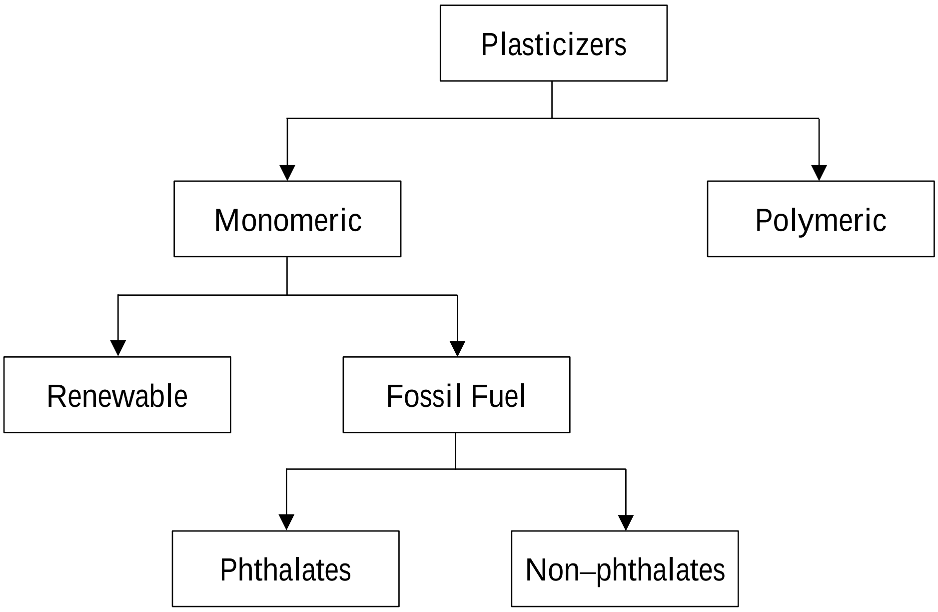
4.1. Introduction

Plasticization of a polymer can be obtained with two main routes, through the use of internal or external plasticizers. The first ones consist in a chemical modification of the polymer chain, using a co–polymerization reaction with a proper co-monomer or functionalizing the macromolecules with suitable compounds, while the latter ones involve the addition of relatively small molecules which are not chemically bonded with the polymer. This is without a doubt the easiest and more flexible method for formulators.

The history of external plasticizers is almost coeval to that one of PVC. Plasticizers have been generally thought to be used with polymers for the first time in 1846, when Shoenbein and Bottger used a plasticizer in nitrocellulose, although the term was not indicated in their patent, nor in later works. Klatte, in its 1913 patent [1], was the first to mention plasticizers, followed by Turkington (high boiling aldehyde in phenol resin) and Lindsay (aromatic phosphates in celluloid) who mentioned plasticizers in their 1924 US patents [2, 3]. In 1930s many other patents were issued, mentioning plasticization of zein (a class of prolamine protein), gelatine, cellulose acetate and vinyl chloride/acetate co–polymers, using many known today plasticizers, such as phthalates and phosphates. The 1930s and 1940s were a florid period for plasticizer synthesis and application [4]. In 1951, the Council of the International Union of Pure and Applied Chemistry (IUPAC) adopted the following definition of a plasticizer:

> *A substance or material incorporated in a material (usually a plastic or elastomer) to increase its flexibility, workability, or distensibility.*

This definition is focused on the imparted properties, without any mention to the chemical nature of plasticizers. Amongst the universe of external plasticizers, a first huge distinction could be made between monomeric[*] or polymeric plasticizers. The firsts are single or simple molecular structure, usually high–boiling esters with MW between 300–600 Da and an overall good thermal stability and chemical inertness. On balance, polymeric plasticizers are made of repeating units, with total MW between approximately 1,000 and 10,000 Da, with typical values around 3000 Da [5]. Polymeric plasticizers have very low volatility and greater permanence inside the finite product, but they impart higher viscosities, with consequent issues during processing. Furthermore they have higher costs that are rarely justified. For these reasons, monomeric plasticizers are the common choice for the majority of applications. Inside the monomeric plasticizers group, a subdivision referred to the provenience of the plasticizer, or the raw materials needed for its synthesis, could be made. In this way we could distinguish between *fossil fuel* and *renewable based plasticizers*. A different subdivision amongst the monomeric plasticizers could be made based on their chemical structure. Hence, we can distinguish aliphatic dicarboxylic acid esters (e.g. adipates, sebacates, etc.), phosphates, benzoates, epoxies, and so on. These chemical families, inside the *fossil fuel based plasticizers* set, could be grouped in phthalates and non–phthalates. The whole classification is reported in Scheme 4.1.



Scheme 4.1: nomenclature used for plasticizer groups

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[*] The term *monomeric* is used in contraposition of *polymeric*. These molecules are low molecular weight compounds. They are not monomers and do not polymerize.

The subdivision between phthalates and non–phthalates is the nodal point of the present research work concerning plasticizers. As previously mentioned, phthalates have been proved to pose risks for human health, particularly acting like endocrine disruptors and influencing reproductive system both during its formation in early years and during reproduction. Actually, these properties are typical of low molecular weight phthalates, intended as those ones whose main side chain is composed of 6 or less carbon atoms. This definition includes BenzylButyl Phthalate (BBP), DiButyl Phthalate (DBP) and Di(2–EthylHexyl) Phthalate (DEHP). While the firsts two have found use mainly in other types of industries, DEHP (Figure 4.1) has been the most widely used for decades in the SLs industry.

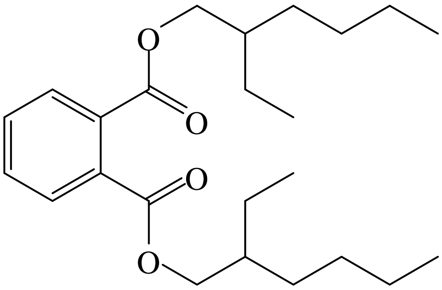

Figure 4.1: chemical structure of DEHP.

However, nowadays the standard phthalates used in automotive industry belongs to the high molecular weight (HMW) class, and are obtained with C10–C11 alcohols. These plasticizers are, for example, Diisodecyl Phthalate (DIDP), Di(2–Propylheptyl) Phthalate (DPHP), Diisoundecyl Phthalate (DIUP) and Diundecyl Phthalate (DUP).

- *Plasticization mechanisms [5-8]*

Independently from their nature, plasticizers act through mechanisms which were described by many authors with different theories, neither of which fully explain the mechanism. This is due to the complexity of the system, which is difficult to simplify. It is therefore more than possible that these theories are not exclusive, and the real mechanism should be a sum of contributions. The principal theories and models are briefly described hereafter.

According to the oldest of these theories, the *lubricity theory*, as the system is heated the plasticizer molecules diffuse into the polymer, weakening the interactions between the polymer chains (Van der Waals forces). This theory was presented by different authors [9, 10], but the common idea behind them is that plasticizers reduce intermolecular friction between the macromolecules, letting them slip one over the other through gliding planes, acting analogously to a lubricating oil. Thus, also the glass transition temperature (T_g) of the polymer lowers, resulting in increased flexibility, softness, and elongation. Although this effect may be easy to visualize, there are several problems with this concept, and the lubricity theory is rarely used by itself to describe plasticization of PVC.

The *gel theory*, the second of the "classic theories", takes into account the polarity of the polymer chains and plasticizers, in particular those ones containing long aliphatic chains which seem to be more effective than short chains or cyclic groups [11, 12]. This theory considers the polymer formed by a three-dimensional network of inter-chain weak secondary bonds. The plasticizer acts inserting itself between these chains, and consequently reducing the rigidity of the gel structure. Thus, the molecules dynamically solvate/desolvate the resin, temporarily opening the polymer structure which is later restored in a casual, different, position. The flexibility of the plasticized polymer is, hence, explained by the reduction of the rigidity of this three–dimensional network through the relative reduction of the numbers of entanglement between polymer chains caused by the presence and mobility of plasticizer molecules [13].

The *free–volume theory* was developed some years later thanks to a more in–depth comprehension of polymer properties as a function of temperature, viscosity and other variables. As the previous cases, this theory was proposed by different authors, but postulated by Fox and Flory [14], and involves an important propriety of polymeric materials known as *glass transition temperature* (T_g), and the concept of *free–volume*. The first one is a characteristic temperature that sets a limit between the rubbery and glass–like state of a polymer, while the latter one is a measure of the internal space available within a polymeric material. When a polymer is in the glassy state, its molecules are tightly organized, the free volume is low and the molecules cannot move with ease. Thus, the material results rigid and hard. Heating the polymer above the T_g, the thermal energy and molecular vibrations create additional free–volume, allowing the polymer chains to move one over the other, yielding a more flexible polymer system. However, not only heat has this effect on free–volume: the functionalization of the polymer backbone with side chains or end groups, or the addition of relatively small molecules such as plasticizers, also lowers the T_g by separating the macromolecules, adding free–volume. Moreover, plasticizers with lower T_g are more efficient in reducing the T_g of the plasticized system [4].

Since the free–volume theory was postulated, few other attempts were made in formulating new theories, which were mainly based upon the ones previously illustrated. The *mechanistic theory*, for example, takes into account the interaction of plasticizer and polymer molecules, assuming weak temporary bonds between them, and self–associations of the plasticizers itself. This dynamic process depends on the plasticizer concentration indeed plasticizer–plasticizer interactions become more frequent and significant at higher concentrations. Such a behaviour can explain the concept of "*antiplasticization*", depicted in Figure 4.2, a theory according to which the addition of small quantities of plasticizer (i.e. less than 15 phr) sufficiently increases free–volume promoting polymer reorganization into a larger number of crystallites.

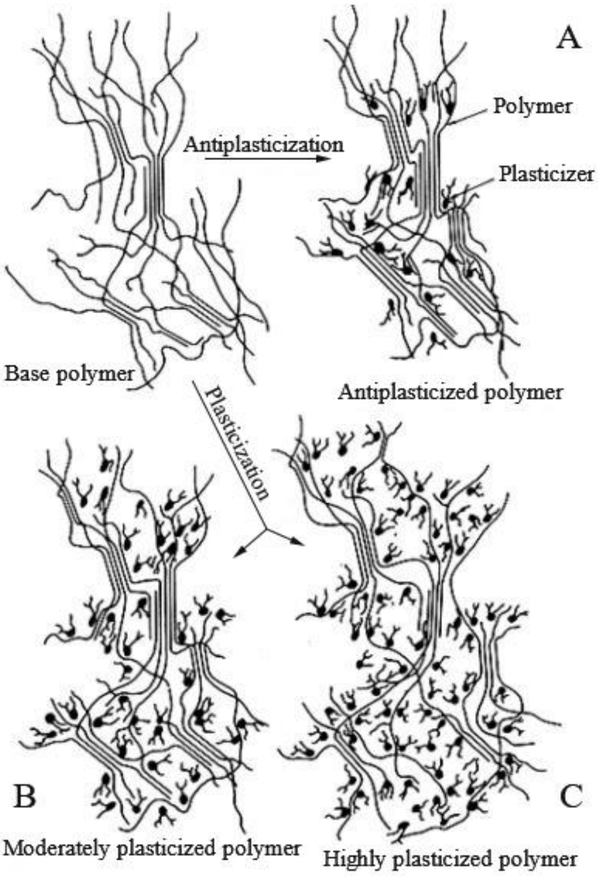

Figure 4.2: simplified representation of plasticization and antiplasticization. Adapted from Sears et al. [15]

These crystalline domains are responsible for higher tensile strength and modulus, resulting in a more rigid material (Figure 4.2–A, Antiplasticized polymer). Further addition of plasticizer may result in slighter increase in crystallinity, but the contribution of the amorphous phase, which is swollen by the plasticizer molecules is greater, resulting in a softer, more flexible, material with better elongation and impact resistance (Figure 4.2–B, Moderately plasticized polymer). At higher concentration of plasticizer, a point could be reached at which the crystallites are dissolved and a gel is obtained (Figure 4.2–C, Highly plasticized polymer).

4.2. Results and discussion

Several of the tested plasticizers, particularly the renewable based ones, were new commercial, or even pre–market products, often with secret formulas and with few information supplied. Hence, all the plasticizers were initially analysed by means of gas–chromatography mass spectrometry (GC–MS) and Fourier transform infrared spectroscopy (FT–IR) in order to build a database of mass and infrared spectra of these molecules and verify the nature of these products.

4.2.1. Plastisol formulation

Due to new and improved requirements sought by car manufacturers, and occurred during the experimentation, plastisols were prepared following two different standard recipes (Recipe A in Table 4.1, and Recipe B in Table 4.2). Some of the selected plasticizers were tested with both the formulations, in order to allow the comparison of the two series of results. Both the recipes are intended to be used for the manufacturing of highly flexible supported SLs.

The quantities reported in Table 4.1 and Table 4.2 are expressed in **phr**, which stands for *parts per hundreds resin*. This is a purely practical measure unit which is commonly used in industrial contexts due to its scalability easiness. In fact, using the values reported in Table 4.1 as example, the recipe could be equally referred to grams, kilograms or tonnes: for each 100 g/kg/t of PVC resin, 75 g/kg/t of plasticizer and 6 g/kg/t of heat stabilizers have to be added.

Table 4.1: standard recipe A, used for 1st batch of plastisols preparation.

Component	Type	Quantity (phr)	Total quantity (phr)
PVC resin	K74	100	100
Plasticizer	See Table 1	75	75
Heat Stabilizer	Ca/Zn	3	6
	ESBO	3	

The first recipe (Table 4.1) employs only one type of PVC resin, emulsion grade with a K–value of 74. The heat stabilization system is composed by a calcium/zinc metal soap and Epoxidized Soybean Oil (ESBO), an available and cheap co–stabilizer. For the second recipe (Table 4.2), two PVC resins, a blend of K82 and K70 grades, were used. The predominant portion is composed by the first one, which is a PVC homo–polymer obtained by micro–suspension. Its high MW should guarantee high mechanical properties. A smaller quantity of a K70 emulsion grade resin is added to thicken the plastisol and also to impart good quality of expanded layers.

Table 4.2: modified recipe B, used for 2nd batch of plastisols preparation.

Component	Type	Quantity (phr)	Total quantity (phr)
PVC resin	K82	75	100
	K70	25	
Plasticizer	See Table 1	75	75
Heat Stabilizer	Epoxy/Zn	4	7
	ESBO	3	

The heat stabilization system is slightly different with respect to that one used in the first recipe, with 4 phr of an Epoxy/Zn compound to further improve the plasticized PVC (pPVC) heat stability.

4.2.2. Mechanical properties

- *Hardness*

Indentation hardness measurements quantify the resistance of a material to plastic deformation. In the case of pPVC material, these values are directly connected to the amount of plasticizer contained in them. Results are reported in Table 4.3.

Table 4.3: Shore A and D of the two series of samples.

Recipe A			
#	*Plasticizer*	*Shore A*	*Shore D*
1	**DPHP**	67	19
2	DUP	69	19
3	DIUP	67	19
4	DOTP	65	18
5	DINTP	70	20
6	DINCH	66	18
7	TOTM	65	18
8	DIDA	66	16
9	DOS	63	15
10	PIV	63	17
11	ATEHC	69	20
12	ISE	65	17
13	AGM	64	18
14	ESBO	65	19
15	ModESBO	64	17
16	ModESBO_1	63	16
17	ModESBO_2	65	19
18	ModESBO_3	63	16

Recipe B			
#	*Plasticizer*	*Shore A*	*Shore D*
1	**DPHP**	61	15
2	DUP	62	14
3	DOTP	61	15
4	DINCH	65	15
5	TOTM	67	17
6	TNTM	67	17
7	DIDA	63	14
8	DBEEA	59	12
9	DOA-TEGDEH	63	15
10	ModA	62	13
11	DOS	57	12
12	DIDS	71	18
13	PPB	58	13
14	PGDB	63	16
15	DP/DE-GDB	59	14
16	P/DP/DE-GDB	60	14
17	IDDPP	56	12
18	EHDPP	57	11
19	PETV	57	13
20	DOZ	62	14
21	RFE	58	12
22	ModESBO	59	13

The comparison of the samples containing the same plasticizer but obtained with the two different recipes is reported in Figure 4.3. It is worth noting that recipe A yields samples with basically higher hardness with respect to samples obtained with recipe B. The only exception to this trend is represented by the samples containing TOTM, probably due to the morphology and size of the plasticizer molecules.

These results are quite unexpected due the fact that recipe B contains a high MW resin (K82) which should impart higher mechanical properties, hardness included. However, industrial know–how possessed by Vulcaflex company allowed to suggest that this effect is progressively less marked increasing the plasticization level and, thus, not so dramatic at the plasticizer loading used in the present work.

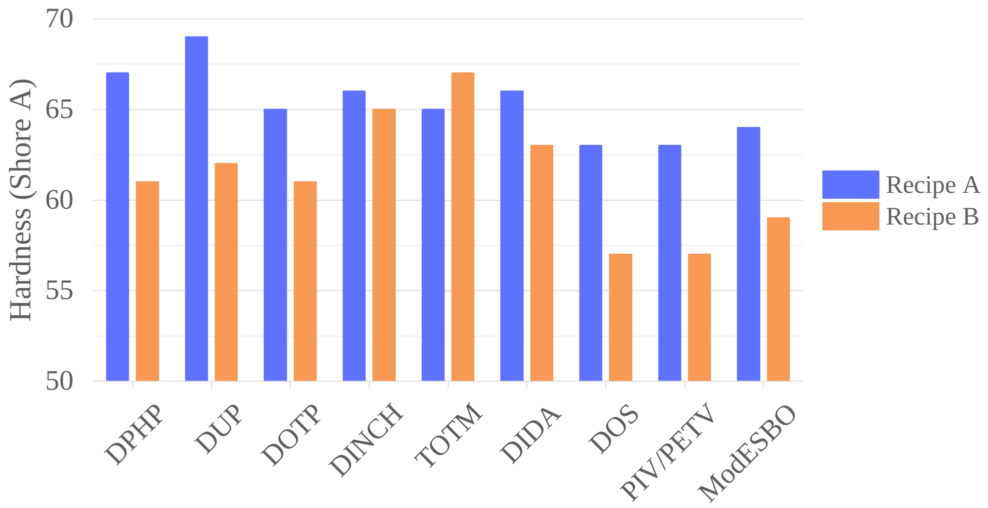

Figure 4.3: differences between hardness (Shore A) of the same plasticizers used in recipe A and B.

The lower hardness measured for samples obtained with the recipe B could be ascribed in part to the presence of a blend of two PVC resins which differ in terms of both K–values (K70 and K82) as well as polymerization techniques used for their production. Theoretically, the blend of PVC resins with K–value differences of 10 units or less, should not significantly affect MW distributions (MWD) of the resulting material. Thus, the blend should not result in a multimodal MWD, and should behave like an intermediate K–value resin [16]. However, the slightly higher K–value difference and the unbalanced ratio (75:25) of the two resins could play a role in this unforeseen result. Furthermore, the two resins are obtained via micro–suspension (K82) and emulsion (K70) polymerization; thus, even if they should have similar properties, they could differ in terms of particles dimension, porosity, and the chemical nature and quantity of residual surfactants. Therefore, different interactions between polymer and plasticizer could be established. Moreover, it is worth noting that, usually, higher K–value resins need higher temperature or longer time for gelation and fusion [17]. Hence, being gelation times and temperatures the same for both series of samples, the possibility of non-optimal process conditions for recipe B, might be taken into account and verified in further investigations.

Anyway, simple hardness values of pPVC materials may not be very useful for the formulator. Thus, it is common practice to calculate a *substitution factor (SF)* [5], which expresses the degree of efficiency of each plasticizer compared to a reference standard. In this case, we choose DPHP which is one of the most common phthalate worldwide used.

The efficiency of each plasticizer, calculated using only the more significant value of Shore A, is reported in Table 4.4 with the equivalent quantity (phr_{eq}) of each plasticizer needed to obtain the same hardness of the reference. These last values are clearly understandable and easy to read: lower results mean that less of that particular plasticizer is required to obtain the same hardness and, hence, flexibility of the pPVC containing the reference plasticizer.

Table 4.4: Substitution factors (SF) and equivalent phr (phr_{eq}).

	Recipe A		
#	*Plasticizer*	*SF*	*phr_{eq}*
1	**DPHP**	1.00	75
2	DUP	1.03	77
3	DIUP	1.00	75
4	DOTP	0.97	73
5	DINTP	1.04	78
6	DINCH	0.99	74
7	TOTM	0.97	73
8	DIDA	0.99	74
9	DOS	0.94	71
10	PIV	0.94	71
11	ATEHC	1.03	77
12	ISE	0.97	73
13	AGM	0.96	74
14	ESBO	0.97	73
15	ModESBO	0.96	72
16	ModESBO_1	0.94	71
17	ModESBO_2	0.97	73
18	ModESBO_3	0.94	71

	Recipe B		
#	*Plasticizer*	*SF*	*phr_{eq}*
1	**DPHP**	1.00	75
2	DUP	1.00	75
3	DOTP	1.00	75
4	DINCH	1.06	79
5	TOTM	1.09	82
6	TNTM	1.08	81
7	DIDA	1.03	77
8	DBEEA	0.96	72
9	DOA-TEGDEH	1.03	77
10	ModA	1.01	76
11	DOS	0.93	70
12	DIDS	1.16	87
13	PPB	0.95	71
14	PGDB	1.03	77
15	DP/DE-GDB	0.96	72
16	P/DP/DE-GDB	0.97	73
17	IDDPP	0.91	68
18	EHDPP	0.93	70
19	PETV	0.92	69
20	DOZ	0.94	71
21	RFE	1.00	75
22	ModESBO	0.96	72

Moreover, they allow an easier comparison of the data obtained for the two recipes, being normalized on the reference plasticizer (DPHP). It results clear that in both recipes phthalates (in red) behave almost identically (SF ≈ 1.00) and that renewable based plasticizers (in green) can be used in less quantities being more efficient than the reference DPHP (SF ≤ 1.00) with the only exception of ATEHC (recipe A). Figure 4.4 reports a comparison of only the plasticizers tested in both the formulations.

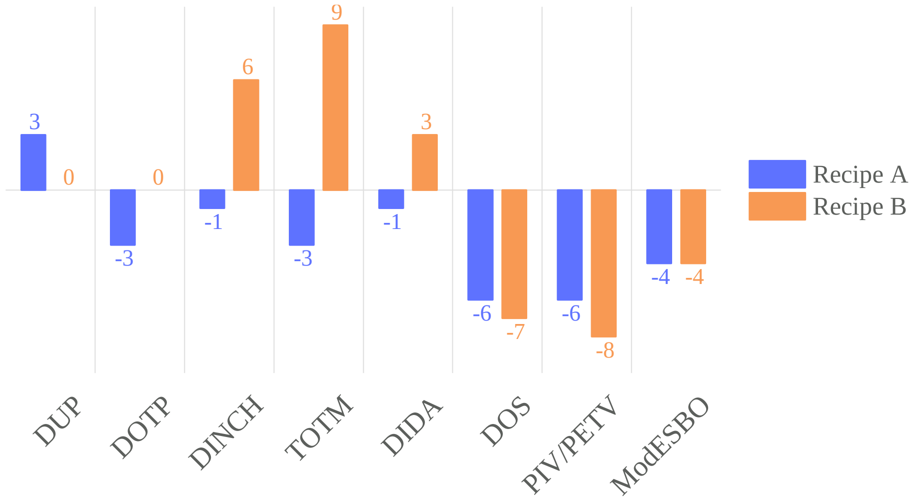

Figure 4.4: percentage differences of plasticizers efficiency in the two recipes compared to DPHP.

Results point out that some of the tested plasticizers, namely DINCH, TOTM and DIDA, have an opposite behaviour when added in the two different recipes, yielding softer materials than DPHP when used with the K74 emulsion–grade resin, and harder materials than DPHP when used with the blend K82/K70 (75:25). Conversely, phthalates, renewable–based plasticizers (PIV/PETV and ModESBO) and DOS show almost identical results.

Such a behaviour could be ascribed to the nature of plasticizers and the interactions between them and the different PVC resins. It must be however pointed out that the magnitude of the uncertainty of the measures is approximatively two points on the Shore A scale.

- *Ultimate Tensile Strength and Elongation at Break*

Ultimate tensile strength (UTS) and elongation at break (EB) of the samples, measured for both the recipes, are reported in Table 4.5. The obtained results are consistent with the ones obtained for hardness measures. Samples obtained following recipe A exhibit slightly higher mechanical properties than samples from recipe B, particularly in the case of renewable based plasticizers (in green in Table 4.5), which show higher tensile strength and comparable elongation at break with respect to formulations containing DPHP.

Table 4.5: Ultimate tensile strength (UTS) and elongation at break (EB) of the two series of samples

Recipe A			
#	***Plasticizer***	***UTS (MPa)***	***EB (%)***
1	DPHP	14,0	618
2	DUP	13,3	586
3	DIUP	14,2	601
4	DOTP	13,1	590
5	DINTP	15,6	521
6	DINCH	12,6	578
7	TOTM	14,7	594
8	DIDA	11,5	584
9	DOS	11,4	634
10	PIV	15,8	630
11	ATEHC	15,6	524
12	ISE	16,0	606
13	AGM	15,9	664
14	ESBO	15,1	535
15	ModESBO	14,5	630
16	ModESBO_1	14,3	639
17	ModESBO_2	15,5	597
18	ModESBO_3	12,8	625

Recipe B			
#	***Plasticizer***	***UTS (MPa)***	***EB (%)***
1	DPHP	14,6	618
2	DUP	12,8	615
3	DOTP	13,2	633
4	DINCH	13,0	624
5	TOTM	12,4	483
6	TNTM	11,9	518
7	DIDA	11,2	592
8	DBEEA	11,0	623
9	DOA-TEGDEH	12,1	544
10	ModA	11,9	592
11	DOS	9,1	590
12	DIDS	13,2	509
13	PPB	10,3	603
14	PGDB	12,4	371
15	DP/DE-GDB	12,2	436
16	P/DP/DE-GDB	13,9	504
17	IDDPP	9,5	618
18	EHDPP	10,1	634
19	PETV	9,6	581
20	DOZ	11,5	647
21	RFE	14,0	627
22	ModESBO	10,7	540

Conversely, all of the plasticizer tested with recipe B show lower properties than DPHP, in particular the renewable based ones, RFE excluded. Other plasticizers that show good tensile strength but very poor elongation results are dibenzoates (Table 4.5, Recipe B, #13–15). Such a behaviour could be ascribed in part to their volatility. Indeed the compounds with lower boiling point (BP) seem to give the stiffer materials. See for example PGDB sample, which having the lower BP (BP of P/DP/DE–GDB, DP/DE–GDB and PGDB, as reported on the technical data sheets (TDS), are 215, 191 and 157 °C @ 5 mmHg respectively), exhibits the worst elongation at break value and, a lower efficiency (i.e. substitution factor) than DPHP and the lowest amongst mono– and dibenzoates. Thus, such a behaviour could be due to the partial removal of the plasticizer at the process temperature, which leads to a stiffer material. The plasticizer loss of the other dibenzoates, however, is partly compensated by the good efficiency of these plasticizers, as seen in Table 4.4. The mono–benzoate, PPB, shows a different behaviour, with quite low tensile strength and very high elongation at break.

With aim to better understand the differences between the tested plasticizer and the two recipes, in Figure 4.5 and Figure 4.6 the comparisons between the UTS and the EB of several samples are reported.

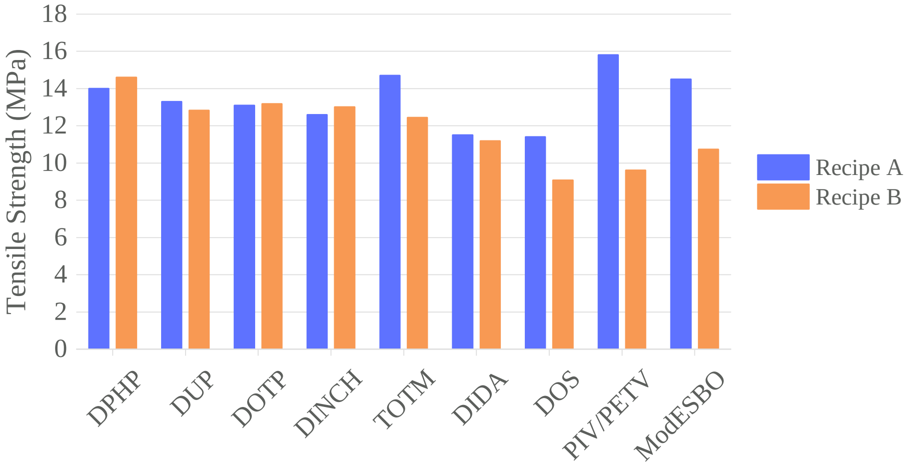

Figure 4.5: Comparison between UTS of plasticizers used in recipe A and B.

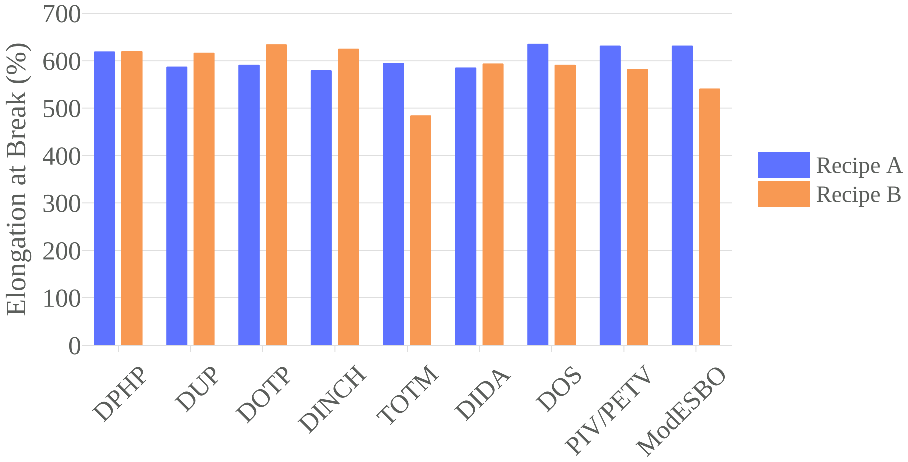

Figure 4.6: Comparison between EB of plasticizers used in recipe A and B.

It is worth noting that phthalates (DPHP, DUP), phthalates–like (DOTP, DINCH) and DIDA show similar properties, with slightly higher elongation values measured on sample obtained with recipe B. All the other plasticizers exhibit instead higher UTS and EB values when added to recipe A, yielding more elastic materials, consistently with hardness results reported in Table 4.4.

As highlighted in Figure 4.7 which reports the differences between UTS values of each plasticizer and the reference (DPHP), all the samples obtained with recipe B result less performant than DPHP containing materials while the addition of TOTM and bioplasticizers (particularly PIV/PETV) yields samples with opposite behaviour in the two formulations.

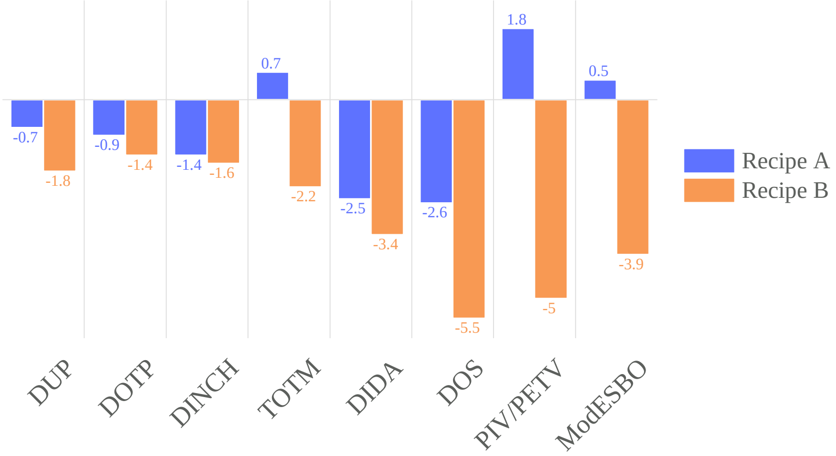

Figure 4.7: Difference between UTS of plasticizer and reference (DPHP).

- *Cold resistance*

The evaluation of cold resistance (CR), a critical property for automotive applications in cold climates, was performed by means of a flex test and rated as per Paragraph 3.2.2.

Table 4.6: Cold resistance evaluation.

	Recipe A	
#	***Plasticizer***	***CR***
1	**DPHP**	3.0
2	DUP	3.0
3	DIUP	2.5
4	DOTP	1.5
5	DINTP	3.0
6	DINCH	2.5
7	TOTM	3.0
8	DIDA	0.0
9	DOS	0.0
10	PIV	2.0
11	ATEHC	4.0
12	ISE	2.5
13	AGM	2.5
14	ESBO	4.0
15	ModESBO	2.5
16	ModESBO_1	1.5
17	ModESBO_2	4.0
18	ModESBO_3	0.5

	Recipe B	
#	***Plasticizer***	***CR***
1	**DPHP**	1.5
2	DUP	0.5
3	DOTP	1.5
4	DINCH	1.5
5	TOTM	2.0
6	TNTM	1.5
7	DIDA	0.0
8	DBEEA	0.5
9	DOA-TEGDEH	4.0
10	ModA	1.5
11	DOS	0.0
12	DIDS	1.5
13	PPB	3.0
14	PGDB	4.0
15	DP/DE-GDB	4.0
16	P/DP/DE-GDB	4.0
17	IDDPP	1.5
18	EHDPP	1.5
19	PETV	0.5
20	DOZ	0.5
21	RFE	2.5
22	ModESBO	1.5

The obtained results, reported in Table 4.6, show that, apart from DIDA and DOS which are well known for their exceptional low–temperature properties (T_g = -104/-106 °C [4]) and confirmed their performances in both the formulations, other plasticizers that gave good results using recipe A are DOTP, ModESBO_1 and ModESBO_3. The samples obtained using recipe B result more resistant than the other ones, with the notable exceptions of benzoates (particularly dibenzoates) and DOA–TEGDEH which were totally destroyed at the end of test, and TOTM which might be considered borderline. These results suggest that the higher elasticity of samples obtained with recipe B, demonstrated by their lower hardness and, to a certain extent, by elongation results, is maintained even at very low temperatures. Such a results could be ascribed to a better thermodynamic compatibility between plasticizers and K82/K70 PVC blend when used together with epoxy/ESBO heat stabilizers. Recipe B, indeed, seems to allow the plasticizer to better perform their plasticization effect

The direct comparison between plasticizers used in both formulations, reported in Figure 4.8, shows the trend already pointed out. Again, the behaviour of TOTM is intriguing, being the only plasticizer of this series that performed worse than DPHP (in recipe B).

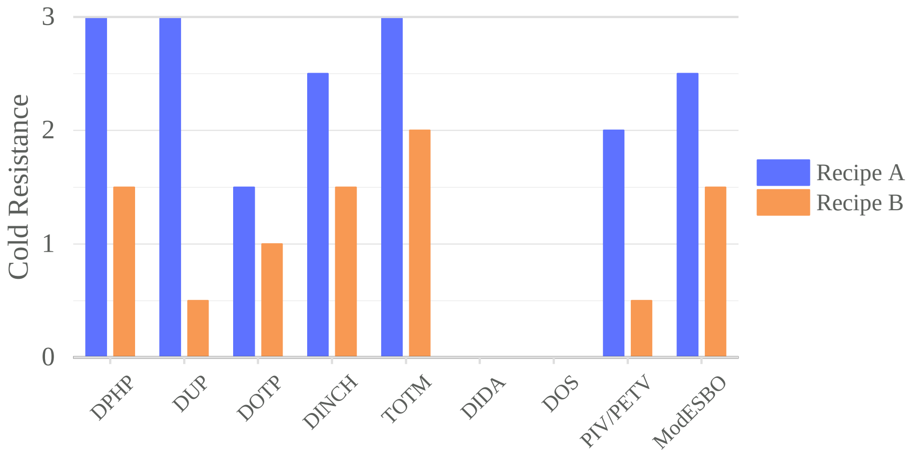

Figure 4.8: Comparison between cold resistance of plasticizers used in recipe A and B.

4.2.3. Thermal and flame properties

- *Thermal stability*

The evaluation of the thermal stability of all the samples obtained with both recipe A and B was carried out. This test is a paramount tool when developing new formulations or testing new additives or combinations, because it gives a good estimation of the resistance and stability of the material at process temperature and allows to determine the more suitable heat stabilization system and the appropriate quantity. In industry practice, results are normally qualitatively assessed by visually examination of the samples, with the aid of a graduated scale, marked every 15 mm to indicate each step outwards of the mobile rack when exits from the oven. However, with the aim at giving quantitative results, the Yellowing Index (YI) was measured on the samples at different intervals of exposure time, by means of a spectrophotometer. The results related to plasticizers formulated with recipe A, expressed as variations of Yellowing Index (ΔYI) with respect to an unexposed sample, are reported in Figure 4.9.

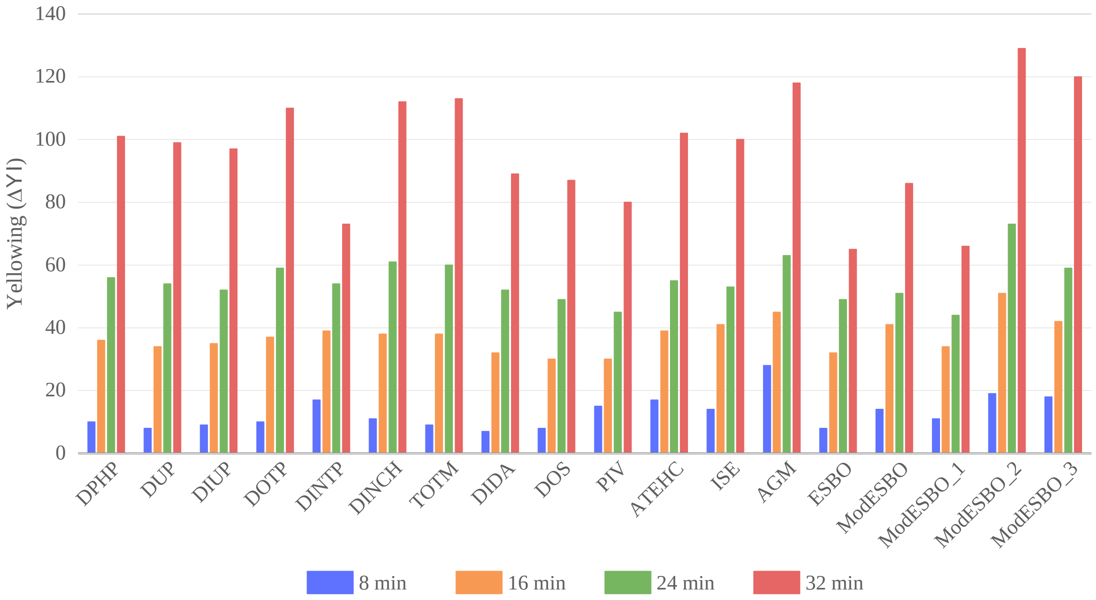

Figure 4.9: Thermal stability of samples obtained with recipe A.

The reported data show that DINCH and TOTM exhibit the worst performance amongst the fossil fuel based plasticizers. Yellowing variations of DIDA, DOS, PIV and particularly DINTP, after 24 and 32 min, are lower than DPHP. It is also worth noting the behaviour of epoxy based compounds, which are commonly used as co–stabilizers. In fact, ESBO, ModESBO and ModESBO_1 exhibit a lower yellowing compared to the reference (DPHP), while ModESBO_2 and ModESBO_3, exhibit the worst results at 32 min and among the worst at 24 min. It is interesting to observe the trends exhibited by the samples containing these two plasticizers, in comparison with the sample with the best performer (ESBO) and the reference (DPHP), reported in Figure 4.10.

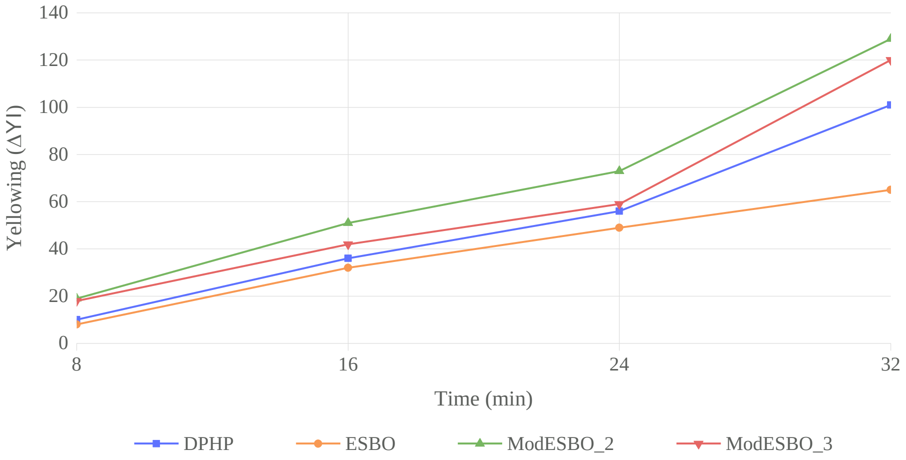

Figure 4.10: *yellowing trend (ΔYI) of DPHP and some of the epoxy plasticizers.*

By comparing the thermal stability of ModESBO_2 and ModESBO_3 with that one of the sample with the best performance (ESBO) and the reference (DPHP) (Figure 4.10), two different trends can be identified. ESBO sample, as though the majority of plasticizers, shows an almost linear increasing of the variation of yellowing index vs time which suggests a slow degradation. ΔYI of ModESBO_3 and ModESBO_2 samples, instead, results similar to that of ESBO until 16 minutes, than it grows slower up to 24 minutes and, finally, at 32 minutes an abrupt increase of the yellowing happens, suggesting a fast degradation of the polymer, visually identified by the blackening and stiffening of the specimen. Such a behaviour could be related to the heat stabilization system, in particular to its interactions with the plasticizer and its behaviour at test temperature. The heat stabilization mechanism was not completely understood, but probably but could probably put in connection with the used PVC resins and in particular to the amount and chemical nature of residual additives derived from the VCM polymerization, such as surfactants and antioxidants.

The results of the test performed on the samples obtained with recipe B are reported in Figure 4.11 and show that they exhibit a poorer stability.

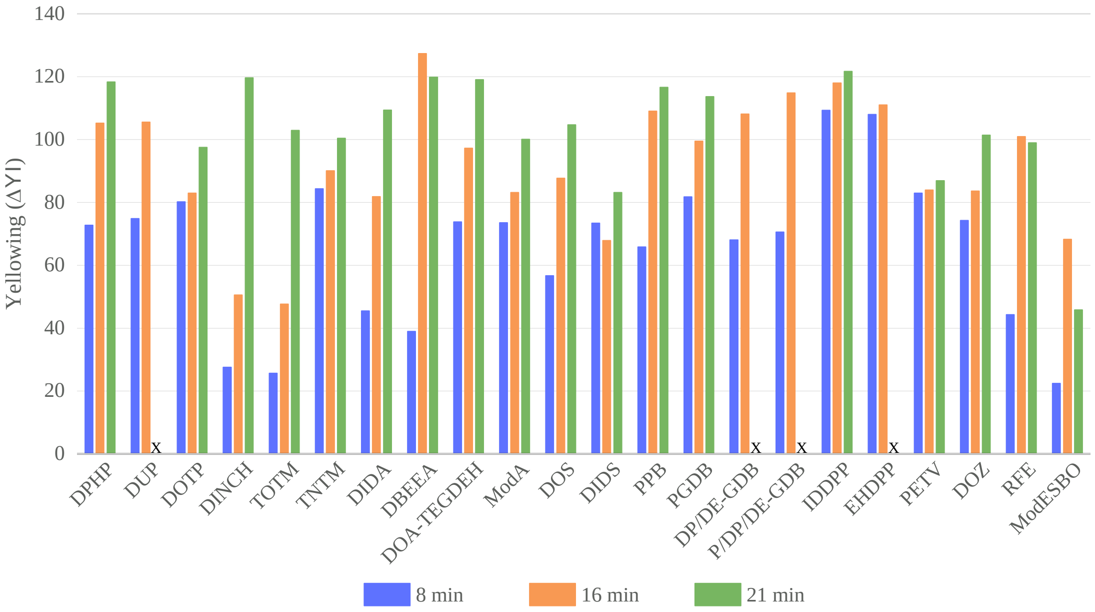

Figure 4.11: Thermal stability of samples obtained with recipe B.

It is worth noting that the reported data refer to a maximum of 21 min as heating time, against the 32 min values correctly recorded on samples obtained with recipe A. The best results are shown by DINCH, TOTM (especially at 16 min) and ModESBO, followed by DIDS and PETV. The latter undergoes a higher initial colouring than DPHP but remains almost unchanged even after 21 minutes. Several samples show lower results at 21 than at 16 minutes. This could be addressed to two different motives: the lower ΔYI @ 21 min of RFE, DBEEA, EHDPP, DP/DE–GDB and P/DP/DE–GDB is caused by severe colour changing of the specimen, which begins to blacken making unreliable the measures of YI obtained by the spectrophotometer, and were not reported in the graph but indicated with a "X"; diversely, RFE and particularly ModESBO exhibit a flexion of the yellowing trend which then resumes its increasing without reaching the blackening of the specimens.

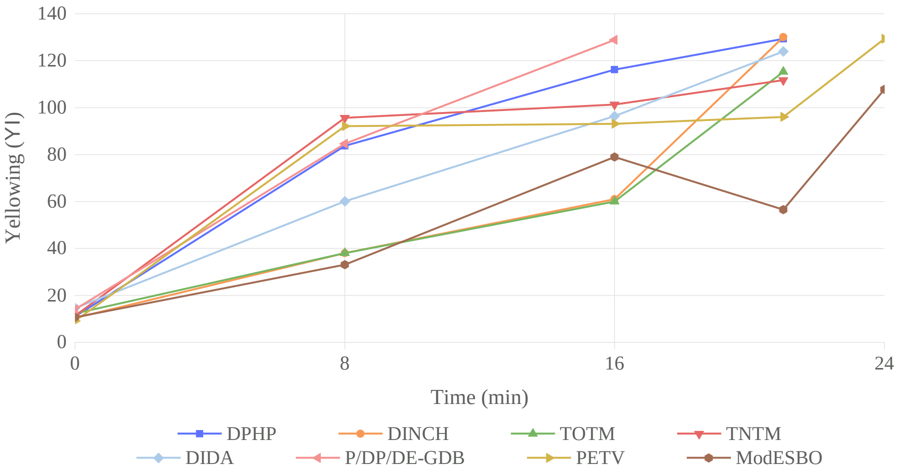

Figure 4.12: yellowing trend (YI) of DPHP (ref) and other plasticizers.

The yellowing s of samples obtained with recipe B are reported in Figure 4.12, showing trends similar to those one registered for samples obtained with recipe A (Figure 4.10).

As can be seen, DPHP degradation is initially quite fast, then decreases up to 21 min; P/DP/DE–GDB has a similar trend but at 8 min the degradation rate increases and blackening is reached in 16 min. TNTM and PETV exhibit higher initial yellowing than DPHP but between 8 and 21 min their degradation almost stops. DINCH and TOTM yellowing increase slowly up to 16 min and then they undergo an abrupt degradation, particularly the first. DIDA has a quite linear trend, positioned halfway between DPHP and DINCH/TOTM. Lastly, ModESBO shows a polynomial–like trend, and at 24 min its degradation is lower than the majority of the other samples at 21 min. The faster colour changes compared to samples realized with recipe A, could also be correlate to the use of the epoxy/ESBO stabilizer system, which is known in industry practice for its characteristic toning towards red when exposed to high temperatures. This reddish tone could be misleading when recording the YI, meaning that samples appear more degraded than they actually are. An explanation of the polynomial–like trends recorded for some of the samples is normally associated to surfactants and other process additives remained in PVC after the polymerization. These compounds may be responsible for the initial discoloration, which appears to be reversible once they are consumed.

Finally, a comparison between the samples obtained with the two recipes after 8 and 16 min of exposure is reported in Figure 4.13 and shows that recipe B samples have lower thermal stability than recipe A ones.

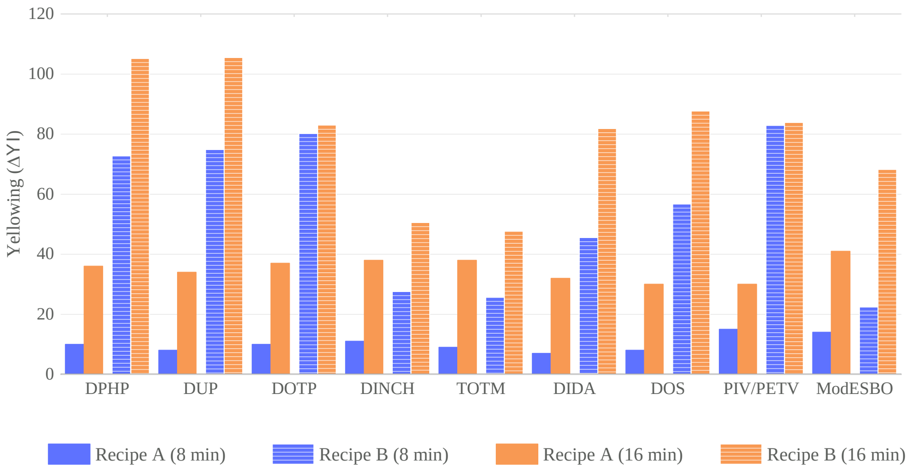

Figure 4.13: Comparison between thermal stability of plasticizers used in recipe A and B.

However, TOTM and DINCH, which were the worsts when used in recipe A, are the best performers amongst fossil fuel based plasticizers when used in recipe B. Their results are, in fact, quite similar particularly at 16 min.

- *Thermal aging*

With the aim to obtain information concerning the resistance of the material to the effect of aging, accelerated weathering tests were carried out for all the samples. The test takes advantage of the colour change of the samples exposed to a moderately high temperature (i.e. 90 °C) which is measured at different interval of times. Results, expressed as variation in respect to the unexposed sample, are reported in Table 4.7.

Table 4.7: Thermal aging data.

Recipe A					
#	***Plasticizer***	***ΔYI @ 90 °C***			
		1	3	5	7
1	**DPHP**	0.7	3	5	8
2	DUP	0.8	4	6	8
3	DIUP	0.7	3	5	8
4	DOTP	0.5	3	4	7
5	DINTP	3	6	8	10
6	DINCH	0.6	3	4	6
7	TOTM	0.6	3	4	7
8	DIDA	0.6	3	4	6
9	DOS	0.5	3	4	6
10	PIV	2	4	5	7
11	ATEHC	3	10	10	14
12	ISE	2	6	8	10
13	AGM	4	9	11	13
14	ESBO	6	12	14	17
15	ModESBO	5	12	15	18
16	ModESBO_1	4	11	14	16
17	ModESBO_2	6	13	17	19
18	ModESBO_3	2	7	9	10

Recipe B					
#	***Plasticizer***	***ΔYI @ 90 °C***			
		1	3	5	7
1	**DPHP**	6	10	11	16
2	DUP	7	12	14	15
3	DOTP	3	10	13	16
4	DINCH	6	13	18	21
5	TOTM	3	13	22	23
6	TNTM	3	13	15	19
7	DIDA	0.9	9	12	12
8	DBEEA	8	25	34	42
9	DOA-TEGDEH	6	18	26	33
10	ModA	2	5	7	9
11	DOS	3	5	9	11
12	DIDS	5	12	19	19
13	PPB	3	26	33	37
14	PGDB	2	18	26	36
15	DP/DE-GDB	4	16	22	28
16	P/DP/DE-GDB	6	17	23	29
17	IDDPP	18	40	50	58
18	EHDPP	18	47	48	55
19	PETV	6	10	15	16
20	DOZ	0.4	4	7	9
21	RFE	8	13	17	20
22	ModESBO	0.8	5	7	8

The obtained data show that both the two series of samples suffer the effect of the moderate heat used for thermal aging and are in accordance with the results of the thermal stability tests. In fact, ΔYI data reported in Table 4.7 are definitely higher for samples obtained with recipe B. The results regarding plasticizers used in recipe A are reported in Figure 4.14.

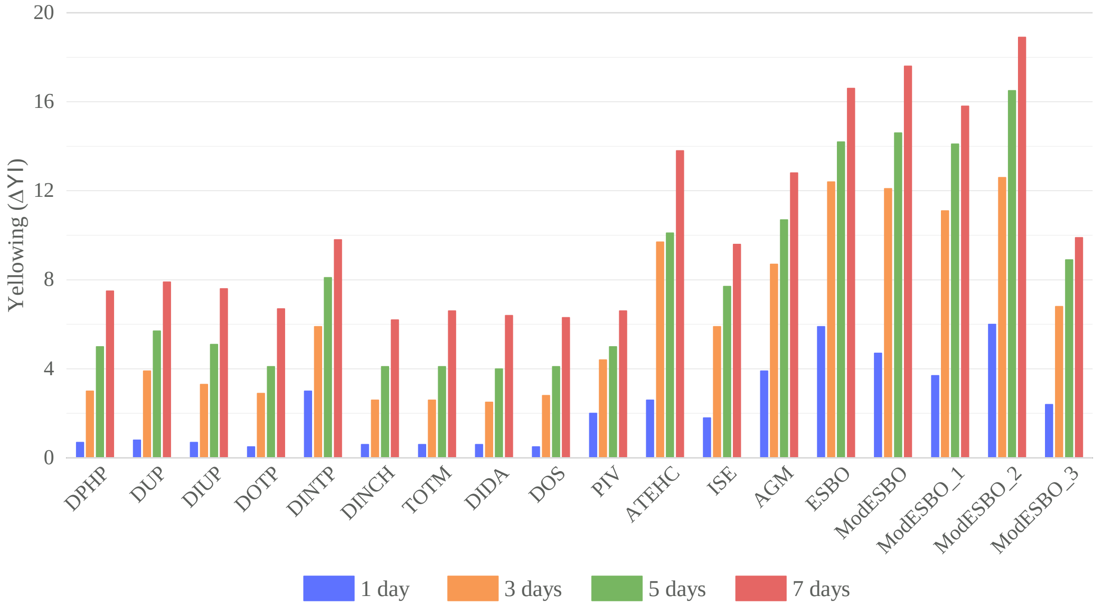

Figure 4.14: Thermal aging of samples obtained with recipe A.

Interestingly, plasticizers that yields better thermal stability (i.e. DINTP, ESBO and ModESBO_1) are those ones that underwent major colour changing in thermal aging test. At the same time, some of the plasticizers that behave poorly in thermal stability test (i.e. DOTP, DINCH, TOTM and ModESBO_3) show good colour retaining after heat aging, with better results than DPHP. There are, also, plasticizers that do not follow this trend. ModESBO_2 exhibits overall major signs of degradation both in thermal stability and thermal aging tests, while the best overall performer in both tests is PIV.

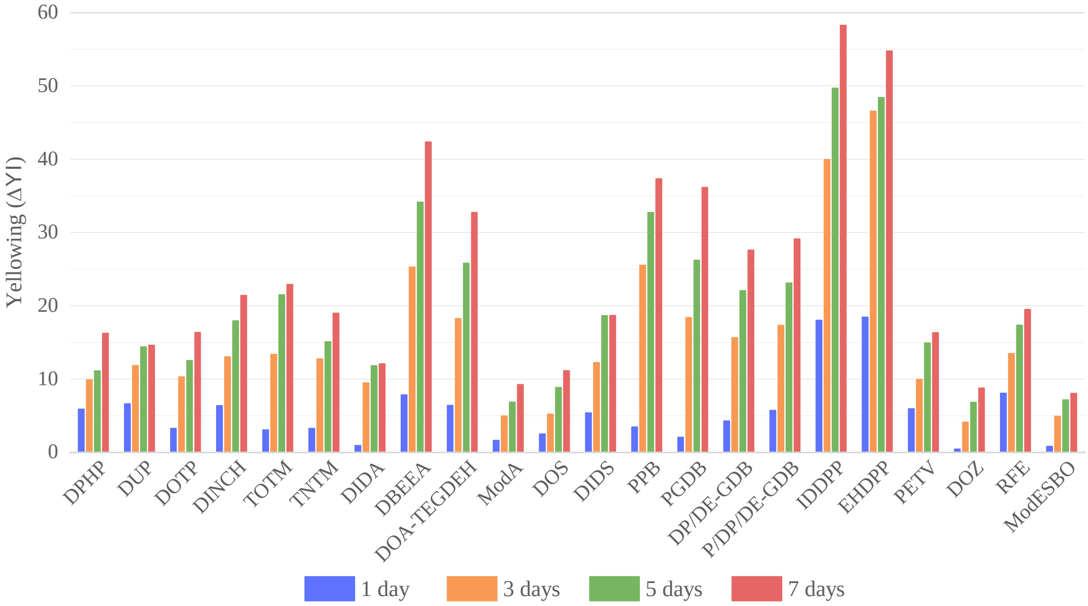

Figure 4.15: Thermal aging of samples obtained with recipe B.

Aged samples of the series obtained with recipe B (Figure 4.15) underwent greater colour changes, on average, than those obtained with recipe A. There is, however, a wide variation between results of the various plasticizers tested. This is particularly the case of the extremely high ΔYI measured on benzoate/dibenzoates (PPB, PGDB, DE/DP–GDB, P/DP/DE–GDB), phosphates (IDDPP, EHDPP), DBEEA and DOA–TEGDEH. These plasticizers exhibited also the worst performance in thermal stability test, with the exception of DOA–TEGDEH which behave similarly to DPHP, as well as PETV. Apart from the aforementioned plasticizers, other samples that have been subjected to colour changes higher than DPHP are DINCH, TOTM, TNTM, DIDS and RFE. These samples exhibited generally good thermal stability (Figure 4.11), as already seen for samples obtained with recipe A. The best results are shown by ModA, ModESBO and DOZ, followed by DOS and DIDA.

A comparison between plasticizers used with the two different recipes is reported in Figure 4.16.

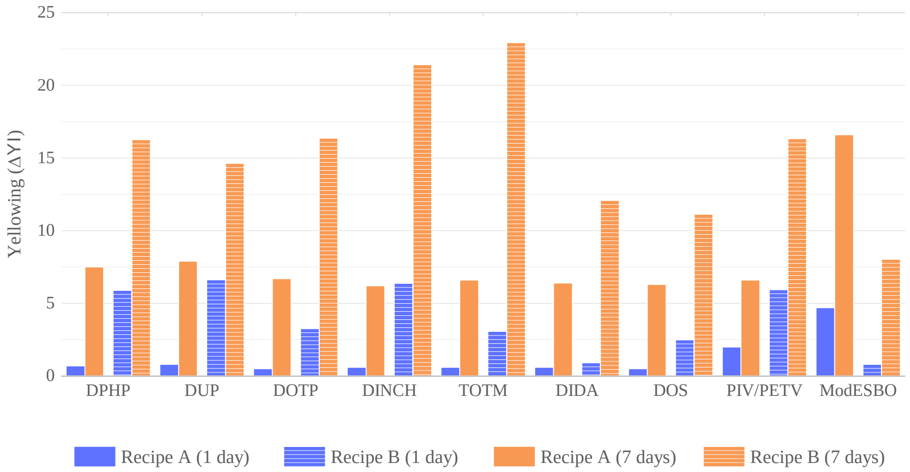

Figure 4.16: Comparison between thermal aging of plasticizers used in recipe A and B.

As already said, samples belonging to recipe B series exhibit lower resistance to thermal aging. Trends are somewhat opposite: if a plasticizer yields good results with one of the formulations, it is likely to show poorer results in the other. This is the case, for example, of DINCH and TOTM which behave far better in recipe A, or ModESBO which shows better results in recipe B. DOS and DIDA, even though perform slightly poorer in recipe B, yields good results in both recipes, with the latter which exhibited almost the same ΔYI after 1 day in each series.

- *Flame resistance*

The flame resistance of all the samples was determined by horizontal combustion test. This test is susceptible to the isotropy and orientation of the sample. This means that when testing a finite material, with a backing textile having uneven warp and weft, specimens must be cut out longitudinally and transversally to the machine direction and, thus, to the orientation of the textile. The test results must then be given as longitudinal or “machine direction” (L, MD) and transversal or “cross machine direction” (T, CMD). However, this is not the case because the pPVC foils obtained in laboratory may be considered anisotropic materials. Knowing how each plasticizer influences the burning behaviour of pPVC is of crucial importance to select and dose opportunely a FR system. It must be bear in mind that a typical limit value required by automotive industries, expressed as burning rate, is 100 mm/min. If a sample has a burning rate below this value, it is considered as complying with the specification. However, the lower the value the better the flame behaviour of the pPVC and, hence, the less need for FRs to be added at the formulation.

Table 4.8: Burning rate of the plasticizers used in both formulations.

	Recipe A	
#	***Plasticizer***	***BR (mm/min)***
1	**DPHP**	145
2	DUP	104
3	DIUP	97
4	DOTP	137
5	DINTP	114
6	DINCH	192
7	TOTM	62
8	DIDA	209
9	DOS	194
10	PIV	95
11	ATEHC	88
12	ISE	139
13	AGM	84
14	ESBO	48
15	ModESBO	158
16	ModESBO_1	165
17	ModESBO_2	60
18	ModESBO_3	206

	Recipe B	
#	***Plasticizer***	***BR (mm/min)***
1	**DPHP**	140
2	DUP	108
3	DOTP	140
4	DINCH	178
5	TOTM	58
6	TNTM	29
7	DIDA	164
8	DBEEA	134
9	DOA-TEGDEH	19
10	ModA	141
11	DOS	162
12	DIDS	123
13	PPB	76
14	PGDB	146
15	DP/DE-GDB	98
16	P/DP/DE-GDB	68
17	IDDPP	0
18	EHDPP	0
19	PETV	83
20	DOZ	158
21	RFE	127
22	ModESBO	169

Results of the horizontal combustion test, expressed as burning rate (BR, mm/min) are reported in Table 4.8. Being strongly dependent on the nature of plasticizer, results are only limitedly influenced by the two different recipes using different PVC resins. Burning rates of recipe A samples are reported in Figure 4.17, for better comprehension. The better performers are ESBO, ModESBO_2 and TOTM, which resulted in burning rates more than 50 % lower when compared to DPHP. Other good results are shown by AGM and ATEHC, while DIUP and PIV are slightly lower than the 100 mm/min limit value. The worst flame behaviour has been exhibited by DIDA, DOS, DINCH and ModESBO_3, with burning rates of approx. 200 mm/min. It is also possible to notice a trend in the homologous series of plasticizers families. Phthalates and terephthalates, in fact, exhibit lower burning rates when increasing the side chain length.

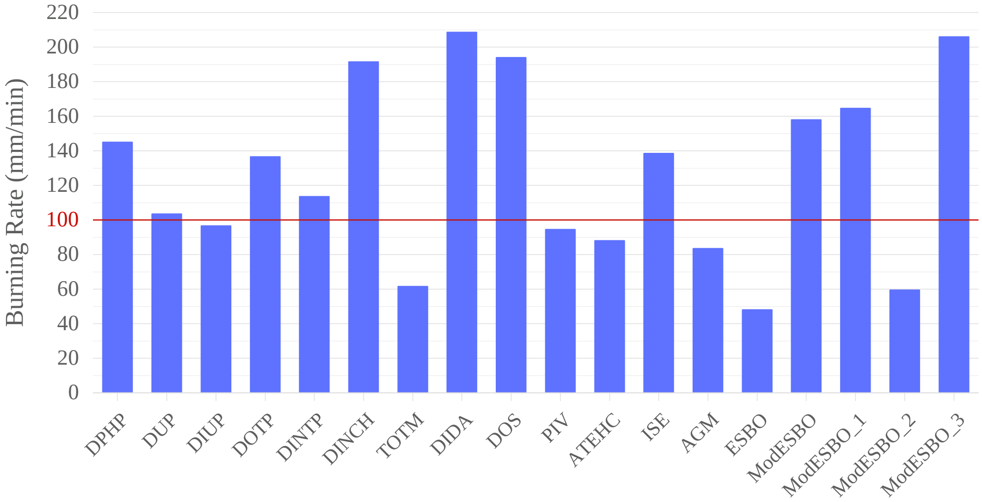

Figure 4.17: Burning rates of the samples obtained with recipe A.

Samples obtained with recipe B (Figure 4.18) exhibit basically lower burning rate values than recipe A ones. Optimal performances have been obtained by DOA–TEGDEH, trimellitates (TOTM, TNTM), most of the benzoates/dibenzoates (PPB, DP/DE–GDB, P/DP/DE–GDB) and PETV. As predictable, IDDPP and EHDPP yielded self–extinguish samples. In fact, phosphates are known to impart fire retardancy properties and are often used as secondary plasticizer to improve flame resistance. As previously seen, also in this series of sample a trend seems to exist in the homologous series of plasticizers families. In particular, it can be observed that burning rates of plasticizers with greater side chains length resulted in lower burning rates: TNTM < TOTM, DUP < DPHP, DIDS < DOS. It is also noticeable an unusual behaviour of the benzoates, with PGDB that imparts a very high burning rate to the sample; DP/DE–GDB has also a quite high burning rate, but the plasticizer which is constituted by a mixture of the same three molecules (i.e. P/DP/DE–GDB) performs better compared to the other two plasticizers.

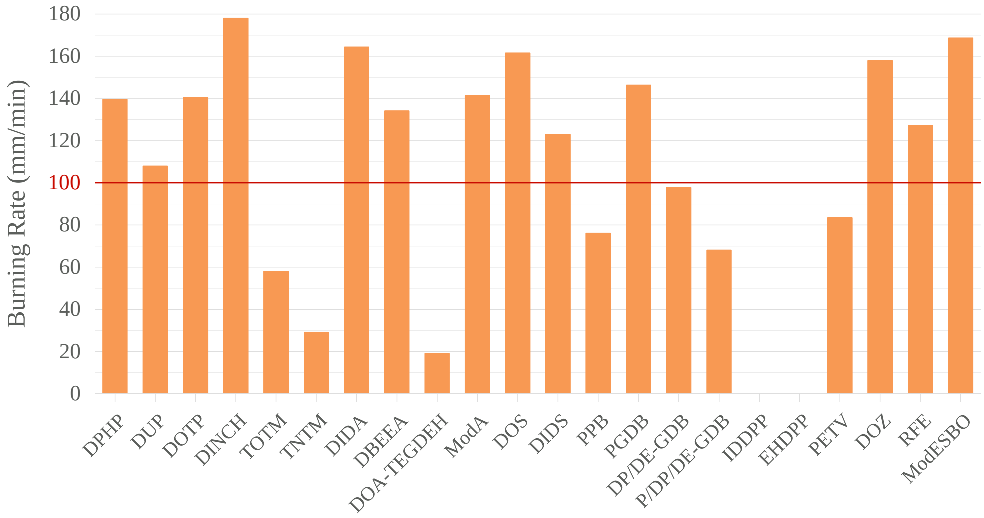

Figure 4.18: Burning rates of the samples obtained with recipe B.

A comparison between plasticizers employed with both formulations is reported in Figure 4.19. Highest differences are visible at high burning rate values, as in the case of DINCH, DOS and DIDA. The other samples show similar burning rates, faintly higher in recipe A formulation.

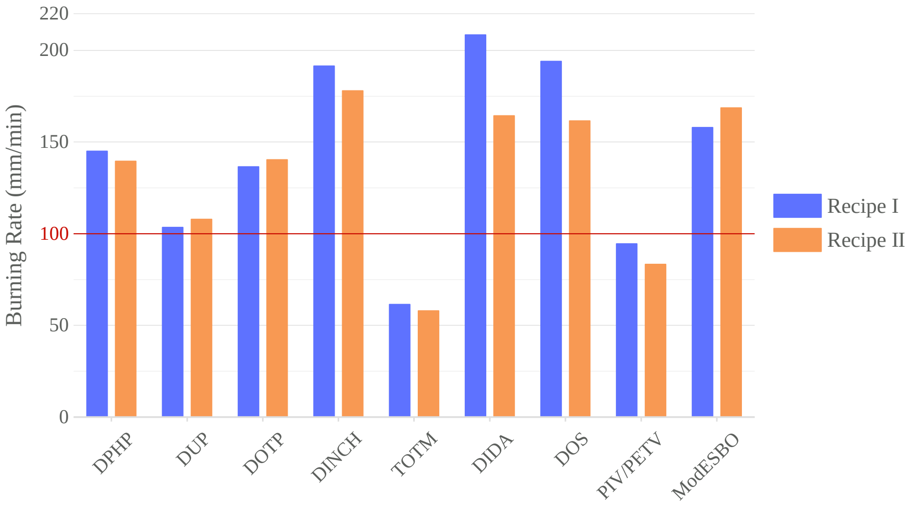

Figure 4.19: Comparison between burning rates of plasticizers used in recipe A and II.

4.2.4. Volatility and migration properties

- *Fogging*

The fog test was carried out for all the samples. This test is one of the many possible measures of the volatile fraction contained in a material. In particular, the test measures a property called *fogging*, which represents the amount of semi–volatiles compounds (SVOC) which could be released by heating and subsequently condensate on a cold surface. Fogging values are of particular importance in the automotive industry, because they are obtained simulating what commonly happens inside a vehicle which is subjected to heating/cooling cycles, for example in summer when hot days are followed by fresh nights. Both the gravimetric (GF, mg) and reflectometric (RF, %) fogging results are reported in Table 4.9.

Table 4.9: Gravimetric and reflectometric fogging results of the two series of samples.

	Recipe A		
#	*Plasticizer*	*GF (mg)*	*RF (%)*
1	**DPHP**	0.82	80
2	DUP	0.73	82
3	DIUP	1.00	94
4	DOTP	2.36	30
5	DINTP	0.62	76
6	DINCH	2.37	32
7	TOTM	0.34	84
8	DIDA	1.63	48
9	DOS	1.38	49
10	PIV	0.26	77
11	ATEHC	1.85	83
12	ISE	27.5	22
13	AGM	0.69	60
14	ESBO	0.15	91
15	ModESBO	1.46	44
16	ModESBO_1	1.19	51
17	ModESBO_2	1.01	45
18	ModESBO_3	1.99	31

	Recipe B		
#	*Plasticizer*	*GF (mg)*	*RF (%)*
1	**DPHP**	0.60	73
2	DUP	0.27	83
3	DOTP	2.94	33
4	DINCH	2.34	32
5	TOTM	0.32	84
6	TNTM	0.41	98
7	DIDA	1.48	49
8	DBEEA	1.27	64
9	DOA-TEGDEH	1.15	60
10	ModA	1.73	49
11	DOS	1.11	53
12	DIDS	0.50	89
13	PPB	94.9	12
14	PGDB	96.9	16
15	DP/DE-GDB	50.9	29
16	P/DP/DE-GDB	52.0	17
17	IDDPP	8.11	38
18	EHDPP	6.57	35
19	PETV	1.10	60
20	DOZ	1.68	47
21	RFE	5.88	33
22	ModESBO	3.13	51

Fogging results are less dependent to the formulation and more influenced by the nature of the plasticizer. Typically, the automotive industries set quite strict limits regarding the results of this test. The reasons of this choice are clearly understandable and absolutely embraceable, because the emission arising from these material (VOC and SVOC) are of concern for vehicle air quality and, hence, for the health of the passengers. Typical limit values are 1.0 mg or less for GF and 90 % or more for RF. However, these limits are intended for the finite materials, which are more complex in terms of construction and formulation of each layer. Moreover, the lacquers applied on the surface, even though they can limitedly contribute to the SVOC fraction, act as a physical barrier to the leakage and emission of substances from the underlying layers. Hence, the test of simple foils as performed in the present work, may use broader limit values: GF is considered optimal when less than 0.6 mg, but acceptable up to 1.5 mg; RF is considered optimal if more than 85 %, but acceptable if 70 % or higher. Results for samples obtained with recipe A are reported in Figure 4.20 (GF) and Figure 4.21 (RF).

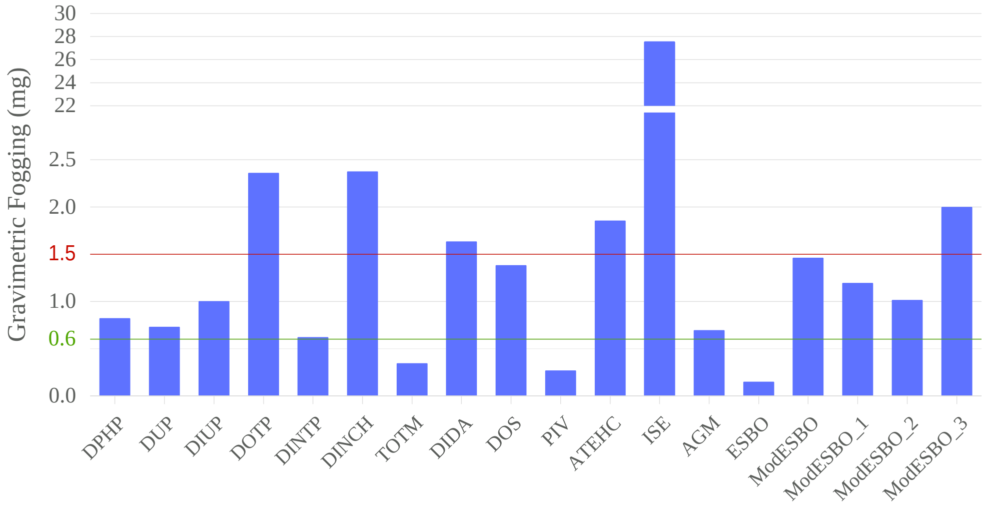

Figure 4.20: Gravimetric fogging of samples obtained with recipe A.

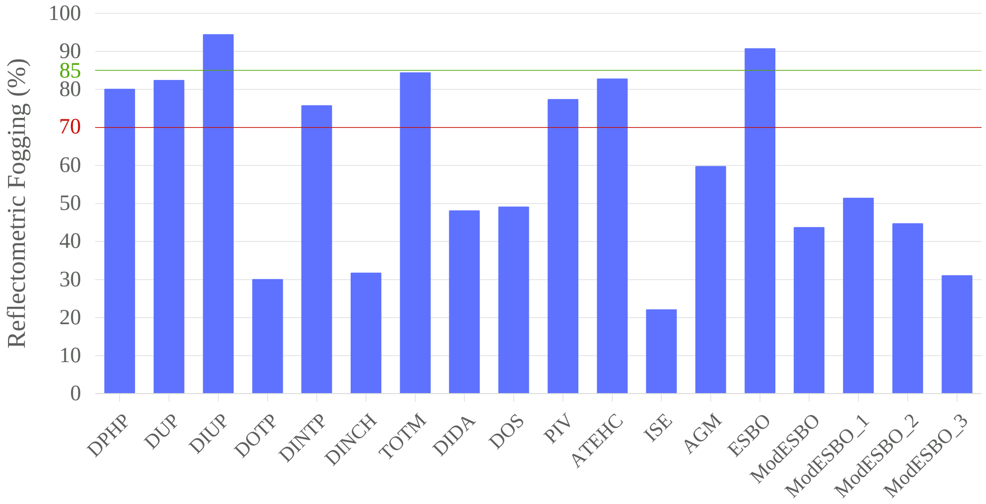

Figure 4.21: Reflectometric fogging of samples obtained with recipe A.

Gravimetric and reflectometric fogging are clearly linked: when the first one increases, the second one decreases. This is due to the method of expressing RF as the gloss percentage of the fogged compared to the clean glass plate. This relationship is, however, not proportional. Results obtained in the gravimetric test revealed poor performance of ISE, DINCH, DOTP and ModESBO_3. The first one exhibits a GF value of 27.5 mg, which is more than 18 times the acceptable limit of 1.5 mg. For the aforementioned reasons, RF value of these plasticizers are the lowest recorded, with the glass plate that retained, respectively, the 22, 32, 30 and 31 % of its initial gloss. The non–proportional relationship previously mentioned is easily observable in the cases of DIDA, DOS, AGM and ModESBO, ModESBO_1 and ModESBO_2. These plasticizers exhibit, in fact, low values of GF (mostly below 1.5 mg) but also low values of RF (mostly below 50 %). Probably, these plasticizers have quite low volatility but once condensed on the cold surface, they are able to form an opaque continuous film that dramatically decreases the gloss value measured. Phthalates, DINTP, TOTM, PIV and ESBO performed extremely well in both tests, particularly the latter with GF = 0.15 mg and RF = 91 %. Also, DINTP results are in great contrast with its lighter homologous DOTP.

Results of samples obtained following recipe B are reported in Figure 4.22 (GF) and Figure 4.23 (RF).

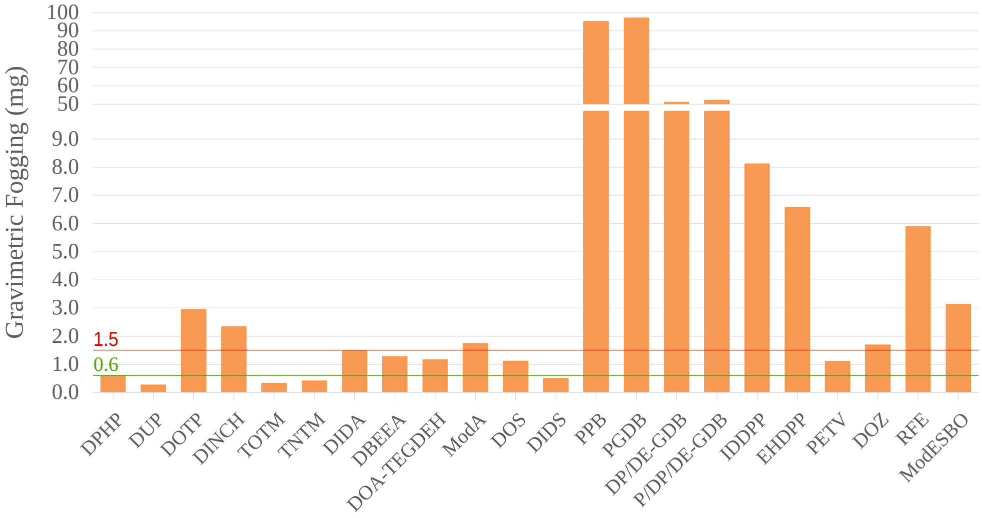

Figure 4.22: Gravimetric fogging of samples obtained with recipe B.

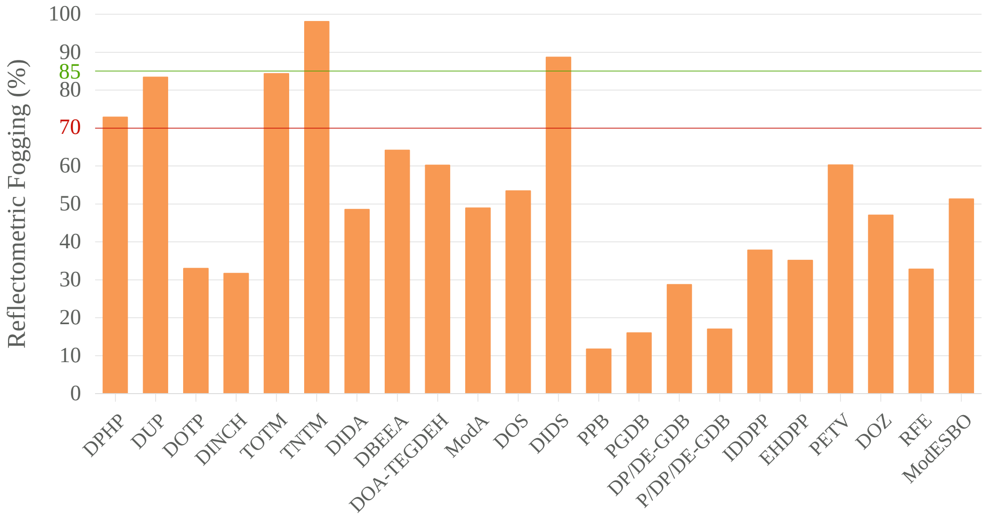

Figure 4.23: Reflectometric fogging of samples obtained with recipe B.

Correspondingly to what observed with samples obtained with recipe A, also in this series of samples different behaviours may be observed. Benzoate/dibenzoates and phosphates yields the worst results, with the lighter species (PPB, PGDB) that produce approximately 100 mg of condensates and less than 20 % of the initial gloss of the glass plates. Thus, these additives are not suitable for automotive interior applications. DINCH and DOTP give also poor results, as well as RFE and ModESBO. Other plasticizers exhibit an uncertain result, with good GF and poor RF results: these samples are the adipates, DOS, DOZ and PETV. Finally, phthalates, trimellitates and DIDS performed well in both the tests, with TNTM that yields GF = 0.41 mg and RF = 98 %.

A comparison between the samples obtained with recipe A and recipe B is reported in Figure 4.24 (GF) and Figure 4.25 (RF).

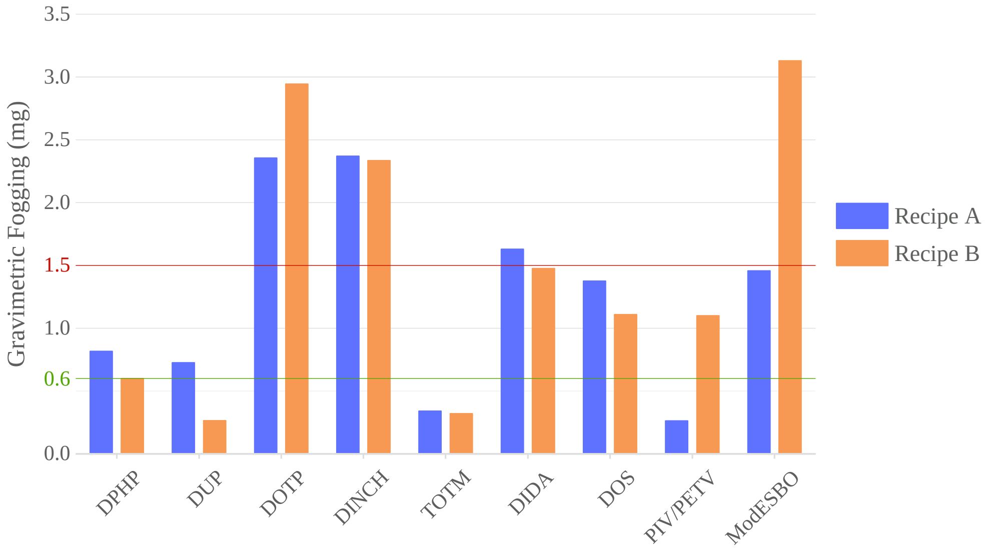

Figure 4.24: Comparison between gravimetric fogging plasticizers used in recipe A and B.

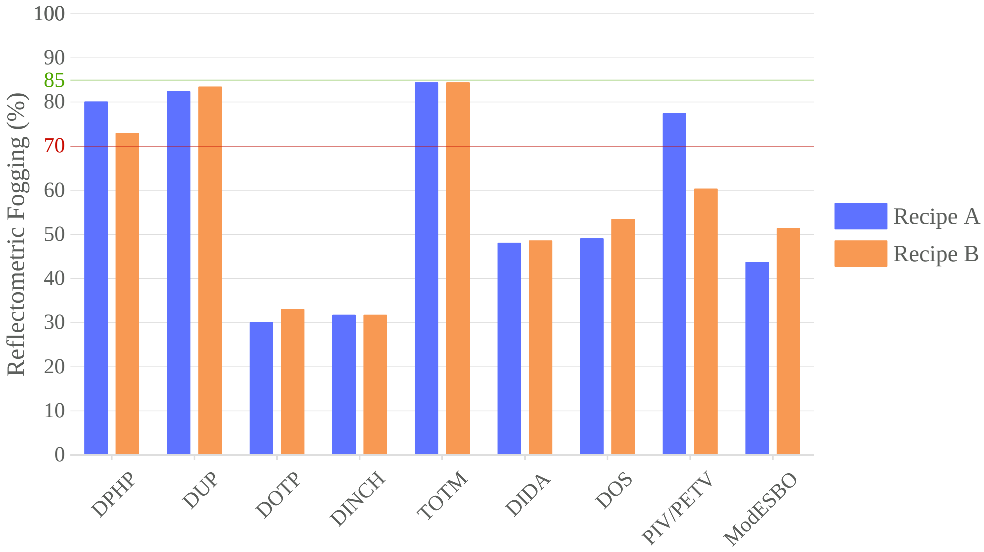

Figure 4.25: Comparison between reflectometric fogging plasticizers used in recipe A and B.

The direct comparison between the two formulations does not show particular differences. Results are quite similar with no relevant trends in any sense, with the only two exceptions being PIV/PETV and ModESBO. The first plasticizer in fact shows optimal performances in recipe A while when used in recipe B it shows good results only in GF test. An opposite behaviour is shown by ModESBO, which exhibits poor RF values and a good GF only when used in recipe A.

- <u>*Odour*</u>

The odour test, as subjective, is of paramount concern in the automotive industry. Substances emanating unpleasant odours are not acceptable for interiors materials. The test was carried out keeping the samples for 3 hours at 60 °C prior to evaluation by five different operators, which rated each sample according to the scale reported in Paragraph 3.2.4. Typically, the automotive industries reject materials with odour values greater than "3". The obtained results are reported in

Table 4.10, where the ratings higher than “3” are given in red for easier reading.

Table 4.10: Evaluation of the odour of the two series of samples.

	Recipe A	
#	*Plasticizer*	*Odour*
1	**DPHP**	2
2	DUP	2
3	DIUP	2
4	DOTP	2
5	DINTP	4
6	DINCH	2
7	TOTM	2
8	DIDA	2
9	DOS	2
10	PIV	4
11	ATEHC	5
12	ISE	5.5
13	AGM	2
14	ESBO	4
15	ModESBO	4
16	ModESBO_1	4
17	ModESBO_2	3
18	ModESBO_3	4

	Recipe B	
#	*Plasticizer*	*Odour*
1	**DPHP**	2
2	DUP	2
3	DOTP	2
4	DINCH	2
5	TOTM	2
6	TNTM	2
7	DIDA	2
8	DBEEA	4
9	DOA-TEGDEH	4.5
10	ModA	3.5
11	DOS	2
12	DIDS	3.5
13	PPB	3
14	PGDB	4.5
15	DP/DE-GDB	4
16	P/DP/DE-GDB	4
17	IDDPP	3
18	EHDPP	3
19	PETV	4
20	DOZ	3
21	RFE	3.5
22	ModESBO	3.5

The obtained data highlight that formulation does not substantially affect the odours released by the pPVC samples and, thus, plasticizers are almost totally responsible for that. Furthermore, bio–plasticizers exhibited the worst results, which could be easily explained by the vegetable origin of these additives. In fact, the majority of these compounds are derived from vegetable oils (i.e. soybean oil) or other raw materials obtained by the chemical or biochemical modification of plant crops. This is, unfortunately, one of the major drawbacks and limitation to the widespread diffusion of these green additives in the automotive industry, despite the efforts of the manufacturers to find effective deodorization techniques for these compounds.

- *Migration*

Migration is intended as the tendency that plasticizers have to move to the surface of the pPVC and leave the material, both towards the atmosphere or being absorbed and transferred to another material or medium. Migration of plasticizers used in the two formulations was evaluated according to different tests, due the different hypothetical application and the specifications required by the different customers. Hence, the data obtained are difficultly comparable, but inside each series various considerations may be done. Table 4.11summarizes the results, expressed as weight decrease percentage of the sample, of the different tests conducted: semi–rigid foil migration (SFRM) and soapy water migration (SWM) or butter migration (BM), as described in Paragraph 3.2.4.

Table 4.11: Migration results of the samples obtained with recipe A and B.

		Recipe A	
#	***Plasticizer***	***SFRM (wt%)***	***SWM (wt%)***
1	**DPHP**	5.4	1.8
2	DUP	3.6	1.5
3	DIUP	3.5	1.0
4	DOTP	8.0	2.0
5	DINTP	5.8	1.8
6	DINCH	8.9	2.1
7	TOTM	0.5	0.8
8	DIDA	6.8	3.0
9	DOS	8.5	2.7
10	PIV	7.6	1.3
11	ATEHC	0.8	0.5
12	ISE	10.6	5.7
13	AGM	4.8	3.2
14	ESBO	3.6	0.0
15	ModESBO	5.4	2.0
16	ModESBO_1	5.3	1.0
17	ModESBO_2	1.2	0.3
18	ModESBO_3	8.9	1.6

		Recipe B	
#	***Plasticizer***	***SFRM (wt%)***	***BM (wt%)***
1	**DPHP**	3.6	3.0
2	DUP	4.6	7.1
3	DOTP	4.5	6.2
4	DINCH	7.5	7.9
5	TOTM	0.7	1.4
6	TNTM	0.9	2.7
7	DIDA	6.9	14.1
8	DBEEA	13.2	17.5
9	DOA-TEGDEH	1.7	0.6
10	ModA	5.8	14.3
11	DOS	3.7	16.3
12	DIDS	6.0	9.5
13	PPB	20.0	9.4
14	PGDB	18.2	2.2
15	DP/DE-GDB	14.4	3.1
16	P/DP/DE-GDB	15.6	3.2
17	IDDPP	15.2	6.0
18	EHDPP	14.9	7.0
19	PETV	4.9	5.1
20	DOZ	8.7	15.4
21	RFE	10.1	8.5
22	ModESBO	4.8	6.7

The tests involving the series of samples obtained with recipe A (Figure 4.26) indicate that some plasticizers are, to a certain extent, resistant to migration in both the medium and, thus, have a good persistence inside pPVC. These plasticizers, with superior performance compared to DPHP, are TOTM, ATEHC, ModESBO_2 and, in a lesser measure, DUP and DIUP. ESBO are not extracted at all by the test in soapy water and performs quite well against semi–rigid foil. PIV, ModESBO_1 and ModESBO_3, instead, show similar or higher migration than DPHP into semi–rigid foils. AGM has an opposite behaviour, being quite resistant to migration into semi–rigid foil but highly extractable in soapy water. All the other plasticizers behave poorly, with particularly high migration values registered by ISE, DINCH, DIDA, DOS and DOTP. Lastly, TOTM is the only sample in the set that exhibits higher plasticizer losses in soapy water than in semi–rigid foil.

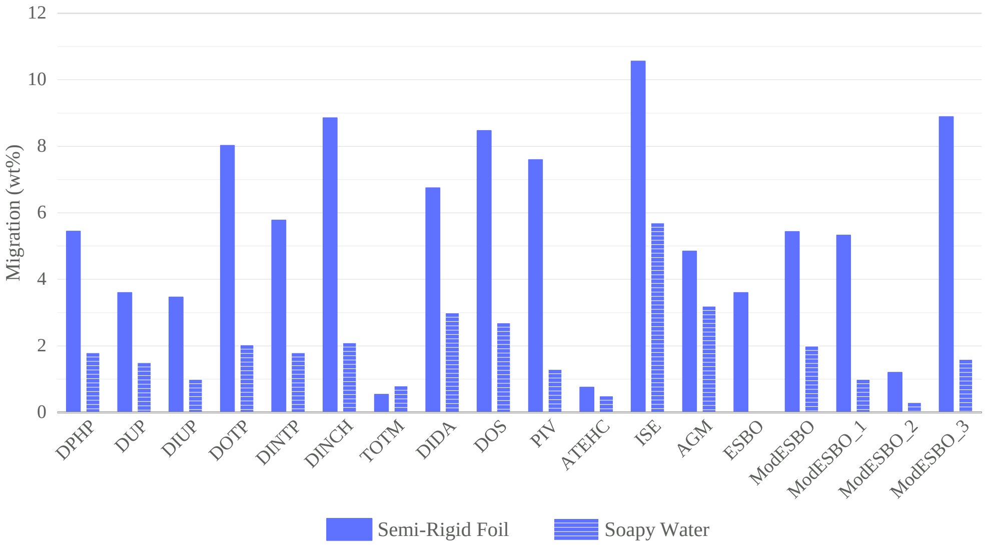

Figure 4.26: Migration performances of samples obtained with recipe A.

The tests performed on recipe B samples (Figure 4.27), semi–rigid foil and butter (not soapy water) migration, show that TOTM, TNTM and DOA–TEGDEH perform globally better than DPHP, with the latter one being almost non–extracted by butter. Also, PETV, DUP, DOTP and ModESBO exhibit a global low tendency to migration. More specifically, semi–rigid foil migration (SRFM) sees optimal performance by the reference (DPHP), trimellitates (TOTM, TNTM) and DOA–TEGDEH, while benzoate/dibenzoates (PPB, PGDB, DP/DE–GDB, P/DP/DE–GDB), show the worst performance, with PPB and PGDB that result in plasticizer losses of the order of magnitude of 20 wt%. These plasticizers obtained poor results also in the fogging tests, and it is arguable that the reason is an extremely low compatibility with PVC. Regarding the butter migration (BM), all the plasticizers are easily extracted with the exception of the reference (DPHP), trimellitates (TOTM, TNTM), dibenzoates (PGDB, DP/DE–GDB, P/DP/DE–GDB) and, in particular, DOA–TEGDEH.

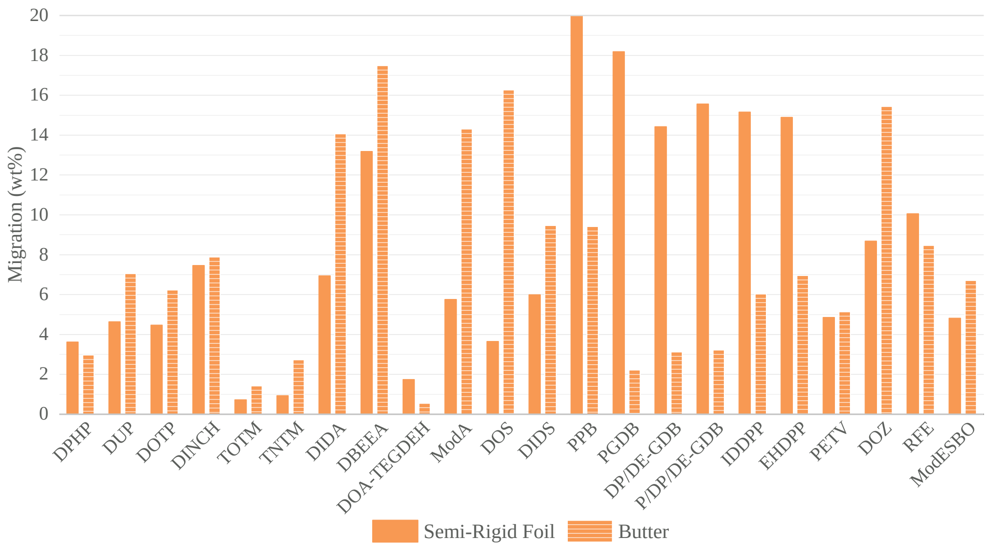

Figure 4.27: Migration performances of samples obtained with recipe B.

4.3. Conclusions

Several compounds were used to plasticize PVC as alternatives to the more common but potentially hazardous phthalates. In fact, even though HMW phthalates are not considered particularly harmful, the trend of both legislators and final users is to move towards phthalate–free materials. Thus, more than 40 plasticizers were screened amongst commercial or pre–market proposal, and more than 30 of them were tested in depth. In particular each plasticizer was added to two different formulations and the obtained samples were subjected to several tests typically performed by PVC synthetic leather producers according to international standards, automotive companies' methods and specifications and, in some cases, Vulcaflex internal methods. A particular attention was given to the determination of mechanical and thermal properties imparted by each plasticizer, together with their volatility and their migration tendency. The obtained results are summarized below.

- *Mechanical properties*

Samples with higher mechanical properties than DPHP were obtained with both recipes. The obtained data show generally higher hardness and tensile properties for samples obtained with recipe A, which is a quite unexpected results. In fact, recipe B is formulated with a K82 PVC resin, which should improve mechanical properties. However, the use of a blend of PVC resin could possibly be responsible for a lack of compatibility with the plasticizers and, thus, for the poorer results. A ranking of the results of mechanical tests performed on plasticizers evaluated in recipe A formulations is reported in Table 4.12.

Table 4.12: Mechanical properties of samples obtained with recipe A.

	Recipe A			
#	*SH$_A$*	*UTS (Mpa)*	*EB (%)*	*CR*
1	DOS	ISE	AGM	DIDA
2	PIV	AGM	ModESBO_1	DOS
3	ModESBO_1	PIV	DOS	ModESBO_3
4	ModESBO_3	DINTP	PIV	DOTP
5	AGM	ATEHC	ModESBO	ModESBO_1
6	ModESBO	ModESBO_2	ModESBO_3	PIV
7	DOTP	ESBO	**DPHP**	DIUP
8	TOTM	TOTM	ISE	DINCH
9	ISE	ModESBO	DIUP	ISE
10	ESBO	ModESBO_1	ModESBO_2	AGM

Recipe A yielded generally good results with bioplasticizers (in green), particularly PIV and AGM, followed by ModESBO_1. The best amongst the fossil fuel based is DOS, due to its low hardness and superior performance at low temperatures, followed by DOTP and TOTM. Almost in every type of test, phthalates (in red) are not amongst the best plasticizers, hence this formulation is particularly suitable for their substitution with other classes of molecules.

Analogously, a ranking of the sample obtained with recipe B is reported in Table 4.13.

Table 4.13: Mechanical properties of samples obtained with recipe B.

	Recipe B			
#	*SH$_A$*	*UTS (Mpa)*	*EB (%)*	*CR*
1	IDDPP	**DPHP**	DOZ	DIDA
2	PETV	RFE	EHDPP	DOS
3	EHDPP	P/DP/DE-GDB	DOTP	DUP
4	DOS	DOTP	RFE	DBEEA
5	DOZ	DIDS	DINCH	DOZ
6	PPB	DINCH	DBEEA	PETV
7	ModESBO	DUP	**DPHP**	DOTP
8	DBEEA	TOTM	IDDPP	**DPHP**
9	DP/DE-GDB	PGDB	DUP	DINCH
10	P/DP/DE-GDB	DP/DE-GDB	PPB	TNTM

Recipe B sees general lower values and also a different trend. Renewable based plasticizers (in green) are not ranked particularly well, while benzoates/dibenzoates and phosphates are particularly good performers. The two phthalates (in red) present in this series of samples yielded especially good results, to the point that in UTS tests none of plasticizers outperformed DPHP. All things considered, **DOZ**, **EHDPP** and **PETV** are amongst the best performers.

- *Thermal properties*

Most of the plasticizers tested impart positive effects on thermal stability, thermal aging and flame resistance, when compared to the reference (DPHP) and the other phthalates (DUP, DIUP), even though these plasticizers (in red) perform generally well in this series of tests. A ranking is reported in Table 1.14.

Table 4.14: Thermal and flame properties of samples obtained with recipe A and B.

Recipe A				*Recipe B*			
#	*TS* (ΔYI_{16min})	*TA* (ΔYI)	*BR* (mm/min)	#	*TS* (ΔYI_{16min})	*TA* (ΔYI)	*BR* (mm/min)
1	DOS	DINCH	ESBO	1	TOTM	ModESBO	IDDPP
2	PIV	DOS	ModESBO_2	2	DINCH	DOZ	EHDPP
3	DIDA	DIDA	TOTM	3	DIDS	ModA	DOA-TEGDEH
4	ESBO	TOTM	AGM	4	ModESBO	DOS	TNTM
5	DUP	PIV	ATEHC	5	DIDA	DIDA	TOTM
6	ModESBO_1	DOTP	PIV	6	DOTP	DUP	P/DP/DE-GDB
7	DIUP	**DPHP**	DIUP	7	ModA	**DPHP**	PPB
8	**DPHP**	DIUP	DUP	8	DOZ	PETV	PETV
9	DOTP	DUP	DINTP	9	PETV	DOTP	DP/DE-GDB
10	DINCH	ISE	DOTP	10	DOS	DIDS	DUP

Recipe A series see PIV, DOS and ESBO as the best substitutes for DPHP. More variegate is the result pattern concerning recipe B, mostly due to the presence of phosphates and, even though more limitedly, benzoate/dibenozates. In fact, these compounds achieved very good results in the horizontal combustion test, with phosphates that impart self–extinguish properties to the pPVC foils, confirming what stated in literature [4, 5, 20]. **ModESBO**, **TOTM** and **DOZ** are the plasticizers that exhibited the best results.

- *Volatility properties*

The results obtained by phthalates (in red) in all of these tests, particularly the odour test, are one of the reasons for their widespread use. In fact, a fewer number of alternative plasticizers give better results than DPHP and other phthalates when compared to the other series of tests.

Results for recipe A samples are reported in Table 4.15.

Table 4.15: Volatility properties of sample obtained with recipe A.

			Recipe A		
#	*GF (mg)*	*RF (%)*	*SRFM (wt%)*	*SWM (%)*	*Odour*
1	ESBO	DIUP	TOTM	ESBO	**DPHP**
2	PIV	ESBO	ATEHC	ModESBO_2	DUP
3	TOTM	TOTM	ModESBO_2	ATEHC	DIUP
4	DINTP	ATEHC	DIUP	TOTM	DOTP
5	AGM	DUP	DUP	DIUP	DINCH
6	DUP	**DPHP**	ESBO	ModESBO_1	TOTM
7	**DPHP**	PIV	AGM	PIV	DIDA
8	DIUP	DINTP	ModESBO_1	DUP	DOS
9	ModESBO_2	AGM	ModESBO	ModESBO_3	AGM
10	ModESBO_1	ModESBO_1	**DPHP**	**DPHP**	ModESBO_2

Renewable based plasticizers gave particularly good results, showing good compatibility that translates in quite low fogging and migration, particularly in the case of ESBO. However, the weak point of these bioplasticizers is, as previously mentioned, odorous emissions which makes it difficult their use as primary plasticizers in SLs for the automotive interior industry. Amongst the possible substitutes for phthalates plasticizers, on materials based on recipe A, the best candidates are **TOTM** and **ESBO**. A ranking of the sample obtained with recipe B is reported in Table 4.16.

Table 4.16: Volatility properties of sample obtained with recipe B.

			Recipe B		
#	*GR (mg)*	*FR (%)*	*SRFM (wt%)*	*BM (%)*	*Odour*
1	DUP	TNTM	TOTM	DOA-TEGDEH	**DPHP**
2	TOTM	DIDS	TNTM	TOTM	DUP
3	TNTM	TOTM	DOA-TEGDEH	PGDB	DOTP
4	DIDS	DUP	**DPHP**	TNTM	DINCH
5	**DPHP**	**DPHP**	DOS	**DPHP**	TOTM
6	PETV	DBEEA	DOTP	DP/DE-GDB	TNTM
7	DOS	PETV	DUP	P/DP/DE-GDB	DIDA
8	DOA-TEGDEH	DOA-TEGDEH	ModESBO	PETV	DOS
9	DBEEA	DOS	PETV	IDDPP	PPB
10	DIDA	ModESBO	ModA	DOTP	IDDPP

Bio–based plasticizers did not perform particularly well in this formulation, and generally few plasticizers outperformed DPHP. These are **TOTM** and **TNTM**, but a mention should be reserved for **DOA–TEGDEH**, especially for its great resistance to migration.

- *Overall performances*

Summarizing the rankings reported above, the overall performance of the plasticizers used in both recipes is reported in Table 4.17.

Table 4.17: overall performances of samples obtained with recipe A and B.

	Recipe A				*Recipe B*		
#	*Mechanical*	*Thermal*	*Volatility*	*#*	*Mechanical*	*Thermal*	*Volatility*
1	PIV	PIV	TOTM	1	DOZ	ModESBO	TOTM
2	AGM	DOS	ESBO	2	DOTP	TOTM	TNTM
3	ModESBO_1	ESBO	DIUP	3	EHDPP	DOZ	DUP
4	ModESBO_3	DIDA	DUP	4	DOS	ModA	DOA-TEGDEH
5	DOS	TOTM	ATEHC	5	RFE	DIDA	DIDS
6	DOTP	DINCH	ModESBO_2	6	PETV	PETV	DOS
7	TOTM	DUP	PIV	7	DINCH	DOTP	PETV

Based on these results, the best plasticizers that could be viable alternatives for phthalates are:

- Recipe A: **PIV**, **TOTM** and **ESBO**, with the limitation posed by the odour test results for the renewable based plasticizers.
- Recipe B: **TOTM**, **DOZ** and **DOTP**, with, however, the poor performance of the bio–plasticizer (DOZ) in the volatility and migration tests.

All these considered, TOTM is the best substitute for phthalates amongst the fossil fuel based plasticizers. Greener alternatives are represented by ESBO, PIV/PETV and DOZ, but issues related to their odorous emissions still needs to be overcome.

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5

Flame Retardants

5.1. Introduction

Flame resistance is one of the key properties that plastic materials should have in order to be used in specific applications, ranging from electric and electronics devices (wirings or components), to household appliances and building components, and, also, automotive parts both for exteriors and, particularly, interiors of vehicles. When exposed to sufficient heat, polymers release flammable volatiles as a result of pyrolysis and decomposition reactions occurring in the solid phase. At this point, the flammable compounds could ignite spontaneously (autoignition) or in presence of an external source, as sparks or flames (flash ignition) [1]. Once ignited, the flammable compounds, referred to as *fuel*, undergo radical oxidation reactions and burn, generating heat which acts as thermal feedback on the endothermal pyrolysis reactions that will then proceed, triggering a self–sustaining cycle. The more heat is produced by combustion reaction, the more the pyrolysis rate increases, resulting in high velocity on the flame front and, thus, on the flame spread. A scheme of the flame propagation and the macroscopic interconnections between the phenomena occurring during combustion is reported in Figure 5.1.

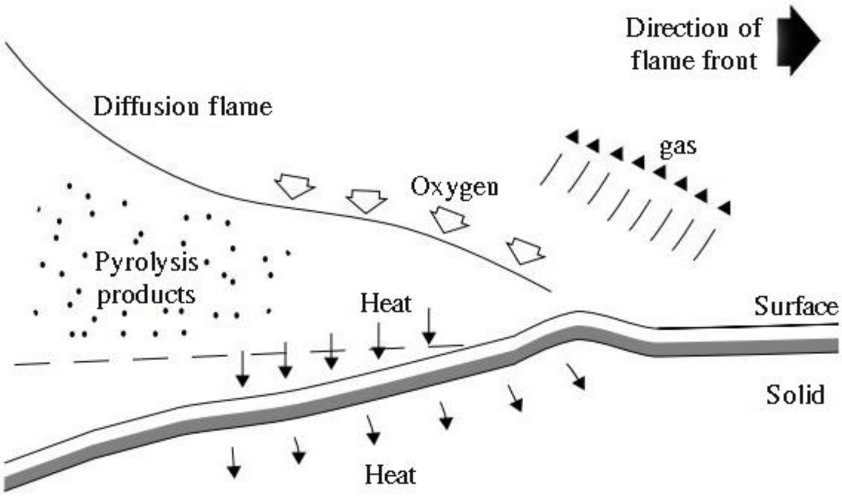
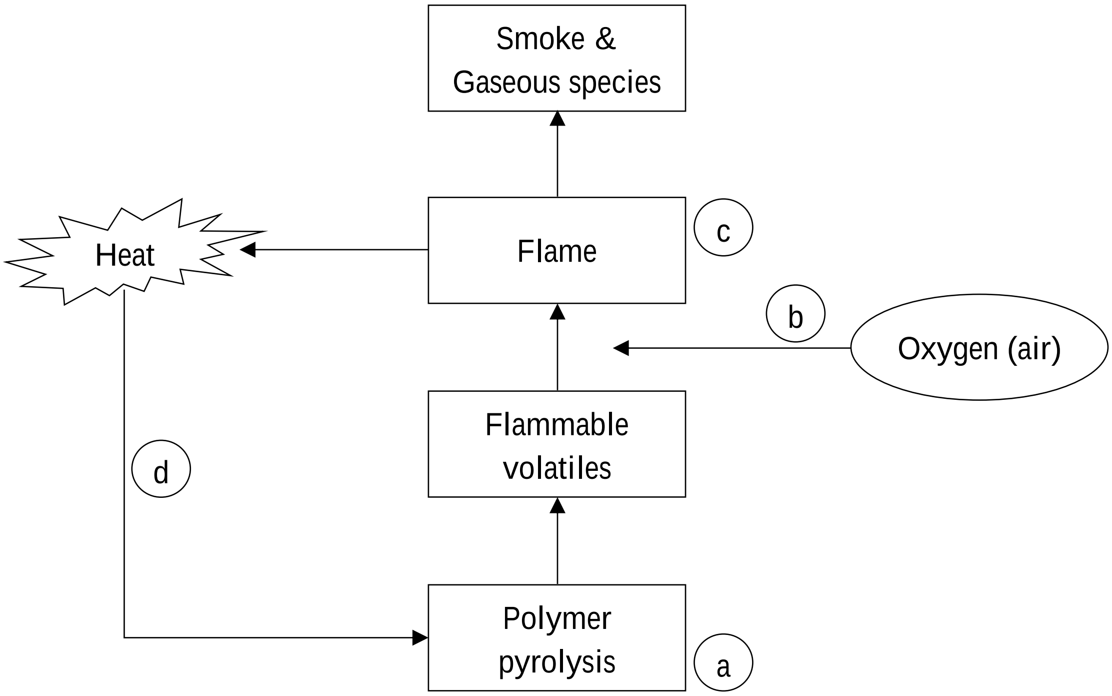


Figure 5.1: representation of the combustion process and flame spread [2].

Typically, flame retardancy is granted by the addition of specific additives known as flame retardants (FRs), that act delaying the ignition of the material and/or decreasing its chance, possibly lending less efficient burning and imparting self–extinguishing effects.



Scheme 5.1: self-sustaining combustion cycle and modes of action of flame retardants (a-d) [1].

These additives have the aim to break the combustion reactions (Scheme 5.1) with different mechanisms of action, which are obtained by:

a) formation of a char surface layers, which are poorly flammable and isolate the fuel from the flame (it acts on the initial pyrolysis reactions);
b) dilution of the oxidizing agent (i.e. oxygen/air), making it less available for the combustion reactions in the flame zone;
c) introduction, in the combustion radical reactions cycle, of chemicals that interfere with flame propagation. Particularly effective compounds are chlorine and bromine atoms, and this flame inhibition is often referred to as “flame poisoning”;
d) reduction of the feedback heat that promotes further pyrolysis reactions, using a heat sink (i.e. a compound that decomposes endothermally) as aluminium hydroxide (ATH, $Al(OH)_3$).

Mechanism “a” is explicated in solid (or condensed) phase, while “b” and “c” happen in vapour phase. Obviously, it is possible to create synergistic systems that simultaneously take advantage of more than one of these pathways. The choice of the FR and hence, to the mechanism of action, is also related to the nature of the polymer which needs fire retardancy. In fact, each material respond diversely to heat, ignition and combustion and, hence, not all of the previously listed mechanisms are suitable for all the possible polymeric materials.

As previously stated, one of the key features of PVC and other chlorinated polymers (i.e. Poly(Vinylidene Chloride), PVDC; Chlorinated Poly(Vinyl Chlorine), CPVC; Chlorinated Polyethylene, PE–C) is the presence, along the polymer chains, of chlorine atoms. In particular, PVC has a chlorine content of 56,8 wt% which is a sufficient amount to make uPVC materials not easily ignitable and easily extinguishable, hence almost not flammable. These assertions are confirmed by rigid PVC flame properties measured by Limiting Oxygen Index (LOI) [3], and flammability standard test UL 94 [4]. The first one measures the minimum concentration of oxygen that will support the combustion of polymer, and is an index of the ease of extinction of a material fire; the latter one is a measure of material's tendency to spread the flame and it is widely used in various specification and building requirements. In fact, rigid PVC has a LOI of 45–49 [5], meaning that an oxygen concentration of 45 vol% is needed to support its combustion[*], and classifies as UL 94 V–0 which means that the samples stop burning within 10 seconds since ignition on a vertical specimen, without the formation of inflamed drips.

However, the high plasticizer loading used to soften PVC and, thus, necessary for the manufacturing of synthetic leathers (SLs) changes the fire response of pPVC which becomes, in most cases, a flammable material. Hence, these products need the addition of FRs in their formulation.

- *Flame Retardants for pPVC*

The most widely used FR for pPVC is antimony trioxide (ATO, Sb_2O_3), which works synergistically with chlorine to produce free radical scavengers and poison the flame. The

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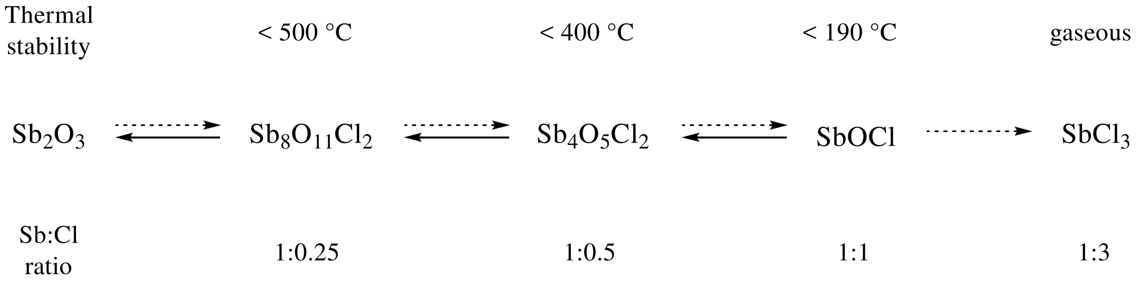
[*] A LOI value lower than 21 indicates that the combustion of the material is self–sustaining in normal atmospheric condition, while a LOI value higher than 21 means that in normal condition a greater concentration of oxygen than that contained in air is needed for the sustaining of the material combustion.

main reason for its large diffusion is the great efficiency on pPVC flame retardancy with few phr of loading. The mechanism of action of ATO is mainly explicated in vapour phase, despite being non–volatile. In fact, during polymer pyrolysis in condensed phase, volatile species as antimony oxychloride (SbOCl) and antimony trichloride ($SbCl_3$) are formed through a complex mechanism which involves progressive chlorination of ATO [6], as illustrated in Scheme 5.2.



Scheme 5.2: reaction scheme between ATO and halogen compounds (i.e. PVC) [7].

The chemical chlorination of ATO (dashed arrows) originates progressively chlorine richer compounds until finally obtaining antimony trichloride. Simultaneously, the intermediate oxychlorides give thermal disproportionation, yielding both antimony trichloride and chlorine poorer species (solid arrows) [7].

All these substances help the transfer of chlorine in the gas phase, promoting its radical scavenging effect. Once in the vapour phase, antimony chlorides react with free radicals with a series of reactions, proposed in Scheme 5.3.

$$\begin{aligned}
SbCl_3^{\bullet} + H^{\bullet} &\longrightarrow SbCl_2 + HCl \\
SbCl_2^{\bullet} + H^{\bullet} &\longrightarrow SbCl + HCl \\
SbCl^{\bullet} + H^{\bullet} &\longrightarrow Sb + HCl \\
Sb + \dot{O}H &\longrightarrow SbOH \\
Sb + O^{\bullet\bullet} &\longrightarrow SbO \\
SbO + H^{\bullet} &\longrightarrow SbOH \\
SbOH + H^{\bullet} &\longrightarrow SbO + H_2 \\
SbOH + \dot{O}H &\longrightarrow SbO + H_2O
\end{aligned}$$

Scheme 5.3: proposed mechanism of reaction between antimony chlorides and free radicals in the flame region [8].

Thus, antimony chlorides (and its halides, more in general) have two different functions in the flame. First, they are a ready source of hydrogen chloride in the early stages of a fire and, then, they produce a "solid spray" of fine particles of SbO, which is an independent flame inhibitor that works even in the absence of halogens [8].

With the aim to phase out the use of ATO, due to its unresolved issues previously discussed (see Paragraph 2.1), other FRs that may be used in pPVC were subjected to testing: i.e. phosphorous–based compounds, inorganic hydroxides/hydroxycarbonates and tin compounds. These FRs act through other of the mechanisms previously pointed out and briefly depicted hereafter.

Phosphorous–containing flame retardants are a class containing a great variety of compounds, including elemental red phosphorous, inorganic phosphates, ammonium polyphosphates, organic phosphates and phosphonates, phosphine oxides and organohalides phosphates. Organophosphates esters could be used as non-flammable plasticizers (e.g. 2–Ethylhexyl Diphenyl Phosphate (EHDPP), Isodecyl Diphenyl Phosphate (IDDPP)), in total or partial substitution of standard plasticizer. All of these additives have different mechanisms of action, including flame poisoning, charring formation and surface vitrification. Flame–inhibition of phosphorous species is similar to that one shown for halogens, with the transfer of volatile species (e.g. H_3PO_4) in the vapour phase and the formation of the highly active PO radical. Formulations containing phosphates, polyols, or other char former compounds, and a blowing agent (i.e. gas source) are used for intumescence flame retardant systems. An example of this triad of compounds is ammonium polyphosphate, dipentaerythritol and melamine. By heating, the phosphate decomposes to phosphoric acid which esterifies the polyol. The ester undergoes further decomposition with char formation, while the thermal decomposition of melamine yields N_2, leading to a volume expansion and to the formation of a thick, porous char layer which helps to isolate the underlying polymer, limiting both the contact with oxygen and the heat transfer to polymer mass. However, intumescent systems are more diffused in polyolefins, and their use in pPVC appears limited. The use of inorganic phosphates/sulphates salts, which are low–melting (below approx. 600 °C) glass forming systems, yield the formation of a viscous fused layer which helps avoiding the contact between virgin polymer and the flame and contributes to the formation and consolidation of char [9].

Inorganic hydroxides and hydroxycarbonates are mostly represented by magnesium hydroxide ($Mg(OH)_2$) and aluminium trihydroxide (ATH, $Al(OH)_3$), but also minerals like boehmite and hydrotalcite [10]. These inorganic compounds are the most common FRs used in plastic materials, particularly ATH which, alone, represents a third of the global market size for FRs [11]. These hydroxides decompose when heated, releasing water in the vapour phase which dilutes the flame. Moreover, being the elimination of water an endothermic reaction, a considerable amount of heat is removed from the system, as illustrated in Scheme 5.4.

$$2\,Al(OH)_3 \longrightarrow Al_2O_3 + 3\,H_2O \qquad 1127\ J/g$$

$$Mg(OH)_2 \longrightarrow MgO + H_2O \qquad 1244\ J/g$$

Scheme 5.4: endothermic decomposition and water release of inorganic hydroxides [8].

Tin compounds are essentially zinc hydroxystannate (ZHS, $ZnSn(OH)_6$), and its dehydrated version, zinc stannate (ZS, $ZnSnO_3$). These compounds are particularly active as synergistic agents that improve the performances of other FRs, ranging from ATO to inorganic hydroxides. At low chlorine content, tin compounds promote char formation, even though their mechanism of action is not fully understood [12]. Another synergistic agent that could be used is zinc borate (ZB, $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$).

5.2. Results and discussion

With the aim to evaluate the effectiveness of each FR system in improving fire and thermal properties, all the obtained samples were analysed by cone calorimeter and horizontal combustion test and their thermal stability was evaluated (Paragraph 3.2.3). Furthermore, their ultimate tensile strength (UTS) and elongation at break (EB) (Paragraph 3.2.2) were determined to put in evidence the effect of these additives on the mechanical properties of the final material.

5.2.1. Plastisol formulation

All the selected additives were added to the same two recipes, Recipe A and B, used for the evaluation of plasticizers (Table 4.1 and Table 4.2, respectively). Diundecyl Phthalate (DUP) was used as plasticizer, common to both recipes, being the best performer amongst (standard) phthalate plasticizers, as demonstrated in Chapter 4.

The method used for samples preparation is the same used previously for the evaluation of plasticizers (Paragraph 3.1). A summary of the combination of FRs used to prepare the samples subjected to testing is reported in Table 5.1.

Table 5.1: list of the samples of both recipes subjected to testing.

	Recipe A	
#	*Sample*	*phr*
1	-	-
2	ATO	2
3	ATH	10
4	ATH	20
5	ATH	30
6	ATH	50
7	ZB	1
8	ZB	2
9	ZB	3
10	ZB	5
11	ZHS	1
12	ZHS	2
13	ZHS	3
14	ZHS	5
15	ZB + ZHS	1+1
16	ZB + ZHS	1+2
17	ATH + ZB	10+1
18	ATH + ZHS	10+1
19	ATH + ZHS	10+2

	Recipe B	
#	*Sample*	*phr*
1	-	-
2	ATO	2
3	HT	5
4	HT	10
5	HT	20
6	Ph1	2
7	Ph1	5
8	Ph1	10
9	Ph2	2
10	Ph2	5
11	Ph2	10
12	CARB	2
13	CARB	5
14	CARB	10
15	CARB	20
16	CHP	2
17	CHP	5
18	CHP	10
19	ATH + ZHS	10+2
20	CARB + ZHS	10 + 2
21	CARB + Ph2	10 + 5

Amongst all the combinations, the standard ATO and ATH + ZHS were tested in both recipes to have a comparison of their effectiveness in the two formulations. Sample #1 with both recipes is a neat pPVC foil, without any FR, but only plasticizer (DUP) and heat stabilizers as per Table 4.1 and Table 4.2.

5.2.2. Mechanical Properties

- *Ultimate Tensile Strength and Elongation at Break*

Ultimate tensile strength (UTS) and elongation at break (EB) of the samples obtained with both the recipes, are reported in Table 5.2.

Table 5.2: Ultimate tensile strength (UTS) and elongation at break (EB) of the two series of samples

Recipe A				
#	*FR*	*phr*	*UTS (MPa)*	*EB (%)*
1	-	-	13.3	586
2	ATO	2	14.0	576
3	ATH	10	12.4	497
4	ATH	20	12.1	480
5	ATH	30	10.5	420
6	ATH	50	9.5	368
7	ZB	1	12.9	517
8	ZB	2	12.7	518
9	ZB	3	13.4	561
10	ZB	5	12.8	539
11	ZHS	1	13.5	561
12	ZHS	2	13.3	563
13	ZHS	3	13.6	553
14	ZHS	5	13.2	517
15	ZB + ZHS	1 + 1	13.1	544
16	ZB + ZHS	1 + 2	13.5	519
17	ATH + ZB	10 + 1	12.2	532
18	ATH + ZHS	10 + 1	12.8	539
19	ATH + ZHS	10 + 2	12.7	556

Recipe B				
#	*FR*	*phr*	*UTS (MPa)*	*EB (%)*
1	-	-	12.8	615
2	ATO	2	11.8	515
3	HT	5	12.4	562
4	HT	10	11.2	475
5	HT	20	8.9	357
6	Ph1	2	11.6	495
7	Ph1	5	12.4	558
8	Ph1	10	11.7	498
9	Ph2	2	11.2	425
10	Ph2	5	11.9	472
11	Ph2	10	11.6	445
12	CARB	2	11.4	519
13	CARB	5	12.3	574
14	CARB	10	10.9	489
15	CARB	20	10.5	478
16	CHP	2	12.6	587
17	CHP	5	12.4	598
18	CHP	10	11.1	506
19	ATH + ZHS	10 + 2	12.4	529
20	CARB + ZHS	10 + 2	11.0	498
21	CARB + Ph2	10 + 5	11.3	516

Samples obtained following recipe A show faintly higher mechanical properties than samples from recipe B. It is worth noting that the UTS of the majority of samples result comparable to that one of DUP (#1) and ATO (#2) (Figure 5.2). Only the addition of ATH greatly influences the mechanical performances of the material, with a UTS deterioration of approx. 30 % at 50 phr loading (Recipe A, #6). A decrease in tensile strength, even though only slight, is shown by adding ZB (Recipe A, #7–10), also in combination with ATH (Recipe A, #17), while when added to ZHS (Recipe A #15-16), its negative effect is mitigate by this latter. As shown in Figure 5.2, elongation at break (EB) values follow the same UTS trend. It is worth noting that all the tested samples display lower EB than the reference material with no FR (#1). Such a behaviour suggests that FRs basically behave as inert fillers, yielding stiffer samples. However, the decrease of elasticity is not extremely marked (except for ATH samples), and it should not constitute a serious issue for the formulator.

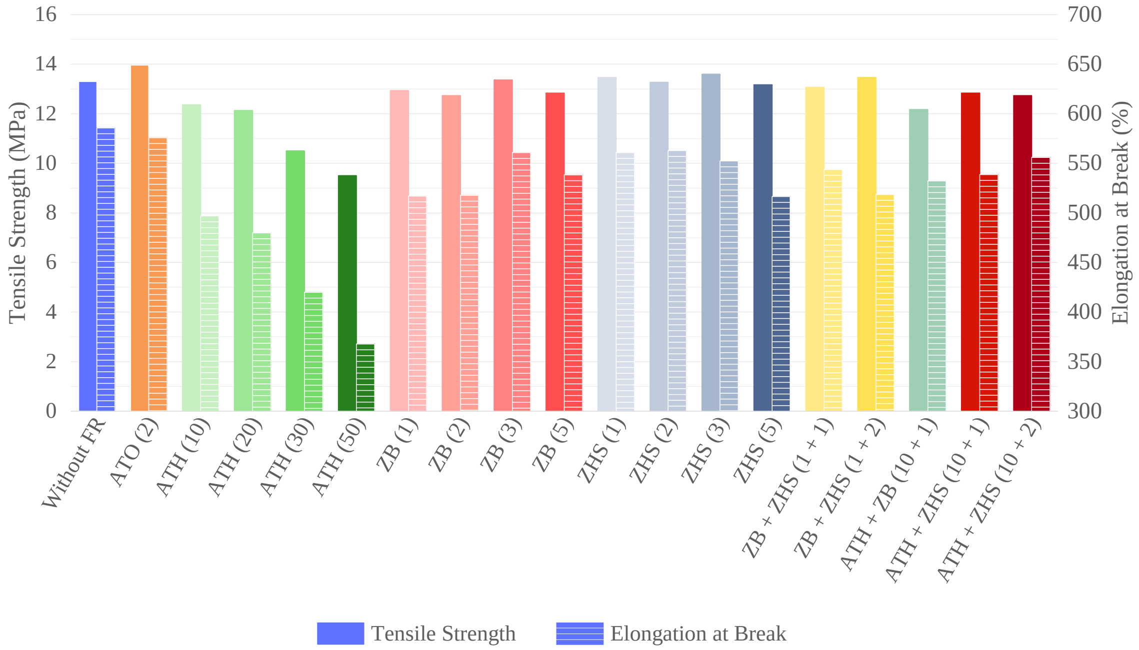


Figure 5.2: Ultimate Tensile Strength (UTS) and Elongation at Break (EB) of samples obtained with recipe A.

Samples obtained with recipe B generally exhibit slightly lower UTS and EB values, probably because of the presence of a blend of PVC resins which affects several properties of the material, as already seen in Chapter 1. However, contrary to recipe A samples, the addition of ATO does not increase the tensile strength (Figure 5.3). Moreover, the obtained data show that, as expected, the effect of the additives in the mechanical properties of the material are more marked at higher loadings. In particular, the addition of HT and CARB, which in low quantities (Recipe B, #3 and #13) impart slightly higher tensile properties than ATO, with recorded values very close to that one obtained for the sample without any flame retardant (Recipe B, #1), at higher loadings lead to the drop of the mechanical properties (Recipe B, #5 and #15). Furthermore it is interesting to note that both the phosphate–based (Ph1, Ph2) and CARB additives show a particular trend with higher UTS and EB values at 5 phr, suggesting a reinforcing effect, to some extent, at intermediate loading, with lesser properties both at higher and lower loading rates.

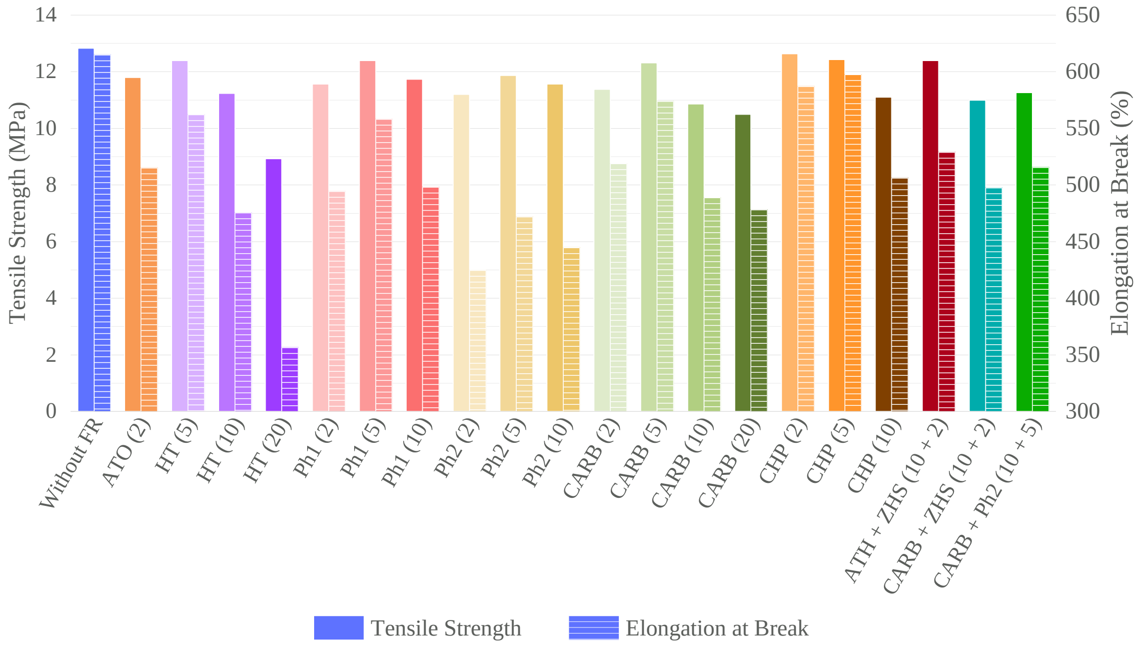


Figure 5.3: Ultimate Tensile Strength (UTS) and Elongation at Break (EB) of samples obtained with recipe B.

5.2.3. Thermal and flame properties

- *Thermal Stability*

The use of flame retardants is likely to affect thermal stability of pPVC, due to the possible activity of these compounds at process temperature. This effect could be either positive or negative, depending on the nature, stability and mechanism of action of a certain FR. With the aim to study the effect of all the selected FRs on the thermal stability of pPVC, all the obtained samples were subjected to thermal stability test at 200 °C (see Paragraph 3.2.3). The obtained results are reported in Figure 5.4 (Recipe A) and Figure 5.5 (Recipe B). First of all it is worth noting that, as reported in Chapter 4, Recipe A samples show lower yellowing than Recipe B ones, also in absence of FRs. For this reason, the results of the latter ones are reported up to 21 minutes: at longer time all the samples undergoes severe degradation and blackening.

As shown in Figure 5, in Recipe A the addition of ATO has a positive effect on the pPVC thermal stability, and the same effect is observed with increasing load of ATH. In particular, ATH (50) is the only FR belonging to recipe A samples that exhibits a faintly better effect on thermal stability than ATO. Conversely, ZB, ZHS and their combinations show higher yellowing even if added in few phr, and severe colour changing at the maximum, but nonetheless modest, loading. The positive effect of ATH results nullified when this FR is combined with ZHS.

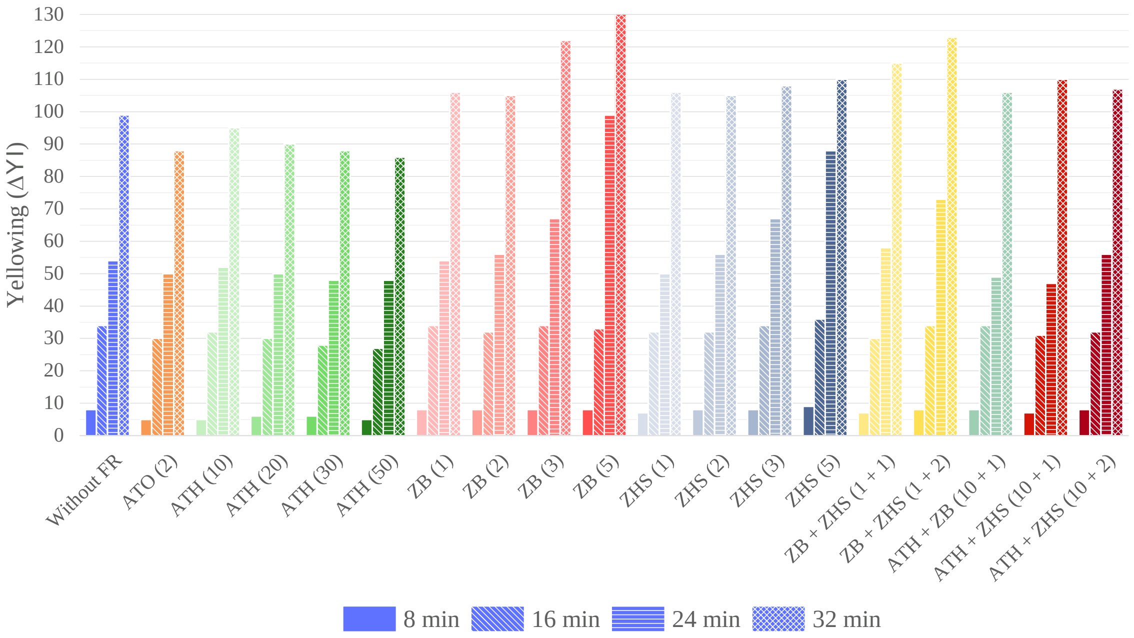


Figure 5.4: Thermal stability of samples obtained with recipe A.

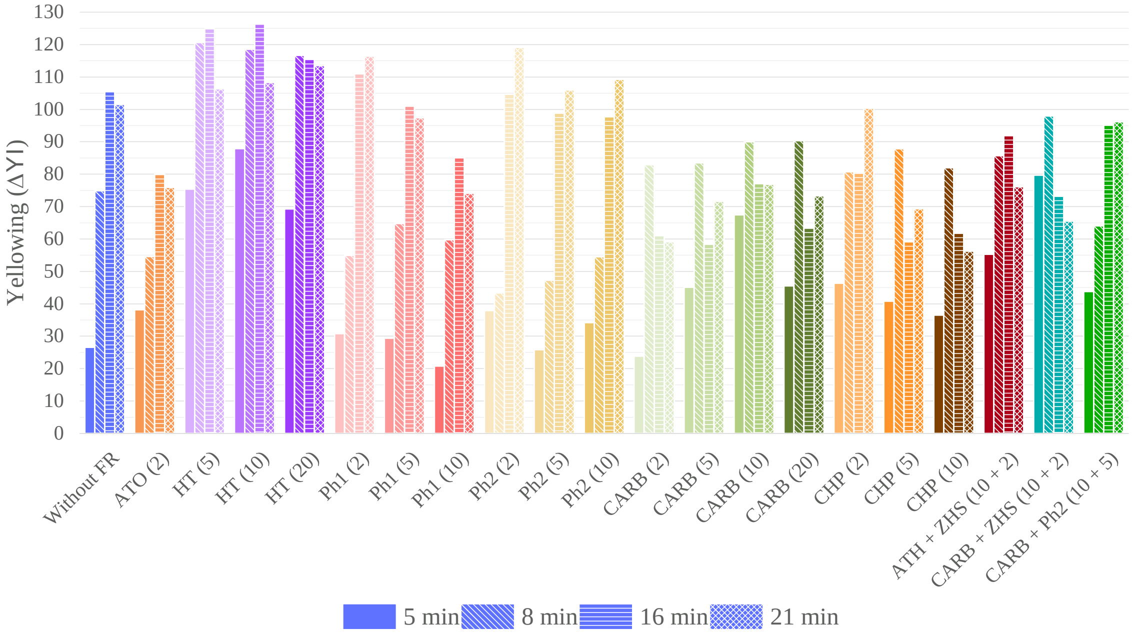
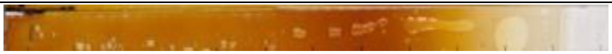
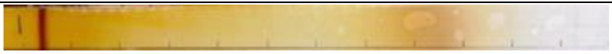


Figure 5.5: Thermal stability of samples obtained with recipe B.

In Recipe B, ATO is still the best FR in terms of improved thermal stability up to 8 minutes. At higher exposure times, FR systems based on CARB, CARB + ZHS and CHP have a better impact on heat stabilization. Phosphate–based FRs have a different behaviour, with Ph1 that improves its performances at higher loadings, while Ph2 is rather detrimental in any case. The addition of HT, at any loading, instead, seems to promote the degradation of the material. It is worth noting that such a test has, above of all, a qualitative nature and sometimes the pure instrumental reading is not correct. As reported in Table 5.3 for Recipe B samples, indeed, HT containing formulations show the formation of bubbles*, mostly at 10 and 20 phr. This phenomenon could be attributed to both physisorbed and interlayer water losses of hydrotalcite at process temperatures [10, 13].

Table 5.3: Exposed specimens of samples obtained with recipe B for visual evaluation.

#	FR	phr	Exposed specimen
1	DUP	-	
2	ATO	2	
3	HT	5	
4		10	
5		20	
6	Ph1	2	
7		5	
8		10	
9	Ph2	2	
10		5	
11		10	
12	CARB	2	
13		5	
14		10	
15		20	
16	CHP	2	
17		5	
18		10	
19	ATH + ZHS	10 + 2	
20	CARB + ZHS	10 + 2	
21	CARB + Ph2	10 + 5	

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* Observing the images in Table 2.3, it seems that other samples formed bubbles during the test, but in these other samples the circular spots are simply caused by the imperfect adhesion of the specimen to the release paper.

- *Flame resistance*

In a given formulation, a FR should be able to reduce the flame spread. Thus, all the samples were subjected to horizontal combustion test and burning rate (BR, mm/min) was calculated and averaged (Table 5.4). It has to be taking in account that the maximum limit value typically demanded by automotive industries is 100 mm/min.

Table 5.4: Evaluation of the burning rate of the two series of samples.

Recipe A			
#	*FR*	*phr*	*BR (mm/min)*
1	-	-	104
2	ATO	2	0
3	ATH	10	96
4	ATH	20	85
5	ATH	30	38
6	ATH	50	0
7	ZB	1	74
8	ZB	2	72
9	ZB	3	71
10	ZB	5	76
11	ZHS	1	50
12	ZHS	2	34
13	ZHS	3	26
14	ZHS	5	0
15	ZB + ZHS	1 + 1	39
16	ZB + ZHS	1 + 2	15
17	ATH + ZB	10 + 1	66
18	ATH + ZHS	10 + 1	31
19	ATH + ZHS	10 + 2	0

Recipe B			
#	*FR*	*phr*	*BR (mm/min)*
1	-	-	108
2	ATO	2	4
3	HT	5	121
4	HT	10	103
5	HT	20	54
6	Ph1	2	62
7	Ph1	5	71
8	Ph1	10	54
9	Ph2	2	90
10	Ph2	5	69
11	Ph2	10	51
12	CARB	2	75
13	CARB	5	63
14	CARB	10	52
15	CARB	20	42
16	CHP	2	60
17	CHP	5	50
18	CHP	10	31
19	ATH + ZHS	10 + 2	20
20	CARB + ZHS	10 + 2	19
21	CARB + Ph2	10 + 5	56

As shown by the data reported in Figure 5.6, all of the FRs added to recipe A lead to the decrease of the burning rate. Moreover, increasing the loading of a FR or FR system enhance the flame resistance of the material, with the exception of ZB, which seems to exert its –modest– function independently from the loading, in the considered interval (1–5 phr). It is worth noting that 3 of these FRs, namely ATH (50), ZHS (5) and ATH + ZHS (10 + 2) show results comparable to that one of ATO, yielding self–extinguishing materials (i.e. BR = 0 mm/min). However, ATH is effective only at 30 phr or more, while ZHS, both alone or as synergist, is greatly effective in increase the flame resistance even at the minimum loading.

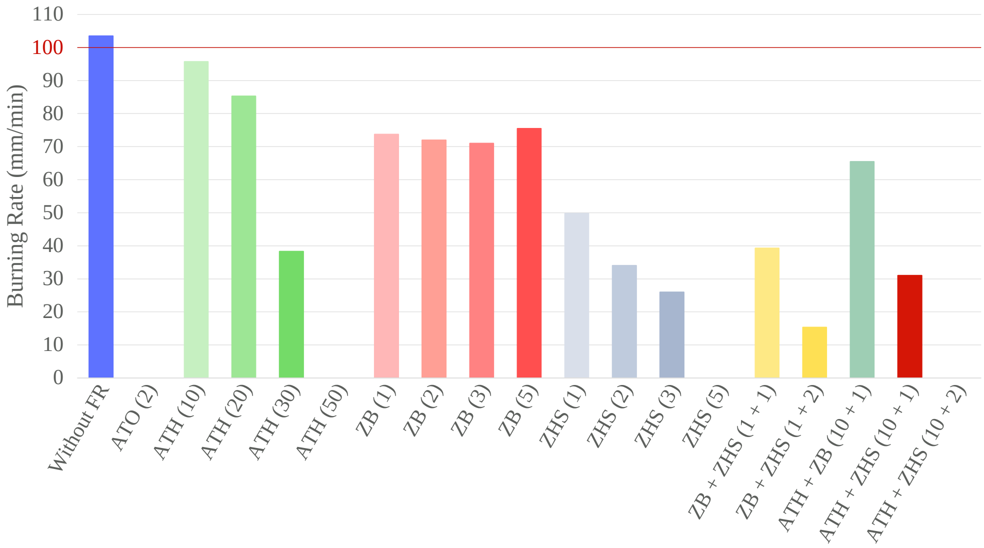

Figure 5.6: Burning rates of the samples obtained with recipe A.

As shown in Figure 5.7, by using recipe B the additives show a lesser effectiveness in decrease the flame spread of the samples with respect to Recipe A. Such a behaviour is partly attributable to the nature of the two formulations. In fact, sample Without FR (Recipe A) achieves a slightly lower burning rate compared to sample Without FR (Recipe B), respectively 103 and 108 mm/min. Furthermore, ATO yielded a self–extinguish material in recipe A, meaning that the sample extinguished before reaching the 1st mark on the sample holder (see Paragraph 3.2.3), while burnt instead when added to recipe B, even though only slowly and for a short distance, resulting in a burning rate of 4 mm/min. Analogously, ATH + ZHS (10 + 2) gave a result of 20 mm/min in recipe B, while it resulted self–extinguishing in recipe A sample.

Anyway, FRs tested in recipe B yielded good but not excellent results, with burning rate lower than that one of neat pPVC, except for HT (5) that, quite surprisingly, has a burning rate higher than 120 mm/min, and HT (10) that is over 100 mm/min. However, only few samples are able to halve the burning rate of the sample without FR. Furthermore, also in this case, increasing loading leads to better performances. The addition of ZHS as synergist yielded the best results amongst ATO alternatives, with burning rates below 20 mm/min at moderate overall loadings.

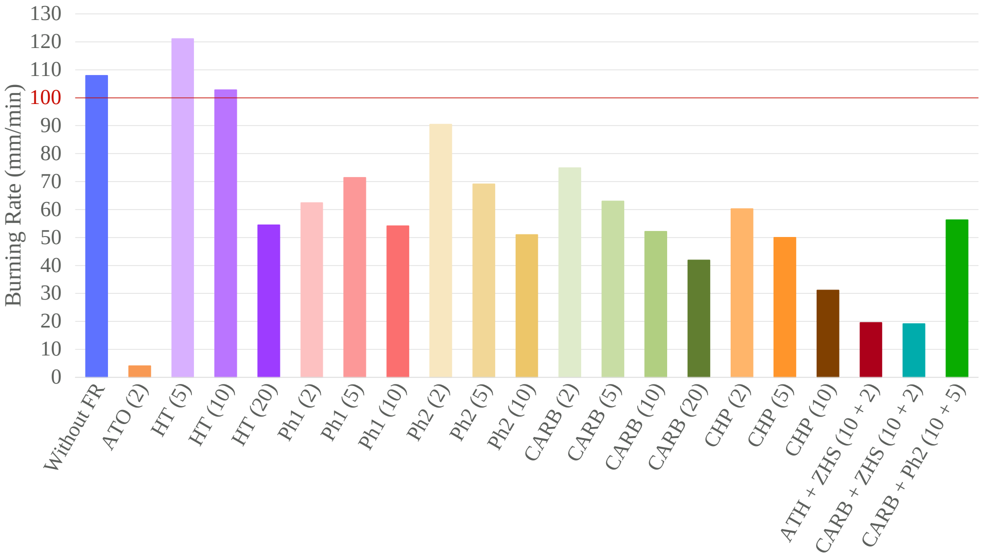

Figure 5.7: Burning rates of the samples obtained with recipe B.

- *Cone calorimetry*

Cone calorimetry is a powerful technique for testing fire behaviour of a wide variety of materials, measuring their response when exposed to a constant and controlled radiant heating generated by a conical electric heater. The cone calorimeter measures the oxygen decrease in the exhaust product stream during the test which correlates with the heat released by the specimen. Despite being not particularly widespread in the automotive industry, this test could provide several interesting information about the fire response of pPVC materials, including Time to Ignition (TI, s), Total Heat Release (THR, MJ/m^2), Fuel Load (MJ/kg), peak Heat Release Rate (pHRR, kW/m^2) and time to peak Heat Release Rate (t–pHRR, s). These tests e were only performed for recipe B samples, and at least 2 specimens per sample were tested. Most relevant results obtained are reported in Table 5.5.

Table 5.5: data obtained from cone calorimetric tests on samples obtained with recipe B.

#	*FR*	*phr*	*THR (MJ/m^2)*	*pHRR (kW/m^2)*	*Fuel Load (MJ/kg)*	*TI (s)*	*t–pHRR (s)*
1	-	-	13.4	317.0	15.4	35	64
2	ATO	2	12.4	266.1	13.0	41	74
3	HT	5	13.9	372.7	15.3	36	55
4	HT	10	16.3	393.4	16.6	37	56
5	HT	20	17.4	390.7	15.6	35	60
6	Ph1	2	13.1	296.3	15.1	30	62
7	Ph1	5	12.5	275.9	13.3	32	62
8	Ph1	10	13.1	286.5	14.3	32	58
9	Ph2	2	13.6	298.5	14.9	32	70

10	Ph2	5	11.3	255.6	12.9	29	65
11	Ph2	10	12.2	263.8	13.3	26	62
12	CARB	2	13.6	278.9	14.5	36	75
13	CARB	5	13.5	258.1	14.7	29	68
14	CARB	10	14.0	245.9	15.5	24	67
15	CARB	20	13.2	239.6	13.5	21	59
16	CHP	2	14.5	265.4	15.3	36	59
17	CHP	5	13.3	249.5	14.6	35	59
18	CHP	10	12.3	238.9	13.6	35	75
19	ATH + ZHS	10 + 2	14.3	252.5	14.8	30	58
20	CARB + ZHS	10 + 2	13.7	246.2	14.3	23	55
21	CARB + Ph2	10 + 5	13.3	247.7	13.8	25	58

The information given by cone calorimetric tests allow a better understanding of the performances of each FR. Two of the most considered variables measured are pHRR and THR, which are direct measures of the heat generated by the combustion of the materials subjected to testing. The first indicates, as the name suggests, the rate at which heat is generated by a fire fuelled by the material under testing and, hence, could be considered as the fire power and the driving force for flame spread. It has been argued that HRR should be considered as the single most important among the fire reaction properties [14]. Differently, THR is the total heat generated during the combustion of the material. Both of these parameters should be lowered as much as possible by a FR, in order to consider it effective. pHRR and THR of all the tested samples are reported in Figure 5.8.

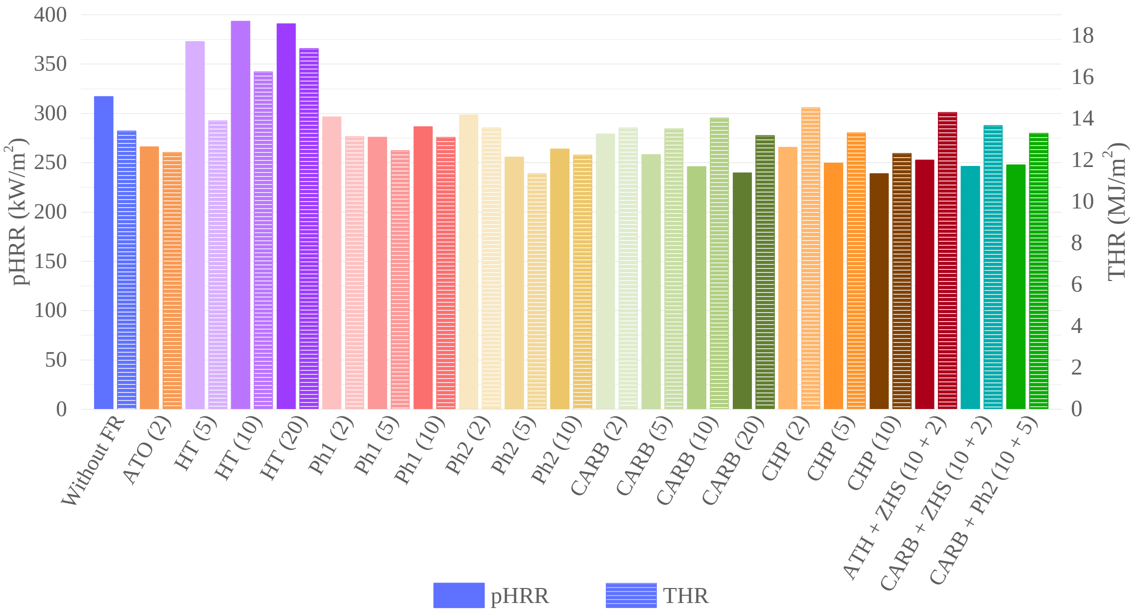

Figure 5.8: pHRR and THR of samples obtained with recipe B.

As reported in Figure 5.8, the majority of the tested FRs are able to reduce pHRR below the value of the neat pPVC sample, and many of them can compete with the performance of ATO, for example Ph2, CARB and CHP at medium to high loading, as well as the 3 FRs combinations. Thus, all these additives reduce flame spread during combustion of pPVC.

An anomalous behaviour is shown by HT containing samples, which exhibit an increase in both pHRR and THR when increasing loading. Being an inorganic compound and, thus, not flammable, HT does not directly contribute to the combustion of the sample, but possibly exerts a catalytic action at certain stages of the combustion reactions series. THR results indicate that the heat produced is quite similar amongst the sample, regardless of the nature and loading of FR (with the notable exception of HT), suggesting that none of these additives is able to lower the heat released during the whole combustion reaction. The only samples that achieved results comparable to ATO are Ph2 (5) and Ph2 (10), suggesting an enhanced effectiveness of phosphate–containing FRs.

In many cases, pHRR and THR values alone are not sufficient to have a definite impression of the fire response of materials subjected to test; thus, it results useful to observe the HRR curves, which gave a direct indication of the evolution of fire. By comparing the HRR curves of all the FR at their maximum loading (Figure 5.9) it results evident that ATO and CHP (10) behave similarly, and both lower and delay the pHRR with respect to the sample without FR.

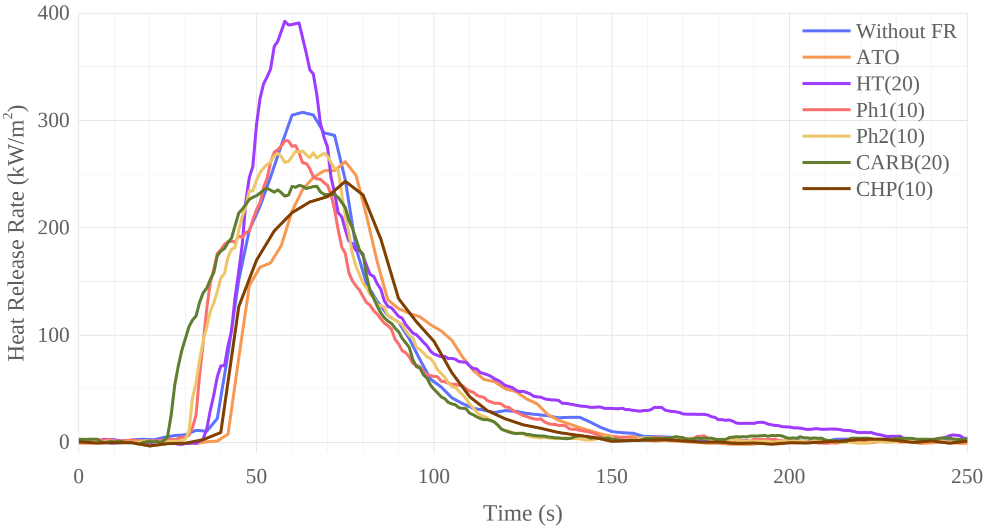

Figure 5.9: HRR curves of FRs at their respective maximum loading.

Conversely, HT (20) sample exhibit a marked peak which occurs in shorter times than the sample without FR. The first phosphate–based FR, Ph1 (10), shows a curve similar to the sample without FR, but with lower pHRR and a first portion of the curve more similar to the other phosphate FR. Finally, Ph2 (10) and CARB (20) exhibits a similar behaviour and shape of the curves, which are less sharpened, with peaks not clearly identifiable, and slightly shifted towards shorter times. The beginning of the slope of HRR curves represents the Time to Ignition (TI), which is another very important parameter, because it indicates the delay at which the material ignites when exposed to the high temperatures developed in a neighbouring fire. Higher values are clearly preferable, and in the scenario of a fire resulting from a car accident, even few more seconds can make a difference. The results reported in Table 5.5 indicate that, for this property, ATO is the more effective amongst the FRs tested, followed by HT and CHP, at all loadings, and CARB (2). A common trend to all of the additives tested at different loadings is the decrease of the TI when increasing the loading. This is particularly the case of CARB, which exhibit a TI of 36 seconds at 2 phr that decreases to 21 seconds at 20 phr. The other time–related variable measured by the cone calorimeter is the time to reach to peak HRR (t-pHRR), which is another important parameter describing the interval from the ignition of the material to the moment of maximum heat released by the fire. The lower the result, the more sudden and abrupt will be the development of fire and the flame spread. Also for this parameter, ATO yields excellent results, and only CARB (2) and CHP (10) performed faintly better (Table 4.8).

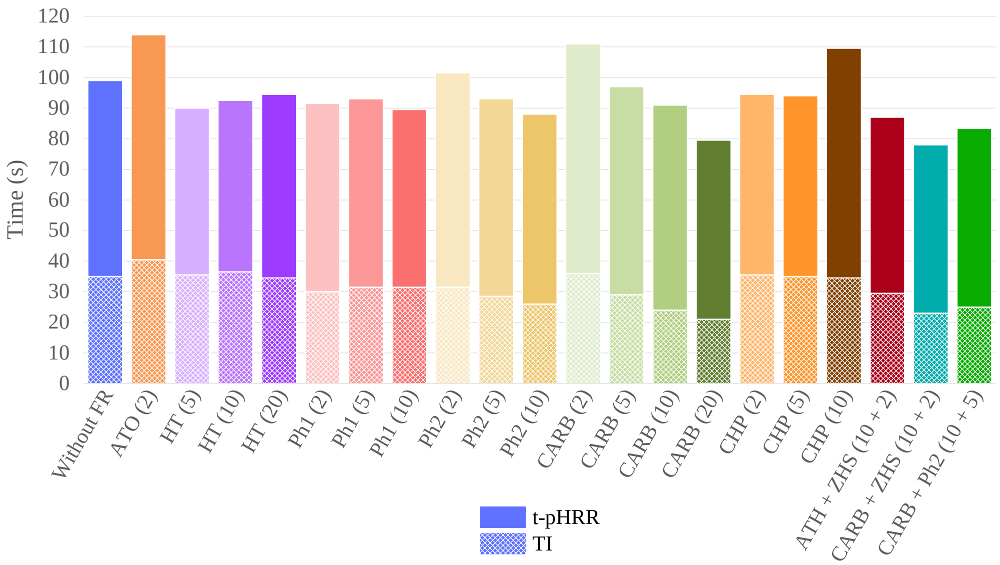

Figure 5.10: total time elapsed to pHRR (sum of TI and t-pHRR).

HT and CHP exhibit an increase of t–pHRR when increasing loading, while an opposite trend is recorded by Ph2 and CARB, and Ph1 shows practically constant values. The sum of these two measured times gives a more precise indication of the time elapsed between the exposure to high temperatures and the reaching of the pHRR and, thus, the maximum fire intensity. This data elaboration is reported in Figure 5.10. The excellent performance of ATO is almost matched by CARB (2) and CHP (10). The overall trends of Ph2 and CARB are verified, confirming that the increase loading of these FRs leads to a decrease of the total time to reach pHRR. Furthermore, a more evident positive trend is observable for hydrotalcite (HT) and calcium hypophosphite (CHP).

5.3. Conclusions

More than 35 FRs and FR systems were evaluated in 2 different formulations, based on different types of PVC resins and heat stabilizers, and with the same amount (75 phr) and type (DUP) of plasticizer. The obtained samples were subjected to tensile and thermal stability tests, as well as flame resistance and flame response analysis. The latter ones, clearly and obviously important for a FR, were investigated by means of horizontal combustion test according to ISO 3795 [15] and cone calorimetry, as per ISO 5660–1 [16] and ASTM E1354–16a [17].

- *Mechanical properties*

Tensile strength results were not particularly surprising, as the addition of FRs at increasing loadings tends to decrease both UTS and EB. Thus, FRs basically acts as inert fillers, increasing the stiffness of the material. With the aim to better evaluate the performances of each FR, mechanical properties and the flame resistance of the materials were contemporarily taken into account. Thus, the comparison between burning rate and UTS for recipe A samples is reported in Figure 5.11.

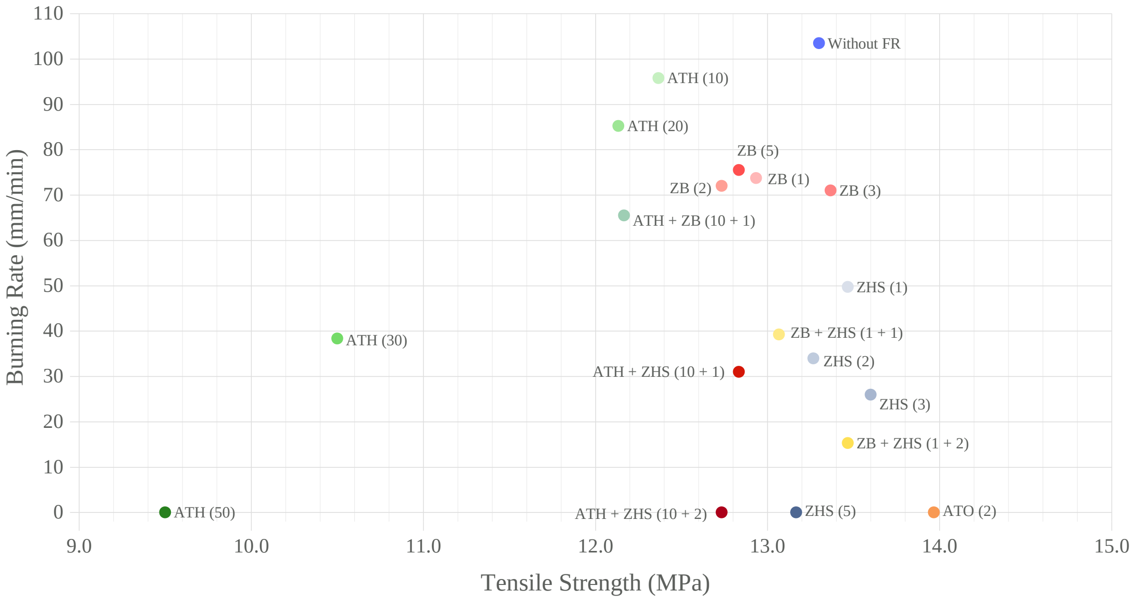

Figure 5.11: Burning rate and tensile strength of recipe A samples.

It results evident that ATO is the best performer when formulated in recipe A, followed by ZHS and its combinations with ZB. All these formulations result indeed fire resistant maintaining at the same time good mechanical properties. ZB alone, instead, is not particularly efficient in reducing the burning rate at any of the loading tested. Furthermore, ATH needs high loading to perform as a good flame retardant, but it drops the mechanical properties of the material. Thus it results not suitable for our purposes. Thus, promising candidates for the substitution of ATO in formulations with recipe A could be those based on zinc hydroxystannate (ZHS), and particularly **ZHS (5)**, **ATH + ZHS (10 + 2)** and **ZB + ZHS (1 + 2)**.

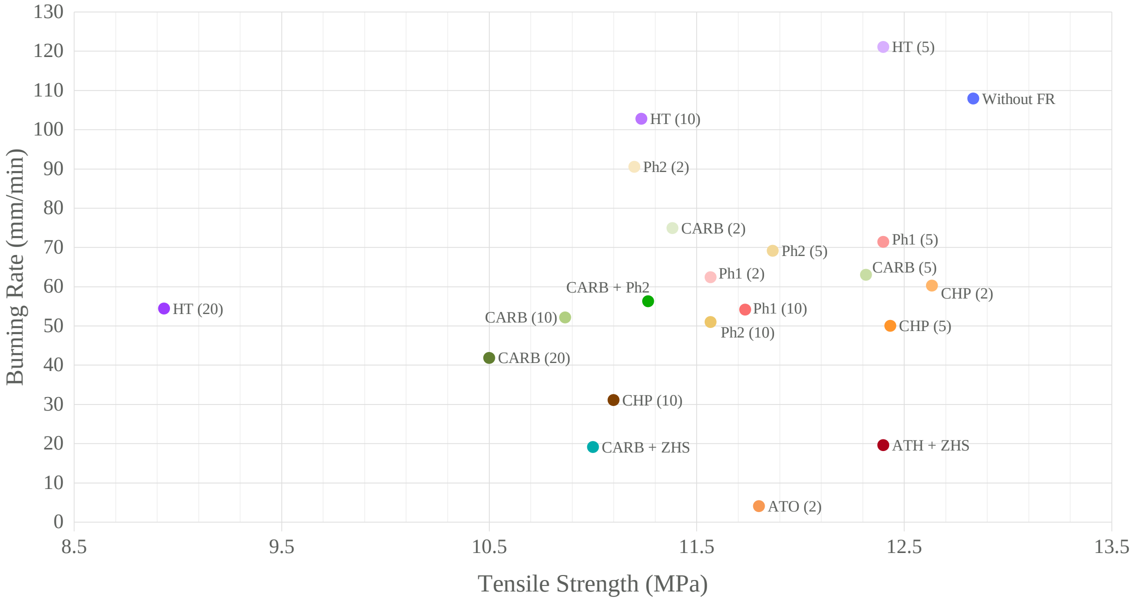

Figure 5.12: Burning rate and tensile strength of recipe B samples.

Using Recipe B (Figure 5.12), ATO containing samples show the lower burning rate, but a decrease in the mechanical properties is evidenced. HT and CHP samples show a quasi–linear trend, with a simultaneous decrease of burning rate and UTS when increasing loading. Amongst the other additives particular trends are observable with Ph1 and Ph2, with seems to have a reinforcing effect when increasing the loading, particular at intermediate values (5 phr).

Anyway the best compromise between flame retardancy and maintenance of tensile properties, apart from ATO, seems to be **ATH + ZHS (10 + 2)**, followed by **CARB + ZHS (10 + 2)** and **CHP (10)**, even though the performance loss in tensile properties is quite marked in these latter ones.

- *Thermal properties*

Thermal stability is indeed influenced by FRs but correctible with the proper selection of the heat stabilization system. As previously discussed, recipe A samples exhibited a better heat stability, possibly due to formulation components and residual polymerization additives in PVC resins. Again, a graphical comparison against burning rate is reported in Figure 5.13.

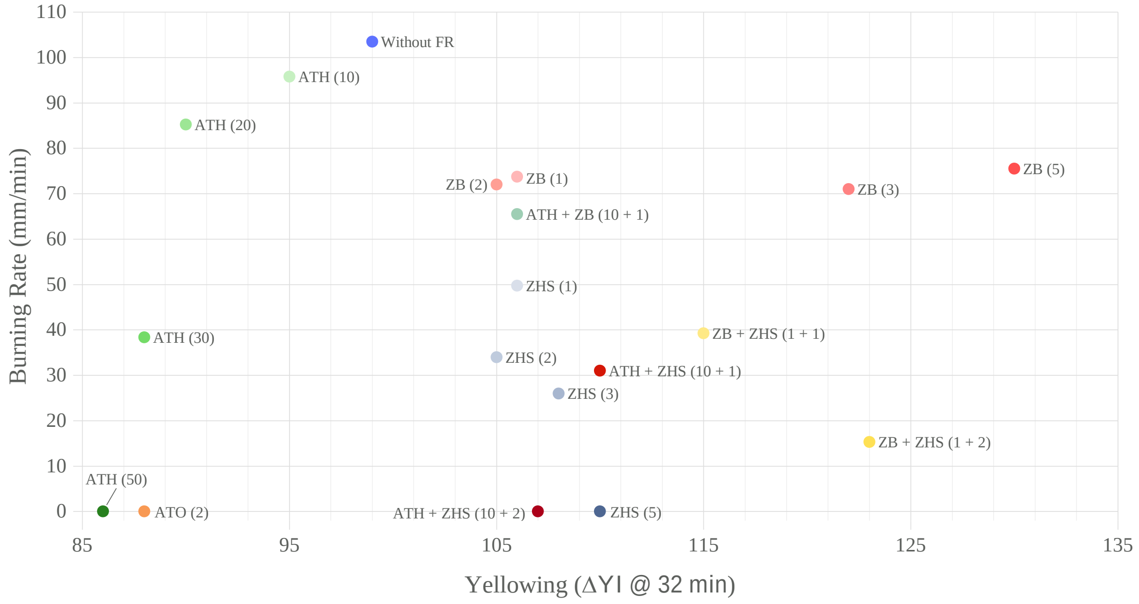

Figure 5.13: *Burning rate and thermal stability (ΔYI @ 32 min) of recipe A samples.*

The best results are here obtained by ATO and ATH (50). The whole series of the ATH samples show a clear trend: increasing the loading results in increased flame and heat resistance (i.e. a decrease in both burning rate and yellowing). However, ATH samples exhibit poor mechanical properties (Figure 5.11) and its use alone is, therefore, definitely limited. Conversely, while not having particular impact on the flame resistance, the effect of ZB is detrimental on the thermal stability particularly when used in combination with ATH and **ZHS**. The latter, while imparts very good flame properties and mechanical properties comparable to neat pPVC, does not exhibit great thermal stability.

Results obtained with recipe B samples are reported in Figure 5.14.

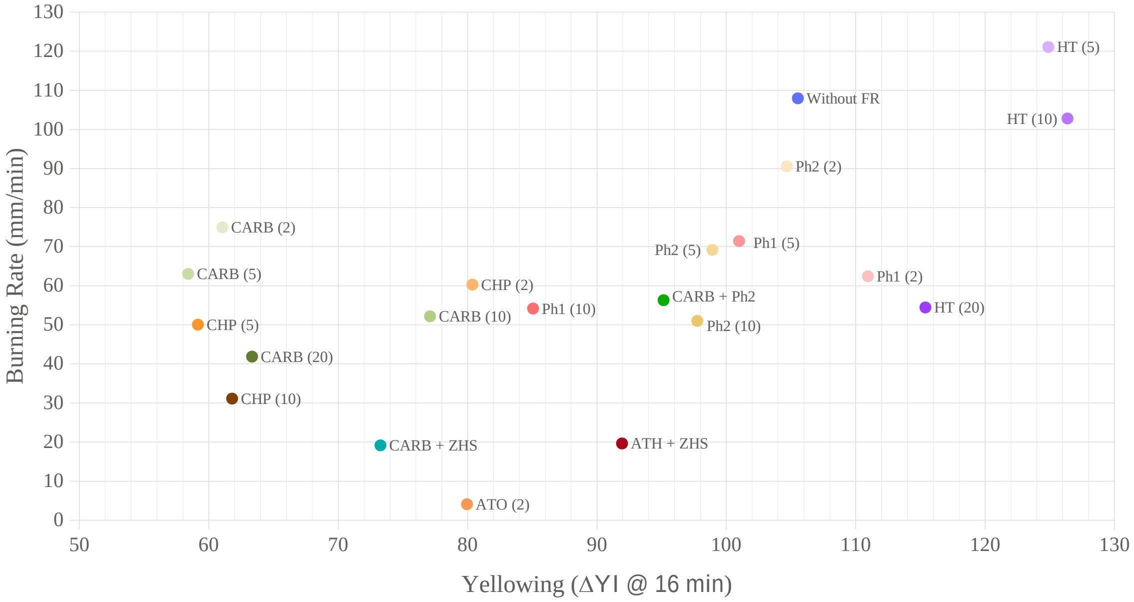

Figure 5.14: Burning rate and thermal stability (ΔYI @ 16 min) of recipe B samples.

As already seen in Paragraph 5.2.3, HT yielded unacceptable blistering, and phosphate–based FRs (Ph1 and Ph2) start to blacken in early stages. The data proposed in the above diagram suggests that these FRs not only yielded reduced heat stability, but also quite poor flame retardancy. Conversely, CARB and CHP at medium to high loading generally impart optimal thermal stability. The best overall results from this perspective are expressed by **CARB + ZHS (10 + 2)**, **CHP (10)** and, even though only to some degree, CARB (20) and CHP (5).

Lastly, cone calorimetry tests were performed, even though only on recipe B samples, to investigate possible correlations with the horizontal combustion test, which is much more widespread in the automotive industry. A direct comparison of burning rate and HRR is reported in Figure 5.15.

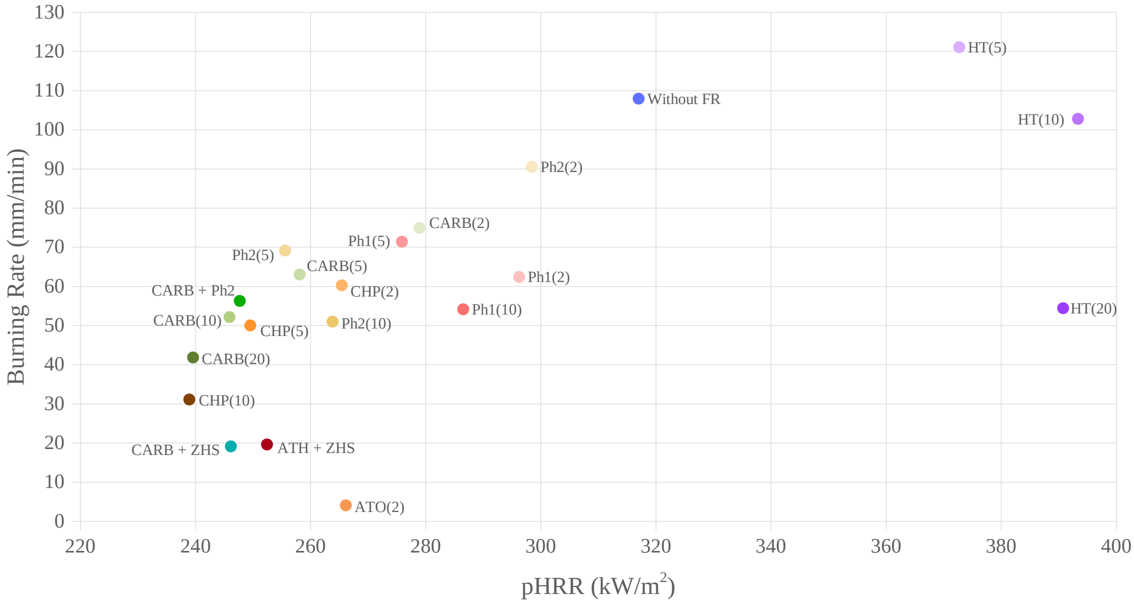

Figure 5.15: Burning rates and pHRR of recipe B samples.

This interpolation shows that, generally, an increase in burning rate corresponds to an increase in pHRR. More precisely, a quasi–linear trend is observable for CARB and CHP, with both burning rate and pHRR that decrease with increasing loading. The situation differs for HT, with burning rate that decreases and pHRR increasing when this FR is added in larger quantities. The behaviour of the phosphates–based FRs is less clear and appears to be random. The additives that approach the performances of ATO, in terms of both low burning rate and pHRR are the combinations with ZHS, CHP (10) and, to a lesser extent, CARB (20). Conversely HT samples exhibit the worst pHRR (also considering the shape of HRR curves, Figure 5.9) and at the same time high burning rates.

The tests performed on the samples obtained with the two formulations allow to argue what below summarized.

- Recipe A: the best alternatives to ATO are ZHS (3), ZHS (5) and ATH + ZHS (10 + 2).
- Recipe B: even though with slightly poorer performances, the best alternatives to ATO amongst the tested are CARB + ZHS (10 + 2), ATH + ZHS (10 + 2) and CHP (10).

After all these consideration, it is arguable that **zinc hydroxystannate** (**ZHS**) is a particularly performant FR, both alone or as a synergist with other inorganic compounds like Aluminium Hydroxide (ATH) or carboxylates mixtures (CARB). Another additive which deserves further testing and an evaluation of possible synergic properties is calcium hypophosphite (CHP).

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6

Blowing Agents

6.1. Introduction

Another important class of additives used in the manufacturing of synthetic leathers is that of blowing agents (BAs). These compounds are used in the formulation of the expanded layer, which is underlying the compact, superficial one (skin). Even though this layer is not critical for mechanical or aspect properties, it is essential to provide the desired thickness to the material maintaining it simultaneously flexible and soft to the touch, that, in a term derived from leather industry and also commonly used in the sector of SLs, is defined as the right "hand". Lastly, the use of foamed layers offers advantages in terms of weight and cost reduction.

The additives used to obtain this foamed, expanded layer should be effective at low loading, give the desired expansion in an extremely controlled process (in terms of time and temperature), and yield what is defined as a good cellulation, which means that the foamed layer should have closed cells, uniform in size and dimensions (Figure 6.1).

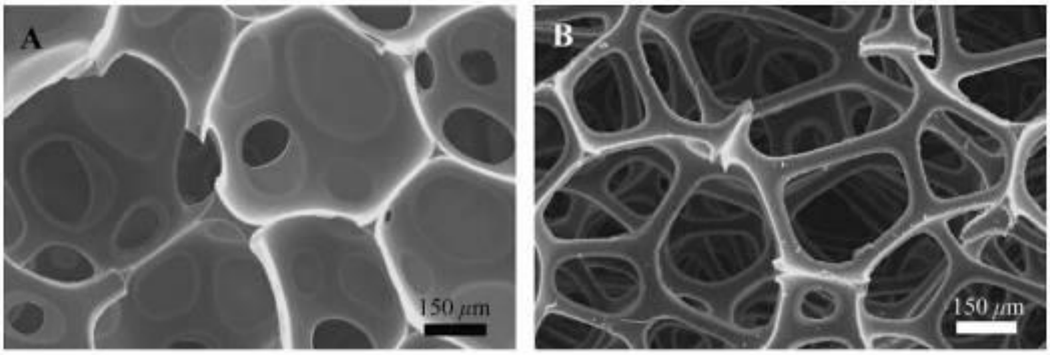


Figure 6.1: example of closed (A) and open (B) cells foams [1].

There are two pathways to obtain foamed layers, based on the nature and mechanism of action of the BAs employed. It is therefore possible to distinguish between *physical* and *chemical* BAs. The physical approach was the first one historically used, with techniques derived from the rubber and latex industry based on the mixing of plastisols and latex with gases under pressure (i.e. CO_2 at 30 atm) or the use of low boiling point solvents like *n*–

pentane. However, these methods are nowadays rarely used and mostly limited to the production of rigid PVC products, with techniques like extrusion–foaming, even though the use of CO_2 to foam PVC is becoming attractive due to the possibility to sequestrate carbon dioxide [2]. Anyway, in the SLs industry, the most used BAs are based on chemical pathways, which use molecules able to thermally decompose and release gases during the fusion and gelation of plastisol. The evolved gases are trapped into the material when it solidifies, creating the foamed layer. The plastisol route used to obtain SLs complicates the selection of an ideal BA, due to many factors, processing temperature and time frame being the most important but not the only. Other essential features for a BA are: good dispersibility, non-toxicity, absence of colour and odour, cost–effectiveness and inertness with the other component of the formulation. Chemical foaming agents can be in turn divided into endothermal and exothermal BAs, based on the absorption or generation of heat during their decomposition. The main difference between these two typologies is the ease to stop the reaction before full decomposition in the case of the first ones, even though they require generally twice the loading respect to exothermic BAs. Representative compounds of this class of chemical BAs are carbonates/bicarbonates, polycarboxylic acid derivatives (i.e. esters and salts) and tetrazoles (e.g. 5–phenyltetrazole). Conversely, the use of exothermic BAs results in a sudden reaction, difficult to control and stop before complete decomposition and, hence, located in a narrow range of temperature. Amongst this class of compounds, hydrazine derivatives, *N*–nitroso and azo compounds are found [3, 4]. This latter family of compounds include the most used chemical BA for pPVC, as well as for many other polymers, which is azodicarbonamide (AZO, $C_2H_4O_2N_4$) (Figure 6.2).

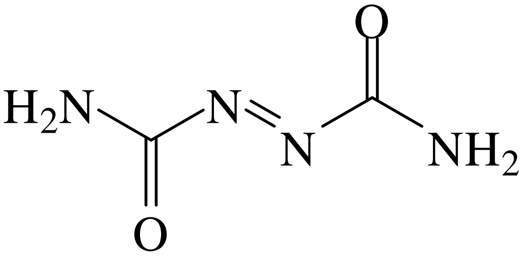
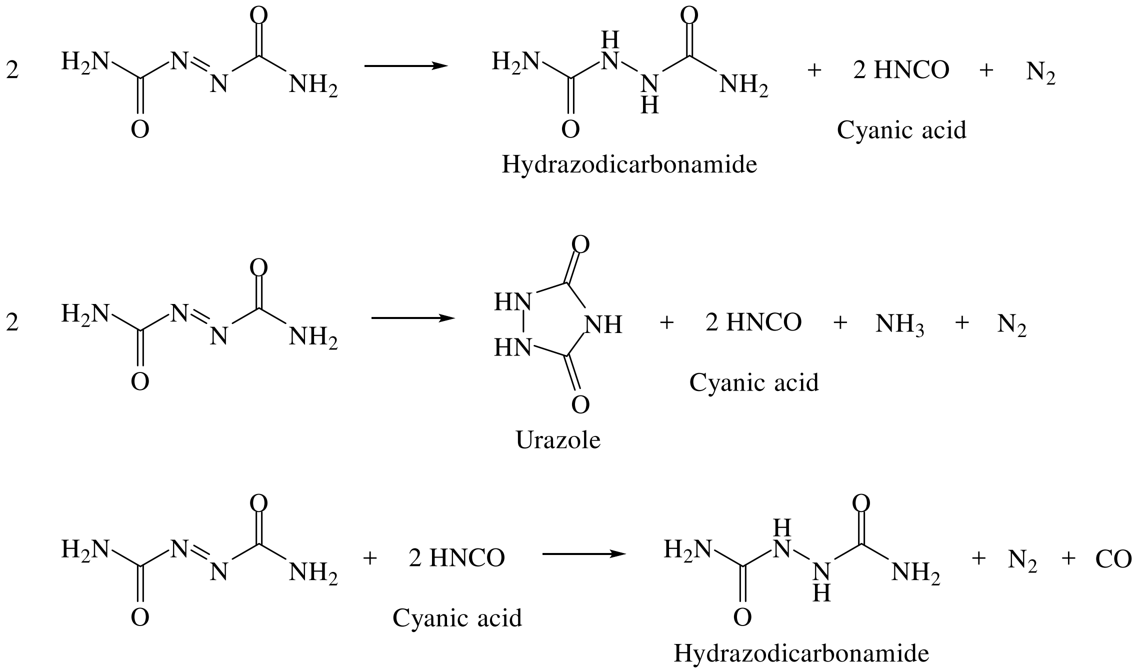


Figure 6.2: chemical structure of azodicarbonamide (AZO).

This compound exothermally decomposes around 205–215 °C, with a typical gas yield of 220 mL/g [4]. The evolved gases are mainly N_2, CO and minor amounts of CO_2 and NH_3, leaving organic residues comprising urazole, biuret, cyanuric acid, urea and ammonium salts (Scheme 6.1).



Scheme 6.1: Azodicarbonamide decomposition reactions [5, 6]

The widespread diffusion of this BA is also due to the fact that its decomposition temperature could be lowered in the range of 155–200 °C by simply adding and dosing activators, called *kickers*, which promote the decomposition of AZO. These compounds are typically organic zinc salts (e. g. zinc octoate) and are added in minor amounts. However, even though AZO is widely used, and not only in plastics but also in food, its use poses more than an issue. In fact, it is considered a respiratory sensitizer, induces occupational asthma, and prolonged exposure to AZO may result in persistent symptoms (Paragraph 2.1), For these reasons, the EU treats this compound as a Substance of Very High Concern (SVHC). With the aim at evaluate substitutes for AZO, few others BAs were selected and subjected to testing.

Another quite known and widespread chemical BA, with exothermic decomposition occurring at approximately 110–160 °C, is 4,4'-Oxydibenzenesulfonyl Hydrazide (OBSH) (Figure 6.3).

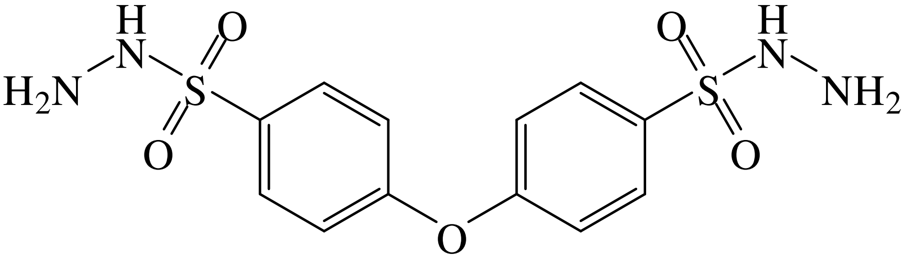


Figure 6.3: chemical structure of OBSH.

This hydrazine derivative decomposes evolving mainly N_2 and H_2O, with a gas yield of 120–150 mL/g [4], which is far lower than the values obtainable with AZO. However, OBSH is a chemical compound which is potentially harmful for human health and the environment (Figure 6.4) even though to a lesser extent than AZO.

Figure 6.4: Hazard labelling of OBSH, CAS no 80-51-3.

Mixes of sodium bicarbonate and citric acid (BIC/CIT) are typical examples of endothermic chemical BAs. These additives decompose, absorbing heat, into CO_2 and H_2O in a temperature range between 120 and 220 °C and with a gas yield in the range of 110–170 mL/g, based on the exact composition [4]. Even though the main constituents are those indicated, manufacturers' formulations often include various other additives in minor amounts, and/or with an overall different ratio of the main components.

Physical BA could be also used, in particular those constituted by expandable microspheres. These microspheres are made of a thermoplastic polymer and filled with a gas: when heated to the process temperature, the thermoplastic polymer softens as the gas expands due to the temperature. This process leads to a great volume expansion of the spheres, which maintains the expanded form when cooled.

6.2. Results and discussion

In order to evaluate the efficiency of each BA in producing foamed layers possessing the desired properties, the expansion yields were determined for all of the additives tested. Subsequently, the cellulation was evaluated and all of the samples were analysed by means of a limited but significant number of tests, to determine their ultimate tensile strength (UTS), elongation at break (EB) and flex resistance (FR) (see Paragraph 3.2.2).

6.2.1. Plastisol formulation

For the purposes of evaluating the foaming properties of the selected compounds, samples containing the different BAs were obtained using recipe A (K74 PVC resin and Diundecyl Phthalate (DUP) as plasticizer, Table 4.1) but with the addition of 1 phr of a black pigment. Such a pigment allows to obtain a dark greyish expanded foil which is better observable under a microscope for the visual evaluation of the cellulation. The *kicker* used with AZO and OBSH is zinc octoate.

The determination of the correct amount of each BA was performed as a preliminary step, producing several plastisols varying the amount of foaming agent in the range between 1 and 6 phr, which were expanded at 200 °C for 60 seconds in a Mathis oven. This process parameters were chosen on the basis of Vulcaflex know–how. Each expanded foil obtained was weighted and measured in thickness, in order to calculate foam density. The obtained curves, reported in Figure 3.5, allowed to individuate the loading necessary for any BA in order to obtain an optimal desired density of 0.40 ± 0.05 g/m^3.

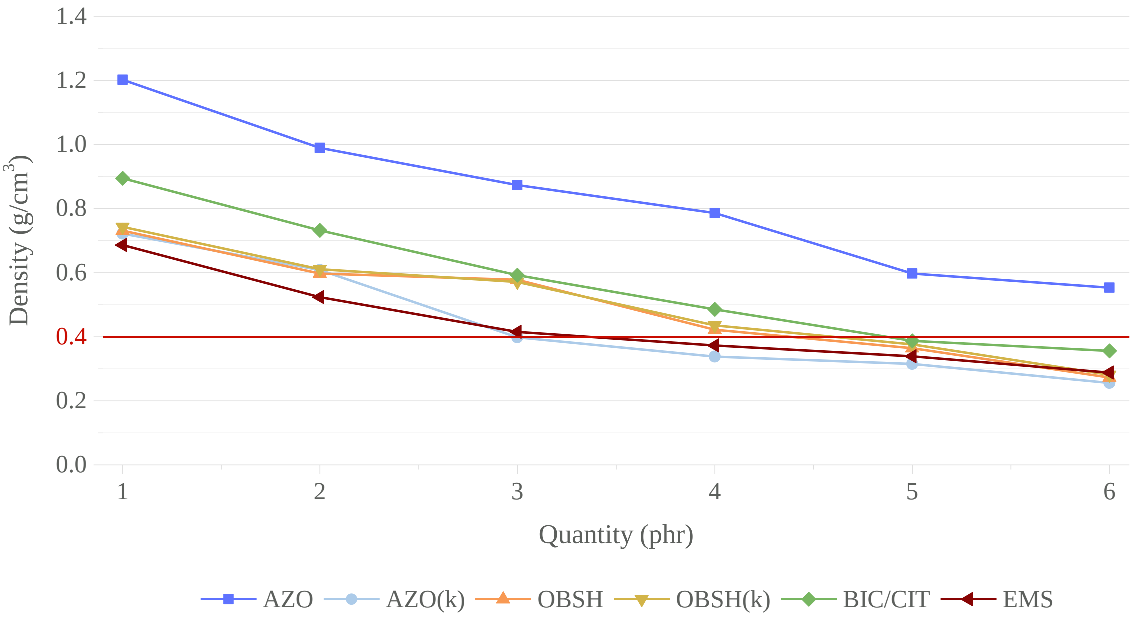


Figure 6.5: foils density obtained after 60 s @ 200 °C, with different loading of BAs.

Thus, the quantity of each BA selected on the basis of these preliminary tests is hereafter reported (Table 6.1).

Table 6.1: list of the samples subjected to testing.

#	*BA*	*Quantity (phr)*	*Kicker (phr)*
1	AZO	3	–
2	AZO(k)	3	0.5
3	OBSH	4.5	–
4	OBSH(k)	4.5	0.5
5	BIC/CIT	5	–
6	EMS	4	–

6.2.2. Foam properties

- *Expansion curves*

In order to verify the yield of each BA, in terms of maximum attainable expansion, tests in Mathis oven at different temperatures and residence times were carried out. The obtained results allowed the tuning of process parameters (temperature and residence time) necessary to obtain with all the samples the desired expansion values (foam density = 0.40 ± 0.05 g/m^3). The data obtained with this tests were used for the preparation of the samples for further testing. The preliminary tests were performed at 180, 190 and 200 °C, with residence times ranging from 30 to 70 seconds: shorter times would result in incomplete gelation and expansion, while longer times usually lead to the collapse of the foam, detectable by the increase of the density after a plateau. Density curves, with the target density values of 0.40 g/m^3 put in evidence, are below reported (Figure 6.6 to Figure 6.11).

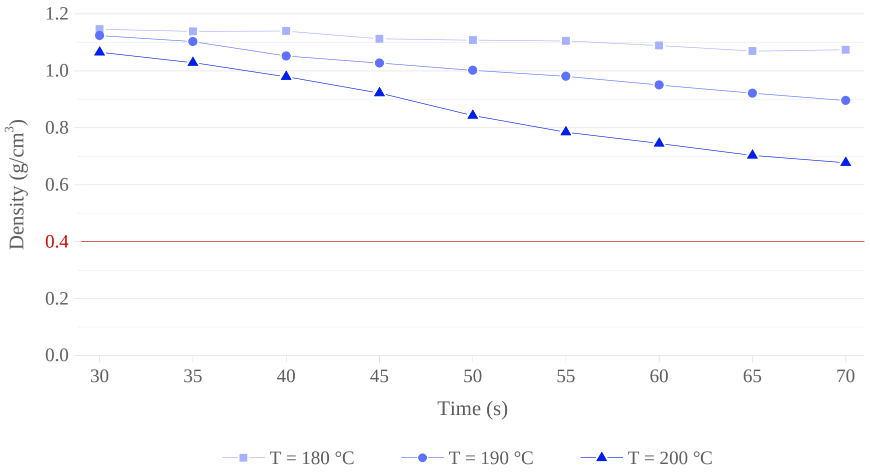


Figure 6.6: Expansion curves of AZO.

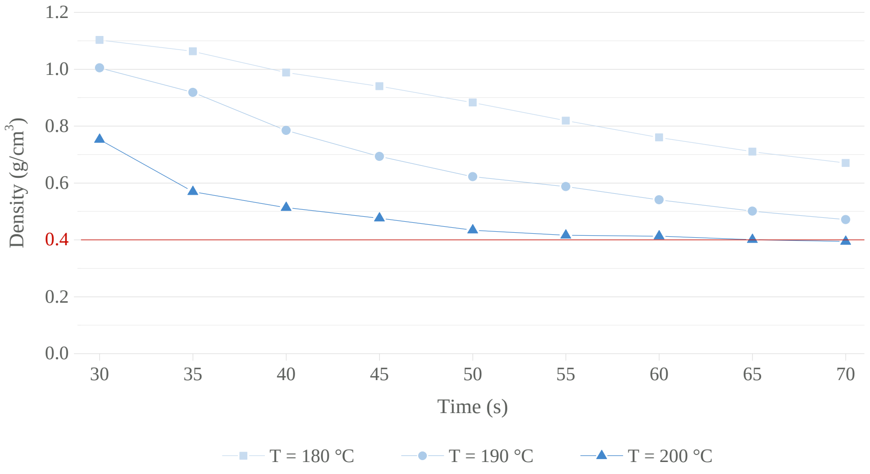


Figure 6.7: Expansion curves of AZO(k).

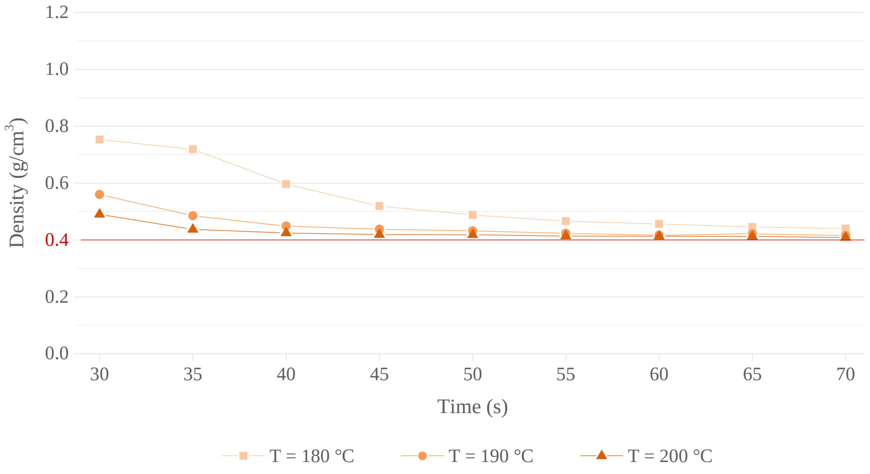


Figure 6.8: Expansion curves of OBSH.

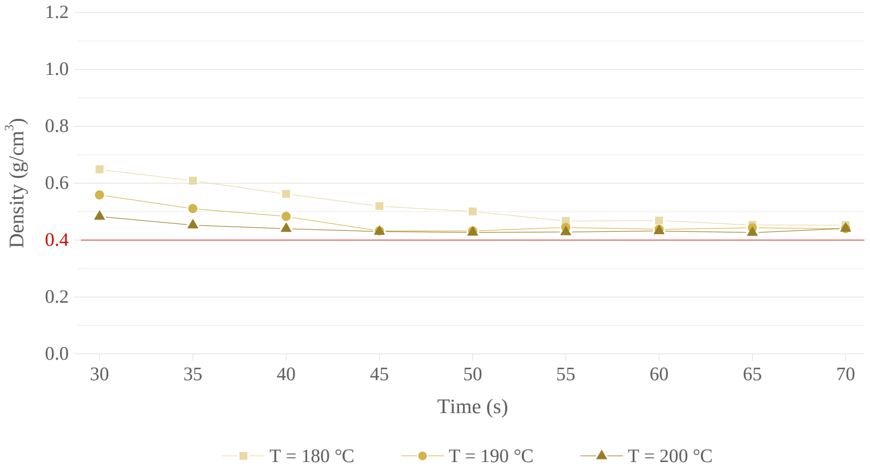


Figure 6.9: Expansion curves of OBSH(k).

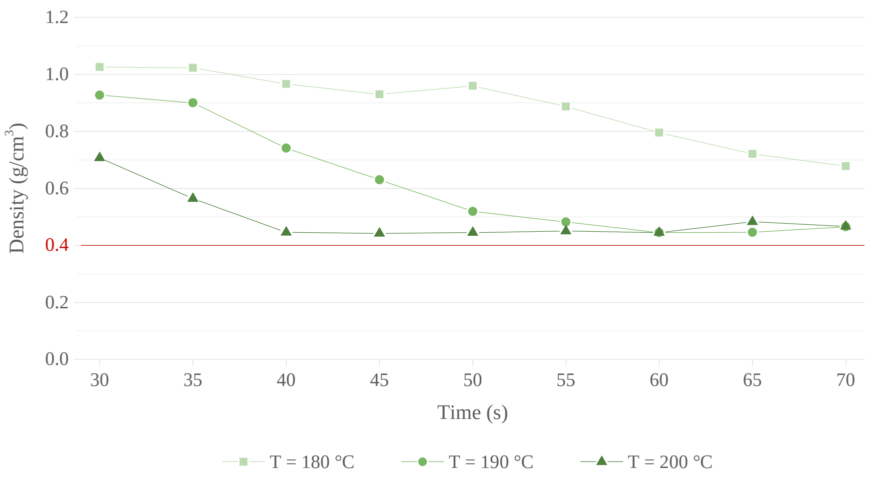


Figure 6.10: Expansion curves of BIC/CIT.

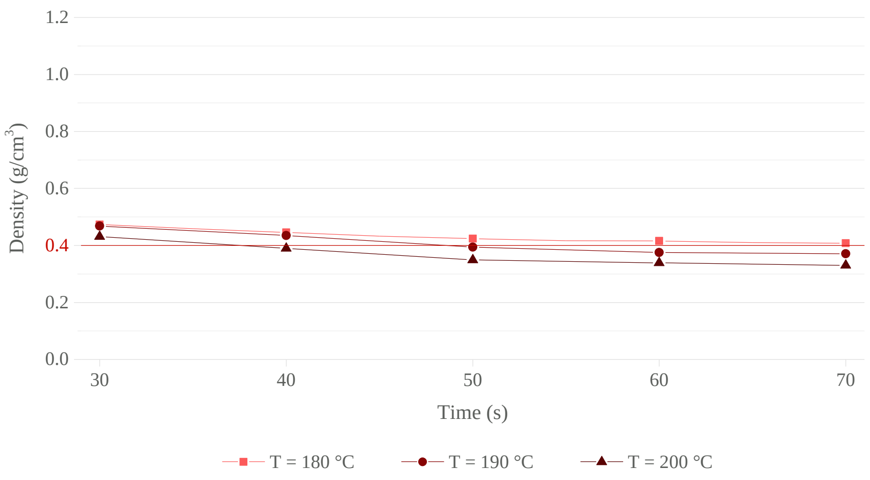


Figure 6.11: Expansion curves of EMS.

The obtained curves allow to observe that in all cases, the increase of process temperature leads to a greater expansion (i.e. lower density), with the partial exception of EMS, that is already effective at 180 °C, and thus shows minor differences at higher temperatures. It is worth noting that AZO is not particularly effective and does not reach the desired foam density neither with 70 s @ 200 °C. However, by adding the kicker, the decomposition rate significantly accelerates, resulting in an efficient foaming system. Conversely, the use of a kicker is not beneficial in the case of OBSH, as it only lowers marginally the densities at 180 °C leaving unaltered the curves at higher temperatures. Finally, BIC/CIT exhibits the most temperature–dependent behaviour amongst the samples, with the curve obtained at 200 °C that reaches a plateau between 40 and 60 seconds, after which the density begins to increase possibly due to cells collapse. Thus, as shown in Figure 6.12, the best compromise to obtain the best overall conditions results to be 60 seconds at 200°C, even if the sample containing AZO without kicker, only reached a density of approx. 0.7 g/cm^3.

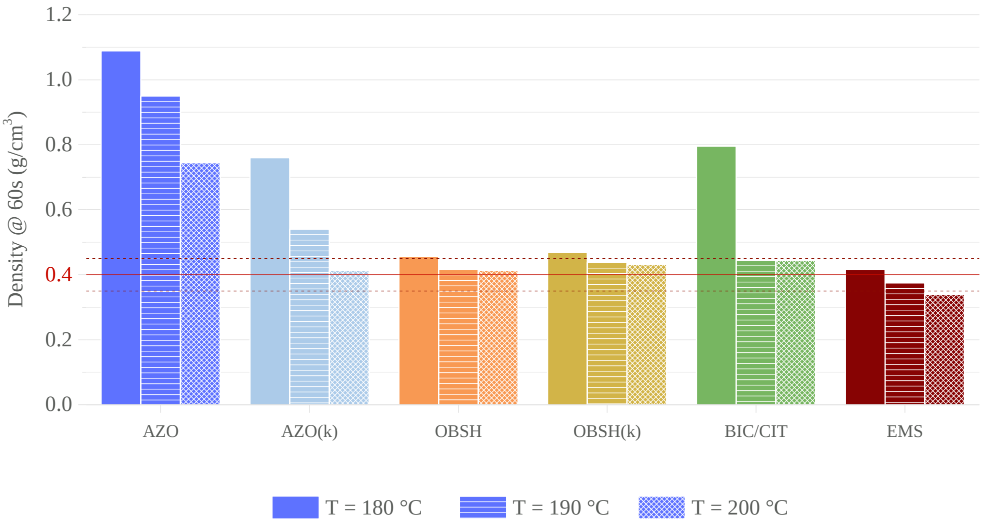
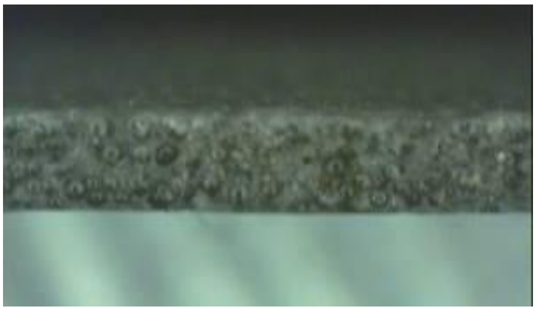


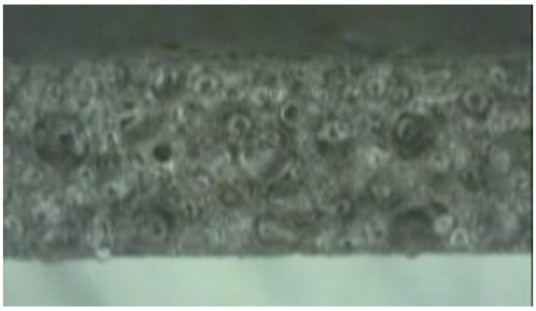
Figure 6.12: densities of foamed samples obtained after 60 s at different temperatures.

- *Evaluation of the cellulation*

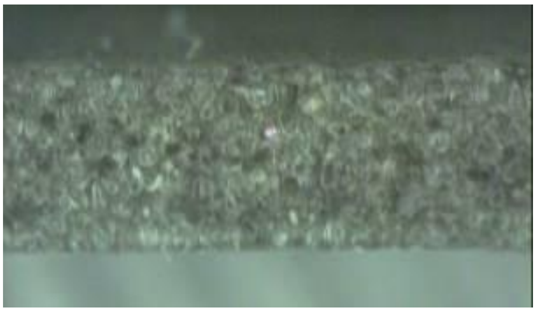
With the aim to evaluate the quality of the cellulation, the section of each foamed sample was observed under a microscope, with a 50x magnification.



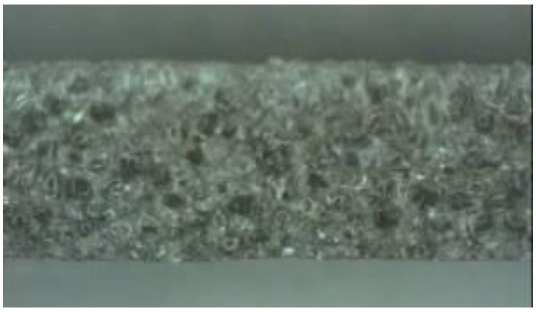
AZO



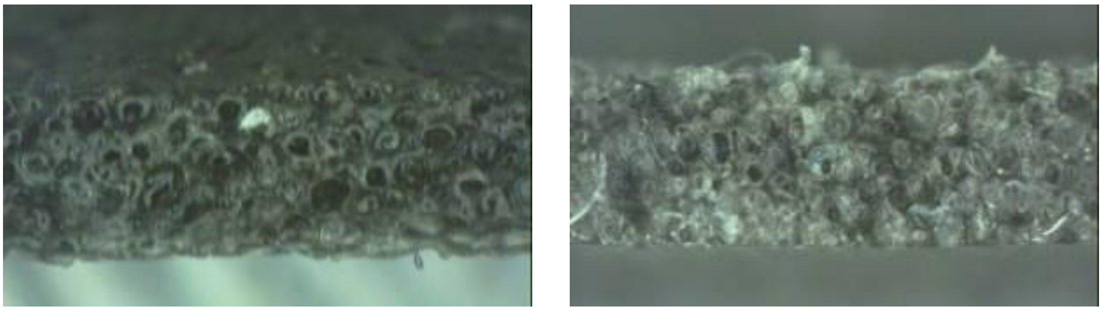
AZO(k)



OBSH



OBSH(k)



BIC/CIT EMS

Figure 6.13: micrographs of sections of foamed sample after 60 s at 200 °C.

The obtained micrographs, reported in Figure 6.13, show the poor expansion obtained for AZO foamed foils in the used gelation conditions. Thus this sample was discarded and not subjected to further testing. The addition of the kicker in AZO(k) sample leads to a better cellulation, even though the cells size results slightly inhomogeneous. OBSH and OBSH(k) exhibit an analogous expansion, and a finer and more homogeneous cells size. The sample obtained with BIC/CIT has coarser but quite similar cells dimensions, while EMS proved to be quite inhomogeneous in size and dimensions of cells.

6.2.3. Mechanical properties

- *Ultimate Tensile Strength and Elongation at Break*

All the foamed samples were analysed by tensile tests. The obtained ultimate tensile strength (UTS) and elongation at break (EB) values (Table 6.2 and Figure 6.14) are comprehensibly lower than those one usually reported for compact samples (see Table 4.5, #2), due to the non–cohesive nature of foamed layers.

Table 6.2: Ultimate tensile strength (UTS) and elongation at break (EB) of the expanded foils.

#	*BA*	*UTS (MPa)*	*EB (%)*
1	AZO(k)	1.7	259
2	OBSH	1.9	228
3	OBSH(k)	2.1	230
4	BIC/CIT	1.7	221
5	EMS	1.3	164

In particular, OBSH samples show the best mechanical resistance, in terms of UTS (Figure 6.14), mainly when in presence of the kicker, while AZO(k) retain higher elasticity. BIC/CIT behave in a similar fashion than the exothermal BAs. Lastly, the performances of EMS are quite poor in both UTS and EB values, possibly due to the reduced compatibility between the thermoplastic shell of the microspheres and the PVC matrix.

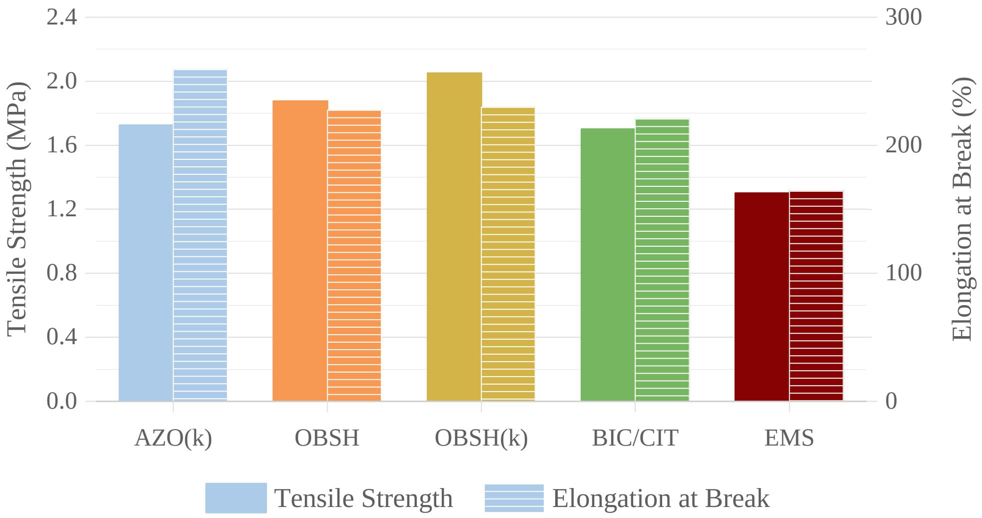


Figure 6.14: Ultimate Tensile Strength (UTS) and Elongation at Break (EB) of the samples.

- *Flex Resistance*

The resistance of foamed samples to flexion was evaluated by means of a Bally flexometer, operated at room temperature and set for 100,000 cycles. Results of the visual evaluation of the samples are reported in Table 6.3, using a rating scale where 0 indicates no cracks and 4 stands for complete fracture of the sample (see Paragraph 3.2.2).

Table 6.3: Evaluation of the samples after flex test.

#	BA	FR
1	AZO(k)	0
2	OBSH	0
3	OBSH(k)	0
4	BIC/CIT	1
5	EMS	3

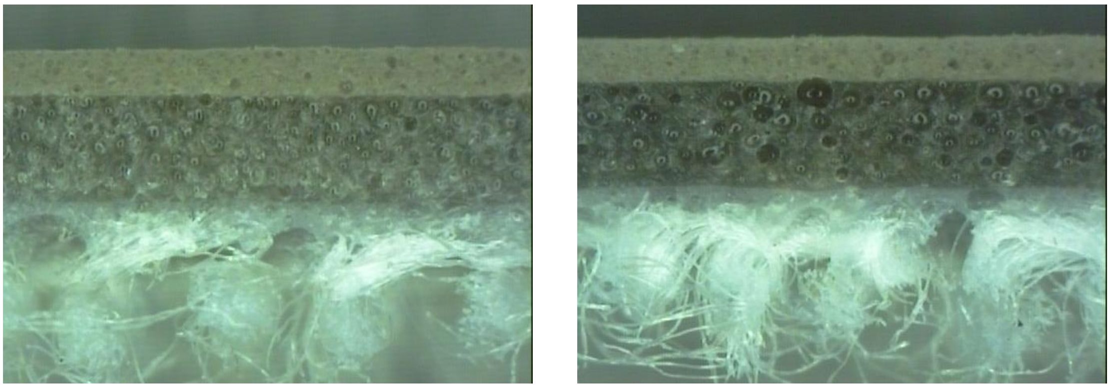
The poor mechanical resistance of EMS is confirmed also by the flex resistance test, while the sample containing BIC/CIT shown only minor cracks. Conversely, the performances of AZO(k) and OBSH are optimal, with undamaged samples after the test.

6.2.4. Industrial test batch

Even though OBSH, amongst the BAs tested, exhibited better performances than ATO(k), due to the non–optimal potential health and environment effects it was not selected for further testing on industrial scale. The candidate chosen was, instead, BIC/CIT which is slightly less performant than AZO(k) and OBSH but with an increased sustainability compared to them.

Hence, BIC/CIT was chosen for the industrial manufacturing of a supported SL, and the obtained material was compared to a standard product obtained with AZO(k). The exact recipe for the plastisol used, as well as the process parameters employed, are an industrial secret and therefore will not be disclosed. It must be noticed, however, that the BIC/CIT additive employed for this industrial production test is an evolved version, in terms of additive formulation improved by the manufacturer, of the one used in the laboratory scale test. Nevertheless, the main components of the mixture remained sodium bicarbonate and citric acid.

As a first step, an evaluation of the cellulation obtained with the industrial process was performed by means of microscopy observations on sections of the finished material. The comparison is reported in Figure 6.15.



a) b)

Figure 6.15: micrographs of sections of the finished materials. a) AZO(k); b) BIC/CIT.

The fine and even cellulation of the expanded layer obtained with AZO(k) were not matched by the one obtained with BIC/CIT. In fact, the latter presents more coarse and uneven cells, even though a closed cellulation was obtained. Subsequently, mechanical tests were performed to determine ultimate tensile strength (UTS), elongation at break (EB) and also tearing strength (TS) and cold resistance (CR) (see Paragraph 3.2.2). Mechanical tests have been performed on samples cut in both machine direction (MD, longitudinal) and cross–machine direction (CMD, transverse) due to the different isotropy of the finished material imparted by the presence of a support textile with different warp and weft. Results obtained are reported in Table 6.4.

Table 6.4: Comparison between the industrial production of AZO(k) and BIC/CIT.

#	BA	UTS (MPa)		EB (%)		TS (N)		CR
		MD	CMD	MD	CMD	MD	CMD	
1	AZO(k)	7.4	6.1	82	187	35	26	0
2	BIC/CIT	8.1	6.2	77	214	36	29	1

These results, even though limited to few mechanical tests, clearly put in evidence the good results obtained by BIC/CIT in a real–world application, even though cellulation (Figure 6.13 and Figure 6.15) and preliminary tests on laboratory scale (Paragraph 6.2.3) suggested a behaviour not comparable with the reference, AZO(k). However, further testing both at laboratory and industrial scale will be done in order to confirm these promising results and to verify the possible range of application of this foaming agent.

6.3. Conclusions

The research for alternative BAs is a particular difficult task, due to the scarcity of compounds which can yield foamed layers in the range of useful process times and temperatures without imparting, at the same time, any other change in the properties of the finished product. It is worth noting that this part of the research project is relatively recent and will be prosecuted in the future, in view of the preliminary but promising result since now obtained.

Amongst the tested additives, OBSH is the foaming agents that yields the best results, but it is potentially harmful for human health and the environment, as previously described, and therefore not the perfect candidate in order to reach the sustainability and security aims of the present work. Conversely, a BA that coincide with the aforementioned targets aims is the non–toxic and green BIC/CIT, and even though the results obtained on a laboratory scale suggested a lesser effectiveness if compared to AZO(k) or OBSH, its future diffusion could be possible. In fact, the first industrial test batches for the production of actual finished materials, manufactured using an improved version of **BIC/CIT**, exhibited performances comparable to the ones obtained with AZO(k). Moreover, due to the presence of a number of similar additives on the market, and to the ongoing research carried out thanks to manufacturers, formulators and research groups, the possibilities to see an effective and sustainable endothermic blowing agent based on bicarbonate and citric acid are definitely likely.

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7

Organic modified nanoclays

7.1. Introduction

The use of finely dispersed, mainly inorganic, fillers in polymers is a well–known practice, pursued to improve primarily their mechanical properties, hence the common term “reinforcement” [1, 2], but also rheological, thermal and even conductivity properties [3, 4]. The last decades saw the introduction and diffusion of nanoscale polymer composites, which immediately pointed out the high potential of the nano–metric dispersion of various additives, and the gained advantages with respect to traditional–scale composites [5, 6]. The common feature of these nano–additives is the high surface area and, thus, the strong interface interactions that can be established with the matrix in which they are dispersed [7]. Amongst the various fillers, clay based compounds have the peculiar property of being natural based inorganic compounds with a layered nature, as shown in Figure 7.1, that can be exfoliated and dispersed to nano–metric scale as single or double silicate layers with thickness in the range of 0.7 and 1 nm respectively. Thus, a dramatic increase of surface area and interfacial interactions with the polymer matrix occurs.

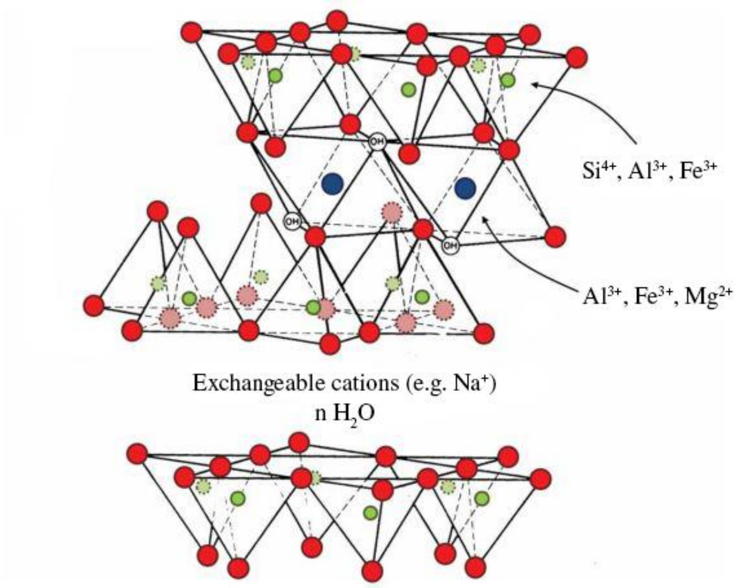

Figure 7.1: montmorillonite structure. Adapted from Paineau [8].

The properties imparted on polymers by these nanoclays have proved to be particularly interesting. For example, studies have proved the positive impact of nanoclays on flame resistance of polymers [9], while others pointed out a certain reduction in migration of plasticizer in pPVC in consequence of the addition of nanoclays [10]. In fact, the presence of these silicate layers dispersed in the polymer matrix makes more tortuous the path towards the surface [11]: the plasticizer molecules would find physical obstacles in their diffusion, which will thus result in a reduced migration. Furthermore, the high aspect ratio gives greater possibility of energy transfer from the two phases, yielding improved mechanical properties [12]. The major drawback related to the use of these compounds is the low compatibility of these additives with polymers, due to the ionic and, thus, hydrophilic nature of phyllosilicates. A way to make them more compatible with a variety of polymers is modify them by means of interlayer cation exchanges [13, 14], obtaining Organic Modified Nanoclays (OMNC). The most used ions for this procedure are ammonium quaternary salts whose exchange efficiency is particularly remarkable, to the point that they are often considered a reference method for the determination of the cation exchange capacity (CEC) [15]. Quaternary ammonium could be substituted with several functionalities, becoming even a surfactant, which can be tailored to maximize the compatibility with different polymers. These tailored ammonium cations act enlarging the interlayer spaces and making the surfaces of the silicate layers more lipophilic and, thus, more compatible with the polymer chains. These two conditions are aimed at favouring the exfoliation of the platelets that constitute the nanoclay.

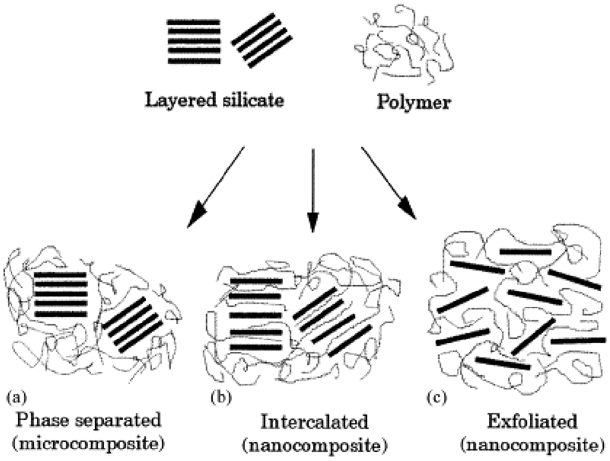

Figure 7.2: schematic representation of different polymer/clay nanocomposites. (Reproduced with permission from Alexandre et al. [16])

Being the proper dispersion into the matrix the most critical issue related to the use of nanoclays, the attention of the researchers has focused on the dispersion methods. As shown in Figure 7.2, the dispersion of layered silicates passes through two steps, intercalation and exfoliation, with the first one being mainly a time–dependent process, while the latter more dependent on the energy input. In particular, the techniques that proved to be more efficient are those ones based on the simultaneous application of heat and shear, otherwise said "melt mixing", like twin–screw extrusion, advanced compounding and injection mould compounding [17]. These techniques are particularly attractive for the industry, due to the wide offered possibility in terms of the nature of polymer, such as various molecular weights, grafting grades, copolymers and also recycled feedstock. Moreover, melt mixing is a solvent–free process and does not involve chemical reactions as, instead required for alternative techniques such as solvent exfoliation or *in situ* intercalative polymerization. For these reasons, the preferred polymers in which nanoclays have been tested are thermoplastics like polyolefins, polyamides, polystyrene, PMMA, PLA and, even though to a lesser extent, PVC [18].

In the case of pPVC SLs, dispersion of nanoclays is particularly challenging, due to the fact that the plastisol route commonly employed is basically a cold process. In fact, the material is heated only briefly, when passing through the gelation ovens, and while being already spread and, thus, not subjected to any mechanical shear. Hence, a different approach for the dispersion of nanoclays was designed, as described in the next section. Another reported issue in the use of OMNC in PVC formulation, particularly with ammonium quaternary salts, is the negative effect on thermal stability of the material. In fact, these organoclays are thought to be responsible for accelerated degradation in the initial stage of polymer decomposition [19].

7.2. Results and discussion

Nanoclays were subjected to testing with the aim of evaluating possible enhancement of mechanical properties, flame resistance and anti–migration capabilities. The performances of each nanoclay in pPVC samples, at different loading, were assessed by measuring ultimate tensile strength (UTS) and elongation at break (EB) (see Paragraph 3.2.2), thermal stability and aging, and flammability properties by means of cone calorimetry and horizontal combustion tests (see Paragraph 3.2.3). Furthermore, their effect on plasticizer migration were determined with semi–rigid foil and butter migration tests (see Paragraph 3.2.4). Obtained results were compared to a sample without additives containing only a standard phthalate plasticizer and heat stabilizers (i.e. neat pPVC) and to antimony trioxide (ATO) flame retardant, added at 2 phr, due to the possible enhancement of fire resistance by the use of nanoclays.

7.2.1. Plastisol formulation

In order to evaluate their effect, nanoclays at different loading were added to the Recipe B, used for the evaluation of plasticizers (Table 4.1). Diundecyl Phthalate (DUP) was used as plasticizer, being the best performer amongst (standard) phthalate plasticizers, as demonstrated in Chapter 4.

The method used for samples preparation is the same used previously for the evaluation of the other additives studied in the present work (Paragraph 3.1). A summary of the different samples subjected to testing is reported in Table 7.1.

Table 7.1: list of the samples subjected to testing

#	*Type*	*Sample*	*phr*
1	Neat pPVC	DUP	–
2	FR	ATO	2
3	OMNC	10A	1
4	OMNC	10A	2
5	OMNC	10A	4
6	OMNC	I34	1
7	OMNC	I34	2
8	OMNC	I34	4
9	OMNC	I34	10
10	NC	HYS	1
11	NC	HYS	2
12	NC	HYS	4
13	NC	HYS	10

Sample #1 is a neat pPVC foil, without any NC, but only plasticizer (DUP) and heat stabilizers as per Table 4.2.

- *Nanoclays dispersion*

Each nanoclays was then added to the neutral formulation in percentages ranging from approx. 0.5 to 5.0 wt%. The procedure for the dispersion of these additives in plastisols was improved, in order to increase the possibility to obtain intercalated or exfoliated nanocomposites, using, as starting point, the few works found in literature [11] as well as the company know–how. However, the used techniques and apparatus were chosen bearing in mind a possible scale–up of the procedure. Hence, only equipment which simulate Vulcaflex industrial processes were used.

Different approaches were followed to disperse the nanoclays. These dispersion tests were performed only on 10A nanoclay, at 4 phr, and an initial evaluation of each technique has been given by observing the characteristic of the plastisol (i.e. thickness, bubbles, presence of aggregates) and of the obtained foils (i.e. colour homogeneity, holes and voids). The pathways attempted are briefly explained hereafter.

i. Plastisol preparation, as described in Paragraph 3.1. This method yielded poor results, as demonstrated by the extremely high viscosity of the plastisol and by the inhomogeneous colour and presence of voids in the foils, after gelation in Mathis oven.
ii. Same as the previous, but with the addition of 0.5–1.5 phr of a dispersing agent, typically used for pigment pastes preparation. The result did not vary compared to the previous.
iii. Preparation of a paste containing 15 wt% nanoclay in plasticizer (DUP), with the aid of a dispersing agent (2 wt%). The obtained thick paste was passed two times through a three–roll mill decreasing the gap between the rolls at the second passage, for finer dispersion. Subsequently, the paste was dosed in a neutral plastisol prepared subtracting the contribution of the plasticizer already present in the nanoclay paste. The paste was difficultly homogenised in the neutral plastisol, and yielded non-optimal foils.
iv. Pre–dispersion of the nanoclay in plasticizer (DUP), using a mechanical overhead stirrer (IKA overhead stirrer, equipped with a R1302 dissolver stirrer) left to mix

the dispersion at high speed for 12 hours. Even this method did not give the expected results, possibly due to insufficient shear stress and the consequent low heat build–up.

All of these tests were performed in order to obtain exfoliation of the silicate layers. However, none of the attempts yielded an ideal result, giving inhomogeneous foils. A procedure that instead gave better results, and that was adopted for the preparation of all samples, is here reported. The PVC resins and the nanoclay powders were high–speed mixed using a food mixer equipped with blender mixing blades, which allowed a good mixing of the powders and an increase of their temperature up to 55–60 °C. This temperature, measured with an infrared thermometer, is however probably not high enough to induce the softening of the PVC, due to the overcoming of its T_g (80–85 °C) [20], and the desired reciprocal interpenetration of the polymer chains and silicate layers. Once this step is over, the powder was transferred to another container and manually mixed with half of the plasticizer expected to be used (i.e. 37.5 phr), obtaining a very thick paste which was passed through a three–roll mill to disrupt the aggregates and homogenize the suspension, and degassed under vacuum for 10 minutes. In this step, the high–speed mix (1,000 rpm) of the dissolver stirrer combined with the high viscosity of the paste give rise to a sensible temperature increase, which reaches 45–65 °C depending on the nanoclay loading. Finally, after the addition of the remnant part of the plasticizer and the heat stabilization system, the plastisol was manually mixed, homogenized through a three–roll mill and degassed a second time. The evaluation of the samples obtained through this pathway was focused on the imparted tensile properties, influence on migration of the plasticizer, thermal and flame resistance.

7.2.2. Viscosity of plastisols

The addition of fillers, nanoclays included, typically gives an increase of the obtained plastisol viscosity. The measure of this property of plastisols is paramount for the process, because in order to be coated on the carrier release–paper, the plastisols need to have a viscosity comprised in a precise range. Hence, if not in the desired range, the viscosity should be adjusted by changing some of the components of the formulation, or adding suitable rheology modifiers. The viscosities of the obtained plastisols after the addition of NC are graphically reported in Figure 7.3. These plastisols were spread without any further rheology modification.

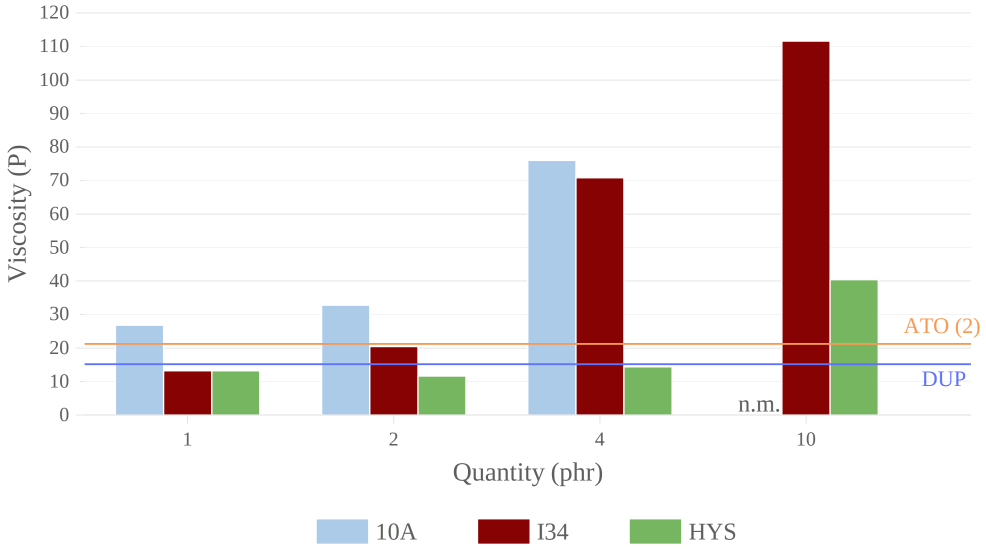

Figure 7.3: viscosity measures of plastisols containing different nanoclays.

The graph reported above also indicates the viscosities of the neat plastisol (DUP, blu line) and the ones containing 2 phr of ATO (orange line), as a reference. It is easy to see how viscosity increases when increasing the loading of nanoclays inside the plastisol. Montmorillonite based nanoclays greatly thickens the plastisol, particularly at loading higher than 4 phr. Sample 10A exhibits the greatest rheology modification, yielding a plastisol with non–measurable (n.m.) viscosity. Conversely, HYS does not modify the viscosity of the plastisol unless 10 phr were added. The potential use of these additives, hence, should be carefully evaluated from the rheological point of view in order to have plastisols that could be effectively spread and coated.

7.2.3. Mechanical properties

- *Ultimate Tensile Strength and Elongation at Break*

One of the main features reported in literature regarding polymer nanocomposites is their increased tensile properties due to the presence of the finely dispersed nano–additives. Results obtained by the organoclays containing samples are reported in Table 7.2 and, for better comparison, in Figure 7.4.

Table 7.2: Ultimate tensile strength (UTS) and elongation at break (EB) of nanoclays samples

#	*Sample*	*phr*	*UTS (MPa)*	*EB (%)*
1	DUP	-	12.8	615
2	ATO	2	11.8	515
3	10A	1	10.7	392
4	10A	2	10.8	389
5	10A	4	10.1	343
6	I34	1	12.4	461
7	I34	2	11.4	394
8	I34	4	11.4	390
9	I34	10	9.5	327
10	HYS	1	12.3	443
11	HYS	2	12.1	427
12	HYS	4	12.2	436
13	HYS	10	11.3	385

As it was expected, the addition of a filler always yields stiffer materials, as demonstrated by the quite lower EB values compared to the unfilled sample or even ATO (2). Moreover, it is also arguable that the addition of reinforcement did not impart a beneficial effect on tensile strength. In fact, all the samples show UTS values lower than the unfilled sample, particularly the series of 10A nanoclay and I34 when added in higher quantities (10 phr). However, both I34 and HYS up to 4 phr exhibit similar UTS values compared to ATO, even though EB is definitely lower. Such a behaviour could be attributed to the non–optimal dispersion of the nanoclay, despite similar trends were previously reported by other authors [18, 21].

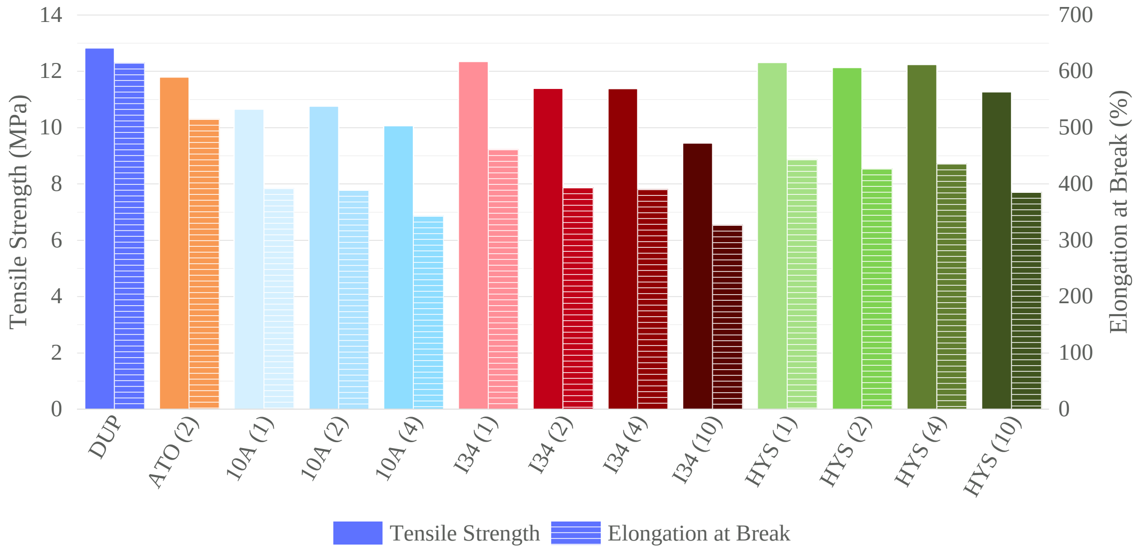

Figure 7.4: Ultimate Tensile Strength (UTS) and Elongation at Break (EB) of nanoclay samples.

7.2.4. Thermal and flame properties

- *Thermal Stability*

As previously reported [19], the ammonium quaternary salts in the organic modified nanoclays catalyse dehydrochlorination reactions, leading to an accelerate degradation of the pPVC materials. This effect is reflected in the thermal stability of the tested samples, as shown in Figure 7.5.

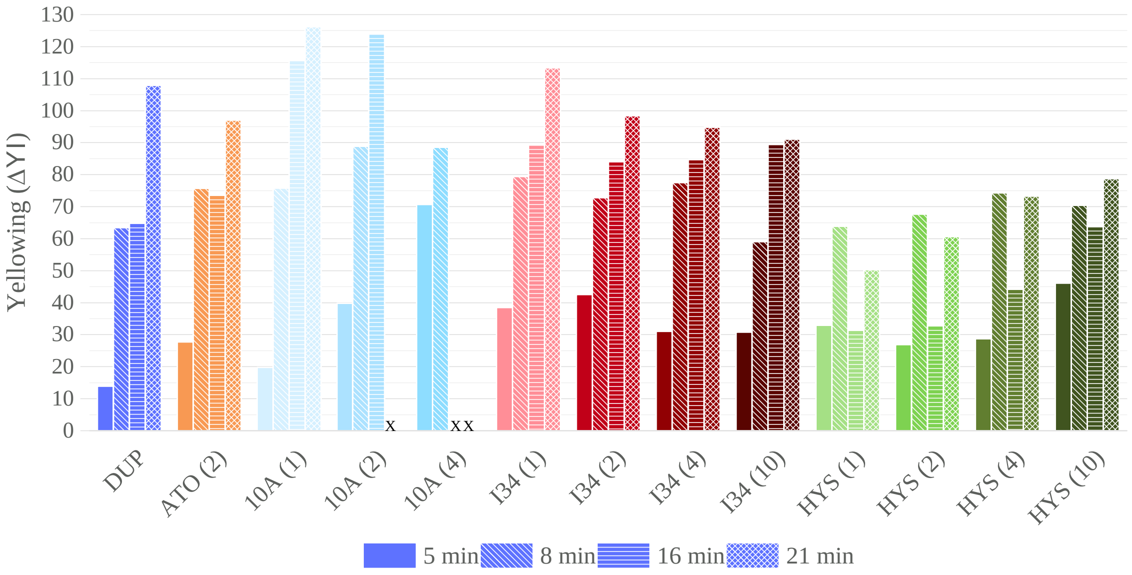

Figure 7.5: Thermal stability of nanoclay samples.

The first noticeable fact is the impossibility to make instrumental readings of 10A (2) sample at 21 minutes, as well as 10A (4) sample at 16 and 21 minutes of exposure at 200°C (marked with X in Figure 4.5). In fact, the performances of these PVC nanocomposites samples at any of the tested loading are clearly unacceptable due to the high occurred degradation in these conditions. The results obtained by I34 specimens seem to be promising, with ΔYI at the highest loading which is lower than DUP and ATO (2) containing materials. However, as shown in Figure 7.6, the result is biased by the much higher initial colouration imparted by I34 (10) to the pPVC foil, which is an undesired effect. This comparison allows also to confirm the good performance imparted at the material by HYS nanoclay at all loadings, but particularly up to 4 phr. In fact, the initial colour of HYS samples, as well as their maximum yellowing, is the most neutral amongst the nanoclays tested, but also compared to ATO and DUP. These results are in accordance to what reported in literature. In fact, the presence of clays seems to provide stability to the PVC system, in particular stabilizing the allylic species that form during dehydrochlorination reactions [22, 23]. However, as previously stated, the presence of ammonium quaternary ions in the OMNCs (10A and I34) is accountable for the accelerated degradation of polymer [19] and, thus, for the far from optimal, if not detrimental, thermal degradability.

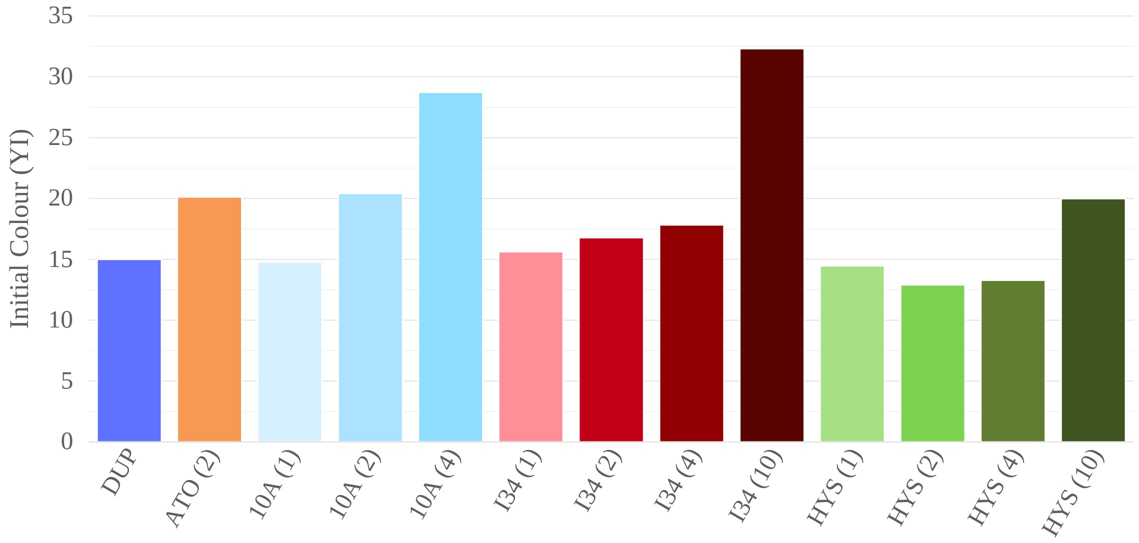

Figure 7.6: Initial colour of the samples loaded with nanoclays.

Yellowing pathways of samples containing HYS, noticeable in Figure 7.5 but better represented by yellowing curves reported in Figure 7.7, follow a singular trend between 8 and 21 minutes, also exhibited by DUP and ATO (2), even though with different entities and time shifts. As previously stated, this trend could be attributed to the amount and chemical nature of the residual surfactants and antioxidants from the polymerization of

VCM. Conversely, 10A (4) and I34 (10) masks this trend, exhibiting a faster yellowing that yields blackening (i.e. complete degradation) occurring at shorter times.

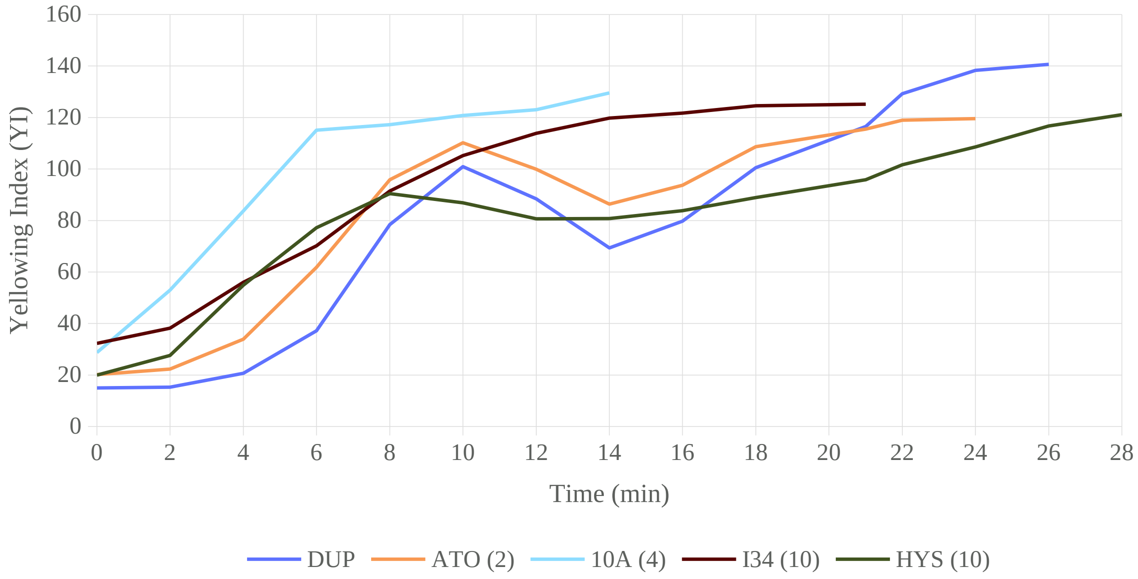

Figure 7.7: Yellowing trends of selected samples.

- *Thermal aging*

All of the nanoclay–containing samples were maintained at 90 °C for 7 days, in order to evaluate the weathering induced by exposure at moderately high temperature. As for thermal stability tests, results are expressed as variation of the yellowing index (ΔYI) with respect to the unexposed sample (Figure 7.8) and show that ATO sample is subjected to the greatest yellowing, while PVC containing only DUP exhibits the best result.

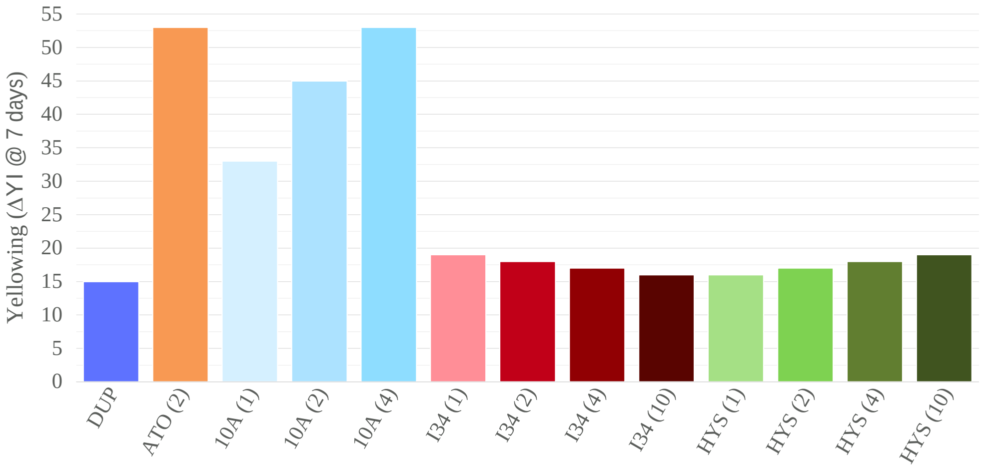

Figure 7.8: Thermal aging of nanoclay samples after 7 days @ 90 °C.

Furthermore, 10A samples display a marked enhancement of yellowing with increasing load, while HYS samples exhibit similar ΔYI to that of DUP, even if a slightly increase of yellowing occurs passing from 1 to 10 phr. The trend shown by I34 is exactly the opposite of HYS, with a slight decrease of the yellowing when increasing the load, suggesting, in this case, a beneficial effect on weathering.

- *Flame resistance*

As mentioned, one of the reported positive effects of the use of nanoclays is the imparted flame resistance. Being a property particularly important that characterizes the pPVC SLs for the automotive industry, an evaluation of the flame retardancy of all the obtained samples by means of the horizontal combustion test, according to ISO 3795 [24], was performed. The results, reported in Table 7.3, are expressed as burning rate (mm/min). A typical limit demanded by automotive industries is 100 mm/min.

Table 7.3: Evaluation of the burning rate of the nanoclay loaded samples.

#	Sample	phr	BR (mm/min)
1	DUP	-	108
2	ATO	2	4
3	10A	1	119
4	10A	2	115
5	10A	4	107
6	I34	1	118
7	I34	2	119
8	I34	4	119
9	I34	10	99
10	HYS	1	116
11	HYS	2	132
12	HYS	4	151
13	HYS	10	110

Despite in the literature it is reported the use of nanoclays to improve the flame resistance of polymeric materials [9, 25, 26], the obtained results show that all the tested samples have BR similar (and also higher) to that one of DUP, and very different from the performances of ATO (Figure 7.9). This fact is quite unexpected, particularly in the case of HYS, which is the only one amongst the nanoclay tested being unmodified and, hence, purely inorganic. It is therefore possible that these particular nanoclays exert a catalytic effect on the combustion reactions, based on the presence of particular cations or on the tubular morphology of the nanoparticles. Another hypothesis for this behaviour, reported also by others [27], could be the interference of the nanoclays in the char layer typically formed during the combustion of PVC, with the result of a non–continuous and, hence, non–effective char layer on the surface of the burning sample. Conversely, the increasing loading of 10A causes a decrease of the burning rate, possibly due to a char–promoting effect of this nanoclay, which contains an aromatic ring on the quaternary ammonium ion used for its organic modification.

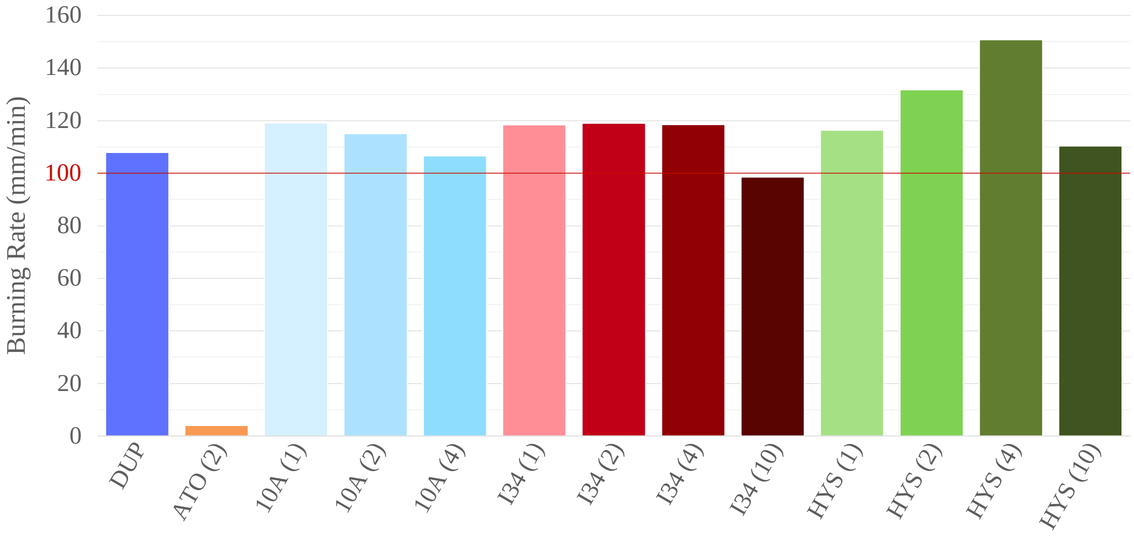

Figure 7.9: Burning rates of the samples loaded with nanoclays.

- *Cone calorimetry*

All the samples loaded with nanoclays were subjected to cone calorimetry analysis, in order to obtain a better comprehension of their flame response. Results obtained for Time to Ignition (TI), Total Heat Release (THR), peak Heat Release Rate (pHRR) and time to peak Heat Release Rate (t–pHRR) are reported in Table 7.4 and Figure 7.10.

Table 7.4: data obtained from cone calorimetric tests on nanoclay loaded samples.

#	Sample	phr	THR (MJ/m^2)	pHRR (kW/m^2)	TI (s)	t–pHRR (s)
1	DUP	-	13.4	317.0	35	64
2	ATO	2	12.4	266.1	41	74
3	10A	1	13.9	372.7	36	55
4	10A	2	16.3	393.4	37	56
5	10A	4	17.4	390.7	35	60

6	I34	1	13.1	296.3	30	62
7	I34	2	12.5	275.9	32	62
8	I34	4	13.1	286.5	32	58
9	I34	10	13.6	298.5	32	70
10	HYS	1	11.3	255.6	29	65
11	HYS	2	12.2	263.8	26	62
12	HYS	4	13.6	278.9	36	75
13	HYS	10	13.5	258.1	29	68

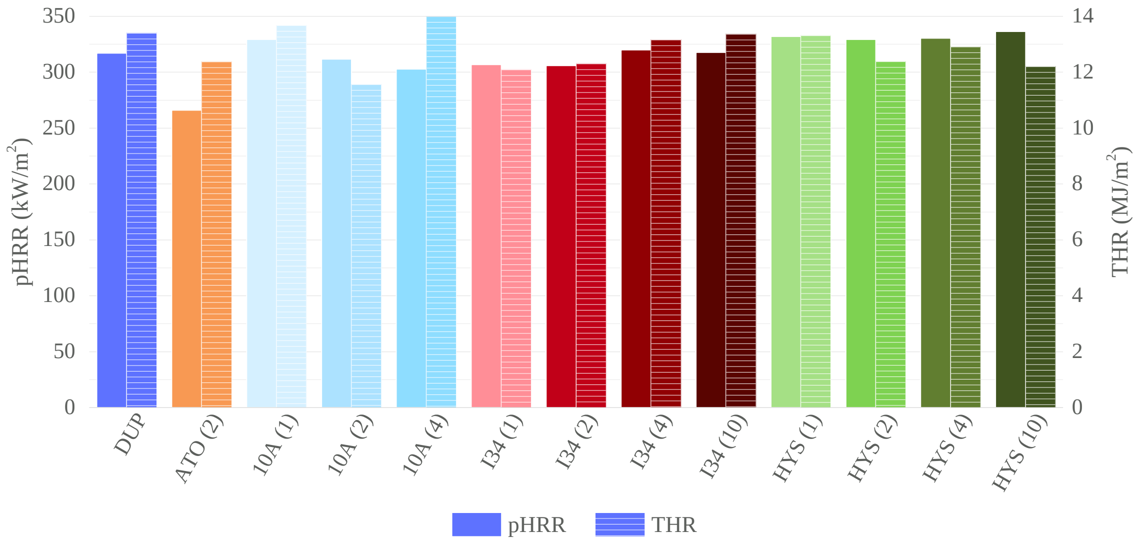

Figure 7.10: pHRR and THR of nanoclay loaded samples.

The sample containing ATO exhibit the best flame response in terms of both pHRR and THR. Samples containing increasing load of 10A nanoclay seem to follow a decreasing trend for pHRR, which falls, at 4 phr, below the value registered for DUP, even though it remains quite far from what obtained with ATO. Diversely, THR shows a minimum lower than ATO, when added at 2 phr but dramatically increases at 4 phr. The other organic modified nanoclay (I34) up to 4 phr shows similar or better results for both pHRR and THR when compared to DUP. At the same time, I34 (1) and I34 (2) show THR values even better than ATO. There is, however, an increasing trend of both these properties when the loading of nanoclay is increased. Lastly, samples containing HYS nanoclay exhibit slightly higher but quite constant pHRR values when compared to DUP, while THR values oscillates, without a clear trend, between the values recorded for DUP and ATO. The overall performances are in accordance from burning rate results obtained by the horizontal combustion test, as clearly visible in Figure 7.11.

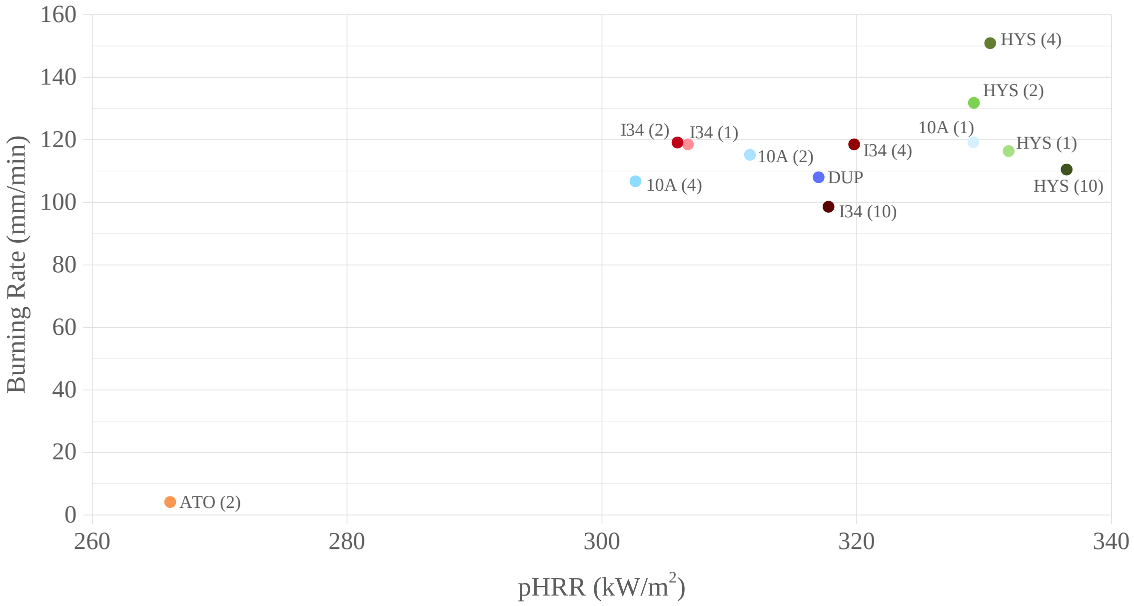

Figure 7.11: Burning rates and pHRR of nanoclays loaded samples.

Such a behaviour seems to confirm the possible detrimental effect of nanoclays in the char formation of burning PVC, as suggested by horizontal combustion tests.

However, a more in–depth comprehension of the performance of these additives could be gained by the analysis of the HRR curves, which graphically represents the fire growth during the test (Figure 7.12).

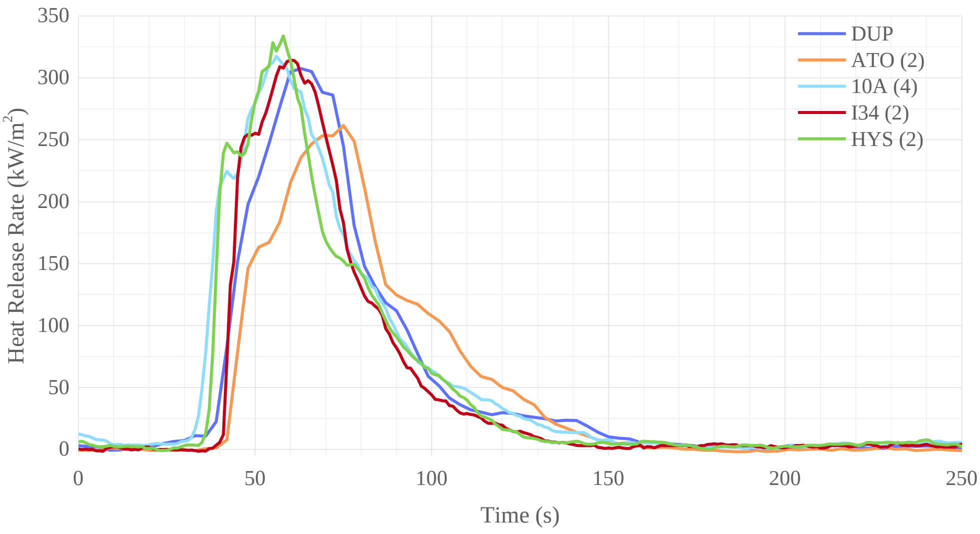

Figure 7.12: HRR curves of nanoclay loaded samples.

Differently from what observed for flame retardants (Paragraph 5.2.3), the curves obtained for nanoclays loaded samples are quite similar to each other and to DUP sample, in terms of shape of the curve, with the exception of the HYS one which appears to be slightly sharper. This means that when ignited, the sample released a great amount of heat in a relatively short time, which is an undesired behaviour for a flame retardant additive. It is also worth noting the presence of a first local maximum of HRR visible soon after the ignition of the all the nanoclay containing samples. This peak, absent in the DUP analysis, could be hence related to a rapid decomposition in which the nanoclay is involved.

All things considered, none of the nanoclays at any of the loading tested impart a sufficient decrease of the heat released by the material during its burning and, thus, are not particularly effective as flame retardants. However, heat release is not the only parameter that could be modified to improve fire retardancy. In fact, also TI and t–pHRR are important measures to be considered, and particularly their sum, which represents the total time elapsed from the exposure of the sample to fire temperatures to the time at which pHRR is reached. The lower these values are, the better the performances as flame retardants. The obtained values for nanoclay loaded samples are reported in Figure 7.13.

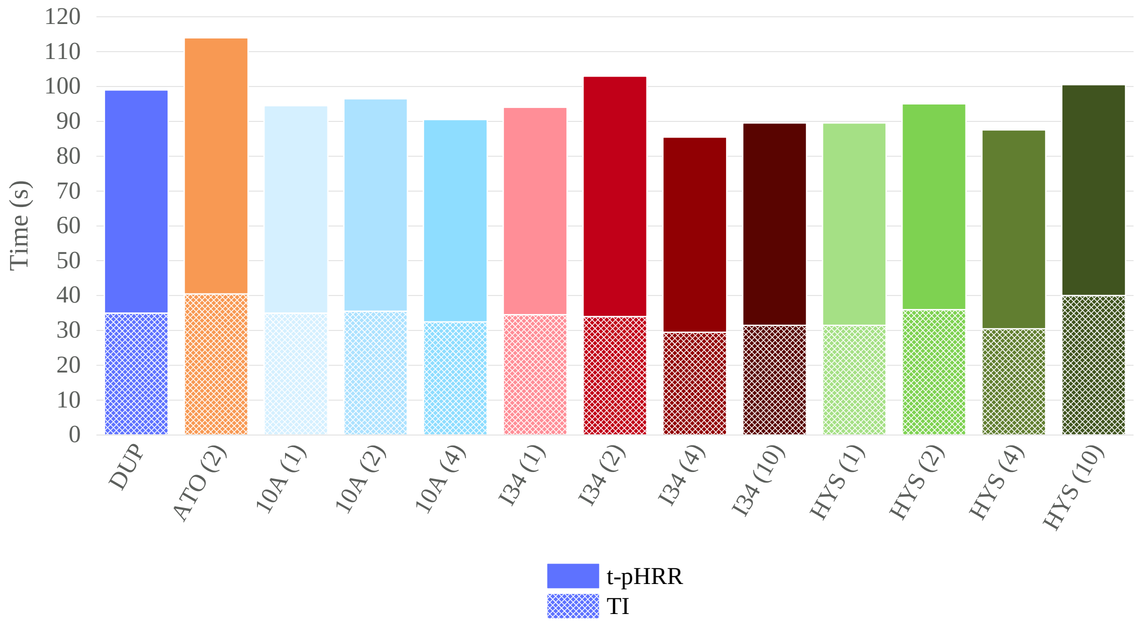

Figure 7.13: total time elapsed to pHRR (sum of TI and t-pHRR).

It results clear the absence of particular trends. Moreover, the totality of the samples exhibits values lower than ATO, and the majority of them are also lower than DUP with the only exception being I34 (2) and HYS (10). The first one, in particular, is also the sample that exhibits the second lowest pHRR amongst the tested nanoclay samples and, thus, the best compromise in terms of heat release and time elapsed to the maximum fire intensity.

7.2.5. Volatility and migration properties

- *Migration*

Data obtained from the two different tests conducted, semi–rigid foil migration (SFRM) and butter migration (BM), as described in Paragraph 3.2.4, are summarized in Table 7.5 and Figure 7.14. Results are expressed as percentage weight decrease of the sample.

Table 7.5: Migration. Results obtained by SRFM and BM tests.

#	*Sample*	*phr*	*SRFM (wt%)*	*BM (wt%)*
1	DUP	-	2.4	7.7
2	ATO	2	3.1	8.4
3	10A	1	4.0	8.2
4	10A	2	5.3	8.0
5	10A	4	3.5	6.9
6	I34	1	2.9	8.7
7	I34	2	4.2	8.4
8	I34	4	3.7	7.8
9	I34	10	3.2	7.0
10	HYS	1	3.5	8.6
11	HYS	2	3.4	8.7
12	HYS	4	4.2	8.6
13	HYS	10	4.5	8.5

The obtained results suggest that the addition of the nanoclays have a negative effect on the plasticizer migration towards other plastic materials (SRFM), here simulated by a semi–rigid PVC foil. In particular, the OMNCs (10A and I34) exhibit a maximum of the weight loss when loaded at 2 phr, while with higher loading the anti–migration effect seems to become effective. This trend, also reported in literature [28], could be attributed to a non–optimal dispersion of the nanoclay which is however counterbalanced by its greater amount in samples at 4 phr or more. Conversely, HYS does not impart any improvement, considering instead that the weight loss increases with increased loading.

Quite different appears to be the effect of the nanoclays on extraction by means of a fat simulant (BM). In this case, in fact, both the OMNCs (10A and I34) exhibit a positive trend when increasing their load, resulting similar or better than ATO at almost any of the loading tested and even better than DUP sample when added at their maximum loading. Diversely, HYS seems to have a slight negative effect, even though not particularly worse than ATO, at any of the loading tested. In particular, the best results were exhibited by 10A, which is modified with an aromatic quaternary ammonium cation. It is arguable that its presence could lead to the formation of intermolecular interactions with the aromatic ring of the phthalate plasticizer (DUP). These interactions could increase the anti–migration properties of 10A when compared to I34, due to the better affinity of the plasticizer with it rather than the butter triglycerides. However, a role could be also played by the form factor of these nano–additives: the organic–modified nanoclays (10A and I34) are plate–like, while the unmodified HYS is nano–tubular. Hence, it is more than likely that platelets are more efficient in render more tortuous the path of diffusing plasticizer.

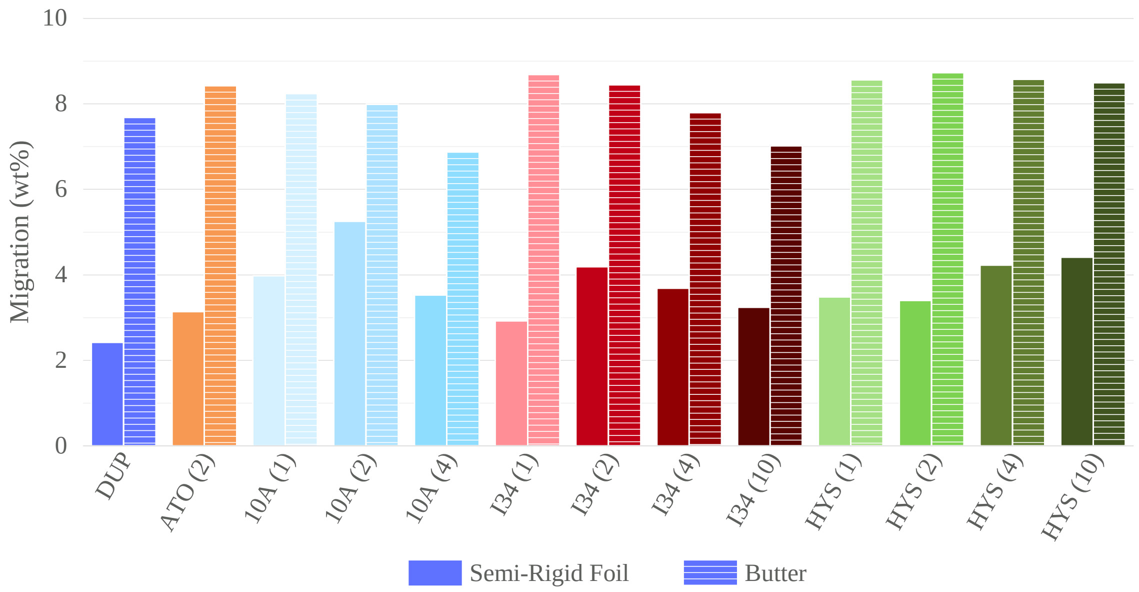

Figure 7.14: Migration results of samples loaded with nanoclays.

7.3. Conclusions

The method designed and tuned for the dispersion of nanoclays, organically modified or not, in pPVC plastisols seems to be still not perfectly capable to render exfoliated or even intercalated nanocomposites. In fact, the performance obtained by all of the nanoclays are at best on par with DUP or ATO samples.

Plastisol viscosity. The addition of these additives yields an increase of the plastisol viscosity which is unacceptable in the case of 10A and particularly problematic for I34, while much more limited is the thickening effect of HYS.

Mechanical properties. The effect on tensile strength is more limited if not worse then what expected. HYS samples exhibit the best UTS values, even slightly higher than ATO. For all of the samples, EB is definitely lower than reference samples, with again HYS that yielded the best performance. The obtainment of stiffer material is a known effect imparted by nanoclay, however, the poor UTS performance suggests an imperfect dispersion with the formation of micrometric aggregates (Figure 7.4).

Thermal properties. Thermal stability (Figure 7.5) is negatively affected by the presence of quaternary ammonium salts, used for organic modification of nanoclays, in sample 10A and, to a lesser extent, I34. Conversely, HYS shows superior resistance at process temperature, with better results than DUP and ATO. Analogously, thermal aging test (Figure 7.8) shows the good performances of I34 and HYS samples, while 10A yields excessive yellowing, particularly at higher loading. However, a consideration on the initial colour changes imparted by these nanoclays (Figure 7.6) allows to identify HYS as the best performer in thermal tests, with some of the results even better than ATO (e.g. initial colour and thermal stability).

Flame properties. Fire response results affected by the addition of nanoclays, even though not in the expected and desired manner. Again, one of the causes, even though possibly not the only one, could be attributed to a non–optimal dispersion of the nanoclays. The most peculiar information obtained by horizontal combustion and cone calorimeter tests is the poor performance of HYS, with BR up to 140 mm/min (Figure 7.9) and pHRR exceeding 325 kW/m^2 on average (Figure 7.10), both result being higher than what recorded for DUP. Furthermore, the sharpness of HRR curve of HYS (Figure 7.12) confirms the tendency to burn rapidly and with high heat development of pPVC material loaded with this nanoclay. Results from the two tests on I34 sample are quite discordant, with BR that decreases while pHRR increases with the increase of nanoclay loading. Diversely, 10A samples show a decreasing of both the measured parameters with increased loading (Figure 7.11). Finally, TI and t–pHRR (Figure 7.13) do not seem to have a clear trend in neither direction, but a mostly random distribution. All things considered, the best results, even though far away from being acceptable, were achieved by 10A and I34 at their maximum loading.

Plasticizer Migration. The last of the properties evaluated is the effect on plasticizer migration, which should be decreased by the addition of layered silicates (Figure 7.14). The tests on semi–rigid foil (SRFM) suggest that 10A and I34 could impart some anti–migration properties starting at 4 phr and higher loadings, while an opposite trend is registered by HYS. The results are analogous for migration into a fat simulant (butter, BM), with poor performances exhibited by HYS and the best performer being 10A. Possible hypothesis to explain these results are related to the tubular rather than plate–like form factor of HYS, and to the nature of the quaternary ammonium ion, containing an aromatic ring more akin to DUP, for 10A.

All the aforementioned considerations confirm that the positive effects related to the use of nanoclays are strictly dependent on the effectiveness of their dispersion in the polymer matrix, which seems to have been obtained only to a certain extent using the technique designed and partly optimized for plastisol applications in the present work. An evaluation of the nanoclays dispersion will be performed on the pPVC samples containing these additives by means of X–ray Diffraction (XRD), to evaluate an eventual increase of the interlayer spaces by the polymer chains [16], and also by means of Transmission Electron Microscopy (TEM) analyses. The data obtained could be hence considered a good starting point for the fine–tuning of the dispersion method in order to verify how, actually, the use of nanoclays could be beneficial for pPVC SLs for automotive interiors applications.

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8

Conclusions

The present research project was carried out in close collaboration with Vulcaflex S.p.A. and deal with the complex thematic of sustainability related to the production of plasticized PVC (pPVC) materials. In particular, the class of products studied belong to synthetic leathers (SLs), which are materials that simulates real leather using quite complex formulations and structures composed by different layers of plasticized PVC, compact and expanded, textiles and finishing lacquers (Figure 1.4). The manufacturing of these materials is nowadays considered a safe process, but still sees a number of issues related to the use of specific compounds belonging to the three main classes of additives in terms of importance and amount used inside SLs. These additives have proved, even though some are still under more exhaustive evaluation, to be potentially harmful for human health and the environment and are both being limited by legislative restrictions and pressures from end users. For all of these reasons, and in order to move towards more safe and sustainable products, the substitution of these additives has become mandatory. In this context, the present work aimed at the research and testing of viable alternatives for the following additives:

1. **Phthalate plasticizers**

More than 30 different plasticizers have been subjected to testing, in order to evaluate their properties in typical SLs formulations. The obtained results (Paragraph 4.3) allowed us to identify few potential substitutes for phthalates plasticizers, namely Trioctyl Trimellitate (**TOTM**, fossil fuel based) and the bioplasticizers Pentaerythritol Tetravalerate (**PIV/PETV**), Epoxidized Soybean Oil (**ESBO**) and Dioctyl Azelate (**DOZ**).

2. **Antimony Trioxide (ATO) flame retardant**

Numerous alternatives to ATO were taken into account, for a total of more than 30 different flame retardant systems. The results (Paragraph 5.3) pointed out that several compounds are able to give good flame retardancy even though not always at the same level than ATO. The better candidates identified are those systems based on Zinc Hydroxystannate (**ZHS**), both alone of combined with inorganic compounds like Aluminium Trihydroxide (**ATH**) and carboxylates mixtures (**CARB**), or to a lesser extent Calcium Hypophosphite (**CHP**).

3. Azodicarbonamide (AZO) blowing agent

The ongoing research for alternative blowing agent than AZO is particularly challenging. Amongst the few possible substitutes identified, the best performances, also confirmed by preliminary industrial tests, are achieved with a non–toxic, optimized, mixture of sodium bicarbonate and citric acid (**BIC/CIT**). Also, OBSH offers an effective alternative, but poses similar issues to AZO in terms of health and environment risks.

However, the technical and scientific evaluation of these additives should not be considered without an economic feasibility estimate. In fact, these new formulations must be sustainable not only from an environmental and health point of view, but also from an economical perspective in order to become appealing and be integrated inside standard production. To evaluate this aspect, a weighted cost analysis is hereafter reported, referred to the previously mentioned additives.

Plasticizers

Name	*Price (€/kg)*	*Price difference (%/kg)*	*Amount* (kg)*	*Cost (€)*	*Cost difference (%)*
DPHP	1.2	–	75	90	–
TOTM	3.0	+150	73^A	219	+143
			82^B	246	+173
ESBO	1.5	+25	73	110	+22
PIV/PETV	2.5	+108	71^A	178	+97
			69^B	173	+92
DOZ	4.0	+233	71	284	+216

* referred to the equivalent quantities, based on the phr_{eq} values (see Paragraph 4.2.2);
^{A} when used in Recipe A; ^{B} when used in recipe B (see Paragraph 4.2.1).

All of the plasticizers that are identified as potential substitutes for phthalates are more expensive than the standard DPHP, even taking into account the equivalent quantities derived from the substitution factors (SF) calculated on the hardness values (Paragraph

4.2.2). The best compromise between performance and costs compared to DPHP are exhibited by ESBO (+22 %), followed by PIV/PETV (+97/+92 %). The use TOTM and DOZ causes cost increases rarely justifiable. However, TOTM remains the best alternative when high–performance, phthalate–free material are required.

Flame Retardants

Name	*Price (€/kg)*	*Amount* (kg)*	*Price difference (%)*	*Cost per compound (€)*	*Cost difference (%)*
ATO	7.5	2	–	15	–
ZHS	18.0	3	+140	54	+260
		5	+140	90	+500
CHP	6.0	10	-20	60	+300
ATH + ZHS	0.8 + 18.0	10 + 2	+151	44	+193
CARB + ZHS	9.0 + 18.0	10 + 2	+260	126	+740

* referred to the phr loading at which they were more effective (see Paragraph 5.3).

Also in the case of flame retardants, the price and loading of ATO give rise to a very low cost per compound and an excellent price/performance ratio. Amongst the alternatives, ZHS is definitely more expensive in terms of price (+140 %) but when used in combination with the inexpensive ATH it becomes the cheaper amongst the alternatives (+193 %). Thus, currently ATH + ZHS (10 + 2) seems to be, considering both performances and cost, the best solution for substituting ATO.

Blowing Agents

Name	*Price (€/kg)*	*Amount* (kg)*	*Price difference (%)*	*Cost per compound (€)*	*Cost difference (%)*
AZO(k)	3.0	3 + 0.5	–	11	–
OBSH	12.0	4.5	+120	54	+400
BIC/CIT	4.0	5	+13	20	+86

* referred to the phr loading at which they yielded foam densities of 0.4 kg/m^3 (see Paragraph 6.2.1);

Amongst the alternatives identified to substitute AZO, OBSH exhibits the best performance, even though poses analogous issues compared to AZO, is however definitely too expensive (+400 %). The price/performance ratio of BIC/CIT is, instead, more than appealing and with constant enhancement of both formulations based on bicarbonate/citric acid, and plastisol recipes, the cost difference with AZO could be further levelled. Thus, BIC/CIT could represent a viable alternative to AZO.

4. Organic modified nanoclays

Lastly, a novel class of additives completely new in the pPVC SLs industry, were subjected to testing in a standard formulation. The evaluation of both organic modified and unmodified nanoclays, focused on mechanical, flame and anti–migration properties. The results of this preliminary tests (Paragraph 7.3) suggest that the continuation of the research project should focus on techniques to disperse them into plastisols. In fact, dispersion resulted a decisive factor in the full development of the potential properties that these nano–additives could enhance on polymers.