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Formulation and Study of New Eco-Friendly Intumescent Polylactic Acid Based Materials

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Abstract

Polylactic acid (PLA) is a biodegradable and bio-based polymer obtained by polymerization of lactide or lactic acid, both arising from renewable resources like cereals' starch. Polylactic acid is also a semycristalline thermoplastic polymer and has mechanical properties in between polystyrene and polyethylene terephthalate. In the last decades the interest on this polymer raised very fast and its industrial production increases very rapidly, in the same way the number of published researches have exponentially increased.

Nowadays the main PLA applications consist on food packaging, disposable tableware, biomedical items and textiles. Future and new PLA applications are focusing towards electric, electronics, and transport field.

The materials for this kind of applications must have good flame resistance properties and several flame and burning tests must be passed before these materials can be applied.

PLA does not have flame resistance properties and burn in air in case of a fire source. Focusing my research to solve this issue, PLA based materials with different flame-retardants additives have been formulated and tested.

Intumescence has been studied as mechanism to achieve good flame resistance properties, and halogen-free, non-toxic and eco-friendly additives have been used trying to maintain the material biodegradability.

New eco-friendly intumescent polylactic acid based materials have been developed, using low load of halogen-free, not toxic and biodegradable additives (6, 10 and 14%).

Bio-based and biodegradable carbonizing agents such as starch, sorbitol, coffee grounds, glycerol phosphate, cellulose and Kraft lignin have been tested (2%), and V-0 UL94 classification, LOI values over 32% and GWIT over 775°C were archived in presence of different amount of ammonium polyphosphate (4, 8.5%) for all the carbonizing tested.

The presence of zinc borate increased the flame resistance of the materials yielding the lowest total heat release in synergy among all carbonizing agents tested.

Summary

1 Introduction

Find alternatives to energy, molecules and polymers arising from fossil resources, is the main challenge in chemistry and engineering science of the 21th century. The future total consumption of non-renewable sources is a fact, this because the fossil fuel production time is longer respect to the human extraction and consumption times. Although the fossil fuel reserves are going to end, innovative technology on discovery new extraction point and innovative kind of perforation permit to find new oil reserves, considered inaccessible before that. This moves repeatedly the deadline far in the future and their exhaustion is not actually a great concern. Actually the main problem arise from the global warming due to an increase of the greenhouse gasses concentration in the atmosphere, among them the carbon dioxide is the most worrying. Using fossil fuel as combustible for transports and to produce energy, the carbon dioxide concentration inevitably increase resulting in the steady warming of the heart surface temperature. This is leading to desertification, melting glaciers, sea level rise and climate changes. Moreover, the growth of world population is increasing the requirements for energy and raw materials. In looking with that, a large scale use of renewable resources is getting mandatory. The renewable energy actually produced is well below the world potential and contributes only marginally to human needs. This is principally due to the lower cost of traditional fossil resources, to political choices, and to technological limitations. Science and technological development are the key for achieving these objectives. There are many proposed sustainable solutions for the energy sector, but so far, only few are competitive compared to use of fossil hydrocarbons. Besides, the major building blocks for the synthesis of most chemical products that we commonly use every day, are obtained from fossil resources. Indeed, 90% of the organic substances derive, through chemical transformations/reactions, from seven oil derivates: methane, ethylene, propylene, butenes, benzene, toluene and xylenes. Approximately only 16% of oil is transformed into chemicals, the main fraction it is used for energy production and fuels.

The replacement of oil with renewable resources will be our primary goal for the future. Actually, a reasonable target is maximize the diversification of energy and chemical sources using renewables resources. The main goal must be the use of the renewable resources for energy and chemicals production in a competitive way compared to fossil resources, in term of costs for process the raw materials into the final products. Only following this route, the renewable resources can be a real alternative option to fossil resources in the future energy and chemicals global market. The progress of the scientific research in order to develop sustainable energy, chemicals and materials are the key to reach this target.

Going in this direction, United Nations Framework Convention on Climate Change stipulate in 1992, an international agreement for reducing the greenhouse gasses concentration and emissions in atmosphere. This agreement was updated in 2005 with the Kyoto protocol that is actually active and see 192 parties agree on reducing greenhouse gas concentrations in the atmosphere to a level that would prevent dangerous anthropogenic interference with the climate system [1].

In addition, the European commission has developed two big program to reduce the fossil fuel consumption founding sustainable research, Europe 2020 and Horizon 2020.

Europe 2020 is a 10 years strategy proposed by the European Commission in 2010 for advancement of the economy of the European Union. It aims at smart, sustainable, inclusive growth with one of the main target "to reduce greenhouse gas emissions by at least 20% compared to 1990 levels or by 30% if the conditions are right, increase the share of renewable energy in final energy consumption to 20%, and achieve a 20% increase in energy efficiency" [2].

Horizon 2020 is the biggest EU Research and Innovation programme with nearly €80 billion of funding available over 7 years from 2014 to 2020 for research and innovation in sustainable resources [3].

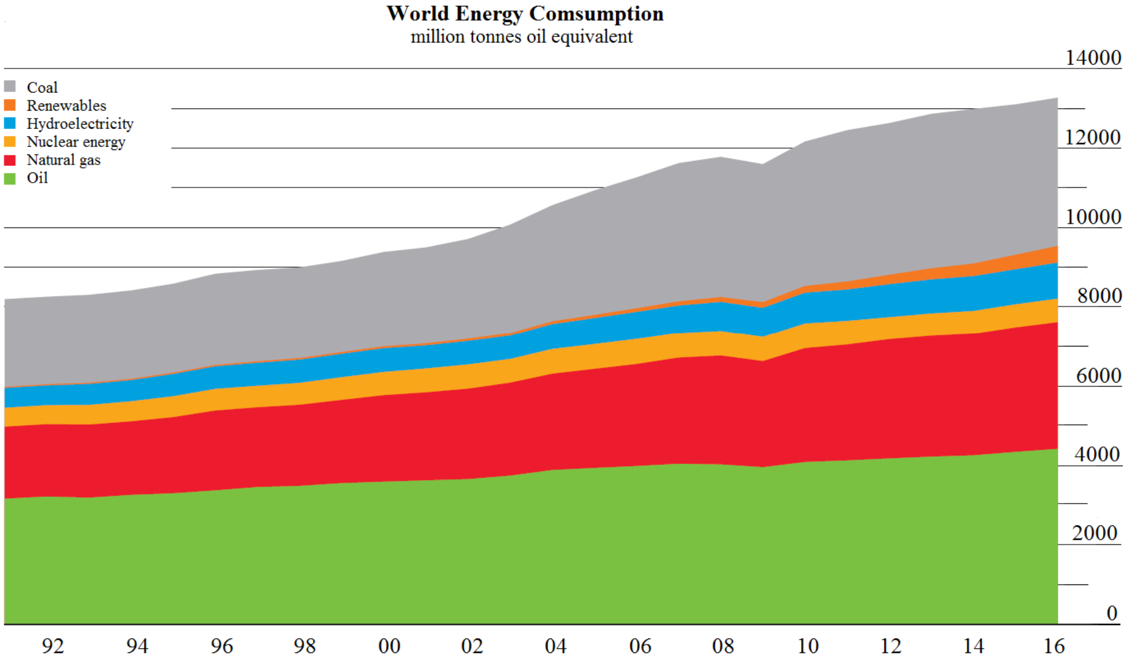

Figure 1: Trend of world consumption of energies [4].

The world consumption of energy shows an increase of the renewable energy consumption in the last decade as a result of these regulations (Figure 1). Although the consumption of renewable energy is the lowest compared to the others, it is currently growing fast. In 2016 the oil provided the largest increment to energy consumption at 77 million tonnes oil equivalent (toe), followed by natural gas with 56 mtoe and renewables with 53 mtoe of increment [4].

These regulations have affected also the production capacity of the bio-based building blocks (Figure 2) that are growing up rapidly.

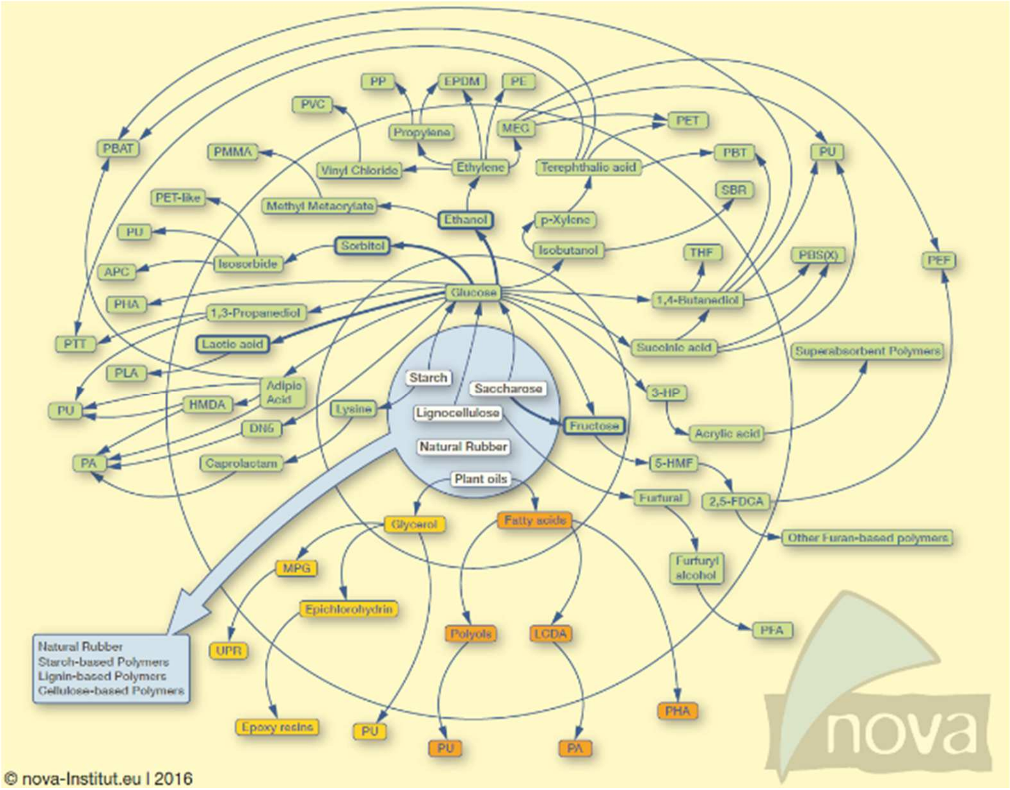

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Figure 2: Schematic representation of the main bio-based route from starting materials, to bio-based building block and bio-based polymer.

A recent investigation made by Nova institute involved the study of different bio-based building blocks as precursor of bio-based polymers. As reported on it, the total production capacity of the main bio-based building blocks is estimated to be 2.4 million tonnes in 2016 and is expected to reach 3.5 million tonnes in 2021 (Figure 3), which means an annual growth of 8% [5].

The most growth are foreseen to be succinic acid, 1,4-butandiol and monoethylene glycol (MEG). Bio based MEG, L-lactic acid (L-LA), ethylene and epichlorohydrin are relatively well established on the market.

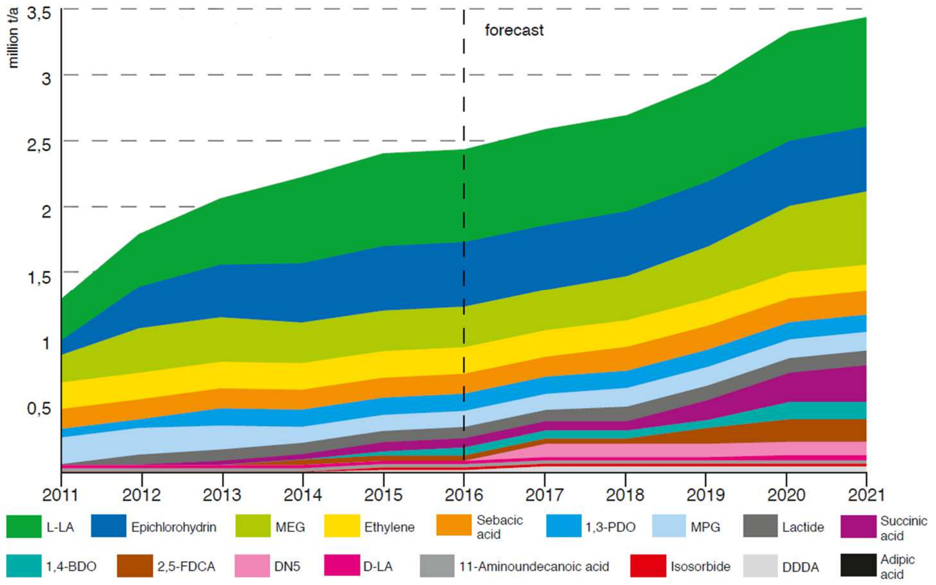


Figure 3: Evolution of worldwide production capacities of the main bio-based building block.

Bio-based polymers growth capacity, in contrast to a 10% annual growth between 2012 and 2014, now is expected to show a 4% annual growth rate from 2015 to 2021. The main reasons for this slower increase in capacity are low oil prices, low political support and a slower than expected growth of the capacity utilization rate. However bio-based polymer are seeing a global growth rates at the same level as conventional polymers, their worldwide production capacity is forecasted to increase from 6.6 million tonnes in 2016 to 8.5 million tonnes in 2021 (Figure 4) [5].

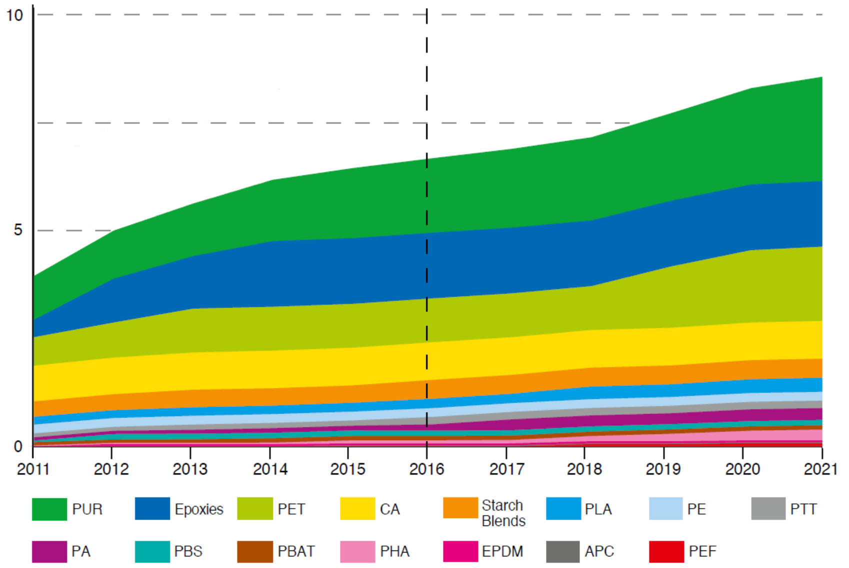


Figure 4: Evolution of worldwide production capacities of the main bio-based polymers.

The most relevant increment is foreseen for the recent bio-based polyhydroxyalkanoates PHA whose production capacity is still small in 2016 and is projected to almost triple by

2021. The second most development is foreseen for polyamides, whose production capacity is expected to almost double by 2021. Bio-based polyethylene terephthalate and bio-based polylactic acid are showing interesting growth as well with an approximately 10% annual growth rate [5].

1.2 Biopolymers

In recent years, green movements, initiatives, and regulations are pushing almost every developed country to reduce the volume of solid polymers waste generated by consumers in order to protect the environment. The use of products made from both natural renewable resources or fossil resources that decompose into environmentally friendly constituents, is increasing steadily and rapidly. These class of materials are defined biodegradable and are a subclass of biopolymers.

It is important to clarify what biopolymers are because also not-biodegradables biopolymers exist. The biopolymers, in fact, are divided into two big classes of materials, biodegradables and non-biodegradables. The biodegradables biopolymers are further divided in other two classes: bio-based or fossil based. Instead, only bio-based polymers can be classified in non-biodegradable biopolymers class.

Moreover it is important to understand what biodegradable and bio-based means. According to the standard ASTM D5488-94 [6], biodegradable polymers refer to polymers that are “capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, or biomass in which the predominant mechanism is the enzymatic action of microorganisms that can be measured by standard tests, over a specific period of time, reflecting available disposal conditions”.

“Bio-based” is a term focused on the raw materials basis, and it is applied to polymers derived wholly or partially from renewable resources. Raw materials are defined as renewable if they are replenished by natural procedures at rates comparable or faster than their rate of consumption [7]. To be exact, a biobased material is “an organic material in which carbon is derived from a renewable resource via biological processes. Bio-based materials include all plant and animal mass derived from carbon dioxide previously fixed via photosynthesis”.

Biodegradable bio-based biopolymers, can be produced by biological systems like microorganisms, plants, and animals; or chemically synthesized from biological starting materials such as corn, sugar, starch, etc. The most used bio-based biodegradable biopolymers are starch and poly(hydroxyl acids).

Non-biodegradable bio-based biopolymers are synthetic polymers produced from biomass or renewable resources such as polyamides from castor oil (polyamide 11), polyesters based on biopropanediol, biopolyethylene (bio-LDPE, bio-HDPE), biopolypropylene (bio-PP), or biopoly(vinyl chloride) (bio-PVC) based on bioethanol from sugarcane, and also natural occurring biopolymers such as natural rubber or amber.

Biodegradable fossil fuel based biopolymers are synthetic aliphatic polyesters made from crude oil or natural gas that are certified biodegradable and compostable. PCL, poly(butylene succinate) (PBS), and certain “aliphatic/aromatic” copolyesters are at least partly fossil fuel-based polymers, but they can be degraded by microorganisms.

Actually, most of the renewable resources based material are much higher in cost and inferior in properties compared to synthetically derived products. In order to decrease this gap, the research and innovation are focusing to develop new synthetic strategies and new processes for obtain environmentally friendly products with similar performances and price to fossil resources based materials.

It is clear that the most interesting biopolymers are the biodegradable bio-based biopolymers, due to their zero carbon dioxide emission that characterize their life cycle.

One of the main well known and in large quantity produced bio-based biodegradable biopolymer is polylactic acid. Polylactic acid is a poly(α-hydroxyalkanoic acid) largely produced by fermentation of renewable resources such as starch and sugarcane.

1.2.1 Introduction to polylactic acid

Polylactic acid was synthetized for the first time by Théophile-Jules Pelouze in 1845 throw polycondensation of lactic acid [8]. In 1932, Wallace Hume Carothers et al. [9] developed a method to polymerize lactide into PLA and subsequently Du Pont in 1954 patented this method. PLA and its copolymers were originally developed as biomedical materials until 1970s, this since this polymers are bioabsorbable and biocompatible. Biomedical uses of polylactic acid consisted of therapeutic and pharmaceutical applications such as drug delivery systems [10], protein encapsulation and delivery [11], development of microspheres [12] and hydrogels [13]. The biomedical application of PLA were recently extended to tissue engineering including scaffold materials [14] and biocompatible materials for sutures [15] and prostheses [16].

In the early 1990s Cargill Inc. managed to obtain high-molecular-weight poly(L-lactic acid) (PLLA) by ring-opening polymerization (ROP) of L-lactide. The ROP polymerization process implemented in industrial scale, permitted in the mid 1990s, to commercialize the PLLA polymer.

PLLA has high mechanical properties in addition to a biodegradable nature, this was the starting point to provide opportunities to replace nondegradable oil-based polymers, such as polyethylene terephthalate (PET) and polystyrene (PS).

Various types of bio-based polymers are now under development, also several PLA types are proposed as promising alternatives to commercial commodities. In particular, PLLA polymers having high L-contents and stereo-complex PLA polymers showing high melting temperatures are now expected to be candidates for high performance materials.

1.3 Lactic acid

1.3.1 History of Lactic Acid

Lactic acid was discovered in 1780 by the experimental chemist Carl Wilhelm Scheele, who isolated “acid of milk” from sour whey [17]. A further description of the history of lactic acid by Holten and Benninga shows that industrial production of lactic acid started in the United States in the 1880s [18]. Avery patented and applied a fermentation process of vegetable sugars [19]. In 1950, the first commercial production of synthetic lactic acid started in Japan [20]. For some decades, synthetic lactic acid competed with lactic acid obtained by fermentation, but currently almost all lactic acid is produced by fermentation.

1.3.2 Chemical structure of Lactic Acid

Lactic acid (2-hydroxypropanoic acid) is one of the simplest 2-hydroxycarboxylic acid (or α-hydroxy acid), in this molecule a chiral carbon atom in alpha position to the carbonyl permits the existence of two lactic acid enantiomers, namely L-lactic acid and D-lactic acid (Figure 5).

(*S*)-Lactic acid
L-(+)-Lactic acid

(*R*)-Lactic acid
D-(–)-Lactic acid

Figure 5: Enantiomer species of lactic acid.

The lactic acid molecule possess both a hydroxyl and an acid functional group, these groups can react together through an intermolecular esterification reactions, leading to the formation of a linear dimer (lactoyl lactic acid). This condensation reaction can proceed to higher oligomers and it is promoted by the water removal. Also the cyclic dimer, lactide, is formed in small amounts by intramolecular esterification of lactoyl lactic acid or by cyclization of higher oligomers. All reactions shown in Figure 6 are equilibrium reactions.

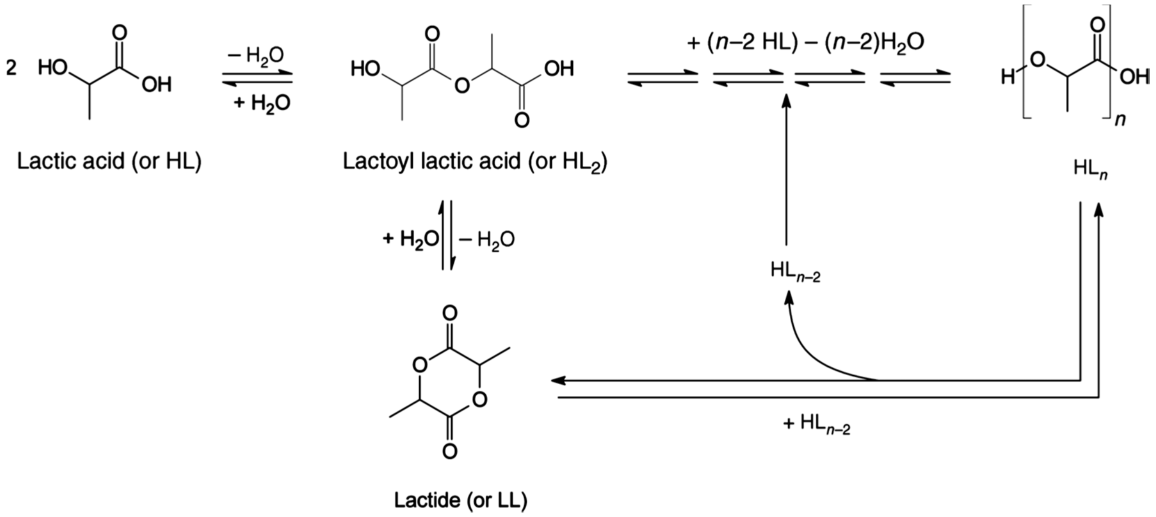


Figure 6: Oligomerization and cyclization reaction of lactic acid.

Due to these reactions, a solution of lactic acid at equilibrium consists of monomeric lactic acid, dimeric lactic acid or lactoyl lactic acid, higher oligomers of lactic acid, and lactide. The ratios between all substances depend on the amount of water present; for example, a 90.1% lactic acid solution contains about 59.3% of monomeric lactic acid, 27.3% of lactoyl lactic acid and higher oligomers [18]. The condensation reactions are also the reason that it is quite difficult to obtain enantiopure solid lactic acid. For this purpose, crystallization is a suitable technique [21].

1.3.3 Production of Lactic Acid by Fermentation

Nowadays, almost all lactic acid available on the market is produced by fermentation. In particular some classes of microorganism are able to convert suitable carbohydrates to L-lactic acid and D-lactic acid. Depending of witch type of microorganism are used the process can be carried out in anaerobic (by bacteria) or aerobic conditions (by fungi).

The sugar conversion into L-lactic acid for example, is made without oxygen, in other worlds in anaerobic process conditions starting from D-glucose. The reaction involves several enzymatic steps inside the microorganism cells, the sugar is first converted to pyruvate, then the pyruvate is reduced to lactic acid. In this way, the microorganism generates energy in the form of ATP that uses in several processes, for example, cell growth, maintenance, and sometimes even motility. In other words, L-lactic acid is mainly produced to keep the cellular processes going [22].

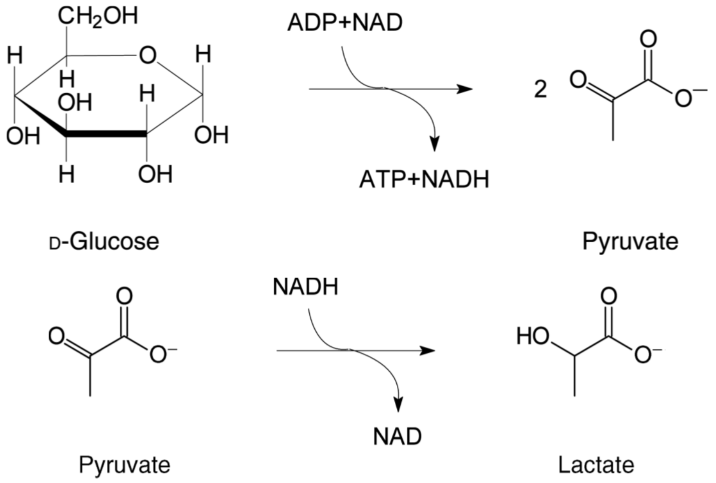


Figure 7: Lactate biosynthetic route in homofermentative bacteria.

The reaction in Figure 7 takes place in the so-called homofermentative lactic acid bacteria (LAB). Homofermentative bacteria produce almost exclusively lactic acid as a fermentation result, in these microorganisms glycolysis reactions split a C6 into two C3 molecules [23]. Lactic acid can be produced also by heterofermentative bacteria that produce a mixture of lactic acid, acetate, CO_2, and ethanol [23]. Heterofermentative bacteria fermentation process is known to use phosphoketolase pathway, this is a route where a C6 is transformed to a C5 sugar (and CO_2) subsequently splitted into a C2 and a C3 molecule. The C3 molecule is then converted to lactic acid whereas the C2 molecule is converted to acetate or ethanol.

Some heterofermentative bacteria show glycolysis and phosphoketolase pathways active at the same moment and produce mostly lactic acid under certain circumstances [24].

Lactococcus lactis is a lactic acid producing microorganisms that do not have a phosphoketolase pathway but can still produce acetate or ethanol from pyruvate as byproduct [25].

Every microorganism has its own benefits and drawbacks, but *lactobacillus* (bacteria) and *Rhizopus* (a fungus) are the most reported [26].

Lactobacillus generally have high productivity, but special and often expensive nutrient requirements. *Rhizopus* needs much less nutrients, but has a lower yield, it needs oxygen, and for its morphology is sometimes difficult to handle. Of course, via genetic manipulation, researchers have tried to make an ideal lactic acid producing microorganism in order to increase the process productivity and the enantiopurity of lactic acid.

Several natural D-lactic acid producing bacterial species exist, for example *Sporolactobacillus inulinus*, *Sporolactobacillus laevolacticus* and *Lactobacillus delbrueckii* [27] [28] [29]. Some patents were also developed for the production of D-lactic acid by a genetically modified microorganism. Several different species such as *Kluyveromyces* and *Escherichia coli* have been claimed so far [30] [31].

1.3.4 Carbohydrates for Lactic Acid Production

In general, any carbohydrate source containing pentoses (C5 sugars) or hexoses (C6 sugars) can be used for the production of lactic acid. Pure sucrose from sugarcane or sugar beets and glucose from starch are available in large amounts and readily fermentable. Disaccharides can also be used, lactose present in whey for example.

Polysaccharides such as cellulose or starch are more complex and need special pre-treatments, like hydrolysis into sugars with specific enzymes prior to fermentation.

In particular, starch occurs in discrete granules and it is usually a mixture of two homopolymers of glucose, amylopectin and amylose. Although some microorganisms are able to convert starch directly to lactic acid, others cannot hydrolyze starch themselves and enzimes like α-amylase and glucoamylase are used in a first step of hydrolysis. Starch can be obtained from corn, wheat, potato, or tapioca [32] and a lignin free cellulose source can be derived from waste paper and used for lactic acid production [33].

1.3.5 Batch and Continuous Fermentation

The fermentation process can be run in batch [34] or in continuous mode [35]. In all scenarios, microorganisms produce an aqueous lactic acid solution containing lactate, counterions, impurities from raw materials, fermentation by-products, residual sugars, polysaccharides, and the microorganism itself. The first step to separate lactic acid is the filtration of microorganism and raw material residue.

Then, lactic acid is purified by saturation with lime, crude calcium lactate obtained is filtered off and acidified with sulfuric acid. Subsequently filtering off the calcium sulphate, and evaporating to obtain a crude viscous lactic acid [17].

1.3.6 Purification of lactic acid

Food and pharmaceutical lactic acid application as well as polymer synthesis, require a high purity grade of lactic acid, this can be obtained in different ways such as:

- active carbon treatment and/or ion exchange process; in order to remove impurities and salts.
- esterification/saponification; esterification of lactic acid with methanol/ethanol yields different boiling points species, these can be easily separated from the impurities by distillation and reconverted in lactic acid by a subsequently saponification [36].
- crystallization; this method can lead to an excellent lactic acid grade, but the yield is generally low.
- distillation; lactic acid can be distilled under low vacuum in order to separate it from higher molecular weight components such as sugar and protein that remain as residue. Lactic acid is obtained as the top product, but the formation of oligomers limit an overall high distillation yield.
- extraction; an extraction and back-extraction process with tertiary amine systems can be a suitable way to purify lactic acid [37] [38].

Lactic acid purified by crystallization may be taken as the benchmark in lactide manufacture, but the unfavourable economics of making crystalline acid from the mother liquor are limiting its commercial use for lactide/PLA production. The use of more efficient raw materials and more performing purification processes that involve lower costs, are the key to reduce the overall cost of lactic acid and mainly, the lactide and PLA commercial costs.

1.4 Lactide

1.4.1 Lactide structures

The dehydrated, cyclic dimer of lactic acid is commonly known as lactide (3,6-dimethyl-1,4-dioxane-2,5-dione). Due to the two asymmetric carbon atoms in the molecule, lactide exists in three different forms (Figure 8).

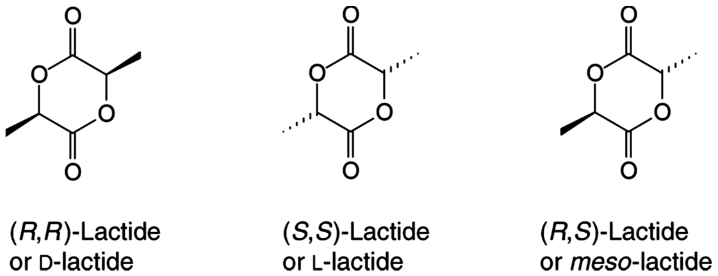


Figure 8: Lactide diastereoisomeric species.

In addition to the three diastereomeric structures mentioned above, also a racemate of D-lactide and L-lactide is commercially available: rac-lactide or DL-lactide.

1.4.2 Production of lactide

The synthesis of lactide was described for the first time by Pelouze in 1845 [39] studying the self-esterification of lactic acid by heating and distilling off water. Later, in 1914 Gruter and Pohl [40] patented an improved procedure where lactic acid was self-esterified at 120-135°C and water removed using an air flow. Then the lactic acid oligomers obtained were converted in lactide adding zinc oxide as cyclization catalyst. One of the main reaction problem is the equilibrium reaction that limit the conversion from oligomer to lactide, so in order to pull the reaction toward the products, the lactide produced was distilled off under vacuum at 200°C.

In the last two decades, several papers have appeared on lactide manufacture [41] [42], the major step forward was the use of a tin catalyst as coordinating catalyst.

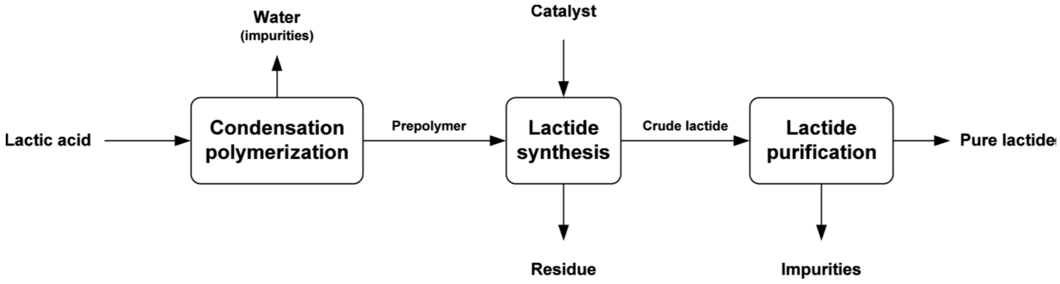


Figure 9: General scheme of lactide manufacture and purification route [43].

As previously described modern lactide production processes involve two main reaction step, the prepolymerization process and the lactide synthesis (Figure 9). Both step can be drown in a batch or in a continuous process. O’Brien et al. patented the prepolymerization process in batch [44]. They worked under partial vacuum at 70-250 mbar and temperatures up to 190°C to dewater lactic acid to a prepolymer with an average polymerization degree (DP) of around 10 in a process time of 6 h.

Continuous prepolymerization has also been described in a number of patents, for example, in a series of stirred tanks or in evaporator-type equipment [45] [46].

Noda and Okuyama reported the further batch synthesis of lactide from DP 15 prepolymer with various catalysts at 4-5 mbar and 190-245°C [42].

Tin catalyst can be considered the best compared to other catalysts and showed the lowest levels of racemization. The catalyst increases the rate of lactide formation catalysing the backbiting reaction of the oligomer hydroxyl end chains group [47].

Tin octoate (stannous 2-ethylhexanoate) was and actually is still the most used catalyst for lactide production, moreover is a liquid catalyst that can be handled easily, is food grade, and is widely available.

In batch processes, the depolymerisation rate is initially constant, but during the synthesis, polyesterification also occurs, and the degree of polymerization of the polyester rises concomitantly. For this reason the melt viscosity of the reaction mixture increases during the reaction and at the end of the batch process, mixing the highly viscous residue becomes very difficult. The mass transfer of lactide from the liquid to the gas phase decreases limiting the lactide separation.

1.4.3 Lactide continuous process production

Gruber et al. described a continuous lactide synthesis in 1992 [45]. In this process the prepolymer is continuously fed inside the reactor, crude lactide is evaporated under vacuum pressure at 4 mbar, temperature 213°C, and using 0.05 wt% tin octoate as catalyst. The process has a residence time of about 1 h.

1.4.4 Purification of lactide

In both processes, batch and continuous, the lactide synthesis reactor produces a crude lactide stream that contains lactic acid, lactic acid oligomers, water, meso-lactide, and further impurities.

Different separation methods for lactide purification are currently employed:

- Distillation; this process was well described in Gruber et al. patent in 1993 [48]. This technique permit to split the multicomponent mixture of lactide, water, lactic acid, and its oligomers into pure fractions. The boiling points of all compounds are in the range of 200–300°C, thus low pressures are used. Distillates and bottoms may be recycled, but the accumulation of impurities from the feed or the production of meso-lactide during the process are the main problems. Since the difference in boiling temperature of lactide and meso-lactide is quite small, this distillation requires many theoretical plates (>30). For example, in the Cargill / NatureWorks process, distillation uses a series of distillation columns in a continuous way [47].

- Solvent crystallization; this method is commonly used in laboratory and involves the lactide purification trough recrystallization from mixtures of toluene and ethyl acetate [47]. Lactide at extremely high purity can be obtained by repeated crystallization with different toluene / ethyl acetate ratios.
- Melt crystallization; this method is preferred for large scale process. Lactide crystallizes easily when melt is cooled down, but the presence of impurities limit the maximum yield [49]. The heat transfer areas and hydrodynamics inside the reactors are the main challenge to influence the productivity of this process, for this reason different types of apparatus as static equipment, falling film crystallizers, vertical column with scraper to remove crystal mass from the cooled wall, and scraped heat exchanger coupled to a wash column can be used [49] [50] [51].

Affordable distillation equipments don’t fully remove all meso-lactide, and consequently, a mixture of lactic units are obtained during the polymerization resulting in PLA copolymers with different thermal properties. Instead, crystallization yields highly pure lactide, suitable for high molecular weight PLA homopolymer.

1.5 Polylactic acid

1.5.1 Polycondensation of lactic acid

Lactic acid can be polymerized to polylactic acid by polycondensation (Figure 10), the condensation reactions occur between the hydroxyl groups and the carboxylic acid groups. The removal of the water formed during this reaction is essential to converts oligomers into polymer.

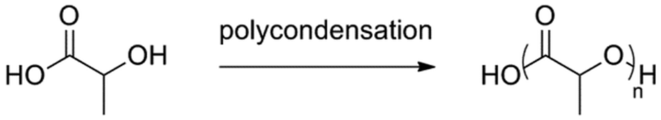


Figure 10: Lactic acid polycondensation.

This direct polycondensation involve different phases, in a first step the lactic acid is dried removing the water contained in the feedstock. Then, a condensation step produces oligomers. The rate determining step in this stage is usually the chemical reaction, which is significantly affected by the catalyst used [52]. Traditional polycondensation catalysts are strong Lewis acids and organometallic compounds. The last step is characterized by melt polycondensation in which oligomers condense generating the polymer chains. The removal of water becomes more difficult and can be rate determining when producing a higher molecular weight polymer. To enhance the polycondensation reaction rather than the transesterification reactions, the water formed in the reaction mixture is removed under vacuum in inert atmosphere conditions.

To improve mass and heat transfer, the melt polycondensation reaction should be carried on in an apparatus having an efficient renewal of phase boundary layers and systems that can handle high-viscosity mass are required such as rotating disk type reactor.

The preparation of a high molecular weight PLA by a direct dehydration condensation reaction is not practicable due to the equilibrium reaction towards high molecular weight polymer. Generally, this type of polymerization is used for obtaining a polymer with low molecular weight, and usually the reaction is stopped when the polymer reach a molecular weight of about few thousands. PLA prepared from polycondensation possessing low molecular weight has poor mechanical properties and therefore is not suitable for many applications. Polymers whit high molecular weight can also be obtained, but the conversion remains low. As example the results of different catalyst tested [53] shown SnO as the most efficient catalyst in terms of molecular weight but the maximum yield obtained at 180°C after 20 hour of reaction is below 40%. Moreover, side reactions occur and they give a negative influence on the properties of the polymer. Indeed the formation of cyclic structures, such as lactide, lowers the overall molecular weight. Furthermore, the lactide is removed with the water under vacuum lowering also the yield of the process even if it is recycled.

1.5.2 Solid-state polycondensation

As has been seen, a limited molecular weight in combination with a low yield are the main disadvantage of PLA prepared by the direct polycondensation. Some progress in increasing the molecular weight of the PLA has recently been achieved with sequential melt / solid polycondensation [54] [55].

In the sequential melt / solid-state polycondensation, a further step is used at the end of the direct polycondensation. During this step the melt-polycondensated PLA is cooled below its melting temperature in order to start the crystallization process. At this point a crystalline phase and an amorphous phase are simultaneously present in the material and the reactive end groups as well as the catalyst, are concentrated in the amorphous phase in between the crystals (Figure 11).

Metal catalysts can promote the solid state polycondensation in the amorphous phase as well as in the melt polycondensation. These catalysts can be metals or metal salts of Sn, Ti, and Zn.

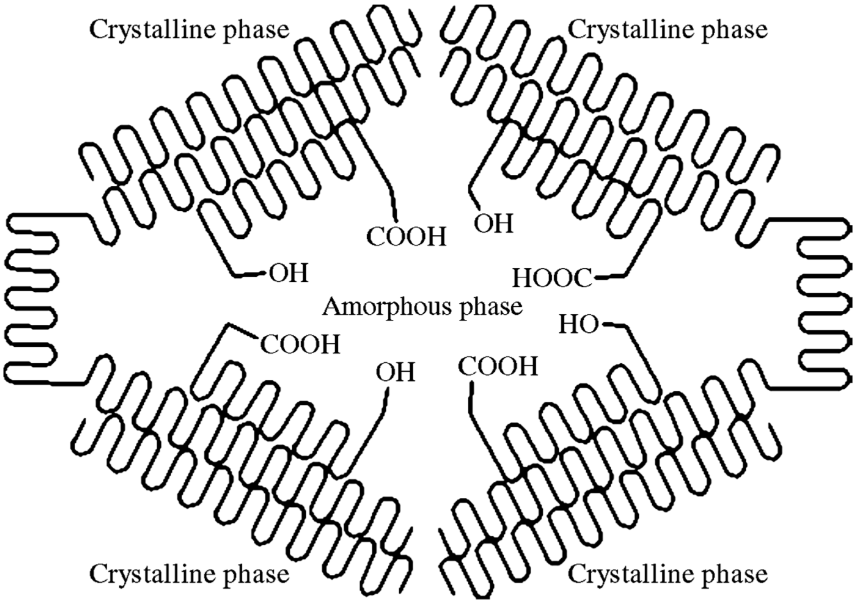


Figure 11: Schematic representation of semicristalline PLA phases [43].

The rate-determining step in the solid-state polycondensation is the mass transport of the water, in the solid state the water formed during the reaction moves slowly because it is tied to its molecular diffusion inside the crystalline and amorphous phases. Thus, the water removal can be enhanced by carrying out the reaction under vacuum conditions in an inert atmosphere.

A process for preparing PLA by the sequential melt / solid state polycondensation has been described and patented [56]. The process involves a liquid-phase polycondensation reaction step followed by crystallization and growth of the prepolymer crystals in a cooling step, and finally a solid-phase polymerization step. The weight-average molecular weight of linear PLA obtained by this process was above 100000 g/mol that in many cases was a 10 times higher compared to the prepolymer. The total process time to prepare the mentioned PLA was about 100 h, starting from lactic acid at 88% of purity.

1.5.3 Azeotropic dehydration

Another way for synthetizing PLA by direct condensation is using an organic solvent to remove the condensation water during the polycondensation step, this method is called Azeotropic Dehydration. As for standard direct polycondensation the lactic acid drying and the oligomers production steps are the same. Then the previously described high viscosity melt polycondensation is eliminated performing this step in solution.

The removal of the water from the reaction medium is easier in this way and higher molecular weight is achievable. The solvent, on the other hand, has to be dried from the using a drying agent (e.g., molecular sieve), and a dried non solvent is required for separating the polymer from the solvent at the end of the process.

Anisole or diphenyl ether are the main solvents used and tin based catalysts such as SnO or $SnCl_2$ are the most effective giving a weight average molecular weights higher than 100000 g/mol [57].

1.5.4 Ring-opening polymerization of lactide

Ring opening polymerization (ROP) has been the preferred route to synthetize PLA since the 1970s. Chemie Combinatie Amsterdam CCA, now known as PURAC, started to produce small volumes of PLLA and copolymers with rac-lactide, glycolide, and ε-caprolactone for biomedical applications [58].

Later starting from the 1990s, the ROP polymerization process was used for high-volume production of PLA grades. In 2002 Cargill and Dow under the name NatureWorks LLC started to produce PLA copolymers of L-lactide and meso-lactide in large scale. In 2009 its production capacity reached 140 ktpa with Ingeo PLA grades [59].

Nowadays, solid D-lactide and L-lactides are available in bulk quantities and can be polymerized into a wide range of polylactides by continuous melt polymerization processes based on static mixing reactors developed by Sulzer and PURAC.

Ring opening polymerization of lactide is usually the most preferred route for preparing high molecular weight polylactide, this due to the fact that the repetitive unit is composed essentially of two condensed molecules of lactic acid. In addition, this catalysed process not involves water formation during the polymerization, so most of the problems related to water removal and hydrolysis of polymer are avoided.

Moreover this type of synthesis permits an accurate control of the polymer stereochemistry, using a pure lactide stereoisomer or a mixture of them is possible to obtain semicrystalline or amorphous polylactic acid and also stereopolymers.

Lactide can be polymerized by melt, bulk n, solution, and suspension polymerization. Each of these methods has its own advantages and disadvantages, but melt polymerization is generally considered the most simple and reproducible method [58].

A large number of catalysts have been studied in the ROP of lactide, the most used are the carboxylates and alkoxides of Sn [60] [61] and Al [62] [63] [64].

During the polymerization, different mechanisms are involved, the predominant mechanism depends on polymerization conditions, catalyst and initiator concentration, and the presence of a solvent.

Tin octoate catalyzed ROP has been studied by many authors, and the coordination-insertion polymerization between tin and lactide, seems to be the main mechanism involved.

Kowalski et al. [65] shown that the polymerization mechanism involves a catalyst activation step (Figure 12), in which tin 2-ethylhexanoate is converted to a tin alkoxide by reaction with a hydroxyl compound, such as aliphatic alcohol or water.

$$\mathrm{Sn(Oct)_2 + ROH \rightleftharpoons Oct\text{-}Sn\text{-}OR + OctH}$$

Figure 12: Tin catalyst activation step.

Then, the polymerization proceeds on the tin-oxygen bond of the alkoxide ligand, whereas the carboxylate itself is inactive in the polymerization.

In the insertion-coordination mechanism, one of the carbonyl oxygen atoms of the lactide temporarily coordinates the tin atom of the alkoxide catalyst specie. This coordination enhances the nucleophilicity of the alkoxide part of the initiator as well as the electrophilicity of the lactide carbonyl group. Then the cleavage of the lactide ester bond makes the lactide open and insert into the alkoxide tin-oxygen bond of the catalyst. In this way, the lactide alkoxide group formed by the ring opening coordinates tin and the latide opened carbonyl group forms a new ester bond with the alkoxides compound that coordinated tin in the previous catalyst activated species. Subsequently propagation is induced by identical coordination and insertion mechanism of additional lactide molecules into the tin-oxygen bond (Figure 13) making the polymer chain grow.

Every initiating molecule is covalently bonded as an end group to each polymer chain, transesterification reactions between polymer and the 2-ethylhexanoate ligands of the catalyst will also give octanoic ester end groups in the polymer.

Lauryl alcohol (1-dodecanol) is usually added as a catalyst initiator, this system shows excellent catalytic activity to give high molecular weight PLLA using L-lactide.

Moreover this catalyst system is biologically safe and approved by the US Food and Drug Administration (FDA) for use in medical and food applications.

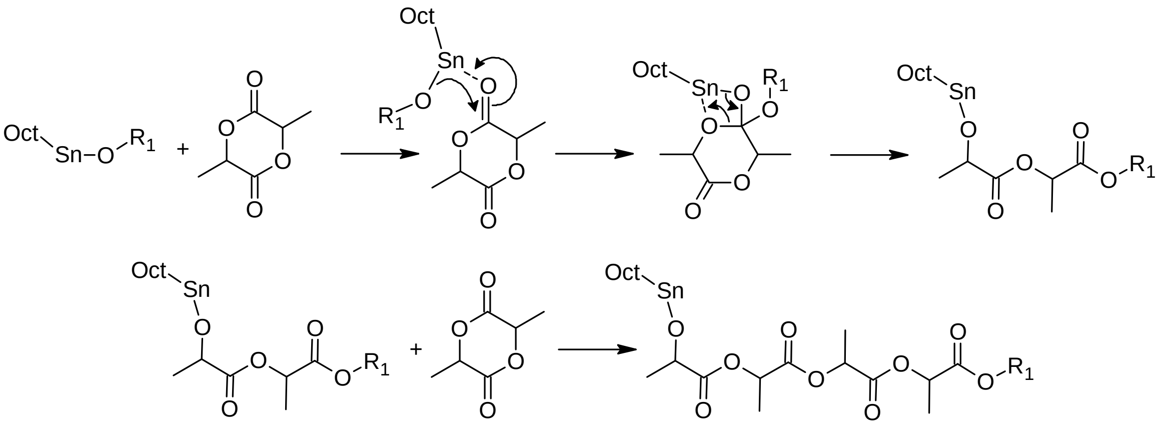


Figure 13: Coordination-insertion mechanism in ROP of lactide with tin octoate.

1.5.5 ROP in industrial process

The most common reactor system used for lactide ROP consist on one or more mixed reaction vessel, the number of vessels can vary depending on the desired polymerization conditions [66]. A combination of this type of reactor and a static mixer has also been developed, plug-flow reactor columns are used for a continuous polymerization process. In this type of reactors agitation blades are used in order to ensure appropriate mixing [67]. ROP can also be performed by reactive extrusion, in this process the residence time and catalyst efficiency are essential to achieve the right polymer molecular weight [68].

At the end of the PLA polymerization process, low molecular weight oligomers unreacted, lactide and the lactide generated by side reaction like backbiting and intramolecular cyclization, need to be removed. This process is carried on by distillation under vacuum in the presence of an inert gas current [69]. During this final step, the catalyst deactivation also occurs. Deactivator agents can be various such as phosphorous containing compounds [70] [71], antioxidants [72], acrylic acid derivatives [73], and organic peroxides [74].

A solid state-state polymerization can be also used in order to reduce the lactide content, and increase the molecular weight of the polymer [75].

The final polymer product must be dried at 60°C under vacuum or with dry air before storage or before future processing, in order to avoid hydrolysis due to the presence of moisture [76].

1.5.6 Polylactic acid stereopolymers

Starting from different types of lactides or from a mixture of them is possible to synthetize PLA with various stereoregolarity:

- Isotatic PLAs; they are formed from pure L-lactide or pure D-lactide obtaining a polymer with the same stereoconfiguration in all repeating unit, poly(L-lactide) (PLLA) or poly(D-lactide) (PDLA).
- Syndiotactic PLA; it has alternating configurations of the sequential stereocenters L and D, poly(meso-lactide) (mesoPLA).
- Atactic/Heterotactic PLA; the atactic has a random distribution of configurations about the stereocenters, while its heterotactic counterpart has regions of stereo-homogeneity, poly(rac-lactide) (PDLLA, racPLA).
- Isotactic stereoblock PLA; it consist on a block copolymer of PLLA and PDLA, poly(l-lactide-co-d-lactide) (PLDA).

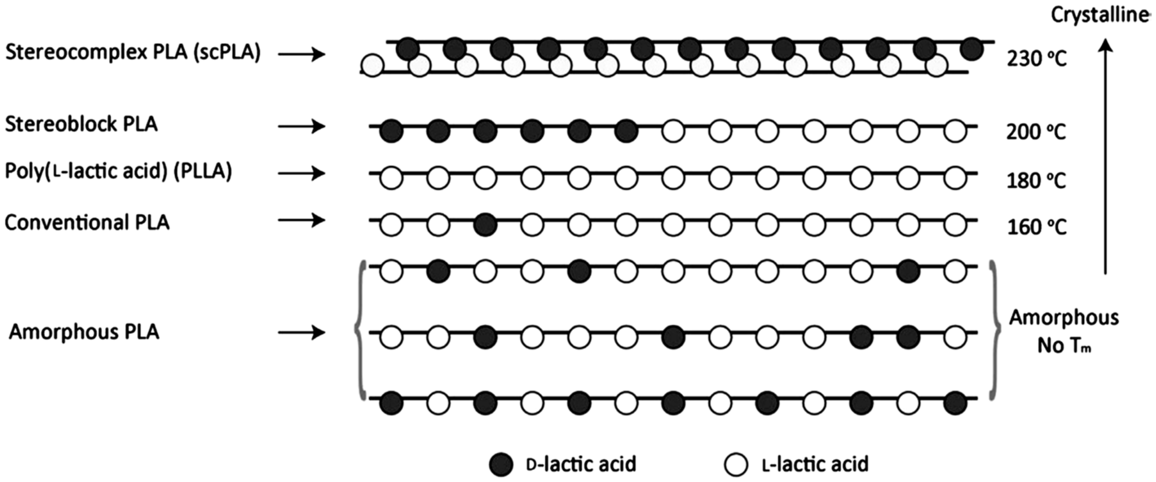


Figure 14: Schematic representation of the various stereoisomeric forms of polylactic acid [43].

As reported in Figure 14, and in Table 1, the melting point and the glass transition temperature change depending on the chain stereoregularity, this is due to the ability of the high enantiopure omopolymers to crystallise.

Table 1: Transition Temperatures of different types of PLA

Transition temperatures	PLLA/PDLA	racPLA	mesoPLA atac. / synd.	scPLA	sbPLA
Tg (°C)	53-63	50-55	40-45 / 34	80-90	50-55
Tm (°C)	160-185	-	- / 153	200-230	185-195

PLLA is semicrystalline with a Tm of 160-185°C, a Tg of 53-63°C, and a crystallization temperature Tc of 100-120°C.

Syndiotactic PLA can be produced from the polymerization of meso-lactide using a stereoselective catalyst like isopropoxide [77]. It is semicrystalline with a Tm of 153°C and a Tg of 43°C, however, its thermal properties are poorer compared to PLLA.

Atactic PLA (PDLLA or racPLA) can be prepared from rac-lactide. It has a Tg of 50-55°C but it has no Tm because it is amorphous, it shows the lowest mechanical properties [78]. Atactic PLA can also be prepared from the random copolymerization of meso-lactide.

PDLA is prepared from D-lactide, it is very expensive and produced only in small quantities.

Stereoblock PLA (sbPLA) can be prepared by solid-state polycondensation of PLLA and PDLA. It has a Tm of 185-195°C and a Tg of 50-55°C.

Stereocomplex PLA (scPLA) is obtained mixing PLLA and PDLA omopolymers. It has a Tm of 200-230°C and a Tg of 80-90°C.

Pure PLLA and PDLA macromolecules can crystallize together into a stronger crystalline structure. The alternation of PLLA and PDLA molecules in the crystal lattice permit the formation of a structure where the macromolecules are closer. In fact, in this particular stereoconfiguration the two polymer chains are less hindered when align in the crystals leading to an increase of the intermolecular interaction energy compared to the crystalline structure obtained in both omopolymers alone [79].

This effect lead to an increase of Tm in both stereoblock and stereocomplex polymers. In the same way, the mechanical and thermo-mechanical properties change. The presence of a crystalline phase increase the degradation times [80] since the crystalline phase possess higher water impermeability.

scPLA is prepared by mixing PLLA and PDLA in solution state [81] or in molten state [82], both processes require long period of time to reach high stereocomplex content. Although in both cases the polymer’s molecular weight decrease, this problem is more emphasized when the mixing is achieved in molten state because the temperature involved is 45-55°C higher than the melting temperature of PLLA and PDLA omopolymers [78].

1.6 PLA Properties

PLA is widely used in packaging and biomedical applications because of its biodegradability characteristics, in addition to its good mechanical and physicochemical properties. The methyl side groups give to the material a hydrophobic behaviour. PLA is soluble in many organic solvents like chloroform, dichloromethane or THF. PLA has higher transparency than other biodegradable polymers, and is superior in weather resistance, and workability.

It is a high modulus thermoplastic polymer with properties in between polystyrene (PS) and polyethylene terephthalate (PET). The polymers obtained from optically active monomers (L-lactide and D-lactide) are semicrystalline while the optically inactive monomers (racemic D,L-lactide and meso-lactide) give amorphous polymers.

Similarly to polyethylene terephthalate, polylactic acid has slow crystallization rate. The highest rates of crystallization occur in pure PLLA in the temperature range of 110–130°C with the formation of spherulitic crystals [83].

Runt et al. [84] presented crystallization kinetics data for copolymers of poly(L-lactide-co-meso-lactide). At a crystallization temperature of 117°C, a copolymer of 0.4% D-content crystallized 60 times faster than a copolymer of 6.6% D-content. At 135°C, the dependence of growth rate on meso concentration was much more significant. Indeed the ratio of crystal growth rates of the 0.4% to 6.6% meso concentration was more than 340 times. Also Kolstad [85] studied the crystallization kinetics of poly(L-co-meso-lactide) and found that the crystallization half time increased approximately 40% for every 1 wt% increase in the meso-lactide content. Moreover, his results show a loss in crystallization ability when this content exceed 15%.

Amorphous PDLLA is typically used for biomedical devices and for slow drug release, while semicrystalline PLLA is selected for applications where higher mechanical and thermo-mechanical properties are required.

Typically its tensile strength range from 50 to 70 MPa, modulus of elasticity of 3000–4000 MPa, elongation at break of 2-5%, flexural strength of 100 MPa, and flexural modulus of 4000–5000 MPa [86] [87] [88] [89]. The typical low elongation at break limits some of its uses, indeed it is brittle at room temperature, fracturing through a crazing mechanism. Different studies are focussed to improve the properties of PLA by copolymerization, blending with other biodegradable polymers, and plasticization.

The copolymerization of L-lactide with minor amounts of meso-lactide or D/L-lactide offers materials with lower brittleness and better film properties.

In general, PLA properties depend on the molecular weight, on the degree of crystallinity, and also on the polymer chain stereochemistry. A higher molecular weight raises Tg, as well as Tm, tensile strength [89], elastic modulus, and lowers the elongation at break. In the same way an increase in crystallinity increase the tensile strength, the elastic modulus and lower the elongation at break [90].

The stereochemistry is very easily controlled by the polymerization with D-lactide, L-lactide, D/L-lactide, or meso-lactide, to form random or block stereocopolymers, while the molecular weight is directly controlled by the addition of hydroxyl containing compounds such as lactic acid, water, alcohols [91]. The ability to control the stereochemical architecture allows precise control over the rate and degree of crystallinity. Although some polymers like PLLA are semicrystalline and so can crystalize under proper conditions, the slow crystallization kinetics that characterize this process gives problems to achieve higher degree of crystallinity during injection moulding and compression moulding processes. In this machinery, the material is rapidly cooled down in order to maintain high the productivity, and only low degree of crystallinity can be achieved.

Increase the crystallinity also means increase the mechanical properties at temperature in between the transition temperature and the melting temperature, where usually the material loose its mechanical properties.

Different ways can be followed to overcome the slow rate of crystallisation, the main are annealing, orientation and nucleation.

1.6.1 Annealing

As reported by Park at al. [92] the Xc (crystallization degree) of quenched PLLA is generally around 3%, while PLLA annealed at 70 and 100°C can reach Xc of 23% and 56%, respectively.

PLLA specimens annealed at 100°C maintain high the value of the storage modulus above Tg due to the presence of more crystallinity that contributes to the mechanical properties.

These data agree with others reported in the literature and in general, the annealing of PLLA is accompanied by increase in tensile and flexural strengths, as well as impact resistance and thermo-mechanical properties [86] [93].

1.6.2 Orientation

Orientation is an excellent way to improve the mechanical properties of amorphous or semicrystalline PLLA films. Biaxial orientation of PLLA film is effective in increasing tensile strength, elongation at break, and elastic modulus. Instead, a monoaxial orientation gives anisotropy with very poor mechanical properties in the normal direction respect to the orientation.

The stretching is typically carried out at a temperature between the Tg and Tm of the material, usually 70-90°C, depending on the method [94].

The tensile strength of a semicrystalline PLLA film can be increased from 50-60 MPa in unoriented film, to 100–200 MPa in biaxially oriented film, while elongation at break can change from 10% to 50-150%. The elastic modulus increase from 2500 MPa to around 3300 MPa [94] [95].

1.6.3 Nucleation

PLA nucleation is a technique used for increasing the crystallization rate during material cooling, this can be obtained by adding nucleation agents able to generate crystal nuclei faster during the material cooling into the melted polymer. In particular nucleation agents increase the temperature of hot crystallization, so during industrial process like injection moulding where the cooling rate are rapid in order to maintain high the productivity of the process, the material starts to crystalize at higher temperature and the final product is more crystalline with respect the material nucleating agent free.

Kolstad at al. [85] showed that talc is an efficient nucleating agent for PLLA increasing the polymer crystallization rate. The results showed that for PLLA with 6% of talc the polymer half-time crystallization at 110°C was reduced from 3 minutes to approximately 25 seconds. For PLLA copolymerized with 3% meso-lactide and with the same percent of talc, the half-time was reduced from about 7 minutes to about 1 minute.

Li and Huneault [96] compared the crystallization kinetics of talc and montmorillonite Closite Na^+ added to PLLA with 4.5% of D-content. They reported that the lowest crystallization induction period and maximum crystallization speeds were observed around 100°C. By adding 1 wt% of talc, the crystallization half-time of PLA was decreased from a few hours to 8 min. In contrast, the montmorillonite tested was less effective as a nucleating agent achieving 30 min as lowest half-time.

Organic compounds such as calcium lactate [97], sodium stearate [98] or benzoylhydrazide compounds [99] and N,N-ethylenebis(12-hydroxystearamide) [100], are also been studied. The addition of 1% calcium lactate induced crystallization of a 90:10 L/D copolymer during the injection moulding cycle [97].

Ke and Sun also reported the detailed thermal behaviours of the starch/PLA blends studied by differential scanning calorimetry [101]. The experimental data were evaluated using the well-known Avrami kinetic model. For comparison, talc was also incorporated into PLA at 1%. Starch effectively increased the crystallization rate of PLA, even at just 1% content, but the effect was less compared to talc.

1.6.4 Plasticization

The addition of a plasticizer is commonly used to increase the elongation at break, the impact resistance and reducing the brittleness. The main effect induced to the polymer involves the decrease of the Tg by increasing the chain mobility. Using particular plasticizers, an increase of crystallinity was also seen in PLA.

Poly(ethylene glycol) [102], triacetine [103], citrate [98], laurate, and sebacate esters [104] are commonly used plasticizers for PLA. The primary effect is the improvement of the polymer ductility and drawability, but also an increase of crystallization rate, as shown by Kulinski and Piorkowskafor for PEG added PLLA [105].

Martin and Avérous [106] tested the addition of PEG with a molecular weight of 400 g/mol, after the addition of 10% of PEG the Young’s modulus of a pure PLLA decreased from an initial value of 2050 to 1488 MPa, and it decreased to 976 MPa with 20%. The elongation at break increased from 9% to 26% and 160%, respectively.

In general, the storage modulus drops in plasticized PLA, the Tg decreases almost linearly with increasing plasticizer concentration, from 67°C for pure PLA to 54 and 46°C with 10% and 20 % of PEG content. Martin and Avérous tested also oligomeric lactic acid (OLA) as plasticizer, the results obtained show a reduction of the elastic modulus of PLLA from 2050 to 1256 MPa with 10% plasticizer and to 744 MPa with 20% plasticizer, while elongation at break increases to 32% and 200%, respectively [106].

Ljungberg et al. showing that stress at break of PLA is lowered from the value of 62 MPa for neat material to 30 MPa in the presence of 15% triacetine and to 35 MPa with 15% tributyl citrate. Elongation at break changes from 6% to 355% and to 350%, respectively, with 15% triacetine and with 15% tributyl citrate [107].

1.6.5 Biodegradability

Biopolymers containing hydrolysable linkages are generally susceptible to biodegradation by microorganism enzymatic catalysis. In general biodegradation reactions occur in aqueous media, so hydrophilic or hydrophobic polymers character affect the phenomenon. More polar are the polymers and more readily can be biodegraded. Also the crystallinity and chain flexibility are important characteristics that affect the polymer degradation.

Biodegradation mechanism include disintegration, dispersion, dissolution, erosion, hydrolysis, and enzymatic degradation.

Generally microbial reactions are sequential, the metabolism end product of a one organism becomes the substrate for another organism [108].

The process involves the microorganism growth on the surface of the polymer and the secretion of enzymes able to break down the chains into oligo- or monomeric units such as hydroxyacids in case of aliphatic polyesters. Then the microorganism consumes these hydroxyacids as carbon sources in order to produce energy. In aerobic environment the carbon dioxide and water are the main degradation products, whereas in anaerobic environment the degradation products are carbon dioxide and methane [109] [110].

The whole biodegradation process can take from days to months to years, and it depends on the type of polymer. PLA breaks down slowly in the soil and, if composted, high temperatures are required to decompose it.

PLA is initially degraded by a nonenzymatic catalysed hydrolysis mechanism. The enzymatic degradation at the beginning of the biodegradation process is slow. This is due to its hydrophobicity nature and to the presence of crystalline regions that act as barriers for the diffusions of enzymatic molecules. It is well known that the crystalline part of PLA is more resistant to degradation than the amorphous part, generally the rate of degradation decreases with an increase in crystallinity.

Subsequently, soil bacteria and fungi microorganism are able to hydrolyse the shorter polymer chain formed, consuming these oligomers with their enzymatic catalysed reactions.

In details bacteria like *Amycolatopsis sp*. and *Kibdelosporangium aridum* [111], and fungi like *Fusarium moniliforme* and *Tritirachium album* [112] release protease and lipase enzymes that are able to hydrolyse the polymeric chain ester groups. Lipase are able to hydrolyse both PLLA, PDLA and PDLLA chain, instead protease like *proteinase K*, *subtilisin*, *a-chymotrypsin* are able only to hydrolyse PLLA. This because *proteinase K* hydrolyses only the ester groups of L-amino acids that naturally occur and in the same way it is able to hydrolyse only the ester bonds between the L-lactic unit present in PLLA, but not the ester bonds between the D-lactic units in PDLA.

1.7 PLA applications

1.7.1 Medical applications

PLA and other poly(α-hydroxyacid) as well as their copolymers have been approved by the U.S. Food and Drug Administration (FDA) and by other regulatory agencies in many countries for implantation in the human body.

These materials remain temporarily in the body and disappear upon biodegradation, so a secondary surgery is no needed to remove them after the defective site is repaired.

A number of products are now commercially available and have successfully been used in the medical field. For instance, biodegradable orthopaedic devices have been reviewed extensively, and they have been replacing metallic ones for the fixation of fractured bones in the forms of plates, pins, screws, and wires [113] [114].

Self-reinforcing PLLA is used where a strong support is required like in bone fixation applications. In this material, polymeric fibre with high modulus are bound together with the matrix of the same polymer without any adhesion promoters.

However, due to the slow degradation rate of PLA, its medical applications have been limited. Copolymers with PGA or poly(ε-caprolactone) (PCL) have been synthesized in order to reduce their crystallinity and increase the degradation rate matching the tissue recovery time. PLLA fibres are used in the form of biodegradable stents in cardiovascular surgery and in surgery where longer support is required [115].

Furthermore, the degradation products and the hydrophobic nature of PLA can cause some problems. Indeed the body can decompose the lactic acid resulting from PLA biodegradation, however lactic acid is a relatively strong acid and its accumulation at the implant site, results in lowering the local pH and an inflammatory response can occur [116]. A large amount of research is under development to overcome these problems, for instance, by using copolymers and blends.

1.7.2 Packaging

The thermoplastic nature of polylactic acid permits to process it with different techniques like extrusion, thermoforming, injection moulding, compression moulding, blow moulding and film blowing. The range of objects obtainable goes from fibres, films, bottles and printed items, making the PLA packaging applications various.

Oriented flexible films, for example, are obtained using plasticizer or blending PLA with other flexible biodegradable polymers. Ajinomoto adopted PLA film for cap seals of a bottle in 2003, and thereafter S&B Foods, Nisshin Oilio, and Asahi Soft Drinks also adopted PLA films for bottle labels [117].

Thermoformed food containers are widely produced, the more commonly are for packaging products that are not to be heated such as eggs, vegetables, fruits, bakery, and blister pack products. PLA is also widely used for single use items like disposable tableware and drinking cups.

NatureWorks Ingeo PLA is one of the most easily processable PLA grade and used as amorphous biopackaging material as a result of its relatively high meso-lactide content.

1.7.3 Agricultural

PLA biodegradability is the basis of agricultural applications consisting of sandbags, weed prevention nets, vegetation nets, vegetation pots, ropes and binding tape. These applications are very interesting because the materials can be left in the ground to decompose without needing to remove it. For this reason, the complete decomposition in the ground is essential but at the same time a structural integrity during their use is compulsory. Moreover, PLA needs to possess properties that permit manufacture on an automatic loom. Tight binding, abrasion resistance, and branching prevention are required. The use of monofilament, yarn, and nonwoven fabric made from PLA loaded with inorganic fillers are example used to satisfy this request.

1.7.4 Electronics and electrical

Nowadays biopolymers applications in electronics are widely studied and developed. Electronics industry has made considerable efforts to improve its environmental profile optimizing the energy efficiency of products and devices, and focusing on the sustainability of the materials used. In fact, the miniaturization of electronic devices such as circuit boards, which are difficult to repair and sometimes hard to recycle, see in biodegradable polymers a suitable choose to reduce the amount of waste. However, severe product requirements have limited the adoption of bio-based polymers for the electronics industry, indeed thermo-mechanical and electrical properties of these polymers remain inadequate for electrical and electronic applications, moreover good flame resistance properties are required.

Engineering thermoplastics made at least in part from renewable resources are nowadays the most used in electrical and electronic devices.

PLA based materials are the greatest promise to replace polycarbonate / acrylonitrile-butadiene-styrene (PC/ABS) blends that are actually the most used in this fields. However, PLA is brittle, and more difficult than PC/ABS to make flame resistant. Compounds based on PLA with various additives or PLA blends with other polymers were studied to overcome these drawbacks. Many studies have been conducted in the last decade to improve PLA thermal, impact and flame resistance, in order to develop materials for office automation equipment and electrical appliances. Sony in 2002 adopted PLA to build the chassis of a portable audio player Walkman by injection moulding. FUJITSU in 2004 developed a glass fibres PLA based material containing a phosphate flame retardant for electric housing devices such as personal digital assistant (PDA), notebooks and mobile telephones.

NEC produced a chassis of a cell phone based on PLA reinforced with kenaf fibre in 2006. TEIJIN CHEMICALS in 2007 formulated a flame retarded stereocomplex PLA based materials for housing of scanner and digital cameras.

Panasonic in 2013 disclosed a moulded housing for a flat display device, composed by 50 wt% of PLA, 40 - 49 wt% lactic acid based copolymer, and silica magnesia catalyst particles as a flame retardant (0.5 – 9 wt%).

Other recent applications are the Bioserie iPhone 5 cover and the Telecom Italia’s Eco cordless telephone made of PLA Ingeo® NatureWorks [118]. Also Samsung Reclaim™ used a blend of PLA (40 wt%) and polycarbonate (60 wt%) for outer casing of its mobile phone [119].

1.7.5 Automotive

The substitution of metal with plastic in automotive lightweighting is the key to reduce the fuel consumption and decrease the related carbon dioxide emissions. Nowadays the plastic content in automotive is about 12% of the total weight [120].

The most used polymers in automotive are polypropylene, polyamides, polyurethanes, and acrylonitrile-butadiene-styrene. Estimates shown that approximately every year 20 millions of vehicles reach the end of their useful lives. While about 80% of these vehicles are recovered and recycled for scrap or second hand parts, the remaining 20% cannot be recycled. Five million tons of nonrecyclable material from vehicles end up in landfills every year. Many of these parts are fossil fuel-based plastics [121]. In this contest it is clear how vehicle parts based on bio-based biodegradable polymers are the way to follow. These materials are completely biodegradable at the end of their useful lives and they would not contribute to plastics accumulation in landfills.

Automotive applications require materials with at least 10 years durability, this can be a problem using biodegradable materials, but can be solved increasing thermal and moisture resistance as well as improving the resistance to weathering.

PLA may be inferior in thermal and impact resistance, and durability in comparison to the most common engineering polymer in commerce, but a range of technologies have been developed improving its thermal and moisture resistance, for example by capping the end groups improving its durability and incorporating UV absorbent increasing resistance to weathering.

In addition, the National Highway Traffic Safety Administration released the Standard No. 302 “Flammability of Interior Materials - Passenger Cars, Multipurpose Passenger Vehicles, Trucks, and Buses”. This standard specifies burn resistance requirements for materials used in the occupant compartments of motor vehicles. Its purpose is to reduce deaths and injuries to motor vehicle occupants caused by vehicle fires, especially those originating in the interior of the vehicle from sources such as matches or cigarettes.

In keeping with that, flame resistance properties are needed for these applications.

Although PLA is very interesting for its biodegradability, the low thermo-mechanical resistance and flammability are limiting its application. However, some PLA based materials were specifically developed. As example, Toyota designed in 2009 spare-tire cover made from PLA and fibres from kenaf [122] and in 2003 introduced in the Raum and Prius models [123] a floor mat consisting of a PLA fibre where polymer end groups were capped to prevent hydrolysis. Röchling Automotive developed a heat and UV resistant PLA compound with 30% of wood fibre called Plantura^{TM} for air filter part.

Mazda Motor Corp. developed a door module part based on PLA and 12 wt% organic additives [124].Even if these materials have founded some applications, a wide range of uses in automotive and transportation fields can be obtained only with good thermo-mechanical properties and, especially, good flame resistance properties.

1.8 Combustion in polymers

1.8.1 General considerations

In 2016, 1,342,000 fires were reported in the United States, fire departments responded to a fire emergency every 24 seconds. 3,390 civilian were dead for fire, statistically one death occurred every 2 hours and 35 minutes. 14,650 civilian were also injured and $10.6 billion were estimated in property damage. As shown in Figure 15, the fires occurred principally as structure fires and vehicle fires.

As in the United States, fire losses occurred in every country, especially in countries where fire protection system are not well developed and fire protections regulation are not strict enough.

Fire is a destructive force of nature, what it touches cannot easily be repaired, rebuilt, or restored to its original form.

This because fire involves a thermo-oxidative decomposition of the materials that converts carbon and other combustible materials into CO_2 and water.

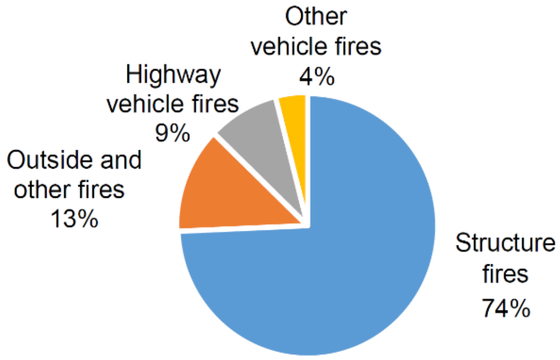


Figure 15: Fire distribution in 2016 based on property loss estimates [125].

I is clear how important is develop and use new materials that do not easily ignites and burns in the presence of a heat source during the daily life. A fire can occur at home, at working places, at public places, driving a car or travelling using public transport. A fire scenario can starts and grows destroying everything if there are combustible materials able to feed the flames. Fire prevention and suitable fire safety regulations are the basis to reduce the risks for people and firefighters.

Fire can be prevented in most cases, but we still experience catastrophic fire losses that result in the loss of wealth, possessions, and life. It is for these reasons that scientists and engineers are studying fire seeking to provide passive fire protection for daily life. The major goal in fire science consist on developing materials that difficultly ignite and if an accidental fire begin, it must be easily and rapidly extinguished before it grows. In particular the fire grow mast be slowed in order to leave time to people to save themselves and for firefighters rescue. Moreover, the toxicity of the combustion products are essentially toxics and smoke are frequently the main reason of death blocking and intoxicating people during their escape from fire.

1.8.2 Combustion

Combustion is a highly exothermic oxidation reaction process that occurs in presence of a combustible, oxygen and a heat source. All carbon-based materials are able to burn or smouldering because the carbon content can be oxidized into CO_2 and H_2O in presence of the right amount of oxygen and heat. The presence of fuel, heat and oxygen at the same time is fundamental to create the condition for combustion, and this particular condition is called fire triangle (Figure 16). If any of the three elements are removed, the fire is extinguished.

The first element in the fire triangle is heat, which is perhaps the most essential of fire elements. A fire cannot ignite unless in the presence a certain amount of heat, and it cannot grow without heat either.

The second element in the fire triangle is fuel. A fire needs a fuel source in order to burn. The fuel source can be anything that can be oxidized, a combustible can be a gas or a vapour or a solid in bulk or in small particles. Once the fuel element of the fire triangle is removed, the fire will go out.

The final but not last element of the fire triangle is oxygen, it is also an essential component of fire since fire needs oxygen to start and continue. That is why one recommendation for extinguishing a small fire is to smother it with a non-flammable blanket, sand or dirt.

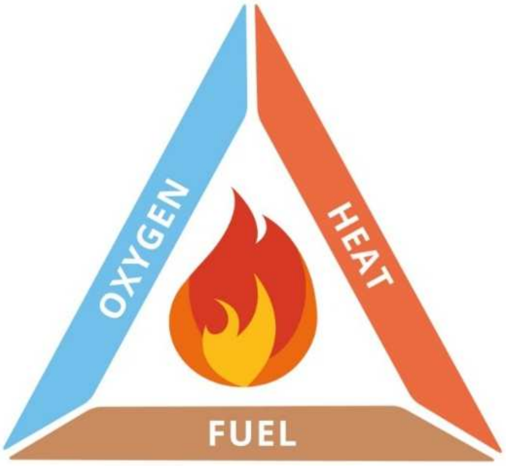


Figure 16: Graphic representation of the fire triangle.

Only inorganics and metals in their highest oxidation state are noncombustible. Even if carbon based materials can burn thought the thermo-oxidative decomposition, for some polymeric materials under some conditions it may be hard to burn, and in some cases under some particular test condition some carbon based materials can be defined as noncombustible.

1.8.3 Polymer combustion

Polymers are solid materials essentially non-volatile and are formed by large molecules, which must be broken down through thermally decomposition into smaller molecules that can vaporize. That said, the fuel is not the solid polymer but are their volatile thermal decomposition products, that burn in the gas phase when mixed with oxygen and ignited. Polymers do not burn in the condensed state because of the low solubility and diffusivity of oxygen inside them and their low oxidation rate at the decomposition temperature. The thermal degradation of the polymer surface occur mainly in a non oxidative conditions rather than in an oxidizing environment. The chemical structure of the polymer determines the thermal stability as well as the degradation temperature and the volatiles generated. The fire point temperature is the temperature of plastics surface at ignition, and this temperature is close to the degradation temperature. Polymers are generally not thermally conductive, so the thermal degradation reactions at the plastic surface are faster than the rate at which heat is absorbed. Consequently, the polymer chemical structure and its characteristic degradation mechanism involved, governs the burning rate, the heat release rate, and the smoke evolution during flaming combustion.

Ignition occurs when the concentration of low-molecular-weight degradation products reaches the lower flammability limit for a particular fuel-air mixture and temperature. As is possible to see in the Figure 17 the lower flammability limit decreases with the increase in temperature, so the higher is the heat of the gas mixture, the lower must be the concentration of fuel required for the ignition.

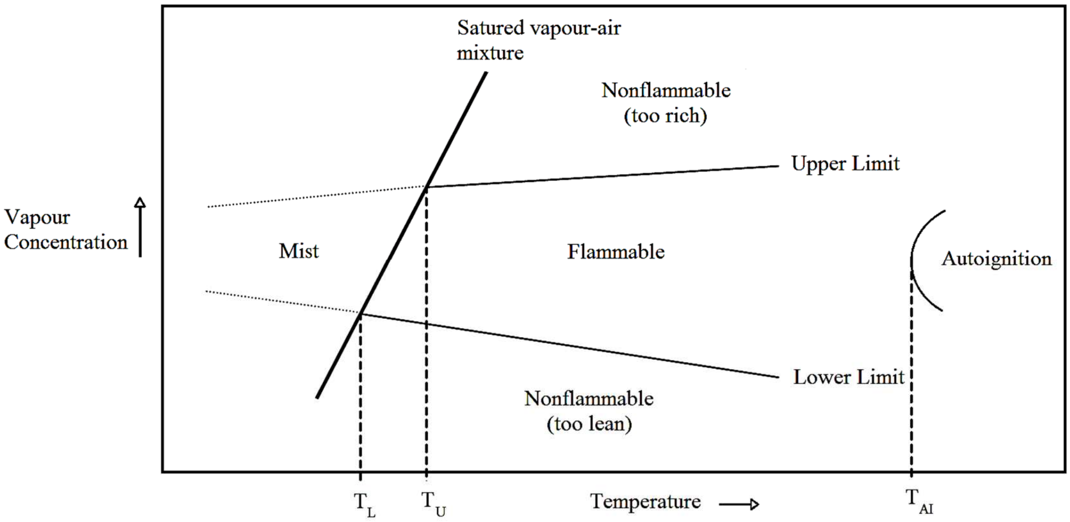


Figure 17: Effect of temperature on flammability limits of combustible vapours in air at a constant initial pressure [126].

The flow of low molecular weight degradation products that leaves the condensed phase feeding the flame, is also related to the amount of heat applied on the material surface. When the burning occurs the volatiles are consumed and heat developed. This heat generated by the combustion give a thermal feedback to the material surface by conduction, convection or radiation. If this thermal feedback is enough to maintain the volatiles concentration over the lower limit, the process became self-sustaining and will not stop until all material is consumed.

This particular condition is well known as polymer combustion cycle and is schematized in Figure 18.

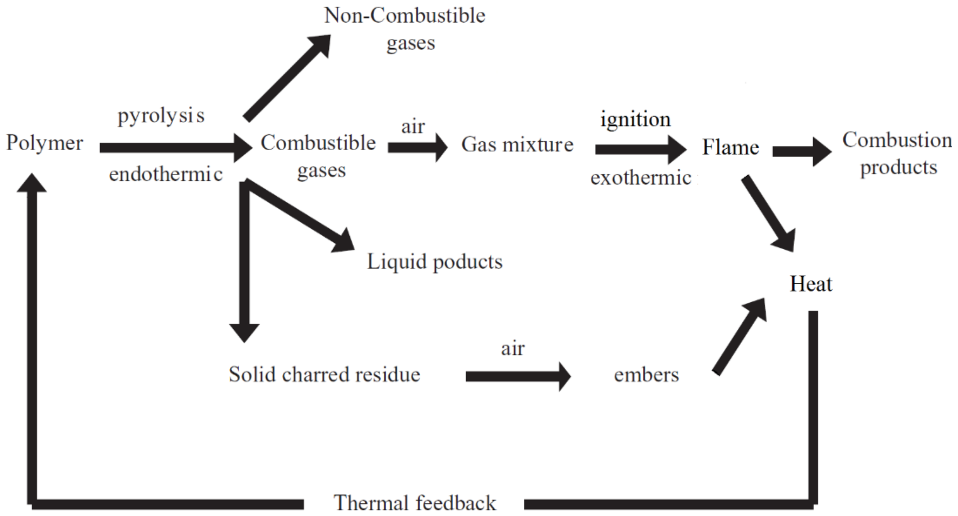


Figure 18: Polymer combustion cycle [127].

The flame spread can be considered as an advancing ignition front in which the outer edge of the flame acts as the source of heat and the source of ignition at the same time [128] [129].

The flame propagation can occur on horizontal, inclined, and vertical surfaces, in parallel or in opposite to the airflow direction. The thermal feedback occurs by radiation when the combustion takes place on a horizontal surface. Instead, when the burning occurs on a vertical surface the thermal feedback is obtained by conduction, convection and radiation [130].

The flame spread affects the fire growth process and different behaviours may be observed:

- Non-propagating fire behaviour, when there is no flame spread beyond the ignition zone.

- Decelerating fire behaviour, when the flame spread rate decreases with time and the flame front propagation stops before covering the entire surface of the material.
- Propagating fire behaviour, when the flame spreads all over the entire surface of the material.
- Accelerating fire behaviour, when the flame spread rate rapidly increases covering the entire surface of the material, the flames front extends far beyond the surface of the material in a relatively short time.

Fire development in a real fire scenario is characterized by the following stages (Figure 19):

Ignition: fuel, oxygen and heat combined in the right amount generate flame trough the exothermic thermo-oxidative reaction.

Growth: with the initial flame as a heat source, additional fuel is generated by convection and irradiation. The flame spread ignites more surfaces and the size of the fire increases. When a fire happen inside a room, the fire can reach the ceiling. The hot gases that are collecting at the ceiling, transfer heat towards anything inside the room, allowing all fuels in the room to come closer to their ignition temperature at the same time. If sufficient fuel and oxygen are available, the fire will continue to grow. When the exposed surfaces will reach their ignition temperature the fire spreads quickly and all combustible items in the compartment are involved in fire. This step is known as flashpoint and is the transition from a growing fire to a fully developed fire.

Fully Developed Fire: during this stage, oxygen is rapidly consumed and the heat release rate of the fire is the greatest, leading to the temperatures reach their peak. In this case, the fire is said to be ventilation controlled. Usually during this stage more fuel is pyrolized respect to the fuel that can be burned with the oxygen available in the compartment. The unburned fuel can leave the room trough openings, and burn outside causing fire spread to upper floors and neighbouring room or building.

Decay Stage: in the decay stage, the fuel becomes consumed, and the fire may change from ventilation to fuel controlled. The heat release rate and temperature inside the room decrease and the fire became less intense.

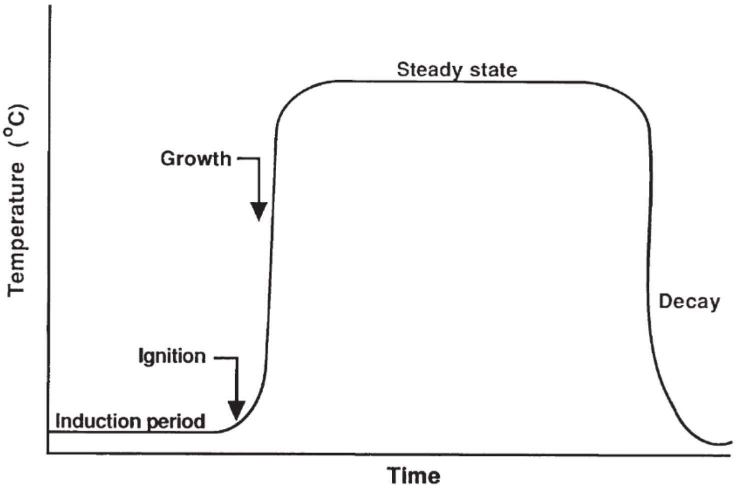


Figure 19: Characteristic stages in a fire [130].

1.8.4 Thermal decomposition of polymers

The combustion of polymers starts with the thermal decomposition of the material when it is exposed to a high source of heat. In this process, the polymer bonds start to break causing the formation of potential fuel molecules. These cleavages consist on bonds and radical scissions, and these fragments generate fire reacting with oxygen in the gas phase.

The different chemistry and structures of the various polymer types influence the decomposition process and the formation of different degradation products that can have different volatility and different resistance to combustion.

Polymeric materials are generally classified in two main categories, thermoplastics and thermosetting in base on their behaviour when heated. Both classes behave differently when heated, but when high temperature are involved, they get either degraded trough one or more of the following processes:

- end-chain scission, individual monomer units are cleaved from the chain ends
- random chain scission along the polymer chains
- chain stripping, atoms or groups not part of the polymer backbone are cleaved off
- cross-linking with the formation of new bonds between the polymer chains

When polymers are subjected to heat, generally, the weakest bonds will break first. More linkages are present in the polymer, like in rubber and thermoset, more linkages must be broken before first volatile molecules are generated. Moreover, cross-linking reactions give rise to eventual char formation and thus, may minimize the volatiles formation. In the following paragraphs, the thermal decomposition pattern of the principal and most diffused polymers will be described.

1.8.4.1 Thermoplastics polymers decomposition

Polyolefins

The main degradative route for polyolefins like polyethylene, polypropylene and their copolymers, is characterized by random chain scission [131]. The degradation proceeds by a free-radical mechanism [132] leading to the formation of low molecular weight alkanes, alkenes and dienes. These reactions are only slightly affected by the differences in the physical structure such as crystallinity, but are influenced by the presence of impurities.

The complete absence of cross-linking reactions prevents the char-formation during the polymer decomposition.

Polyamides

For linear aliphatic polyamides, such as PA-6 and PA-6.6, the thermal degradation is influenced by two major factors: the strength of the weakest chain bonds around the amide group and the tendency to form three-dimensional structures resulting in gel formation.

The bonds cleavage randomly occur preferentially at the –NH–CH_2– bond [133], leading to the formation of linear and cyclic oligomers. These random scissions give rise to NH_3, CO, and CO_2, low molecular weight fragments, and subsequent degradation products from them. Considering these gases, only CO is flammable, but the volatiles generated from the smaller polymer chain fragments provide the major fuel components.

Polyesters

The most known and diffuse linear polyester is poly(ethylene terephthalate) (PET). As for many polyesters, its thermal degradation is dominated by random chain scission based on β-CH hydrogen transfer trough a six membered ring transition stage [134]. At temperatures close to 290°C, the random chain scissions generates oligomers with olefinic and carboxylic end groups [135]. Homopolymerization of these vinyl ester ends group, followed by chain-stripping with the loss of a substituted carboxylic acid, will produce unsaturation along the main chain of the polymer. Then, these unsaturated linkages can cyclize to give a highly cross-linked and aromatic polymer [136].

The final degradation products are: acetaldehyde as the main flammable product, CO, CO_2, ethane, and very small amounts of other fuels such as methane and benzene [133].

Polystyrene

The polystyrene thermal degradation involves a single step characterized by random scissions process with the production of the volatile monomeric styrene in high amount close to 40%, followed by significant amount of dimer and other oligomers and smaller amount of benzene and toluene.

The oligomers are formed by intramolecular radical transfer reactions during the depolymerisation process, competing whit the formation of the monomer [137].
The combustion of polystyrene is characterized by the formation of high amount of smoke arising from the formation of not completely combusted aromatic species like benzaldehyde, benzoic acid, phenol, and benzyl alcohol.

Polyvinyl Chloride

The poly-vinyl chloride thermal degradation consists on autocatalytic chain stripping process involving the dehydrochlorination reaction by β-elimination to release hydrogen chloride and to form a conjugated polyene [138].
Acids, such as HCl, catalyse the β-elimination and the decomposition is auto catalytic and very rapid. At higher temperature, the polyene undergoes further cross-linking, cyclization and aromatization processes to produce a complex pattern of hydrocarbons with aromatic materials predominating.
If the aromatic hydrocarbons only contain a few rings, they may generate soot particles and toxic smoke, if they are large and well cross-linked the residue may form a stable protective char layer [139]. The concomitant char formation and HCl production give to this polymer good flame resistance properties. HCl is a reasonably efficient free radical trap, it removes high energy H· and HO· radicals from the flame zone quenching the fire, but it is also corrosive and toxic.

Polytetrafluoroethylene

The polytetrafluoroethylene thermodecomposition consist on end chain scission. Because of the high strength of the carbon-fluorine bond, PTFE is not easy to cleave and the reaction occurs solely by breaking of carbon-carbon bonds. The degradation products are mainly the monomer tetrafluoroethylene (C_2F_4) and difluorocarbene (CF_2), other products are generated by the reactions between these two molecules, and are hexafluoropropene (C_3F_6), perfluorocyclobutane (C_4F_8) [140]. Under certain conditions, carbonyl fluoride (COF_2) can evolve during the combustion of this polymer and hydrolyses to produce toxic carbon monoxide and hydrogen fluoride [141].

Polymethylmetacrylate

Polymethylmetacrylate thermal decomposition gives principally the formation of the monomer, methylmethacrylate. Low molecular weight polymer decomposes by end chain scission, while polymer with higher molecular weight decomposes by end chain scissions and random chain scission [142].

Both mechanisms involve radical scissions with the formation of the monomer units. This process is also known as unzipping depolymerisation.

Polyacrylonitrile

Polyacrylonitrile thermal decomposition is strictly correlated to the process condition. This polymer is well known to be used for carbon fibre production through several thermal processes under controlled condition [143]. Although these thermal processes can lead to carbon fibres, that is a material with good flame resistance properties, in a non controlled thermal process like a fire scenario this material burns easily. The decomposition processes involved are mainly cyclisation and chain scission leading to the volatiles formation, moreover chain stripping decomposition resulting in the release of hydrogen cyanide [144]. These processes generate also a residue that at higher temperature decomposes by random chain scission and rearrangements producing ethyne, ethane, benzene and higher aromatics.

1.8.4.2 Thermosets thermo-decomposition

Epoxy resins

Epoxy resins are one of the most important thermosetting polymers for high-performance composites. Their thermal stability as well as flammability depends on the structure of the monomer, the structure of the curing agent and the cross-linking density. In general, the thermal stability increases with increasing cross-linking density for the analogous resins. The thermal degradation starts with the dehydration of the secondary alcohols in the glycidyl group leading to an allylic group formation. The C-O bond in the allylic group is thermally less stable than the original C-O, and at higher temperature chain scission occurs at that position generating both aliphatic and aromatic segments. The aliphatic segments break down into acetone, allyl alcohol, methane, ethylene, acetaldehyde and starting curing molecules. The aromatic segments may release phenol and generate char trough cross-linking reactions and structure rearrangements [145].

Phenolic Resins

Phenolic resins are polymers prepared by treating phenol with formaldehyde. The resulting materials are fully cross-linked thermosetting polymers. The characteristic chemical structure imparts high chemical resistance and thermal stability but low toughness and mechanical resistance. Depending on their structure, phenolic resins can self-extinguish quickly or burn very slowly when they are ignited in air. For this reason, they are considered materials with low flammability due to their high temperature resistance and high char yielding.

The thermal degradation of phenolic resins is characterised by a complex mechanism with at least two different processes that lead to the formation of a stable and resistant char structure. The first process involves the water release by phenols condensation leading to biphenyl ether cross-links. Subsequently structure rearrangements, radical recombination and ring condensation lead to char formation and decomposition gases such as carbon monoxide, carbon dioxide, acetone, and low molecular weight hydrocarbons [146]. At higher temperature, aromatic fragments like phenol, cresol, methylenebisphenol, and dimethylphenol volatilize [147].

Polyurethanes

Polyurethanes are a class of polymers widely used for rigid or flexible foams, elastomers and as thermoplastic materials. They are obtained by the polymerization of diisocyanates and diols resulting in urethane groups between these units. The use of isocyanates or polyols with more than two functional groups or a curing agent, leads to a complex cross-linked structure. The thermal decomposition of polyurethanes depends on the polyol and isocyanate chemistry. In general, the thermal decomposition starts with the polymer fragmentation leading to the formation of isocyanates and alcohols. Subsequently, these oligomers decompose generating primary amines, olefins and carbon dioxide, alongside the urethane groups can rearrange in secondary ammine releasing carbon dioxide.

At higher temperature, these molecules brake down by radical scissions with the formation of various gaseous species, such as carbon dioxide, water, amines, aldehydes, ethers, radical aliphatic fragments, acetonitrile and hydrogen cyanide [148].

All the degradation processes described before lead to the formation of volatiles fragments, light molecules and gasses. These compounds leave the condensed phase and mix with oxygen in the gas phase. Then, radical reaction processes between this radical fragments and oxygen generate a complex exothermic chain reaction visible as flame. This process is also known as oxidative degradation.

1.8.5 Oxidative degradation

The oxidative degradation, also known as autoxidation, involves subsequent radical rearrangement, propagation, fragmentations and combination reactions, with both the original polymer and decomposition products. These complex reactions are reported in the Figure 20, this pathway is well known as Bolland and Gee reaction scheme [149] [150] [151].

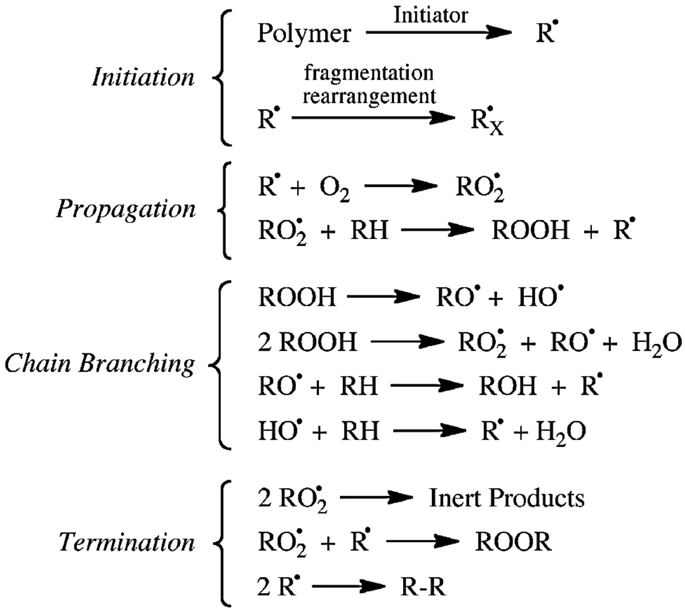


Figure 20: Oxidative degradation reactions scheme by Bolland and Gee, adapted from Gryn'ova at al. [152].

The Bolland and Gee scheme has been found to be a useful model for many aliphatic polymers such as aliphatic polyamides, polyesters and certain vinyl polymers. In the first reaction, the heat is the initiator for the thermal decomposition process, the radical formation can be also the result of photo-degradation or depolymerisation by trace of catalyst and impurities. This reaction scheme is autocatalytic, the radical propagation mechanism generates new radical species that are ready to react with oxygen molecules increasing the heat generated in the gas phase, and this heat is commonly visible as flame.

1.9 Flame retardancy

Flame retardancy means that "something has been done to a material so that when exposed to a flame, either the material will retard the growth and propagation of that flame, or it will retard (slow) the growth and propagation of any flames that may come from the material once it has been ignited" [153]. In other words fire retardant means that the material will be harder to burn and not that it will not burn.

A flame-retardant material may self-extinguish after being ignited if the external flame is removed, or in other cases, just burn slowly once ignited. The requirements for a flame-retardant material like self-extinguishment or slow burn rate are dictated by the specific regulatory test under which the material is rated and sold, which in turn is governed by fire risk scenarios. A fire risk scenario is a risk assessment study based on the material fire behaviour in a particular situation. This study involves the potential of the material to become ignited and its contribute to the fire growth. The results leads to determine how a material will support in negative or positive way the fire growth.

1.10 Strategies for fire resistance

The strategies for increasing the flame resistance properties are focused on the fire triangle. Indeed, limiting or isolating one or more constituents of the fire triangle is essential to obtain less favourable condition for the thermo-oxidation process and to retard the combustion.

There are several ways to limiting the contribution to the combustion of the fire triangle constituents, both chemical and physical.

The chemical actions can occur in the gas phase or in the condensed phase:

- in the gas phase the radical reactions can be quenched using particular species that are able to trap the radicals, shutting down the flame and reducing the thermo-oxidative process below a critical value. Generally, this process is carried on with halogenated additives, these molecules reacting in the gas phase interfere with the combustion, leading to the formation of toxic and irritating species not completely burned like CO, halogenated dioxin and acids;
- the action in the solid phase is obtained with additives able to react with the polymer breaking down its chain. This causes a decrease in the polymer viscosity during the exposure to the fire, and the material can flow away from the flame easily. Is important that the material drips without the production of flammable drops.

  Other additives able to act in the solid phase are the char promoters. These additives react with the polymer generating double bonds and aromatic rings causing the formation of a carbonaceous layer on the surface of the material.

The physical actions consist on:

- cooling the material during the degradation using species that degrade trough endothermic reactions;
- forming a protective layer on the material surface in order to limits or isolating the fuel from heat and oxygen;
- diluting the gas phase with non-combustible species like H_2O and CO_2, this species are generated by specific chemicals during the material decomposition. They act retarding the combustion by diluting oxygen and the combustible degradation product in the gas phase.

The strategies described above are feasible using specific molecules or compounds known as flame retardants.

1.11 Flame retardant

Flame retarded materials are generally obtained adding particular molecules called flame retardants into the starting material. These additives are generally mixed and dispersed inside polymers matrices or added as protective layer like prints in wood or fibres.

Flame retardants “FR or FRs” are various and can act in different way, alone or in synergy each other. In polymer based materials, a flame retardant is any additive that allows a polymer to retard a flame, or any polymer that shows the ability to slow fire growth when ignited. Non-combustible or ignition resistant are different terms respect to flame retarded, and must not be confused. A material that is non-combustible or ignition resistant either cannot be combusted, so cannot be ignited with a particular heat source and the thermo-oxidative decomposition cannot occur. Instead, a flame retarded material can show non-combustibility or ignition resistance under certain burning test condition and burn easily under different set of test condition, for instance, cone calorimeter test with different heat source.

1.11.1 Halogen flame retardants

Halogen-containing fire-retardant chemicals are one of the largest groups of additives in the plastics industry.

They are generally used as additives, but in suitable cases, halogenated molecules are introduced into the polymer chain by copolymerization or blending [154].

Halogen flame retardants may function in either the vapour and the condensed phase. As thermally reactive species, they can react with the polymeric matrix to produce aromatization, and they can act in the gas phase as radical scavenger.

The action of the fire retardant depends on the structure of the additive and on the polymer chemistry. The degradation temperature of the polymer is related to its structure, while the decomposition temperature of the halogen-containing fire-retardant additive is related to the energy of the carbon-halogen bond. The order of stability for the halogen compounds is F > Cl > Br > I. Iodine compounds are not sufficiently stable for commercial applications, whereas fluorine compounds are too stable, so not useful and no versatile for polymers.

Bromine or chlorine compounds are the most used, the choice is dependent on the type of polymer for which it will be used. In particular, the suitable halogenated flame retardant is selected to match the decomposition temperature of the polymer. Moreover, it must have a thermal stability suitable to the polymer processing temperatures.

Bromine compounds are more cost-effective but are more susceptible to photochemical degradation than chlorine compounds.

Action in the condensed phase:

The condensed phase acting flame retardants are halogenated paraffin or polychlorinated biphenyls.

The action mechanism involves various step and the C-X bond will be the first to break, generating a halogen radical and an organic radical:

$$\text{R-X} \longrightarrow \text{R}\cdot + \text{X}\cdot$$

The halogen radical, X·, can abstract a hydrogen atom from any molecule to form HX specie:

$$\text{RH} + \text{X}\cdot \longrightarrow \text{HX} + \text{R}\cdot$$

In case of halogenated paraffin, the broken C-X bond has a vicinal hydrogen atom that gets abstracted by the radical halogen atoms, and a double bond is produced. In chlorinated paraffin, this mechanism is known as dehydrochlorination.

$$\text{-CH}_2\text{-CHX-} \longrightarrow \text{-CH}_2\text{-C}\cdot\text{H-} + \text{X}\cdot \longrightarrow \text{-CH=CH-} + \text{HX}$$

$$\text{CH}_2\text{-CHX-CH=CH-} \longrightarrow \text{-CH=CH-CH=CH-} + \text{HX}$$

The presence of the double bond and the HX make easier the subsequent cleavage of allylic C-X bonds [155]. These mechanisms involve the formation of a polyene that can generate cross-links within the polymer and the further aromatization process leads to a reduction of the volatiles species.

In polyhalogenated byphenils the mechanism involves only the abstraction of the polymer hydrogen atoms. The absence of a hydrogen atom in these halogenated biphenyls, as in decabromodiphenyloxide (DBDPO), prevents the formation of HBr from decomposition of the additive itself.

The radicals produced by the thermal decomposition of a halogenated fire retardant can interact with the melted polymer to form HX and polymeric macroradicals [156]. These macroradicals influence the polymers decomposition. Furthermore, the additive radical species can affects this process interfering with the further radical decomposition processes. The halogenated additives interferes in the polymers chemical decomposition pathways resulting in the reduction of volatiles, and in some cases less flammables volatiles are generated [157].

Action in the gas phase:

The action in the gas phase is the principal and most effective way of acting of the halogenated flame retardants. This consist on generating halogen radical species able to interrupt the radical chain mechanism during the thermo-oxidative process in the gas phase.

The mechanism involves various step:

Release of the halogen radical (X·, Cl· or Br·) from the flame-retardant R-X:

$$R\text{-}X \longrightarrow R\cdot + X\cdot$$

Formation of halogen acid HX:

$$RH + X\cdot \longrightarrow HX + R\cdot$$

Neutralization of energy-rich radicals:

$$XH + H\cdot \longrightarrow H_2 + X\cdot$$

$$XH + HO\cdot \longrightarrow H_2O + X\cdot$$

The H· and HO· species are the main species responsible to the autocatalytic thermo-oxidative process that occur in the flame.

The radical hydrogen atoms in the gas phase consume oxygen during the thermo-oxidative process, through the branching reactions [158]:

$$H\cdot + O_2 \longrightarrow HO\cdot + O$$

$$H_2 + O \longrightarrow HO\cdot + H\cdot$$

In parallel the hydroxyl radical species oxidize carbon monoxide trough the following reaction [159]:

$$HO\cdot + CO \longrightarrow CO_2 + H\cdot$$

Carbon dioxide and new hydrogen radical are the reaction products, hydrogen radical is ready to react with other oxygen molecules generating an autocatalytic process.

The branching reaction increases mainly the radical concentration in the gas phase, whereas the oxidation of carbon monoxides is highly exothermic and increase the temperature generating heat.

The halogenated flame retardant acts trapping the H· and HO· radicals reducing the overall rate of thermal oxidation process.

1.11.1.1 Chlorine based flame retardants

The most used chlorine based flame retardants are chlorinated paraffins and alicyclic chlorinated molecules.

Chlorinated paraffins are liquid or solid depending on their chlorine content that range between 40 to 75%, respectively.

They have low thermal stability. Indeed, at around 180°C they start to degrades, and are used in materials with low processing temperatures such as PVC, polyurethanes, polypropylene and polyethylene.

Alicyclic chlorinated known as Dechlorane Plus has a chlorine content about 65% and high thermal stability. Around 350°C it starts to melt and degrades.

Dechlorane Plus has been used since 1960s for application based on polyolefins and polyamides like polypropylene and nylon.

1.11.1.2 Brominates based flame retardants

The different degradations temperature of the plastic materials leaded to produce a wide range of brominated compound. Brominates based flame retardants are various and can be organized in different classes in base on their structure:

Tetrabromophthalic anhydride, that is used in polyesters, polyurethanes, and in polyvinylchloride, where can acts also as plasticizer if esterified with aliphatic alcohols.

Hexabromocyclododecane (HBCD) is used as flame retardant in expandable and extruded polystyrene foam in which is very effective at low concentrations.

Tetrabromobisphenol A (TBBA) is the most used flame retardant nowadays, it is mainly used in epoxy resins for printed circuit boards. It is generally cured with the epoxy resin in form of brominated epoxy oligomers, in order to allows high thermal stability and excellent electrical properties for circuit boards.
In form of brominated polycarbonate oligomers are suitable for polycarbonate and polybutylene terephthalate applications. In form of bis(2,3-dibromopropyl ether) is used in polypropylene application.

Polybrominated biphenyl ethers (PBDEs) like decabromobiphenyl ether with high thermal stability up to 300°C used in high-impact polystyrene, polypropylene and polyethylene.
*Octabromobiphenyl ethe*r with less thermal resistance is used in acrylonitrile butadiene styrene resins.

Tribromophenol is used as a reactive alcohol in unsaturated polyester applications, and as tribromophenyl allyl ether in polystyrene and in other thermoplastic applications. By reacting with ethylene dibromide, bis(tribromophenoxy) ethane is obtained, which is excellent flame retardant for ABS.

Dibromostyrene used as monomer in copolymers with styrene or in grafted copolymers with polypropylene. Can be used as brominated polystyrene homopolymer for blends or as brominated polystyrene with reactive end groups in order to increase the compatibility with polyamides and polyesters.

Brominated alcohols like tribromoneopentyl alcohol is a reactive flame retardant for polyurethanes. Its high solubility in urethanes allows reaction of the single hydroxyl functionality to form pendant urethane groups.
Dibromoneopentyl glycol is mainly used in thermoset polyester resins. This molecule is also suitable for use in rigid polyurethane because of its high bromine content and high reactivity.

1.11.1.3 Environmental concerns

The safety of brominated fire retardants is under scrutiny since 1985, when it was discovered that under certain conditions, pyrolysis of brominated diphenyl ethers could lead to the formation of brominated dioxins and furans. The possible production of toxic compound during a fire or during end life incineration has become an issue in Europe and actually most of the halogenated flame retardant are under REACH and RoHS investigation concerning their health and environmental risk assessments. Moreover, some brominated flame retardants were proved to have properties which cause them to persist bioaccumulating in the environment [160] [161] [162] [163].

Different brominated flame retardant are actually under investigation whereas the use of certain has already been limited. The European commission directive 2003/11/EC indicated that penta- and octa-bromodiphenyl ether compounds shall not be placed on the market or used as a substance or as a constituent of preparations in concentrations greater than 0.1% by mass. Additionally, items may not be placed on the market if they, or flame-retarded parts thereof, contain these compounds in concentrations higher than 0.1% by mass. Furthermore, since 1 July 2006, PBDEs (other than deca-BDE) and PBBs are banned in electrical and electronic applications according to the “RoHS” directive [164]. Deca-BDE is actually under investigation because its high persistence in the environment, moreover the investigation is focused on its neurotoxic effects and the possible formation of more toxic and accumulative degradation products.

1.11.2 Phosphorus based flame retardants

Phosphorus based flame retardants include red phosphorus, inorganic phosphates, and organophosphorus compounds.

1.11.2.1 Red phosphorus

Red phosphorus is suitable for polymers containing oxygen such as polyamides (PA), poly(ethylene terephthalate) (PET), poly-(butylene terephthalate) (PBT), or polycarbonate (PC), but can be used in polyolefins, ABS, high-impact polystyrene (HIPS), epoxy resins, as well.

It acts in the condensed phase during the polymer degradation. Reacting with oxygen, red phosphorus is oxidized into phosphoric acid or phosphoric anhydride. Upon heating, these compounds generate polyphosphoric acid, which catalyses the dehydration of organic

compounds promoting charring for a physical barrier formation. Moreover, it has proved to be active in the gas phase as radical trap [165] [166].
Red phosphorus can react with atmospheric moisture to form toxic phosphine gas and ignite easily in air. For these reasons, the commercial product is often stabilized and encapsulated, but handling and processing safety concerns, and its characteristic red colour, limit its use.

1.11.2.2 Inorganic phosphates

Inorganic phosphates are widely used as flame retardant additives for thermoset and thermoplastic. Moreover, they are used in intumescent systems for coatings and paints.
Ammonium phosphates and diammonium phosphate were widely used to impart flame resistance properties to a wide variety of cellulosic materials such as paper, cotton, and wood [167]. However, the formulations based on these salts are generally nondurable, due to their solubility in water and their easily migration outside of the material matrix.
Ammonium polyphosphate (APP) replaced these salts in a wide range of applications, because relatively insoluble in water and very versatile. Commercial products differ in crystalline forms, in molecular weights, and in phosphorus content, particle sizes, and solubility. Moreover, ammonium polyphosphate has very good thermal stability and can be used in high temperature applications.
The way of action is the same already described for red phosphorus. APP undergoes endothermic reactions during the material degradation generating phosphoric acid and related acids, these latter catalyse dehydration reactions promoting a protective char layer as physical barrier.

1.11.2.3 Organophosphorus

Organophosphorus additives work well in oxygen containing polymers such as polyesters, polyamides or polyurethanes [168], but poorly efficiently in hydrocarbon-based polymers. They act as charring promoters trough cross-linking reaction with the polymer matrix.
Aluminium diethyl phosphinate is one of the most used for thermosets and thermoplastics. During the material degradation, the phosphinate partly vaporises and partly decomposes to volatile diethyl phosphinic acid and an aluminium phosphate residue. It acts both in the condensed phase contributing to charring of the polymer matrix and thus protecting the substrate against heat and oxygen attack. In parallel it acts in the gas phase removing from

the combustion zone the high energy radicals H· and OH·, quenching the flame propagation [169].

Another interesting and well studied organophosphorus flame retardant, acting in both condensed and gas phase, is 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide known as DOPO and its derivates [170].

DOPO compounds are efficient flame retardant in epoxy resins as reactive and non-reactive system. DOPO flame retardant for polyester and polyamide fibres has also found commercial success. Recently P-N and P-O bonded DOPO derivatives have found application in polyurethane foams and engineering thermoplastic. On the other hand, the synthesis of DOPO and its derivate involve several reaction steps and the use of not environmental friendly molecules and reaction processes.

Triphenyl phosphine oxide, diphenyl phenyl phosphonate [171] and triphenyl phosphate [172] are very effective flame retardants for thermoplastic, in particular for polyethylene terephthalate, acting in the vapour phase. They volatilize quantitatively from the bulk and inhibits the flame reactions by radical trap mechanism.

1.11.3 Inorganics flame retardants

1.11.3.1 Hydrated minerals

The hydrate minerals act in both condensed and gas phase. The energy consumption during their endothermic decomposition with the characteristic release of water, resulting in dilution of the combustion gases and cooling of the polymer.

The most used are aluminium hydroxide and magnesium hydroxide. Their endothermic decomposition leads to the formation of their oxides releasing water molecules as shown below:

$$2\,Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

$$Mg(OH)_2 \rightarrow MgO + H_2O$$

The endothermic decomposition of aluminium hydroxide involves 298 kJ/mol. The release of water starts from 205°C diluting the combustible gases and leading to the reduction of heat release and smoke evolution. Aluminium hydroxide is principally used in thermoplastics materials such as polyolefins and polyvinyl chloride, used for wire and cable applications. These applications generally have to pass strict smoke evolution requirements, so high load levels up to 40 to 60 % are usually required.

This lead to meet difficulties to obtain good mechanical properties and good performance simultaneously.

Magnesium hydroxides has a higher decomposition enthalpy and decomposition temperature, 380 kJ/mol and 320°C respectively. This makes it more suitable for higher temperature thermoplastics. Combinations of aluminium hydroxide with magnesium hydroxide can be used to reduce heat release and smoke evolution over a range of temperatures. Due to their higher decomposition temperature and cost, magnesium hydroxide is generally used in thermoplastic and thermosetting resins that are processed above 200-225°C. Like aluminium hydroxide, the magnesium hydroxide loadings required are higher, usually between 50% and 70% [173] [174]. Nevertheless, these additives are more expensive since high purity and surface treatment are required in order to increase the dispersion and distribution into the polymers matrix.

Aluminium hydroxide and magnesium hydroxide are not suitable to be used in thermoplastic polyester, as they catalyse their decomposition and depolymerisation reactions.

1.11.3.2 Antimony trioxide

Antimony trioxide is a compound used is synergy with most halogenated compounds, its presence increases the efficiency of the halogenated compounds. This allows to achieve equivalent flame resistance performance with lower halogen compounds content, compared to using the halogenated compound on its own. Antimony oxide is nonvolatile, but reacting with the halogenated compounds in the condensed phase where volatiles antimony oxyhalide (SbOX) and antimony trihalide (SbX_3) are formed.

$$Sb_2O_3 + 2HX \rightarrow 2SbOX + H_2O \quad 250\,°C$$

$$5SbOX \rightarrow Sb_4O_5X_2 + SbX_3 \quad 245\text{-}280°C$$

$$4Sb_4O_5X_2 \rightarrow 5Sb_3O_4X + SbX_3 \quad 410\text{-}475°C$$

$$3Sb_3O_4X \rightarrow 4Sb_2O_3 + SbX_3 \quad 475\text{-}565°C$$

Figure 21: Antimony trioxides - halogen synergism reactions.

This process facilitate the transfer of the halogen and antimony into the gas phase where they function as radical scavengers [175].

The Antimony trioxides interaction with the halogen compounds involves different reaction at temperature range from 250 to 600°C. This lead to a continuous stream of radical scavengers in the gas phase quenching the flame.

It is used for thermoplastic applications based on polyvinyl chloride and polyethylene, but is not suitable for polycarbonates and polyesters where acts as a depolymerizing catalyst decreasing the polymer molecular weight.

Antimony trioxides has suspected carcinogenic potential for humans.

1.11.3.4 Borates

The most efficient and multifunctional borate containing flame retardants are zinc borate compounds $xZnO \bullet yB_2O_3 \bullet zH_2O$.

These compounds varying in zinc-borate ratio and in water content (Figure 22). Different ratio and different water content influence their thermal stabilities and a range of different compounds with different degradation temperature make them very versatile for a wide group of polymers.

$2ZnO \cdot 3\,B_2O_3 \cdot 3.5H_2O$	Firebrake ZB	290°C
$2ZnO \cdot 3\,B_2O_3$	Firebrake 500	>500°C
$4ZnO \cdot B_2O_3 \cdot H_2O$	Firebrake 415	>415°C
$4ZnO \cdot 6B_2O_3 \cdot 7H_2O$	ZB-467	170°C
$2ZnO \cdot 2B_2O_3 \cdot 3H_2O$	ZB-223	200°C

Figure 22: Different commercial grades of zinc borate and their degradation points.

Zinc borate is a real multifunctional flame retardant [176], it is an anti-dripping and char-promoting agent; it is a smoke and afterglow suppressant. In electrical insulator plastics, it suppresses arcing and tracking.

It can act alone or in synergy in both halogen-based and halogen-free systems. It can replace antimony trioxide in halogen-containing systems, catalysing the release of halogens by forming zinc halides and zinc oxyhalides, but usually are used together. It is also used in synergy with aluminium hydroxide, and in general it catalyses the formation of char creating a protective layer of glass.

In halogen-free system, zinc borate can be used together with aluminium hydroxide, magnesium hydroxide, red phosphorus, ammonium polyphosphate, also in intumescent systems. During the material combustion, a layer of borate ceramics is formed and protects the underlying materials. Borosilicate glass can be formed at the combustion temperatures in presence of silica.

Zinc borate is used as a flame retardant in a wide range of plastics such as polyvinyl chloride [177], polyolefins [178], polyamides [179], epoxy resins [180], polyesters, thermoplastic elastomers, rubbers, cellulose fibres and textiles. It is also used in intumescent paints, adhesives, and pigments [181].

1.11.4 Intumescence

Intumescence is a special case of flame retardant action in the condensed phase [182]. Intumescent systems act at the early stage of the polymer combustion interrupting the evolution of gaseous fuels through a combination of charring and foaming at the surface of the burning polymer. This resulting foamed cellular charred layer acts as a physical barrier, protects the underlying material from the action of the heat flux or flame, inhibiting heat and oxygen transfer into the undecomposed bulk, and slows down diffusion into the gas phase of the fuel formed.

This system is usually composed of three components: an acid source, a carbonization agent, and a blowing agent. The acid source in general, is an acid or a precursor for catalytic acidic species such as ammonium salts or phosphates. Carbonization agents are mainly hydroxyl-containing compounds, such as pentaerythritol and starch . Blowing agents are compounds that can produce gases on heating, in the temperature range corresponding to the development of the intumescence process. Melamine, urea, and urea–formaldehyde resins are typical blowing agents.

Various acid sources molecules can be used:

- Inorganic acid such as phosphoric acid, sulfuric acid and boric acid.
- Ammonium salts such as ammonium phosphates, ammonium polyphosphates, ammonium borates, ammonium polyborates, ammonium sulfates and halides.
- Phosphates of amine or amide, like melamine phosphate, reaction products of urea or guanidyl urea with phosphoric acids, and reaction product of ammonia with P_2O_5.
- Organophosphorus compounds such as tricresyl phosphate, alkyl phosphates and haloalkyl phosphates.

Carbonizing agents are different and can be small molecules or polymers:

- Molecules rich in hydroxyl groups such as mono-, bi-, tri-pentaerythritol, sorbitol, mannitol, dextrins, cyclodextrins, methylol melamine.
- Polymers rich in hydroxyl groups like starch and cellulose.
- Char former polymers such as polyamides 6, polyurethanes, polycarbonates, phenol-formaldehyde resins and chlorinated paraffins.

The most common blowing agents are urea, urea-formaldehyde resins, dicyandiamide and melamine.

Other compounds can be used in synergy with the intumescent system like inorganic agents such as clays, zinc borates, zeolites and metal oxides. These inorganics compounds concentrates in the char structure increasing its stability and efficiency during the combustion.

The intumescent system synergy action involves the dehydratation and aromatization reaction between the acid source and the carbonizing agent or the polymer. In the same range of temperature, the blowing agent vaporizes and decomposes to noncombustible gases. The acid source can act in different way simultaneously: it can catalyse the aromatization reaction, it can cross-link with the aromatics species improving the char stability, and it can act in the gas phase as diluent or radical trapping [183].

The carbonizing agents is not necessary when the treated material has an intrinsic charring behaviour, as for example most of polyamides, polyurethanes and carbohydrate polymers like cellulose or starch. In contrary to char former polymers, the presence of a carbonizing agent is required for polyolefin. Polypropylene is the most studied with intumescent additive system in order to replace halogen-containing flame retardant. Intumescent flame retardant formulations for polypropylene are: ammonium polyphosphate, melamine and pentaerythritol [184]; ammonium polyphosphate, melamine phosphate and pentaerythritol [185] in addition with a charring polymer [186] or with an inorganic agent [187].

High loading content of intumescent flame retardants leads to a decrease in the mechanical properties of the polymer, indeed conventional intumescent systems show efficiency only from 20 wt% loading in polypropylene. Moreover, acid sources and charring agents are globally hydrophilic chemicals and have problems such as moisture sensitivity and poor compatibility in polymer matrix, in particularly in polyolefins, where they can migrate losing their efficiency . These intumescent systems can be very active in the polyesters due to the presence of hydroxyl groups, for this reasons the polymer and additives degradation may occur during the materials processing, so their degradation during mixing can results in a further decrease in the mechanical properties of the materials.

The wide variety of chemicals that can be used as acid, carbonizing or blowing agent, allows tailor-made intumescent systems able to be very efficient for a large group of polymers to be developed. This implies that intumescent flame retardant system are the best candidates to replace halogens containing flame retardant.

1.12 Bench scale fire tests

This section describes the common fire tests used for evaluating the fire resistance properties of flame retarded materials. Moreover, these techniques are used for investigate the resistance to combustion of the materials prepared during this research project.

Bench scale tests are used to characterize the ignition and combustion behaviour of materials under different exposure conditions that are representative of the growing stage of a fire.

1.12.1 Small heat source ignition tests

1.12.1.1 Limiting oxygen index

The Limiting Oxygen Index (LOI) is the minimum percentage of oxygen in an inert gas mixture that support the combustion of the sample.

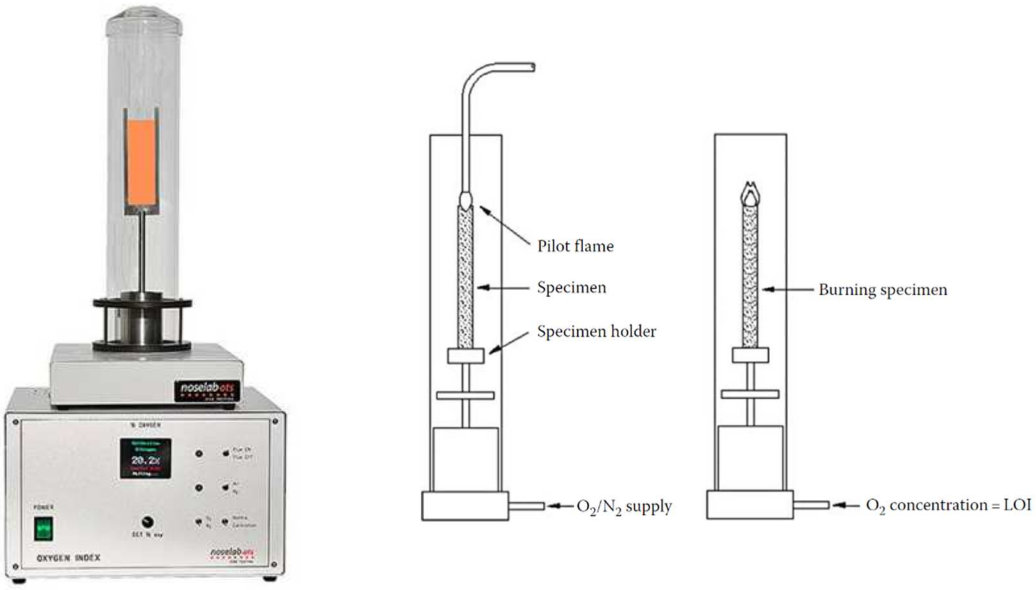


Figure 23: Limiting oxygen index apparatus.

The LOI is measured by placing the samples in a flow of oxygen/nitrogen gas and increasing the concentration of oxygen until the sample will support combustion in a candle like manner. The flame is applied with a burner in the top surface of the sample and the lowest oxygen concentration that maintain the combustion within certain limits according to ISO 4589-2 or ASTM D2863 is the value used as the index. Usually samples that achieve LOI values higher than 27% are considered self-extinguishes in case of fire in air.

1.12.1.2 UL94

Underwriters Laboratory developed the most commonly used test method to characterize polymer flammability This method is well known as UL 94 standard, it is the “20-mm Vertical Burning Test; V-0, V-1, or V-2.” The method is described also in ASTM D 3801 and IEC 60695-11-10. A schematic representation of the test setup is shown in Figure 24.

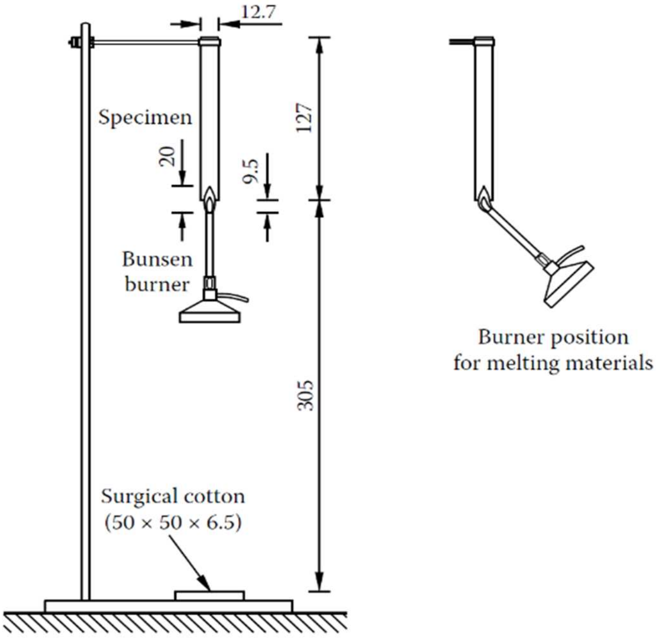


Figure 24: Schematic representation of UL94 test.

The test is carried out by applying the flame at the bottom edge of the specimen for 10 seconds, then the flame is removed to a distance of at least 150 mm. Upon flame removal, the specimen is observed for flaming and its duration time recorded. As soon as the flame ceases, the burner flame is reapplied for an additional 10 seconds, then removed again. The flaming duration, and the glowing after the second flame application is recorded. In addition, the ignition of the cotton piece placed beneath the specimen by dripping flamed particles from the test specimen is recorded.

The material rating V-0, V-1, V-2 requirements are reported in the Table 2, if the V-2 classification is not reached the material is considered “no rating”.

Table 2: Criteria for rating materials in UL94 test in vertical position.

Criteria conditions	V-0	V-1	V-2
Afterflame time for each individual specimen t_1 or t_2	≤10s	≤30s	≤30s
Total afterflame time for any condition set (t_1 plus t_2 for the 5 specimens)	≤50s	≤250s	≤250s
Afterflame plus afterglow time for each individual specimen after the second flame application (t_2+t_3)	≤30s	≤60s	≤60s
Afterflame or afterglow of any specimen up to the holding clamp	No	No	No
Cotton indicator ignited by flaming particles or drops	No	No	Yes

1.12.1.3 Glow wire ignition test

Glow wire ignition test is performed by heating a metal wire to a pre-determined temperature (glow wire element). When the setting temperature is reached and a stable reading is attained, the element is pressed on the sample surface under a pre-set force of 1N for 30 seconds by using a specific apparatus (Figure 25). The ignition, duration of flame and flame height are recorded. In the case of dripping material igniting the tissue paper placed beneath the specimen, this event is also recorded in accordance to IEC 60695-2-12/12/13. Glow wire testing can be performed on both end products and raw material test plates with different thickness, usually from 1 to 3 mm.

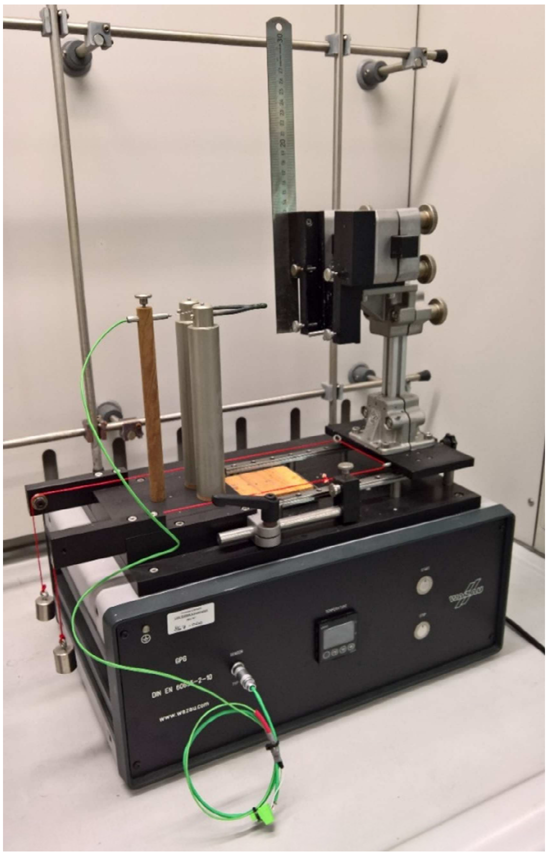


Figure 25: Glow wire apparatus.

GWT (IEC 60695-2-11) is used when glow wire testing is performed on an end product. It is expressed as the temperature at which the sample does not ignite or self-extinguishes within 30 seconds after removal of the heated element. In addition, the ignition of tissue paper produced by flamed drips does not occur.

GWFI means Glow Wire Flammability Index (IEC 60695-2-12) and is related to the raw material used in the end product. This index is determined by conducting the glow wire test on a test plate of a raw material of a given thickness. The Glow Wire Flammability Index (GWFI) is the highest temperature at which the material does not ignite or self-extinguishes within 30 seconds after removal of the heated element.

GWIT means Glow Wire Ignition Temperature (IEC 60695-2-13). This temperature is determined by testing the raw material used in the end product by conducting the glow wire test on a test plate of a given thickness. The GWIT is the temperature 25 K higher than the maximum test temperature at which sustained and continuous flaming combustion does not occur for a time longer than 5 seconds for any single flame event. These tests are at the base of electric and electronic materials applications and stringent requirements are needed for connections in attended and unattended appliances carrying different currents. As example, in Figure 26 is reported the glow wire requirements for connections in unattended appliances.

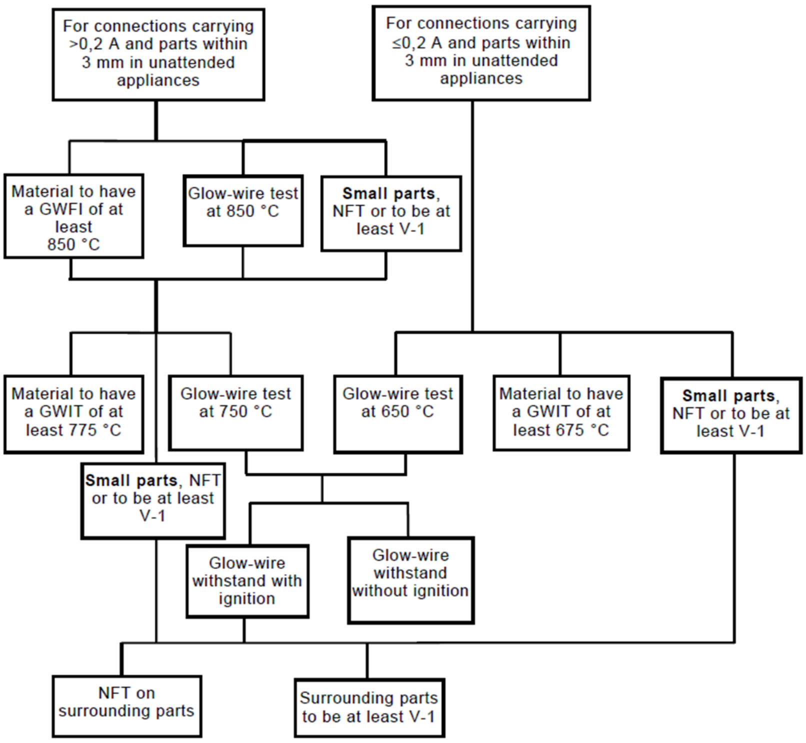


Figure 26: Flow chart with glow wire requirements for connections in unattended appliances.

1.12.1.4 Oxygen consumption cone calorimeter

Cone calorimeter test is one of the main test used worldwide to study the flame resistance properties of materials in different case of fire scenario. It consists on applying a calibrated heat flux on the material surface. A glow, cone-shaped metal coil is used as radiant heat flow source. In this way, the material is forced to degrade and if a combustible gas mixture is generated, a high voltage sparkler igniter ignites the mixture and burning occurs.

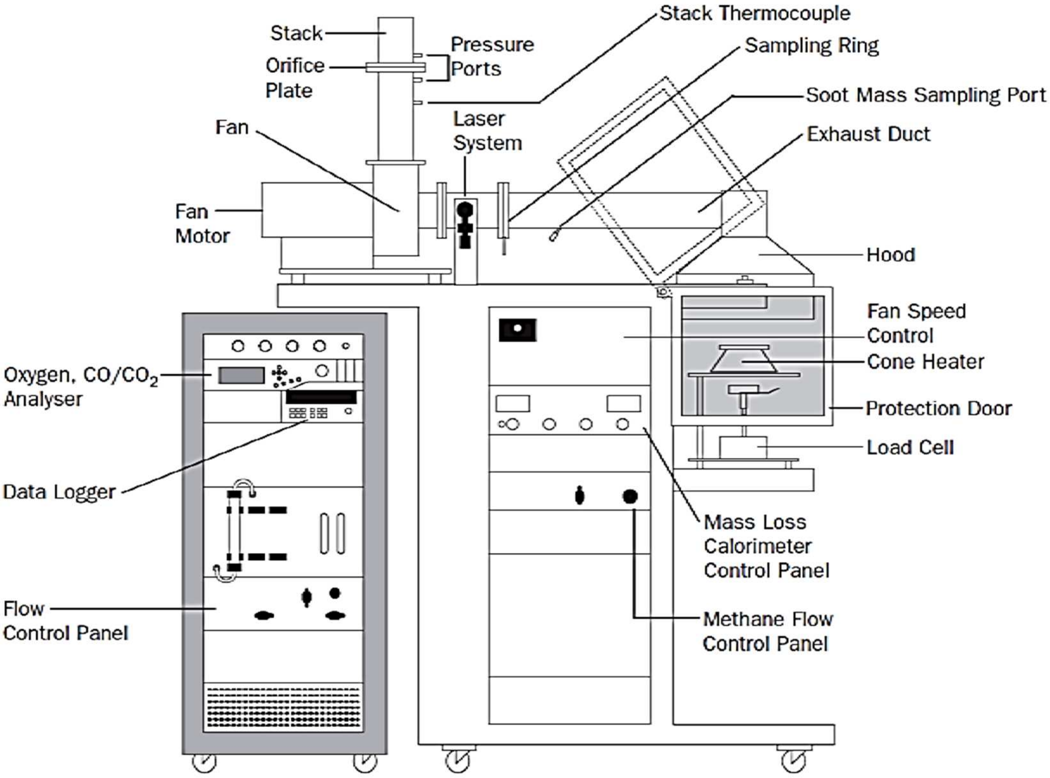


Figure 27: Oxygen consumption cone calorimeter apparatus.

The apparatus (Figure 27) simultaneously records the weight loss of the specimen, the smoke production and the oxygen depletion during the combustion. Moreover, the gas analyser detects the carbon monoxide and carbon dioxide produced during the combustion. The instrument converts the oxygen depletion in energy released as heat release rate (HRR) during the combustion. The characteristic result is reported on a HRR curve as a function of time. From such a curve, it is possible to obtain specific values that are essential to understand and to compare the materials flame resistance properties, such as time to sustain ignition (t_{ig}), peak of heat release rate (PHRR), time to peak of heat release rate, total heat release (THR), etc. ISO 5660 regulates this technique and square specimen (100x100 mm) with different thickness (1-50 mm) can be tested in horizontal and vertical position under a wide range of radiant heat flux (10-100 kWm^{-2}).

2 Aim

The aim of my PhD research was to improve the flame resistance properties of polylactic acid (PLA), which is a bio-based and biodegradable thermoplastic semi-crystalline polymer. PLA is actually one of the best candidate as alternative to polymers derived from fossil fuel. PLA has very poor flame resistance properties and burns in air, this lack limits the polymer application in automotive, electric and electronic fields. Intumescence has been selected as the best strategy to improve flame resistance properties using not toxic and environmentally friendly additives, in order to maintain the biodegradability of the material.

In addition, low loads of additives were tried in order to preserve the mechanical properties of PLA. Indeed, these compounds are suitable for many applications where good elastic modulus and relatively high yield stress are required. However, the brittleness due to a low elongation at break is a limit for many other applications.

3 Materials and methods

3.1 Polymer

Poly L-lactic acid L100M with high content of L isomer >99.7% (grade L100-M) was supplied by Sulzer.

3.2 Acid sources

Clariant Exolit® AP 423 ammonium polyphosphate and Exolit® OP 1240 aluminium diethyl phosphinate have been used as high temperature acid source.

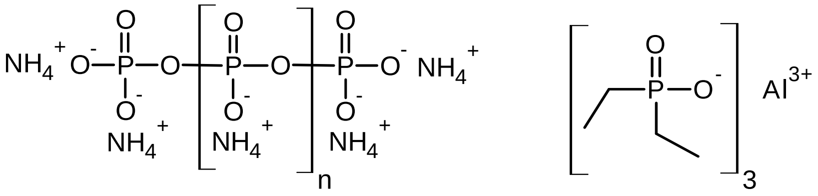


Figure 28: Ammonium polyphosphate and aluminium diethyl phosphinate structures.

3.3 Carbonizing agents

Starch, cellulose, sorbitol, glycerol phosphate, coffee grounds and Kraft lignin have been used as bio-based and biodegradable carbonizing agents.

Starch from potato, sorbitol and glycerol phosphate disodium salt were purchased from Sigma Aldrich. Coffee grounds waste were collected from the faculty coffee bar (from Serenissima Ristorazione), they were washed with water and hexane in a Soxlhet extractor, milled and sieved with 71 micron sieve. Kraft lignin was kindly provided from Oak Ridge National Laboratory-University of Tennessee Knoxville.

Cellulose was obtained from partial acid hydrolysis of commercial medical cotton fibres.

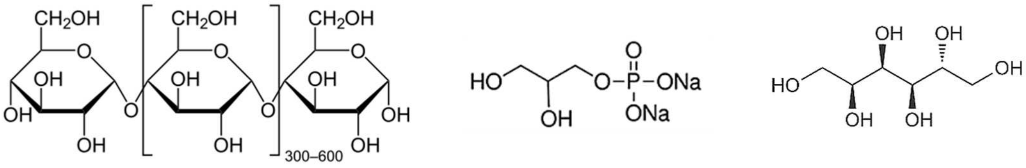


Figure 29: Starch, glycerol phosphate disodium salt and sorbitol structures.

3.4 Blowing agents

Thor AFLAMMIT® PMN 525 Melamine Cyanurate (Figure 30) has been used as the main blowing agent. In addiction, expandable graphite EG GHL PX 95 HT supplied by LUH and calcium carbonate from Sigma Aldrich were also tested.

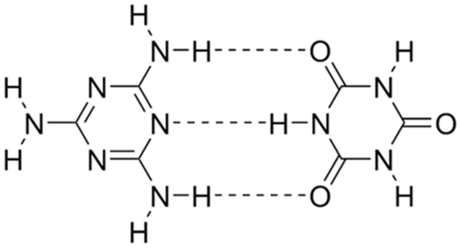


Figure 30: Structure of melamine cyanurate.

Melamine cyanurate starts to degrade at 350°C, it undergoes endothermic decomposition to melamine and cyanuric acid, acting as a heat sink in the condensed phase. The melamine sublimes working as blowing agent and as inert gas source diluting the oxygen and the fuel gases present at the point of combustion.

Expandable graphite (EG) consist in graphite intercalated with sulphate molecules. At high temperature, the intercalated molecules gasify, producing enough pressure to push adjacent graphite layers apart. In particular, the EG grade used starts to degrade at 230°C generating expanded flakes with a specific volume of 100 cm^3/g.

Calcium carbonate is stable up to 500°C, but in presence of acids, the carbonate group reacts with H^+ to form calcium bicarbonate that decompose to H_2O, carbon dioxides and calcium carbonate.

3.5 Inorganics

AFLAMMIT® PCI 511 zinc borate supplied by Thor has been used as vitrifying and char stabilizer agent ($2ZnO \times 3B_2O_3 \times 3.5H_2O$). Commercial talc and clay (Dellite72T from Laviosa, Italy) were used as char stabilizer.

3.6 Tests methods

3.6.1 Tensile test

The tensile tests were carried out according to ISO 527-2 using the universal testing machine INSTRON 5966, and a strain gauge extensometer with a gauge length of 80 mm in order to measure the strain between 0-0.5% where the elastic modulus was calculated (segment slope 0.05-0.25%). The strain rate used was 50 mm/min and the specimen protect mode was turned on in order to avoid the pretensions during the specimens clamping. The test was performed at 22-23°C and 35-45 % relative humidity. For each compounds the results were obtained from the average of five specimens.

3.6.2 Flame tests and ignition test

LOI

Limiting oxygen index were determined using a Noselab ATS Oxygen Index according to BS EN ISO 4589-2. Pure nitrogen, moisture-free air and oxygen were used as calibration and testing gasses.

UL 94

UL 94 tests in vertical position were carried out according to IEC 60695-11-10 and using a bunsen flame calibrated following ASTM D 5207-03.

Glow wire test

Glow wire tests were accomplished using a WAZAU Glow wire testing device GPD DIN EN 60695-2-10. Compounds classified as “no rating” in UL94 test have not been tested.

Cone calorimeter test

Cone calorimeter tests were performed with a GOVMARK CC-2-X apparatus equipped with a gas analyser and gas sampling system for the quantitative analysis of oxygen, carbon dioxide and carbon monoxide. The apparatus was calibrated daily and all tests were performed according to ISO 5660.

3.6.3 Thermogravimetric analysis

TGA/FTIR

The infrared spectroscopy of the degradation gasses evolved from TGA analysis was performed with a Perkin Elmer Spectrum One using a gas cell connected to Perkin Elmer TGA4000 thermo-balance. Perkin Elmer transfer line TL 8000 was used to drive the evolved gases to the FTIR gas cell, both heated at 280°C.

TGA/GC-MS

The thermogravimetric analysis was performed with Mettler Toledo TGA/DSC 2 and the degradation product were collected by a gas station containing 250 μL vacuum chambers able to collect the degradation gasses during the thermogravimetric analysis. A transfer line heated at 300°C is used to interconnect the TGA with the gas station and with the GC-MS system. The thermogravimetric analysis is carried out using a temperature run of 20°C/min from 35°C to 500°C in air.

The mass spectroscopy analysis of degradation products was accomplished with Thermo scientific ISQ LT single quadrupole mass analyser and Trace 1300 gas chromatography station. Thermo TQ-SQC 15m x 0.25mm x 0.25µm was used as gas chromatography column. The method scans from 54-650 m/z with a start temperature of 40°C, held for 1 min, then in temperature ramp at 10°C/min until to 280°C and held for 5 minutes. Helium with 1.2 ml/min flow in splitless was used as carrier gas.

4 Research approach

Polylactic acid thermal decomposition occurs at 350-380°C, and the main mechanisms of decomposition involve different types of chain scission and fragmentation [188] [189]:

- Depolymerisation by backbiting or cyclization into lactide.
- Beta elimination with the acrylic acid formation.
- Transesterification and hydrolysis with the formation of oligomers and lactic acid.
- Radical fragmentations with the production of propionic acid, acetaldehyde, carbon monoxide and carbon dioxide.

Considering this complex reactions pathway, a range of different volatiles are generated as fuel. For this reason, acting in the condensed phase and in the gas phase as the same time is the best choice to improve flame resistance properties.

Halogenated compounds were been discarded because their degradation products can be very toxic, corrosive, also they contribute to ozone depletion. Hydrate minerals such as aluminium hydroxide was been discarded due to the high load required, this can lead almost certainly to the worsening of the PLA mechanical properties. Intumescent flame retardant systems take action in both condensed and gas phase, and this strategy was been the preferred route for retarding the combustion of the polylactic acid. In addition, the use of non-toxic, environmentally friendly and bio based compounds as acid source, carbonizing and blowing agent into the intumescent systems, was considered the best innovative and promising route to follow trying to produce a fully bio based and biodegradable material with good flame resistance properties.

4.1 Formulations

The additive compositions and loads were selected and formulated also considering recent results published on scientific literature. Intumescent systems based on ammonium polyphosphate (30 %) and starch (10 %) [190] or ammonium polyphosphate (10%) and β-cyclodextrin (10%) [191] work well as intumescent flame retardant systems for polylactic acid, indeed these compounds achieve V-0 classification in UL-94 test. However, the lack of data concerning the mechanical properties of these latter materials pushed to start with formulations containing lower amount of additives, in order to not significantly affect the mechanical properties of the polymer. The hydroxyl groups of the carbonizing agent can be very effective on the degradation of the polymer, they can react with the ester groups of the polymer leading to the cleavage of the polymer chains and causing reduction of the molecular weight of the polymer.

Different compounds were prepared without carbonizing agent trying to observe if PLLA could itself behave like carbonizing (Table 3). Ammonium polyphosphate AP 423 (8.5%) was used with different blowing agent (2%) such as melamine cyanurate, expandable graphite and calcium carbonate. Moreover, ammonium polyphosphate (8.5%) and melamine cyanurate (2%) were tested in presence of inorganic compounds (1%) such as clay, talc, and zinc borate trying to enhance the char formation.

Aluminium diethyl phosphinate OP1240 (8.5%) was tested with melamine cyanurate (2%) in presence of zinc borate (1%).

Different loads combinations of ammonium polyphosphate (4, 8.5%) and melamine cyanurate (0, 2%) were used in presence of carbonizing agent (2%) such as starch, sorbitol, coffee grounds, glycerol phosphate disodium salt and Kraft lignin respectively. In addiction, zinc borate (1%) was used trying to increase the char stability.

Aluminium diethyl phosphinate (8.5%) and melamine cyanurate (2%) were used with starch and sorbitol (2%), these OP containing compounds were also tested in presence of zinc borate (1%).

All materials were dried under vacuum in an oven at 4 mbar for 14 hours before be mixed and compounded.

Polylactic acid pellets and sorbitol were dried at 65°C. Glycerol phosphate disodium salt was dried at 150°C in order to eliminate the coordination water molecules due to its very high hydrophobicity. All other additives were dried at 110°C.

For each formulation, 2 kilograms of compound were prepared by dry mixing polymer pellets plus the additives in defined weight percentage. This amount was required to mould a sufficient number of specimens in order to perform all fire and mechanical tests.

Then, the polymer pellets and the additives powders were melt mixed into a co-rotative twin-screw extruder Coperion ZSK 18ML, simultaneously the extruded compounds wires were cooled down with cold water and pelletized.

Table 3: Compounds formulations.

Compound Name	Acid % $^{w}/_{w}$	Carbonizing % $^{w}/_{w}$	Blowing % $^{w}/_{w}$	Inorganic % $^{w}/_{w}$
PLLA	-	-	-	-
AP8M2	AP 8.5%	-	Melamine Cyan. 2%	-
AP8M2c	AP 8.5%		Melamine Cyan. 2%	Clay 1%
AP8M2t	AP 8.5%		Melamine Cyan. 2%	Talc 1%
AP8M2z	AP 8.5%		Melamine Cyan. 2%	Zinc Borate 1%
OP8M2z	OP 8.5%		Melamine Cyan. 2%	Zinc Borate 1%
AP8EG2	AP 8.5%		Exp. Graphite 2%	-
AP8CC2	AP 8.5%		Calcium Carb. 2%	-
St2AP4	AP 4%	Starch 2%	-	-
St2AP4M2	AP 4%		Melamine Cyan. 2%	-
St2AP8M2	AP 8.5%		Melamine Cyan. 2%	-
St2AP8M2z	AP 8.5%		Melamine Cyan. 2%	Zinc Borate 1%
St2OP8M2	OP 8.5%		Melamine Cyan. 2%	-
St2OP8M2z	OP 8.5%		Melamine Cyan. 2%	Zinc Borate 1%
So2AP4	AP 4%	Sorbitol 2%	-	-
So2AP4M2	AP 4%		Melamine Cyan. 2%	-
So2AP8M2	AP 8.5%		Melamine Cyan. 2%	-
So2AP8M2z	AP 8.5%		Melamine Cyan. 2%	Zinc Borate 1%
So2OP8M2	OP 8.5%		Melamine Cyan. 2%	-
So2OP8M2z	OP 8.5%		Melamine Cyan. 2%	Zinc Borate 1%
Gp2AP4	AP 4%	Glycerol Phosphate 2%	-	-
Gp2AP8	AP 8.5%		-	-
Gp2AP4M2	AP 4%		Melamine Cyan. 2%	-
Gp2AP8M2	AP 8.5%		Melamine Cyan. 2%	-
Co2AP8	AP 8.5%	Coffee Grounds 2%	-	-
Co2AP4M2	AP 4%		Melamine Cyan. 2%	-
Co2AP8M2	AP 8.5%		Melamine Cyan. 2%	-
Co2AP8M2z	AP 8.5%		Melamine Cyan. 2%	Zinc Borate 1%
KL2AP4	AP 4%	Kraft Lignin 2%	-	-
KL2AP4M2	AP 4%		Melamine Cyan. 2%	-
KL2AP8M2	AP 8.5%		Melamine Cyan. 2%	-
KL2AP8M2z	AP 8.5%		Melamine Cyan. 2%	Zinc Borate 1%
Ce2AP8M2z	AP 8.5%	Cellulose 2%	Melamine Cyan. 2%	Zinc Borate 1%

(AP) ammonium polyphosphate, (OP) aluminium diethyl phosphinate, (M) melamine cyanurate, (c) clay, (t) talc, (z) zinc borate, (St) starch, (So) sorbitol, (Gp) glycerol phosphate, (Co) coffee grounds, (KL) Kraft lignin, (Ce) cellulose

Subsequently, all pelletized materials were dried under vacuum at 70°C for 14 hours, then the dried compounds were injection moulded using an injection moulding machine Negri-Bossi VE 70 240. Different shape specimens were moulded:

- Dog-bone shape specimen according to ISO 294-1 and ISO 527-2(Figure 31).
- Square plates with thickness of 2 mm according to ISO 294-3 (Figure 32).

- Square plates with thickness of 3 mm according to ISO 294-5 (Figure 33).

Dog-bone shaped specimens were used for tensile test following the ISO 527-1.

The square plates with thickness of 2 mm were used for Glow wire test IEC/EN 60695-2-12 (GWFI) and IEC/EN 60695-2-13 (GWIT).

The square plates 3 mm thick were used for cone calorimeter tests according to ISO 5660.

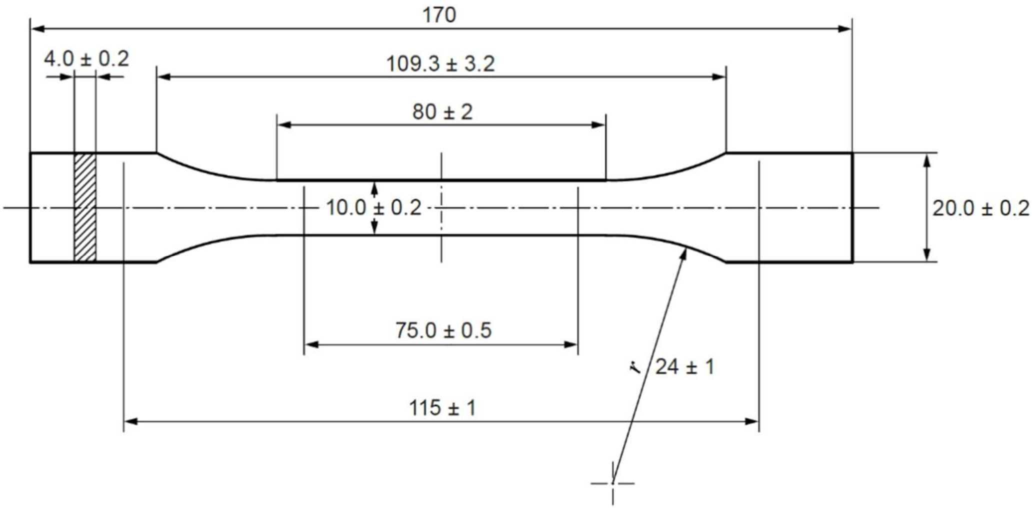


Figure 31: Dog-bone shape specimen dimensions in mm according to ISO 527-2.

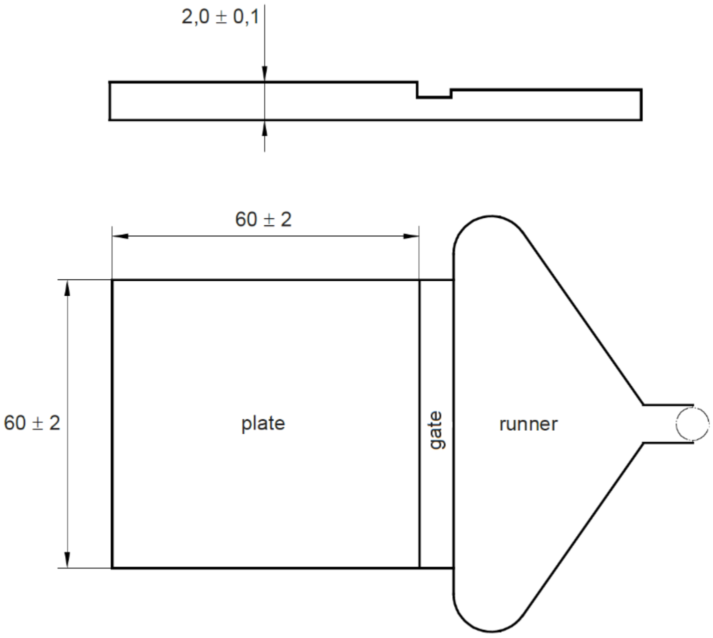


Figure 32: Square plate specimen dimensions in mm according to ISO 294-3.

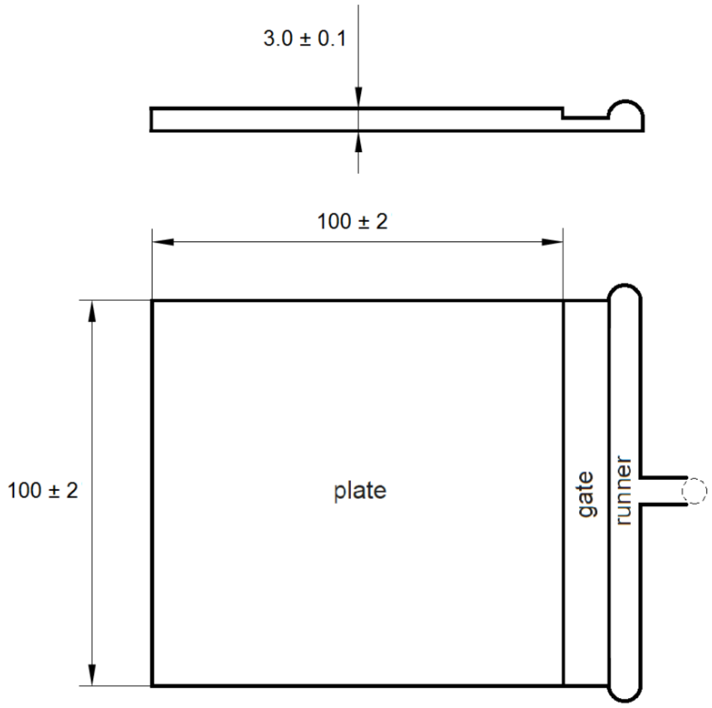


Figure 33: Square plate specimen dimensions in mm according to ISO 294-5.

Others 3 mm thick square plates were cut with a bandsaw into appropriate specimens (Figure 34) in order to perform limiting oxygen index test and UL 94 vertical test, following ISO 4589-2 and IEC 60695-11-10 respectively.

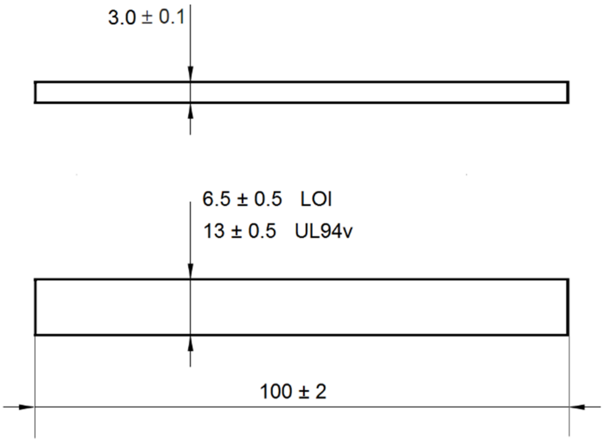


Figure 34: LOI and UL94v specimen dimensions in mm.

5 Results and discussion

5.1 Tensile tests

The tensile test results are reported in the Table 4. The average curves of tensile tests, the elastic modulus, the ultimate stress and elongation at break of all compounds classes are displayed in comparison in the Figure 35-Figure 46. The various compounds are grouped according to the type of carbonizing agent used, in order to investigate the effect of different amount of additives over the mechanical properties of the materials respect the pure PLA as a control.

Table 4: Tensile test results

Compound Name	Elastic modulus		Ultimate Stress		Elongation at Break	
	GPa	σ	MPa	σ	%	σ
PLLA	3.67	0.03	67.5	3.4	3.6	0.7
AP8M2	3.73	0.08	49.3	0.4	17.3	5.3
AP8M2c	3.97	0.09	50.3	0.5	25.2	10.6
AP8M2t	3.76	0.11	57.6	1.3	9.7	2.8
AP8M2z	3.60	0.08	45.7	7.5	2.9	1.5
OP8M2z	3.88	0.15	29.4	3.2	1.1	0.2
AP8EG2	3.77	0.06	54.9	0.5	8.9	0.7
AP8CC2	3.78	0.05	48.2	0.3	4.4	0.8
St2AP4	3.81	0.04	57.1	0.3	6.1	1.1
St2AP4M2	3.85	0.04	55.9	1.0	3.6	0.2
St2AP8M2	4.01	0.17	43.2	5.3	1.9	0.5
St2AP8M2z	3.89	0.10	51.4	0.7	9.9	2.8
St2OP8M2	4.43	0.20	45.6	1.3	1.9	0.1
St2OP8M2z	4.31	0.09	26.9	1.6	0.8	0.1
So2AP4	3.45	0.13	37.9	7.2	1.7	0.5
So2AP4M2	3.61	0.05	49.8	5.7	2.7	0.5
So2AP8M2	3.49	0.13	51.2	1.0	2.8	0.1
So2AP8M2z	3.49	0.08	32.9	2.7	1.4	0.2
So2OP8M2	4.00	0.06	47.3	0.6	2.5	0.2
So2OP8M2z	4.01	0.13	40.5	1.3	1.6	0.1
Gp2AP4	3.76	0.05	51.6	2.0	2.1	0.1
Gp2AP8	3.76	0.09	39.5	8.1	1.6	0.5
Gp2AP8M2	3.59	0.10	43.9	5.5	2.1	0.4
Co2AP8	4.09	0.07	52.1	0.3	8.6	2.2
Co2AP4M2	3.91	0.06	57.5	0.7	3.3	0.2
Co2AP8M2	3.87	0.16	49.4	1.3	7.2	1.8
Co2AP8M2z	3.90	0.18	45.9	0.5	3.0	0.3
KL2AP4	3.90	0.05	56.7	0.6	4.0	0.6
KL2AP4M2	3.94	0.01	56.7	0.4	5.9	0.9
KL2AP8M2	4.20	0.03	53.2	0.6	6.2	0.6
KL2AP8M2z	4.22	0.04	52.9	0.2	5.9	0.4
Ce2AP8M2z	4.01	0.05	51.5	0.4	4.4	1.2

(AP) ammonium polyphosphate, (OP) aluminium diethyl phosphinate, (M) melamine cyanurate, (c) clay, (t) talc, (z) zinc borate, (St) starch, (So) sorbitol, (Gp) glycerol phosphate, (Co) coffee grounds, (KL) Kraft lignin, (Ce) cellulose

All carbonizing free compounds (Figure 35 and Figure 36) showed a decrease of ultimate stress compared to pure PLLA. The talc containing compound showed the higher value. For all carbonizing-free compounds except OP8M2z, the maximum stress matched the yielding stress. On the contrary, the OP8M2z didn't achieve the yielding point and it broke with an ultimate stress less than half respect to the control.

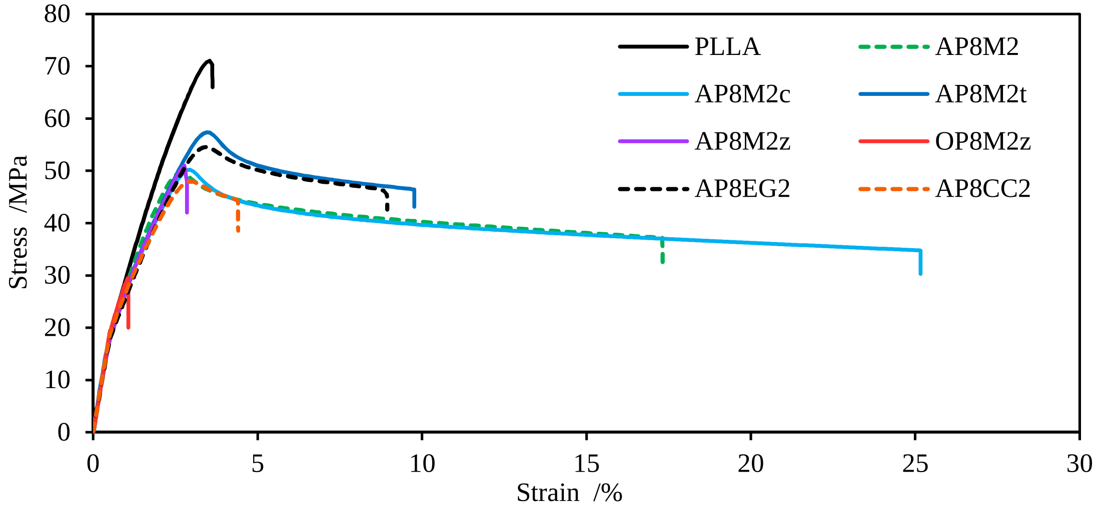


Figure 35: Average curves of the carbonizing free compounds tensile tests.

The elastic modulus didn't change much in the series, most of elastic modulus have increased slightly respect to the control, only AP8M2z showed a little decrease.

Elongation at break increased more significantly in AP8M2 and AP8M2c compounds, in presence of clay, the material reached 25% elongation at break. The lowest values was measured for OP8M2z, just 1% of elongation at break.

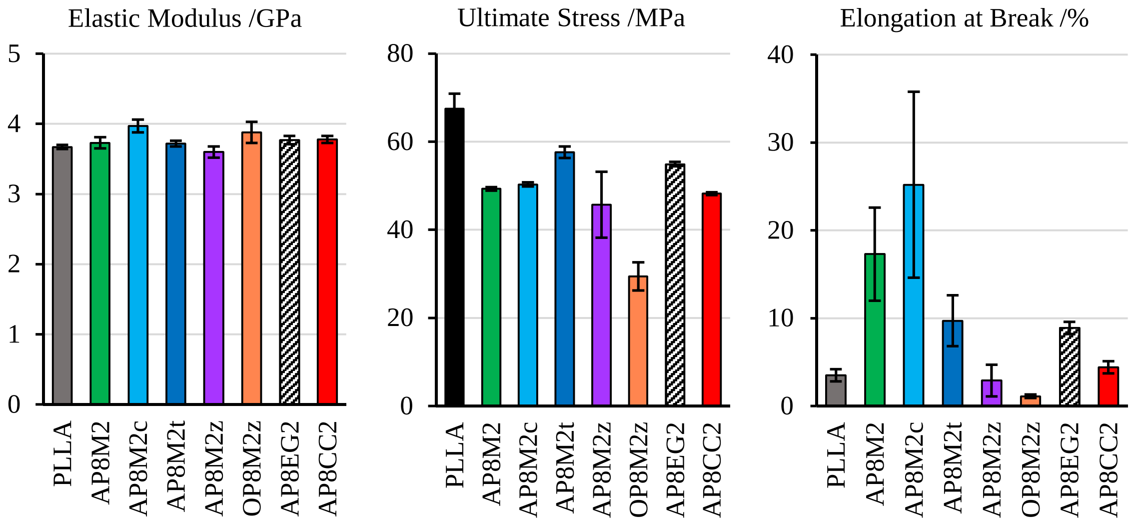


Figure 36: Tensile test results of the carbonizing free compounds in comparison.

Starch containing compounds (Figure 37 and Figure 38) showed a decrease of maximum stress respect to pure PLLA. The compound with the lower additive load (St2AP4M2) had the higher value of maximum stress. On the contrary, the compounds with higher additives loads showed lower maximum stress, the lowest value was recorded for the St2OP8M2z compound. The elastic modulus of the ammonium polyphosphate containing compounds increased as the total additives loads increased. The highest value was obtained for OP containing compounds. Zinc borate determined a decrease of elastic modulus respect the compound without it. Elongation at break is double (6%) in St2AP4 and is decreased increasing the load additives, only the St2AP8M2z compound has a different behaviour showing higher elongation break respect to the general trend. St2AP8M2, St2OP8M2 and St2OP8M2z broke before the yielding point, this can relate to an increase of the brittleness of the material.

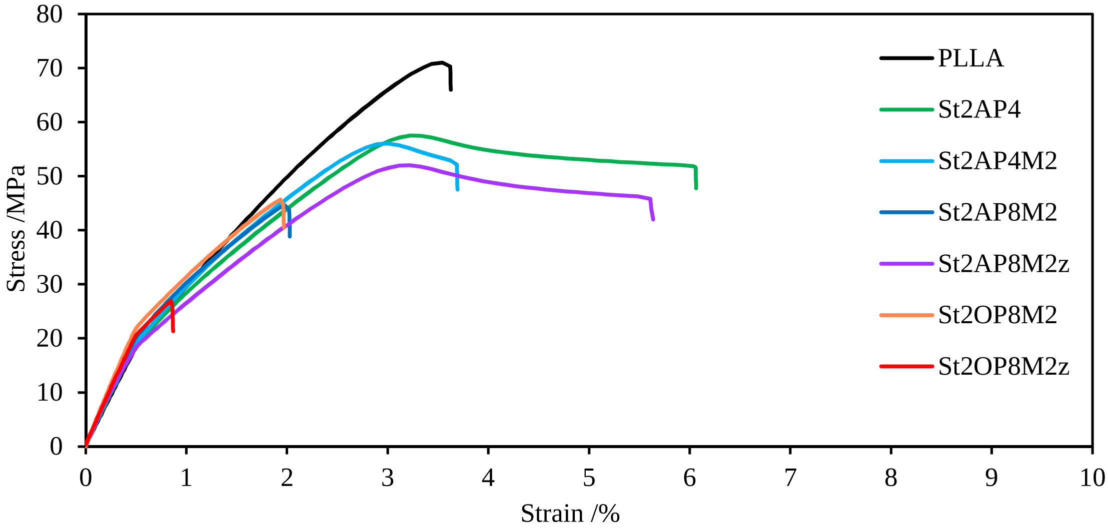


Figure 37: Average curves of the starch containing compounds tensile tests.

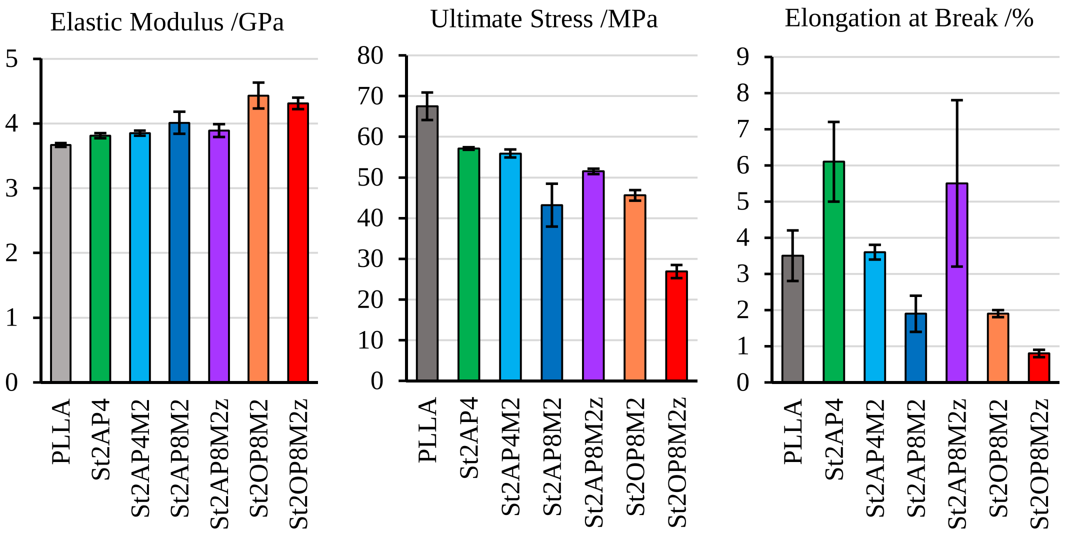


Figure 38: Tensile test results of the starch containing compounds in comparison.

Sorbitol containing compounds (Figure 39 and Figure 40) showed a decrease of maximum stress respect pure PLLA. Moreover, all the sorbitol containing compounds showed an elongations at break lower respect to the control. In general, the sorbitol presence leaded to an increase of the brittleness of the materials. The increase of brittleness can be related to a decrease of the polymer molecular weight. The polymer degradation results from the partial glycolysis of the polymer due to the reaction with the sorbitol hydroxyls groups during the melt mixing. The degradation in presence of sorbitol can be very effective since it is the carbonizing agent with the highest weight percentage of hydroxyls group. In addition, sorbitol melts at 95°C achieving high dispersion into the material during the extrusion process. The elastic modulus didn’t change much in compounds with ammonium polyphosphate and is increased up to 4 GPa in diethyl aluminium phosphinate containing compounds.

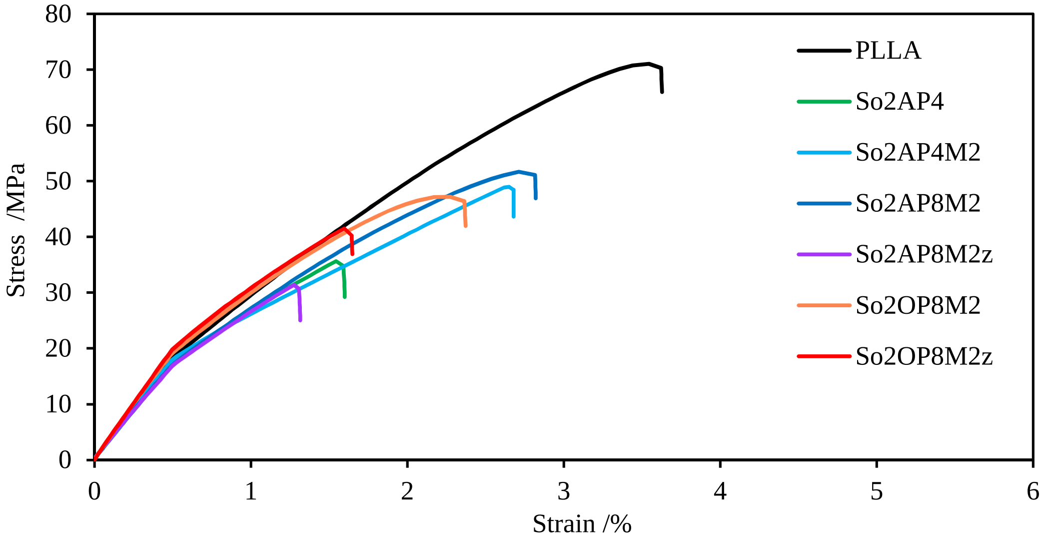


Figure 39: Average curves of the sorbitol containing compounds tensile tests.

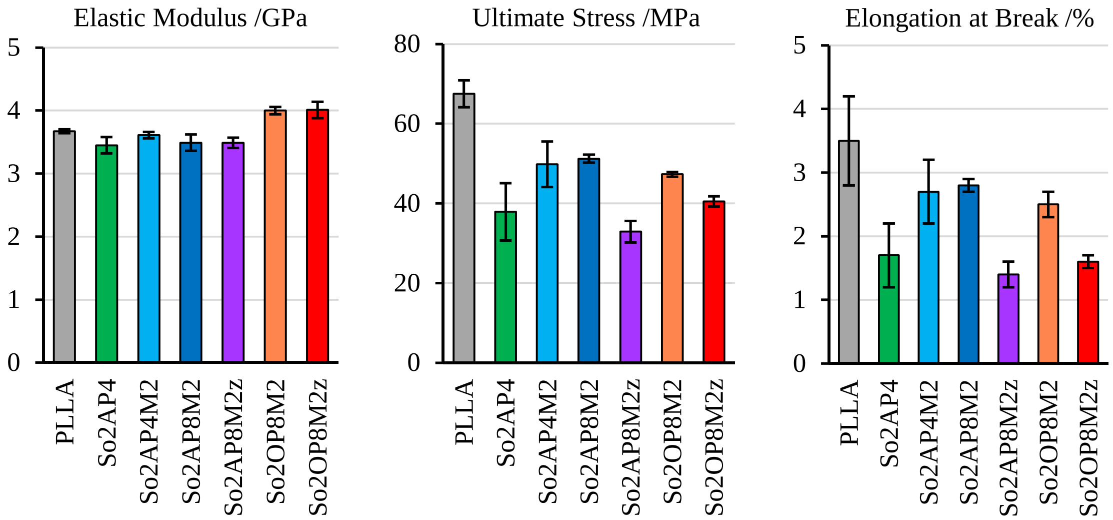


Figure 40: Tensile test results of the sorbitol containing compounds in comparison.

The glycerol phosphate containing compounds (Figure 41 and Figure 42) showed lower maximum stress and lower elongation at break respect to pure PLLA. All glycerol containing compounds broke before reaching the yielding stress. The elastic modulus was not much affected, changing slightly respect to the control.

As in the presence of sorbitol, the increase of brittleness can be related to the glycolysis of the polymer due to the reaction with the hydroxyls groups in the glycerol phosphate. In addition, glycerol phosphate is highly moisture sensitive and can adsorb water as coordination molecules very difficult to remove. The presence of moisture inside the material leads to an increase of the polymer degradation by the hydrolysis of the ester groups during the melt mixing and injection moulding processes.

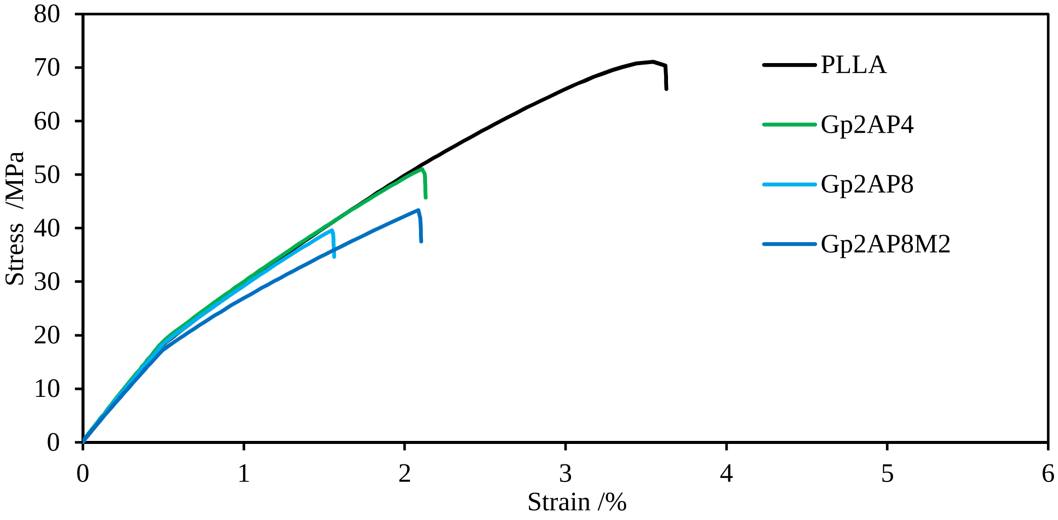


Figure 41: Average curves of the glycerol phosphate containing compounds tensile tests.

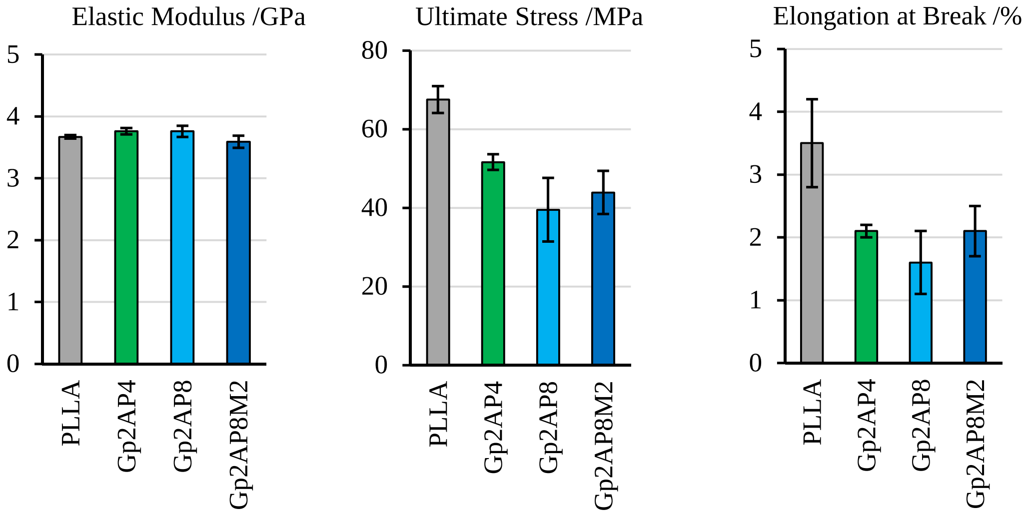


Figure 42: Tensile test results of the glycerol phosphate containing compounds in comparison.

Glycerol phosphate containing compounds were very brittle, the Gp2AP4M2 compound was very problematic to mould. Gp2AP4M2 dog bone specimens got broken during the extraction from the mould when they were injection moulded, and no suitable specimens were obtained in order to perform the tensile test.

The maximum stress of coffee grounds containing compounds (Figure 43 and Figure 44) decreased with increasing total additives loads.

The elastic modulus is generally increased for all compounds, in the Co2AP8 the value reach 4.1 GPa respect to 3.7 GPa of the control.

The elongation at break remained the same or did improve, an increase of brittleness is not occurred in the presence of coffee grounds. Co2AP8 and Co2AP8M2 had an elongation at break double respect to the control.

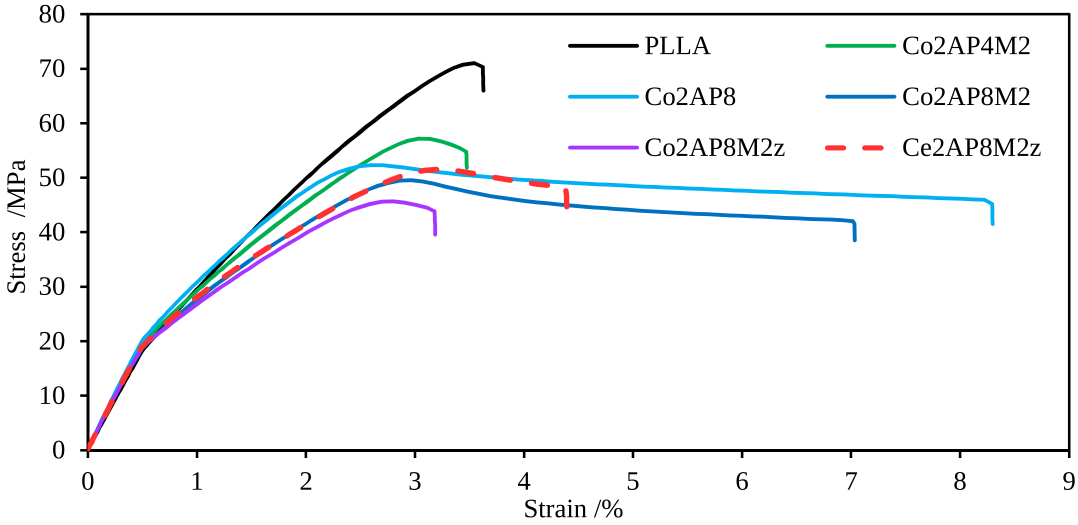


Figure 43: Average curves of the coffee grounds and cellulose containing compounds tensile tests.

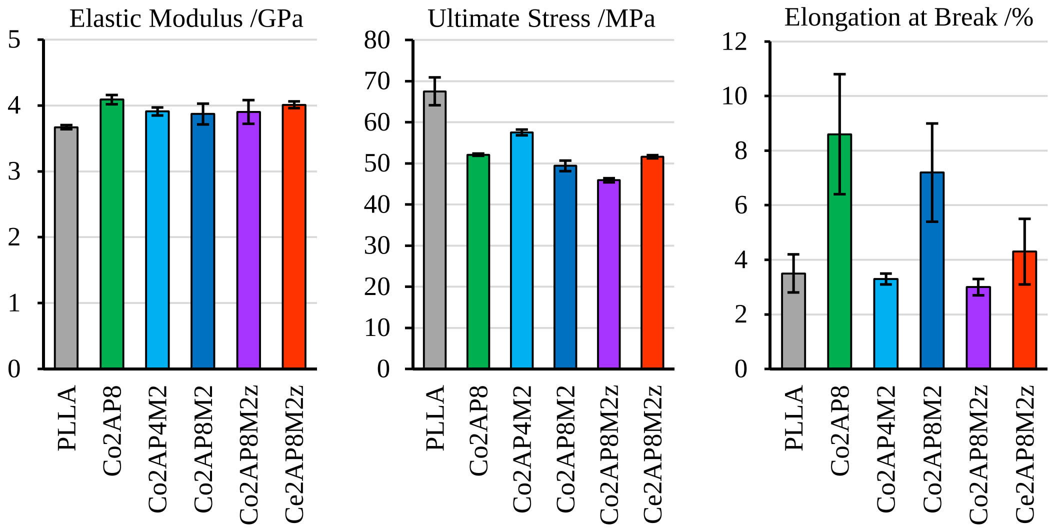


Figure 44: Tensile tests results of the coffee grounds and cellulose containing compounds in comparison.

Cellulose containing compound (Figure 43 and Figure 44) had lower yield stress respect to the control, but its elastic modulus and elongation at break are slightly increased.

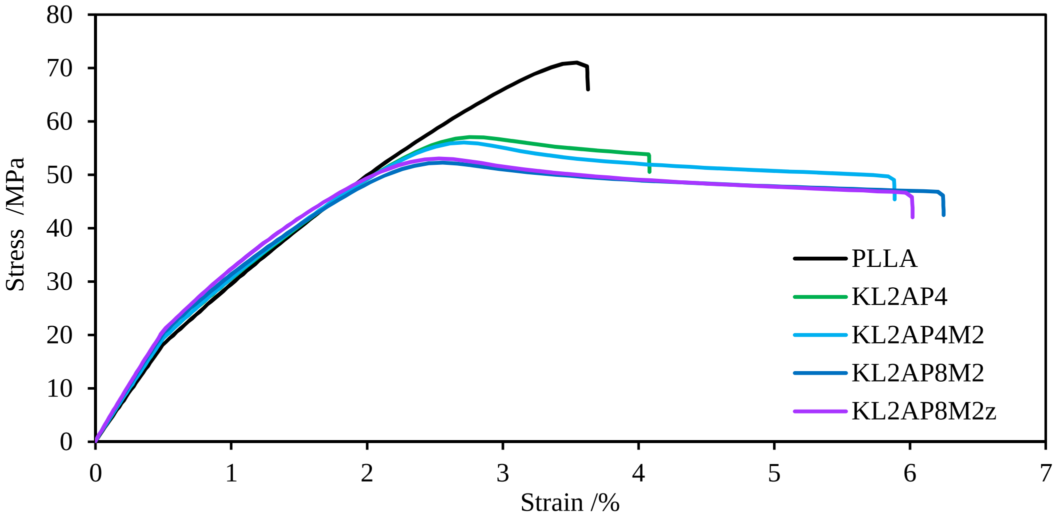


Figure 45: Average curves of the Kraft lignin containing compounds tensile tests.

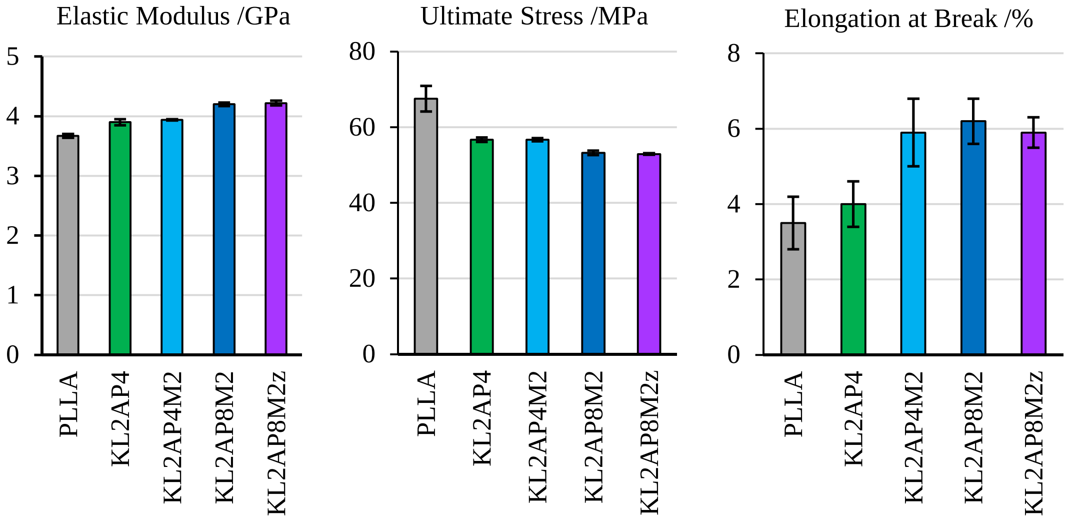


Figure 46: Tensile tests results of the Kraft lignin containing compounds in comparison.

In general, Kraft lignin containing compounds (Figure 45 and Figure 46) showed lower yield stress respect to pure PLLA. The maximum stress decreased slightly as the amount of the total additives load increased. Unlike what has been observed for the other carbonizing agent classes, the elastic modulus is increased with the additives load as well as the elongation at break. Kraft lignin containing compounds showed generally an increase on the elongation at break reaching values close to 6% in all melamine cyanurate containing compounds (KL2AP4M2, KL2AP8M2 and KL2AP8M2z).

5.2 Bench scale flame test results

5.2.1 Small-scale flame tests and ignition tests results

The results of flame tests and glow wire test are reported in Table 5. Limiting oxygen index tests were the first tests attempted for each compounds, followed by UL-94 test in vertical position and eventually complemented by the glow wire test.

Table 5: Small scale flame and ignition tests results.

	Flame Tests		Ignition Test	
Compound Name	LOI %	UL94 V class	GWFI °C /2mm	GWIT °C /2mm
PLLA	<27	no rating	825	850
AP8M2	<27	no rating	-	-
AP8M2c	30.0	V-2	>950	775
AP8M2t	37.0	V-2	>950	775
AP8M2z	28.5	V-2	>950	800
OP8M2z	<27	V-0	>950	775
AP8EG2	<27	no rating	-	-
AP8CC2	27.5	no rating	-	-
St2AP4	32.5	V-0	>950	825
St2AP4M2	36.2	V-0	>950	800
St2AP8M2	36.4	V-0	>950	825
St2AP8M2z	37.5	V-0	>950	750
St2OP8M2	<27	V-0	>950	800
St2OP8M2z	<27	V-2	>950	800
So2AP4	36.1	V-0	>950	875
So2AP4M2	36.9	V-0	>950	825
So2AP8M2	40.3	V-0	>950	850
So2AP8M2z	48.5	V-0	>950	800
So2OP8M2	<27	V-0	>950	800
So2OP8M2z	<27	V-0	>950	800
Gp2AP4	42.4	V-0	>950	975
Gp2AP8	43.3	V-0	>950	950
Gp2AP4M2	50.3	V-0	>950	875
Gp2AP8M2	43.5	V-0	>950	850
Co2AP8	33.7	V-0	>950	850
Co2AP4M2	32.1	V-2	>950	825
Co2AP8M2	31.8	V-0	>950	775
Co2AP8M2z	35.3	V-0	>950	775
KL2AP4	29.1	V-2	>950	825
KL2AP4M2	29.2	V-0	>950	825
KL2AP8M2	30.0	V-0	>950	850
KL2AP8M2z	34.6	V-0	>950	850
Ce2AP8M2z	37.6	V-0	>950	775

(AP) ammonium polyphosphate, (OP) aluminium diethyl phosphinate, (M) melamine cyanurate, (c) clay, (t) talc, (z) zinc borate, (St) starch, (So) sorbitol, (Gp) glycerol phosphate, (Co) coffee grounds, (KL) Kraft lignin, (Ce) cellulose

All compounds with a LOI under 27% are considered self-sustaining in case of fire in air [192], and for this reason their LOI value have not been further investigated in detail. Reaching a self-extinguishes behaviour is necessary to achieve good flame resistance properties, thus all compounds with LOI values under 27% are considered not suitable for applications where flame resistance is required.

Polylactic acid burns self-sustaining in air and a limiting oxygen index value under 27% was obtained as expected. Indeeed, the LOI value is 20-21% as reported in many research works [190] [191] [193].

Limiting oxygen index results showed values under 27% in AP8M2, AP8EG2, AP8CC2 and in all aluminium diethyl phosphinate containing compounds.

All compounds containing carbonizing agents or inorganics agents that reach LOI values equal or higher than 27% are considered self-extinguish material.

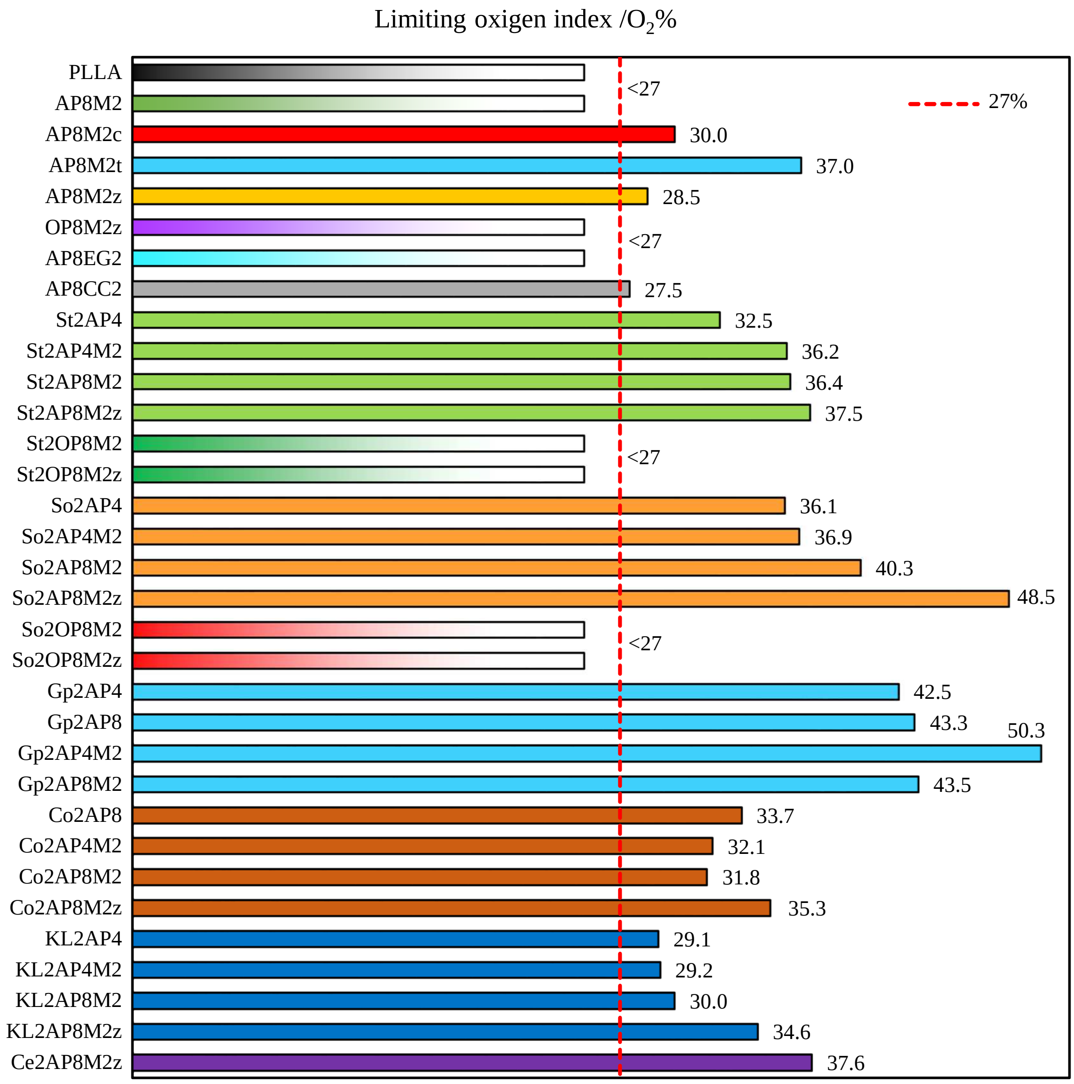


Figure 47: Limiting oxygen index test results.

The presence of carbonizing agents (2%) or inorganic agents (1%) in addition to APP (4%) and melamine cyanurate (2%), is sufficient to achieve a self-extinguishes behaviour. Polylactic acid was found to form char by acting itself as carbonizing agent but a stable char formation was obtained only with the addition of carbonizing or inorganic agents. Calcium carbonate was chosen as blowing agent but acts as inorganic agent too, improving the char stabilization. In bicarbonate form, obtained by its reaction with acids, it decomposes generating water, carbon dioxide and carbonate. In carbonate form, it starts decomposing around 600°C generating carbon dioxide and calcium oxide that concentrates into the char residue, hence increasing its stability.

Aluminium diethyl phosphinate is a commercial flame retardant used in polyesters but seems not to be effective in polylactic acid. Indeed, all OP containing compounds reached a LOI lower than 27% showing a self-sustaining behaviour.

Thermogravimetric analysis showed a marked decrease of the decomposition temperature of polylactic acid in presence of OP. As an example, in Figure 48 are reported the thermogravimetric curves of neat OP and pure PLLA, in comparison with So2OP8M2, So2OP8M2 and OP8M2z. The decomposition temperature of OP is about 80°C higher than PLLA and when they are mixed the gap increase to 110°C, and to 130°C in the presence of zinc borate. The degradation temperature of the material decreased, but the additive degradation temperature remained unaltered. This means that the effect of the OP starts to act when the entire polymer has already been completely decomposed into combustible volatiles. Indeed, aluminium diethyl phosphinate degrades and acts in the condensed phase improving the char formation, as well as in the gas phase where diethyl phosphinic acid produced by its decomposition acts as radical trap. The first and the second weight loss steps of the OP additive consist on the loss of diethyl phosphinic acid [194]. The residue contains the remaining diethyl phosphinate that condense into cross-linked species like aluminium alkyl phosphates.

The lower decomposition temperature can be associated to the presence of aluminium ions that catalyse the depolymerisation of PLLA. Aluminium ions are reported on many papers to be active as polymerization catalysts for lactide [195]. At higher temperature, they can act in the opposite way reducing the energy required to break the polymer chain, thus increasing the depolymerisation rate of the polymer. This lead to a lower decomposition temperature of the compound respect to the pure PLLA.

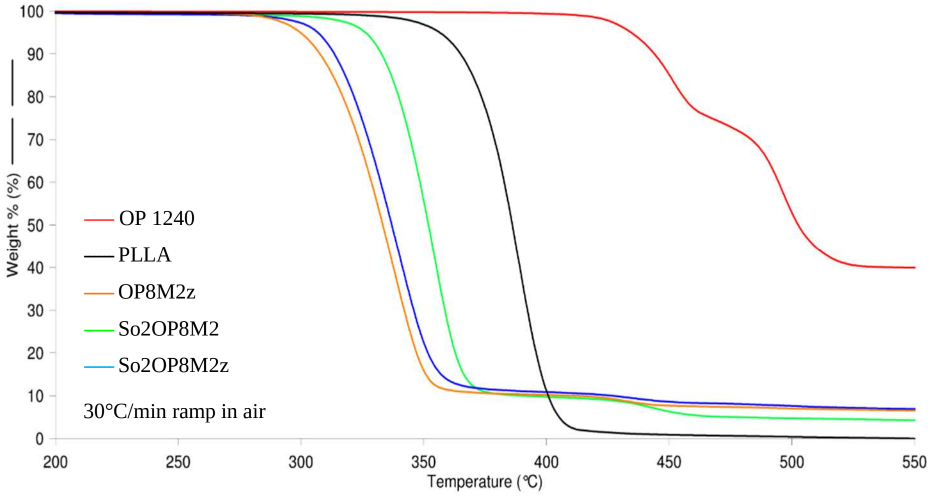


Figure 48: Thermogravimetric analysis of neat aluminium diethyl phosphinate and pure PLLA in comparison with aluminium diethyl phospinate and sorbitol containing compounds.

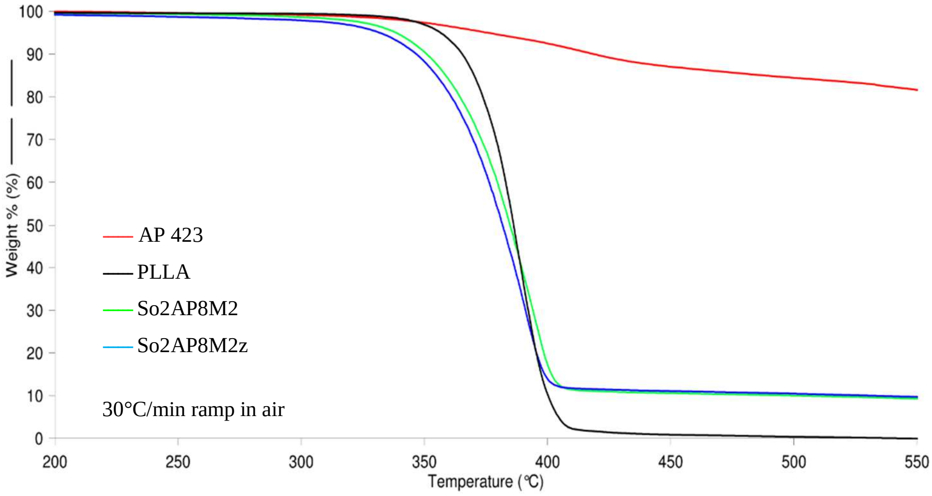


Figure 49: Thermogravimetric analysis of neat ammonium polyphosphate and pure PLLA in comparison with ammonium polyphosphate and sorbitol containing compounds.

Neat ammonium polyphosphate starts decomposing at the same temperature of pure PLLA (Figure 49) gradually releasing ammonia and water up to 580°C. Then, it starts to fragment into P_2O_5 which volatilises, at that temperature [196]. Sorbitol containing compounds with 8.5% of ammonium polyphosphate and 2% of melamine cyanurate start to decompose at temperatures close to the starting decomposition temperature of the aluminium diethyl phosphinate compounds (3% of weight loss around to 300°C for both). However, as it can be seen in Figure 49, the weight loss is slower in comparison, achieving the maximum rate at a temperature about 20°C lower than the temperature of maximum decomposition rate of the pure PLLA, and decreases of about 25°C with the further presence of zinc borate. The main weight loss step of So2OP8M2 compound takes place within 60°C c.a., starting from 300°C to 360°C. On the contrary, the main decomposition step of So2OP8M2 compound starts at 300°C and it is completed at 410°C, occurring within a 110°C temperature range. At 360°C, the OP containing compound lost 90% of its weight whereas the APP containing compound reach a weight loss of about 10% at the same temperature. This can be related to a better efficiency in char formation in the presence of ammonium polyphosphate respect to aluminium diethyl phosphinate, because a lower flow of volatiles evolves from the bulk material.

The talc containing compound AP8M2t gave a LOI value 37%, a relatively high value considering that is obtained in absence of carbonizing agent. However, this compound achieved only V-2 classification in UL 94 vertical test.

The compounds with APP and starch showed LOI values higher than 32%, the maximum value is obtained for the zinc borate containing compound with a LOI of 37.5%.

The compounds with APP and sorbitol reached LOI values higher than 36%, the maximum value is again obtained for the zinc borate containing compound with a LOI of 48.5%.

The compounds with APP and glycerol phosphate gave LOI values higher than 42%, the maximum value is achieved for the Gp2AP4M2 compound with a LOI of 37.5%.

The compounds with APP and coffee grounds gave LOI values higher than 31%, the maximum value is shown for the zinc borate containing compound with a LOI of 35.5%.

The compounds with APP and Kraft lignin gave LOI values higher than 29%, the maximum value is obtained for the zinc borate containing compound with a LOI of 34.6%.

The compound with APP and cellulose gave a LOI of 37.6, this value is close to the values obtained with the same additives loads for the starch and zinc borate containing compounds. These similar values can arise from the similar chemical composition of starch and cellulose, since they have the same weight percentage of hydroxyls in their polymeric structures. Other compounds with cellulose have not been prepared, so other correlation with starch containing compounds are not possible in order to confirm this assumption.

The results of UL94 tests showed V-0 classification for all compounds with APP and starch, sorbitol and glycerol phosphate respectively. No carbonizing free compounds reached V-0 or V-1 classification. PLLA achieved no rating classification, as well as AP8M2, AP8EG2 and AP8CC2.

Coffee grounds containing compounds achieved V-0 classification in all formulation with 8.5% of ammonium polyphosphate, the Co2AP4M2 compound reached only V-2 classification leading to the cotton ignition, caused by the material burning drops during the UL94 test.

Kraft lignin containing compounds achieved V-0 classification in all formulations with ammonium polyphosphate and melamine cyanurate, the KL2AP4 reached only V-2 classification leading to the cotton ignition with its burning drops.

Cellulose containing compound reached V-0 classification.

All aluminium diethyl phosphinate containing compounds reached V-0 classification except St2OP8M2z compound reaching V-2 classification only. This self-sustaining behaviour seen in LOI test is in contrast with the V-0 classification achieved in UL94 tests. The reason of these results arises from the high melting rate showed by these compounds during the flame application in the bottom edge of the specimen. The materials melt very easily and flow away from the flame, rather than dripping. In this way, the material leaves the flame zone application before reaching temperatures sufficiently high to generate enough fuel to maintain the combustion.

On the contrary, during the LOI test the flame is applied at the top of the specimen and the material melts but doesn’t flow away rapidly, reaching temperatures sufficiently high to produce enough volatiles to sustain the combustion after the ignition.

Based on the results was possible to see a correlation between LOI values and UL94 classification, it is possible to say that in the presence of carbonizing agents all compounds with a LOI value over 32 reached V-0 classification. Considering Kraft lignin containing compounds, the threshold seems to be lower, around 29-30%. In electronics application, UL94 V-1 or V-0 is required, V-0 is mandatory for application in strict contact with printed board circuits.

The glow wire ignition tests were attempted for all compounds that reached V-2 classification or higher in the UL94 test and compared with pure PLLA. The compounds without UL94 rating classification have not been tested. The tests were performed in specimens 2mm thick and the results are reported in Figure 50.

Pure PLLA showed a glow wire flammability index (GWFI) of 825°C and a glow wire ignition temperature (GWIT) of 850°C, the GWIT is higher than GWFI meaning that once the material is ignited, it burns completely, according to the self-sustaining behaviour already seen in LOI test and UL94 test. All compounds tested showed a GWFI higher than 950°C, which means the self-extinguish of the flames in less than 30 seconds after the removal of the glow wire. As it is possible to see in the Figure 50, the GWIT decreased by increasing the additives loads in all carbonizing containing series except Kraft lignin containing compound where the trend is the opposite.

Glycerol phosphate and sorbitol containing compounds achieved the highest values with Kraft lignin, followed by coffee grounds starch and cellulose, respectively. In this test, as well as in the LOI and UL94 tests, the dripping away from the heat source leaded to good performances in these tests. As a supporting evidence to confirm this observation, glycerol phosphate and sorbitol containing compounds reached the highest GWIT.

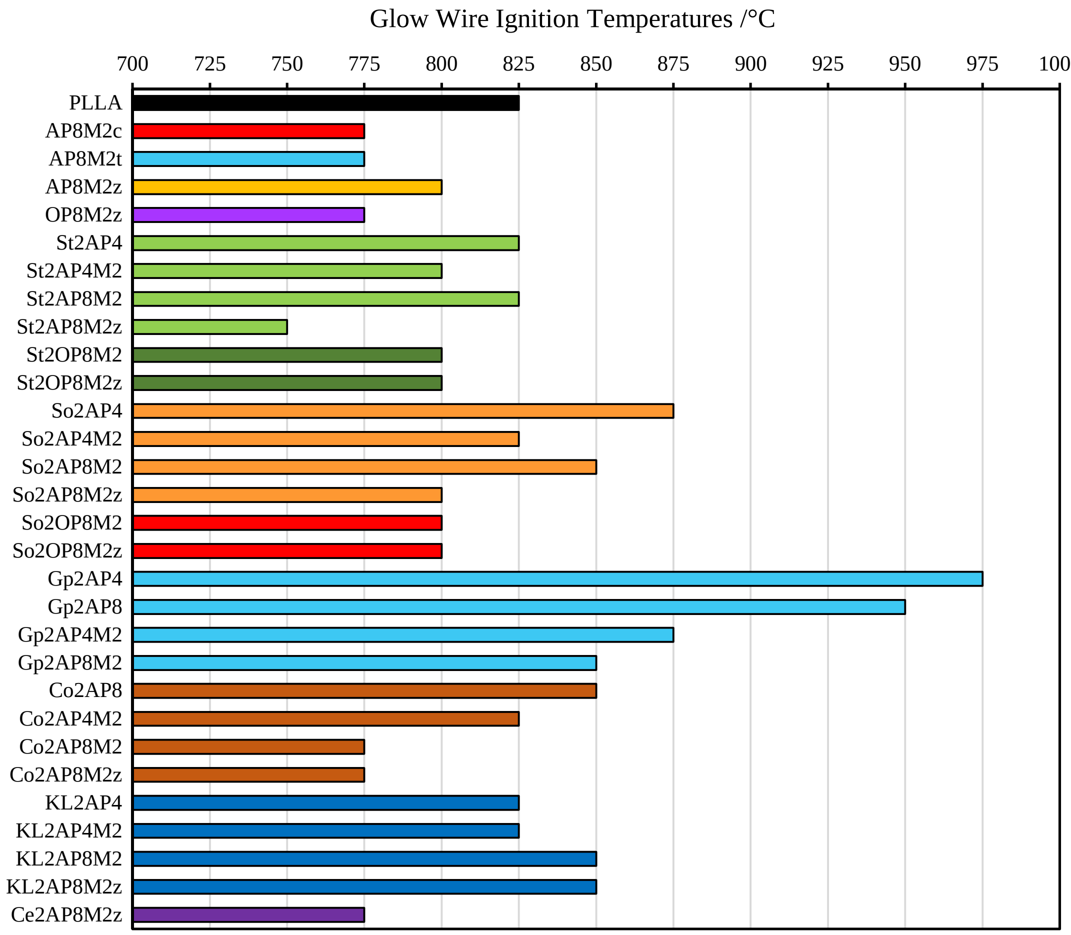


Figure 50: Glow wire ignition temperature results.

Increasing the additives loads, the char formation is enhanced and the material becomes less viscous and flows away from the heat source less rapidly, thus achieving lower ignition temperature.

However, considering that a GWFI of 850°C is required for insulating materials in unsupervised appliances carrying a current higher than 0.2 amperes, all compounds tested achieved values over 950°C. Moreover, all compound tested except St2AP8M2z, reached GWIT equal or higher than 775°C. St2AP8M2z compound reached lower GWIT of 750°C. A GWIT of 750° is required for supervised appliances carrying a current higher than 0.5 amperes. On the other hand, a GWIT of 775°C and V-1 classification is required for unattended appliances carrying a current higher than 0.2 amperes. It is important to remember that these small-scale test results must be confirmed by further tests on the final products and for this reason the thickness of the corresponding finished components must be equal or lower than the thickness of the test specimens. The glow wire results obtained are strictly related to the 2 mm specimen thickness, and can be slightly different in specimen with lower or higher thickness, usually higher GWIT values are obtained for specimen less thick. Nevertheless, 2 mm thick specimens cover a wide range of appliances in common uses and glow wire test over different thickness are not been performed.

5.2.2 Cone calorimeter test results

The cone calorimeter tests were been carried out at the Centre of fire and hazardous science of the University of Central Lancashire in Preston UK during a period abroad in my doctorate. All the compounds have been tested and pure PLLA was been taken as control. Squared plates 100x100 mm and 3 mm thick were tested in triplicates in horizontal position, 60 mm below a radiant heat flux of 35 kWm^{-2} in accordance with the ISO 5660. The gap of 60 mm was chosen in order to avoid the direct contact between the cone and the intumescing specimens during the char expansion. A radiant heat flux of 35 kWm^{-2} was selected in order to investigate the flame resistance of the materials in conditions comparable to an early stage fire [197]. In these test conditions, the synergistic action of the intumescent flame retardants systems was studied and the material ability to retard or to extinguish the fire under a forced combustion condition, has been investigated.

The time to ignition (t_{ig}), peak of heat release rate (PHRR), total heat release (THR) and the residue percentage left at the end of the test, are reported in Table 6. The compounds heat release curves are reported in Figure 51 - Figure 57 in comparison with pure PLLA.

The carbonizing agent free compounds with ammonium polyphosphate and melamine cyanurate (Figure 51) showed a different behaviour. In particular AP8M2 showed worse results respect to pure PLLA. Instead, in presence of inorganic agents, more efficient char formation occured. In general, the PHRR are lower than the control, but as it can be seen in the Figure 51, the combustion continues for longer time, in particular the char barrier is not efficient enough and the specimens burn for more than 20 minutes.

The aluminium diethyl phosphinate containing compounds showed the worst behaviour during the combustion. For all OP containing formulations, the PHRR and the total heat release are larger compared to the values obtained with pure PLLA, and the ignition occured 40-50 seconds earlier (Figure 51, Figure 53 and Figure 54).

Table 6: Cone calorimeter tests results.

Compound	t_{ig}		PHRR		THR		Residue
Name	s	σ	kW/m^2	σ	MJ/m^2	σ	%
PLLA	92.4	5.5	387	9	70.2	2.3	3.2
AP8M2	79.2	2.3	437	10	72.5	1.4	8.3
AP8M2c	64.6	1.2	157	1	37.4	6.2	23.3
AP8M2t	65.4	1.3	169	6	50.5	1.6	24.9
AP8M2z	100.6	5.4	185	15	56.4	3.2	16.9
OP8M2z	51.7	1.2	471	29	69.4	2.6	6.5
AP8EG2	71.5	5.6	322	16	65.3	2.1	11.4
AP8CC2	81.6	7.3	249	14	63.2	3.4	14.6
St2AP4	67.9	1.4	357	10	71.5	0.4	4.4
St2AP4M2	67.6	4.1	323	5	71.3	0.2	4.9
St2AP8M2	75.0	1.5	216	3	56.8	1.7	16.2
St2AP8M2z	60.3	2.4	148	4	21.0	1.0	60.0
St2OP8M2	51.0	1.8	580	17	76.8	0.6	4.6
St2OP8M2z	40.5	1.5	504	4	76.6	0.1	5.6
So2AP4	98.8	5.5	251	20	64.3	1.3	11.4
So2AP4M2	95.4	2.3	331	8	70.8	0.2	4.7
So2AP8M2	99.2	4.5	269	3	36.1	12.5	43.5
So2AP8M2z	96.8	5.9	191	16	34.7	2.4	39.5
So2OP8M2	51.1	0.7	585	13	75.6	0.5	4.2
So2OP8M2z	40.2	2.6	459	22	71.9	0.2	7.2
Gp2AP4	99.8	1.7	421	7	73.7	0.2	5.6
Gp2AP8	106.0	0.7	264	2	54.0	3.4	22.9
Gp2AP4M2	105.6	3.1	287	9	71.1	0.3	6.0
Gp2AP8M2	103.2	4.2	199	6	8.2	0.6	80.8
Co2AP8	68.0	2.0	239	4	64.7	0.9	11.9
Co2AP4M2	65.9	0.2	313	2	71.5	0.7	5.3
Co2AP8M2	53.1	2.0	238	6	62.7	6.4	14.7
Co2AP8M2z	60.3	2.5	195	34	54.7	17.5	19.5
KL2AP4	80.2	2.0	371	10	71.4	1.0	4.6
KL2AP4M2	71.9	0.5	363	6	71.1	0.2	5.1
KL2AP8M2	72.4	2.4	297	5	50.6	0.5	26.6
KL2AP8M2z	68.8	1.2	235	1	50.8	0.9	15.5
Ce2AP8M2z	50.3	1.8	197	5	58.7	3.1	20.0

(AP) ammonium polyphosphate, (OP) aluminium diethyl phosphinate, (M) melamine cyanurate, (c) clay, (t) talc, (z) zinc borate, (St) starch, (So) sorbitol, (Gp) glycerol phosphate, (Co) coffee grounds, (KL) Kraft lignin, (Ce) cellulose.

Expandable graphite containing compound ignited 20 seconds earlier than the control and reached rapidly its peak of heat release rate (Figure 52). Althought the PHRR is lower compared to control, the time to reach it is half respect pure PLLA. Calcium carbonate containing compound showed a time to sustain ignition 10 seconds lower and a PHRR of about 65% respect to the control. However, it kept burning for longer and a second large peak of heat release rate occured after the char formation.

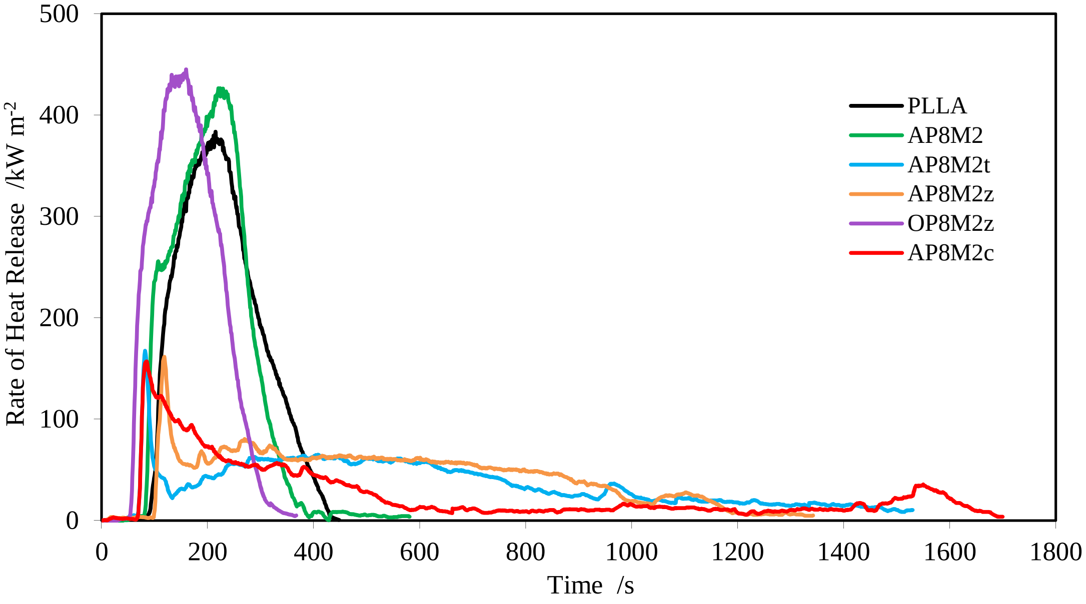


Figure 51: HRR average curves of PLLA and carbonizing free compounds based on APP and OP with melamine cyanurate.

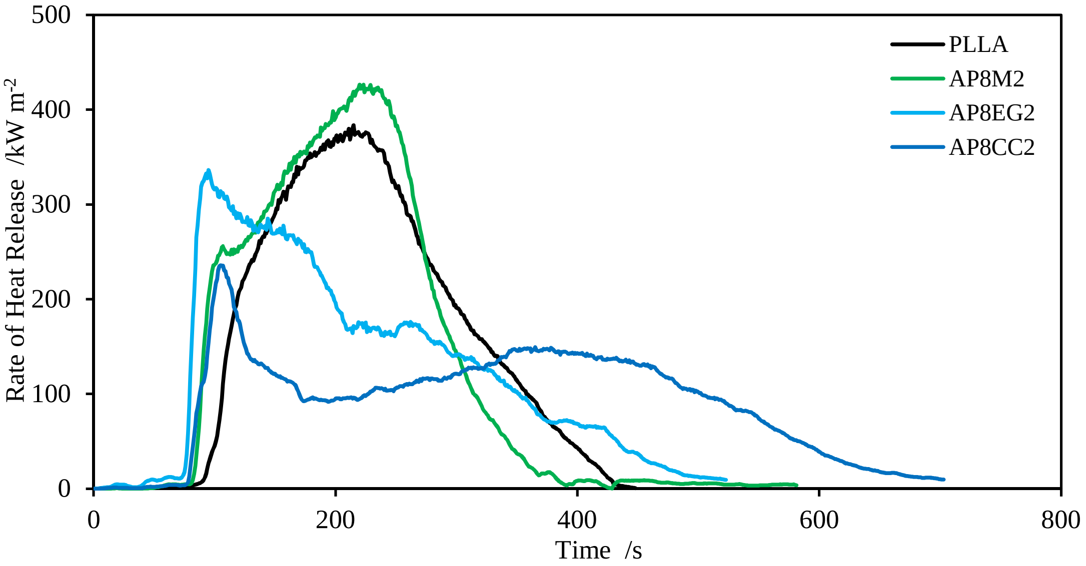


Figure 52: HRR average curves of PLLA and APP containing compounds with different blowing agent.

The carbonizing agent containing compounds showed better results in terms of fire resistance due to a more efficient char barrier formation. Excellent flame resistance properties were obtained in the presence of carbonizing agents and 8.5% of ammonium polyphosphate AP. The best results in terms of total heat release and peak of heat release rate were obtained with the further presence of zinc borate.

The starch containing compounds have lower peak of heat release rate but showed a time to sustain ignition 20-30 seconds less than pure PLLA (Figure 53). In presence of 8.5% ammonium polyphosphate a good char barrier is formed (Figure 58), the PHRR is less than 60% of the control value, and in presence of zinc borate the value decreased further down to 40%.

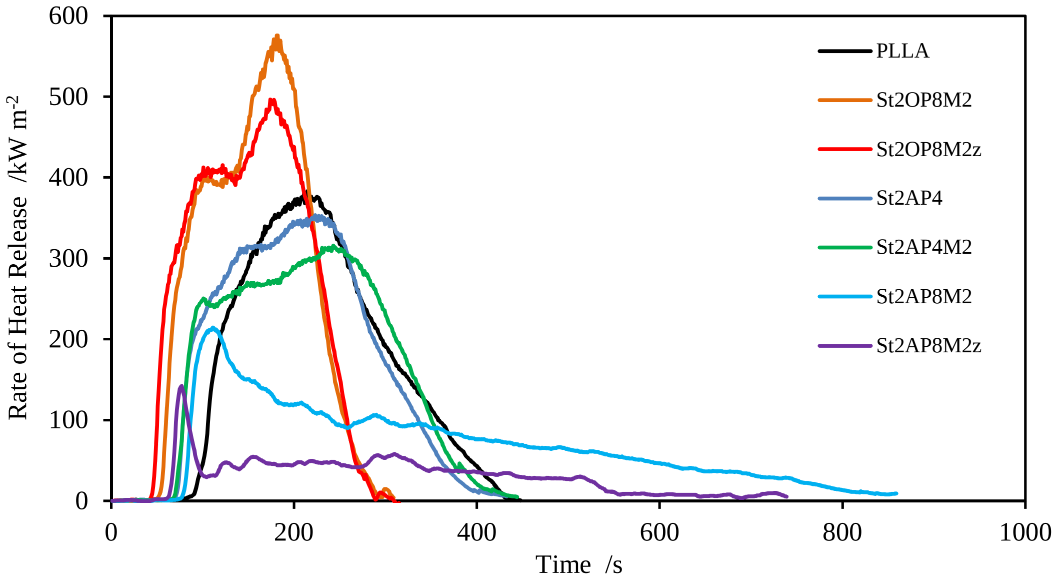


Figure 53: HRR average curves of PLLA and starch containing compounds.

The sorbitol containing compounds (Figure 54) showed a time to sustain ignition close to the pure PLLA; moreover, they all have lower peaks of heat release rate, the lowest value being recorded in the presence of zinc borate. In the presence of 8.5% ammonium polyphosphate, the PHRR is less than 70% respect to the control pure PLA, and in presence of zinc borate the value decreased to 50%. The residual weight for 8.5% APP containing compounds is about 40%. The sorbitol containing compounds with 4% APP showed better results without the presence of melamine cyanurate. As reported in the Table 6 and in Figure 54, PHRR and total heat release values are lower for So2AP4 respect to So2APM2, while the residue is higher.

The glycerol phosphate containing compounds (Figure 55) showed a time to sustain ignition 10 seconds longer respect to pure PLLA. Only Gp2AP4 compound showed a PHHR and THR higher respect to the control. The other compounds showed a PHRR lower than 75% respect to the control; in particular, the Gp2AP8M2 showed the lowest value in total heat release and the higher value of residual weight among all materials tested. For glycerol phosphate containing compounds, good results were achieved without the use of zinc borate.

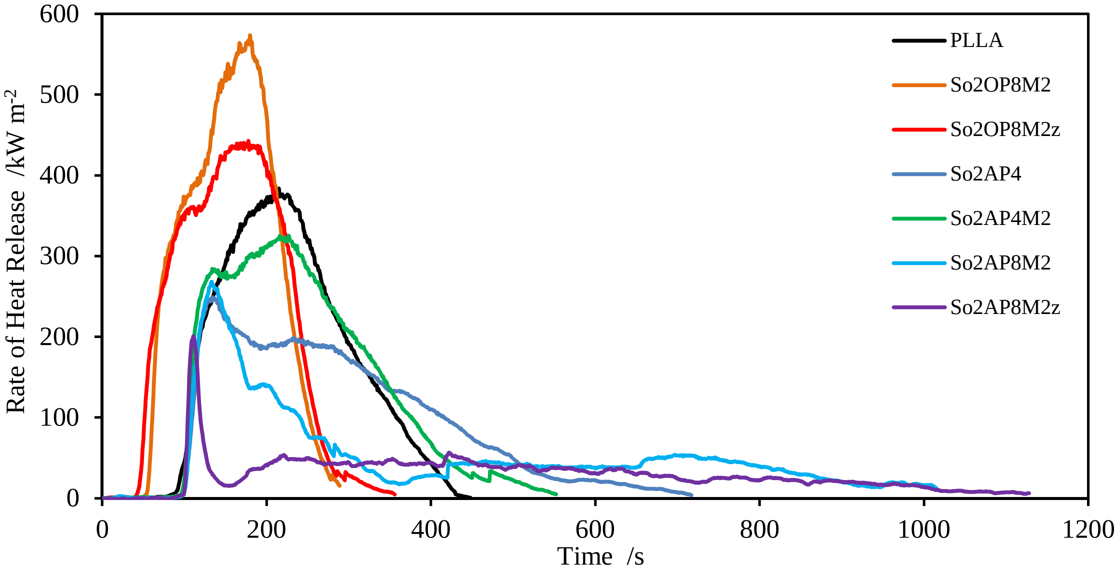


Figure 54: HRR average curves of PLLA and sorbitol containing compounds.

The Gp2AP8M2 compound self-extinguishes in 4 minutes with less char formation on the surface of the specimens. Moreover, the presence of melamine cyanurate seemed to favour the char formation, as it can see from the data reported in Figure 55. The presence of melamine cyanurate leaded to the reduction of the heat release rate earlier respect to the compound without it. This means that melamine cyanurate improved char formation and this finding is further confirmed by comparing the results reported in Figure 60. By comparing Gp2AP4M2 with Gp2AP4, the latter compound without melamine showed a poorer char formation behaviour. The same conclusion can be drawn by comparing Gp2AP8 with Gp2AP8M2. This result may not be easily seen in Figure 60 but further support to this conclusion comes from the residue values reported in Table 6.

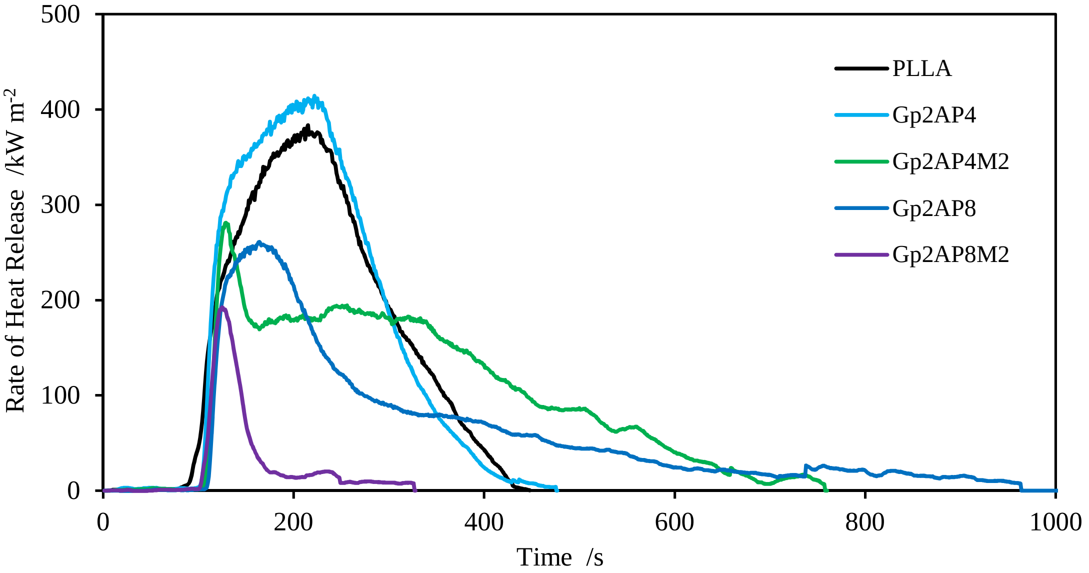


Figure 55: HRR average curves of PLLA and glycerol phosphate containing compounds.

Indeed, these data showed that in the presence of melamine cyanurarate, the residue percent is four time larger than in the absence of such compounds (formulation Gp2AP8M2 respect to Gp2AP8).

The coffee grounds containing formulations (Figure 56) showed a time to sustain ignition 30-40 second shorter than pure PLLA. The peak of heat release rate relative to compounds with 8.5% of APP were lower than 65% of the control and have resulted in a good char barrier respect the 4% APP containing compound CoAP4M2 (Figure 61). This latter compound showed a total heat release value close to the pure PLLA value and a PHRR around 80% of the control. The zinc borate containing compound Co2AP8M2z showed the best results with a PHRR of 50% respect the pure PLLA and a residue of 19.5%.

The cellulose containing compound (Figure 56) showed good results in terms of fire resistance, although the time to sustain ignition was 40 seconds shorter than the control, the PHRR value has almost halved respect to the control.

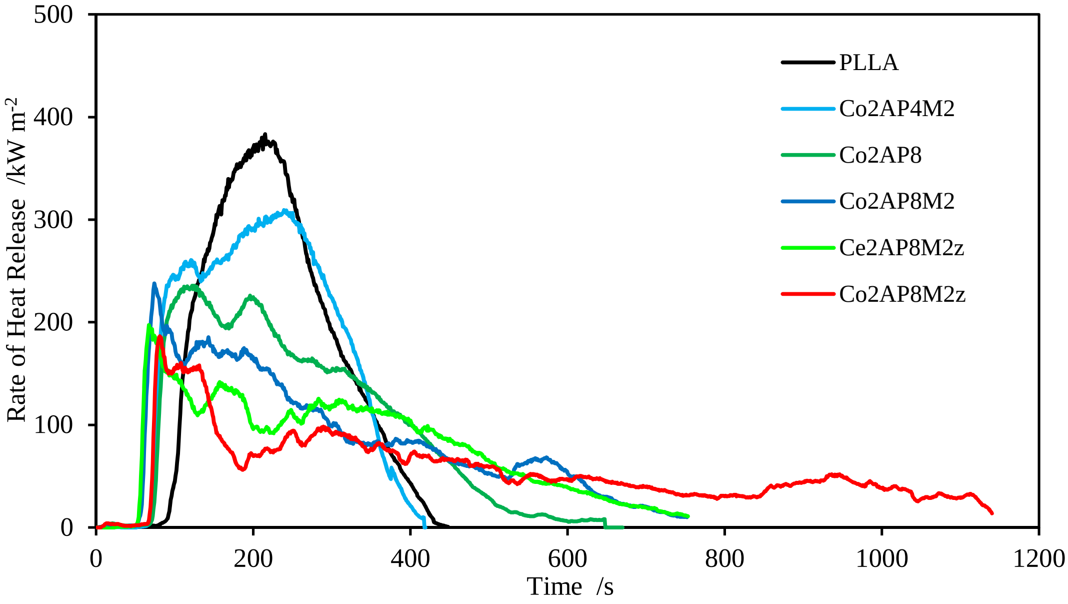


Figure 56: HRR average curves of PLLA, coffee grounds containing compounds and cellulose containing compound.

The Kraft lignin containing compounds (Figure 57) showed a time to sustain ignition 10-20 seconds shorter than pure PLLA. The PHRR and THR values for compounds with 4% of APP were close to the pure PLLA, as it can be seen in Figure 62. The char formation was poor. In presence of 8.5% APP, better results were obtained; the PHRR of KL2AP8M2 compound was 75% respect pure PLLA and in presence of zinc borate the value decreased further down to 60%. Although this two compounds have different PHRR, the THR values were the same, this because KL2AP8M2z burned two time faster than KL2AP8M2.

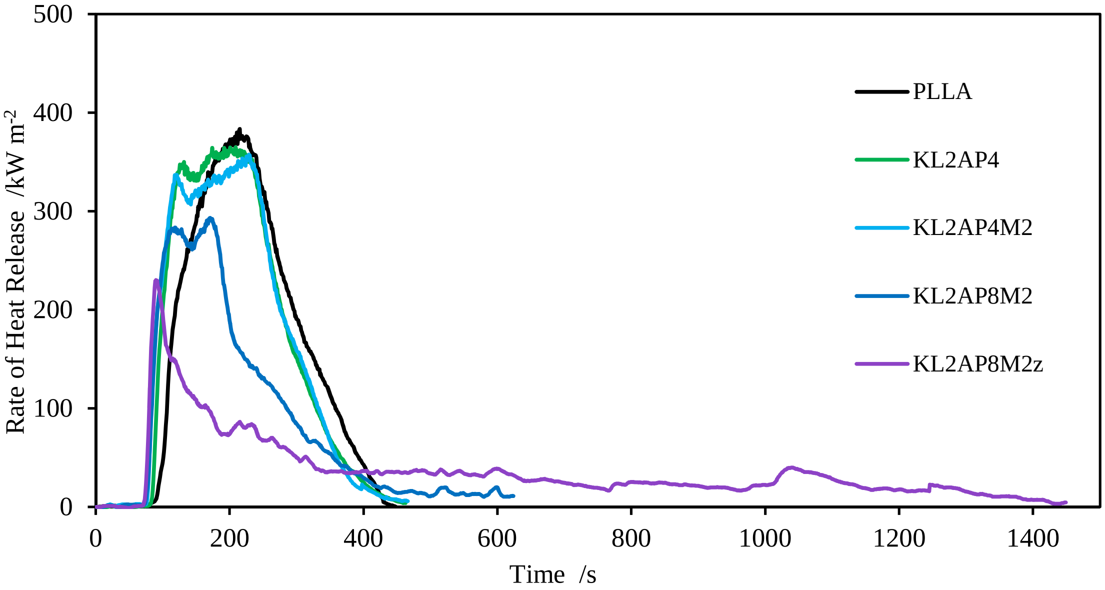


Figure 57: HRR average curves of Kraft lignin containing compounds.

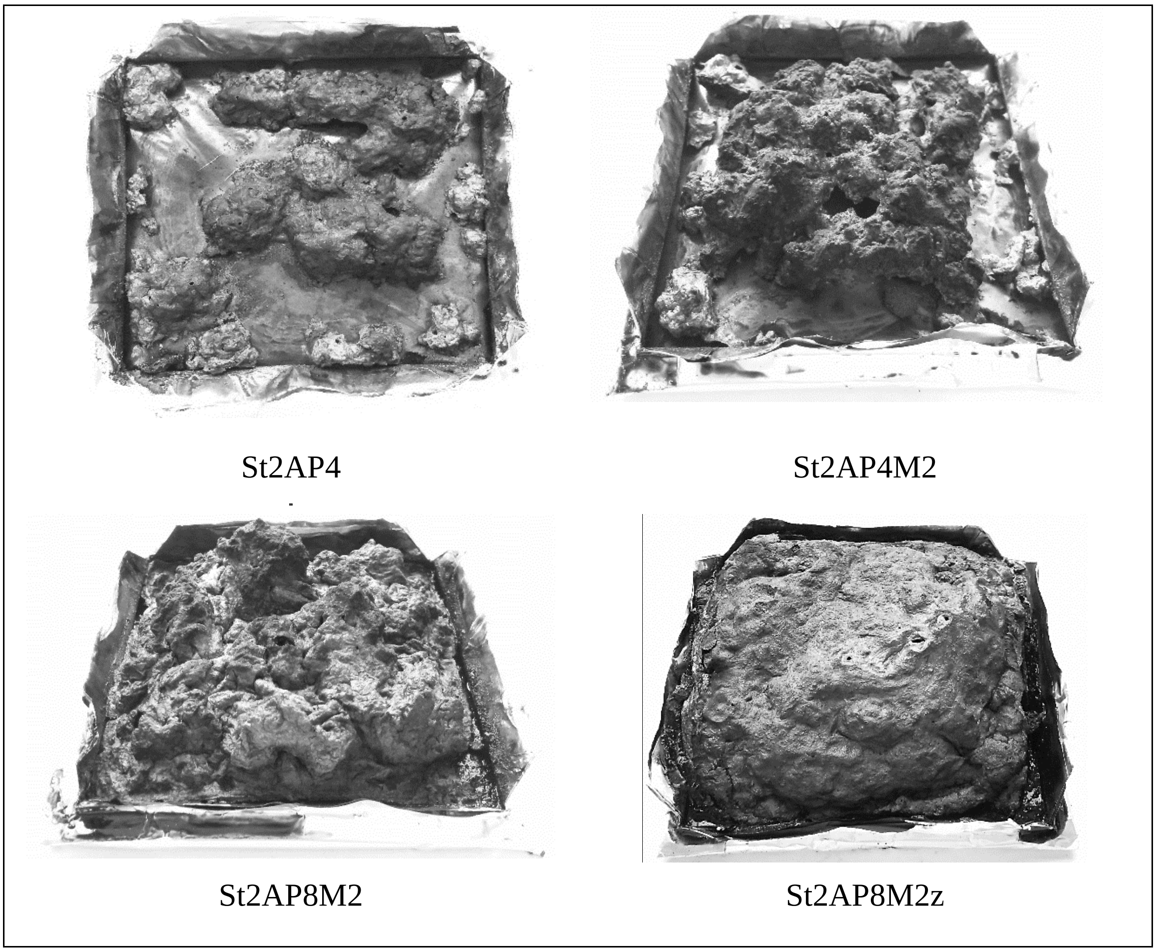
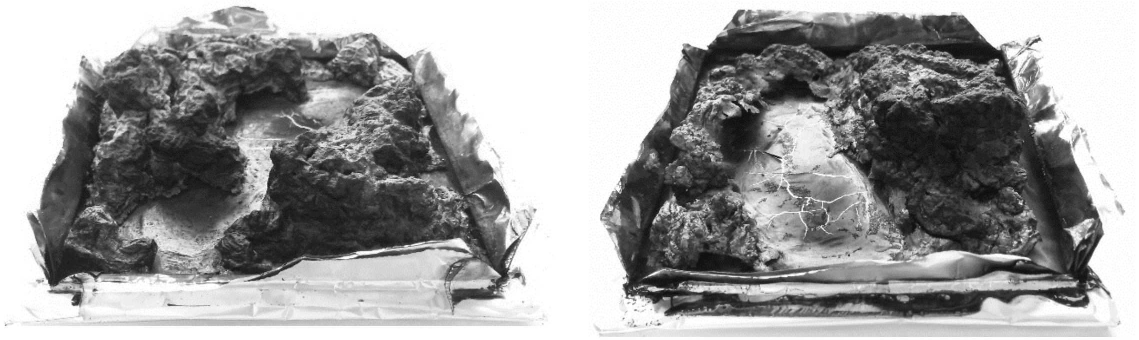


Figure 58: APP and Starch containing specimens residue after cone test.

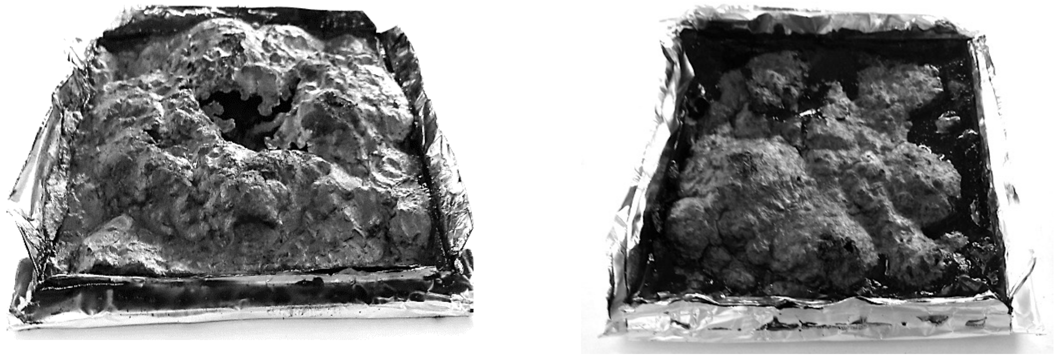


So2AP4 So2AP4M2

So2AP8M2 So2AP8M2z

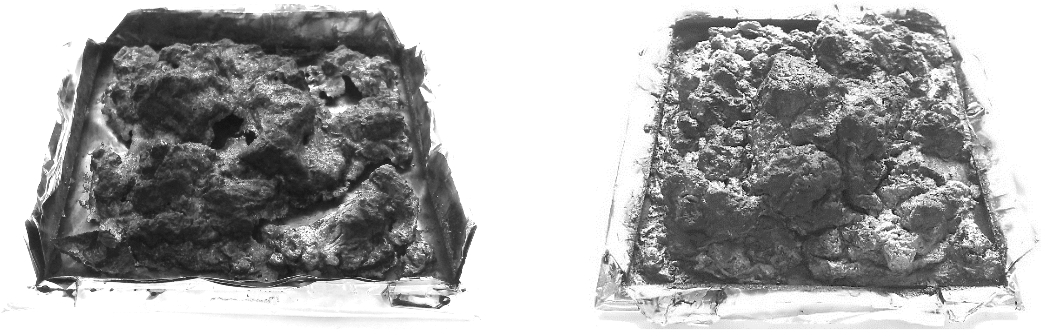
Figure 59: APP and sorbitol containing specimens residue after cone test.

Gp2AP4 Gp2AP4M2

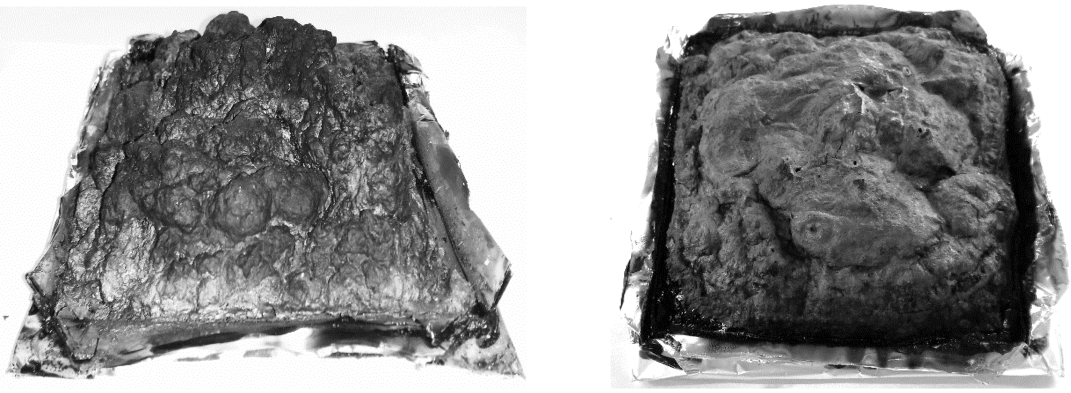


Gp2AP8 Gp2AP8M2

Figure 60: APP and glycerol phosphate containing specimens residue after cone test.

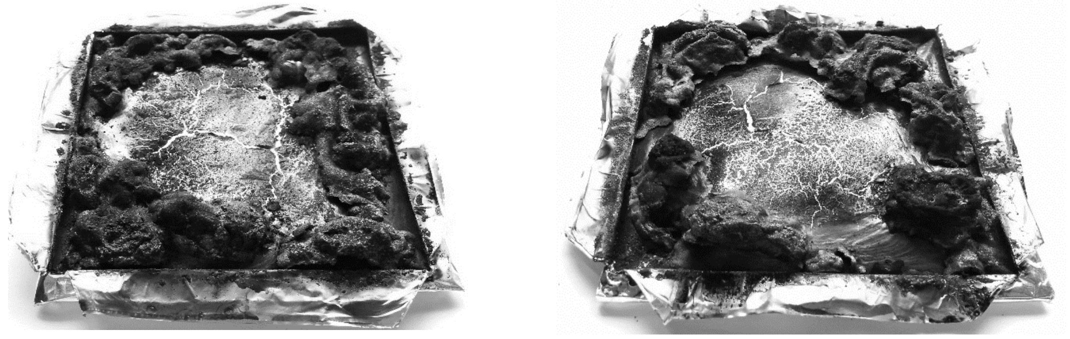


Co2AP4M2 Co2AP8

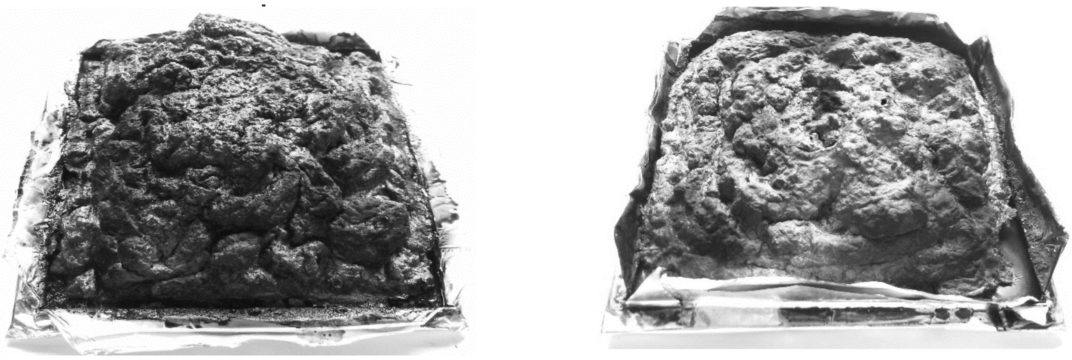


Co2AP8M2 Co2AP8M2z

Figure 61: APP and coffee grounds specimens residue after cone test.



KL2AP4 KL2AP4M2



KL2AP8M2 KL2AP8M2z

Figure 62: APP and Kraft lignin containing specimens residue after cone test.

To sum up, ammonium polyphosphate 8.5% containing compounds showed the best flame resistance properties, giving also a good char formation when a carbonizing agent is present. Moreover, zinc borate improved the char stability in all compounds. The compounds containing 4% APP showed worse results; for all those compounds, the char formation occurred but the char formation wasn't enough to completely cover the material surface and didn't protect it efficiently. In this way, the material kept burning in the areas where the char didn't cover the surface (Figure 58 and Figure 62).

The OP containing compounds showed the worst flame resistance properties producing higher total heat release than pure PLLA. Furthermore, the times to sustain ignition were 40-50 seconds shorter than the control.

Some of the carbonizing agents used in this work were very effective in char formation. Glycerol phosphate was the best in terms of fire extinguishing, giving the lowest total heat release in Gp2AP8M2 (8 MJ/m^2 compared to 70 MJ/m^2 of the control). The other additives, ranked in order of decreasing effectiveness were: starch with 21 MJ/m^2 in St2AP8M2z, sorbitol with 35 MJ/m^2 in So2AP8M2z, Kraft lignin with 51 MJ/m^2 in KL2AP8M2, coffee grounds with 55 MJ/m^2 in Co2AP8M2 and cellulose with 59 MJ/m^2 in Ce2AP8M2z. In parallel, Glycerol phosphate showed the longest time to sustain ignition compared to all the other XAP8M2 compounds, followed by sorbitol, starch, Kraft lignin, and coffee grounds containing compounds. In general, for all carbonizing agents, the presence of zinc borate reduced the time to sustain ignition, making the material starts to burn earlier; but its presence reduced the peak of heat release rate of about 40-50 kW/m^2 compared to 8.5% APP compounds without it.

The Gp2AP8M2 compound showed the lowest total heat release and the highest residue percentage in cone calorimeter test, it self-extinguished in less than five minutes without generating a great amount of char (Figure 60). At the end of the test, a large part of material remained in molten state unlike all other compound that result on rigid carbonaceous char formation.

These results suggested to investigate more in details the decomposition products of the various carbonizing containing compound. The aim of this part of the project was to clarify if they also act in the gas phase by some mechanisms or in the condensed phase by promoting the formation of decomposition products less volatile or less combustible.

In order to investigate these hypotheses, thermogravimetric analysis coupled with infrared spectroscopy and with gas chromatography mass spectroscopy were carried out.

The instrumental parameters used for this technique are reported in methods section. The FTIR analysis of the degradation products of pure PLLA under inert atmosphere (N_2) showed that at the maximum decomposition rate temperature, a mixture of CO, CO2, CH_3CHO, lactide and oligomers is formed. Figure 63 and Figure 64 report the main peaks present in the gas mixture evolved in inert atmosphere.

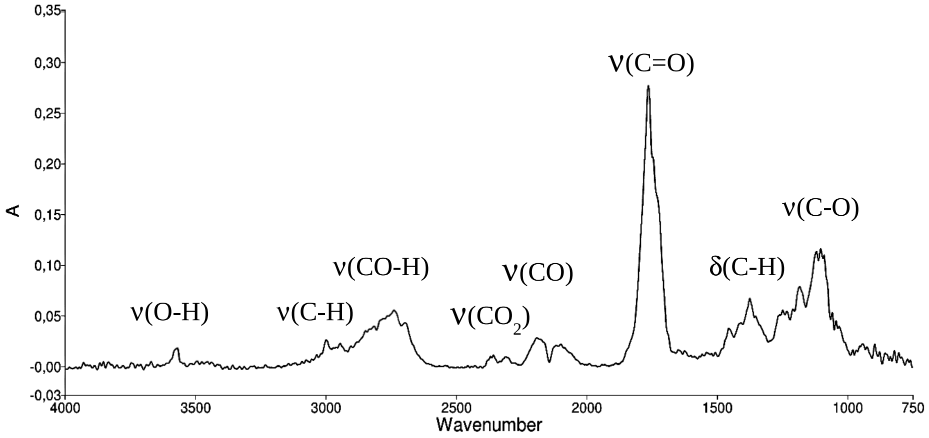


Figure 63: FTIR spectra of decomposition products of PLLA in inert atmosphere at maximum decomposition rate temperature.

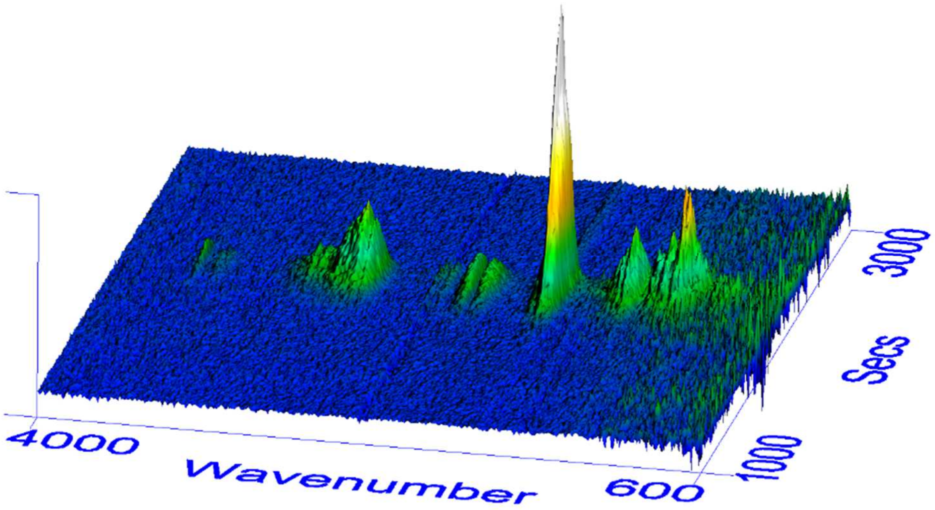


Figure 64: FTIR of evolved decomposition product of PLLA in inert atmosphere.

Peaks at 2180 cm^{-1} and 2115 cm^{-1} are characteristic of carbon monoxide. The peak in the range 2400-2270 cm^{-1} with a maximum at 2350 cm^{-1} is characteristic of carbon dioxide stretching. Peaks at 2740-2700 cm^{-1} and peak at 1760 cm^{-1} are characteristic of aldehydes, stretching of CO-H bonds and stretching of carbonyls group respectively, mainly due to acetaldehyde. The peaks in the range 1100-1050 cm^{-1} are relative to C-O stretching of alcohols (R-OH) and ester (COO-R). The peaks at 1260-1250 cm^{-1} is relative to the C-O stretching between carbonyl carbon and oxygen in ester groups (CO-OR). The small peak at 3575 cm^{-1} is related to the stretching of O-H bond.

The TGA-FTIR analysis of pure PLLA was then performed in air and Figure 65 shows the results. The peaks relative to carbon dioxide (2400-2250 cm^{-1}) were much more intense, respect to the same peaks obtained in inert atmosphere (Figure 64), whereas the peaks relative to the CO-H stretching of aldehyde (2740-2700 cm^{-1}) have a much lower intensity. Moreover, the peaks at 1180 cm^{-1} relative to C-O stretching of alcohols shows increased intensity and a new peak at 3700 cm^{-1} relative to the stretching of alcohol O-H bond appeared for the first time. A further increase of the peaks around 3000 cm^{-1} can be related to the stretching of O-H bond of carboxylic acid groups. The change of the degradation product pattern can be explained by the oxidation of the aldehydes species by the oxygen molecules in air. Aldehydes are fully oxidized into carbon dioxide, with a very limited conversion to their correspondent acids. In addition, the simultaneously presence of acid groups and hydroxyls group can be attributed to the formation of linear PLLA oligomers such as dimer, trimer but also lactic acid itself.

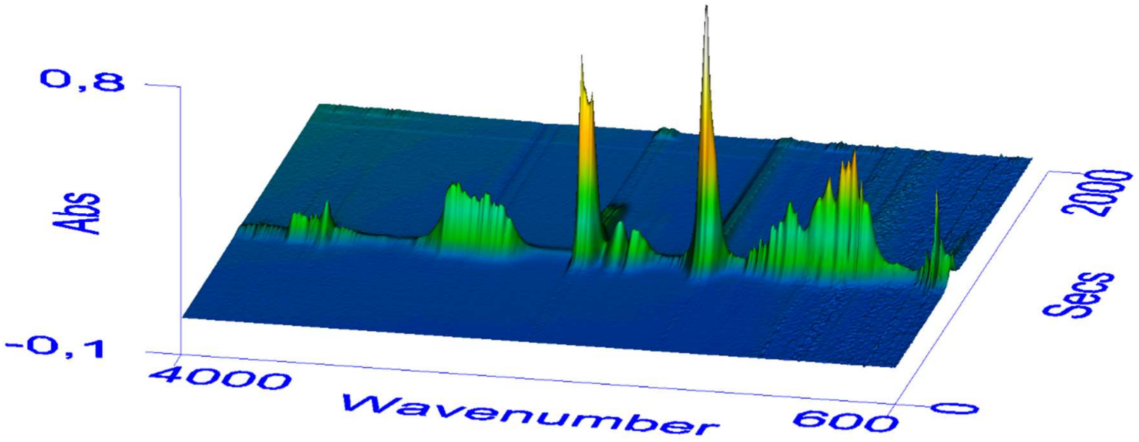


Figure 65: FTIR of evolved decomposition product of PLLA in air.

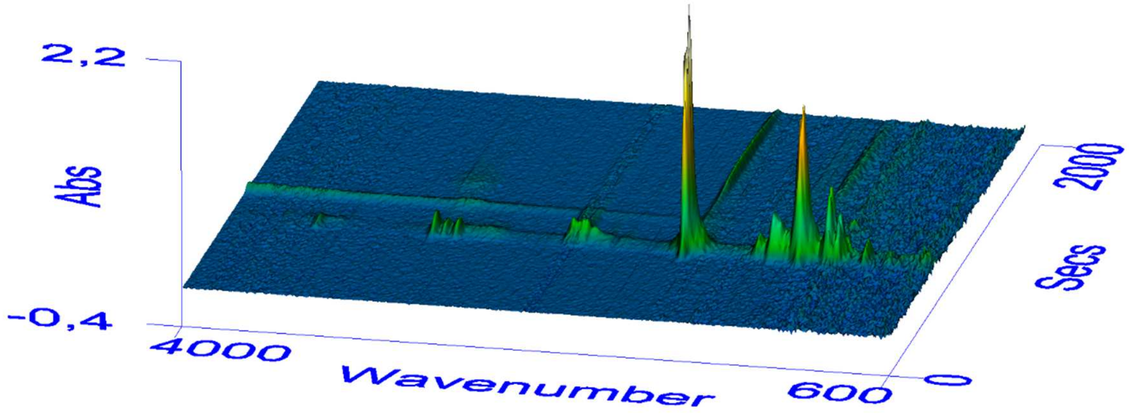


Figure 66: FTIR of evolved decomposition products of So2OP8M2 in inert atmosphere.

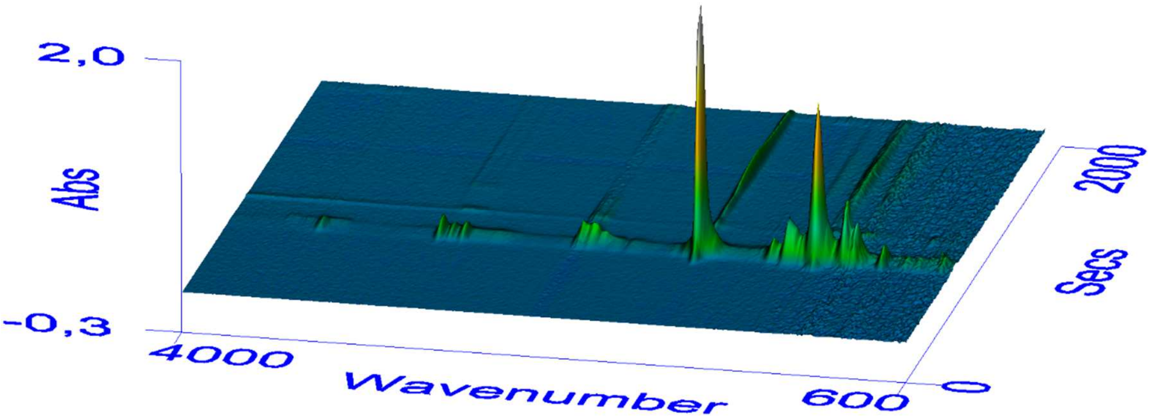


Figure 67: FTIR of evolved decomposition products of So2OP8M2 in air.

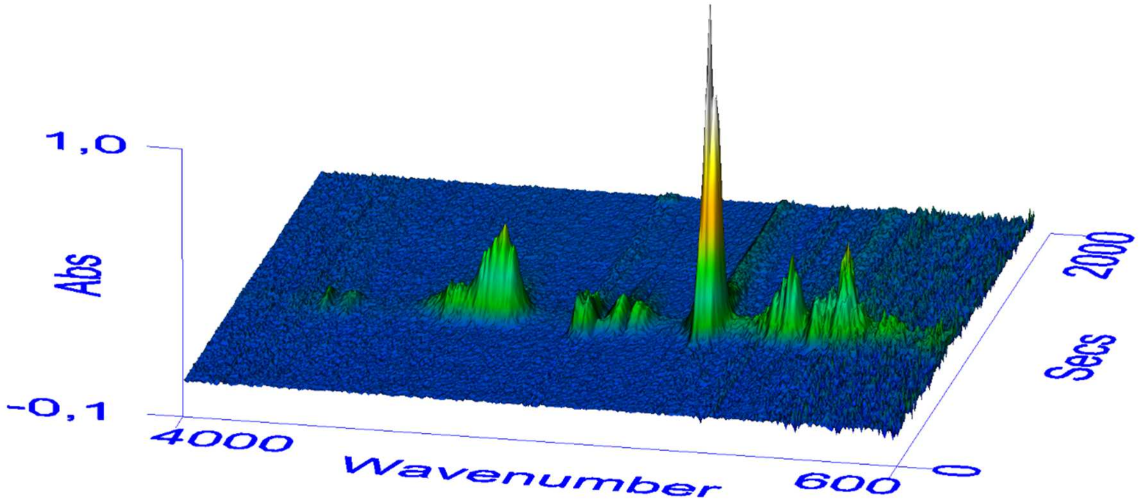


Figure 68: FTIR of evolved decomposition products of So2AP8M2 in inert atmosphere.

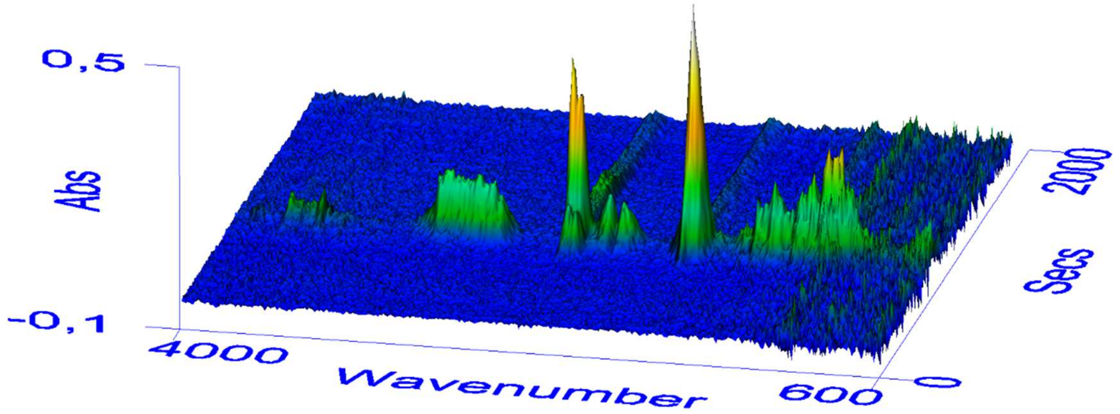


Figure 69: FTIR of evolved decomposition products of So2AP8M2 in air.

Sorbitol containing compounds with ammonium diethyl phosphinate OP and ammonium polyphosphate APP (So2OP8M2, So2AP8M2) were analysed with TGA-FTIR in inert atmosphere and in air. The results are reported in Figure 66 and Figure 68 for inert atmosphere and Figure 67 and Figure 69 for air, respectively. Their spectra at maximum degradation rate are compared with the pure PLLA in Figure 70 and Figure 71.

The presence of aluminium diethyl phosphinate leads to the formation of lactide as main degradation product both under inert atmosphere and in air (Figure 70 and Figure 71). The peak at 1790-1785 cm^{-1} is relative to the stretching of carbonyls group in the lactide ring, while the peak at 1250-1235 cm^{-1} is the characteristic peak of stretching between the carbonyl carbon and the oxygen in the ester groups. The production of lactide as main degradation product in presence of OP, confirmed the hypothesis that aluminium ions act as depolymerisation catalyst promoting the decomposition of the polymer by cyclization reactions. Moreover, the presence of air didn’t affect this mechanism so the lactide evolved as the main fuel.

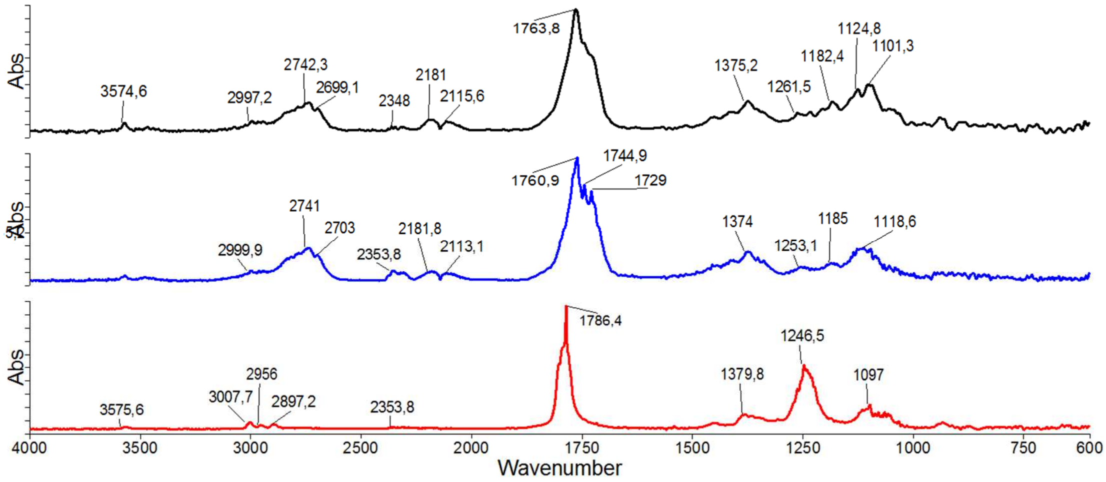


Figure 70: FTIR spectra of decomposition products of PLLA (black), So2OP8M2 (red) and So2AP8M2 (blue) at maximum decomposition rate in inert atmosphere.

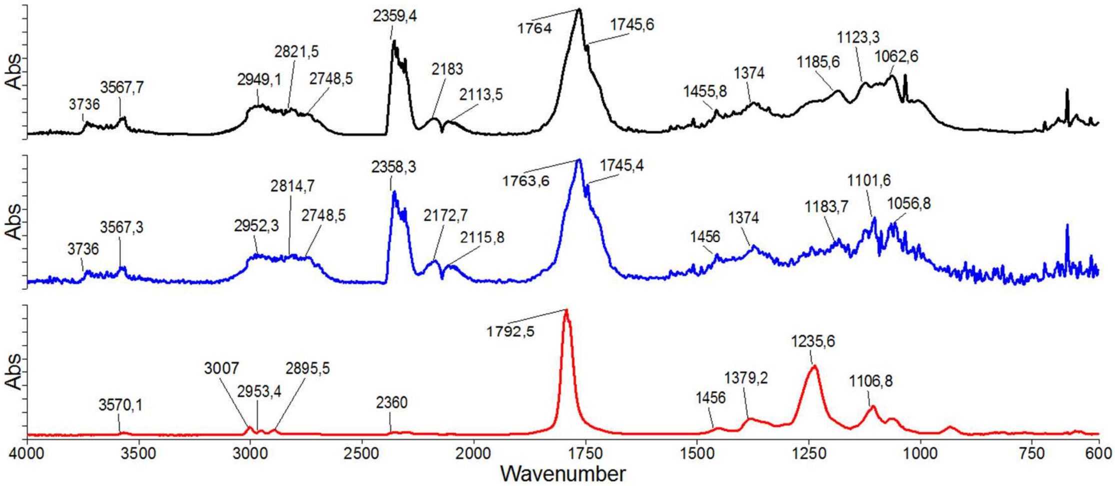


Figure 71: FTIR spectra of decomposition products of PLLA (black), So2OP8M2 (red) and So2AP8M2 (blue) at maximum decomposition rate in air.

The ammonium polyphosphate containing compound So2AP8M2 showed a degradation pattern similar to pure PLLA both in inert atmosphere and in air (Figure 70 - Figure 71). Under inert atmosphere, a minor difference was observed, mostly relative to a slightly increase of carbon dioxide and different carbonyls peak (1745/1729 cm^{-1}).

The same analysis was carried out for the other carbonizing agents. In agreement with the observation for the sorbitol containing formulations, the FTIR spectra shows the same decomposition products obtained from pure PLLA, both in air and in inert atmosphere. For this reason, they have not been reported. The TGA-FTIR analyses leaded to identify the formation of lactide as main decomposition product of aluminium diethyl phosphinate containing compound. Unfortunately, these analyses didn’t provide interesting information about the action of ammonium polyphosphate and carbonizing agents. This results suggested to consider that their ways of action is active solely in the condensed phase. However, the excellent fire resistance observed for the Gp2AP8M2 formulation in cone calorimeter test was not fully understood yet. TGA-GC/MS analyses were carried out in order to obtain more information about the nature of the various decomposition products.

The TGA-GC/MS analyses were performed on PLLA, So2AP8M2, St2Ap8M2, Gp2AP8M2, Co2AP8M2 and KL2AP8M2 compounds. 250 μL of the decomposition product gas mixture evolved in air at max decomposition rate (370-380°C), were collected and analysed. The instruments parameters and methods used are reported in the method section. The mass spectrometer detector used had a cut off at 54 m/z and the fragments under this value could not be detected. Acetaldehyde is one of the main aldehydes formed by the decomposition of PLLA but along with carbon dioxide (44 g/mol) and carbon monoxide (28 g/mol), they remained not quantified because of the limit mass detection of the mass spectrometer.

The action of the intumescent system additives in the condensed phase was studied by detecting heavier fragments arising from oligomers or aromatized species.

The gas chromatography column available had limited separation capability. For such reason, the decomposition species produced were eluted rapidly and remained overlapped in the chromatogram. They gave rise to a narrow peak as shown in Figure 72. Fortunately. the mass spectra were not too complex to investigate and interesting results have been obtained.

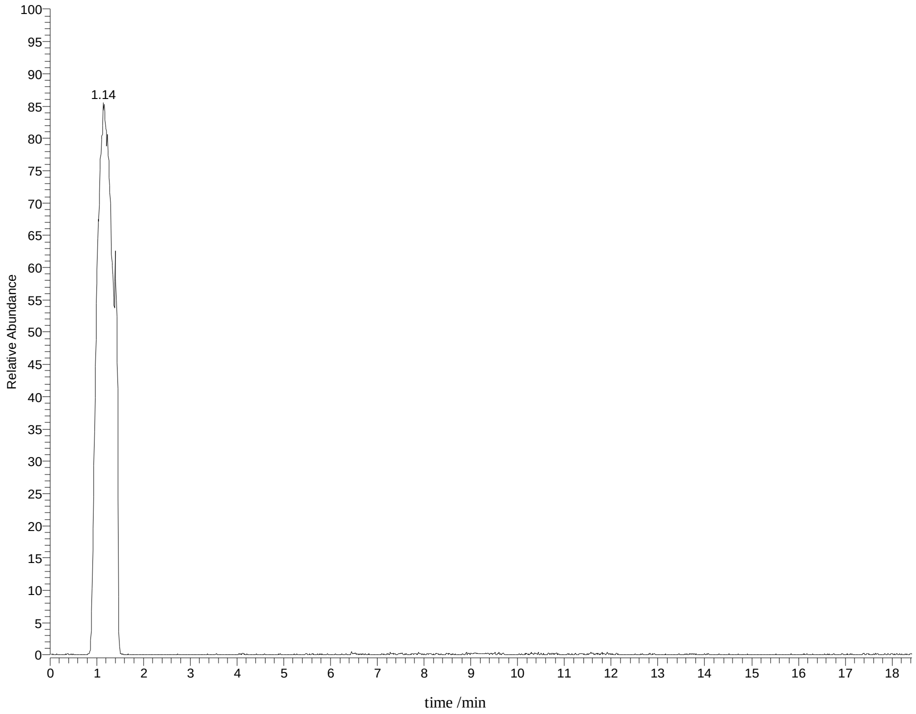


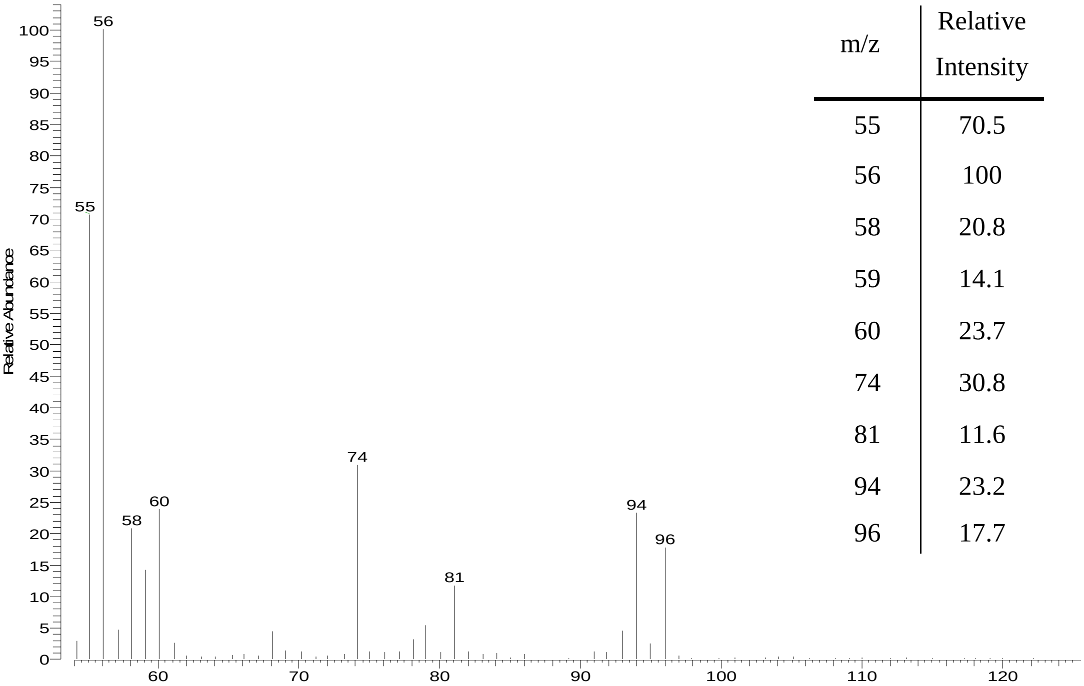
Figure 72: Chromatogram of PLLA decomposition products.

Pure PLLA decomposition products mass spectrum is shown in Figure 73. The main fragmentation products detected over 54 m/z are listed below in order of decreasing relative intensity:

- 56 m/z relative to C_3H_4O molecular ion (methylketene and 2-propenal).
- 55 m/z relative to C_3H_3O radical ion (acrylic acid after the loss of OH group and 2-propenal after the loss of H).
- 74 m/z relative to $C_3H_6O_2$ molecular ion (propionic acid, and a-hydroxy propionaldehyde).
- 60 m/z relative to $C_2H_4O_2$ molecular ion (acetic acid)
- 94 m/z not well identified C_6H_6O (phenol) or/and C_7H_{10} or/and $C_8H_{12}O_5$ double charged molecular ion.
- 58 m/z relative to C_3H_6O molecular ion (propionaldehyde).
- 96 m/z relative to C_6H_8O molecular ion (molecule resulting from the aldol condensation between propionaldehyde and 2-propenal).
- 59 m/z relative to $C_2H_3O_2$ molecular ion (acetate).
- 81 w/z relative to $C_6H_{10}O_5$ molecular ion double charged (linear dimer).

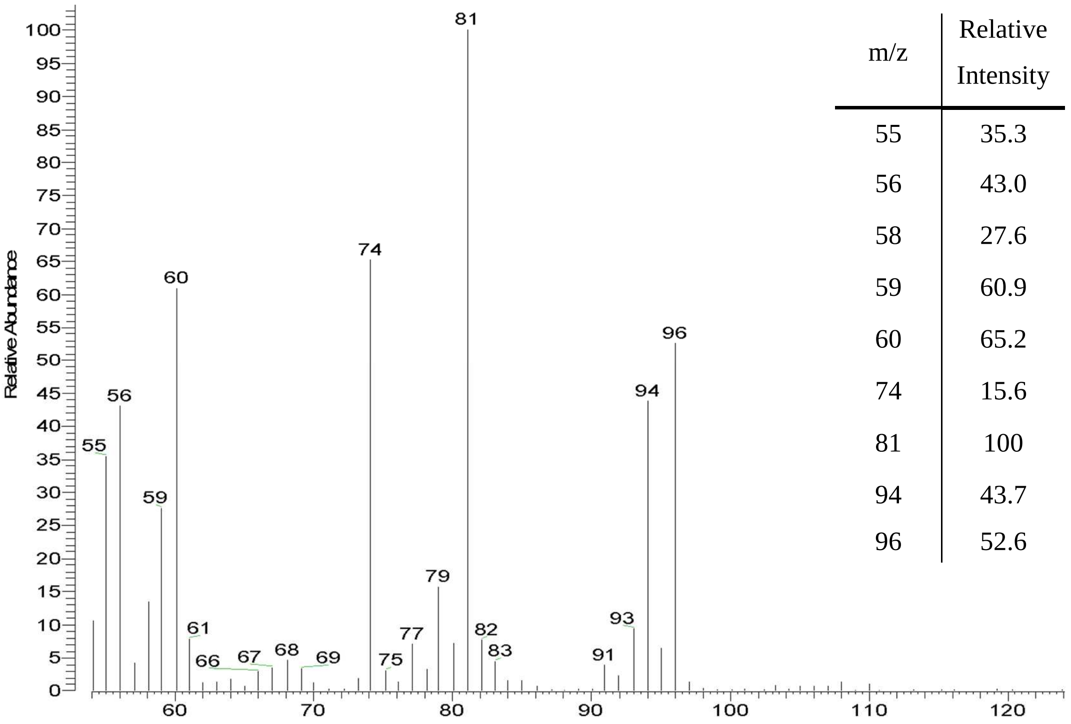
The peaks at 55, 56, 58, 59, 60 and 74 m/z are relative to the presence of aldehydes and their relative acids, as confirmation of the results yet seen for the TGA-FTIR analysis performed in air.

The peak at 81 arises from the dimer and the peaks at 94 and 96 arise from the aldol condensation and dehydration of the aldehydes, catalysed by the presence of the acid species such as acetic acid, acrylic acid and propionic acid. No other peak have significant intensity at m/z values larger than 96.



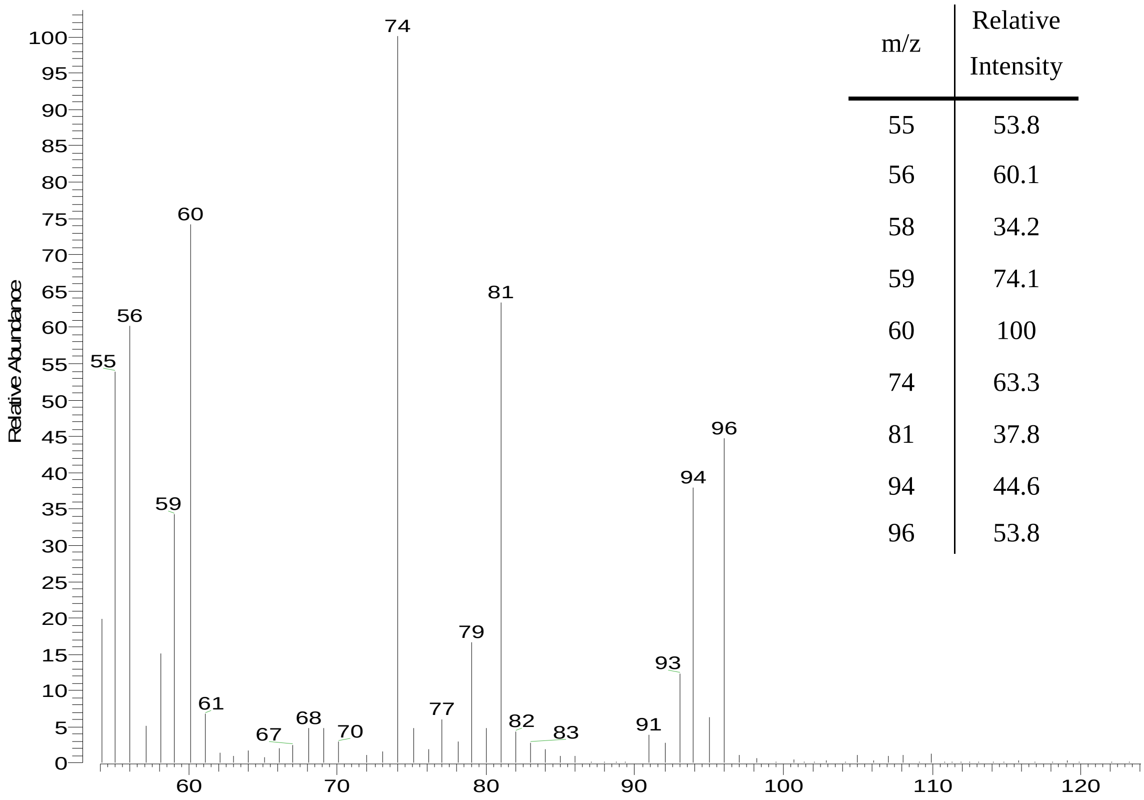
m/z	Relative Intensity
55	70.5
56	100
58	20.8
59	14.1
60	23.7
74	30.8
81	11.6
94	23.2
96	17.7

Figure 73: Mass spectrum of pure PLLA degradation products.



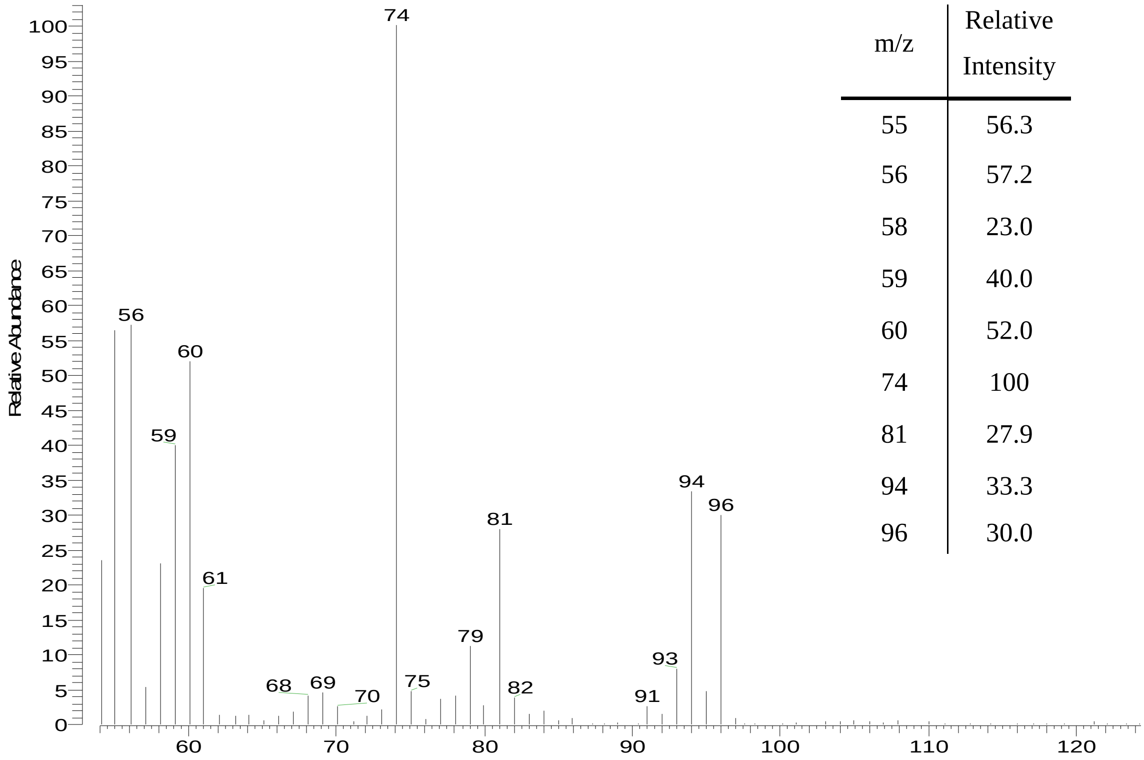
m/z	Relative Intensity
55	35.3
56	43.0
58	27.6
59	60.9
60	65.2
74	15.6
81	100
94	43.7
96	52.6

Figure 74: Mass spectrum of starch containing compound St2AP8M2.



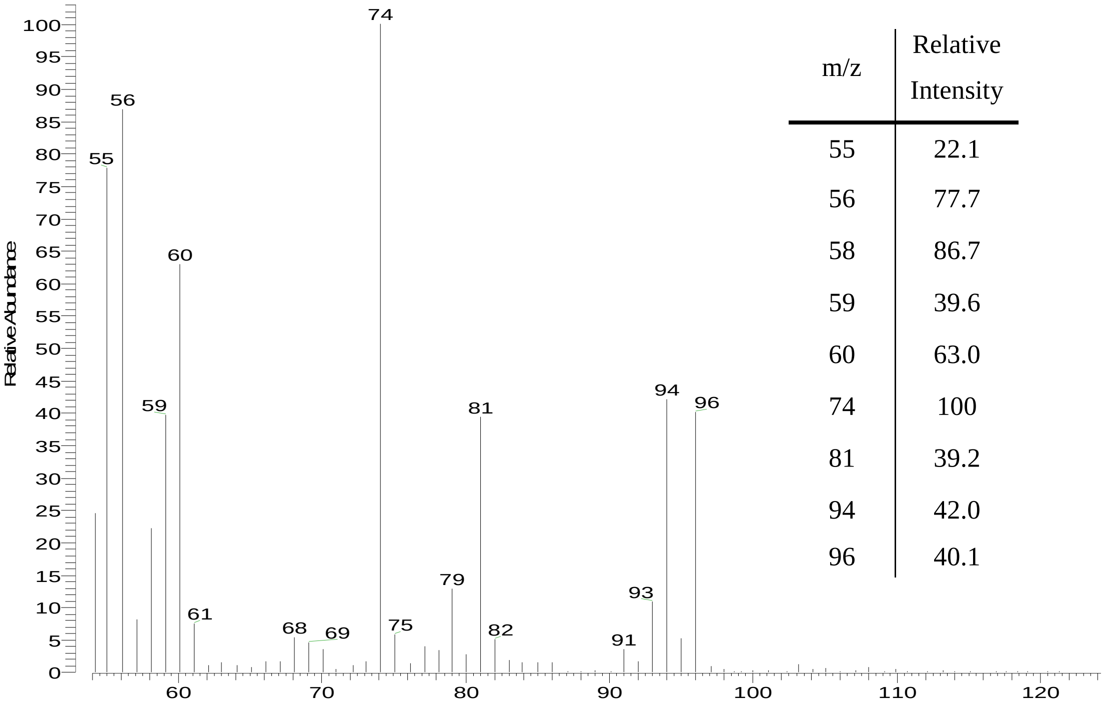
m/z	Relative Intensity
55	53.8
56	60.1
58	34.2
59	74.1
60	100
74	63.3
81	37.8
94	44.6
96	53.8

Figure 75: Mass spectrum of sorbitol containing compound So2AP8M2.



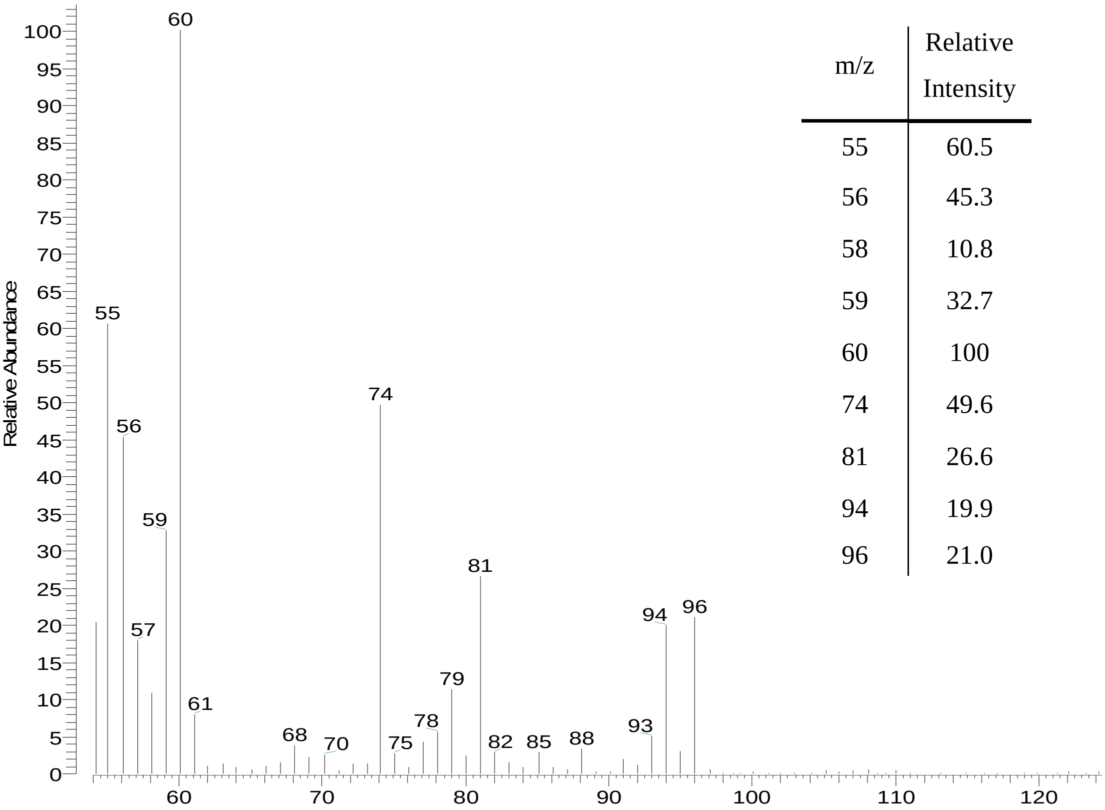
m/z	Relative Intensity
55	56.3
56	57.2
58	23.0
59	40.0
60	52.0
74	100
81	27.9
94	33.3
96	30.0

Figure 76: Mass spectrum of coffee grounds containing compound Co2AP8M2.



m/z	Relative Intensity
55	22.1
56	77.7
58	86.7
59	39.6
60	63.0
74	100
81	39.2
94	42.0
96	40.1

Figure 77: Mass spectrum of Kraft lignin containing compound KL2AP8M2.



m/z	Relative Intensity
55	60.5
56	45.3
58	10.8
59	32.7
60	100
74	49.6
81	26.6
94	19.9
96	21.0

Figure 78: Mass spectrum of glycerol phosphate containing compound Gp2AP8M2.

The mass spectra of ammonium polyphosphate containing compounds with carbonizing agents show a different distribution of the decomposition products respect pure PLLA.

Starch containing compound has the main intensity peak at 81 m/z relative to the presence of the dimer (Figure 74), followed by the peaks at 74 m/z relative to propionic acid and the peak at 60 m/z relative to acetic acid. Moreover, the peaks relative to the condensed aldehyde species at 94 and 96 m/z are increased.

The main peaks seen for pure PLLA at 55 and 56 m/z species, related to the acrylic acid and 2-propenal, have lower intensity. These light molecules in presence of APP are less favoured and this behaviour can be related to the formation of less volatiles species in the condensed phase, where these molecules can undergo cross-linking and aromatization reactions that maintain them in the condensed phase. Moreover, the increase of the acid species produced can act in synergy with the intumescent system improving the char formation. The sorbitol, glycerol phosphate and Kraft lignin containing compounds have the main intensity peak at 74 m/z relative to propionic acid. The 60, 81, 94 and 96 m/z peaks have the same intensity for all these compounds, even if it was slightly decrease respect the 56 and 55 m/z peak. In particular, their relative intensity is the highest in starch containing formulation, followed by the sorbitol (Figure 75), coffee grounds (Figure 76) and Kraft lignin (Figure 77) containing compounds where the ratio is the lowest in comparison to the other carbonizing agent.

Glycerol phosphate containing formulations have the highest intensity peak at 60 m/z relative to acetic acid (Figure 78). The production of acetic acid in a relatively high amount can be considered as one of the reasons why this compound showed high fire resistance in cone calorimeter, in addition to the highest time to ignition and the highest residue percentage.

6 Experimental section

6.1 Compounding

The materials compounding was carried out in a co-rotative twin screw extruder Coperion ZSK 18ML (Figure 80), which has two screw with 18 mm of diameter and length 40 L/D. Screw profiles has different section for melting, mixing and degassing as show in Figure 79.

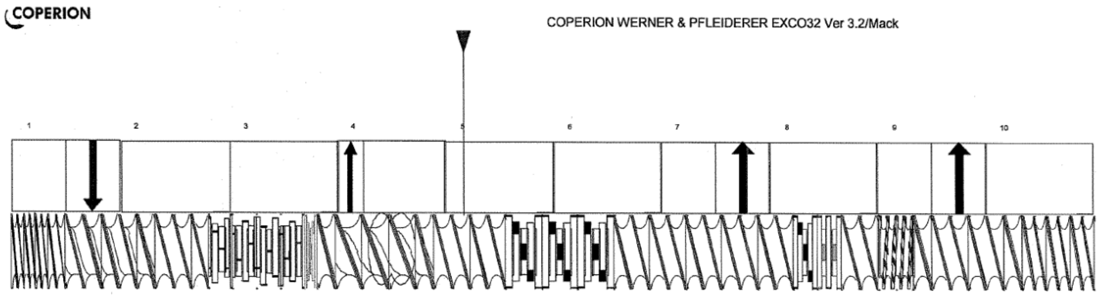


Figure 79: Section profiles of the extruder screws.

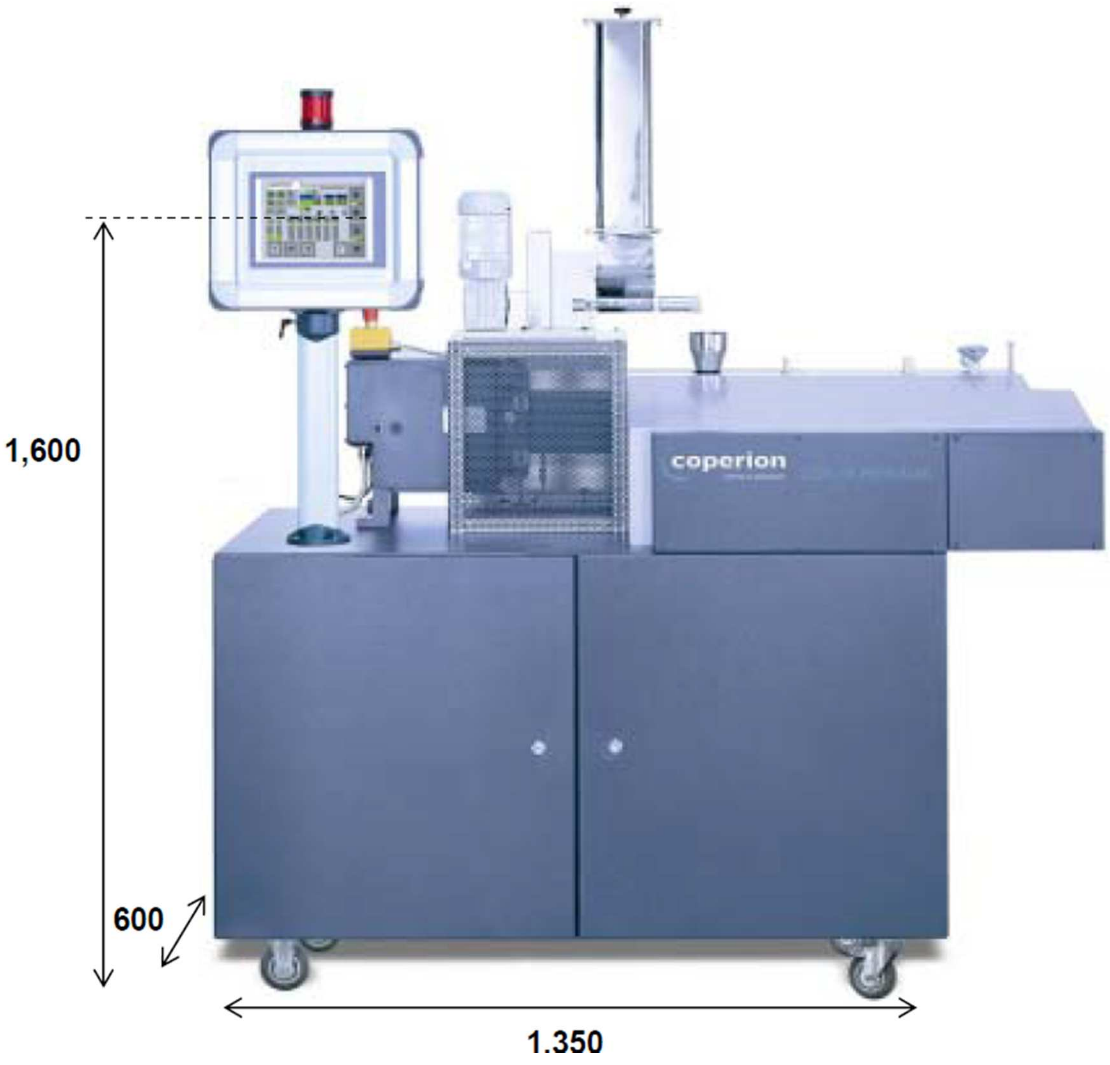


Figure 80: Coperion ZSK co-rotative twin screw extruder.

The extruder barrel is divided into seven sections each with a separate temperature controller, in order to design a suitable temperature profile for the compounding process to be carried out.

The temperature profiles used for compounding the different formulations are reported in Table 7. Screw rotation speed was set at 250 rpm for all the compounding tests.

The residence time of compounds under this condition was about 20-30 seconds and was measured by spiking a small amount PLA yellow masterbatch in the main feed throat.

Table 7: Temperatures of the screws sections.

Section	1	2	3	4	5	6	7
Temperature °C	170	175	180	185	185	180	175

6.2 Injection moulding

The injection moulding of the material was performed with a Negri Bossi VE 70 240 injection moulding machine. The samples were moulded into different shapes specimens:

- Dog-bone shape specimen according to ISO 294-1 and ISO 527-2.
- Square plates with thickness of 2 mm according to ISO 294-3.
- Square plates with thickness of 3 mm according to ISO 294-5.

Temperature profiles suitable to injection moulding PLLA were used (150-190°C), and in order to obtain relatively fast cycles of moulding, the mould temperature was set to 30°C. A compete cycle of moulding took place in 1 minutes for the dog bone specimens and square plate 3 mm thick, while 45 seconds for square plate 2 mm thick.

The parameters related to the screw dosage, screw injection velocity, screw pressure and post pressure were adjusted to obtain the specimens free from defects.

7 Conclusions

New eco-friendly intumescent polylactic acid based materials have been developed, using low loads of halogen-free, not toxic and biodegradable additives (6, 10 and 14%). Bio based and biodegradable carbonizing agents such as starch, sorbitol, coffee grounds, glycerol phosphate, cellulose and Kraft lignin have been tested (2%), in synergy with different amount of ammonium polyphosphate (4 and 8.5%), and melamine cyanurate (0 and 2%). All carbonizing agent containing compounds tested, achieved V-0 UL94 classification except St2AP8M2z, Co2AP4M2 and KL2AP4. V-0 UL94 classification is the best rating class of the test and is required for material application in strict contact with electronic circuits. Moreover, the LOI test results showed for all these latter compounds a self-extinguishes behaviour in air in case of fire. Starch containing compounds showed LOI values over 32% with a maximum value of 37.5% achieved by St2AP8M2z. Sorbitol containing compounds showed LOI values over 36% with a maximum value of 48.5% achieved by So2AP8M2z. Glycerol phosphate containing compounds showed LOI values over 42% with a maximum value of 50.3% achieved by Gp2AP4M2. Coffee grounds containing compounds showed LOI values over 31% with a maximum value of 53% achieved by Co2AP8M2z. Kraft lignin containing compounds showed LOI values over 29% with a maximum value of 34.6% achieved by KL2AP8M2z. The cellulose containing compound (Ce2AP8M2z) reached a LOI value of 37.6%. The presence of zinc borate increased the flame resistance of the materials yielding the highest LOI values.

Carbonizing agent free compounds did not reach V-0 or V-1 UL94 classification, and therfore are not suitable materials for electric and electronics applications. In particular, AP8M2, AP8EG2 andAP8CC2 showed no rating in UL 94 test and they showed self-sustaining behaviour with LOI values under 27%, whereas talc, clay and zinc borate containing compounds achieved only V-2 classification.

All carbonizing containing compounds achieved a glow wire flammability index (GWFI) higher than 950°C and a glow wire ignition temperature equal or higher than 775° except St2AP8M2z, reaching a GWIT of 750°C. A GWFI of 850°C is required for insulating materials in unsupervised appliances carrying a current higher than 0.2 amperes. A GWIT of 750° is required for supervised appliances carrying a current higher than 0.5 amperes. On the other hand, a GWIT of 775°C and V-1 classification is required for unattended appliances carrying a current higher than 0.2 amperes.

The carbonizing agent containing compounds showed better results in terms of fire resistance due to a more efficient char barrier formation, as it can possible to see from the cone calorimeter test results. Excellent flame resistance properties were obtained in the presence of carbonizing agents and 8.5% of ammonium polyphosphate APP. According to LOI values, the best results in terms of total heat release and peak of heat release rate were obtained with the further presence of zinc borate. The 4% APP containing compounds showed worse results in term of fire resistance respect to the compounds with 8.5% of APP; for all those compounds, the char formation occurred but it wasn't enough to completely cover the material surface and didn't protect it efficiently during the cone calorimeter test.

All diethyl aluminium phosphinate containing compounds showed a self-sustaining behaviour in air in case of fire obtaining LOI values under 27%, moreover the cone calorimeter test showed higher total heat release and higher peak of heat release rate respect pure PLLA.

The material decomposition and the decomposition products have been investigated in order to identify the main way of actions of these intumescent systems. It was seen that additives more reactive such as sorbitol and glycerol phosphate lead to obtain the highest results in flame resistance properties. Indeed they act as dripping agents as well as char promoters, producing higher amount of acetic acid and propionic acid that are able to improve the char formation by acting as acid sources catalysing the aromatization reactions. The presence of aluminium diethyl phosphinate favoured the lactide production increasing the PLLA depolymerisation, these molecules leave earlier and easily the condensed phase, and they burn faster respect the decomposition products generated in pure PLLA.

The mechanical properties of the additivated PLLAs arising from the tensile tests, showed in general a decrease of the maximum stress respect the pure PLLA. This behaviour is enhanced by species with higher content of hydroxyl group such as glycerol phosphate and sorbitol, where the specimens broke before reaching the yielding in most of them. Sorbitol containing compounds showed a decrease of the maximum stress around 70-50% respect to the control (50 to 35 MPa respect 70 MPa of the PLLA), glycerol phosphate containing compound showed a decrease of the maximum stress, the values reached the 70-57% of the control (50 to 40 MPa respect 70 MPa of the PLLA).

In the same way, the elongation at break in sorbitol and glycerol phosphate containing compounds decreased leading to an increase of the brittleness of the material. The elastic modulus remained close to the control value giving the possibility to use these materials in applications where the final product is subject to lower tensions respect to the maximum stress reached by the materials.

Additives less actives showed an elongation at break equal or higher than pure PLLA, as seen in presence of cellulose, coffee grounds and Kraft lignin containing compounds, where in some cases the elongation at break is double or higher.

Indeed KL2AP8, KL2AP8M2 and KL2AP8M2z showed an elongation at break close to 6% respect to 3.6% of pure PLLA, and the elastic modulus increased along the series from 3.9 to 4.2 GPa respect to 3.7 GPa of the control. The yielding stress values are lower respect to the control but are the highest compared to all the other carbonizing agents tested, showing a decrease of the value that reached the 57-81% of the control.

Co2AP8 and Co2AP8M2 showed an elongation at break double or higher, 8.6% and 7.2% respectively and an elastic modulus of 4.1 GPa and 3.8 GPa.

These results hold great promise for innovative products and completely novel applications because the good flame resistance properties obtained with relative low loads of bio-based and environmentally friendly additives. Moreover, the compounding techniques used in this work reflect the production chain of the nowadays plastics processing industry, involving the use of a co-rotative twin-screw extruder and an injection moulding machine. The use of these techniques leaded to obtain materials with properties close to a real materials application scenario.

However, the lack of data in scientific publications, that are strictly comparable to this work, make not possible a comparison with the state of art for intumescent PLLA based materials. Indeed, there are very few publications concerning the processing of intumescent PLLA based materials with these latter processing techniques, especially injection moulding, and no one is focused on bio-based and environmentally friendly intumescent additives at low concentrations as on this work.

A fortiori, the results arising from this research can be considered innovative and can be very promising as a reference to comparison with further research works, especially to comparing the mechanical properties.

Further developments based on this research work can be focused to improve the mechanical properties of the best formulations prepared to match the market requirements where the material is applied in products in strict contact with relatively high heat source, in particular where the temperature are close to the glass transition temperature of the materials or 10-20°C higher. Preliminary differential scanning calorimetry tests (DSC), not reported in this work, showed glass transition temperatures of these materials close to the control (45-55°C). In order to increase the mechanical properties at those temperatures, an increase of crystallinity or the use of stereocomplex PLA is required. The increase of crystallinity can be attempted by annealing treatments or changing the injection moulding parameters used. Considering that the compounds were injection moulded with a mould at 30°C to obtain a fast cycles, the crystallinity can be improved by increasing the mould temperature. This will lead to longer cycles but the crystallinity can increase as well as the heat deflection temperature (HDT). Using the stereocomplex PLA is possible to achieve glass transition temperatures around 80-90°C, but it is more expensive and the processing of this material requires temperature 50°C higher than PLLA, and the degradation rate of the polymer in presence of the intumescent formulation studied can be increased.

Further studies can be attempted to correlate the loss on the mechanical properties with the degradation of the materials during the compounding processes. Melt flow index test (MFI) or gel permeation chromatography analysis (GPC), can be done for study the decrease of the molecular weight of the material in different extrusion and printing condition, so it is possible to adjust the parameters condition with the aim to reduce the material degradation.

Other tests can be attempted to study the biodegradability of the prepared materials, even if all additives are environmentally friendly the biodegradability can be changed respect to the pure PLLA.

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