



PLA composites: From production to properties[☆]



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ARTICLE INFO

Article history:

Received 17 January 2016
Received in revised form 22 March 2016
Accepted 4 April 2016
Available online 13 April 2016

Keywords:

PLA - Poly(lactic acid)
Composites
Fibers
Fillers
Calcium sulfate anhydrite
(Nano)composites
Production
Properties

ABSTRACT

Poly(lactic acid) or polylactide (PLA), a biodegradable polyester produced from renewable resources, is used for various applications (biomedical, packaging, textile fibers and technical items). Due to its inherent properties, PLA has a key-position in the market of biopolymers, being one of the most promising candidates for further developments. Unfortunately, PLA suffers from some shortcomings, whereas for the different applications specific end-use properties are required. Therefore, the addition of reinforcing fibers, micro- and/or nanofillers, and selected additives within PLA matrix is considered as a powerful method for obtaining specific end-use characteristics and major improvements of properties.

This review highlights recent developments, current results and trends in the field of composites based on PLA. It presents the main advances in PLA properties and reports selected results in relation to the preparation and characterization of the most representative PLA composites. To illustrate the possibility to design the properties of composites, a section is devoted to the production and characterization of innovative PLA-based products filled with thermally-treated calcium sulfate, a by-product from the lactic acid production process. Moreover, are emphasized the last tendencies strongly evidenced in the case of PLA, i.e., the high interest to diversify its uses by moving from biomedical and packaging (biodegradation properties, “disposables”) to technical applications (“durables”).

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Abbreviations: All, CaSO₄ anhydrite II; All_c, All coated; All_{CB5}, All coated by Biomax[®] Strong 100; All_{III}, CaSO₄ anhydrite III; APP, Ammonium polyphosphate; ATH, Aluminium trihydroxide; BCNW, Bacterial cellulose nanowhiskers; BCP, Biphasic calcium phosphate; BS, Biomax[®] Strong 100; CB, Carbon black; CF, Carbon fibers; CMF, Cellulose microfibrils; CNTs, Carbon nanotubes; CNW, Cellulose nanowhiskers; CS, Calcium sulfate; DMTA, DMA, Dynamic mechanical (thermal) analysis; DOA, Dioctyl adipate; EG, Expanded graphite; FR, Flame retardant(s), flame retardancy, fire retardant; GF, Glass fibers; GTA, Glyceryl triacetate; HA, Hydroxyapatite; HDT, Heat distortion temperature; HRR, Heat release rate (rate of heat release); IM, Impact modifier(s); LA, Lactic acid; LOI, Limiting oxygen index; MCC, Microcrystalline cellulose; MFI, Melt flow index; MMT, Montmorillonite; M_n, Number average molecular weight; MP, Melamine phosphate; M_w, Weight average molecular weight; NCC, Nano-crystalline cellulose; NFs, Natural fibers; NG, Natural graphite; OMLS, Organomodified layered silicates; PCL, Polycaprolactone; PDLA, Poly(D-lactic acid) or poly(D-lactide); PER, Pentaerythritol; PGA, Polyglycolide; PHA, Polyhydroxyalkanoates; pHRR, Peak of heat release rate; PLA, Poly(lactic acid) or polylactide; PLGA, Poly(lactide-co-glycolide) or poly(D,L-lactide-co-glycolide); PLLA, Poly(L-lactic acid) or poly(L-lactide); POSS, Polyhedral oligomeric silsesquioxanes; PP, Polypropylene; REX, Reactive extrusion; ROP, Ring opening polymerization; RWF, Recycled wood fibers; SA, Stearic acid; sc-PLA, PLA stereocomplexes; SEM, Scanning electron microscopy; T_{5%}, Onset of thermal degradation; TCP, Tricalcium phosphate; T_d, Max. temperature of degradation; TEM, Transmission electronic microscopy; T_g, Glass transition temperature; TGA, Thermogravimetric analysis; T_m, Melting temperature; TTI, Time to ignition; UV, Ultraviolet light.

[☆] This review is part of the *Advanced Drug Delivery Reviews* theme issue on “PLA biodegradable polymers”.

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1. Introduction

The extraordinary growth and interest for the utilization of biopolymers are connected to a big number of factors including consumer demand for more environmentally-sustainable products, the development of new bio-based feedstocks, and especially, to increased restrictions for the use of polymers with high “carbon footprint” of petrochemical origin, particularly in applications such as packaging, automotive, electrical and electronics industry, etc. [1–8]. In this context it is expected that novel technological advances will lead to the biopolymers market boom, not only in the traditional sectors such as packaging, but also in transportation, in the automotive and electronics industry, or in other applications with higher profit potential such as the biomedical field [9–14].

1.1. The emergence of bioplastics

The market of biopolymers is growing every year and important new demands can be expected from applications which offer clear benefits for customers and environment. A 2014 report published by BCC Research has estimated in 2014 the global bioplastic demand at more than 1400 kt (metric kilo tonnes), whereas it is predicted an increasing to about 6000 kt in 2019, which represents a CAGR (compound annual growth rate) of 32.7% for the five-year period, 2014 to 2019 [4]. Furthermore, in correlation with the important demand of bioplastics, it is expected that the global production capacities will increase to more than 7.8 million tonnes in 2019 [15], whereas the biobased/non-biodegradable and biodegradable polymers will represent about 84% and 16%, respectively.

The rapid emergence of bioplastics is one of the major stories of the last decade [4]. Once billed as biodegradable plastics, the theme for renewably sourced plastics has shifted in the recent years to sequestration of CO₂ and to sustainability. In order to maximize the impact of biopolymers, it is noteworthy also mentioning that there is a growing trend to combine the bio-based with petrochemical-based polymers, a key-approach allowing to extend their consumption and market as durable products used in cars, electronics, and elsewhere [16,17]. The focus has shifted to the total “carbon footprint”, and the bio-based polymers not only can replace existing polymers in various sectors, but can also provide new combinations of properties.

Unfortunately, for certain requests such as in packaging or engineering sectors, the biopolymers cannot be fully competitive with polymers from the category of commodity or engineering thermoplastics (e.g. PS, PE, PP, PET, etc.). PLA has good mechanical properties

(particularly, high tensile strength and Young’s modulus, good flexural strength) [18], which are even higher than those of PS, PP, PE, or other polymers. The tensile strength and elastic modulus of PLA are comparable to those of PET, but unfortunately PLA is very brittle, with less than 10% elongation at break and low toughness, which limits its use in applications that need plastic deformation under high stress [19]. For packaging applications, it is stated that PLA films have mechanical properties comparable to those of PET, whereas the lower glass transition temperature is considered a disadvantage, especially in applications (e.g., hot packaging) requiring resistance at high temperature [13]. Regarding the characteristics of films, the gas permeability coefficients to CO₂, O₂, N₂ and H₂O(g) have been reported as being higher than for PET [13,18], therefore these properties need further improvements. The shortcomings or advantages of PLA will be more evident from the next sections of this review.

However, the development of special formulations of biopolymers (the case of PLA) is clearly in its early stages, therefore, a further progress is expected to be made. Currently, many R&D works have as main objective the production—using different techniques, of new grades of biopolymers characterized by improved characteristics (process-ability, higher mechanical and thermal resistance, flame retardancy (FR), tailored electrical properties, long durability and stability, etc.) to allow their utilization in engineering sectors and in applications requiring higher added value. Nowadays, the market turns to more “durable” biomaterials, but on the other hand, the interest for utilization in the pharmaceutical and medical applications (drug delivery systems, healing products and surgical implant devices, orthopaedic devices, bioresorbable scaffolds for tissue engineering and others [9,20,21]) is remaining of high actuality. Nevertheless, it is important to remind that some designed bio(co)polymers and tailored based products could show properties of interest for biomedical applications, such as biocompatibility, biodegradation to non-toxic products, high bio-activity, process-ability to complicated shapes with appropriate porosity, ability to support cell growth and proliferation, also appropriate mechanical characteristics [20,22,23].

1.2. Recent trends for PLA: from biomedical and packaging, to technical applications

Even that a generally recognised definition of the concept “biopolymers” does not exist, we will accept that they are mainly as follows: (a) based on renewable resources and biodegradable; (b) based on renewable resources but not biodegradable; (c) based on fossil resources and biodegradable.

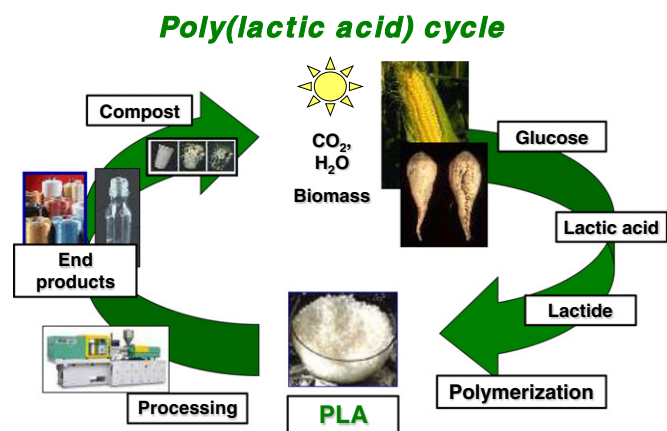


Fig. 1. PLA life cycle starting with corn and sugar-beet; the biological systems use the solar energy by the process of photosynthesis (adapted, from the Ref. [8]).

Bioplastics such as polylactide (PLA), polyhydroxyalkanoates (PHA), thermoplastic starch, bio-polyethylene, bio-polyamides, etc., are polymers that are made from renewable resources. Some bioplastics are also biodegradable (e.g. bio-based PLA, non-renewable polyesters such as PCL (polycaprolactone)) [24,25]. However, following some legislative restrictions, the “biodegradability” at the end-life cycle is a desired condition required by end-users to increase the attractiveness and environmental impact of their products.

Poly(lactic acid) or polylactide (PLA), is industrially obtained respectively, through the polymerization of lactic acid (LA) or by the ring-opening polymerization (ROP) of lactide (the cyclic dimer of lactic acid, as an intermediate) [7,13,26–28]. PLA is not only biocompatible and biodegradable (N.B. under controlled composting conditions), but it is a thermoplastic aliphatic polyester produced from non-fossil renewable natural resources by fermentation of polysaccharides or sugar, e.g. extracted from corn, potato, cane molasses, sugar-beet, etc., therefore allowing the biological cycle to come full circle (Fig. 1) with PLA biodegradation, as well as the photosynthesis process [28,29]. Nowadays, other bio-based sources such as fermentable sugars from non-food cellulosic biomass, agricultural wastes, non-food crops (e.g. switchgrass), etc., are considered as alternative allowing carbon neutral cycles, thus new technological progress is expected from the utilization and diversification of PLA feedstocks [30], other than agricultural foods (i.e. instead of corn-derived dextrose).

Initially, the main uses of PLA have been limited to medical applications such as implant devices, tissue scaffolds, internal sutures, and others, because of polymer high cost, low availability and limited molecular weight [7,31–33]. In the last years, new techniques which allow the economical production of high molecular weight PLA have decisively contributed to its larger utilization, and PLA has gained enormous attention as an alternative to petrochemical-based synthetic polymers (PET, PS, PE, etc.) in packaging and/or textile sectors [13,34].

Therefore, following the interest for the utilization of this biopolyester it is predicted a rapid growth in PLA production global capacities (Fig. 2) to about 800 kt/year [35], whereas the main applications will be represented by food and beverage packaging, textiles, “durables” such as engineering components for automotive and electronics, and so on [2,3,13,26,36–40]. The last trends show clearly that the growth of PLA production indeed comes from the demand of long-lasting bioplastics in industry sectors such as electronics and automotive, end-user markets requiring similar performances and processing characteristics that match those of existing polymers, traditionally derived from petroleum or other fossil resources [41,42]. In this context, new PLA based products (composites, nanocomposites, tailored formulations, etc.) with improved performances are needed to satisfy the specific application requirements.

Regarding the biomedical sector, at the present time the demands of market for special PLA based products exist but still remain much smaller (i.e., with respect to the packaging materials), therefore it is assumed that the realization of new PLA formulations with high added value is remaining of high interest. PLA and its copolymers are widely concerned in medicine because they are between the most promising eco-friendly products for use in the human body (nontoxic, biodegradable and bioabsorbable) [9,43].

This review attempts to highlight an insight on the current research, results and key trends in the field of material composites based on PLA. It presents the main developments of PLA properties using traditional reinforcements, micro- and/or nanofillers, specific additives and reports selected results in relation to the preparation and characterization of PLA composites designed with specific end-use properties. On the other hand, it is important to mention that this contribution belongs to a special issue of *ADDR* entitled “*PLA biodegradable polymers*”. By considering the multiple aspects that can be overviewed, it is assumed that some more specific information connected to the properties and utilization of PLA composites in different sectors (e.g., biomedical applications) will be additionally developed by other contributions in the frame of this special issue.

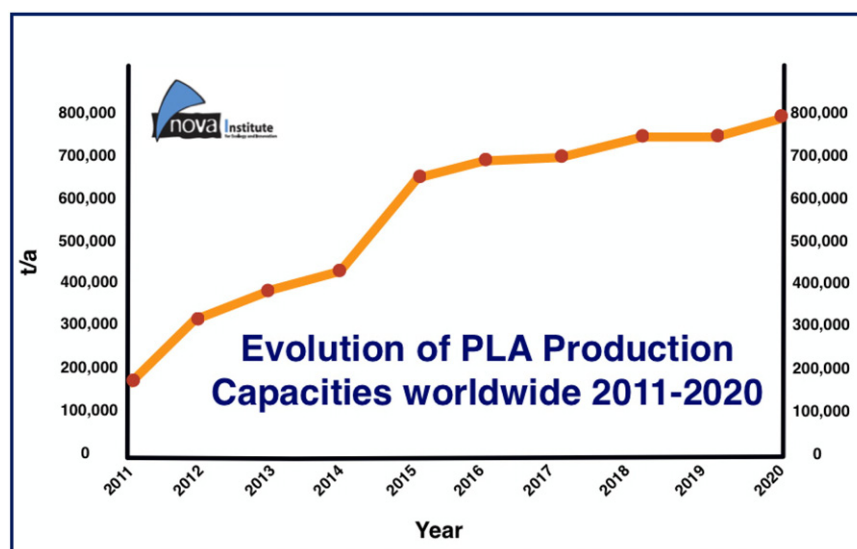


Fig. 2. Evolution of PLA worldwide production capacities (2011–2020) (adapted, source nova-Institute, Ref. [35]).

2. Production of PLA composites

In order to maximize the benefits and versatility of PLA, it is necessary to understand and combine the relationship between the properties of polyester matrix and characteristics of dispersed phases (reinforcing fibers, micro- and nano-fillers, additives, etc.), their compatibility and interactions, stabilizing or degradation effects, influences of manufacturing process on the characteristics of final products, and so forth. This section summarizes the most relevant information and last developments in relation to the PLA as polymeric matrix and is discussing the main techniques used for the production of PLA composites.

2.1. Short overview: production and PLA as polymeric matrix

By considering the production at large industrial scale, PLA is a relatively new polymer because the first full-scale plant capable to produce 140,000 metric tons per year was started in Blair, Nebraska, USA in 2002 [38]. Therefore, PLA needs some time to become an effective key-biopolymer in the market or to be produced in tailored grades and properties, similarly as assortment to the actual engineering or traditional polymers. On the other hand, environmental, economic and safety challenges, have provoked the scientists and industrial producers to partially substitute petrochemical-based polymers with biopolymers, from either categories, biodegradable or non-biodegradable. The interest for “PLA” is clearly attested by an impressive number of scientific papers and reviews [7,13,14,19,26,27,34,44–55] connected to its fabrication, modification and processing.

Firstly, it is noteworthy mentioning that the nomenclature of PLA prepared by following different routes or containing different content of L- and D-enantiomers (isomers) is sometime contradictory [27]. Polymers derived from lactic acid (LA) and obtained by polycondensation are usually referred to as poly(lactic acid) and the ones prepared from lactide by ring opening polymerization (ROP) as polylactide. Both types are commonly referred to as PLA, and this abbreviation is used here.

LA (2-hydroxypropionic acid), is an organic acid which can be produced by chemical synthesis or by fermentation. LA the basic building block for PLA, is made by a fermentation process using 100% annually renewable resources [13,37,50,56,57]. The interest in the fermentative production of LA has increased due to the prospects of environmental friendliness and because are used renewable resources instead of petrochemicals [26,58]. Moreover, the advances in the

fermentation of sugar-containing materials have significantly reduced LA production costs.

Chemically synthesized LA gives the racemic mixture (50% D and 50% L). On the other hand, the fermentation process is very specific, allowing the production of essentially one major stereoisomer; i.e., LA consists of about 99.5% of L-isomer and 0.5% of D-isomer [59].

The most common way to obtain high-molecular-weight PLA is through ROP of the lactide, i.e., the cyclic dimer of LA. In the first step of the process, the water is removed in a continuous condensation reaction of aqueous LA to produce low molecular weight oligomers or prepolymers [26,28]. Next, the prepolymer is catalytically converted through an internal transesterification by ‘back-biting’ reaction to the cyclic dimer (i.e., lactide) and then purified. Production of cyclic lactide results in three potential forms: D,D-lactide (called D-lactide), L,L-lactide (called L-lactide) and L,D- or D,L-lactide (called *meso*-lactide). As it is displayed in Fig. 3, only D- and L-lactide are optically active stereoisomers. The molten lactide mixture is then purified by distillation under vacuum and used following the polymerization process to produce different PLA grades with finely controlled physical and chemical properties [26]. Interestingly as information, according to the main supplier of PLA (NatureWorks), the *meso*-lactide is up to two times more susceptible to ROP reactions than L-, D-, or *racemic* lactides, which can mean less catalyst usage, lower processing temperatures, or both [60].

Table 1 shows the melting temperatures of different lactides including also the *racemic*-lactide (*rac*-lactide), which is an equimolar mixture of D- and L-lactides.

At this time exist two major routes (Fig. 4) to produce PLA at industrial scale [28,37,59,61,62]:

- Direct polycondensation of lactic acid (LA)
- Ring-opening polymerization (ROP) via the cyclic dimer (lactide)

The first route (a) involves the removal of water by condensation and the use of solvent under high vacuum and temperature [13,43]. Using this method, only low to intermediate molecular weight PLA can be produced, mainly due to the difficulties of removing water and impurities. It was reported that between the disadvantages of this technique are the relatively large reactor required, the need for evaporation, recovery of the solvent, significant change of color and racemisation [59,62]. One way to solve this problem is the use of a chain-extension method (route c, in Fig. 4), but the properties of PLA obtained in this way can be somewhat affected by the applied procedure [63].

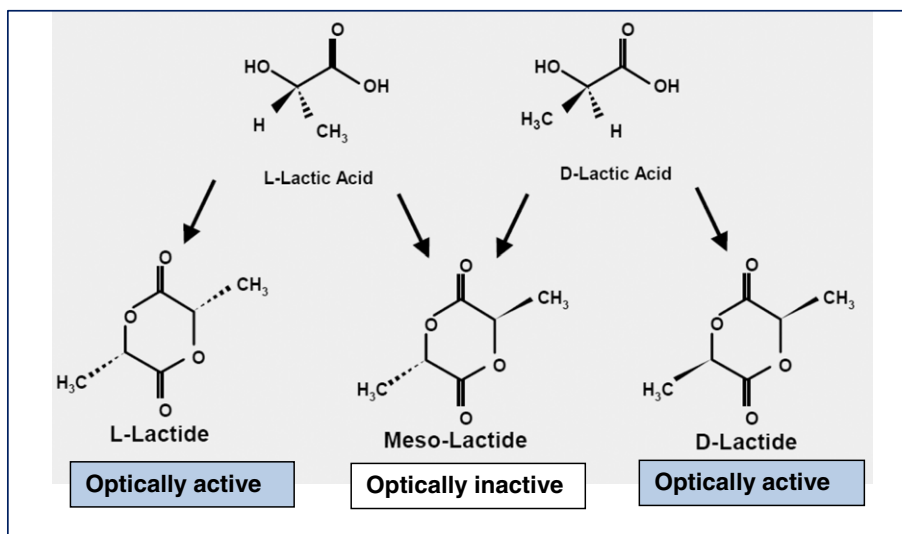


Fig. 3. Starting stereoisomers of lactic acid and lactide (adapted, with permission from the Ref. [26]).

Table 1
Thermal properties of lactides [61].

Lactide type	Melting point (°C)
L-lactide	95–98
D-lactide	95–98
meso-lactide	53–54
rac-lactide	122–126

It is also noteworthy mentioning that Mitsui Toatsu Chemicals has patented an azeotropic distillation using a high boiling solvent to remove the water in the direct esterification process and to obtain PLA of high molecular weight [64].

Actually, the main way to obtain high-molecular-weight PLA is through ROP of lactide (route b) carried out commonly by using a stannous octoate based catalyst, but for laboratory demonstration other catalysts or methods of polymerization are often employed [26, 43,53,61,65]. Additionally, the biosynthesis of PLA using enzymes is a new challenge, both in terms of research and industrial implementation [63,66].

Currently, NatureWorks LLC, the actual leader in the market for PLA technology and production, focuses on a multi-step procedure involving the ROP of lactide. The process (Fig. 5) does not use any solvents [28]. It starts with the condensation reaction of aqueous LA to produce low molecular weight PLA prepolymer. Next, the prepolymer is converted into a mixture of lactide stereoisomers using tin catalysis to enhance the rate and selectivity of the intramolecular cyclization reactions. Impurities are removed in the distillation step, and the *meso*-lactide is separated. Afterwards the “*meso*” fraction is combined with the low D-lactide fraction (in fact, essentially L-lactide) to produce a large portfolio of PLA grades. PLA of high molecular mass is produced using an organo tin-catalyst by ROP of the lactide in the melt, completely eliminating the use of costly and environmentally unfriendly solvents [62]. After polymerization, the residual lactide monomer is removed and recycled within the process.

However, as aforesaid, for laboratory demonstrations other catalysts or techniques are often employed, and in this context, it is expected that in short time new progress and significant improvements in PLA

technology will be reported [61]. In order to make the manufacturing of PLA economically viable, Jacobsen et al. [68] together with some people from our research group, have developed a new catalytic system (i.e., an equimolar amount of triphenylphosphine and stannous octoate) for the polymerization of lactide by reactive extrusion (REX) which can be further used to produce continuously PLA in large quantities and at lower costs. However, due its advantages connected firstly to a low residence time and specific features, especially where is used the twin-screw extruder as “reactor” equipment, the REX process has been developed in the last years at both, laboratory or plant scale to produce PLA-based products [69–71].

It is also noteworthy to mention that at industrial scale the ROP of lactide results in a “family” of PLA copolymers having different isomer ratios, while the actual technology is allowing controlling the molecular weights of macromolecular chains. The thermal, mechanical, and biodegradation characteristics of PLA are known to depend on the choice and distribution of stereoisomers within the polymer chains. Poly(L-lactide) (PLLA), i.e., the product resulting from the polymerization of L-lactide, due to its availability is preferred whenever higher mechanical strength and longer degradation time are required [52]. The optical purity of PLA has strong effects on the structural, thermal, barrier and mechanical properties of the polymer. PLA with L-content greater than ~90% tend to be (semi)crystalline, while the grades with lower optical purity are amorphous [7,13]. Besides, the melting temperature (T_m) and glass transition temperature (T_g) of PLA are decreasing, more or less, by increasing D-isomer content (Table 2).

It is generally agreed that the choice of the PLA matrix (point of view isomer purity, molecular, rheological and thermal properties, method of processing, etc.) is of key-importance for the production of composites. However, between the different other factors, it is also essential to take into account the requirements of application. It is important also to remind that PLA is usually delivered as granules previously crystallized during the final steps of fabrication process, to obtain a certain degree of crystallinity (dependent also on isomer content, Table 3).

PLAs with low D-isomer content are mostly indicated in applications requiring (semi)crystalline polymers, while those with higher percentage of D-isomer are generally used where amorphous polymers are necessary, such as heat seal layers needing low activation temperature.

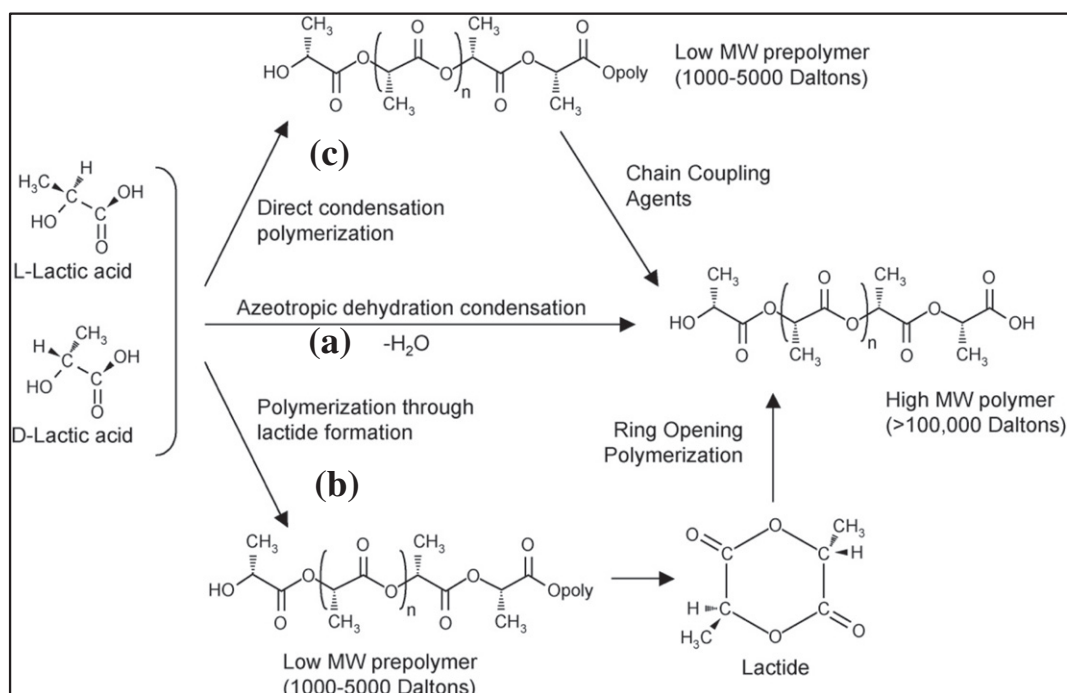


Fig. 4. Polymerization routes to produce PLA (adapted, with permission from the Ref. [7]).

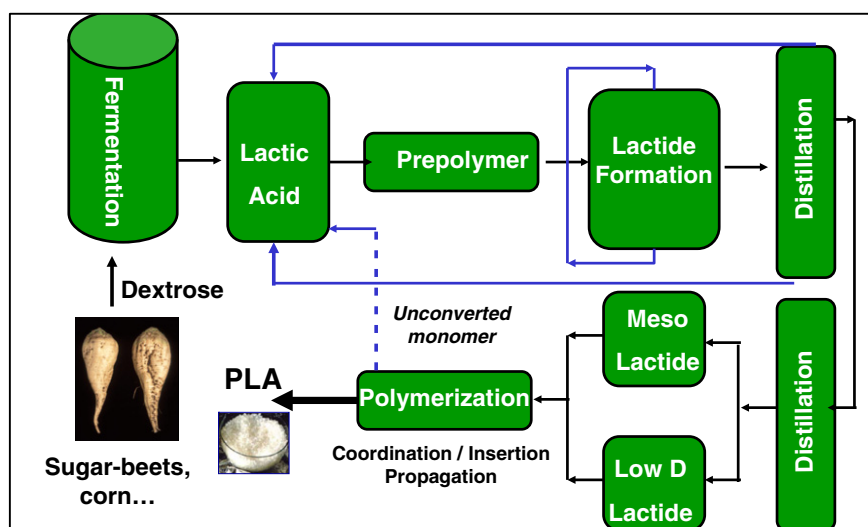


Fig. 5. Non-solvent process for the production of PLA (adapted, from the Refs. [62,64,67]).

However, because the engineering applications are demanding a high thermal stability and/or utilization at high temperature, the general tendency is to use a PLA matrix with extremely low D-isomer content which can exhibit higher melting temperature and degree of crystallinity.

Furthermore, important advances are expected to be obtained by utilization as polymeric matrix of PLA stereocomplexes (sc-PLA) produced by combining PLLA and PDLA using different methods [47,53,73–76]. This “topic” has generated a wide interest for both, academia and industry, thus an impressive number of studies and reviews are specifically focused on the production and current understanding of sc-PLA properties [70,71,73–75,77–80]. In fact, one of the most important characteristic features of sc-PLA is the high melting point, i.e. with about 50–60 °C greater than those of poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) homocrystallites [53,77,78,81]. The mixing using different methods of PLLA and PDLA gives sc-PLA having high melting temperature, i.e. around 220–230 °C. It is reported also that stereocomplexation enhances the mechanical properties, thermal, and hydrolysis resistance of PLA-based materials [47,55,74,79]. These improvements arise from a peculiarly strong interaction between L-lactyl and D-lactyl unit sequences, thus the stereocomplexation approach could open a new way for the preparation of biomaterials for biomedical applications such as drug delivery systems [47,82], but also for the production of composites requiring resistance at high temperature and/or high HDT (heat distortion temperature) [78,80].

On the other hand, it is important to mention that by comparing to other polymers commonly used in hot packaging (e.g. PS, PMMA, etc.), the relatively low T_g of PLA is considered a disadvantage (T_g about 60 °C, for PLA with high isomer purity). Therefore, for increasing the T_g of PLA materials different approaches have been considered: a) by realization of sc-PLA is reported a quite limited growing of T_g , i.e. of about 5 °C [67]; b) chain extension, e.g., with diisocyanates [83]; c) cross-linking [84], other methods. According to a review published

by Baker et al. [84] a promising way to increase T_g can also be to attach large, sterically demanding groups directly onto the polymer backbone, to anchor polar groups on pendant chains to increase chain-chain interactions, or include rings or other rigid elements along the polymer backbone. Furthermore, to overcome the shortcomings connected to a low T_g and to allow the use of PLA at high temperature, other interesting methods have been considered as well: addition of reinforcements, promoting of PLA crystallization, nano-alloying PLA [29] and blending PLA with polymers having high T_g (PC, PMMA, etc.) or crystallization ability such as PA [85], etc.

Nevertheless, it is also important to remind that PLA has a slow crystallization rate [86] when is compared with many other thermoplastics showing ability to crystallize. In fact, this is a kind of “Achilles’ heel”, limiting PLA use in high-performance applications, because this parameter is particularly essential to control PLA degradation rate, thermal resistance, as well as optical, mechanical and barrier properties. Melt-blending has proved to be an effective route to prepare and disperse the sc-PLA within PLLA matrix. The addition of less than 5% sc-PLA was found to be of high effectiveness in nucleating PLLA matrix with additional contribution in faster kinetics of crystallization [81].

In relation to the biomedical sector, it is necessary to point out that PLA and derivative copolymers are between the most utilized biodegradable polymer materials [9,57,63,87], since their properties can be tuned by changing the (co)polymer composition. To give only a selected example, the copolymers of PLA (both L- and D,L-lactide forms) and polyglycolide (PGA), known as poly(lactide-co-glycolide) (PLGA), are hydrolytically unstable and the changes in copolymer composition allow to design their rate of biodegradation. Thus, PLGA copolymers are used as biodegradable polymers in biomedical applications such as sutures, drug delivery devices and tissue engineering scaffolds, and so on [87,88].

As a final point, it is assumed that the choice and characteristics of PLA matrix (stereochemistry, molecular, thermal and mechanical properties) can effectively play a key-role in determining the performances of biocomposites, their process-ability and biodegradability.

Table 2
Primary transition temperatures of selected PLA copolymers [7].

Copolymer ratio	Glass transition temperature (°C)	Melting temperature (°C)
100/0 (L/D,L)-PLA	63	178
95/5 (L/D,L)-PLA	59	164
90/10 (L/D,L)-PLA	56	150
85/15 (L/D,L)-PLA	56	140
80/20 (L/D,L)-PLA	56	125

2.2. Main techniques for the production of PLA composites

Because of its versatility, it is generally agreed that the production and processing of PLA (e.g. by injection molding, compression molding, extrusion, spinning, etc.) and its (nano)composites can be realized with similar equipment [7,34,89], such as in the case of traditional polymers.

Table 3

Characteristics and applications of PLA grades (with 0.3–5% D-isomer content) produced in a demonstration plant by Sulzer (adapted, from the Ref. [72]).

Grade	Applications	MFI ^a (g/10 min)	D-isomer, % (by chiral GC)	T _m , °C	Crystallinity ^b , %
L100-HH	Extrusion, thermoforming, sheets, films, fibers	3	< 0.3	180	45–55
L100-H	Extrusion, thermoforming, sheets, films, fibers	6–7	< 0.3	180	45–55
L100-M	Injection molding, staple fibers	14–15	< 0.3	180	45–55
L99-L	Injection molding	30	1	173	40–45
L98-H	Continuous yarns	6–7	2	165	35–40
L97-HH	Oriented films, bi-axially stretched, blown films	4	3	160	25–35
L96-HH	Extruded sheets for thermoforming, extrusion	3	4	157	20–30
L96-H	Extruded sheets for thermoforming, extrusion	6–7	4	157	20–30
L95-M	Amorphous parts, injection molding	22–23	5	153	20–25

^a MFI = melt flow index, mean values at 2.16 kg/190 °C.^b PLA (granules) delivered by supplier.

In relation to this section, it was found of interest to display the main grades of PLA currently produced by NatureWorks LLC (Table 4) under the trademark Ingeo [90]. It is indicated the primary application, with the remark that these PLAs are supplied with precisely adjusted L/D-ratios, specific molecular and rheological parameters. Following the different requirements connected to the production method, processing and application, it is noteworthy mentioning that many of them are used as polymeric matrix to produce PLA composites via various techniques (see hereinafter).

As aforementioned, PLA has very interesting properties (e.g., high tensile strength and rigidity, i.e. Young's modulus) but also some drawbacks (low-flexibility, ductility, impact resistance and heat distortion temperature (HDT); long injection molding cycle time due to a small rate of crystallization, high sensitivity to moisture and low resistance to hydrolysis, etc.) [40]. Therefore, many efforts are realized to enhance PLA properties via different techniques and modifications, adding reinforcements and various dispersed phases, by blending, alloying and/or copolymerizing, by realizing physical treatments, etc. [38,91]. Moreover, PLA based products with specific end-use properties (high

speed of crystallization [86,92], toughness and impact resistance [93, 94], flame retardancy (FR) [3,95,96], antistatic to electrical conductive properties [97–100], anti-UV and antimicrobial characteristics [101–103], etc.) have been recently produced for novel applications as new PLA bio(nano)composites [104].

With few modifications and adaptations, the production of PLA composites is realized using the following techniques:

- a) Melt-compounding using typical procedures, for example dry-mixing all or some of the components with high speed mixers, followed by compounding in a wide range of melt-blending equipment such as internal mixers, single- or twin-screw extruders, Buss kneaders, etc.

The processing conditions (shear, temperatures, mixing time, etc.) are determined by the type of equipment, nature of dispersed phase(s), blend composition, desired end-use product properties, etc. It is worth recalling that the polyester-based matrix (i.e., PLA) is very sensitive to

Table 4

Main PLA grades commercialized by NatureWorks LLC under the trademark Ingeo (adapted, from the Ref. [90]).

Categories	Grade	Key features
Extrusion/Thermoforming (series 2000) General purpose, transparent extrusion grade	2003D	Used as is or as part of a formulated blend using traditional extrusion equipment
	2500HP	High viscosity & designed to crystallize during processing
Injection Molding (series 3000) Designed for injection molding applications	3001D	Unlubricated, medium-flow grade
	3052D	Lubricated, medium-flow grade
	3100HP	Medium viscosity, designed for medium-flow injection molding
	3251D	Lubricated, ultra-high flow grade
	3260HP	Designed to crystallize during processing for higher heat deflection temperature (HDT)
Films & Sheets (series 4000) Designed for the production of oriented films, card-stock and graphic arts	4032D	High heat films
	4043D	General purpose films
	4044D	Reactive extrusion grade
	4060D	Heat seal layer for films
	6060D	Amorphous- extrusion into mechanically drawn staple fibers, low melt binder polymer in a sheath-core configuration
Fibers/Nonwovens (series 6000) (selected grades) Designed for fiber processes from mono- to multi-filaments as well as spunbond & melt-blown products. Melting point from 130 °C to 170 °C, with amorphous to semi-crystalline grades	6100D	For lower fiber shrinkage, where higher dimensional stability is required
	6201D	Continuous filaments/staples for dyed fiber applications
	6202D	Staple fibers/spunbond for nonwovens, non-dyed fiber applications
	6252D	Melt-blown
	6260D	Designed for melt-blown fiber processing or extrusion into mechanically drawn staple fibers
	6362D	Designed especially for fiber products where an amorphous structure is desired
	6400D	Monofilaments/BCF/ multifilament products
Injection Stretch Blow Molding (series 7000) Designed for use in injection stretch blow molded (ISBM) bottle applications	6752D	Sheath polymer for spunbond applications
	7001D	General propose, ISBM bottle grade
	7032D	Heat-set ISBM bottle grade
Foams (series 8000) Designed for expanded foam sheets	8052D	Expanded foam sheets
	10361D	Amorphous/low-melting, high-flow resin
Binders & Adhesives (series 10000) Thermoplastic binder grades for various applications (printing, adhesives, building, etc.)		

temperature, shearing and hydrolysis, so that all precautions should be applied to avoid its degradation [7]. It is imperiously required to limit the content of water in PLA for all compositions at 50–250 ppm whatever the processing conditions, and this can be problematic in the case of some natural fibers (NFs) used as reinforcements or of fillers containing crystallization water.

Clearly, the melt-compounding method is highly preferred in the context of sustainable development since it avoids the use of organic solvents, which are not eco-friendly and can alter the life cycle analysis (LCA) of PLA. Moreover, this approach is easier up-scaled to larger-scale and to industry, whereas the twin-screw extrusion is the preferred method for PLA modification by REX or for the addition of masterbatches, impact modifiers, fibers, fillers, additives, or of selected polymers, which can increase the performances of PLA [105].

b) **Solvent-based methods** (e.g. solvent-casting) are chosen especially in the incipient phase of the research, mostly at small laboratory scale. Besides, due to low quantities of active pharmaceutical

ingredients (API), this technique is remaining of interest for the bio-medical sector. This approach can lead to some differences in the proprieties of PLA based products (PLA composites) with respect to those obtained using the processing of PLA in the molten state. Rhim et al. have prepared PLA films by thermo-compression and solvent-casting methods, and characterized selected properties, such as the mechanical and thermal performances [106]. The films prepared by thermo-compression showed better thermal stability than those obtained by solvent-casting and a surprisingly much higher tensile strength (44 MPa with respect to about 17 MPa, respectively). On the other hand, the solvent-cast films were very ductile (elongation at break of 203%) compared to the films realized by compression-molding (elongation of only 3%).

c) **Other methods:** the production of composites based on PLA can imply the polymerization of lactide on the surface of dispersed phases for better compatibility/higher performances [107,108], the physical blending of PLA (as fibers) with natural or synthetic fibers [109], utilization of pultrusion as technique [110] to produce PLA

Table 5
Methods of fabrication of PLA composites.

Methods of fabrication	PLA matrix	Nature of dispersed phase	Ref.
<i>Melt-compounding</i>			
Melt-compounding using a twin-screw mini-extruder	PLA extrusion grade, MFI = 2–10 g/10 min	Talc and kaolinite	[113]
Melt-compounding using a twin-screw mini-extruder, followed by injection molding	PLA (2002D NatureWorks): $M_w = 215,000$ and dispersity (M_w/M_n) = 1.9, D-isomer ~4.2%	Two types of talc, micrometric and sub-micrometric particles	[114]
Melt-compounding of PLA with up to 20 wt. % natural micro-powders using an internal mixer	PLA with M_w of 126,000 and dispersity of 1.48; D-isomer = 4.1%.	Natural micro-powders (agricultural by-products such as oat husks, cocoa shells, and apple)	[115]
Melt-compounding using an internal mixer	PLA extrusion grade with $M_n = 130,000$	Bacterial cellulose nanowhiskers modified with lactic acid oligomers	[116]
Melt-compounding using a twin-screw extruder, hot pressing	PLA (2002D, NatureWorks), MFI (at 210 °C/2.16 kg) of 6 g/10 min	Nonwoven flax fibers and impact modifiers	[117]
Melt-compounding with twin-screw and single-screw extruders, followed by injection molding	PLA (3051D, NatureWorks): $M_w = 171,000$, $M_w/M_n = 2.3$; D-isomer = 3.7 – 4.6%.	Reinforcement fibers of abaca and man-made cellulose, glass fibers	[118]
Melt-compounding using a twin-screw extruder, injection molding to produce testing specimens	PLA (2003D, NatureWorks) with $M_n = 155,500$ and D-isomer = 3.5%, MFI = 2.9 g/10 min	Glass microspheres up to 25 wt. % were added into PLA	[119]
Melt-compounding using a twin-screw extruder, PLA composites with up to 30 wt. % talc	PLA commercial injection-grade (Revode 201), no additional information	Up to 30% talc was added into PLA	[120]
Melt-compounding in a co-rotating twin-screw extruder	PLA (2100D, NatureWorks): $M_w = 180,000$ –210,000	Wood flour, talc and organo-silanes	[121]
Melt-compounding using a twin-screw extruder, followed by injection molding	PLA (3001D, NatureWorks): 1.4% D-isomer	Talc and ethylene bis-stearamide (EBS)	[89]
Melt-compounding PLA with up to 5% kenaf in an internal mixer, compression molding	PLA (NatureWorks): $M_n = 98,600$; $M_w = 194,800$	Kenaf bast fiber with diameters in the range 70–100 μm , lengths of about 1 mm.	[122]
Melt-compounding PLA with up to 40 wt. % CaCO_3 using a twin-screw extruder	PLA ($M_w = 180,000$, $M_w/M_n = 1.7$, D-isomer = 4%, $T_m = 155^\circ\text{C}$)	Precipitated CaCO_3	[123]
Melt-compounding PLA with 2.5 wt. % of treated or untreated MCC and CMF using a laboratory two roll mill	PLA (4032D, NatureWorks) with a melting point of 160 °C	Microcrystalline cellulose (MCC) with mean particle size of 20 μm and cellulose microfibrils (CMF) with diameters from 5 to 15 μm	[124]
<i>Solvent casting</i>			
Hydroxyapatite (HA) or g-HA were mixed in PLA/ chloroform solution (20 wt. % HA in PLA)	PLA ($M_n = 100,000$) prepared by ROP of lactide with stannous octanoate as catalyst	HA needle-like particles were surface treated by ROP of lactide to obtain g-HA.	[108]
PLA was reinforced with up to 25% (vol. fraction) of biphasic calcium phosphate (BCP); Composites for fracture fixation	PLA with an L/D,L ratio of 70/30 (Boehringer Ingelheim), intrinsic viscosity of 6.1 dl g ⁻¹	BCP with a Ca/P ratio of 1.56; BCP consisted of a mixture of 70 wt% β -TCP (tricalcium phosphate) and 30 wt% HA	[23]
Solvent casting to obtain PLA films with 0.1 and 0.5 wt. % cellulose nanowhiskers (CNW)	PLA (4032D, NatureWorks)	Microcrystalline cellulose (MCC) was used to produce CNW	[125]
<i>Other methods</i>			
Pultrusion technique for reinforcing PLA with up to 50 wt.% long jute fibers	PLA (TERRAMAC TE-8000, Unitika)	Jute yarns with filaments diameter in the range 20–100 μm	[111]
Carding PLA fibers with up to 70 wt. % kenaf, hot pressing	PLA with mean fiber length of 52 mm, no other information	Kenaf with mean fiber length of 60 mm, no additional information	[109]
Carding fibers of PLA with up to 40 wt. % cellulose, injection and compression molding	PLA fibers (6.7 dtex- produced using PLA 6202D, NatureWorks) with a T_m of 160–170 °C	Regenerated cellulose fibers (1.3 up to 15.0 dtex)	[126]
PLA of low-polymerization degree was grafted onto sisal fibers, blending with PLA	PLA (3051D, NatureWorks), with a MFI of 10–30 g/10 min	Sisal fibers with diameters in the range 25–200 μm	[127]
Recycled wood fibers (RWF) treated with 0.5% silane in a K-mixer, melt-blending with PLA	PLA (3001D, NatureWorks): MFI (190 °C/2.16 kg) – 15 g/10 min	Up to 20 wt. % RWF into PLA RWF was a blend of hardwood and softwood	[128]

reinforced with long fibers [111], co-extrusion (fibers, films, sheets), hot pressing using the film stacking method [112], etc. Table 5 shows selected examples from the state of the art in relation to the methods of fabrication of PLA composites, type and characteristics of matrix, nature of dispersed phases.

3. PLA reinforced with fibers and fillers

3.1. PLA reinforced with fibers

First of all, it is important to point out that due to the need to find renewable solutions, many companies are developing new products using the natural fibers (NFs) as raw materials. Furthermore, a big number of reviews and numerous scientific publications concern the utilization of NFs to produce reinforced bio-based polymers [91,129–138] and this is considered between the key trends. The primary driving forces for their utilization in the production of biocomposites are the lower cost of NFs with respect to synthetic fibers, their low density, high specific strength and stiffness, a large game of properties and characteristics, availability, processing features, and so on [129,138].

Table 6 shows selected mechanical properties of different fibers traditionally used to produce polymer composites. The mechanical performances of composites are determined by several factors such as: the type of polymeric matrix, nature and characteristics of fibers (including type, extraction method, aspect ratio, surface treatment, etc.), fiber loading, interfacial strength, composite manufacturing process, fiber dispersion and orientation, compatibility, etc. [138].

However, the hydrophilic nature of fibers is a major problem for all NFs if they are used as reinforcement in polymers. As mentioned elsewhere, PLA is very sensitive to temperature, shearing and hydrolysis, therefore is stable in the molten state provided that it is adequately dried with a maximum acceptable water content of 50 ppm in the case of processing at high temperature. Accordingly, it is of prime importance to dry PLA, but also to dry/dehydrate the dispersed or reinforcing phases (such as NFs) added into the polyester matrix and processed at high temperature using the melt-compounding approach. Moreover, it is often reported in the literature that the high moisture absorption of NFs are disadvantages that need to be considered, particularly during shipment and long-term storage, as well as during processing of composites [138,140].

On the other hand, due to the thermal degradation/decomposition of NFs, the compounding temperatures must be commonly restricted to max. 200 °C. However, to increase the surface hydrophobicity of NFs and to reduce the sensitivity to water absorption (owing also to the presence of a great number of hydroxyl groups on their surface), surface pre-treatments and chemical functionalization constitute a challenging and important pre-processing step in composite preparation [141].

Table 6
Mechanical properties of different fibers [139].

Fiber	Density, g/cm ³	Young's modulus (GPa)	Tensile strength, MPa	Elongation at break (%)
Flax	1.54	27.5–85	345–2000	1–4
Ramie	1.5–1.56	27–128	400–1000	1.2–3.8
Hemp	1.47	17–70	368–800	1.6
Jute	1.44	10–30	393–773	1.5–1.8
Sisal	1.45–1.5	9–22	350–700	2–7
Coconut	1.15	4–6	131–175	15–40
Cotton	1.5–1.6	5.5–12.6	287–597	7–8
Nettle	1.51	24.5–87	560–1600	2.1–2.5
Kenaf	1.2	14–53	240–930	1.6
Bamboo	0.6–1.1	11–17	140–230	N.A.
E-glass	2.5	70	2000–3500	2.5
Carbone	1.4	230–240	4000	1.4–1.8

Chemical approaches have been more investigated than physical ones, with better improvements obtained to date. Chemical treatments include modification with alkali, acetyl, silane, acryl, permanganate, peroxide, isocyanate, titanate, zirconate, use of maleic anhydride grafted coupling agents, etc. as reviewed recently for NFs by Pickering et al. [138].

However, many NFs (flax, kenaf, hemp, jute, wood, different forms of cellulose extracted from NFs, etc.) have been mixed with PLA and selected examples are given below.

3.1.1. PLA–flax

In order to determine if the biopolymers (including PLA) reinforced with NFs can be used in the automotive industry, composites with up to 30% (volume fraction) of randomly scattered flax have been manufactured using a film stacking technique and compared to polypropylene (PP)–flax composites [136]. The tensile strength and Young's modulus of PLA and PLA–flax were found to be better than those of PP–flax composites. However, PLA–flax composites have proved to be very close as mechanical properties to those of glass fiber polyester composites, results found as very promising for the development of biocomposites for structural applications.

Siengchin et al. [117] have been modified PLA (2002D, NatureWorks) by melt-compounding with Biomax Thermal 300 (a composition of wax/ethylene acrylate copolymer/butyl acrylate) and Palaroid BPM-500, aided as thermal and acrylic impact modifiers, respectively. Then, the polymeric matrices as sheets and nonwoven flax fibers (a flax mat, of 220 g/m²) have been used to produce sheets of PLA–flax mat and modified PLA–flax mat composites (20 wt. % flax mat) via hot compression molding. The incorporation of flax mat increased the stiffness of PLA markedly, whereas the impact resistance of PLA was highly enhanced by addition of flax mat and of acrylic impact modifier.

In the study reported by Oksman et al. [135] because of the brittle nature of PLA, up to 15% triacetin (glycerol triacetate) was added as plasticizer into PLA and PLA–flax composites in order to improve the impact properties. Composites with 30 and 40 wt. % flax were produced by melt-compounding using a twin-screw extruder. The processing and the properties of composites were compared to those of most commonly PP–flax composites which are used today in automotive panels. The mechanical properties of PLA–flax composites were found to be promising, because the tensile strength was found with about 50% better compared to similar PP–flax composites (Fig. 6). On the other hand, somewhat surprisingly, the addition of plasticizer has proved to have a negative effect on the mechanical and impact properties. Accordingly, the authors have suggested that the interfacial adhesion (PLA–flax) needs to be further improved. Therefore, other research groups have been considered the physical and chemical

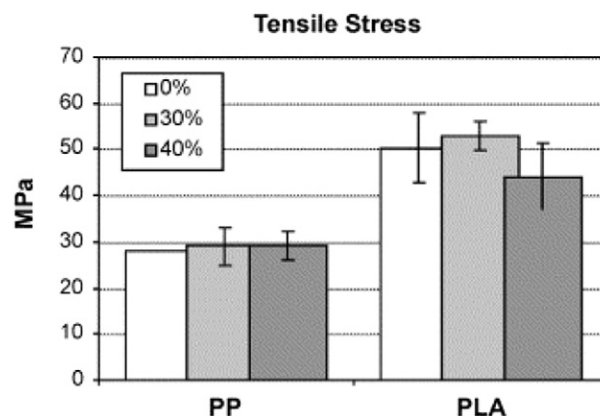


Fig. 6. Tensile strength of PLA–flax composites compared to PP–flax (with permission, from the Ref. [135]).

modification of flax fibers. Flax fiber surface was modified by alkali treatment, corona discharge, maleic anhydride grafting and aminopropyltriethoxysilane treatment [142], interstitial polymerization to replace the water in the fiber [143], or by other methods.

3.1.2. PLA–kenaf

The utilization of kenaf as natural fiber for PLA reinforcement has been the subject of many studies [109,122,144,145], whereas Toyota can be cited between the first companies that have developed the PLA–kenaf composites for automotive applications. Firstly, it is noteworthy mentioning that the adequate preparation of fibers for good interfacial properties with the polyester matrix (which is very sensitive to water) can open the way to more performant PLA composites.

Lee et al. [109] reported the fabrication of PLA–kenaf composites in three steps: a) the carding of PLA with up to 70 wt. % kenaf (both as fibers) followed by b) treatment with 1, 3 and 5 pph (parts per hundred) 3-glycidoxypropyltrimethoxysilane to obtain silane treated prepressed mats, and finally, c) hot-pressing to obtain composites for characterization. The effects of silane coupling agent on composite properties were found highly beneficial: increased heat deflection temperature (HDT), reduced water swelling, improved mechanical characteristics for biocomposites with respect to the neat PLA. The HDT values of composites steeply increased with kenaf fiber loading; already at only 10% kenaf (silane treated) the HDT was much greater (above 140 °C) than that of neat PLA (HDT of 57 °C). Nevertheless, following other studies, it was reported the possibility to produce PLA–kenaf composites even with very low kenaf loading (1–5%) [122]. The addition of kenaf (fiber of 70–100 µm diameter and length of 1 mm) into PLA increased the storage modulus and thermal properties, improved the crystallization rate, whereas the good fiber wetting by the polymeric matrix was assessed by SEM. Furthermore, based on the mechanical properties of PLA–kenaf composites (at 70 vol.% kenaf), i.e., Young's modulus (6.3 GPa) and the tensile strength (62 MPa), Nishino et al. [146] have concluded that kenaf can be a good reinforcement candidate for high performance biodegradable polymer composites.

3.1.3. PLA–glass fibers (GF) and PLA–carbon fibers (CF)

It is generally recognized that the glass fibers (GF) are between the most common and performant reinforcements used in the industry of material composites. For instance, based on a literature survey, the authors of this review have found that, somewhat surprisingly, the number of studies concerning the PLA–GF composites is not so high.

RTP Company is between the first industrial producers of PLA–GF compounds [147]. These composites due to their performances overcome partially the shortcomings of unmodified PLA because they have the mechanical and thermal properties necessary to allow their using as eco-friendly alternative to reinforced petroleum-based plastics. As it is shown in Table 7, the reinforcing of PLA with GF leads to higher tensile and flexural strength with respect to neat PLA, spectacular increase of HDT (from above 51 °C to 160 °C), better impact properties.

Jaszkievicz et al. [118] have reported the results of a study regarding the comparative mechanical properties of composites based on PLA and PP, both reinforced with 30% natural fiber abaca, man-made cellulose and GF. As a consequence of higher initial modulus of PLA, it was

found that all composites based on PLA possess an improved stiffness in comparison to PP. The obvious reinforcing effect of man-made cellulose and GF was ascribed to their geometries and performances.

Concerning the biomedical applications, an important number of studies are focused on the utilization of bioactive GF–PLA composites [148–153] as possibility to use more performant bioresorbable materials. By reinforcing PLA with 40 vol.-% bioactive GF the flexural strength reached 220 MPa (only 125 MPa for the neat PLA), whereas the flexural modulus was 14.3 GPa (2.9 GPa for PLA). Therefore, it was concluded that the mechanical properties of PLA can be increased in composites to the level of bone tissue [148].

Carbon fibers (CF) [154] due to their properties (excellent tensile strength, low density, high thermal and chemical stability, thermal and electrical conductivity, other features) have been considered between the reinforcing fibers of interest for PLA. PLA–CF composites are important for utilization in the biomedical sector [155–158], as well as for special engineering applications [159].

On the other hand, interestingly as approach for the production of carbon fibers (CF), Thunga et al. [160] have reported the possibility to use bio-renewable fibers such as from lignin/PLA blends, as precursors for conversion to CF.

3.1.4. PLA–cellulose and other PLA composites

Cellulose is the most abundant biomass material in nature [161]. Many studies and rich information in the literature are linked to the utilization of different forms of cellulose extracted from NFs (cellulose micro-fibers, microcrystalline cellulose (MCC), cellulose nanowiskers (CNW), cellulose nanocrystals, etc.) [124,161,162] and of PLA as matrix, to produce PLA–cellulose micro- and nanocomposites [107,116,118,126,134,163–169]. Cellulose-reinforced polymer composites have received much attention due to their structural reinforcing, light weight, biodegradable, non-toxic, low cost and recyclable characteristics [170]. Utilization of cellulose (as micro- or nanofibers) for the reinforcement of PLA is a relatively new research field and this topic is showing an increased interest, with a marked orientation in the last time for the production and characterization of PLA–cellulose nanocomposites [40,141,171,172].

From an industrial point of view, one of the main drawbacks of cellulosic fibers is the strong hydrophilic nature of their surface, which leads to weak polymer/fiber interfacial interactions and to a decrease of the mechanical properties [161]. However, PLA can be easily degraded at high temperature in the presence of water or residual moisture. Courgneau et al. have used cellulose fibers (ca. 99.5% cellulose) for PLA reinforcement and potential utilization in automotive sector [165]. The incorporation of cellulose fibers by melt-compounding using a twin-screw extruder induced a slight drop of PLA molecular weights due to the combined effect of the shearing at high temperature and hydrolysis of PLA chains, this polyester being highly sensitive to small amounts of moisture. The composites exhibited a well-dispersed morphology, but generally a weak adhesion PLA–cellulose fibers was evidenced.

On the other hand, the hydroxyl groups from cellulose fiber surfaces offer many possibilities for chemical modification (e.g. using silanes). PLA–recycled wood fiber (RWF) composites with a small amount of silane were compounded using a kinetic-mixer and processed using an injection molding machine [128]. The tensile strength remained the same irrespective of the RWF content, but both tensile modulus and storage modulus of composites increased with the RWF content. No reduction in the number-average molecular weight (M_n) was observed for neat PLA and PLA–10% RWF–0.5% silane composite after injection molding; but a substantial reduction in M_n was found at higher loadings of RWF (i.e. at 20 wt. %).

Braun et al. [107] have used the hydroxyl groups available on the surface of cellulosic fibers to initiate lactide polymerization and the reactive compatibilization with PLA. Various processing strategies were investigated: (1) blending commercial PLA with the fiber, (2) one-step process in which lactide is polymerized in the presence of fibers

Table 7

Comparative characteristics of PLA and selected polymers reinforced with 30% glass fibers (adapted from the Ref. [147]).

Propriety	PLA	PLA–30% GF	PP–30% GF	PBT–30% GF
Tensile strength, MPa	62	114	76	124
Flexural strength, MPa	108	145	112	190
Flexural modulus, MPa	3830	11240	4830	8270
Izod impact resistance, J/m (notched specimens)	16	53	107	96
Heat deflection temperature, °C (0.455 MPa)	51	160	157	213

alone, or (3) reactive compatibilization in the presence of high molecular weight PLA. The composites prepared by simultaneous introduction of lactide and high molecular PLA at the beginning of the reaction have shown superior mechanical properties compared to the composites made by either purely mechanical mixing or solely polymerization of lactide in the presence of cellulosic fibers.

To produce PLA composites characterized by specific FR properties, Fox et al. [173,174] have prepared POSS–cellulose hybrids using monofunctional-POSS reactants (e.g. glycidylphenyl-POSS [170]). The cross-linked network formed during melt-blending between cellulose, POSS, and PLA helped to produce composites with improved FR, rheological, and mechanical properties relative to other intumescent formulations [174].

Costes et al. [175] from our research group, have studied the production of FR PLA composites containing micro- and nano-crystalline cellulose (abbreviated respectively, MCC and NCC) and phosphorus combinations. Phosphorus was introduced either by chemically grafting (by reacting MCC with phosphorous acid) or by co-additive melt-blending using a bio-based phosphorous agent, i.e., aluminum phytate. In both cases, the charring effect of cellulose was enhanced. Using 20 wt% of phosphorylated MCC allowed reaching V0 category according to UL-94 vertical testing, but did not result in significant reduction of pHRR in cone calorimeter test (this was obtained in the presence of aluminum phytate). However, the increased specific surface area of NCC was found to be more beneficially for the improvement of FR properties of PLA, because of the formation of better insulating charred layers.

Furthermore, to produce PLA intumescent formulations with FR properties, in the Bourbigot' group [176], in the traditional ammonium polyphosphate (APP)/pentaerythritol (PER) system, PER was substituted by starch and lignin as biosourced materials. Compared to the PLA/APP/PER composites the composites containing lignin and starch showed lower LOI values, but still commercially acceptable (superior to 32%), and superior UL ratings (V0 against V2 rating).

In the same topic, FR compositions of PLA with aluminium hydroxide (ATH), short carbon fibers (CF) and modified montmorillonite (MMT) were prepared via direct melt-blending. By replacing in PLA–ATH composites a portion of ATH by modified MMT and CF, the tensile strength and elongation at break were significantly improved. Moreover, by co-addition of MMT and short CF, in fire tests a more effective insulation layer has been formed on the ablating surface of composites. Noticeable, following UL 94V testing a V-0 rating was obtained, without burning drips.

Nevertheless, for more details concerning the PLA (nano)composites characterized by FR properties we recommend as support information a recent review published by us and our collaborators [3].

Finally, it is a key point to note that the hydroxyl groups from the surfaces of fibers (e.g. cellulosic fibers) offer many possibilities for the chemical modification with different grafting agents (silanes, titanates, isocyanates, anhydrides, etc.), thus further progress and improvements in the performances of PLA composites can be expected by applying these methods, but also by combining synergistically the properties of micro- and nano-dispersed fillers with those of fibers.

3.2. PLA composites with fillers

Generally speaking, the fillers are combined with the polymers to either reduce the cost or to modify the physical, rheological, optical or other properties of the polymeric compounds [177].

If the fillers do not decrease the molecular, thermal and mechanical characteristics of PLA, their utilization can be an effective route to cost reduction, but also the source of improved mechanical parameters, e.g. increase of modulus/stiffness at room temperature or elevated temperature, especially in those PLA grades which allow a high degree of crystallinity.

As it was reported in the literature, PLA was mixed with various microfillers (talc, carbonaceous fillers, hydroxyapatite, inorganic carbonates and sulfates, mica, kaolin, etc.) and various nanofillers (organo-modified layered silicates (OMLS), graphite derivatives, carbon nanotubes (CNTs), sepiolite, halloysite, polyhedral oligomeric silsesquioxanes (POSS), silica, ZnO, others nanoparticles). Because the PLA-nanocomposites have been concerned in some recent contributions published by us and other scientists [3,40,178–180], hereinafter the nanofillers will be less mentioned and the comments will be mainly focused on the PLA composites containing microfillers.

3.2.1. PLA–talc

Due to its intrinsic characteristics and effectiveness in the improvement of PLA performances at different loadings, talc is one of the most considered fillers for mixing with PLA. The addition of talc into PLA can speed up PLA crystallization, increase the stiffness and heat resistance, improve the dimensional stability and barrier properties, reduce the molding time and production costs, and so on. This is assessed by an important number of studies, patents and the very large information regarding the PLA–talc composites [89,113,120,121, 181–214]. Firstly, it is worth mentioning that whatever the loading, talc has a marked nucleating effect on PLA crystallization [89,113] if the matrix has the ability to crystallize. Isothermal crystallization half-times ($t_{1/2}$) were found to decrease nearly 65-fold by the addition of only 2% talc with respect to the neat PLA [89]. This can lead to faster cycles of processing (e.g. by injection molding) and increased crystallinity, a key-parameter determining finally the level of resistance at high temperature. Petchwattana et al. [189] have studied the effects of up to 10 wt. % talc in promoting the crystallization of PLA using fillers of different particle size, namely 1, 5 and 30 μm , as nucleating agents. Talc was found (even at 1 wt. %) to be an effective nucleating agent for accelerating the crystallization rate in PLA, whereas the finer talc led slightly to higher degrees of crystallinity. In this context, it is noteworthy mentioning that many suppliers are actually delivering submicronic grades of talc (e.g., obtained by a special delaminating (jet-milling) process), and which can be highly effective in the nucleation and important increasing of the degree of crystallinity of PLA [183]. Furthermore, a good affinity between the macromolecular chains of PLA and talc it is generally assumed [113].

On the other hand, the reinforcing effect of talc, increase of thermal stability and heat distortion temperature (HDT), are more advanced in highly filled composites. Shakoor et al. [183] have prepared and characterized the mechanical and thermomechanical properties of PLA filled with up to 30 wt.% ultra-fine talc (Fig. 7 shows its morphology as evidenced by SEM). By addition of 30 wt. % talc the Young's modulus increased from a value of 4.1 GPa for the neat PLA up to 9.8 GPa for

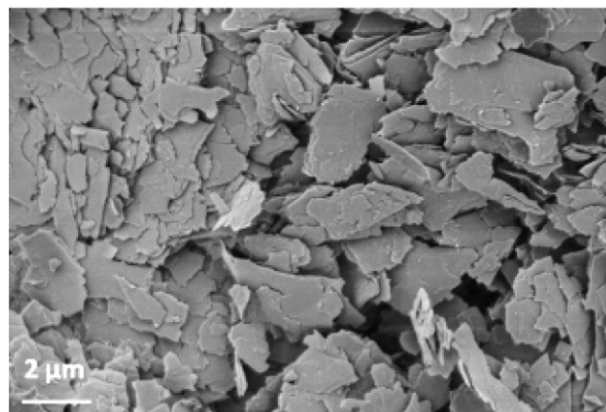


Fig. 7. SEM morphology of talc (Jet fine 3CC) used for the crystallization of PLA (with permission from the Ref. [183]).

composites, the reinforcing effect being also confirmed by the rise of storage moduli evidenced using DMA (Dynamic Mechanical Analysis).

3.2.2. PLA–carbonaceous fillers

Utilization of carbon micro- and nano-fillers (carbon black (CB), graphite and graphite/graphene derivatives, single and multiwalled carbon nanotubes (CNT), fullerenes, etc.) in the industry of polymer composites has been attracted great scientific and industrial interest due to the high technological potential of such materials in many applications [215–217]. Due to their intrinsic characteristics the CNTs [216] are between the most considered nanofillers for mixing with various polymers (N.B. PLA is included). Thus, many reviews are in relation to the synthesis, structural and functional properties of CNTs [217–219].

PLA was used as polymeric matrix to produce micro- or (nano)composites containing carbonaceous fillers of different geometry [100,179,220–223]. The PLA–carbonaceous fillers can show improved nucleating, mechanical, thermal and FR properties, tailored electrical and thermal conductivity, other specific features [3,224–229]. The composites characterized by electrical conductive properties can be promising as materials for the fabrication of sensors with sensitivity to strain, temperature or organic solvents [220,230], but also for the realization of technical items showing electromagnetic shielding (e.g. the case of foamed PLA composites containing carbon black (CB) or carbon nanofibers [98]).

On the other hand, a big number of studies have revealed that the combination of fillers of different geometry can dramatically improve PLA specific properties. To increase the electrical conductivity of PLA foams, Wu et al. [223] have used a combination of CNTs and CB. The electrical conductivity can be improved because the CNTs play the role of ‘bridge’, connecting CB particles and forming better network structure, due to their higher aspect ratio. At the same loading of filler, for the PLA composite foams the electrical conductivity followed the order:

CB–based sample < CNT–based sample < CB/CNT–based sample.

Both, the dispersion state [231] and the surface functionalization of CNTs [232,233] were found to be very important for the final morphology, electrical percolation threshold and thermal stability of PLA–CNT compounds.

It’s a key point to discuss in this section the case of graphite fillers, nowadays rediscovered as exotic materials of the 21st century, due to an exceptional charge transport, thermal, optical, and mechanical properties [234]. Recently, it was evidenced an marked interest for the utilization of graphite and graphite derivatives (micro- or nano-fillers) in combination with various polymers, including PLA [3,99,235–240], to produce either, micro- and nanocomposites [241,242] designed with specific end-use properties. Graphite is consisting of graphene nanosheets which exhibit unique structural features and physical properties. Its effectiveness is evidently, higher where the graphite layers are separated and functionalized, and this is conceivable via different techniques [243,244]. Graphite/graphene (essentially an isolated single-atom plane of graphite [234]) (nano)fillers are suitable for applications where their properties like rigidity, heat stability, lubricant ability, thermal or antistatic to electrical conductivity are required. However, many research works are devoted to the exfoliation of previously intercalated graphite using different methods and to its adequate functionalization [245]. Graphite/graphene derivatives (intercalated/expandable graphite [238,240], expanded graphite [3,235,237], exfoliated graphite nanoplatelets [99,241], etc.) have been associated with PLA matrix to produce (nano)composites by various techniques (once more there is a preference for melt-compounding [235,237], mixing in solution [246], other methods).

Kim et al. [241] have produced *via* melt-blending method and characterized the proprieties of PLA micro- and nano-composites obtained by the addition into PLA of respectively, natural graphite (NG) having micrometric particles (i.e. about 500 μm) to those of exfoliated graphite

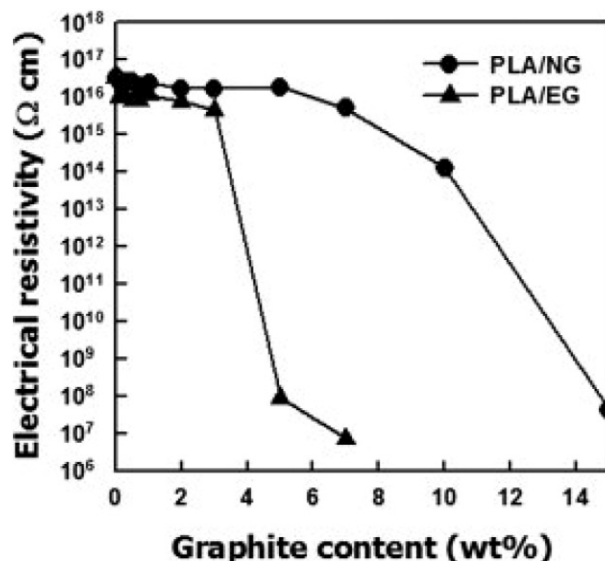


Fig. 8. Electrical resistivity of PLA/exfoliated graphite and PLA/natural graphite (NG) composites as function of graphite content (with permission from the Ref. [241]).

obtained at laboratory scale by acid treatments and following the rapid thermal expansion at high temperature. Better morphology, thermal, mechanical and electrical properties were revealed in the case of nano-composites, i.e. using graphite nanoplatelets (small stacks of graphene). As a key-example (Fig. 8), the percolation threshold for electrical conduction of PLA–exfoliated graphite nanocomposites was found to be at 3–5 wt. %, which is far for lower graphite content than that (10–15 wt. % NG) of PLA–NG composites.

Nevertheless, for extending PLA applications range, it has been demonstrated by us and our partners of research [235,237], that commercially available expanded graphite (EG) microfillers (mean diameter (d_{50}) of 36 μm , dimension of primary particles of 35 nm) can be melt-blended with PLA using different techniques of addition. In correlation with filler loading, the PLA–EG composites were characterized by improved properties with respect to the neat PLA matrix: rigidity as evidenced by the values of Young’s modulus in the tensile tests; improved crystallization kinetics, moderate increase in thermal stability, antistatic to conductive electrical properties, etc. Interestingly as remark regarding the morphology of composites, TEM analysis evidenced even the presence of graphene layers within PLA matrix. Additionally, as demonstrated by DMTA, melt-blending PLA with EG led to the enhancement of storage modulus (Fig. 9), and associated

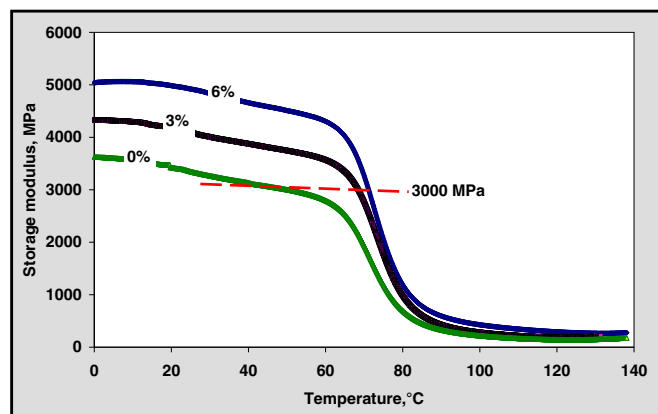


Fig. 9. Evolution of storage modulus vs. temperature: neat PLA and PLA–expanded graphite composites (adapted, with permission from the Ref. [237]).

with the enhancement of crystallinity, this allows the use of PLA–EG composites in applications requiring higher temperatures of utilization.

It is worth mentioning that the fire measurements by cone calorimetry on PLA–EG samples proved also the beneficial role of graphite in the decrease of pHRR (peak of heat release rate). As example, the addition of 6% EG leads to a pHRR reduction of about 30% with respect to neat PLA (Fig. 10a), whereas no significant difference between TTI (time to ignition) was observed. The important amount of char formed during burning (Fig. 10b) was ascribed to the additional expansion of graphite layers provoked by both, the heat and gases/products of combustion. In fact, this assumption is supported by TEM observations on the residue after burning (Fig. 10c), images that have revealed even the presence of exfoliated graphene nanolayers.

In the frame of other study (Fukushima et al. [235]), it was revealed that the co-addition of EG and organically modified montmorillonite (i.e., Cloisite 30B) into PLA using the melt-blending technique provides (nano)composites that show significant enhancements in rigidity, thermal stability and FR properties with respect to the polymer matrix. The improvements of thermal and mechanical parameters were ascribed to the good (co)dispersion and to the co-reinforcement effect of fillers, whilst the fire retardant (FR) properties were found to be related to their combined action.

Still, like for CNTs, the number of studies regarding the FR properties of PLA–graphite composites is enough high. To produce FR biobased composites, up to 10 wt. % expandable graphite (previously intercalated with sulphuric acid) was added into PLA using a co-rotating twin screw extruder [238]. Then, the effects of filler addition have been examined (by TGA, cone calorimeter measurements and UL 94V testing). The best FR results were reported at minimum 5 wt. % (UL 94V test) and at 10 wt. % graphite loading following the cone calorimeter testing. Based on the TGA, at 5–10 wt. % graphite, a very limited acid catalysis of PLA chains was assumed.

On the other hand, synergistic effects in terms of FR have been observed between expandable graphite and ammonium polyphosphate (APP) [240]. The optimal synergism it is reported for a PLA–15% APP/graphite system with the 1:3 weight ratio of APP to graphite. In these experiments, PLA composites with 15 wt. % of APP/expandable graphite (1:3) showed a LOI (limiting oxygen index) value of 36.5% and V-0 rating in UL-94V tests. Accordingly, FR properties were greatly improved with respect to the composites containing only APP or expandable graphite.

3.2.3. PLA–hydroxyapatite

PLA–hydroxyapatite (HA) composites [108,158,247–269] are of high interest especially for biomedical applications since they combine the osteoconductivity and bone bonding ability of HA with the absorbability and the easy processing of PLA and its copolymers.

Gültekin et al. [270] have studied the effects of various parameters such as (co)polymer type, HA loading (10–40 wt. %) and surface modification with silane coupling agents, on the mechanical and microstructural properties of the composites. Based on the tensile testing, the best results were reported for PLLA composites containing HA treated with 1 wt. % aminofunctional silane and PDLA–HA treated with 0.5-wt. % mercaptopropyltrimethoxy silane. Following also the surface modification of HA with silane derivatives, Zhang et al. [271] have reported for PLA–HA composites improved interfacial adhesion and ultimate mechanical properties (e.g. the bending strength was enhanced with about 28%). Nevertheless, the mechanical strength still fails to meet the demands of the fixture of weight bearing bones. Thus, in some studies the carbon fibers (CF), which are widely used as a reinforcing material in the bone implant due to their great biocompatibility and high strength, have been associated with HA [157]. After the degradation in vitro for 3 months, the flexural strength and flexural modulus of the PLA–CF/HA felt respectively, only 13.2% and 5.4%, whereas it

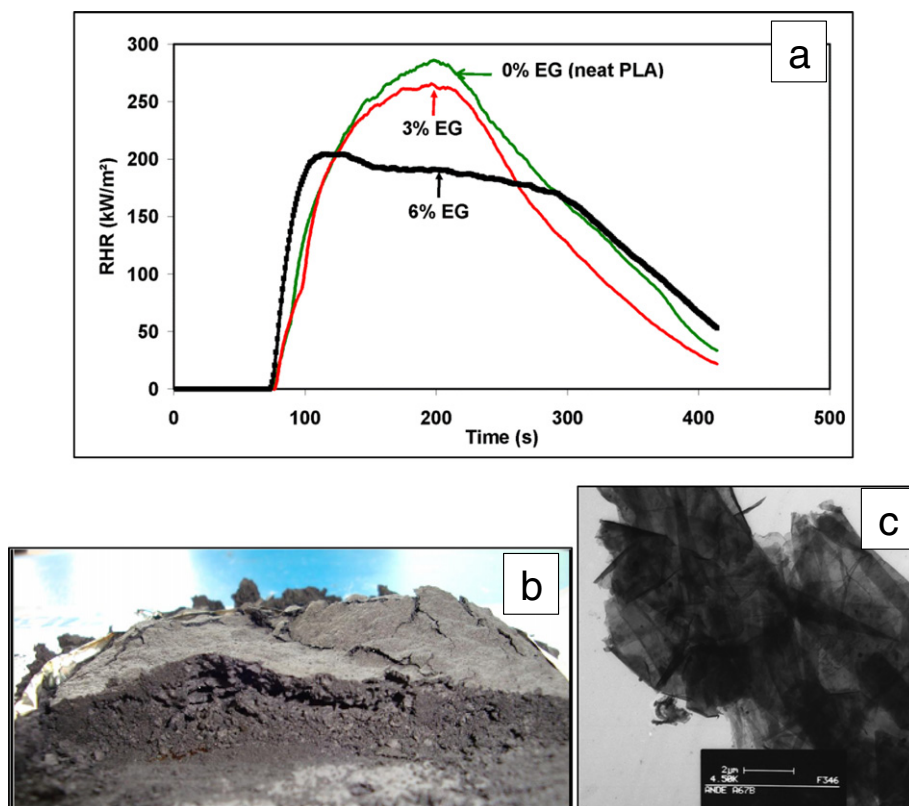


Fig 10. (a–c). (a) HRR plotted against time at a defined heat flux of 35 kW/m²: neat PLA compared to PLA–EG composites with different loadings of expanded graphite (EG); illustration of the residual char formed following the cone calorimeter testing of PLA–EG composites (b) and TEM image of the residual product (c) (adapted, with permission from the Ref. [237]).

was not reported variation in pH values [158]. In fact, due to its alkalinity, HA can neutralize the acidic species formed following the degradation of PLA by hydrolysis and this can prevent the body from the negative effects of acidity.

3.2.4. PLA–barium sulfate ($BaSO_4$)

Remaining in the field of biomedical applications, it is noteworthy mentioning the interest for the utilization of PLA–barium sulfate ($BaSO_4$) composites [272,273].

For developing radiopaque pancreatic stents the PLA–4 wt. % $BaSO_4$ composites were investigated by Lämsä et al. [274]. The authors concluded that the stent material (PLA– $BaSO_4$) was not more toxic than the reference (i.e., steel material) in the rat pancreas during 21-days observation period.

Yang et al. [275] have studied the effects of precipitated $BaSO_4$ modified with stearic acid. The morphologies, mechanical properties and thermal stability of samples with increased $BaSO_4$ loading (up to 30 wt. %) were investigated. The results showed that PLA (a grade previously filled with 10% $CaCO_3$) was toughened and reinforced simultaneously by incorporation of precipitated $BaSO_4$. The highest impact toughness and elongation at break were achieved at 15 wt. % $BaSO_4$, while the elastic modulus increased monotonically by growing $BaSO_4$ amount.

3.2.5. PLA–calcium carbonate and β -tricalcium phosphate

Calcium carbonate ($CaCO_3$) in both variants, as micro- and nano particles, has been used to produce respectively, PLA micro- and nano-composites. Kim et al. [276] have compared the effects of the addition by melt-mixing into PLA of micro- and nanosized $CaCO_3$ treated with calcium stearate (1 wt. %). The modification of $CaCO_3$ particles enhanced the mechanical properties (tensile strength and modulus) of PLA-based composites, the improvements being more important by incorporation of nanosized $CaCO_3$ (amounts of up to 30 wt. %). On the other hand, the decreasing in the thermal stability of PLA composites (with respect to neat PLA) was ascribed to the basic nature of $CaCO_3$.

In relation to the utilization in biomedical applications (e.g. composites for realization of implants) it is noticeable the association of β -tricalcium phosphate and $CaCO_3$ to produce poly(D,L-lactide)-composites for bone replacements [277]. Following a similar objective, i.e. realization of implants, Schiller et al. [278,279] have combined the

poly(D,L-lactide)– $CaCO_3$ for faster degradation, and poly(L,L-lactide)–calcium phosphate composites, to ensure mechanical stability and protection. To overcome problems like inflammatory reactions caused by acidic products following PLA degradation, the polyester was combined with basic filler ($CaCO_3$). The filler neutralises the lactic acid produced during polymer degradation (pH values are well stabilized) and consequently, is increased the bioactivity of the material.

3.2.6. PLA composites with other fillers

From a quick review of the state of the art it comes out that list of micro- and nanofillers already used for mixing with PLA and to produce micro- and (nano)composites is much longer: layered silicates [180, 280], mica [281–284], kaolin [113,285–288], zeolites [289–293], glass beads/microspheres [119], wollastonite [293–295], boehmite alumina [296,297], others.

It is worth mentioning that a great number of adequately modified fillers can lead to PLA nanocomposites which show remarkable improvements of properties evidenced even at very low nanofiller loading (usually 3–5%). For shortness, we will limit our comments concerning the huge potential of nanofillers. However, we recommend for more details and information, a recent review published by us and focused on PLA–nanocomposites [40].

Table 8 shows selected examples illustrating the key-role of filler addition on PLA properties.

On the other hand, it is important to precise that not all fillers have a beneficial effect on PLA properties. Unfortunately, the addition into PLA of some metal oxides (e.g., calcium oxide (CaO), magnesium oxide (MgO), zinc oxide (ZnO)) or other metallic compounds (e.g., layered double hydroxides), usually leads to the advanced degradation of PLA chains resulting in a sharp reduction of the thermo-mechanical properties of the polyester matrix. Moreover, it is of interest to note that to achieve the recycling of PLA to lactide, different “unzipping” depolymerization catalysts have been investigated with particular attention to alkali earth metal oxides, such as CaO and MgO [308].

Finally, it is important to take into account that the effect of mineral fillers on main properties of polymer composites depends on a big number of factors, such as filler loading and its inherent properties, filler particle size and shape, filler/polymer adhesion, method of fabrication to assure the good filler dispersion within the polymer matrix, and last but not least, the methods and conditions of processing [293].

Table 8
Selected examples assessing the key-role of fillers on PLA properties.

Filler	Beneficial effects into PLA	Reference
Talc	- Marked nucleating effect on PLA crystallization - Effective nucleating agent, the finer talc led to higher degree of crystallinity - Addition of 30 wt. % talc leads to the increase of Young's modulus from 4.1 GPa (neat PLA) to 9.8 GPa for composites	[89,113] [189] [183]
CNT	- Antistatic to electrical conductivity, good/improved thermal and mechanical properties (tensile strength and modulus), flame-retardant, crystallization, etc.	[3,40,179,225–227]
CNT and CB Graphite derivatives	- PLA with increased electrical conductivity - Percolation threshold and electrical conductivity adding exfoliated graphite - Addition of expanded graphite: higher rigidity (Young's modulus and storage modulus), improved crystallization kinetics, moderate increase in thermal stability, FR properties (alone or in synergistic blends with OMLS)	[223] [241] [235,237]
Layered silicates	- Stiffness, high tensile and flexural strength, increased HDT, flame-retardant properties, better processing (kinetics of crystallization), barrier properties, etc.	[3,40,178,282,298–300]
Hydroxyapatite	- Composites designed for biomedical applications with specific end-use properties (osteoconductivity and bone bonding ability), reinforcing effects	[270,271]
Calcium carbonate	- HA neutralize the acidic species formed following the degradation of PLA Addition of up to 30 wt.% micro- and nanosized $CaCO_3$ previously treated with calcium stearate enhanced PLA mechanical properties	[158] [276]
Fillers/additives used in FR systems	- PLA/ $Al(OH)_3$ composite is capable of reconciling flame resistance with feedstock recycling of PLA to cyclic monomer - PLA intumescent formulations with FR properties using ammonium polyphosphate (APP)/pentaerythritol (PER) or starch and lignin - Synergistic effects in terms of FR between expandable graphite and APP - PLA composites assessing FR properties obtained using (nano)fillers and traditional FR additives (melamine derivatives, metal hydroxides, phosphorous derivatives such as APP or phosphinates, etc.)	[301] [176] [240] [3,176,240,300,302–307]
Treated ZnO CaO, MgO	UV screening and antibacterial properties “Unzipping” depolymerization catalysts allowing PLA recycling	[40,102,103] [308]

4. Case study: PLA–calcium sulfate composites designed with special end-use properties

Composites of PLA–CaSO₄ (calcium sulfate (CS), anhydrite or hydrated forms) have been firstly considered in biomedical applications for bone repair, in situ forming scaffolds or for the realization of implant materials comprising antibiotics, drugs or other therapeutic agents [309–315]. CS was considered an unusually biocompatible material which is completely resorbed following its implantation [312].

Following an original study developed by our research group [316], and in response to the demand for enlarging PLA applications range while reducing its production cost, it was demonstrated that commercially available PLA can be effectively melt-blended with previously dried gypsum [316–321], a by-product directly issued from the lactic acid (LA) production process (Fig. 11).

In fact, the basic constitutional unit of PLA, LA (2-hydroxypropanoic acid) is obtained by carbohydrate fermentation using appropriate bacterial strain. Following the treatment with calcium hydroxide, the broth containing calcium lactate is filtered to remove cells, carbon treated, evaporated and acidified with sulphuric acid to get LA and calcium sulfate [28,58,322]. For each kilogram of LA produced, about 1 kg of gypsum is formed as a coproduct [322]. Only small quantities of gypsum produced under current conditions are used as soil conditioners for replacing mined gypsum. Therefore, there is a need for new prospects in which gypsum can be made more profitable in parallel with the reduction of costs of LA and PLA. However, to decrease the amount of this by-product (gypsum), some technological improvements in LA production are already considered [28].

This section will reveal that this coproduct from LA manufacture, i.e. gypsum, can be used as microfiller to produce PLA composites designed with specific end-use properties. This is due to unexpected favourable interactions existing between calcium sulfate (CS) and PLA, and owed to the possibility to obtain highly loaded composites (i.e., up to 50 wt. % filler) with quite well-distributed particles using the conventional melt-compounding approach. From the perspective of “green chemistry”, as well as economics, CS is a logical filler choice for cost reduction of PLA due to its availability as a waste stream from LA production [323].

4.1. Calcium sulfate (CaSO₄) as filler for melt-mixing with PLA

Calcium sulfate (CS) hemihydrate (CaSO₄·0.5H₂O)—the by-product obtained from LA production process was provided by Galactic s.a. and dried at various temperatures to obtain several forms of CS anhydrite (Fig. 12). CS hemihydrate can be found in α- and β- forms in function of the production method [324]: α- CS hemihydrate is typically obtained by the wet dehydration of gypsum dihydrate in an autoclave (under pressure), β- CS hemihydrate is formed by dry-dehydration (usually at temperatures above 100 °C, under air). This last filler (i.e. β- CS hemihydrate) was used as raw-material for the production of anhydrites in the frame of experimental studies [316].

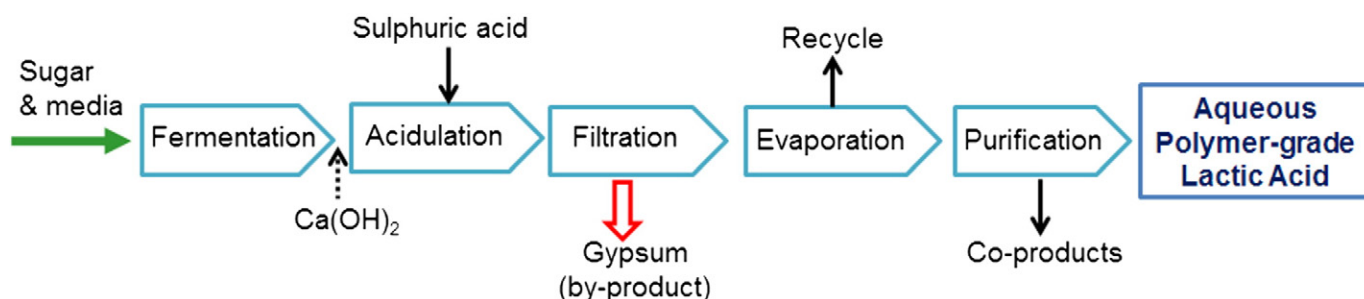


Fig. 11. Gypsum as by-product resulted from the lactic acid production process (adapted, from the Ref. [28]).

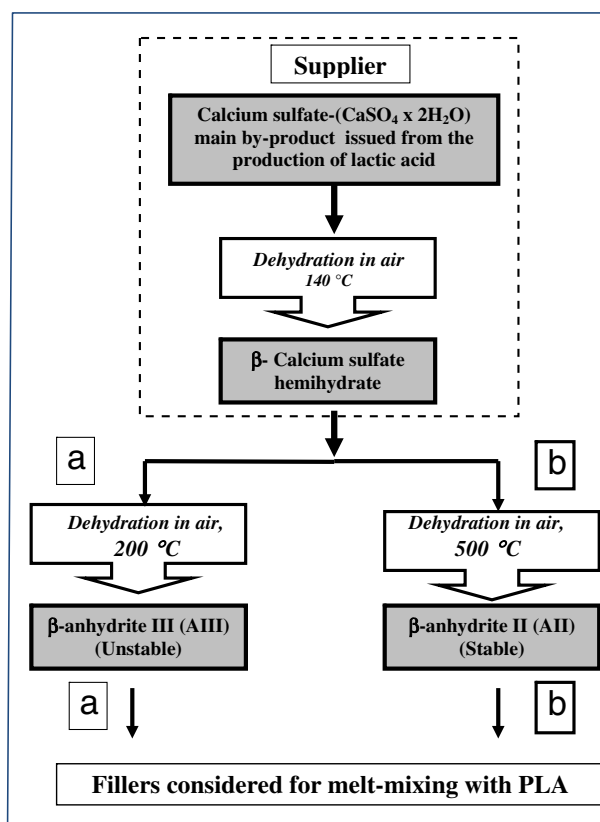


Fig. 12. Experimental routes considered for the preparation of fillers for melt-blending with PLA: (a) β-anhydrite III route; (b) β-anhydrite II route (with permission, from the Ref. [319]).

PLA is stable in the molten state provided that it is adequately stabilized and dried with a maximum acceptable water content of 250 ppm, or even below 50 ppm in the case of processing at high temperature [7]. Therefore, it is of prime importance to dry (dehydrate) also the CS hemihydrate (CaSO₄·0.5H₂O) prior to melt-compounding. As aforementioned, drying gypsum, i.e. CS dihydrate, under atmospheric pressure (at above 100 °C) favors β-CS hemihydrate formation. Further increasing the temperature allows producing unstable β-anhydrite III (AIII) (formed at about 200 °C) and stable β-anhydrite II (AII), generated according to the experimental procedure at 500 °C. Following different investigations, it was concluded that the β-anhydrite form AII is much better suited for melt-blending with PLA than AIII, which is by far too sensitive to atmospheric water absorption (Fig. 13). It is important to point out that CS anhydrites, i.e., AIII or AII, can react very quickly or very slowly with water, thus they have received the name, respectively, soluble and insoluble anhydrite.

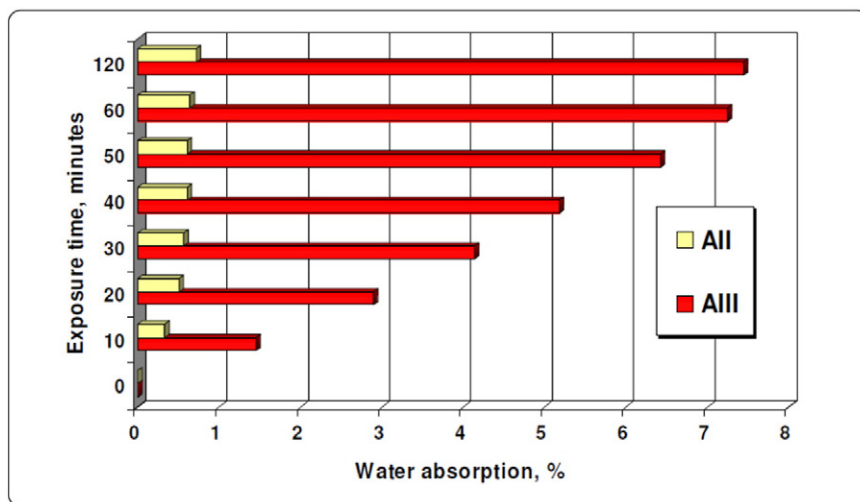


Fig. 13. Comparative water uptake of AII and AIII at different exposure time under atmospheric conditions (adapted, with permission from the Ref. [316]).

4.2. Highly filling PLA with β -calcium sulfate anhydrite II (AII)

In a first study [316], PLA composites have been produced by melt-blending PLA ($M_{n(PLA)} = 74,500$, dispersity index = 2.1, D-isomer content = 4.3%) and previously dried CS hemihydrate (d_{50} ranging from 9 to 43 μm) in a Brabender bench scale kneader at the temperature of 190 $^{\circ}\text{C}$. Due to PLA sensitivity towards hydrolysis, it has firstly demonstrated that formation of β -anhydrite II (AII) by adequate thermal treatments is a prerequisite. In contrast, even at lower loading of filler, the melt-blending PLA with AIII or CS hemihydrate triggered substantial decrease in the molecular weights of PLA. In the absence of any surface treatment, higher mechanical performances were obtained for particle size close to 10 μm , thus AII ($d_{50} = 9 \mu\text{m}$) was selected for more comprehensive studies [316,318,325–327]. In composites, adding up to 50 wt. % AII into PLA, the tensile strength (Fig. 14a) gradually

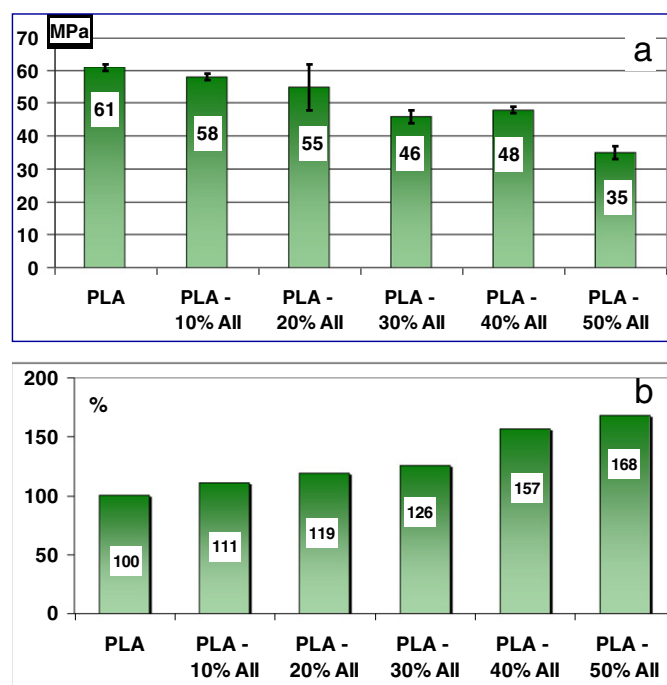


Fig. 14. (a, b). Tensile strength of neat PLA compared to PLA-AII composites (a); Increase of Young's modulus (in %) by filling PLA with up to 50 wt. % AII (b); (adapted, with permission from the Ref. [316]).

decreased with filler content passing from 61 MPa (neat PLA) to 35 MPa. In contrast, Young's modulus (Fig. 14b) increased with filler loading with about 70% adding 50 wt. % AII.

Nevertheless, a tensile strength higher than 45 MPa typically found for the composites filled with 30–40 wt. % AII was considered as an optimistic result in the perspective of potential applications.

To evaluate the affinity between the PLA matrix and AII particles, the recorded tensile data have been compared with the prediction values obtained using classical models, i.e., of Einstein and Nicolais–Narkis. Accordingly, it was concluded that favourable interactions are more likely dominant between AII particles and the ester functions of the PLA backbone [316]. Well-dispersed β -AII particles with various geometries and quite broad size distribution were clearly evidenced by SEM analysis (Fig. 15 (a, b)) at the surface of cryofractured composites. It is worth pointing out that such quality of dispersion and interfacial adhesion was obtained without any previous surface treatment of particles and using a short time of melt-compounding.

From TGA measurements it has been found that PLA-AII composites are characterized by good thermal stability, as the addition of filler (AII is thermally stable) is leading to composites with equal, or even higher thermal stability than the neat polyester matrix. Furthermore, as it was demonstrated by DMTA (Pluta et al. [327]), filling PLA with AII is leading to the increase of the storage modulus in a broad temperature range (Fig. 16). Therefore, due to unexpected favourable interactions existing between CS and PLA, the dehydration of gypsum hemihydrate to form β -anhydrite II (AII) might not only be economically viable, but utilization of this filler can also open the way to highly filled PLA-AII composites characterized by good thermal and mechanical properties.

4.3. Surface treatments of anhydrite II (AII)

To offer better value, usually the fillers are "coated" and/or surface-treated to improve mechanical properties, moisture-resistance, reduce surface energy and melt viscosity, enhance dispersion and processing characteristics, etc. [182,328–332]. Surface modifiers such as fatty acids and their salts, silanes, titanates, zirconates, etc., are generally indicated for the treatment of mineral fillers. This transforms the original hydrophilic surface into a hydrophobic one, reducing the water absorption and weakening the forces of attraction between the particles of filler. For instance, a surface treatment, such as the coating with stearic acid (SA) can dramatically reduce the surface energy of the mineral particles [328,329,332].

Blends of dried CS (β -anhydrite II form (AII) with d_{50} of 9 μm) having various AII/SA ratios (from 99.6:0.4 up to 98:2, by weight) were used to produce PLA-AII composites [333]. The comparative DSC analysis of

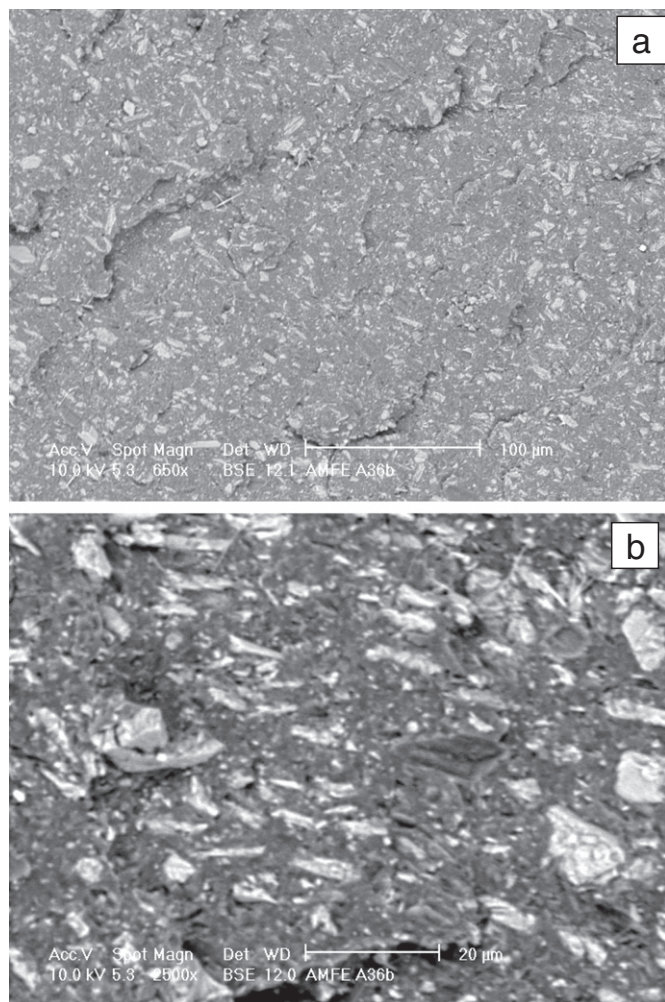


Fig. 15. (a, b). SEM pictures of cryofractured surfaces of PLA–40 wt.% All composites at low (a) and high magnification (b) (adapted, with permission from the ref. [316]).

composites has firstly proved that the addition of All filler coated by 2% SA (All_c) conferred cold crystallization properties to PLA matrix, likely as a result of SA effects (Fig. 17). Additionally, in relation to the thermal stability as determined by TGA, it was observed that, somewhat

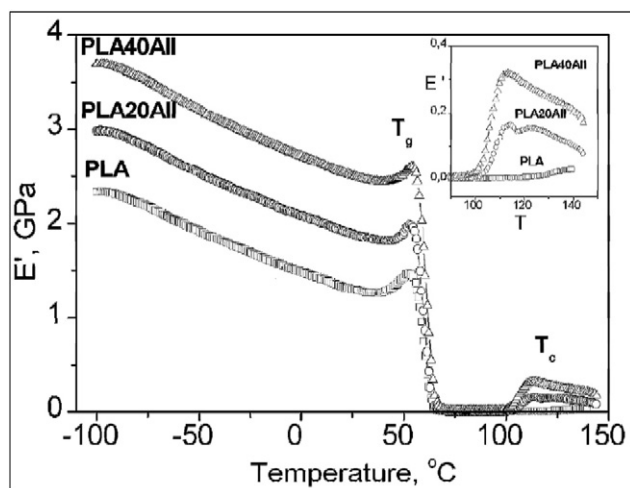


Fig. 16. Dependencies of storage modulus (E') versus temperature: unfilled PLA compared to PLA–20 wt.% All and PLA–40 wt.% All composites (adapted, with permission from the Ref. [327]).

surprisingly, all PLA–All_c composites were characterized by slightly higher thermal stability compared to the composites containing non-coated All. This improvement was ascribed to the modification of the dispersion and/or size of All triggered by the coating with SA, with beneficial influence on the thermal stability of composites. Regarding the mechanical properties, the increase of filler content decreased the tensile strength properties and interestingly enough, in all cases utilization of All_c (All/SA in 98/2 ratio by weight) led to lower tensile strength values, the differences being more evident at higher filling, i.e. 40 wt.% (Fig. 18).

In this context it is noteworthy mentioning that in the group of Pukánszky et al. [334], PLA–CS (All) composites were prepared from PLA ($M_n = 88,500$ g/mol and dispersity (M_w/M_n) = 1.8, D-isomer less than 2%) and a natural CaSO_4 filler (All) to study the developed structure in microcomposite and the interaction between components. The filler (d_{50} of $4.4 \mu\text{m}$) was coated with SA to modify the interactions with the polymeric matrix. Mechanical properties changed only slightly with increasing the amounts of uncoated filler, but the coating resulted in a drastic change of tensile properties. The quantitative estimation of interfacial interactions and their comparison to existing data proved that the interaction of PLA and CaSO_4 corresponds to values observed in other mineral filled polymers. On the other hand, the reinforcing effect of the coated filler with SA was found extremely poor.

Concerning the impact properties, it has been reported that in some cases, the incorporation of mineral fillers at levels needed to produce useful effects, triggers a significant decrease in the impact resistance. Indeed, at increased filler loading (30 or 40 wt.%) a dramatically drop in impact resistance was reported for PLA–All composites with respect to neat PLA [316]. Interestingly, by using All_c excellent impact performances are seen even at high filling (e.g. an increasing of 170% by filling with 40 wt.% All_c with respect to the addition into PLA of a similar amount of non-treated All). From the perspective of impact performances, SA seems to be an excellent surface modifier for All, which can reduce the interactions between filler and polyester matrix (PLA) [334], allowing obtaining the required good dispersion, easy debonding and prompt microvoids formation, as effect of the impact sollicitation. Besides, the All/SA ratio and SA percentage in composites are reported to play a key-role in maximizing the impact resistance of highly filled PLA (Fig. 19).

Last but not least, it is important to point out that additional experiments were realized to produce highly filled composites (e.g. PLA–40% All) using All with different surface treatments, i.e. metal stearates, silanes, etc. Substantial improvements in thermal stability and mechanical properties (tensile strength and modulus), were obtained where the filler was previously silanized, e.g. by 1–2% [3-(methacryloyloxy)propyl]trimethoxysilane.

4.4. Addition of plasticizers into PLA–All composites

Unfortunately, as aforementioned, at filler amount higher than 20 wt.% All, the composites are characterized by low impact resistance [316]. Thus, for some applications such as the extrusion of films or fabrication of containers – blown, thermoformed and injection molded, these composites do not have the toughness/impact resistance or the ductility required for processing (e.g., to avoid the susceptibility to break down during extrusion) and they need to be modified in order to fulfil these requirements. Plasticizers are frequently used, not only to increase the flexibility and ductility of glassy polymers, but also to improve the dispersion in filled systems, and also the processability. The ideal plasticizer for PLA can be any product (preferable, biodegradable), sufficiently non-volatile and which has a relatively low molecular weight to produce a substantial reduction of glass transition temperature (T_g) and adequate mechanical properties, i.e., a decrease of Young's modulus, an increase in ductility and impact resistance [19,335–337]. It is well-known that for instance the monomer, lactide itself, is considered as one of the best plasticizers for PLA [68,338], but its drawback

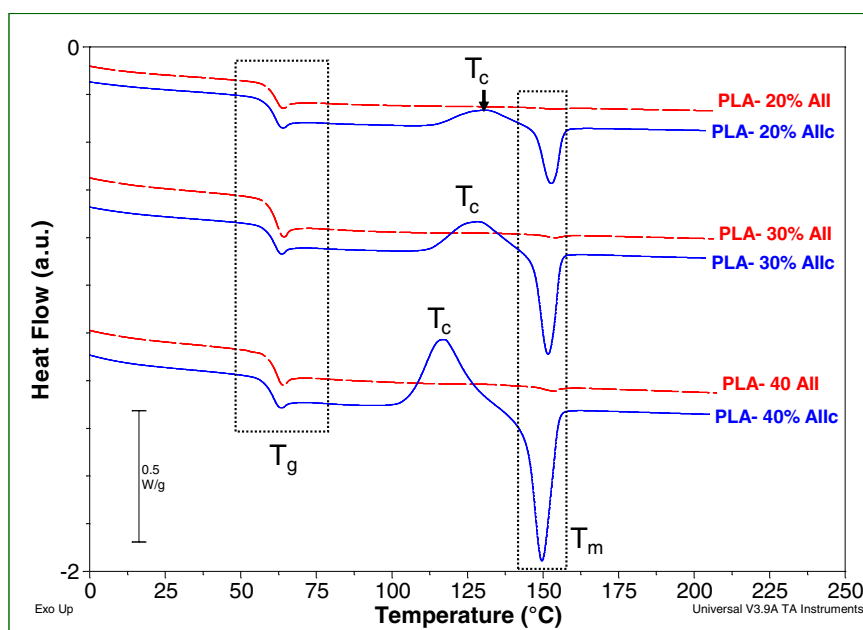


Fig. 17. Comparative DSC measurements on PLA-(20–40) wt. % All and Allc composites (second heating, with ramp of 10°C/min) (adapted, from the Ref. [333]).

is the very quick migration to the polymer surface, which is observed when PLA with high content of lactide is processed. To find out other alternatives, different commercial or synthesized plasticizer systems have been considered: oligomers of lactic acid (OLA) [339–341]; partial fatty acid esters, glycerol esters, citrates, citrate oligoesters, dicarboxylic esters [68,135,342–348]; higher molecular weight plasticizers like poly(ethylene glycol) [349–354]; poly(propylene glycol) [355–357], and more recently, polymeric adipates [358–360].

Among the different commercially available products shown to work well for improving PLA toughness/impact properties, low molecular weight esters, i.e., bis(2-ethylhexyl) adipate (DOA), glyceryl triacetate (GTA), as well as polymeric adipates (Glyplast 206/3NL – it will be noted hereinafter Glyp3 and Glyplast 206/7 – Glyp7), characterized by different molecular weights have been added as third component into highly filled PLA–All composites via melt-compounding [326].

The efficiency of low molecular weight esters (GTA, DOA) and polymeric adipates (Glyp3 and Glyp7) has already been considered with different PLA grades, their effectiveness being confirmed mainly at high amount of plasticizer, i.e., 15–20 wt. % [336,358]. Often, at high percentage of plasticizer, the PLA compositions are characterized by low tensile strength with respect to the neat PLA. Accordingly, in order to preserve the mechanical performances of highly filled

PLA–All composites (40 wt. % filler) at good level, the percentage of plasticizer was limited to 10 wt. % [326]. Regarding the thermal stability of composites containing plasticizers (i.e., PLA–40% All–10% plasticizer), due to the volatility of plasticizers, was not surprising a deterioration of the thermal properties compared to the composites without plasticizer. Because GTA and DOA are characterized by higher volatility when compared to Glyp, an advanced decrease in the thermal stability of the composites obtained with these low molecular weight plasticizers was evidenced, e.g., by the lower value of the onset of thermal degradation ($T_{5\%}$). By contrary, PLA–All–Glyp compositions do not exhibit any significant loss under 300 °C, result that can be connected to the possibility of processing at higher temperature.

The SEM analysis of the cryofractured samples (Figs. 20 (a–d)) have revealed that the composites plasticized with polymeric adipates contain larger aggregates than the blends performed using low molecular weight plasticizers – in which case, particles with lower dimension were observed. This result seems to indicate that the low molecular weight plasticizers tend to further improve the dispersion state of All in the related composition, when compared with the polymeric plasticizers. Additionally, for the ternary blend (PLA–All–DOA) the phase separation of plasticizer (DOA) from the matrix was clearly stressed out (Fig. 20a). Undeniably, it is important to remind that in PLA–DOA

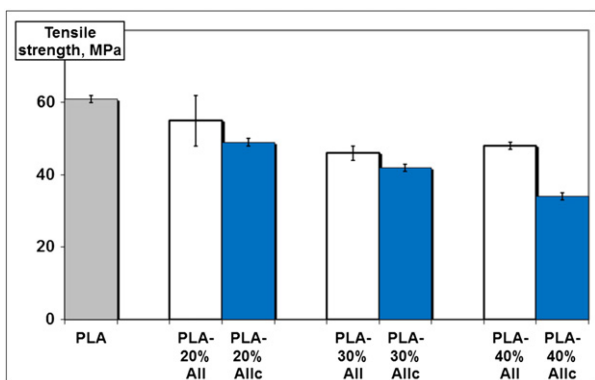


Fig. 18. Tensile strength of neat PLA with respect to PLA–All composites with/without filler treated by stearic acid (adapted, from the Ref. [333]).

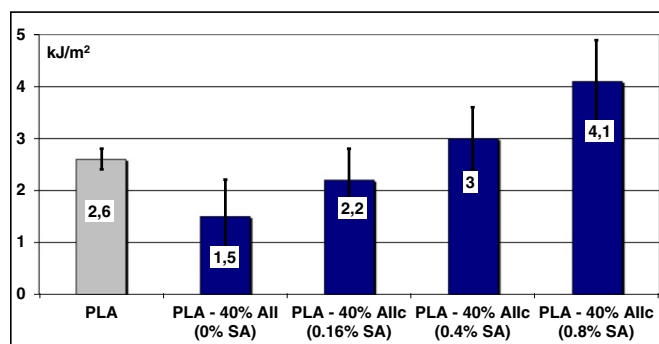


Fig. 19. Notched impact resistance (Izod) of neat PLA compared to PLA–40 wt. % All composites, where All is coated with different percentages of stearic acid (it is indicated the wt. % of SA in composite) (adapted, from the Ref. [333]).

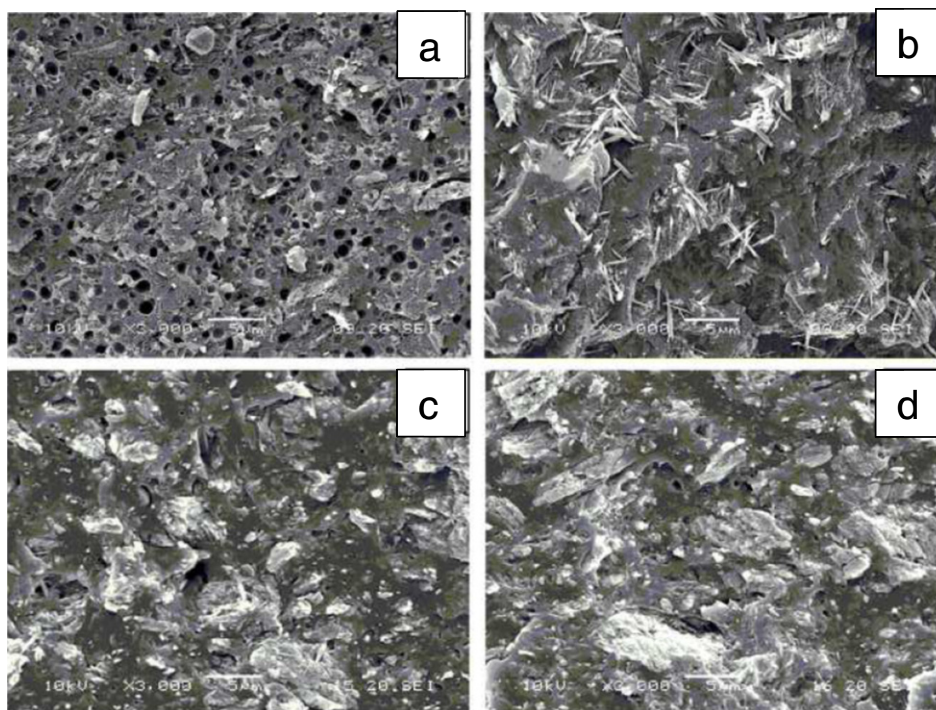


Fig. 20. (a–d). SEM pictures of the cryofractured composites (PLA–40% AII–10% plasticizer): **a**- DOA; **b**- GTA; **c**- Glyp3; **d**- Glyp 7 (adapted, with permission from the Ref. [326]).

blends the PLA matrix becomes saturated with this plasticizer at a certain concentration (at about 5 wt. %) and above this amount a phase separation can occur [336].

Regarding the mechanical properties, addition of plasticizer (10 wt. %) into PLA–AII compositions led to a decrease of both, tensile strength and Young's modulus. Because the plasticizer behaves like a solvent when mixed with a polymer, the macromolecular chains cohesion is decreased and tensile strength properties are thus reduced. It is interesting to stress out that the maximum tensile strength of PLA–AII composites containing 10 wt. % plasticizer was obtained using polymeric plasticizers (31 MPa) instead of low molecular weight plasticizers such as GTA (26 MPa) or DOA (only 18 MPa). The more important decrease of tensile strength recorded using DOA is not surprisingly due to its limited miscibility with PLA. On the other hand, the impact resistance values (see Fig. 21) obtained using polymeric adipates—Glyp3 and Glyp7, i.e. 3.0 and 3.6 kJ/m² respectively, represent an attractive increase of the impact performances with respect to the composites without plasticizer, i.e. PLA–40% AII (only an impact resistance of 1.5 kJ/m²). Moreover, addition of low molecular weight plasticizers into PLA–AII compositions, i.e., DOA and GTA, led to a more spectacular increase of

impact resistance (values of 4.4 and 6.4 kJ/m², respectively). As remark, the PLA–AII–GTA composites showed also the most significant increase of the nominal strain at break. Following the mechanical properties, it was concluded that the addition of GTA and Glyp in PLA–AII compositions has shown the most attractive compromise of both impact and tensile strength properties, and these ternary compositions seem to be the most adaptive for further applications where the toughness is a critical requirement.

4.5. Addition of impact modifiers

It is generally recognized that the brittleness of PLA and PLA based composites is a main drawback which is limiting PLA applications, from commodity to high engineering/performance materials, thus various strategies have been considered to improve PLA toughness [93,94,361–376].

Regarding the PLA–AII composites, unfortunately, at filler amount higher than 20 wt. %, they were characterized by lower impact resistance than the neat PLA [316]. As aforementioned, addition of selected plasticizers, a general approach used to increase the impact resistance of polymers, presents some drawbacks such as, the decrease of tensile strength properties and of glass transition temperature (T_g). Additionally, the thermal stability of plasticized PLA is usually decreased due to the volatility of plasticizers that have been incorporated into the polyester matrix [326].

Another important option that can be followed for increasing impact resistance/toughness is represented by addition into PLA of selected impact modifiers (IM) [93,377–383]. Among the different commercially available products, some specific ethylene copolymers are between the most considered IMs to improve PLA toughness [12,364,384–386]. The main issue in producing toughened plastics is the adequate dispersion of the elastomer as small domains, which will initiate the plastic deformation and will absorb the impact mechanical energy. Following preliminary studies, it was found that the addition of Biomax® Strong 100 (BS) – (supplier DuPont) remarkably improved the impact properties of PLA. The notched Izod impact resistance increased from 2.6 kJ/m²—value obtained for the pristine PLA, to 4.6 kJ/m² by addition

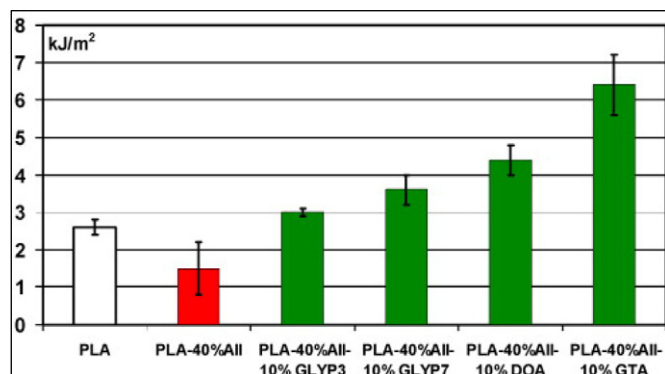


Fig. 21. Notched impact resistance- Izod of different PLA composites with/without plasticizer (% by weight) (with permission, from the Ref. [326]).

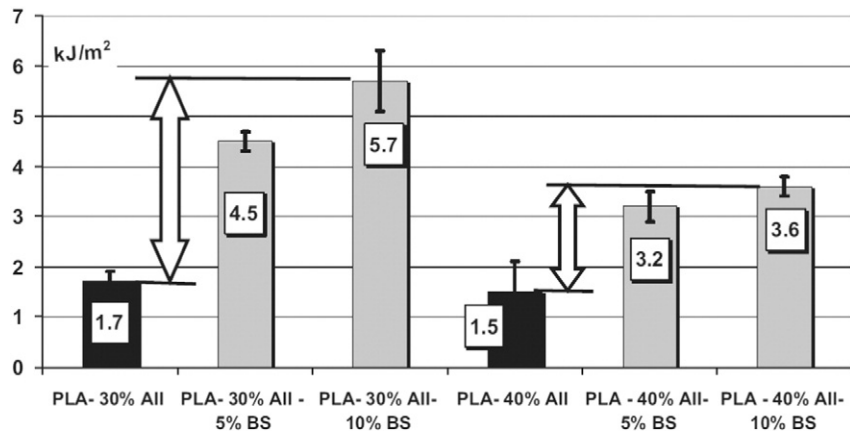


Fig. 22. Notched impact resistance (Izod) of PLA–AII composites with/without BS as impact modifier (with permission, from the Ref. [319]).

of 5 wt. % ethylene–acrylate copolymer (i.e. BS) or even to more than 12 kJ/m² by addition of 10 wt. % BS into PLA [319]. In a second experimental step, the IM (up to 10 wt. % BS) has been added into the highly filled PLA–AII compositions (30–40 wt. % filler) and these composites were characterized with particular attention paid to the impact properties (Fig. 22). Accordingly, the addition of up to 10 wt. % BS led to a surprising two- to three-fold increasing of impact resistance (Izod), excellent thermal stability and typically good filler dispersion (conform SEM investigation).

Furthermore, Pluta et al. [377] have compared two techniques for the addition of BS into PLA–AII composites: (1) the direct melt blending of all components (PLA, 40% AII and 10% BS) in a single step and (2) the previously coating *via* solvent casting of AII by BS, followed by the melt-mixing of coated filler (noted as AII_{CBS}) with PLA. Selected SEM

micrographs of the tensile fractured surfaces of selected PLA compositions are shown in Fig. 23 (a–d).

By comparison with the composite without IM (i.e. PLA–40 wt. % AII, with an impact resistance of only 1.5 kJ/m²), the addition of BS led to a major increasing of the impact properties. Obvious, better results were obtained using BS-coated filler (AII_{CBS}), i.e. a value of 5.4 kJ/m², than by the direct mixing of all components (3.6 kJ/m²). In fact, the presence of BS-layer at the interface between PLA matrix and AII filler, improves distinctly the ability of composites (PLA–AII_{CBS}) to dissipate the energy provided during impact loading. By considering the thermo-mechanical properties and structural modifications, it was assumed that the “core (filler)–shell (elastomer)” approach ascribed to AII_{CBS} could disclose a practical interest in production of PLA composites designed with improved impact resistance over a wider temperature region.

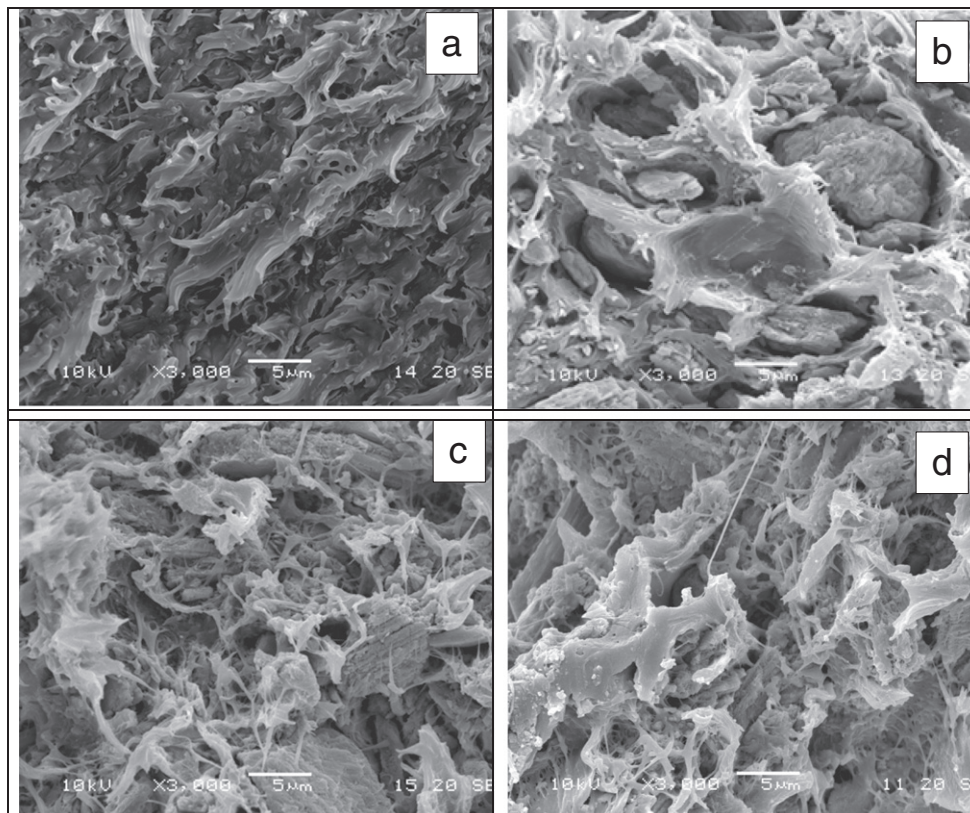


Fig. 23. (a–d). SEM micrographs of the tensile fractured surfaces: (a) PLA–BS, (b) PLA–AII, (c) PLA–AII–BS, and (d) PLA–AII_{CBS} (adapted, with permission from the Ref. [377]).

4.6. PLA–calcium sulfate composites with flame retardant (FR) properties

PLA composites are of interest for the fabrication of electrical/electronic devices or automotive items requiring good mechanical, thermal and FR properties. As for traditional engineering polymers, different approaches can be investigated to produce PLA with tailored FR properties. Among them, has to be mentioned the addition into PLA of selected nano- and microfillers, frequently in association with FR additives [3,95]. Usually the FR compositions are complex, while the list of nanofillers with FR effectiveness in PLA is relatively long: organo-modified clays [235,299,300,387–392], carbon nanotubes (CNT) [3,229,393,394], other types of nanoparticles, or their combinations with traditional FR additives [173,174,303,395].

In many cases are wanted synergies with traditional FR additives such as melamine derivatives [302–304], metal hydroxides [300,305,306], phosphorous derivatives such as ammonium polyphosphate (APP) [176,240,304,307] or phosphinates [396], etc. Unfortunately, most of the products that can provide PLA with flame retardancy, sometimes trigger problems such as the loss of mechanical and thermal properties due to the degradation of the polyester matrix, aspects that need to be considered when targeting a potential application. Unfortunately, because of their flammability and dripping during combustion, PLA–All composites cannot be recommended for applications where advanced FR properties are required, thus the possibility to produce FR PLA–All composites has been investigated.

4.6.1. Hybrid (nano)composites with FR properties

In order to obtain PLA–All composites characterized by specific end-use FR properties, the co-addition of selected organo-modified layered silicates (OMLS) was considered [3,298,397]. Two organo-modified layered silicates (OMLS) have been used as nanofillers for melt-mixing with PLA and All: Bentone 104 (noted as B104)–supplier Elementis Specialties and Cloisite 30B (C30B) – supplier Southern Clay Products [298]. SEM analyses of ternary compositions (PLA–All–OMLS) have once more evidenced the good dispersion of the microfiller (All) into PLA matrix (Fig. 24), thus it was not excluded an additional beneficial effect due to the co-addition and intercalation of OMLS between PLA macromolecular chains.

Regarding the thermal and mechanical performances of hybrid (nano)composites obtained by the co-addition of All and OMLS, these materials are characterized by quite high tensile strength and rigidity, whereas an important increase in thermal stability (of about 20°C for $T_{5\%}$) with respect to neat PLA was evidenced by TGA. This was ascribed to a synergistic effect conferred by the dispersion of nano- and micro-filler into the polyester matrix.

OMLS have received much attention for their positive influence on the thermo-mechanical and barrier properties, but also in terms of flame retardancy, because OMLS are leading to the formation of a ceramic protective surface layer during combustion [398,399]. Since All is inert to the flame, there is no heat of combustion added by the

micro-filler presence, nor additional endothermic effect during heating as observed with specific FR fillers such as aluminium hydroxide or magnesium hydroxide. As illustrated in Fig. 25, during UL94 HB testing PLA and PLA–All composites burn with drips (behaviour which could limit their utilization in electrical applications), whereas the (nano)-composites (PLA–All–OMLS) burn without drips and an important charring is formed owing to the presence of nano-clay.

In another context, the specificity of fire tests can be for discussion. Accordingly, the FR properties conferred by OMLS are sometimes better displayed by using the cone calorimeter testing, frequently at a heat flux of 35 kW/m². In these tests, the neat PLA started to burn after 75s and has shown the highest pHRR, i.e., of 374 kW/m². For all formulations containing OMLS, an intumescent char was formed and in all cases the presence of All increased the time to ignition (TTI) compared to PLA–OMLS nanocomposites or to neat PLA. Furthermore, the formation of the char layer is believed to be principally responsible for the reduction of HRR during cone calorimeter experiments. Indeed, the PLA–All–OMLS hybrid (nano)composites have shown the most important reduction of pHRR (i.e. of about 40%) with respect to neat PLA [298].

It is noteworthy mentioning that these results were validated by up-scaling (Fig. 26) using twin-screw extruders as main equipment (e.g. Leistritz type ZSE 18 HP-40D). Selected OMLS and All microfillers (e.g. All from LA process or as alternative, calcium sulfate (All) manufactured from high purity natural gypsum) were used as dispersed phases. Interestingly in relation to the FR properties, the fire tests by cone calorimetry proved a decrease by more than 45% of pHRR with respect to neat PLA, result that was reasonably ascribed to a better morphology/dispersion obtained using the twin-screw extruder, assumption validated by SEM analysis.

4.6.2. PLA–CaSO₄ (All)–melamine phosphate as halogen free FR composites

Unfortunately, PLA–All–OMLS (nano)composites cannot be classified according to UL 94V test, which can be a key-requirement for a potential utilization in electronic applications. Thus, following another experimental approach, PLA–All composites with advanced FR properties, i.e., the category V0 (UL-94V test), have been obtained using selected non-halogenated FRs.

After the preliminary testing of different melamine based products with PLA, Melapur MP (melamine phosphate, today the product of BASF), has been selected for melt-blending with PLA (3051D, NatureWorks) and All (β -anhydrite II, 9 μ m) [401]. It is noteworthy mentioning that MP can be successfully used to obtain FR polymeric composites (based also on PLA [303]), while in many papers and reviews [402] is given information about its FR mechanism. As it was evidenced by TGA measurements (Fig. 27), the addition of MP into PLA or in PLA–All blends is leading to composites showing the decrease of the max. temperature of degradation (T_d) with respect to the neat PLA matrix and PLA–All composites. This result was ascribed to the degradation of PLA due to presence of water molecules and of acidic species produced following the heating of FR additive, i.e., MP.

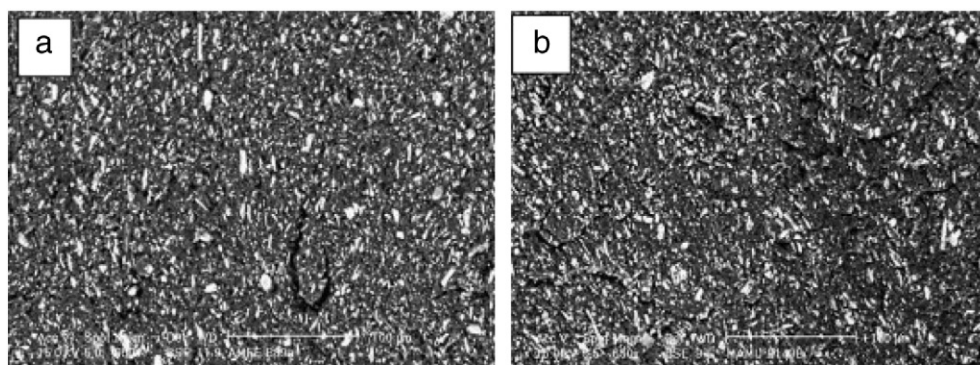


Fig. 24. SEM pictures of the cryofractured surfaces of hybrid (nano)composites: PLA–40% All–3% B104 (a) and PLA–40% All–3% C30B (b) (adapted, with permission from the Ref. [298]).

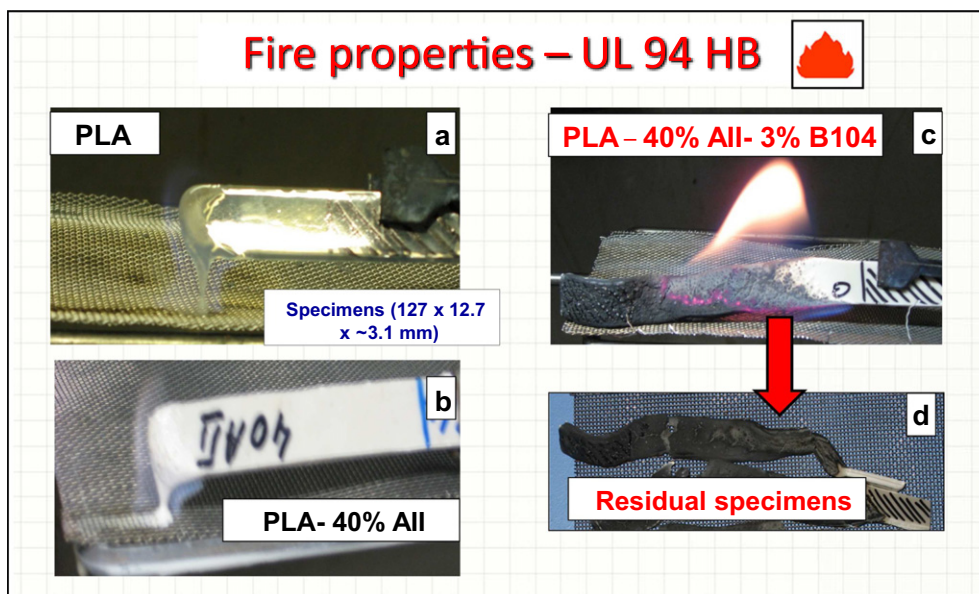


Fig. 25. Illustration of the behaviour during UL94 HB testing: specimens burned with drips (PLA (a) and PLA-40% AII (b)) and without drips (PLA-40% AII-3% B104 (c)), and residual specimens (d) (adapted, based on the Refs. [298,400]).

Fig. 28 shows the aspect of residual specimens (3.2 mm thickness) following the UL 94V (vertical) fire testing. Depending on formulation, different behaviours were observed. On one hand, PLA-AII composites cannot be classified according to UL 94V due to the dripping and combustion of specimens up to the holding clamp. On the other hand, co-addition of AII (25 wt. %) and MP (15 wt. %) allowed only a V2 rating, while a classification V0 is reached by increasing the loading of FR product (i.e. MP) at 25 wt. % in PLA compounds. In addition, regarding the FR properties of these composites, it is noticeable that the limiting oxygen index (LOI) of PLA-25 wt. % AII (LOI = 23%) increased to above 33% following the co-addition of 25% MP into PLA-AII. Lastly, by considering the overall performances of PLA-AII-MP composites (good tensile strength and rigidity, (values of 40 MPa and 4300 MPa (Young'modulus), respectively), FR properties, i.e. V0 category, etc.) it is assumed that these FR PLA composites are of potential interest for further utilization in engineering applications.

4.7. Final considerations regarding the properties and applications of PLA-CaSO₄ composites

PLA can be effectively melt blended with previously dehydrated gypsum, so called CS anhydrite II (AII), by-product from LA fabrication process. These two products (PLA and AII) from the same source as origin can lead by melt mixing to polymer composites characterized by promising thermo-mechanical performances (thermal stability, rigidity, tensile strength, etc.) ascribed to the good filler dispersion and appropriate interfacial properties. Utilization of AII produced by using natural gypsum is also an alternative [316,334, 403]. Moreover, like for other mineral-filled polymers, addition of a third component into PLA-AII compositions, i.e., plasticizers, impact modifiers, nucleating agents, clays, flame retardants (FRs), etc., has been considered to obtain new PLA composites with specific end-use performances (Table 9).

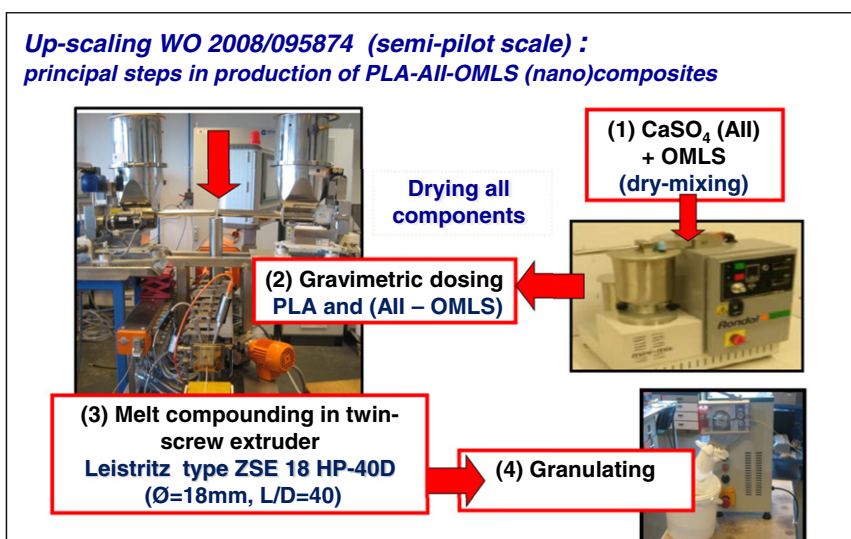


Fig. 26. Production of PLA-AII-OMLS hybrid (nano)composites at semi-pilot scale (adapted, from the Ref. [400]).

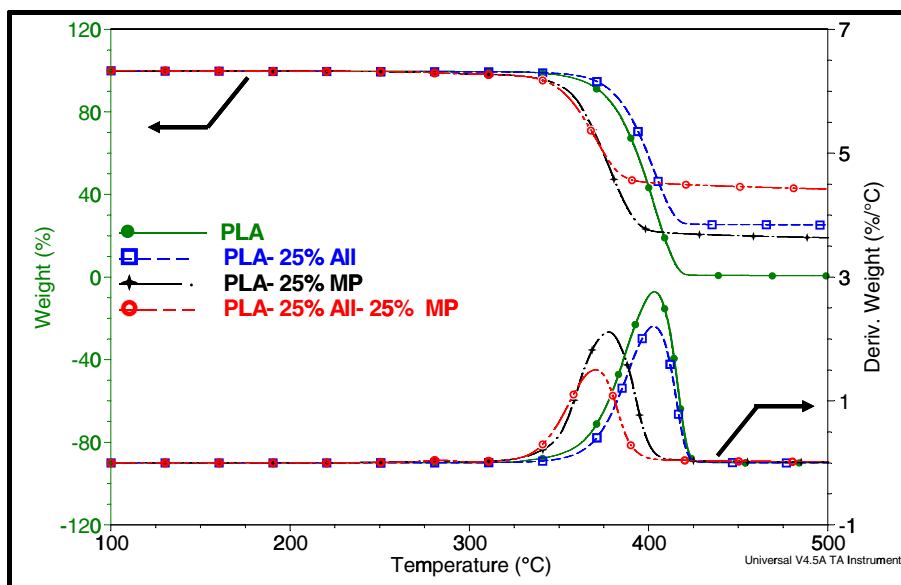


Fig. 27. TGA and d-TG of binary (PLA–MP and PLA–AII) and of ternary composites (PLA–AII–MP) with respect to the neat PLA (under N_2 , ramp of $20^\circ C/min$).

5. Summary and future prospects

PLA, a polyester produced from renewable resources, has actually a key-position in the market of biopolymers and is used for various applications, going from biomedical, packaging and textile fibers, to engineering items. Nowadays, the market of PLA turns from “disposable” (packaging and textiles) to more “durable” materials. However, the utilization in biomedical sector of PLA products of high added value is remaining of high interest (drug delivery systems, surgical implant devices, orthopaedic devices, etc.).

Unfortunately, PLA suffers from some shortcomings (low-ductility and toughness, glass transition and heat distortion temperature, rate of crystallization; high sensitivity to moisture and fast degradation by hydrolysis, etc.). In addition, specific end-use properties are required for the different applications, such as flame retardancy, antistatic to conductive electrical characteristics, anti-UV, antibacterial or barrier characteristics, and so on.

Thus, the reinforcing of PLA matrix with natural or synthetic fibers, the addition of micro- and nanofillers associated with selected additives, is considered as a powerful method allowing obtaining specific end-use characteristics and major improvements of properties.

This review is an insight on the current research, recent progress and key trends in the field of PLA and of material composites based on PLA. In this goal, different aspects have been concerned, going from the

production and selection of PLA matrix, to the preparation and characterization of composites designed with specific end-use properties.

PLA composites are very promising materials since they can show improved performances (high strength and rigidity, enhanced thermal stability, higher HDT and better processing (crystallization ability), low flammability, antistatic to conductive electrical characteristics, barrier properties, and so forth), while maintaining the specific properties of biodegradability of the polymer matrix.

With few exceptions, the methods to produce PLA composites remain similar to those used for other polymers, with a preference for the melt-compounding approach. The most representative PLA composites are reviewed in relation to the nature of dispersed phases (reinforcing fibers, fillers, additives, etc.) and by assessing the enhancements induced in the mechanical, thermal, FR, specific end-use properties, etc. with respect to the neat polyester matrix. On the other hand, there is a special focus on some composites designed for biomedical applications, such as PLA reinforced/filled with hydroxyapatite, several calcium salts, barium sulfate etc. To limit the length of this contribution, the realizations in the field of PLA nanocomposites are less developed here.

It is also noteworthy to mention that some micro- and nano-reinforcements for PLA (e.g. cellulose derivatives) are under current development, and in this context can be predicted a growing trend for the production and use of new PLA (nano)composites, mainly based on renewable bioresources.

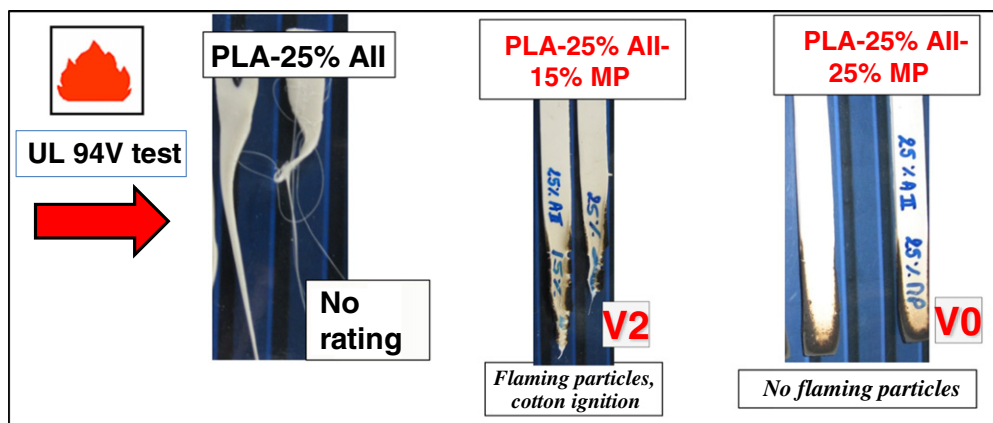


Fig. 28. Classification of PLA–AII composites (without/ with MP) according to UL-94V test and illustration of residual specimens after the vertical burning test.

Table 9
Innovative PLA–CaSO₄ (All) composites obtained by valorisation of gypsum by-product from lactic acid fabrication process (adapted, from the Ref. [377]).

PLA composites/ [References]	Main characteristics	Potential utilization
PLA – CaSO ₄ (All) [316,318,321,327,333]	Rigidity (high modulus), good tensile strength and thermal stability, barrier properties	Biodegradable rigid packaging, engineering applications
PLA – All – plasticizers (impact modifiers) [326,377]	Improved impact resistance and toughness, crystallization properties	Packaging, applications requiring ductility and impact resistance
PLA – All – clays [8,298,397]	Increased time to ignition and low rate of heat release (cone calorimetry), UL 94HB – HB category, anti-dripping properties	Technical components requiring FR properties
PLA – All – halogen-free flame retardants [8,401]	Advanced flame-retardant properties, i.e. V0 rating according to UL 94V test obtained by co-addition of All and selected halogen-free FRs (e.g. MP)	Engineering applications requiring V0 rating such as electrical or electronic devices

Furthermore, to illustrate the possibility to design the properties of composites, a special section was devoted to the production and characterization of innovative PLA-based products filled with thermally-treated calcium sulfate microfiller (anhydrite II), a by-product obtained in the lactic acid production process. Addition of a third component into PLA–All compositions, i.e., plasticizers, impact modifiers, nucleating agents, organo-modified clays, FR additives, etc., has been considered to obtain new composites with specific end-use performances.

Regarding the perspectives, important advances (e.g. point of view enhancement of properties) are expected to be obtained by utilization as polymeric matrix of PLA stereocomplexes, of engineered PLA blends and alloys produced by reactive extrusion (REX). It is also assumed that the development of composites based on PLA is clearly in its early stages compared to the case of petrochemical polymers. Obviously, the level of performances is typically determined by the nature of dispersed phases, their adequate thermal stability, good interfacial adhesion properties and dispersion within the polymer matrix. Hence, the adequate selection and surface modification, the specific treatments to limit PLA degradation and finally the good dispersion, still remain a challenge for obtaining better performances. Thus, it is believed that further work needs to be done with the fibers and fillers of interest for their surface treatment (compatibilization and functionalization) using various techniques and adequate (pre)mixing with the polyester matrix. For the biomedical sector, in the attendance of biocomposites more performants and tailored with specific end-use properties, the controlled degradation of polymeric matrix is remaining a key-issue.

Very promising developments in the synergy aspects are furthermore expected by realization of hybrid PLA (nano)composites and efforts should be made in this direction. Co-addition of micro- and nanofillers, their combination with conventional additives, utilization of combinations of fillers and reinforcing fibers, etc., represent possible approaches leading to new PLA composites designed with specific end-use properties for various applications, going from the biomedical to the engineering sectors.

Acknowledgements

The authors wish to thank the Wallonia Region and European Community for general support in the frame of the Convergence program: SINOLISS, POLYTISS and TECHNOPLY projects, the FEDER 2014–2020 program: PROSTEM, MACOBIO and BIOMAT projects. M. Murariu thanks also to the Wallonia Region, Nord-Pas de Calais Region and European Community for the financial support in the frame of INTERREG projects—MABIOLAC (grant FW 1.3.17) and NANOLAC (grant FW 1.1.8).

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