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Biodegradable Polylactide-Based Composites

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Abstract

The aim of this chapter is to introduce to the use and possible applications of polylactide-based composites. Polylactides are biodegradable aliphatic polyesters, which are widely used in medical and ecological-friendly fields. First of all, a deep description of main characteristics of polylactides is shown. This chapter summarizes many concepts, which comprehend a general view of polylactide biopolymers such as synthesis and structures, physical-chemical and mechanical characterization and possible applications of final products. Then, an overview of composites based on polylactides and their benefits compared with bare polylactides are described.

Keywords: Polylactide, poly(lactic acid), composite, biodegradable, biopolymer, polyester, biocompostable, bone repair, nanocomposite

1. Introduction

Polylactide or poly(lactic acid) (PLA) is the front runner in the emerging biopolymer market with the best availability and the most attractive cost structure [1]. Although PLA existed for several decades, its use has been limited to biomedical applications due its high cost. However, in the new century processing of PLA has been developed in the industry in a large-scale production promoting its commercialization as a commodity plastic [2].

To date, PLA is one of the most used biodegradable polymers in the field of biomedical applications and eco-friendly industrial production. A clear advantage of this polymer is its possibility of polymerization coming from renewable resources as starch, but it is not the only one: stiffness of polylactides are similar to some commodity polymers as polyethylene,

polypropylene and polystyrene [3] and products derived from its degradation process are nontoxic for the human body and also do not leave any footprint in the landfills [4].

2. Synthesis

The monomer of PLA is lactic acid. Although this monomer can synthesize from petroleum, almost all lactic acid available on the market is produced by fermentation. During fermentation a suitable carbohydrate is converted to lactic acid by microorganisms without the presence of oxygen, hence, under anaerobic conditions. Fermentation of sour whey resulted in the discovery of lactic acid in 1780, when it was isolated by C. W. Scheele [5].

Lactic acid is the simplest α -hydroxyacid that contains a chiral carbon atom and exists in the following two enantiomeric forms: L-lactic acid and D-lactic acid. Monomer forms a stable cyclized dimer, that is, lactide. Consequently, dimer presents three different structures, namely L-lactide, D-lactide and DL-lactide. Isotactic, optically active and crystalline homopolymers are obtained if either L- or D-lactide dimers are polymerized. However, DL-lactide or copolymers of L- and D-dimers polymerize obtain atactic, nonactive optically and amorphous polymers [6].

Polymerization of this lactic acid is carried out by polycondensation [7], instead of polymerization of the dimer that occurs by ring opening polymerization [8]. Polymerization started from lactide dimer allows to obtain high level of molecular mass due to a chain polymerization mechanism and this is the mechanism that is normally used for production.

3. Polylactide characterization

3.1. Physical-chemical and mechanical characterization

Poly lactides have a glass transition (T_g) value around 60°C. This characteristic point refers to a change in the mobility of amorphous chains. Hence, atactic homopolymer shows a value of 60°C, but crystalline homopolymers that have some restriction in the mobility of amorphous phase could present T_g values up to 70°C depending on the thermal treatment used for crystallization [9, 10].

Isotactic polylactides (pure PLLA and PDLA have same properties) crystallize forming a homocrystal, which melts in the range of 160–190°C depending on the molecular mass and shows a crystallinity fraction around 35% [9]. This value is calculated using one of the different values for theoretic melting enthalpy extrapolated from experimental analysis by different researches, being the most common values 93.6 [11] and 106 J/g [12].

Depending on the crystallization conditions, PLLA can crystallize in α , β or γ polymorphs [13, 14]. The most common form usually is the orthorhombic α crystal [15], while trigonal β form is obtained under high drawing conditions and high temperatures [16, 17]. Besides, γ poly-

morph is obtained through epitaxial crystallization on special substrates with organic solvents [18]. Recently, the existence of a α' crystal has been reported, which can be identified as a disordered α form, with the same 10_3 helical conformation but different lateral packing [19].

As with other enantiomeric polymers occurs [20], polylactides also form thermally stable crystals when 50–50 wt.% of PLLA and PDLA enantiomers are blended [21]. The formation of stereocomplex crystals is favored with low molecular mass [22, 23] or isothermal treatments above homocrystal melting [24, 25]. These crystals melt at 50°C above the homocrystals and their formation is favored if a pretreatment at temperatures above the melting temperature of α crystals is carried out. This pretreatment allows the formation of homocrystal nuclei and increases the crystallization rate of stereocomplex during the isothermal crystallization step [26].

In regard to the mechanical properties, PLAs display high tensile modulus (3 GPa [27]) and yield strength (50–70 MPa [28]) but low elongation at break (5–7%) that result in a brittle behavior of the material.

3.2. Biodegradability

Ester groups in polylactides allow hydrolytic degradation of polymer chains. The degradation mechanism depends on factors, which can be assigned to two groups: (a) related to material as molecular weight, crystallinity, comonomer structure, porosity, etc; and (b) related to the media: temperature, pH, solute concentration, enzymes, etc. [29].

For bulky materials, there are three kinds of degradation mechanisms: surface erosion, bulk erosion and core-accelerated bulk erosion [30]. A surface erosion mechanism takes place when the hydrolytic degradation rate of the material surface in contact with water (containing catalytic substances as alkalis and enzymes) is much higher than the diffusion within the material. In contrast, a bulk erosion mechanism occurs when hydrolytic degradation takes place homogeneously, irrespective of the depth from the material surface. As it can be foreseen, the hydrolytic degradation mechanism changes from the bulk to surface erosion when material thickness becomes higher than the critical [31]. On the other hand, some authors report that polylactides degradation mechanism proceeds via core-accelerated bulk erosion, when the material is thicker than 0.5–2 mm, due to the accelerated degradation sustained by oligomers and monomers trapped and accumulated in the core part of the materials [32]. Hence, depending of the thickness of the PLA piece, the degradation mechanism proceeds via bulk (<0.5–2 mm), core accelerated (between 0.5–2 and 74 mm) and surface erosion (>7.4 cm). In general, chains in the crystalline region are hydrolysis resistant compared to those in the amorphous regions because the access of water molecules to the chains inside the rigid crystalline regions is prohibited. Such crystalline regions are called “crystalline residues.”

Concerning to enzymatic degradation, no study of specific enzymes for the biodegradation of polylactides has been reported [33]. Williams reported the enzymatic hydrolysis of polylactides in the presence of proteases as pronase, bromelain and proteinase K, being the latter a protease with a strong activity in hydrolizing proteins, particularly keratin [34, 35].

4. Strategies to changes polylactide properties

4.1. Blending

Easier strategy to change properties of a pure polymer is blending with other polymers. These blends could be miscible or immiscible depending on solubility parameters and specific interactions established between counterparts. Miscibility of blends is governed by thermodynamic law, in which the free energy of mixing in the blend must be negative [30]. Polylactide is miscible with polyvinylphenol (PVPh) [36–39], poly(styrene-co-vinylphenol) [40, 41], polyhydroxybutirate (PHB) [42], poly(methyl methacrylate) (PMMA) [43], poly(vinyl acetate) [44] and poly(ethylene oxide) [45].

Phase separation induced by immiscible blends has been commonly used for improving fragile commodity polymers as PS and PMMA with a rubber modification leading into HIPS [46] and high impact PMMA [47]. However, the modifications in polylactides with biodegradable polymers as polycaprolactone (PCL) are an efficient way to toughen polylactides [48].

4.2. Copolymerization

Modification in the synthesis process with other monomers is other way to tune the properties of polylactides. Comonomers as etylenglycol or ethylene oxide [49, 50], propylene oxide [51] and trimethylcarbonate [52] have been reported for polymerization with lactide units. However, cyclic comonomers are suitable to polymerize by ring opening polymerization (ROP) with lactide such as lactones or macrolactones. The most investigated systems are poly(glycolide-lactide) [53, 54] and poly(lactide-co-caprolactone) copolymers [55–57]. Recently, some studies in search of more biodegradable copolymers are using macrolactones as γ -valerolactone [58].

Moreover, starting the polymerization of lactide or lactic acid with polymer containing hydroxyl groups leads into graft copolymers. This strategy is welcomed to increase the miscibility with other polymers and hydrophobicity as it occurs with poly(vinyl alcohol) [59].

5. Polylactide-based composites

Composites combine two (or more) different components: a continuous phase, called matrix, acts as binder and distributes homogeneously the forces through whole composite; and a discontinuous phase, called reinforcement, fundamentally is used to carry the applied load. Depending on the form of the reinforcements, they are arranged in different groups, of which two most important are fibers and particles. Normally, the aim of the reinforcements is to enhance the stiffness and tensile strength of the matrix, although sometimes fillers are used to reduce the price of the final product or modify the physical, rheological, optical or other properties. However, more important is the interface between both components to assure good transmission among constituents of the composite.

Efforts made for advancing in technology lead to the scientific community to introduce nanoscale in material science and consequently in polymer science. It must pay special attention in nanocomposites, because it is foreseen remarkable improvement in properties with less quantity of reinforcement than micro or macroscale composites.

Different families of reinforcements can be classified into function of their chemical nature and it is analyzed the effect that induces in polylactides.

5.1. Organic reinforcements

5.1.1. Natural fibers

These composites are very attractive because both matrix and reinforcement are obtained from renewable resources. But comparing to synthetic ones they have some characteristics to take into account [60]:

- Natural fibers degrade at low temperatures (<200°C). Hence, processing of polylactide/natural fibers composite must be made carefully.
- Natural fibers are hydrophilic and absorb moisture easily. Polylactides can degrade faster and wettability of fibers produces swelling and distorsion in the interface due to a lack in dimensional stability.
- Natural fibers have low microbial resistance. Long-time storages are not ideal for these composites.

Environmental friendly materials with a full degradation capability promote the interest of these composites, especially in the automotive industry. Different natural plant fibers have been used to obtain polylactide-based composites: agricultural natural fibers as jute, kenaf, sisal and flax and also inexpensive agricultural residues as wheat straw, corn stover, soy stalks and their hybrids [61].

- Jute/polylactide [62]: Alkali-, permanganate- and peroxide-treated composites exhibit lower thermal stability, whereas silane-treated composites show a higher thermal stability when compared to untreated composites. However, a better fiber matrix adhesion improves the abrasive wear resistance of the jute fiber-reinforced composites.
- Kenaf/polylactide [63]: The effects of the silane-coupling agent on composite properties is highly beneficial leading to increased moduli and heat deflection temperatures as well as reduced water swelling. Moreover, an optimal formulation comprised of 50% kenaf and 50% PLA fibers with three parts of silane-coupling agent represents an optimal formulation to manufacture automotive headliners.
- Sisal/polylactide [64]: Mechanical properties of PLLA/sisal fiber composites (improved with caustic soda treatment) confer high strength, high modulus sisal-PLLA composites, because of effective stress transfer at well-bonded fiber to matrix interfaces.
- Flax/polylactide [65]: Mechanical properties of polylactide and its composites with flax are greater than those of related polypropylene/flax fiber composites and concretely the specific

tensile strength and modulus have demonstrated to be very close to values obtained in glass fiber polyester composites.

Moreover, micro- and nanoscale improve the mechanical properties of natural fiber-based composites; hence, cellulose microfibrils (CMF), cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC) are the new tendencies.

Composites of polylactide with silane-modified cellulose microfibrils (CMFs) coming from sisal fiber (SF) showed a maximum impact strength which was 24% higher than that of virgin PLA [66].

However, the most important feature of using nanofibrils is the dispersion in the matrix, because fibrils are hydrophilic and the matrix hydrophobic. To overcome this, feature some researches disperse CNF in polylactides by a new method obtaining increments in the modulus and strength (up to 58 and 210%, respectively) demonstrated the load-bearing capability of the CNF network in the composites [67].

Although crystallinity degree of polylactide/CNC nanocomposites remain similar to that of neat homopolymer, the crystallization rate has been notably increased (1.7–5 times) boosted by the presence of CNC, which act as nucleating agents during the crystallization process. In addition, structural relaxation kinetics of PLLA chains has been drastically reduced by 53 and 27% with the addition of CNC [68].

5.1.2. Synthetic fibers, nanofibers and nanotubes

5.1.2.1. Carbon-based reinforcements

Carbon fiber (CF) is made from organic polymers, where hexagonal carbon structures acquired a fibrillate form. Helped by their excellent specific properties supported by low weight (high stiffness, tensile strength, chemical resistance, thermal stability and low thermal expansion) carbon fibers have a widespread application in different sectors such as aerospace, civil engineering, military and competition sports. However, still remain to overcome the price because they are relatively expensive when correlated with natural fibers, glass fibers or polymeric fibers. However, most futuristic than carbon fiber composites are these with nanofibers, nanotubes or graphene.

- Carbon nanotubes (CNT)

Since the discovery by Iijima in 1991 [69], carbon nanotubes have been investigated as their unique properties [70, 71, 72] make them interesting fillers to develop polymer nanocomposites. CNTs influence in the physical-chemical properties, as well as in the mechanical, electrical and biocompatible properties of polylactides.

It has been reported that CNT influence in the crystallinity without changes in dimension of the crystal assisting in the disorder-to-order (α' -to- α) transition. However, results obtained from Hoffman-Weeks plot reveal that equilibrium melting temperature increase with CNT content, while thickness of crystal layer and amorphous layer of PLLA both decreased with increasing CNT contents of polylactide matrix [73]. Moreover, structural

aspects as physical aging [74] and thermal degradation [75] of polylactide matrix is notably affected by the presence of these CNTs.

However, compatibilization of CNTs increment the efficiency of the composites [76]. Pyrene-end-polylactide has been founded as a good interface stabilizer in polylactide/CNT composites. Therefore, modified CNT influence in polylactides in much greater manner than comparing results obtained without modification of CNTs [77].

Besides, polylactide stereocomplexation is clearly favored by CNT content [78]. The addition of small amounts of MWCNTs combined with a mild thermal treatment extends the processing window for the preparation of polylactides exclusively crystallized in the stereocomplex form, instead of the homocrystal formation.

With other point of view, conductivity of polymer matrices with nanofiller addition has been increased even with very low percentages of conductive carbon nanotubes composites [79].

In the biomedical field, also, polylactide/MWCNT composites have been carefully analyzed due to the possible cytocompatibility of the CNTs when polylactide matrix degrades [80, 81]. Instead of nanocomposite system shows adequate biocompatibility, degradation products may induce adverse effects on cell metabolism and proliferation, paying special attention in lactic acid presence and the quality of the MWCNT suspension [82]. However, an extensive *in vitro* evaluation including final degradation products is needed to enable a comprehensive prediction of the overall success or failure of newly developed degradable nanocomposites.

- Graphene

Graphene is a single-atom thick graphite sheet. It is structurally very similar to silicate layers and chemically analogous to carbon nanotubes, due to its huge specific surface area is considered as ideal reinforcing nanofiller in the fabrication of multifunctional polymer nanocomposites, superior mechanical strength, remarkable electronic and thermal properties [83]. As it could be expected to achieve its maximal reinforcing efficiency, graphene sheets must be homogeneously dispersed in the polymer matrix to prompt the interfacial stress transfer between graphene and polymer matrix [84].

An effective nanofiller has been found when graphene is functionallized with octadecylamine (ODAG) in well-exfoliated solution/casting process. Due to the good hydrophobic compatibility between organic counterparts, interfacial adhesion and consequently crystallization, mechanical properties and thermal stability are improved [85].

5.1.2.2. Other organic reinforcements

Slit die extrusion, hot stretching and quenching is proposed as a new technique to construct well-aligned, stiff poly(butylene succinate) (PBS) nanofibrils in the PLA matrix for the first time [86]. The high strength, modulus and ductility are unprecedented for PLA and are in great potential need for packaging applications. However, this technique opens a new way for the development of new composite materials based on polymeric fibers.

5.1.3. Inorganic reinforcements

Bioresorbable polymers play great relevance in biomedical field. Due to its excellent mechanical properties related to stiffness and tensile strength, polylactides are proposed for using in implants with safety-critical applications [87]. Hence, fixation and bone reconstruction are compulsory for a good health and reconstruction of the damaged zone. Most of implants based on polylactide polymer are focused on bone repair; however, radiopacity and other properties are too of great interest.

5.1.3.1. Bone repair

In this context, inorganic reinforcements play the most important role, because the natural bone is formed up to 70 wt. % by calcium phosphate very similar to hydroxyapatite (HA) [88]. HA is an inorganic compound, which helps the differentiation of osteoblasts in regeneration of the bone structure [89]. For this reason, incorporation of HA into PLA matrices has been widely reported [90, 91, 92, 93].

Tricalcium phosphate (β -TCP) has been also widely used due its bioactivity and biodegradability. Its degradation rate is incremented 3–12 times compared with HA [94] and this favors bonding of bone to the bioceramic [95]. However, combination of β -TCP and HA in denominated biphasic calcium phosphates (BCP) shows the advantages of both components: reactivity of β -TCP and stability of HA. BCP with 60–40% of HA-TCP incubated in simulated body fluid produces the precipitation of needle-shaped apatite crystals [96], allowing polylactide/BCP composites for fracture fixation plates [97].

Furthermore, discovery of bioactive glasses by L. L. Hench in 1969 catapults the use of these inorganic particles in tissue engineering due to their excellent biocompatibility and the ability of bone bonding [98]. A common characteristic of bioactive glasses and ceramics is a time-dependent kinetic modification of the surface that occurs upon implantation [99]. Bioactive glasses originate a superficial layer of calcium deficient carbonate, which permits a chemical adhesion to bone. This adhesion is appealed as bioactivity and is associated with the formation of carbonated hydroxyapatite (HCA) when glass is implanted or in contact with simulated body fluids [100, 101]. The HCA layers formed on a scaffold made of 45S5Bioglass® immersed in SBF takes a “cauliflower” typical morphology [99] and allows osteogenic formation [102].

Some researches of PLA/bioactive glass composites have been reported [103, 104]. However, melt processing of bioglass with polylactides affects the thermal stability of the composite [105], and to overcome this handicap, protection of bioactive ceramic with and acrylic plasma treatment has been proposed [106]. An easier treatment than plasma has been proposed by A. Larrañaga by covering these particles with a mussel inspired polydopamine coating, which results in a bioactive composite [107].

5.1.3.2. Radiopacity

Although alternative radiopacifiers have been proposed in bibliography [108, 109], barium sulfate (BaSO_4) is still the gold standard for medical applications [110]. Incorporation of BaSO_4

particles to polymer matrices enables surgeons to accurately place and to monitor any migration of the implant over time.

Singularly, barium sulfate submicron particles added to polylactide matrix enhance deformation at rupture and confer high toughness to fragile polylactides [111]. Consequently, the addition of these submicron barium sulfate particles enables a radiopaque and tough polylactide composite.

5.1.3.3. Nucleating effect

The influence of the nature of the filler on the mechanical properties of PLA has been reported for two silicated clays, both having a platelet-like shape [112]. Talc is a more efficient filler regarding mechanical reinforcement of PLA as compared to kaolin. This better reinforcing effect in the case of talc is ascribed to its higher affinity with the PLA. It was also evidenced that talc has a nucleating effect on the PLA crystallization [113], while kaolin has no or very limited effect on the crystallization behavior of PLA. In conclusion, the existence of crystallographic relationships between the structures of the filler and the polymer crystals is also a key parameter for the observation of a nucleating effect.

6. Future trends and perspectives

Although polylactide has been researched for various decades, still remain being the gold standard in biodegradable polymers. In fact, development of new techniques as 3D printing includes in its commercial version polylactide material. It seems as if polylactides will be investigated for long years and could carve out a place in commodity plastics.

7. Conclusions

Polylactide composites broaden the possibilities of application of neat polylactides. Biodegradable matrix allows validity for ecological packaging and biomedical applications and their composites improve the potential use of these materials.

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