Polylactic Acid (PLA)-Based Nanocomposites: Processing and Properties

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Abstract Polylactic acid (PLA) is the most comprehensively explored biodegradable and renewable thermoplastic polyester. It has the capacity to substitute polymers from fossil fuel-based resources. However, certain properties such as uncontrolled degradation, poor thermal properties, gas permeability, and profound brittleness characteristic may restrict the wide-scale utilization of PLA. Consequently, nano-based reinforcements have been widely exploited to upgrade some of the shortcomings. With the advancement in the field of nanotechnology, PLA nanocomposites have emerged as an excellent material. These materials have a big potential for applications in food packaging, medical applications, and tissue cultures. This chapter mainly assesses the different types of nanocomposites from PLA in terms of reinforcing materials. The resultant composite structures are correlated for different processing methods with the quality and factors of dispersion of reinforcements.

Keywords PLA · Nanocomposite · Biodegradable · Renewable
Polyester · Food packaging · Medical applications

1 Introduction

Lately, the use of biopolymers has been increased due to more environmentally aware consumers and the concern about global warming. These polymers are recognized biomaterials that may also be used in our daily life as a replacement of conventional polymers and plastics (Albertsson and Karlsson 1994; Ali et al. 1994).

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M. L. Sanyang and M. Jawaid (eds.), *Bio-based Polymers and Nanocomposites*,
https://doi.org/10.1007/978-3-030-05825-8_11

Due to the widespread reliance on polymers, scientific and engineering efforts are carried out for the innovation, advancements, and reformations of these materials. Polylactic acid (PLA), a compostable polymer derived from endless sources (mainly starch and sugar), has been considered as a promising material to decrease the solid waste disposal and suitable material for household goods and packaging applications (Luo et al. 2018). PLAs are aliphatic polyesters of lactic acid used mainly in the biomedical field such as implant devices, internal sutures, and tissue scaffolds, because of its low availability, high cost, and limited molecular weight (Rasal et al. 2010; Michael et al. 2016). It has some properties similar to conventional plastics (like polyethylene or polyethylene terephthalate). Moreover, the processing techniques are quite similar. Different forms of fibers, films, plastic containers, and other household products are manufactured from PLA granulates.

2 Overview of PLA

The structural formula of PLA is given in Fig. 1. Lactic acid (2-hydroxypropionic acid) is a simple chiral molecule that exists as two enantiomers, L- and D-lactic acid. In this way, the term "polylactic acid" refers to a family of polymers: poly-L-lactic acid (PLLA), poly-D-lactic acid (PDLA), and poly-D,L-lactic acid (PDLLA). Furthermore, DL-PLA is a syndiotactically alternating D,L-copolymer or a copolymer having L and D units. PLLA has achieved enormous consideration for its brilliant biocompatibility and physical properties. However, its lengthy degradation periods and high crystallinity of its fragments are the major concerns for widespread applications.

The chemistry of PLA involves the processing and polymerization of lactic acid monomer (Hoque et al. 2005). PLA with higher than 90% PLLA tends to be crystalline, while the lower optically pure is amorphous. The melting temperature and the glass transition temperature of PLA increase with the amount of PLLA. The density of amorphous and crystalline PLLA has been reported as 1.248 and 1.290 g/ml, respectively. Generally, PLA is soluble in acetonitrile, dioxane, chloroform, methylene chloride, 1,1,2-trichloroethane, and dichloroacetic acid. On the other hand, PLA is partially soluble at room temperature and completely soluble at boiling temperature in ethyl benzene, toluene, acetone, and tetrahydrofuran. The major beneficial properties of PLA are given below.

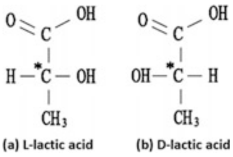

Fig. 1 Structural formulas of **a** L-lactic acid and **b** D-lactic acid

- Transparency: PLA has an excellent property of transparency. Due to this property, PLAs are used in the radio control toys, drones, aerospace, automotive, prototyping, and many more.
- Eco-friendly: Besides being derived from renewable resources (e.g., corn, wheat, or rice), PLA is biodegradable, compostable, and recyclable (Drumright et al. 2000; Sawyer 2003). Its synthesis also utilizes less CO_2 (Dorgan et al. 2001; Hutmacher et al. 2008). These eco-pleasant characteristics make PLA an attractive biopolymer.
- Biocompatibility: The most striking property of PLA is its biocompatibility. PLA does not produce poisonous or cancer-causing consequences in local tissues (Athanasiou et al. 1996). When PLAs are implanted in living organisms including the human body, they hydrolyze to hydroxy acid. It is then integrated into the tricarboxylic acid cycle and expelled (Kimura et al. 1988). Moreover, PLA degradation outcomes are harmless (up to a specific composition) which is the main reason for biomedical applications (Athanasiou et al. 1996; Eling et al. 1982; Kimura et al. 1988). The Food and Drug Administration (FDA) has also approved PLA for direct contacting with biological fluids (Gupta et al. 2007).
- Processability: PLAs can be manufactured by various techniques. PLAs can also be synthesized industrially with novel economical polymerization systems. Some common methods include extrusion, injection molding, injection stretch blow molding, casting, thermoforming, blown film, foaming, blending, fiber spinning, and compounding (Linnemann et al. 2003; Okada 2002; Schugens et al. 1995).
- Energy savings: PLA demands 25–55% less energy to produce than conventional polymers, and this requirement can be further cut down to less than 10% in the near future (Vink et al. 2003). The energy-saving characteristics of PLA synthesis are substantially strategic with respect to cost.

Although PLA has some prospective advantages, it has shortcomings as well, which restrain its exploitation in specific uses. These disadvantages are listed below.

- Brittleness—PLA is a very brittle material. In tension, it shows under 10% of elongation at fracture (Hiljanen-Vainio et al. 1996; Rasal and Hirt 2009). The tensile strength of PLA films ranges between 50 and 70 MPa with an elongation of 4% at break and an elastic modulus of ~ 3 GPa. It shows an impact strength of 2.5 kJ/m^2 (Anderson et al. 2008). These mechanical characteristics are more or less comparable to polyethylene.
- Slow degradation rate—The degradation rate of PLA is influenced by the PLA crystallinity, molecular mass and its arrangement, permeability, surface characteristics, and the stereoisomeric content. The slow degradation rate of PLA raises some concerns. In some cases, degradation could follow several years (Bergsma et al. 2006). There was report of a second surgery almost 3 years after implantation to remove a PLA-based implant (Incardona et al. 1996).

- Hydrolysis rate and thermal resistance—As the hydrolysis rate is fast and thermal resistance is poor, the PLA-based food package is inappropriate for hot liquid.
- Hydrophobicity—PLA is somewhat hydrophobic in nature. The contact angle between PLA and stagnant water is around 80°. Also, PLA is less coherent to biological cell. It is also reported that it could stimulate an incendiary reaction with anatomical liquids at straight association (Burg et al. 1999; Ratner 1995).
- Lack of reactive side chain groups—PLA is chemically passive without any lateral chain clusters for reaction. That is why exterior and volume reformations through chemical reaction are difficult activity for PLA.

Due to those limitations, blending PLAs with flexible polymers or reinforcing with inorganic or natural fillers are common approaches to enhance the mechanical characteristics of PLAs.

3 Processing of PLA

The monomeric building block of PLA is lactic acid. Lactic acid can be produced by bacterial fermentation as well as petrochemical route. Sugar or starch obtained from vegetable sources (e.g., corn, wheat, or rice) (Hoque et al. 2013a) is used for these processes. Commercial PLAs are copolymers of both poly-L-lactic acid (PLLA) and poly-D, L-lactic acid (PDLLA). They are manufactured from L-lactides and D, L-lactides (Auras et al. 2004; Nampoothiri et al. 2010; Saeidlou et al. 2012). The L-lactic acid spins the plane of polarized light clockwise; on the contrary, D-lactic acid turns it counterclockwise. Lactic acid produced by petrochemical routes is a 50/50 mixture of the D and L forms. That is why it becomes optically inactive. Since the fermentation method is eco-friendlier, it has been exploited significantly to synthesis PLA since the 1990 (Anderson et al. 2008). In the bacterial fermentation process, an augmented breed of Lactobacillus is employed to transform corn starch into lactic acid (Dorgan et al. 2000). The L-isomer is the main product of naturally occurring PLAs in the fermentation process (99.5% of the L-isomer and 0.5% of the D-isomer) (Anderson et al. 2008; Vink et al. 2007).

Polymers of lactic acid can be constructed by a number of methods, including azeotropic dehydrative condensation, direct condensation polymerization, and chain formation via lactide development (Fig. 2). Notably, economically viable high molecular weight PLA resins are produced via the lactide ring-opening polymerization route (Garlotta 2001; Ikada and Tsuji 2000; Martin and Averous 2001).

The optical integrity of PLA dictates the structural, barrier, thermal, and mechanical properties. Ninety percentage or more L-isomer-containing PLA polymers become crystalline, while depleted L-isomer comprising PLAs is amorphous. For PLA blends with less than 1% of D-isomer, injection molded techniques can be exploited. However, with less crystallinity PLA combinations with greater D-isomer composition (i.e., 4–8%) are convenient for extrusion, thermoforming, and blow

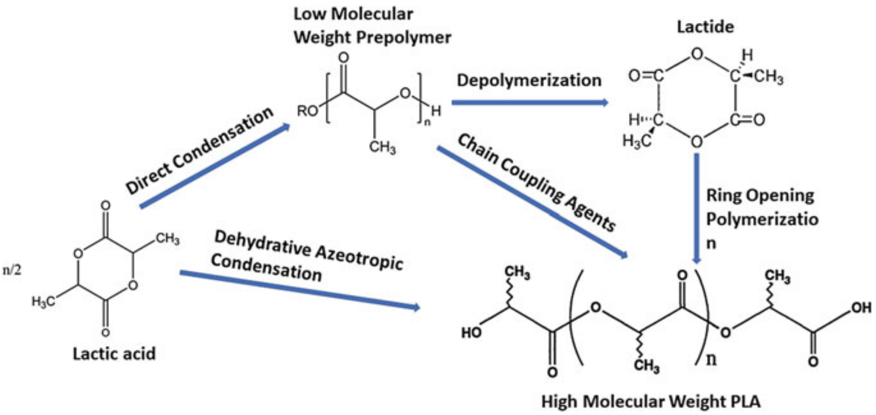

Fig. 2 Synthesis of PLA from L- and D-lactic acids. Adapted from Auras et al. (2004)

molding. Pure PLA typically is poor heat- and shock-resistant. Therefore, reinforcements, plasticizers, and other mixtures are added to augment their properties.

4 PLA-Based Nanocomposites

Mechanical and thermal properties of the PLA matrix are enhanced by incorporating inorganic and organic materials. Macro- , micro- , and nano-reinforcements are commonly employed to make PLA-based composites. The main advantage of nano-reinforcements is the quantity required to produce desired properties in PLA. Typically, PLA nanocomposites with only 0.5–8 wt% reinforcement are adequate for this purpose. Different types of nano-fillers that are used to make PLA-nanocomposites include carbon nanotubes (CNT), layered silicates, hydroxyapatite, layered titanate, and aluminum hydroxide. In PLA nanocomposites, the nanofiller is in nanoscale (i.e., <100 nm) at least in one dimension. Recently, Raquez et al. (2013) comprehensively reviewed PLA-based nanocomposites. Nanofillers can be classified based on their shape:

i. Layered nanofillers: They are nanolayered materials. Their thickness is approximately 1 nm. Customary one-dimensional nanofillers are sheets of silicates, different clays, and graphene.
ii. Whiskers or nanofibers: These shapes have an average diameter of below 100 nm. Carbon nanotubes (CNTs) and nanocellulose are the familiar instances.
iii. Nanoparticles: This three-dimensional shape should have an average diameter of below 100 nm as well. Silica particles, polyhedral oligomeric silsesquioxane (POSS), and metal oxides are the most common.

These nanofillers mainly improve mechanical and thermal properties. But, some other properties may also be improved. These include flame retardant (FR), antistatic, antibacterial effect, conductive, UV protection, and gas barrier. Nanofillers provide a way to extend and improve the existing properties of PLA (Raquez et al. 2013).

4.1 Layered Ceramic/PLA Nanocomposite

As PLA is chiefly hydrophobic in nature, the homogenous dispersion of the hydrophilic ceramic-layered structures is a major concern. They are often unable to be uniformly dispersed in the polymer matrix. Figure 3 shows different types of intercalation/dispersions behavior of layered ceramics in a PLA-based matrix. Commonly, adaption is needed to amplify the interaction between the layered ceramics and PLA by the addition of organic minerals during dispersion (Dash et al. 2008; Parida et al. 2006).

PLA/layered ceramics nanocomposites are mainly prepared by intercalation with solvent, melt, or in situ. Among them, solvent intercalation is one of the simplest procedures to synthesise nanocomposites. In this method, a solvent plays the major role by dissolving the PLA for easy dispersion of the ceramic nanofiller in the solution (Cumkur et al. 2015). Here, the polymer is first allowed to make a solution with suitable dissolvable. And then, the nanofillers are added and stirred for dispersion in the solution. High-speed cyclone and/or sonication techniques are used for adding the nanofiller suspension to the polymer solution. In melt intercalation, a mixture of PLA and layered ceramics is first heated above the glass transition or melting temperature of PLA. Then, the heated mixture is blended using shear forces in an extruder. Nevertheless, the interaction of the layered ceramics with hydrophobic PLA is improved usually through surface modification of the ceramic nanofillers.

In in situ polymerization technique, polylactides are mixed with layered ceramic fillers with a catalyst, and then, in situ polymerization by ring opening takes place to form PLA nanocomposites. Paul et al. (2005) produced PLLA/organo-modified

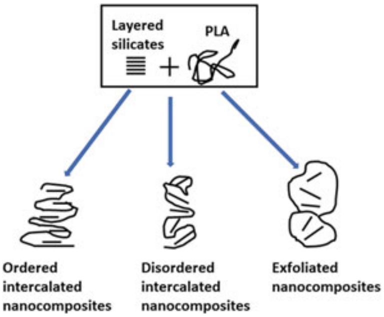

Fig. 3 Structures of layered silicate–polymer nanocomposites (the concept was redrawn from Raquez et al. 2013)

montmorillonite nanocomposites with both intercalated and exfoliated structures by employing the in situ ring-opening polymerization of poly-L-lactides. They realized that the modification of nanofiller acted a major role in dispersion phenomenon. When modified montmorillonite Na was exploited, exfoliation of PLA on layered structure took place (Paul et al. 2005).

Krikorian and Pochan (2004) reported that the degree of clay miscibility with the matrix and the clay distribution condition in the PLLA matrix both considerably affected the crystallinity and ultimate structure of the nanocomposites. They suggested that the nucleating efficiency of PLA crystals with organoclays during intercalation was greater than that during exfoliation. As a consequence, overall bulk crystallization was much higher in the intercalated system than that in the exfoliated system. In addition, they concluded that the spherulite growth was significantly greater in the fully exfoliated nanocomposite due to lower nucleating efficiency (Krikorian and Pochan 2004).

Nanosilica fillers' addition shows advancements in different properties of PLA. The improved properties include tensile, flexural, heat distortion temperature, gas permeability, crystallization rate, biodegradability, and so on. These properties were mainly dictated by the structure of the composites. In this case, the amount and the quality distribution of the reinforcement in the PLA matrix are the two major variables. Different polymeric compatibilizers are added to increase the interaction of silica/PLA for the uniform dispersion of the silica nanofillers (Sinha Ray et al. 2002). Mainly, epoxy and maleic anhydride-based polymeric compatibilizers are used.

In case of clay-based nanoparticles, the organic modifiers were used to increase the intimate contact between clay nanoparticles and the PLA matrix (Tehrani et al. 2014). Comparatively, clays are inexpensive and can provide considerable developments in mechanical and thermal properties of PLA (Lagarón and Cabedo 2014). That is why they are very common nowadays. Most often, a simple melt blending method was used for the fabrication of the composite structure. For the clay-based nanoparticles, Li et al. (2014) investigated PLLA/PDLA/clay nanocomposites. They suggest that dispersion can be improved by enhancing shear force during melt blending (Li et al. 2014). According to their study, clay fillers normally yield higher mechanical strength. So, a rigid structure can be prepared. In an interesting study, Lai et al. (2014) investigated the *N*,*N*-bis(2-hydroxyethyl)-*N*-methyl-*N*-tallow ammonium chloride modified nanoclay addition in PDLLA matrix in melt intercalation process. They reported a tremendous increase in ductility (i.e., with an elongation of 208% at break) of PLA/clay nanocomposites. The extensively exfoliated and uniformly dispersed clay platelets along with the highly plasticized interphase around these clay platelets were observed in their study. The high ductility may be evolved for high level of exfoliation and high dispersion which results in multiple shear banding in the amorphous PLA structure (Lai et al. 2014).

4.2 Layered Double Hydroxide/PLA Nanocomposites

In recent years, layered double hydroxide (LDH) as a layered nanostructure became very popular due to its various unique properties which are not found in traditional layered silicates. LDH has mainly two layers. One layer is the positively charged metal hydroxide sheets, and another is the intercalated anions. Water molecules are also attached to the structure (Mandal et al. 2009). The general formula is recorded as $\left[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2\right]A^{n-}{}_{x/n}yH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations like Mg^{2+} and Al^{3+}, respectively, and A^{n-} are interlayer anions like $CO_3{}^{2-}$, Cl^-, and $NO_3{}^-$ (Costa et al., 2007). The benefits of using LDHs in nanocomposites include the suitability of organo-LDHs for intercalation of hydrophobic polymers and absence of trace heavy metals. LDH platelets have a high aspect ratio, tunable layer charge density, and low production cost. As there are strong electrostatic interactions between highly charged hydroxide layers and intercalated anions, it is difficult to efficiently disperse and to some extent to exfoliate (Chiang and Wu 2010).

In order to simplify the intercalation of polymeric chains between LDH layers, sometimes a pre-treatment of the nanofiller is required. For these, organic or polymeric anions like alkyl carboxylates, alkyl sulfates, and acrylates can be readily incorporated into the LDH interlayers by ion exchange or in situ polymerization reactions (Manzi-Nshuti et al. 2009). Another improvement of dispersion of LDH was studied by Katiyar et al. (2010). They explored the synthesis of PLA/LDH nanocomposites by ring-opening polymerization (ROP) of LA as shown in Fig. 4 (Katiyar et al. 2010). In this study, two types of LDH carbonate (LDH-CO_3) and laurate-modified LDH (LDH-C12) were investigated as LDH nanofillers. LDH-C12 was used to obtain exfoliated nanocomposites. But there was a problem with molecular weight of PLA which was significantly reduced after in situ polymerization. The possible reason could be chain termination promoted via LDH surface hydroxyl groups or metal-catalyzed degradation.

Katiyar et al. (2011) also examined the barrier properties of resulting PLA/LDH nanocomposites manufactured by extrusion technology in the presence of laurate-intercalated LDH (LDH-C12). They also compared with MMT clay, i.e., Cloisite 30B which is an organo-modified montmorillonite (Katiyar et al. 2011). Two different approaches for nanocomposite synthesis were compared, i.e., pot addition and masterbatch way by an in situ intercalative ROP. It was found that PLA/Cloisite 30B nanocomposites exhibited significant enhancement in oxygen and water vapor barrier properties comparing to those of PLA/LDH-C12 nanocomposites.

4.3 Glass/PLA Nanocomposites

Glass particle-reinforced PLA nanocomposites were developed for better mechanical properties. It was reported that inclusion of a glass microsphere

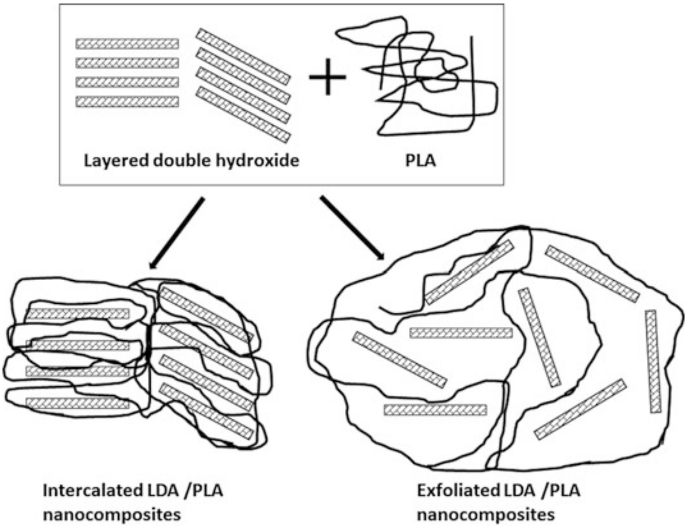

Fig. 4 Schematic illustration of in situ ring-opening polymerization of LA in the presence of LDHs. Reproduced from Katiyar et al. (2010)

uniformly throughout the matrix improves the Young's modulus, flexural modulus, impact strength, flexural strength, and thermal properties of PLA (Malinowski et al. 2015). As expected, the total elongation at fracture was decreased in tension test. Surface free energy was significantly influenced owing to the composite admixing (Malinowski et al. 2015). In this context, another fully biodegradable composite structure with PLA and calcium phosphate soluble glass particles were developed by Navarro et al. (2005). They suggested that the incorporation of phosphate glass particles into PLA significantly accelerated the degradation of the PLA and induced the formation of calcium phosphate precipitates at the composite surface (Navarro et al. 2005). Huda et al. (2008) found that both mechanical and thermophysical properties of glass fiber-reinforced PLA composite showed improved performance with the corresponding properties of neat PLA.

4.4 Silica/PLA Nanocomposites

Generally, hard fillers such as nanosilica are used to improve the strength, adhesion, durability, and abrasion resistance of conventional polymer composites. Zhu et al. (2010) demonstrated that the oleic acid (OA)-modified SiO_2 nanoparticles were effective fillers for improving the flexibility of PLA even though tensile strength decreased the nanocomposites drastically than that of the pristine PLA. In another study, Yan et al. (2007) reported the surface-modified silica nanoparticles with a L-lactic acid oligomer by direct grafting onto the surface of the silica nanoparticles.

The loading of grafted SiO_2 nanoparticles in PLLA matrix greatly improved the toughness and tensile strength of the composite structure because of the uniform dispersion of nano-SiO_2 in the PLA matrix. They also found that the incorporation of ungrafted SiO_2 nanoparticles into PLLA actually deteriorated the mechanical properties of the composites (Yan et al. 2007). Other studies also found that the addition of 2-methacryloyloxyethyl isocyanate (MOI) or trimethyl hexamethylene diisocyanate (TMDI) significantly imparted superior mechanical properties of the SiO_2/PLA nanocomposites with much higher elongation compared to neat PLA (Chen et al. 2010, 2012). Another study demonstrated that simple melt-compounded PLA/spherical nano-SiO_2 composites showed better thermal stability than that of neat PLA (Wen et al. 2011). In this case, they proposed grafting of PLA chains with SiO_2 without any surface modification additives (Wen et al. 2011). Here, they did not measure the mechanical properties of the nanocomposites.

4.5 Titanium Dioxide/PLA Nanocomposites

Due to large surface areas, titanium dioxide nanoparticles possess significant photocatalytic and magnetic properties. They also showed exceptional hydrophilicity, great toughness, and antibacterial properties. PLA/TiO_2 nanocomposites were studied with a view to photodegradability (Nakayama and Hayashi 2007), improvement of toughness (Meng et al. 2011), the crystallization kinetics (Liao et al. 2007), and cancer cells treatment (Chen et al. 2007). Li et al. (2011) investigated the TiO_2 nanowire/PLA nanocomposites which showed covalent bonding between TiO_2 surface and PLA through in situ melt polycondensation. They claimed strong interfacial interaction and homogenous distribution of inorganic nanowires in PLA matrix (Li et al. 2011). This strong interaction between TiO_2 and PLA displayed significantly higher glass transition temperature and thermal stability, compared with pure PLA. Luo et al. (2009) investigated that the effect of initial grafting and polymerization with lactic acid on the surface of TiO_2 nanoparticles. They showed that the TiO_2/PLA nanocomposites prepared by melt blending with PLA and grafted TiO_2 resulted in improved mechanical properties (Luo et al. 2009). Zhuang et al. (2009) have found that the in situ polymerization of L-lactides in the presence of organically modified TiO_2 nanoparticles showed markedly improved thermal and mechanical properties of PLA matrix.

TiO_2 acts as a wonderful photocatalyst in the degradation of organic pollutants due to its effective photostability, reusability, non-toxicity, and cheap as well. Thus, the relatively low photodegradability of a PLA matrix can be extremely enhanced by TiO_2 nanoparticles addition. Besides photodegradation, TiO_2-coated substrates can be used as antibacterial materials (Cai et al. 2003). The antibacterial effect is common for biological cells. These cells can be successfully killed with photocatalytic activity of TiO_2 particles that are incorporated into the cells. The biological cells can also be cultured onto the surface of a substrate with TiO_2 coating. The same effect can be found here too.

4.6 Zinc Oxide/PLA Nanocomposites

Like TiO_2, zinc oxide nanoparticles have excellent antibacterial action for which they are used as nanofillers for PLAs. Another property of ZnO is intensive UV absorption. But, the addition of ZnO nanoparticles and other Zn derivatives into PLA at melt-processing temperatures leads to severe degradation of the polyester matrix. A sharp reduction of thermomechanical characteristics was noticed for the PLA nanocomposite with untreated ZnO reinforcements (Murariu et al. 2011). These problems can be overcome by various surface treatments of nanofillers with selected additives (i.e., stearic acid, stearates, fatty amides). Surface-treated ZnO with triethoxy caprylylsilane was found to be very effective for the improvement of thermomechanical characteristics of the PLA nanocomposite (Murariu et al. 2011). In another study, PLA–ZnO nanocomposites with surface-treated ZnO rod-like nanoparticles showed excellent barrier properties and a good antibacterial activity against gram-positive and gram-negative bacteria (Pantani et al. 2013). Bussiere et al. (2012) also discovered that surface-treated ZnO played an anti-nucleating role in the crystallization of PLA nanocomposites. Anžlovar et al. (2018) studied the nanocomposites of ZnO/PLA (prepared by melt processing) in terms of degradation behavior of PLA. They found that nano-ZnO performed as an obstructer of PLA crystallization process and shifted the polymer glass transition temperature to lower temperatures. They also confirmed that nano-ZnO participated as a reactant and an accelerator in the degradation reaction of PLA (Anžlovar et al. 2018).

4.7 Alumina/PLA Nanocomposites

Alumina/PLA composites have some unique applications. They have shared interaction via polar coupling and hydrogen bonding, which creates good adhesion between these two different materials. Alumina is a ceramic material. It is widely used clinically because it exhibits highly bioinert characteristics, excellent corrosion resistance, and improved strength. It is also used in a large number of dental and orthopedic applications. Sometimes, alumina coatings are used that provide tissue growth and maxillofacial reconstruction (Vallet-Regí et al. 1998). This is of practical interest in PLA, which contain carboxylic ester groups in the structure and can provide strong interactions with alumina particles.

4.8 Fe_3O_4/PLA Nanocomposites

Fe_3O_4 nanoparticles have attracted much attention due to their wide prospective functions in many areas, such as pigments, sorbents, coatings, flocculents, catalysts, gas sensors, ion exchangers, and lubricants (Liang et al. 2012; Mu et al. 2017;

Shabanian et al. 2015). Fe_3O_4 nanocomposites have exhibited promising usages in diverse fields such as magnetic recording, magnetic data storage devices, toners and inks for xerography, magnetite/polymer composite microbubbles, magnetic resonance imaging, wastewater treatment, bioseparation, and medicine (Prasad et al. 2018; Sajjadi et al. 2017; Xia et al. 2017). Furthermore, Fe_3O_4 nanoparticles can be easily produced by co-precipitation methods in the presence of appropriate surfactants (Chen et al. 2005). Zheng et al. took advantage of the super-paramagnetic properties of Fe_3O_4 nanoparticles in order to elaborate the mechanism behind magnetic-induced shape memory PDLLA nanocomposites (Zheng et al. 2009). The mechanism depicted seemed to be quite simple. Under magnetic field, magnetic nanoparticles became heated due to inductive heating within the composites that was applied to thermally induce a shape memory transition (Razzaq et al. 2012). The formulation of PDLLA/Fe_3O_4 nanocomposites used in shape memory outcome was also very clear cut. It was carried out by solution/precipitation methods (Zheng et al. 2009). They confirmed the strong interactions between PLA matrix and the magnetic nanoparticles via hydrogen bonding with different types of characterization techniques. Recently, Taccola et al. (2011) have reported on the elaboration of free-standing PLA nanofilms containing super-paramagnetic Fe_3O_4 nanoparticles. According to their analysis, the resulting nanofilms can be used in the biomedical field (Taccola et al. 2011).

4.9 Calcium Carbonate/PLA Nanocomposites

Calcium carbonate ($CaCO_3$) is widely used in the area of paint, paper, rubber, plastics, biomedical devices, etc. (Hoque et al. 2013b). It is one of the cheapest reinforcing materials. Researches have been done to prepare nanosized $CaCO_3$ with special shapes and a limited size distribution. Due to the problems of high surface energy and particle agglomeration, surface modifiers such as stearic acid, titanates, silanes, and zirconates are employed (Gu et al. 2009). A group of scientists from China investigated the impact of nano-$CaCO_3$ addition on the crystallization characteristics of PLA nanocomposite (Liang et al. 2013). According to their study, crystallization onset temperature, crystallization temperature, and crystallization end temperature of nano-$CaCO_3$/PLA nanocomposite were found to be at higher temperatures as compared to that of the neat PLA. The crystallinity of the nano-$CaCO_3$/PLA nanocomposites elevated with higher amount of the nano-$CaCO_3$. They speculated that this improvement in degree of crystallinity was related to the heterogeneous nucleation of PLA matrix on the nano-$CaCO_3$. Nekhamanurak et al. (2012a) investigate the influence of two plasticizers, polyethylene glycol and tributyl citrate, on the thermomechanical properties and fracture behavior of nano-$CaCO_3$/PLA nanocomposite. They showed that the incorporation of plasticizers improved the thermal properties of PLA. They also confirmed that the fracture behavior of nano-$CaCO_3$/PLA nanocomposites changed from brittle to ductile with the addition of plasticizers.

In another study, Nekhamanurak et al. found that the addition of silica in nano-$CaCO_3$/PLA nanocomposites had a profound effect on the mechanical and fracture behavior (Nekhamanurak et al. 2012b). They confirmed that compared to PLA-$CaCO_3$ nanocomposite, incorporating $CaCO_3$@SiO_2 at the same content increased elastic modulus, % elongation at break, and notched impact strength of PLA nanocomposites. They also concluded that surface modification of $CaCO_3$ with a SiO_2 layer was a beneficial option for better compatibility between PLA matrix and nanofillers. Kumar et al. (2014) also suggested that surface treatment by stearic acid was needed to improve inorganic nanofillers/polymer. The $CaCO_3$ modification induced homogeneous and fine dispersion of nanoparticles into PLA polymer as well as strong interfacial bonding between the two phases. An increase in the glass transition temperature (T_g) and storage modulus of the resultant nanocomposites was observed with the increase of $CaCO_3$ ratio. Shi et al. 2013 investigated the effect of poly(butylene adipate-co-terephthalate) (PBAT) addition on the mechanical properties of PLA/$CaCO_3$ nanocomposite. They observed that with the addition of PBAT impact strength increased; however, the tensile of the nanocomposite showed a decreasing tendency (Shi et al. 2013).

5 Other Nanocomposites

The nanofillers can improve material properties with the consideration of some controlling factors. The size, shape and amount of the filler, the filler/polymer interaction, and dispersion characteristics with polymeric matrices are the most important (Chow 1978). There are several nanofillers that have been investigated in the design of PLA-based nanocomposites in contrast to layered silicates or inorganic salts. Besides these, there are some other nanofillers which have not been commonly used for the preparation of PLA-based nanocomposites. Some of the examples are CNTs, polyhedral oligomeric silsesquioxanes (POSS), cellulose nanofibers, lignin nanoparticles, etc.

5.1 Carbon/PLA Nanocomposites

Carbonaceous materials like CNT are the most common nanofillers for composite fabrication. Graphite and carbon black have been also extensively used nanofillers. They enhance mechanical resilience and thermal/electrical conductivity. Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. The main property of CNTs is surface functionalization. This property is used to increase solubility and obtain uniform dispersion in the polymer matrix.

Solvent evaporation, in situ polymerization, and melt blending are the main processes for manufacturing polylactic acid–carbon nanotube blends (Chiu et al. 2008). Oxidation is the common chemical modification strategy on CNT surfaces. During oxidation, carboxylic acid or hydroxyl groups are introduced on the surface of CNTs (Fig. 5).

Graphite–PLA-based nanocomposites are also popular. Fukushima et al. report a silica–graphite–PLA-based nanohybrid made from expanded graphite and organically modified montmorillonite through a melt blending technique. The composite has excellent thermal stability, fire retardancy, and mechanical strength. The crystallization process is accelerated by graphite nanolayers. Montmorillonite is used for the enhancement of thermal resistance (Fukushima et al. 2010). Recently, a nanocomposite has been prepared by melt blending from PLAs and graphite. This nanocomposite not only showed improved thermomechanical and fire retardant properties, but also has higher Young's modulus as compared with PLAs (Murariu et al. 2010).

In short, the carbonaceous nanofillers enhance the mechanical strength of the PLA matrix. There are mainly two modes: (i) the physical interaction and intercalation of the polymer–filler–polymer are high and (ii) due to nucleation effect and enhancement of crystallinity. But higher cost of production limits their industrial application. But, the versatility and the improvement they provide to PLA are promising and so these are becoming popular day by day.

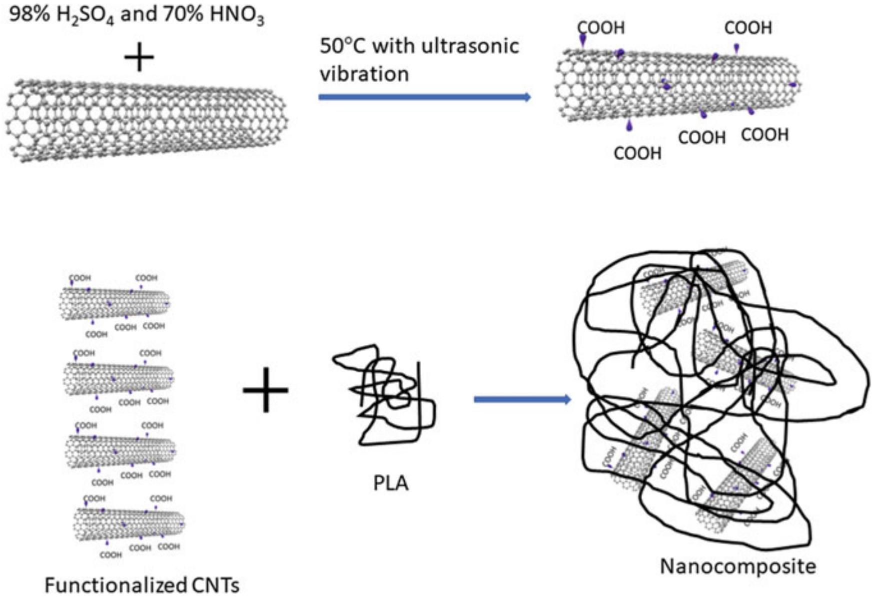

Fig. 5 Surface modification or functionalization of carbon nanotube-based materials. Redrawn from Chiu et al. (2008)

5.2 Cellulose/PLA Nanocomposites

Cellulose nanofibers (CNFs) originated from renewable biomass have drawn considerable attention as an option for reinforcing PLA. In this regard, a slurry of plasticizer and cellulose fibers was blended with the PLA melt in an extruder for composite making (Oksman et al. 2006). The results showed that the cellulose fibers improved the mechanical properties of the PLA. The scientists from Japan have also investigated cellulose microfibrils/PLA nanocomposite in terms of mechanical properties (Suryanegara et al. 2009; Iwatake et al. 2008). For the improvement of dispersion of microfibrils in PLA, an organic solvent was added in the batch. They reported that the resultant composites showed improved Young's modulus and tensile strength than neat PLA. Tingaut et al. (2009) reported well-dispersed acetylated MFC in a PLA matrix. The dispersion of nano- to submicron-wide web-like network fibers was possible because the grafted acetyl groups allowed reduced hydrogen bonding between cellulose microfibrils. They showed that acetylated MFC provided more translucent nanocomposites with reduced hygroscopicity and improved thermal stability versus unmodified MFC (Tingaut et al. 2009).

In another study, CNF/PLA nanocomposites were developed by twin screw extrusion without any surface modification treatment (Jonoobi et al. 2010). They showed that the tensile modulus and strength increased from 2.9 to 3.6 GPa and from 58 to 71 MPa, respectively, in 5 wt% CNF nanocomposites with respect to that in neat PLA. Nakagaito et al. (2009) reported a production process of microfibrillated cellulose (MFC)/PLA nanocomposites by stacking method without any organic additives. They concluded that the modulus, strength, and strain at fracture of the composite structure increased linearly with the MFC content. They confirmed that the enhancement in toughness in MFC/PLA composites was believed to be the major advantage.

5.3 Lignin/PLA Nanocomposites

Lignins are aromatic polymers which constitute a large component of the cell walls of plants. Several studies were completed on nanocomposites containing lignin and PLA. Gordobil et al. (2014) showed that the incorporation of organosolv process yielded lignin from almond shells and caused degradation of both failure strength and Young's modulus. However, acetylation of the lignin was found to improve the mechanical properties as compared to unmodified lignin (Gordobil et al. 2014). Spiridon et al. (2015) studied the mechanical and thermal properties of unmodified lignin/PLA composites. This study established a rise in mechanical properties and impact strength in PLA–lignin composites without modification treatment of the lignin–PLA system (Spiridon et al. 2015).

5.4 POSS/PLA Nanocomposites

Recently, polyhedral oligomeric silsesquioxanes (POSS) have attracted a lot of attention as reinforcing isotropic nanofiller. Their dimensions are in the range of 1–3 nm (Fina et al. 2010). These POSS nanoparticles consist of a cage-like siloxane structure surrounded by eight organic R groups. These R groups can be designed as either non-reactive or reactive. For polymer blending, non-reactive R groups are needed, and for copolymerization, reactive R groups are needed (Moniruzzaman and Winey 2006).

Comparing with commercially available and common nanofillers such as clays and CNTs, POSS nanoparticles have the smallest size, together with a low density. But the incorporation of POSS nanoparticles can be used in a wide range of polymers through simple blending or copolymerization. And POSS improved mechanical properties such as strength, modulus, rigidity, and reduced flammability (Kuo and Chang 2011). POSS nanostructures may also be used as scaffolds for drug delivery due to their nonvolatility (Ghanbari et al. 2011; Kawakami et al. 2010; Wu and Mather 2009).

6 Conclusions and Future Perspectives

The bio-based polymer industry is already competing with fossil fuel-based chemical industry, which has amplified in the last 20 years and so (Babu et al. 2013). The production of bio-based polymers and other chemicals from renewable resources has turned out to be a certainty. The current technological approach is driven toward cellulose-based feedstocks, stems, leaves, and solid municipal waste streams. More and more of these technologies are already in the development stage to introduce new bio-based polymers with higher performance and value (Carus et al. 2011).

Fantastically, encouraging progresses in the collaborative aspects are additionally expected by the achievement of hybrid PLA nanocomposites and attempts should be formulated in this direction. For instance, recently Pal et al. prepared cellulose nanocrystal (CNC) and reduced graphene oxide (rGO)-reinforced PLA hybrid composite and found good dispersion of CNC and rGO within the PLA matrix with higher tensile strength and thermal stability in addition to antibacterial response and better biocompatibility (Pal et al. 2017). In another case, Dhar et al. of Indian Institute of Technology Guwahati proposed a novel noninvasive approach of orienting non-toxic bioderived magnetic cellulose nanocrystal (CNC)/PLA composite in the presence of low magnetic fields, with potential applications for high-performance engineering applications (Fig. 6) (Dhar et al. 2016). For distinctive end-use applications in the biomedical to the engineering sectors, new PLA composites should be designed with the addition of combinations of fillers and reinforcing fibers of micro- and nanoranges, their combination with conventional

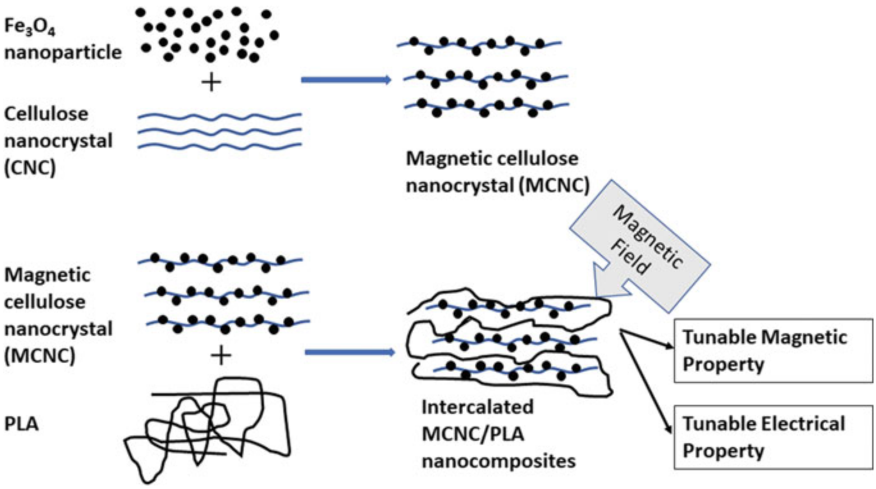

Fig. 6 Schematic illustration of magnetic cellulose nanocrystals-based PLA nanocomposite. The concept was redrawn from Dhar et al. (2016)

additives. The future development of novel PLA-based bio-nanocomposites with improved properties and multifunctionality can be visualized as a promising theme of research, as well as the advantage of their synergistic combination with inorganic nanosized solids. Their unique properties should be a solid base to develop new applications and opportunities for biocomposites in the twenty-first-century "green" materials world.

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