

# Effect of Nano-Additives on PLA/Nanocomposite Properties

Subjects: Polymer Science

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Poly(lactic acid) (PLA) is considered the most promising biobased substitute for fossil-derived polymers due to its compostability, biocompatibility, renewability, and good thermomechanical properties. However, PLA suffers from several shortcomings, such as low heat distortion temperature, thermal resistance, and rate of crystallization, whereas some other specific properties, i.e., flame retardancy, anti-UV, antibacterial or barrier properties, antistatic to conductive electrical characteristics, etc., are required by different end-use sectors. The addition of different nanofillers represents an attractive way to develop and enhance the properties of neat PLA. Numerous nanofillers with different architectures and properties have been investigated, with satisfactory achievements, in the design of PLA nanocomposites.

Keywords: poly(lactic acid) (PLA) ; nano-additives ; nanocomposites ; synthesis

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## 1. PLA/Metal Oxides

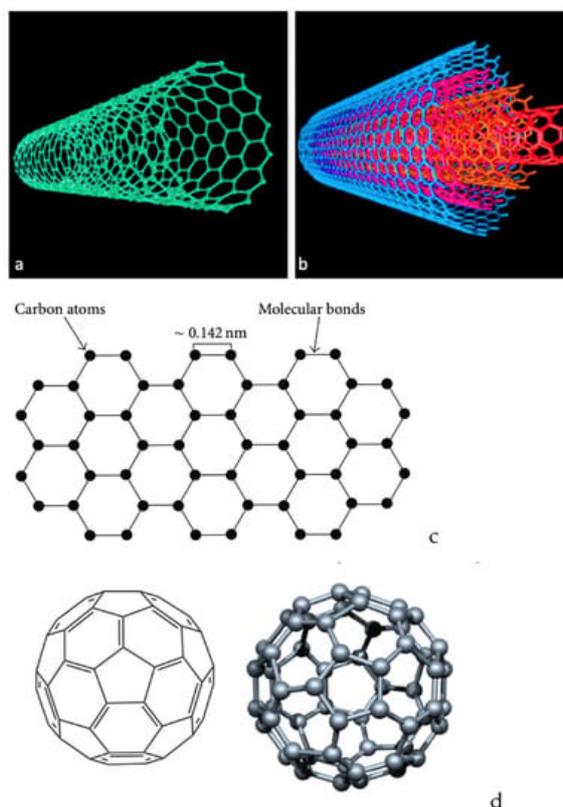
Interest in the investigation of PLA/metal oxides containing nanoparticles has rapidly grown in recent years because of their numerous properties. Particularly, the design of metal-containing nanocomposites is a current trend in scientific research due to their high-potential practical application of antimicrobial and antiviral materials <sup>[1]</sup>. A series of metal oxide nanoparticles have been synthesized including silica dioxide (SiO<sub>2</sub>), titania dioxide (TiO<sub>2</sub>), zinc oxide (ZnO), magnesium oxide (MgO), boron oxide (BO), and aluminum oxide (Al<sub>2</sub>O<sub>3</sub>). They exhibit a variety of morphologies such as sphere, triangular, star, nanotubes, nanorods, nanowires, etc. The preparation of polymer-metal oxide nanocomposites with a nanophase-separated structure requires the homogeneous dispersion of the metal oxide NPs as well as a reduction in the size of the polymer-metal oxide interface, since it may alter the physical property of the nanocomposites <sup>[2]</sup>. Due to a high density and limited size, metal oxide NPs present interesting results in terms of chemical and physical properties. In general, properties including thermal stability, toughness, glass transition temperature, optical, tensile strength, etc. are found to be improved by the formation of such nanocomposites with PLA. Therefore, these nanocomposites are widely used in numerous applications, from active surface coating to biomedical applications including structural materials <sup>[3][4]</sup>. This chapter provides a general overview of the recent studies involved in the fabrication of PLA/metal oxide nanocomposites.

## 2. Carbon-Based PLA/Nanocomposites

### 2.1. Carbon Nanotubes (CNTs)

In spite of PLA's advantages, its mechanical as well as electrical and thermal properties could be further improved so as to expand the application fields. The most effective way to overtake this disadvantage is the filling of a PLA matrix with the introduction of nanoscopic dimensions of carbon-based fillers (**Figure 1**) with a high aspect ratio, such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), graphene nanoplatelets, and spherical nanoparticles. Upon good dispersion in the PLA matrix, such nano-additives have been found to generate an increase in both the degree and the rate of crystallization, since they provide additional sites for crystallization; in other words, they serve as additional crystallization nuclei <sup>[5][6][7]</sup>. Their excellent mechanical properties, such as high modulus in the direction of the nanotube's axis and excellent electrical conductivity that varies from insulating to metallic and the hollow structures of CNTs, have expanded their usage as fillers <sup>[8]</sup>. The growing interest towards carbon-based nanomaterials, including CNTs, mainly relates to their intriguing properties as conductive fillers for the fabrication of electric/electronic devices, for which production volumes have become dramatically elevated in recent years <sup>[9]</sup>. CNTs exhibit a highly specific surface area that allows for low loadings to tune the polymer key properties concerning their mechanical, thermal, electrical, and biological performance. CNTs that possess a wall structure consisting of a single graphite sheet closed in a tubular shape are called

single-walled carbon nanotubes (SWCNTs), while those consisting of a plurality of graphite sheets each arranged into a tubular shape and nested one within the other are named multi-walled carbon nanotubes (MWCNTs). MWCNTs consist of smaller diameter single-walled tubes inside larger diameter tubes and may vary from a double-walled nanotube to as many as fifty concentric tubes, exhibiting diameters varying between 2 and 100 nm [10]. They have exceptional mechanical properties, aspect ratio, electrical and thermal conductivities, and chemical stability, and hence are considered excellent candidates for the creation of multifunctional materials [11][12].



**Figure 1.** Carbon-based nano-additives. Three-dimensional presentation of (a) SWCNTs and (b) MWCNTs [13]; (c) schematic representation of a graphene sheet [14] and (d) 2D and 3D illustration of the fullerene C60 structure [15].

## 2.2. Graphene

In the case of graphene, it is naturally derived from graphite, which is composed of a layer of less than 100 nm and can be divided into sheets (Figure 1c) around 1–2 nm thick. The physical structure of graphene with its large specific surface area makes it have a better reinforcing effect than other nanofillers [16][17]. Graphene has high mechanical strength and electron mobility, and thus may be facilitated as a filler, even at low amounts in a polymer matrix due to its highly specific surface area and chemical interaction with the matrix by the formation of strong bonds [18][19]. Due to its two-dimensional arrangement of  $sp^2$ -bonded carbon atoms, graphene has been shown to enhance the wear resistance and reduction of friction. Graphene's incorporation of polymer matrices has resulted in composites exhibiting superior mechanical strength while retaining their flexibility, as well as tailorable thermal and electrical conductivity as a consequence of the generated graphene network in the matrix [20]. Another form of graphene that can be used as nanofillers are graphite nanoplatelets (GNPs) or graphite nanosheets (GNS), which also possess great mechanical, thermal, and electrical properties [21]. The aforementioned fillers of graphene or its derivatives (graphene oxide, reduced graphene oxide) are utilized in varying concentrations as fillers in a PLA matrix in order to prepare nanocomposites with enhanced properties via different techniques [19][22]. Based on the unique properties of graphene, graphene-based polymer composites are expected to offer enhanced electrical and thermal conductivity, improved dimensional stability, higher resistance to microcracking, and increased barrier properties above the matrix polymer [11].

## 2.3. Carbon Nanofibers (CNFs)

Nanosized carbon-based reinforcements such as carbon nanofibers (CNF) into pure thermoplastic matrices have proven to be valuable for manufacturing polymer matrix composites with enhanced mechanical performance and functionality. Carbon nanofibers have a highly specific area, elasticity, and great strength due to their nano-sized diameter. Concerning CNFs, they are characterized by diameters ranging between 50 and 200 nm, being different from the conventional carbon fibers that have diameters in the order of micrometers. Due to the preparation process employed, CNFs possess improved properties, while they can offer property enhancements similar to CNTs in a more cost-effective way [6].

Therefore, they are utilized as fillers in order to enhance mechanical and electrical properties as well as the thermal conductivity of polymers [23]. Critical parameters for enhancing the mechanical and electrical properties are weight fraction of the filler, filler length, and its orientation. Overall, carbon-based nanomaterials offer the possibility to combine PLA properties with several of their unique features [14].

## 2.4. Fullerene

Fullerene is a unique nano-allotropic form of carbon. Similar to carbon nanoparticles (graphene, carbon nanotubes, nanodiamonds), fullerene has been reinforced in polymeric matrices [24][25][26][27]. Fullerene and derived nanofillers affect the structural, electrical, thermal, mechanical, and physical properties of polymeric matrices. However, the main encounter in the formation of the polymer/fullerene nanocomposite is the dispersion and miscibility with the polymeric matrices. Studies have shown that the incorporation of carbon-based nanofillers with various dimensionalities such as zero-dimensional (0D) fullerenes offers an effective approach to PLA nanocomposites with synergistic enhancements in the electrical and mechanical properties when exposed to external stimuli [28]. For that reason, polymer/fullerene nanocomposites have been applied in solar cell, super-capacitor, electronic, and biomedical devices and systems [26].

## 3. PLA Nanocomposites with Natural Nano-Additives

Currently, amongst the key-priorities of the industry and academic sector is the replacement of petroleum-derived and unsafe complexes by the increasing inclusion of natural and green compounds that can be obtained from diverse renewable resources. To achieve promising results, cost-efficient and eco-friendly extraction methods have been designed over the years. Once these green alternatives have been isolated, they are successfully applied to many fields with very assorted aims of utilization such as coagulants, adhesives, dyes, additives, or biomolecules [29]. The main challenge is to develop high-performance polyphenol-reinforced thermoplastic composites, where the use of natural fillers replaces the usual chemical additives with non-toxic ones, not only to improve the final performance but also to increase the desired multifunctionalities (structural, antioxidant, and antibacterial) [30]. Polyphenols comprise an enormous family of secondary metabolites that are stored in vacuoles of vegetal cells such as esters or glycosides. While this family of compounds is vast, they share some mutual properties, such as the formation of coloured complexes with iron salts, oxidation by potassium permanganate in alkaline media, and easy electrophilic aromatic substitution-coupling with diazonium salts and aldehydes [31][32]. Lignin and tannins are considered polyphenols with high molecular weights. Thus, not only do they possess typical features of the polyphenols group, but the presence of a large number of hydroxyls provides them with the ability to create bonds to reach a stable cross-linked association within several molecules, such as carbohydrates or proteins. This unique characteristic differentiates them from the common group of polyphenols.

## 4. PLA/Ceramic Nanocomposites

The development of ceramic nanoparticles with improved properties has been studied with much success in several areas such as in synthesis and surface science. Ceramics are defined as solid compounds that are formed by the application of heat and sometimes pressure, comprising at least two elements, provided one of them is a non-metal or a metalloid. The other substance(s) may be a metal or another metalloid.

The properties that these versatile materials exhibit include high mechanical strength and hardness, good thermal and chemical stability, and viable thermal, optical, electrical, and magnetic performance. In general, ceramic components are formed as desired shapes starting from a mixture of powder with or without binders and other additives, using conventional technologies, including injection molding, die pressing, tape casting, gel casting, etc. The sintering of the green parts at elevated temperatures is furthermore essential to reaching densification. Ceramics are a class of biomaterials extensively employed in biomedical devices [33]. Owing to their ability to be fabricated into a variety of shapes, along with their high compressive strength, variable porosity, and bioactive properties in the body, ceramics are widely facilitated as implant materials. The high similarity in the chemical composition of some ceramics such as calcium phosphate with human bone minerals makes them suitable for use as orthopaedic implants (human skeleton, bones, and joints) and dental materials. These materials show excellent bioactivity, high biocompatibility, and excellent osteoconduction characteristics [34].

## 5. Nanoclays

Among the variety of nanofillers, nanoclays are the oldest and potentially one of the most interesting and versatile ones [35]. Clays are divided into several classes, such as kaolinite, montmorillonite, sepiolite, smectite, chlorite, illite, and halloysite based on their particle morphology as well as chemical and mineralogical composition. Due to their wide

availability, relatively low cost, and relatively low environmental impact, nanoclays have been studied and developed for numerous usages. Approximately 30 different types of nanoclays can be found, which depending on their properties are used in different applications [36].

With the rapid growth of nanotechnology, clay minerals are increasingly used as natural nanomaterials. Nanoclays are nanoparticles of layered mineral silicates with layered structural units that can form complex clay crystallites by stacking these layers [37]. An individual layer unit is composed of octahedral and/or tetrahedral sheets. The different structures of nanoclays are basically composed of alternating tetrahedral silica sheets “SiO<sub>2</sub>” and alumina octahedral layers “AlO<sub>6</sub>” in ratios of 1:1 when one octahedral sheet is linked to one tetrahedral sheet as kaolinite or halloysite. In ratios of 2:1, this structure created from two tetrahedral sheets sandwiching an octahedral sheet such as montmorillonite and sepiolite yields the proportion of 2:1:1 (chlorite). It has been reported that the different types of nanoclays affect the properties of PLA/clays nanocomposites [38].

Solvent casting [39], melt blending [40], and in situ polymerization techniques [41] have been extensively used to synthesize nanoclays containing PLA composites. In recent years, nanoclays have been given great consideration due to being able to improve and significantly enhance mechanical and thermal properties, barrier, and flame resistance properties, as well as in their use in the accelerated biodegradation of polymers [35]. However, it has been reported that the different types of nanoclays affect the properties of PLA/clays nanocomposites [38]. Although organic montmorillonite (MMT) [42], bentonite [43], and halloysites nanotubes (HNTs) [44] are the most widely used nanoclays in the synthesis of PLA nanocomposites, the use of other clays with different morphologies, such as sepiolite (a fibrous silicate that has microporous channels running along the length of the fibers) [45] and palygorskite (a fibrous silicate with a needle-like morphology) [46] has also been reported in the literature.

Several studies have shown significant improvement in the properties of PLA because of the addition of nanoclays [47]. At present, nanoclays such as organic montmorillonite (MMT), bentonite, and halloysites nanotubes (HNTs) are being greatly considered as they possess the potential tendency to extensively improve the thermal, mechanical, and functional properties of polymers. However, it has been observed that the properties of synthesized nanocomposites are affected by the amount of nanoclays that is added to the PLA matrix due to the incompatibility between the hydrophobic polymer and the hydrophilic natural nanoclays [48][49]. Specifically, this was observed in the case of MMT nanoclays that present a hydrophilic nature, thus hindering their uniform dispersion in the hydrophobic organic PLA matrix [50]. Studies have reported that the mechanical properties of bio-nanocomposite films improved if a small content of nanoclays was added into the packaging materials. Nevertheless, the mechanical properties of the films declined with a further increase in nanoclay concentration [51][52]. **Table 1** overviews the mechanical properties of PLA nanocomposites containing different nanoclays.

**Table 1.** PLA/nanoclays composites and their mechanical properties as found in the literature.

Sample	Content of Nanoclay	Tensile Strength	Young's Modulus	Elongation at Break	Flexural Strength	Impact Strength	Bibliography
PLA/Halloysite	3% wt.	Increase of 14% compared to neat PLA	Increase of 50% compared to neat PLA	Increase of 3% compared to neat PLA	-	-	[42]
PLA/Kenaf fiber (30%)/MMT	1% wt.	Increase of 5.7% compared to PLA/Kenaf	Increase of 39.61% compared to neat PLA	-	Increase of 46.4% compared to PLA/Kenaf	Increase of 10.6% compared to PLA/Kenaf	[53]
PLA/Aloe vera fiber (30%)/MMT	1% wt.	Increase of 5.72% compared to PLA/Aloe vera	Increase of 18.84% compared to neat PLA	-	Increase of 6.08% compared to PLA/Aloe Vera	Increase of 10.43% compared to PLA/Aloe vera	[48]
PLA/Kenaf/Aloe vera/MMT	1% wt.	Increase of 23.2% compared to PLA/Kenaf Increase of 11.46% compared to PLA/Aloe vera	Tensile Modulus Increase of 24.61% compared to neat PLA	-	Increase of 56.43% compared to PLA/Kenaf Increase of 12.63% compared to PLA/Aloe vera	Increase of 57.5% compared to PLA/Kenaf Increase of 54.27% compared to PLA/Aloe vera	[49]

Sample	Content of Nanoclay	Tensile Strength	Young's Modulus	Elongation at Break	Flexural Strength	Impact Strength	Bibliography
PLA/PCL/MMT	4% wt.	Increase of 15% compared to the blend	Increase of 26% compared to the blend	-	-	Decrease of 33% compared to the blend	[54]
PLA/Halloysite nanotubes (HNTs)	9% wt.	Decrease of 10.7% compared to neat PLA	Increase of 10.8% compared to neat PLA	Decrease of 46% compared to neat PLA	Decrease of 7.3% compared to neat PLA	Decrease of 51.4% compared to neat PLA	[55]

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