

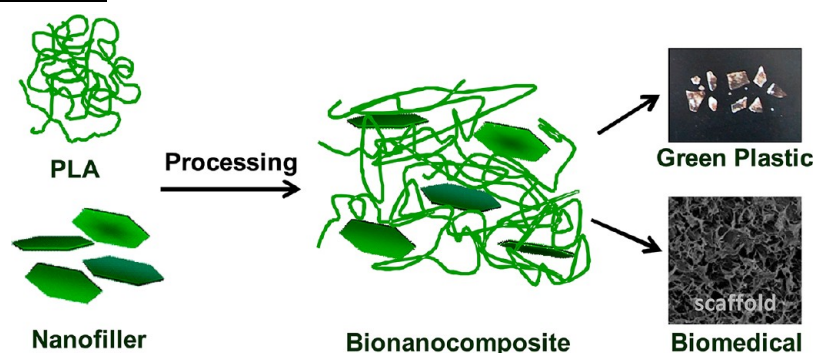
Polylactide-Based Bionanocomposites: A Promising Class of Hybrid Materials

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CONSPECTUS



Polylactide (PLA) is the oldest and potentially one of the most interesting and useful biodegradable man-made polymers because of its renewable origin, controlled synthesis, good mechanical properties, and inherent biocompatibility. The blending of PLA with functional nanoparticles can yield a new class of hybrid materials, commonly known as bionanocomposites, where 1–5% nanoparticles by volume are molecularly dispersed within the PLA matrix. The dispersed nanoparticles with their large surface areas and low percolation thresholds both can improve the properties significantly in comparison with neat PLA and can introduce new value-added properties.

Recently, researchers have made extraordinary progress in the practical processing and development of products from PLA bionanocomposites. The variation of the nanofillers with different functionalities can lead to many bionanocomposite applications including environmentally friendly packaging, materials for construction, automobiles, and tissue regeneration, and load-bearing scaffolds for bone reconstruction. This Account focuses on these recent research efforts, processing techniques, and key research challenges in the development of PLA-based bionanocomposites for use in applications from green plastics to biomedical applications.

Growing concerns over environmental issues and high demand for advanced polymeric materials with balanced properties have led to the development of bionanocomposites of PLA and natural origin fillers, such as nanoclays. The combination of nanoclays with the PLA matrix allows us to develop green nanocomposites that possess several superior properties. For example, adding ~5 vol % clay to PLA improved the storage modulus, tensile strength, break elongation, crystallization rate, and other mechanical properties. More importantly, the addition of clay decreases the gas and water vapor permeation, increases the heat distortion temperature and scratch resistance, and controls the biodegradation of the PLA matrix.

In biomedicine, researchers have employed the design rules found in nature to fabricate PLA-based bionanocomposites. The incorporation of functional nanoparticles in the PLA matrix has improved the physical properties and changed the surface characteristics of the matrix that are important for tissue engineering and artificial bone reconstruction, such as its thermal and electrical conductivity, surface roughness, and wettability. Finally, of the introduction of bionanocomposite biocompatible surfaces on drugs, such as antibiotics, could produce delivery systems that act locally.

1. Introduction

Biodegradable polymers can be defined as polymers that can degrade and gradually be absorbed or eliminated by the body. This degradation is induced by either hydrolysis or chain scission caused by metabolic processes.^{1,2}

However, specific conditions in term of pH, humidity, oxygenation, and the presence of some metals are required to ensure the biodegradation of such polymers.¹ From the perspective of sustainability and environmental concerns, polymers manufactured from renewable sources that are

completely degradable at the end of their useful life are ideal candidates for the development of bionanocomposites, because these materials will be able to close the material loop after use.

Recently, a number of biobased polymers, such as thermoplastic starch, polylactide or poly(lactic acid) (PLA), chitosan, and poly(hydroxyl butyrate), are now commercially available. However, the most promising and extensively studied polymer in this field is PLA.^{3–6} The great interest in PLA-based bionanocomposites is directly supported by the significant increase in the number of scientific publications, as shown in Figure 1.

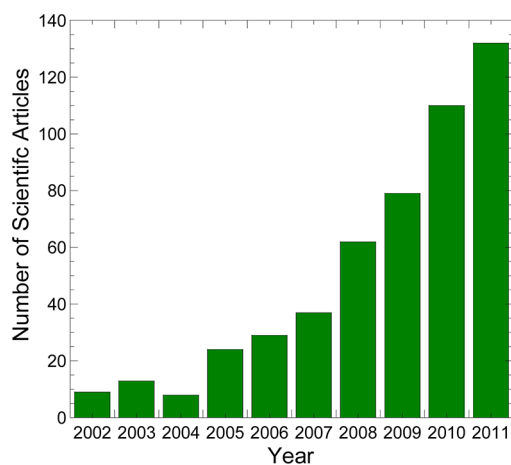


FIGURE 1. Number of scientific works published since 2002 based on Scopus (accessed January 04, 2012) using keywords polylactide and nanocomposites and poly(lactic acid) and nanocomposites.

PLA is a renewably derived thermoplastic polyester and is completely biodegradable and bioabsorbable.⁷ Poly(lactic acid) and polylactide are the same chemical products and both are abbreviated as PLA. The only difference between them is how they are produced. Lactic acid (LA) is the most extensively produced carboxylic acid in nature, and the current industrial production of LA is based on the microbial fermentation of carbohydrates.⁷ High molecular weight PLA is synthesized by ring-opening polymerization of LA, and aluminum and tin alkoxides are the most commonly used catalysts for this polymerization reaction. However, because of chirality, LA has two optically active isomers: L-LA and D-LA. The optical purity of LA is very important during production of high molecular weight PLA (refer to Figure 2) since a small amount of enantiomeric impurities during synthesis can drastically change the properties of PLA, such as the crystallinity and biodegradation rate.

Over the past few years, a great deal of research and development effort has emerged around the hybrid organic–inorganic systems, and in particular, attention has been given to those in which nanofillers are dispersed in a polymer matrix.^{8–13} This class of materials is called polymer nanocomposites and shows unique value-added properties that are completely absent in neat matrices and conventional composites.^{8–13} Researchers believe that the interaction between filler and matrix at a nanoscale level is the basis for new and novel properties of the nanocomposites as opposed to conventional composites.^{8–13} In recent years,

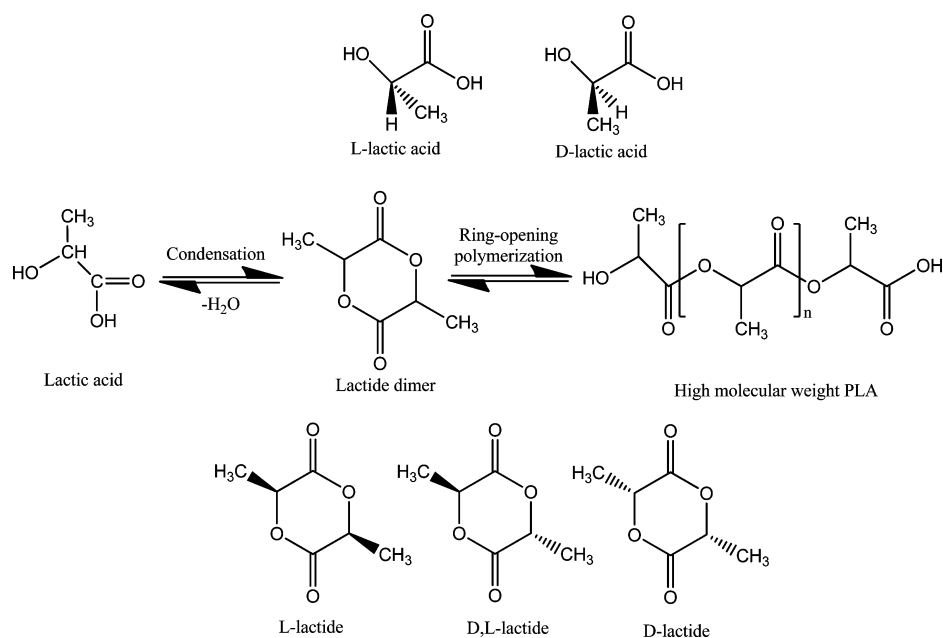


FIGURE 2. Stereoisomers of lactic acid, synthesis of lactide dimer and high molecular weight PLA, and diastereomeric forms of lactides.

TABLE 1. Physical Properties of Pure Poly(L-lactide) (PLLA)

properties	typical value
density	1.25–1.30 g/cm ³
melting temperature	170–190 °C
glass transition temperature	50–65 °C
heat of fusion	93–203 J/g
tensile modulus	6.9–9.8 GPa
tensile strength	0.12–2.26 GPa
elongation at break	12–26%

special attention has been given to the benefits of polymer nanocomposite technology to improve the inherent properties of biopolymers.^{2,14–18} Such materials are called “bionanocomposites” and have created a fascinating interdisciplinary research field that brings together materials science, nanotechnology, and biological science. They also have generated huge interest for use in many applications from green plastics to biomedical products.

When we consider the variety of biopolymers, potential nanoparticles, and end-user applications, the field of bionanocomposites is immense. Recent opportunities to improve food quality and shelf life while reducing plastic waste have stimulated the exploration of new bionanocomposite-based packaging materials.^{7,19} Similarly, improved mechanical and thermal properties make bionanocomposites very attractive in the automotive and construction industries.²⁰ On the other hand, the balanced mechanical properties, functionalities, and biocompatibility of bionanocomposites provide an exciting platform for the design and fabrication of new materials for biomedical applications.^{2,21} In this regard, a number of exciting application concepts are currently under development, such as sutures, tissue engineering, drug delivery systems, and surgical implants, including architecturally fabricated stents that could replace conventional metallic ones.

Although PLA possesses good mechanical properties (refer Table 1), high processability, and less energy dependence, successfully developing PLA-based bionanocomposite materials for use in many applications also depends on additional properties, such as lower gas permeability, fast crystallization, higher ductility, flexural strength, surface roughness and reactivity, hydrophilicity, and fast degradation. As current research has shown, the incorporation of natural (such as clay) and synthetic (such as carbon nanotubes, hydroxyapatite, novel metal, etc.) nanoparticles into PLA matrix can offer the opportunity to develop bionanocomposites with the targeted material performance. This Account highlights the main results of the academic and industrial research on this subject, giving a short overview on the key research challenges, as well as important references for future in-depth study.

2. Nanofillers

Over the past decade, researchers have extensively used various types of nanofillers for the preparation of advanced nanocomposite materials with balanced properties by exploiting the advantages that nanometer-size fillers offer. Compared with conventional fillers, nanometer-size fillers possess such properties as huge interfacial area per volume of particles, large number density of particles per particle volume, and particle–particle correlation arising at low volume fraction.

Nanofillers are defined as fillers that have at least one dimension less than 100 nm (1 nm = 10⁻⁹ m). Depending on the dimensionality, there are four different types of nanofillers: (i) zero-dimension nanoparticles (all dimensions <100 nm); (ii) one-dimensional nanofibers, such as carbon nanotubes (CNTs) (diameter <100 nm); (iii) two-dimensional layered silicates such as clays (thickness <100 nm); (iv) three-dimensional interpenetrating networks, such as polyhedral oligomeric silsesquioxanes (POSSs) (all dimensions <100 nm). Researchers generally choose one of the four nanofillers based on the application's requirements. For example, for the enhancement of mechanical and barrier properties, two-dimensional nanofillers are preferred. On the other hand, for the fabrication of functional nanocomposites, such as to improve optical and electrical properties, spherical nanoparticles are more suitable; while for rigidity and strength, fiber-like nanofillers are preferred.

Nanofillers can be made from a wide range of materials, the most common being silicates, CNTs, POSSs, metals, metal-oxide ceramics, and metal nonoxide ceramics. Recently, other materials have been used for nanofillers such as polymers and compound semiconductors; however, the former categories are used for the majority of polymer nanocomposite applications. The potential inherent characteristics of the most commonly used nanoparticles are shown in Figure 3.

During the past few years, all types of nanofillers have been used for the preparation of composites with different types of environmentally friendly polymer resins.^{8,14} However, bionanocomposites based on PLA and clays have attracted great interest in today's materials research, because these substances can significantly enhance the bionanocomposite properties especially when compared with neat PLA. These improvements can include high moduli, increased strength, flexibility, and heat resistance, decreased gas permeability and flammability, and increased rate of crystallization and control of degradability. Moreover,

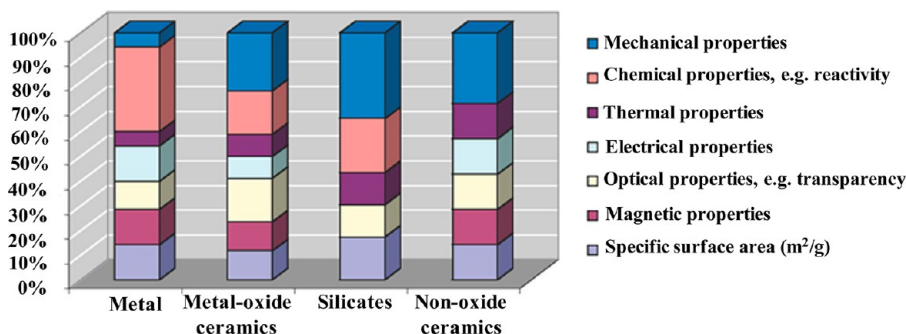


FIGURE 3. Properties of the most commonly used nanofillers for polymer nanocomposites.

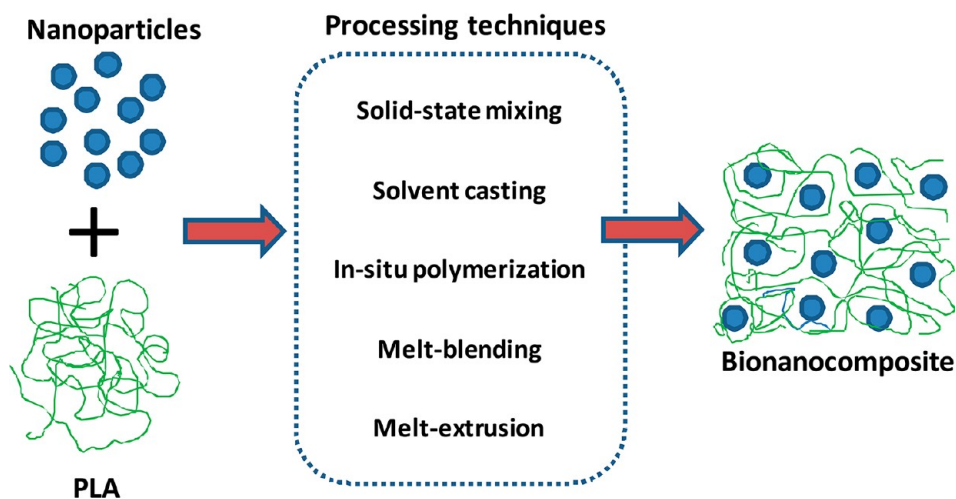


FIGURE 4. Methods generally used for the preparation of polymer nanocomposites.

clays are naturally abundant, economical, and, most importantly, benign to the environment and humans. The most commonly used one is montmorillonite (MMT), a natural phyllosilicate extracted from bentonite. The raw chemical formula of MMT is $(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$. The specific surface area of MMT is equal to 750–800 m^2/g , and the modulus of each silicate sheet is around 200–220 GPa.²² The interlayer thickness of hydrated MMT is equal to 1.45 nm, and the average density is $\rho = 2.385 \text{ g/mL}$.

3. Preparation and Processing Characteristics

In recent years, a number of methods have been developed for the production of PLA-based bionanocomposites (refer to Figure 4).^{14,23} During nanocomposite formulation, nanolevel dispersion is the most important characteristic to achieve, in order to have increased interfacial or surface area for polymer–filler interaction, improved cooperative phenomena among dispersed particles, or a higher degree of confinement effects. In the case of PLA, the primary challenge is to find the right chemistry to provide the best thermodynamic driving force to disperse fillers at a

nanolevel. To this end, researchers are using two approaches. One approach involves the incorporation of functionality into the PLA matrix by grafting, copolymerization, or blending with other polymers. Another approach is the functionalization of nanoparticle surfaces to improve the compatibility with the PLA matrix. Moreover, in the case of nanoclays that have layered structure, researchers are using ion-exchange chemistry to decrease the inherent van der Waals forces among silicate layers to improve the delamination of silicate platelets in the PLA matrix.¹⁴

Among the preparation methods, melt-blending or -extrusion is considered a promising approach for the fabrication of PLA-based bionanocomposites because of its versatility, compatibility with current polymer processing equipment, and environmental friendliness since no solvents are used. However, to optimize melt-processing conditions, it is essential to have a nanolevel dispersion of particles and at the same time ensure structural integrity of the nanofillers (particularly for CNTs). Apart from that, the processing method and regime should have minimal adverse effects on the PLA matrix; that is, degradation should be avoided.

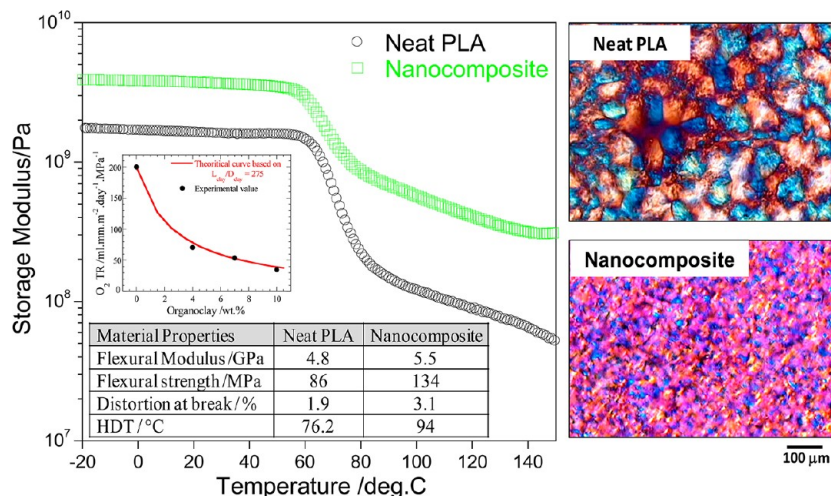


FIGURE 5. Property improvements of bionanocomposite with organoclay (content = 4 wt %) compared with neat PLA.

Furthermore, to establish a structure–property relationship, a certain qualitative measure of the degree of nanoparticle dispersion in the polymer matrix is necessary. However, researchers are facing challenges when analyzing the true dispersion state of nanoparticles in nanocomposites. Qualitative understanding of the dispersion state of nanofillers in a polymer nanocomposite is very important. Among the characterization techniques used are transmission electron microscopy,²⁴ electron tomography,²⁵ small-angle X-ray scattering,²⁶ rheology,²⁷ etc. It is important to note that the degree of nanoparticle dispersion in nanocomposites should be analyzed by complementary methods, because there is no one technique that can fully characterize the nanocomposite structure.

4. Bionanocomposites as Green Plastics

PLA shows huge promise for sustainable development because it is derived completely from renewable resources, and hence production is sustainable. PLA can significantly contribute to the control of green-house gas emission because of carbon capture during plant growth and the eventual complete biodegradability of the PLA matrix.^{6,7} At the end of their lives, products can be composted, and PLA will degrade to produce carbon dioxide, water, and energy. Because of all these features, PLA receives tremendous attention as a replacement for fossil fuel based plastics, polyethylene, polypropylene, etc., and it is the most promising and extensively used biobased polymer. However, for PLA to compete with most of the commonly used commodity polymers, the technical performance of PLA must be improved without compromising inherent green features. For example, to use PLA in packaging materials, the oxygen

and water vapor permeability along with ductility must be improved. Similarly, for automotive applications, the flexural properties, heat distortion temperature, resistance to impact, and long-term durability of injection molded parts of PLA must meet a certain level of performance specifications. Unfortunately, neither neat PLA films nor injection molded parts can currently meet the requirements for packaging and automotive applications. Another serious drawback of PLA is its relatively slow crystallization rate. Since PLA is a semicrystalline polymer, controlled crystallization rate and morphology are extremely important in determining the mechanical properties and biodegradability of PLA.

Of particular interest is the clay-containing bionanocomposites that consist of PLA and organically modified clay (organoclay), which often exhibit concurrent improved properties compared with those of neat PLA or PLA-based conventional composites. For example, low volume (~5%) additions of organoclay particles show flexural modulus enhancements with respect to neat PLA comparable to that achieved by ~15% loading of conventional filler, such as talc.²⁰ The lower loadings also facilitate processing and reduce component weight. However, the most important feature of PLA/clay nanocomposites is the unique value-added properties not normally possible with traditional fillers, such as improved heat distortion temperature and flexural properties, reduced permeability, and optical clarity. Also clay minerals are environmentally friendly and do not significantly affect the inherent compostability of the PLA matrix after nanocomposite formation.^{4,19,28}

Pure clay generally contains interlayer hydrated sodium or potassium cations. Obviously, in this state, clay particles

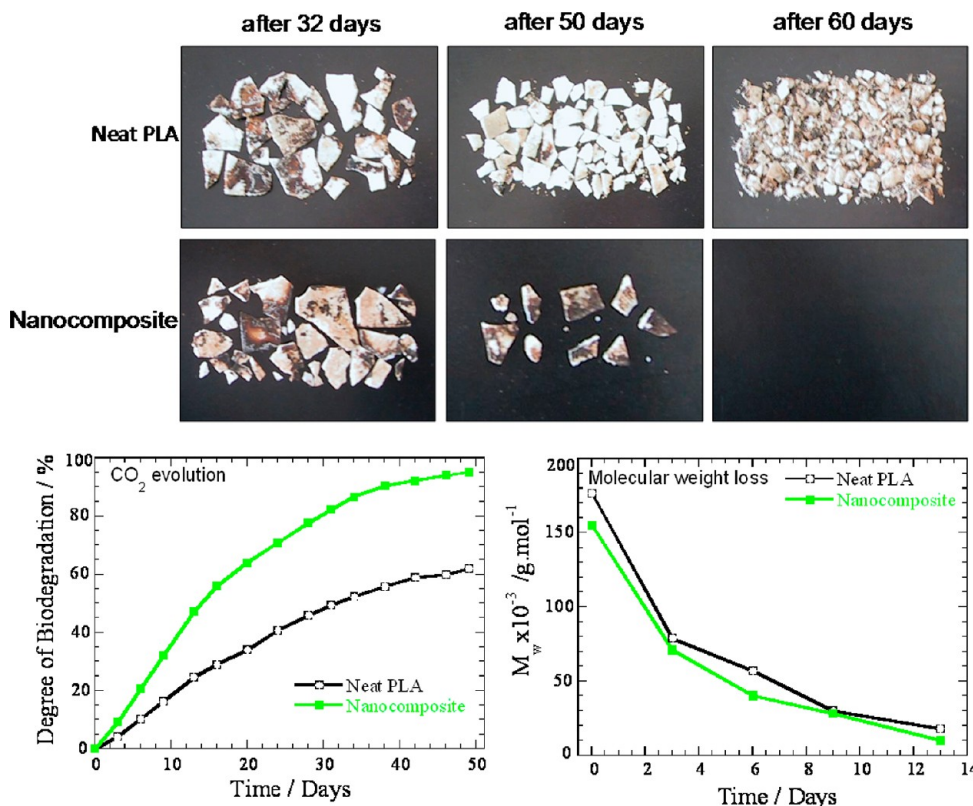


FIGURE 6. Biodegradability test results of neat PLA and bionanocomposites prepared with organically modified clay (content = 4 wt %).

are not compatible with the PLA matrix.^{8,14} To improve the thermodynamically favorable interactions between clay particles and the PLA matrix, researchers generally convert the normal hydrophilic surface to an organophilic one, making the intercalation of PLA chains possible. Generally, this can be done by ion-exchange reactions with cationic surfactants including primary, secondary, tertiary, and quaternary alkylammonium or alkylphosphonium cations.⁸ The strong interfacial interactions between the PLA matrix and organoclay lead to a high level delamination of silicate layers in the PLA matrix that eventually increases the aspect ratio of dispersed silicate layers and results in concurrent improvement of PLA properties (refer to Figure 5).^{4,19,28} For example, the incorporation of 4 wt % organoclay particles shows an impressive improvement of the tensile and flexural modulus of PLA. Similarly, organoclay improved the plastic deformation temperature (under a specific load) of PLA by 18 °C. This property improvement is very important for automotive applications. On the other hand, bionanocomposites show great promise in providing excellent oxygen gas barrier properties for the development of environmentally friendly packaging materials.^{14,29,30} This significant improvement in permeability is due to the presence of highly delaminated silicate layers in the PLA matrix

that delay the molecular pathway and make the diffusive path more tortuous. Researchers also found that thermal stability of PLA improved after nanocomposite formation with clay.^{29,31} Although most reported PLA/clay bionanocomposites showed improved mechanical and material properties, low ductile properties of PLA matrix are still a serious scientific challenge.

Besides the improvements in the mechanical, thermo-mechanical, and gas barrier properties, the resulting bionanocomposites exhibit higher crystallization^{32–34} and biodegradation rates (refer to Figure 6).^{29,31,35} However, the effect of organoclay on biodegradability of bionanocomposites is not unambiguous because the mode of attack by microorganisms depends on the nature of original clay and the chemical structure of surfactants used to modify pure clay.³⁵ Some authors found that a significant improvement in the barrier properties has an adverse effect on the biodegradability of composites.³⁶ Other researchers studied the effect of cationic and anionic clays, as well as their calcination products on the hydrolytic degradation rate of both amorphous and semicrystalline PLA. Like previous observations, the study by Zhou and Xanthos showed that the degradation of the PLA matrix is directly dependent on the surface characteristics of the clay used and the thermal

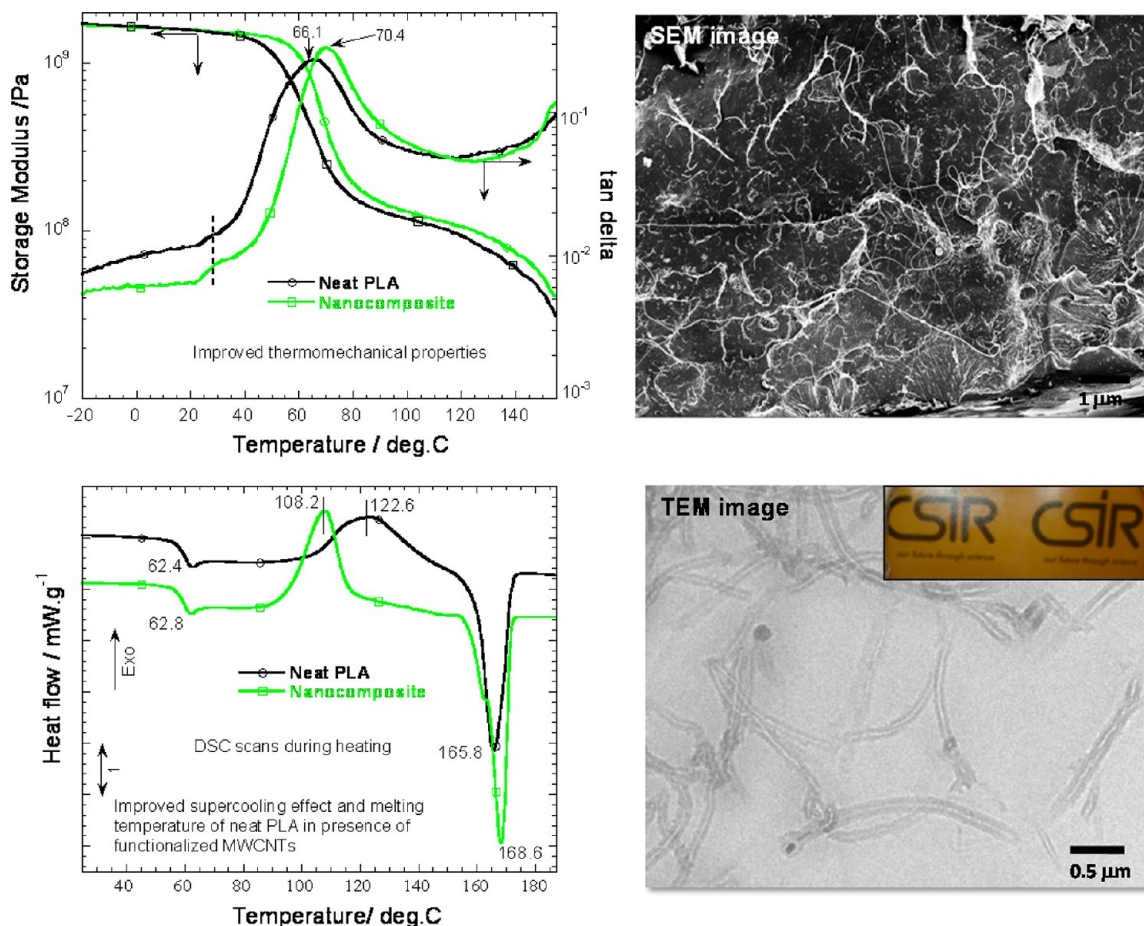


FIGURE 7. Morphology and property improvements of bionanocomposite with functionalized carbon nanotubes (1 wt %) compared with neat PLA.

history of prepared composites.³⁷ Nevertheless, all this information gives us a tremendous opportunity to fine-tune the rate of biodegradation of resulting hybrids by clever selection of organoclays.

Although much research attention has been given to the fabrication of PLA/clay green plastics because of their exceptional mechanical and physical properties with respect to neat PLA, some other inorganic layered solids, such as layered double hydroxides (LDHs), show some new formulation and improved mechanical and thermal properties over those of the neat PLA.^{37,38} However, reported works are very limited because of strong electrostatic interaction between highly charged hydroxyl layers and intercalated anions, the delamination of LDH layers at the nanolevel is very difficult to achieve. On the other hand, because CNTs have extraordinary high modulus (~1 TPa) and strength (~60 GPa), excellent electrical conductivity (~500 S/cm) and thermal conductivity (~100 w/mK) and stability (~900 °C), they also have received serious attention for the preparation of PLA-based bionanocomposites with possible applications in sporting goods, antistatic packaging, automotive, etc.^{39–44}

Of late, a number of reported works are available on the preparation and characterization of CNTs (both single- and multiwalled)-containing PLA hybrids using both pure and surface oxidized/functionalized CNTs, and most of these works have focused on enhanced modulus, thermal, and electrical properties of the final hybrids. In a recent report,⁴⁴ a concurrent improvement in the inherent properties of PLA, such as electrical conductivity, glass transition temperature, crystallization kinetic, dynamic mechanical properties, strength, and elongation at break have been achieved by improving the interfacial interaction between the nanotubes' outer surfaces and the PLA chains (refer to Figure 7 and Table 2).

In addition to the most commonly used nanofillers, such as clays and CNTs, other inorganic and organic fillers, such as silica,⁴⁵ POSS,⁴⁶ titanium dioxide (TiO₂),⁴⁷ silver nanoparticles,⁴⁸ cellulose and starch nanocrystals,⁴⁹ and whiskers,⁵⁰ have been used to improve the physical properties of neat PLA. For example, because of the known capability of absorbing ultraviolet (UV) light to produce oxygen moieties, TiO₂ nanoparticles and nanoplatelets

TABLE 2. Tensile Properties and Electrical Conductivity of Bionanocomposites of PLA and Functionalized MWCNTs

injection molded samples	tensile properties			
	modulus, GPa	strength, MPa	elongation, %	dc conductivity, $S \cdot cm^{-1}$
PLA	6.1 ± 0.3	61.0 ± 4.1	1.5 ± 0.4	$(9.1 \pm 0.8) \times 10^{-4}$
nanocomposite	5.7 ± 0.4	61.6 ± 4.6	2.7 ± 0.1	$(9.7 \pm 0.7) \times 10^{-4}$

have been incorporated to improve the photodegradation of the PLA matrix.⁵¹ Under UV light, the active oxygen species start degrading by attacking interfacial PLA chains, forming carbon-centered radicals, and accelerating chain cleavage.⁴⁷ In addition to photocatalytic activity, TiO₂ nanoparticles also have good magnetic and antibacterial properties.

5. Bionanocomposites as Biomedical Materials

Today, the most frequently used biodegradable polymer for biomedical applications is PLA because it can be synthesized under controlled conditions and hence has predictable properties, such as flexural modulus, tensile strength, and biodegradation rate.⁷ In addition, PLA has excellent biocompatibility *in vivo* and a good osteoconductivity.⁵² Although PLA has good mechanical and physical properties including biodegradability and biocompatibility, it does not have some of the fundamental characteristics of biomaterials. For example, in the tissue engineering areas, not only should PLA stimulate and support tissue growth, but the growth rate of new tissue and the degradation rate of PLA should be the same. Furthermore, the PLA scaffolds should be able to maintain the structural stability *in situ* during tissue growth. Therefore, development of PLA-based multicomponent functional biomaterials has received much research attention, and the fabrication of PLA-based bionanocomposites using biomimetic concepts is a popular subject area for researchers.

The reconstruction of damaged tissue, artificial supports for cell growth, and locally acting drug-delivery systems are the most common applications of bionanocomposites.¹⁸ To guide tissue regeneration in three dimensions (3D), one must convert bionanocomposites to a 3D scaffold with high porosity and homogeneous distribution of pores. These characteristics are crucial to have uniform distribution of cells and adequate transport of nutrients and cellular wastes. Although bionanocomposites with good dispersion and delamination of nanoparticles can be prepared by a number of methods, researchers have employed additional processing techniques, such as gas-induced foaming, thermally induced phase separation, and surface leaching, to fabricate bionanocomposite scaffolds.⁵³ Two such scaffolds have been developed in our laboratory (refer to Figure 8).

Owing to the chemical similarities with mineralized human bone tissue, bionanocomposites containing hydroxylapatite (HA) are the most extensively utilized biomaterials for tissue engineering and artificial supports of cell growth.^{52,54} The main composition of HA is tricalcium phosphate $[Ca_{10}(PO_4)_6(OH)_2]$, and it is generally synthesized by sol-gel methods.⁵⁵ The benefits of nano-HA over conventional HA are a large surface area to volume ratio, superior functional properties, and crystallinity similar to biological apatite, which would support greater impact with implanted cells. Based on this information, a number of articles have been published on the preparation and characterization of PLA/nano-HA composites.⁵² Although published works have shown that the physical properties of PLA as a biomaterial are improved after composite formation with nano-HA, its mechanical properties were significantly reduced, which limits using PLA/nano-HA composite as a load-bearing material. To overcome this drawback and have a better energy-dissipation mechanism, the nano-HA surface was modified with PLA oligomer (oligo-HA) and blended with high molecular weight PLA.⁵⁶ In the presence of oligomer, a nanolevel dispersion of HA particles was achieved, which led to the practical improvement of flexural strength and modulus and impact strength. The improved mechanical properties of this composite are due to the role of oligo-PLA as a compatibilizer between high molecular weight PLA and HA particles; however, these improvements restricted the nano-HA loading to 4 wt %. Nevertheless, PLA/oligo-HA bionanocomposite containing 4 wt % PLA-grafted nano-HA shows significant improvement in cell growth compared with PLA/HA biocomposite. This author believes this improvement could be due to the nanolevel dispersion of HA particles in the PLA matrix, which offers a huge biocompatible surface for cells to grow.

Based on the fact that all living cells are carbon based and CNTs are made completely of carbon, there is tremendous interest in developing CNT-containing bionanocomposites of PLA for biomedical applications. Also, CNTs have very high inherent electrical conductivity along with a huge potential to offer much-needed structural stability for bionanocomposite-based scaffolds. Recently, we explored a number of techniques to transfer the outstanding properties

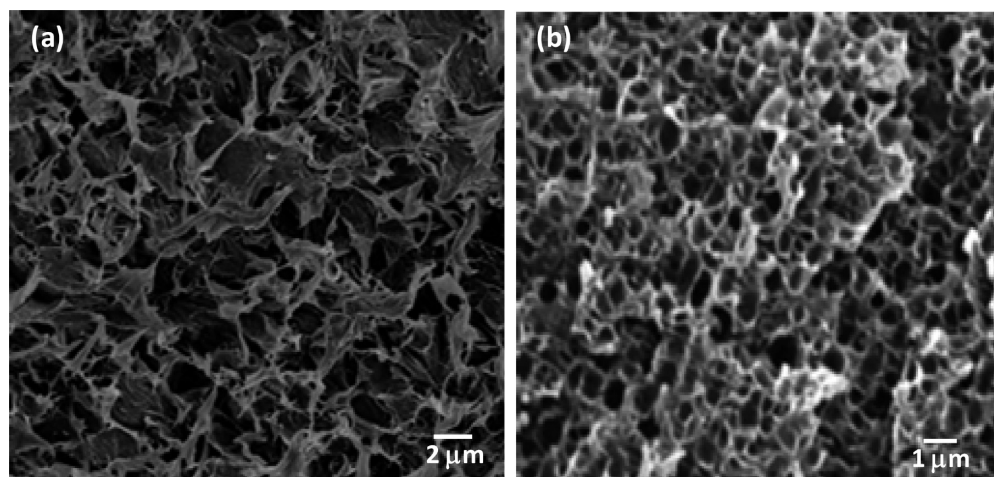


FIGURE 8. Bionanocomposite scaffolds prepared using (a) solvent-casting particulate etching method and (b) gas-induced foaming.

of CNTs from the nanoscale to microscale and develop conductive bionanocomposites with a balance of mechanical properties.⁴⁴ The conductive bionanocomposites can direct the cell growth and stimulate the tissue healing process. For example, PLA/MWCNT composites have shown significant improvement in osteoblast proliferation and calcium production when alternating current was applied to the substrate.⁵⁷ Research has also shown that the nature of functional groups on CNTs' outer surfaces seems to play an important role in the mechanism of interactions with cells. Similarly, researchers have incorporated both CNTs and HA into PLA matrix to produce composites with the synergetic effects of both fillers.⁵⁸

Although PLA/CNT composites have shown huge promise for developing functional biomaterials for biomedical applications, the toxicity and biocompatibility of pure CNTs, functionalized CNTs, and finally, CNT-containing bionanocomposites are not clearly answered yet. A number of papers have been published on this topic, but reported results are very contradictory and lack specific conclusions.^{59–61} Therefore, extensive research on the toxicological effect and pharmacological development of pure and functionalized CNTs is important, which will hopefully lead to an acceptable framework for the safe use of CNTs or CNT-based bionanocomposites in biomedical applications.

Since nanoparticles (particles $\sim 10^3$ to 10^5 atoms) generally exhibit unique physical, chemical, and biological properties compared with their bulk counterparts, recent studies have also focused on the development of PLA-based bionanocomposites incorporating nanoparticles from novel metals.^{62–65} Research has also shown that nanoparticle properties are significantly influenced by their size and

shape. Moreover, homogeneous dispersion of metal nanoparticles can change the surface roughness and wettability of the PLA matrix, which eventually improves the adhesion of living cells on the bionanocomposite surface. Silver, gold, and platinum are the most commonly used metal nanoparticles for the development of bionanocomposites of PLA. The main research concept is to have controlled release of functional nanoparticles when they are dispersed in the PLA matrix. For example, throughout the ages, silver has been commonly used to prevent infection by killing a wide range of microorganisms; however, the influence of silver nanoparticles on bacteria is still debatable. Therefore, homogeneous dispersion of silver nanoparticles in the PLA matrix would allow nanoparticles to be released in a controlled manner during the degradation of the matrix. The higher thermal conductivity (due to the presence of metal nanoparticles) of the bionanocomposite can speed up the overall degradation process of the PLA matrix. This eventually stops the antibacterial effect of silver nanoparticles for an extended period of time. Metal and semiconductor clusters (~ 10 to 10^3 atoms) have also emerged as biocompatible nanofillers for PLA.

6. Future Outlook

The main objective of this Account was to give nonspecialist readers a general understanding about PLA-based bionanocomposites, a promising class of hybrid materials. Research and development activities for PLA bionanocomposites are expanding rapidly, with new materials design concepts and applications being developed in academic, industrial, and government research laboratories worldwide. The recent increased availability of various types of functional nanoparticles is a major factor for the rapid development of

bionanocomposites of PLA. The ultimate goal, though, is to design PLA-based bionanocomposites with just the properties desired.

The large-scale production of bionanocomposites with a controlled nanolevel dispersion of filler is still a major challenge. The inconsistent supply of nanofillers may be the main reason for this. In addition, well-established structure–property–processing relationships of bionanocomposites are crucial to design materials with desired properties and also for further market infiltration. Another important aspect is the quantitative understanding of toxicological effects and pharmacological developments of both nanofillers and developed bionanocomposites.

Originally, the development of high-performance bionanocomposites containing nanoclays and PLA was the main focus area. Increasingly however, we are seeing the rapid development of bionanocomposites of PLA incorporating various types of new and novel functional nanoparticles. The development of PLA-based bionanocomposites is still considered to be an emerging research area, and, just recently, they have become part of modern technology. However, the uses of PLA bionanocomposites in environmentally friendly packaging and in bone implants are rapidly growing application areas.

The future development of novel nanohybrids of PLA with controlled mechanical properties (particularly ductility), biodegradability, and surface functionality can be envisaged as multidisciplinary research efforts with a wide range of application possibilities. For example, in the future, the fundamental structure of bionanocomposites seems to originate by introducing stem cells, where PLA bionanocomposite scaffolds will be able to mimic the *in vivo* and *in vitro* growth of tissues and organs. Similarly, this will also produce photodegradable green plastic films for agriculture and food packaging applications. In addition, PLA bionanocomposites will play a significant role in developing environmentally friendly vehicles and housing.

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BIOGRAPHICAL INFORMATION

Suprakas Sinha Ray is chief researcher and director of DST/CSIR National Centre for Nanostructured Materials, CSIR. He is one of the most active and highly cited authors in the field of polymer nanocomposite materials, and recently, he has been rated as

one of the top 50 high impact chemists in the world (Feb. 2011, Thomson Reuter). Professor Sinha Ray is author and coauthor of 10 book chapters and 121 articles in international journals, as well as holder of several patents.

FOOTNOTES

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The authors declare no competing financial interest.

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