



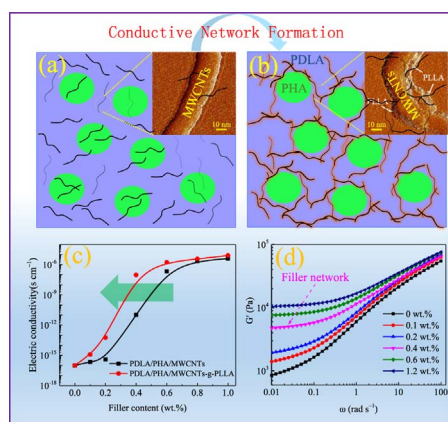
Design of bio-based conductive and fast crystallizing nanocomposites with controllable distribution of multiwalled carbon nanotubes via interfacial stereocomplexation



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GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a novel route was proposed to fabricate entirely bio-based conductive nanocomposites with a low percolation threshold of conductivity (ϕ_c) and enhanced crystallization and mechanical performances. In order to achieve this objective, poly(D-lactide)/poly(hydroxyalkanoate) (PDLA/PHA) nanocomposites with multi-walled carbon nanotubes (MWCNTs) and MWCNTs-g-PLLA (prepared via ring opening polymerization of L-lactide with grafting degree of 17%) were designed and fabricated. The grafting of PLLA facilitates the selective distribution of MWCNTs in the sole PDLA phase via interfacial stereocomplexation, which in combination with the volume exclusion effect of PHA leads to a lower value of ϕ_c ($\phi_c = 0.32$ wt%) compared to that of the unmodified MWCNTs ($\phi_c = 0.56$ wt%). The localization of MWCNTs-g-PLLA in the PDLA phase was directly confirmed by scanning electron microscopy, transmission electron microscopy and supported by crystallization analysis by differential scanning calorimetry, X-ray diffraction, and polarizing optical microscopy. The presence of MWCNTs, in particular, the MWCNTs-g-PLLA significantly enhanced the crystallization rate of PDLA. Furthermore, MWCNTs networks in the nanocomposites were monitored by rheological analysis when the MWCNTs and MWCNTs-g-PLLA loading reached a critical value. The MWCNTs networks not only resulted in conductivity, but also strong reinforcement of the nanocomposites. For example, tensile strength of the PDLA/PHA blends increased from 32 to 50 MPa after the formation of MWCNTs network and leveled off at higher

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MWCNTs loadings. The bio-based conductive nanocomposites reported in this study exhibit significant potential in antistatic films and (semi-)conducting materials.

1. Introduction

Doping electrically conductive fillers such as carbon black [1–3], carbon nanotubes [4–6], and graphene [7–10] into insulated polymer matrix can generate electrically conductive polymer composites (CPCs) with excellent electrical conductivity, which can be applied as anti-static materials, electromagnetic interference shielding materials, sensors, and conductors [11]. Normally, the insulator-to-conductor transition occurs when the content of conductive fillers reaches a critical value which is defined as the percolation threshold (ϕ_c). Conductive network is formed in the polymer matrix at the ϕ_c . However, the conductive fillers, in general, show high ϕ_c values because they are usually randomly dispersed in polymer matrices. For example, Cheah et al. reported that carbon black required a loading of 15–20 wt% to achieve the optimized value of ϕ_c in polymer matrix [12], while the value of ϕ_c for multiwalled carbon nanotubes (MWCNTs) which possess high-aspect-ratio is about 2.0 wt% [13,14]. Notably, the high loadings of conductive fillers lead to difficulty in processing, deterioration in mechanical properties, and high cost of the final products. Therefore, decrease in the values of ϕ_c is extremely important and highly desirable for the fabrication of high-performance CPCs.

In the pursuit of CPCs with lightweight, high-strength, and low-cost, extensive research efforts have been devoted to investigate and explore polymer/MWCNTs composites in recent years. As expected, addition of a small amount of MWCNTs with high-aspect-ratio can impart the matrix polymers with excellent overall performance, in particular, electrical conductivity [15–17]. Way of dispersion of the MWCNTs in the polymer matrix plays a significantly important role in deciding the final properties such as conductivity and mechanical performance of the composite. It has been proved that the uniform dispersion is not the best way to achieve the lowest value of ϕ_c of MWCNTs. Recent reports revealed that addition of MWCNTs into immiscible polymer blends allowed the formation of selective dispersion morphology such as localization at the interphase or the continuous phase, which highly depended on the interfacial energy, affinity of MWCNTs with each polymer, viscosity of the two polymers, as well as their mixing mode [18–22].

Moreover, biodegradable polymers such as poly(lactide) (PLA) and poly(hydroxyalkanoate) (PHA) have attracted considerable interest because of the environmental issues caused by the petrochemical polymers. Till date, MWCNTs-filled PLA/poly(ϵ -caprolactone) blend nanocomposites were developed to obtain environmentally friendly materials with electrical conductivity because of the favorable localization of the MWCNTs in the poly(ϵ -caprolactone) phase [19,23]. Lee and Jeong prepared PLA/maleic anhydride-grafted polypropylene (PP) blend (50/50 by wt%) composite films filled with different pristine MWCNTs contents of 0.0–10.0 wt% [24]. It was found that the PLA domains were well dispersed in the PP matrix of the immiscible PLA/PP blends and that the MWCNTs were localized selectively and uniformly in the PP matrix of the composite films. Accordingly, the electrical resistivity of the composite films decreased considerably from $\sim 10^{10}$ to $\sim 10^1 \Omega \text{ cm}$ with the increment of the MWCNTs content. On the other hand, Nasti et al. reported the preparation of double percolated blends of polystyrene (PS), PLA, and MWCNTs starting from a PS masterbatch containing 2 wt% MWCNTs [25]. This two-step process resulted in a double percolated morphology where PS percolated the PLA phase, and MWCNTs percolated the PS phase. Double percolation led to a very low value of electrical ϕ_c of about 0.45 vol% MWCNTs on total volume and an electrical conductivity of $10^{-9} \text{ S cm}^{-1}$. Park et al. reported that the MWCNTs preferred to locate more in the poly(propylene carbonate)

(PPC) phase than in the PLA phase in the PPC/PLA/MWCNTs composites due to the lower interfacial tension of the PPC/MWCNTs composites compared to that of the PLA/MWCNTs composites [26]. The electrical conductivities of the PPC/PLA/MWCNTs composites were higher than those of the PPC/MWCNTs and the PLA/MWCNTs composites, which was likely due to the selective localization of the MWCNTs in the PPC phase (continuous phase). However, seldom attention has been paid to the dispersion of MWCNTs in PLA/PHA systems.

On the one hand, PLA is synthesized by ring-opening polymerization (ROP) of lactide or by condensation polymerization of the lactic acid monomers [27]. It possesses several merits such as bio-based and biodegradable features, easy melt processability, and thermal and chemical resistance [28]. However, brittleness, low crystallization rate, and high cost limit its applications. On the other hand, PHA belongs to a group of biomass polyesters produced via fermentation of sugars or lipids by bacteria that utilize the polymer for carbon and energy storage in their cells [29]. PHA possesses properties similar to those of traditional thermoplastics and can be degraded completely into water and carbon dioxide by microorganisms in soil, sea, or sewage [30–32]. Although PHA offers several potential benefits such as flexibility, its applications are limited due to its less robust physical properties [33]. A combination of PLA and PHA may generate balanced mechanical properties. Takagi et al. [34] studied the morphology, mechanical properties, and biodegradability of PLA/PHA blends, and found that the incorporation of PHA resulted in an increase in the impact toughness; however, decrease in the tensile strength of PLA. Noda et al. [35] reported that the elongation at break of the PLA/PHA blends was improved significantly when 10% PHA was added, which was ascribed to the increase in the amorphous phase of the blend.

In this study, we attempted to fabricate conductive PLA/PHA/MWCNTs nanocomposites with balanced mechanical performance and enhanced crystallization rate by controlling the distribution of MWCNTs. To control the distribution of MWCNTs, poly(L-lactide) (PLLA) was in situ grafted onto the surface of MWCNTs resulting in the generation of MWCNTs-g-PLLA nanohybrids which were subsequently blended with poly(D-lactide) (PDLA) and PHA to fabricate final PDLA/PHA/MWCNTs-g-PLLA nanocomposites. The grafted PLLA chains were expected to strongly interact with the PDLA matrix forming PLA stereocomplex at the interface which was capable of localizing the MWCNTs in the PDLA matrix and acted both as nucleating agent and reinforcing agent as well [36]. The morphology, crystallization behavior, electrical conductivity, and mechanical properties of the PDLA/PHA/MWCNTs nanocomposites were systematically investigated.

2. Experimental section

2.1. Materials

Neat PDLA ($M_n = 7.0 \text{ kDa}$, $\text{PDI} = 1.6$) was synthesized by ROP of D-lactide (99% purity) which was provided by Shenzhen Esun Industrial Co., Ltd., China. PHA (EM5300F, $M_n = 75 \text{ kDa}$, $\text{PDI} = 1.5$) was supplied by Ecomann Technology Co., Ltd., China. L-lactide (99% purity) was provided by Nantong Jiuding Biological Engineering Co., Ltd., China. Hydroxyl functionalized MWCNTs with a hydroxyl group content of approximately 3.06 wt%, diameter of 10–20 nm, and length of 10–30 μm were supplied by Chengdu Organic Chemicals Co., Ltd. Tin (II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) was purchased from Aladdin Chemical Reagent, China. Toluene, chloroform, and methanol with a purity of 99% were purchased from Sinopharm Group Chemical Reagent Co.,

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