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Biodegradable silica rubber core-shell nanoparticles and their stereocomplex for efficient PLA toughening

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ABSTRACT

In the effort to overcome the shortcomings such as brittleness and poor mechanical stability, and increase the competitive edge of renewable poly(lactic acid) PLA over conventional petroleum-based thermoplastics, silica rubber core-shell nanoparticles for effective PLA toughening were successfully synthesized by sequential ring opening polymerization (ROP). The core-shell structure was designed with silica as inner core, P(CL-*m*LA) as ‘rubber’ middle layer and terminal PDLA chains (SiO_2-*r*-PDLA), to facilitate the stereocomplex formation with PLLA matrix for enhanced interface control. The PLLA/SiO_2-*r*-PDLA nanocomposites were fabricated through solution blending-injection molding process. Nuclear magnetic resonance (^1H NMR and ^{13}C NMR) results confirmed the presence of grafted ’rubber’ and PDLA chains from the surface of silica particle. In addition, PLLA/SiO_2-*r*-PDLA nanocomposites showed tremendous improvement in thermal and mechanical properties using differential scanning calorimetry (DSC) and tensile testing, respectively. Besides the formation of stereocomplex in the nanocomposites, a detailed study on the melt stability of these stereocomplex nanocomposites revealed a ‘memorized’ stereocomplex behavior, *i.e.*, having the ability to perfectly reassemble after re-crystallization from melt (melt memory effect), when rubber segment is present. Finally, structure-deformation mechanisms were studied using scanning electron microscopy (SEM) and small angle x-ray scattering (SAXS). From SAXS, crazing was clearly observed whereas SEM revealed fibrillated structures. Thus, crazing and fibrillation are the key deformation mechanisms in PLLA/SiO_2-*r*-PDLA system. The exciting new fillers could open up new horizons for PLA advanced composites applications.

1. Introduction

Poly (lactide) (PLA) is the most extensively researched synthetic biopolymer due to its intrinsic properties, namely, biodegradability, biocompatibility, renewability, thermal processability and excellent mechanical properties [1–4]. The large scale production of PLA from renewable resources has made this green material a promising candidate to replace the petroleum-based polymers. Moreover, PLA exists in diverse stereoregular microstructures (tacticities), such as, isotactic (-SSSS- or –RRRR-), syndiotactic (*meso*) (-SRSR-) and atactic/heterotactic (*rac*) (-SSRR-) PLA, in which isotactic PLA are highly crystalline, while the atactic poly(D,L-lactic acid) (PDLLA) is amorphous [4,5]. However, PLA suffers from shortcomings such as brittleness, poor mechanical stability, inadequate recrystallization ability and poor gas barrier properties, which have significantly limited the competitive edge of PLA over conventional synthetic thermoplastics [5,6]. As such, many programs have been developed to improve the property deficiency of PLA, including copolymerization, polymer blends, cross linking, stereocomplexation of PLA, addition of fillers and nucleating agents into PLA matrix etc. [7–9]. Recently, researchers have developed keen interests on PLA based bio-nanocomposites by incorporating relatively new organic/inorganic fillers as reinforcements in PLA matrix [8,10–13]. For example, we and other research groups have demonstrated various nanoscale fillers that can be used as reinforcements, for instance, organo-clay [14,15], graphene oxide

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(GO) [13] and carbon nanotubes (CNTs) etc. [16–19]. In the field of organic/inorganic composites, silica is important inorganic filler used as reinforcement because of its low cost and availability in the market. It has been previously explored in polymeric composite systems for material toughening [20,21]. For example, Ziong et al. [22] fabricated PLA/nanosilica composite by extrusion in the presence of epoxidized soybean oil (ESO). The fabricated nanocomposites had enhanced mechanical properties, for instance, the elongation and notched impact strength of PLA/silica/ESO nanocomposite with 5 wt % nanosilica and 15 wt % ESO were ~42% and ~11 kJ/m^2, respectively. These were much higher than neat PLA or PLA/nanosilica composite without ESO. Also, Hao et al. [23] prein the pared PLA/nanosilica composites by melt compounding PLA and rigid spherical silica particles of various sizes. The resultant nanocomposites revealed improved thermal stability, ascribed to a silica network structure dominated by particle-particle and particle-polymer interactions. In another study, Odent et al. [24] obtained tough PLA based material from ternary melt of PLA, rubber-like copolyester (ε-caprolactone-*co*-D, L-lactide) and silica nanoparticles. The fabricated nanocomposites exhibited 15-fold enhanced toughness, ascribed to the peculiar round-like to co-continuous phase transition of the rubber-phase in the matrix. However, the combined silica and rubber as integrated nanofiller for PLA toughening has not been previously explored.

Other programs for PLA improvement include, tailoring impact and toughness performance by incorporating additives, primarily core-shell particles [25]. Core-shell particles provide another route to improve the properties of PLA with advantages such as, consistent morphology, non-filtering of nanosize particles, translucent propensity, extreme stability and compatibility with secondary tougheners. The core-shell particles toughen polymers by cavitation of inner core and small particles act as crack terminators [10,26]. Since its discovery in 1987 by Ikada and coworkers [27], stereocomplexation between PLLA and PDLA has emerged as an important strategy of tailoring the interface adhesion. This strategy has also been reported to improve thermal stability of PLA products [28–30].

From the above discussion, development of a system comprising of silica-rubber-PDLA (SiO_2-*r*-PDLA) core-shell nanoparticles in PLLA, could further divulge interesting PLA properties for specialty applications. In this paper, it is envisaged that covalently bound silica-rubber-PDLA core-shell nanoparticles will radically improve thermo-mechanical properties of PLLA, due to stereocomplex interactions between PDLA segments and PLLA matrix. To the best of our knowledge, this is the first report describing the synergistic property improvements through covalently bonded rigid silica nanoparticles and rubber segments. The presence of silica-rubber-PDLA nanoparticles in the matrix and its stereocomplex formation with PLLA will provide stress relief and bridging effects during deformation, thus improving toughness without sacrificing strength and modulus.

2. Results and discussion

2.1. Synthesis and characterization of SiO_2-r-PDLA and SiO_2-PDLA nanoparticles

In composite materials, there often exists a conflict between strength and toughness. To circumvent this challenge, our group has designed and adopted a rigid-rubber-matrix strategy in composite fabrication with great success [31]. This strategy has been applied in synthesis of SiO_2-*r*-PDLA nanofillers to concomitantly enhance strength and toughness of PLLA. SiO_2-*r*-PDLA nanofillers are ‘core-shell’ particles, synthesized in a three-step approach as follows: modification of raw silica to amino modified silica; grafting of rubber segment onto amino modified silica and subsequent grafting of PDLA chains as outer shell (Scheme 1).

Successful grafting of the rubber or (P(CL-*m*LA)) and PDLA chains onto silica has been confirmed by ^{1}H NMR and ^{13}C NMR. As can be seen in Fig. 1(A), signals at δ ~1.4 (methyl protons) and δ ~5.2 ppm (methine protons) were assigned to PLA units and different methylene protons of PCL units appear at chemical shifts δ ~1.3, 1.6, 2.3 and 4.1 ppm [3,32]. To further confirm existence of the rubber segment in SiO_2-*r*-PDLA, Fig. 1(B) representing SiO_2-PDLA, disclose the absence of chemical shifts at δ ~2.3 and δ ~4.1 ppm assigned to PCL units [33]. Further analysis of SiO_2-*r*-PDLA nanofillers using ^{13}C NMR reveals well separated peaks at different spectral ranges (Figure S1). Both ^{1}H NMR and ^{13}C NMR results confirm the successful synthesis of SiO_2-*r*-PDLA. After using HF solution to etch the silica core, the molecular weight and distribution of the synthesized nanofillers are determined using GPC. The M_n of rubber-PDLA in SiO_2-*r*-PDLA is: 14500 g/mol, with rubber or (P (CL-*m*LA)): 8200 g/mol and PDLA block in SiO_2-PDLA: 5600 g/mol, PDI: 1.16 (see Table S1 Supporting Information). It is shown that there is a substantial increase of molecular mass, undoubtedly, arising from sequential incorporation of D-LA into Si-rubber. TEM image shows the morphological structure of SiO_2-*r*-PDLA, with a diameter of the core in the range of 20 nm (Figure S2). More importantly, the number of amino functional groups in SiO_2-NH_2 has been evaluated using acid-base back titration method using the method reported by Hak-Sung Jung et al. [34]. The density of $-NH_2$ group on the nanoparticle surface is about 2.95 ea/nm^2. Calculations are included in supporting information and the These results are comparable to the values obtained by other researchers using Titration [34].

Thermal stability of the filler and as-prepared nanocomposites were investigated by thermal gravimetric analysis (TGA). The results showed that stereocomplexation between PLLA matrix and PDLA chains attached to nanofillers enhanced thermal properties of the nanocomposites (Figure S3 and S4). In addition, DSC experiments are carried out to investigate thermal behavior of fabricated nanocomposites. Figure S5 shows DSC traces of (A) PLLA, (B) 10% SiO_2-PDLA, (C) 10% SiO_2-*r*-PDLA, (D) 5% SiO_2-*r*-PDLA and (E) 2.5% SiO_2-*r*-PDLA. As can be seen, PLLA and nanocomposites depict a glass transition temperature (T_g), cold crystallization temperature (T_c) and melting temperature (T_m) (Table 1). It is worthwhile noting that PLLA has small cold crystallization peak and one broad melting peak at around 150 °C, compared to the nanocomposites. On the other hand, PLLA/10%-SiO_2-PDLA show one broad melting peak at around 150 °C and a sharp peak at 210 °C. The peak at 210 °C is characteristic of stereocomplex crystallites [13]. On the contrary, PLLA nanocomposites with 2.5%, 5% and 10% SiO_2-*r*-PDLA exhibit double melting peaks (a minor peak, followed of a major peak at higher temperature) at T_{m1} (140 °C) and T_{m2} (155 °C) for homo-crystallites and additional melting peak at about 200 °C, attributed to stereocomplex crystallites. As noted, DSC curves for all PLLA/SiO_2-*r*-PDLA show double melting peak phenomenon, which has been widely reported in PLA studies. For instance, Yasuniwa et al. [35] investigated double-melting behavior of PLLA and proved the recrystallization in the melting process using DSC. This phenomenon is largely ascribed to existence of polymorphic forms or melting of a metastable crystalline form, which crystallizes immediately into a more stable one [36–38]. In addition, it is clear that cold crystallization and melting enthalpies of PLLA/SiO_2-*r*-PDLA nanocomposites are highly dependent on nanofillers content. Undoubtedly, cold crystallization and melting enthalpies decrease with increasing SiO_2-*r*-PDLA nanofillers content. Table 1 summarizes thermo-mechanical properties of PLLA and as-prepared nanocomposites obtained from DSC, DMA and tensile tests. From DSC results, further scrutiny on melt stability of stereocomplex