



Selective localization of carbon nanotube and organoclay in biodegradable poly(butylene succinate)/polylactide blend-based nanocomposites with enhanced rigidity, toughness and electrical conductivity



Veluri Sivanjineyulu^a, Kartik Behera^a, Yen-Hsiang Chang^{b,c}, Fang-Chyou Chiu^{a,b,*}

^a Department of Chemical and Materials Engineering, Chang Gung University, Taoyuan 333, Taiwan

^b Department of General Dentistry, Chang Gung Memorial Hospital, Taoyuan 333, Taiwan

^c Graduate Institute of Dental and Craniofacial Science, Chang Gung University, Taoyuan 333, Taiwan

ARTICLE INFO

Keywords:

- A. Nanocomposites
- B. Electrical properties
- B. Mechanical properties
- B. Thermal properties

ABSTRACT

Carbon nanotube (CNT) and organo-montmorillonite (15A) were used individually and simultaneously as reinforcing fillers to fabricate poly(butylene succinate)/polylactide (PBS/PLA) blend-based nanocomposites. Poly(butylene succinate-co-lactate) served as compatibilizer for the PBS/PLA blend. Morphological results demonstrated that the added CNT was distributed mainly in the PBS matrix, whereas the added 15A was selectively localized within the dispersed PLA domains. Adding only 15A produced a quasi co-continuous PBS-PLA morphology. DSC results confirmed the nucleation effect of CNT on the crystallization of PBS and PLA, whereas 15A facilitated only the nucleation of PLA. The CNT exerted greater influence than 15A on the samples' rheological properties. The Young's modulus and impact strength of the nanocomposites increased up to 4.2 and 2.8 times, respectively, compared with those of the blend. The electrical resistivity of the blend decreased by up to 11 orders at 3 phr CNT loading. The electrical-percolation threshold was constructed at 0.5 phr CNT loading.

1. Introduction

Nanoscale-filler-based polymer composites (nanocomposites) are eliciting considerable academic and industrial research interests because of their excellent properties compared with conventional blends/composites. Various combinations of polymers and nanofillers have been designed to study their potential in improving the chemical and physical properties of parent polymers with minimal addition of nanofillers (ca. < 3 wt%) [1–4]. The resultant performance of nanocomposites is determined based not only on the dispersion status of added fillers but also on the evolved interfacial morphology [5,6]. Among the nanofillers investigated, carbon nanotubes (CNTs) [3] and organoclays [1,7] are the most appropriate materials to be used to enhance the performance of parent polymers. CNTs were first synthesized by Iijima [8] in 1991, and the first polymer nanocomposite utilizing CNTs as filler was manufactured in 1994 by Ajayan et al. [9]. Since then, extensive studies on CNT-added nanocomposites emerged with the aim to achieve unique mechanical and electrical properties. Similar to CNTs, organically modified montmorillonite (O-MMT) is an excellent candidate for the fabrication of high-performance polymer nanocomposites. Montmorillonite (MMT, layered structure) comprises

of 1-nm thin individual layers, consisting of a central octahedral alumina sheet sandwiched between two tetrahedral silica sheets. The pristine MMT exhibits hydrophilic characteristics and requires organic modifications to show an affinity to hydrophobic polymers.

To date, the extensive usage of petroleum-based and non-biodegradable polymers has resulted in such crises as depletion of petroleum resources and environmental pollution. To mitigate this propensity, scientists have exerted effort to develop and synthesize bio-sourced/biodegradable polymers with eco-friendly characteristics [10]. Among the biodegradable polymers available, poly(butylene succinate) (PBS) and polylactide (PLA) have drawn the interest of researchers because of their renewability, biocompatibility and fine properties [11,12]. PBS is an emerging biodegradable polyester synthesized through condensation of 1,4-butanediol and succinic acid. It can be commercially produced from biomass as well. PBS possesses desirable mechanical properties and remarkable reprocessability. Thus, it is recognized as a promising environmentally benign alternative material to traditional commodity plastics. The applications of PBS include production of packaging film and injection-molded parts, and has been investigated as modifier for PLA [13,14]. However, the low-melt viscosity and insufficient rigidity of PBS often hinder its further applications. Several techniques have

* Corresponding author at: Department of Chemical and Materials Engineering, Chang Gung University, Taoyuan 333, Taiwan.
E-mail address: maxson@mail.cgu.edu.tw (F.-C. Chiu).

been employed to overcome these drawbacks; these techniques include blending, reinforcement with fillers and copolymerization. The development of PBS blends/composites is one of the feasible approaches to achieve enhanced properties at a low cost [15–17].

PLA is one of the most attractive aliphatic polyesters due to its environmentally benign characteristics and high modulus. It can be produced from agricultural resources and has been employed in biomedical applications, such as sutures, bone tissue engineering and drug delivery systems. However, PLA has some drawbacks, including low toughness and inadequate gas barrier properties, which limit its industrial applications [18–20]. The manufacture of PLA blends containing other degradable and flexible polymers (such as PBS) is an economic and convenient approach to broaden the application of PLA. Studies have shown that PLA/PBS blends display immiscible characteristics, which limit the improvement of its physical properties [17,21,22]. Therefore, studies [23–26] have utilized various compatibilizers to modify the interfacial morphology of PLA/PBS blends and achieve desirable properties. Poly(butylene succinate-co-lactate) (PBSL) was recently demonstrated as a good component as it acts as film clarity enhancer, compatibilizer and plasticizer in PLA-based blends/composites. Shibata et al. [23] reported that addition of 1–10 wt% PBSL to PLA considerably enhanced the mechanical properties and crystallization rate of PLA.

The properties of polymer blends can be further improved through addition of (nano)fillers to obtain blend-based (nano)composites. Indeed, the distribution of filler(s) and the adhesion between polymers and filler(s) play key roles in controlling the final properties of nanocomposites. Fillers such as metal oxides, calcium sulphate whiskers, organoclays, nitrogen-doped graphene and cellulose nanocrystals have been used to reinforce PBS/PLA blends [25–28]. These fillers not only promoted the reinforcement of PBS/PLA blends but also enhanced the adhesion between polymer components. Wang et al. [27] reported that incorporation of carbon black (CB) into PBS/PLA blend resulted in enhanced compatibility of the immiscible blend. They found that the selective localization of CB within PBS matrix enhanced the processability, stiffness and thermal stability of PBS/PLA blend. Chen et al. [25] found that an epoxy-functionalized organoclay (TFC) can act as compatibilizer for PBS/PLA blend. They reported that when a small amount of TFC was added into the blend, the TFC layers became fully exfoliated and localized mainly in PLA phase. On the basis of the structural (aspect ratio, dimension and alignment), electrical, mechanical and thermal characteristics of CNTs, the addition of CNTs into polymer blends opens new approaches for achieving high-performance nanocomposites [29–31]. Wu et al. [30] studied CNT-filled PLA/poly(ϵ -caprolactone) (PCL) blend-based ternary nanocomposites and observed that added CNTs acted as reinforcement and compatibilizer in immiscible PLA/PCL blends. In addition to incorporating one kind of filler, a growing number of investigations nowadays is geared towards utilizing hybrid filler systems, which is one of the successful methods used to develop high-performance polymer nanocomposites [5,15,32,33]. Chiu [32] recently investigated the effect of adding halloysite nanotube and organoclay on the thermal and mechanical properties of blend-based poly [(butylene succinate)-co-(adipate)] (PBSA)/maleated polyethylene nanocomposites. The rigidity of PBSA evidently increased after the formation of the multi-component nanocomposites. Bouakaz et al. [33] examined the effects on morphology and tensile properties of PLA/PCL blends after simultaneous incorporation of organoclay and epoxy-functionalized graphene. Enhanced compatibility and improved properties were observed in the nanocomposites. Recently, we reported the effect of incorporating CNT/organoclay as hybrid fillers on the morphology, thermal and mechanical properties of polypropylene/PBS blend-based nanocomposites. The mechanical and rheological properties of the blend were considerably improved after the formation of nanocomposites [15].

Multi-component polymer nanocomposites are envisaged to show increased versatility and potential in various applications. Studies on CNT- and hybrid filler-added PBS/PLA blend-based nanocomposites

were less reported. The influences of the individual and/or simultaneous addition of different nanofillers on various properties of PBS/PLA blends should be systematically investigated from the industrial and academic viewpoints. In this study, PBS/PLA blends and blend-based nanocomposites were prepared through inclusion of CNT and/or O-MMT via a conventional melt mixing method. The dispersibility of CNT/O-MMT within the blend matrix was characterized, and the effect of nanofiller(s) addition on the phase morphology of PBS/PLA blend was investigated. The crystal structure and thermal/mechanical properties of neat components, blends and nanocomposites were evaluated and compared. The rheological properties and electrical resistivity of the blends after forming the composites were also highlighted in this work.

2. Experimental

2.1. Materials and samples preparation

This study used biodegradable PBS (Bionolle #1001) purchased from Showa Denko K.K. (Japan) and commercial grade PLA (2500HP) supplied by NatureWorks Ingeo (USA). The PBSL (AZ71T, Mitsubishi Chemical Corporation, Japan), with ca. 3 mol% lactate content, was used as compatibilizer for the PBS/PLA blend. The multi-walled CNT (ICT-030), which has a cylindrical structure with an average diameter of < 40 nm and length of 1–30 μ m, was supplied by Golden Innovation Business Co. LTD. (Taiwan). Cloisite C15A (layered structure and denoted as 15A), was used as another nanofiller for the preparation of nanocomposites. 15A is organically modified MMT, purchased from Southern Clay Products Inc. (USA). As per company data sheet, the cation exchange capacity of 15A is 125 mequiv/100 g; the corresponding organic modifier content is about 40 wt%. The modifier is dimethyl dihydrogenated tallow quaternary ammonium ion of tallow composition is ca. 65% C18, 30% C16, and 5% C14. The thermal stability and morphology of CNT and 15A are shown in supplementary data (Figs. S1 and S2).

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.compositesa.2018.08.009>.

Prior to the fabrication of the PBS/PLA blends and composites, the components were vacuum dried for 12 h at 80 °C to remove any absorbed water. The prescribed ratios of the components were melt mixed using Thermo Haake PolyDrive mixer (R600) at 190 °C for 10 min at a rotor speed of 60 rpm. The designation and formulation of the prepared samples are tabulated in Table 1. We denoted the blends PBS/PLA-70/30 (weight ratio) and PBS/PLA/PBSL-60/30/10 (weight ratio) as SA and SAL, respectively. SAL-T#, SAL-C# and SAL-T#C# indicate the # phr of CNT (T) and 15A (C) loaded into the SAL blend-based composites. For example, SAL-T3 is the PBS/PLA/PBSL blend-based composite with 3 phr CNT inclusion, and SAL-T1C1 is the composite with 1 phr each of CNT and 15A. Neat PBS and PLA were also melt treated under the same condition for comparison. For further characterizations, the melt-mixed samples were subsequently compression-molded at 190 °C for 5 min to prepare specimens of ASTM standard (mechanical properties tests) and 40 mm \times 10 mm \times 2 mm rectangular stripes (electrical

Table 1
Samples designation and formulation.

Designation	Composition	Parts (wt%)
PBS	PBS	100
PLA	PLA	100
SA	PBS/PLA	70/30
SAL	PBS/PLA/PBSL	60/30/10
SAL-T#	PBS/PLA/PBSL/CNT	60/30/10/# [*]
SAL-C#	PBS/PLA/PBSL/15A	60/30/10/# [*]
SAL-T#C#	PBS/PLA/PBSL/CNT/15A	60/30/10/#/15A [*]

#: number; ^{*}: parts per hundred polymer resins (phr).

Download English Version:

<https://daneshyari.com/en/article/8943115>

Download Persian Version:

<https://daneshyari.com/article/8943115>

[Daneshyari.com](https://daneshyari.com)