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ORIGINAL PAPER

Morphological and rheological characterization of multi-walled carbon nanotube/PLA/PBAT blend nanocomposites

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Abstract Biodegradable poly (lactic acid) (PLA)/poly (butyleneadipate-co-butyleneterephthalate) (PBAT)/multi-walled carbon nanotube (MWNT) polymer blend nanocomposites were prepared by using a laboratory-scale twin-screw extruder. Fractured surface morphology of the polymer blend/MWNT nanocomposites were examined via SEM. Furthermore, cross sectioned samples obtained using an ultra-microtome was observed via TEM. In addition, effects of both MWNT reinforcement and phase affinity of MWNT on thermal and rheological properties of the PLA/PBAT blends were investigated by TGA and rotational rheometer. Immiscible PLA/PBAT blend with MWNT nanocomposites showed two-step thermal degradation. The onset temperature of thermal degradation started in the PLA much earlier than in the PBAT. Nonetheless, based on TGA data, it was found that the MWNT enhanced thermal property of the PLA/PBAT blend/MWNT nanocomposites. Rheological properties revealed that both shear and complex viscosities showed unique shear thinning behavior due to selectively localized MWNT dispersion state.

Keywords Nanocomposite · Poly (lactic acid) · Biodegradable polymer · Multi-walled carbon nanotube

Introduction

Polymer/carbon nanotube (CNT) nanocomposites have attracted much attention due to their enhanced thermal, mechanical, electrical and other physical properties

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compared to those of pure polymers or polymer blends [1–4], while quality of the polymer nanocomposites is generally determined by CNT alignment, CNT-polymer adhesion, and CNT dispersion in polymer matrix [5–8]. Therefore, many researchers have paid much attention to CNTs as one of the most promising reinforced nanomaterials due to their extraordinary properties such as high mechanical strength, high aspect ratio and excellent thermal and electrical conducting properties [9]. However, intrinsic aggregation and entanglement of each CNTs bundles in the polymer matrix have been considered as main problems in the polymer/CNT nanocomposites. Therefore, various techniques to homogeneously disperse CNTs into polymer matrix have been studied in various ways [9–14]. In addition, polymer blending methods have also been extensively used in many engineering applications for improving polymeric material properties and commercializing polymer products. Recently, biodegradable polymer blends have drawn a lot of attentions as advanced polymeric systems [15–17]. Both poly (lactic acid) (PLA) and poly (butyleneadipate-co-butyleneterephthalate) (PBAT) are the most common biodegradable polymers which are studied for the purpose of replacing commodity polymers in near future. In addition, their blend system has attracted many interests because it complements brittleness of the PLA with an elastomeric property of the PBAT. PLA is a linear aliphatic thermoplastic polyester which is synthesized by ring opening polymerization or by condensation polymerization of the lactic acid monomers [18]. PLA possesses many good merits due to its melt processability, thermal and chemical resistance [19]. However, due to its brittleness and high cost, without blending it, itself, has been regarded as less attractive material for its application. On the other hand, the PBAT, synthetic biodegradable aliphatic aromatic copolyester synthesized by esterification of 1, 4-butanediol with aromatic dicarboxylic acid and then polycondensation with succinic acid, is attractive while its other properties such as melt viscosity, softness and gas barrier properties are not sufficient for its application to various final products [20].

In this study, PLA and PBAT blends of different composition with a fixed ratio of 2 wt% MWNT content were prepared using a laboratory-scale twin-screw extruder. The MWNT was introduced as a potential filler in the biodegradable polymeric blends. Morphology and thermal properties of the PLA/PBAT/MWNT nanocomposites were characterized by SEM, TEM and TGA. Viscoelastic properties of these nanocomposites were also examined using a rotational rheometer. Based on these investigations, we found that morphological and rheological properties were correlated with physical properties of MWNT in the immiscible PLA/PBAT blend.

Experimental

Materials

Both PLA and PBAT were used as base materials for the biodegradable polymer blend system. PLA resin (2002D, NatureWorks Co., USA) had a melting temperature of 210 °C with melt index of 4–8 g/10 min, and PBAT resin

(G8060, Ire Chemical., Korea) with a melting temperature of 125 °C and melt index of 2 g/10 min. Pristine MWNTs (Iljin Nanotech Co., Korea) with a diameter of 10–15 nm, length 5–15 μm and a purity of 95%, prepared via a thermal chemical vapor deposition method, were adopted as reinforcing fillers.

Preparation of PLA/PBAT/MWNT nanocomposites

Before the melt processing, both PLA and PBAT resin were dried in a vacuum oven at 80 °C for 24 h in order to remove any trace of moisture to prevent potential hydrolytic degradation during the melt processing in the extruder. In general, the hydrolytic degradation reduces molecular weight of the biodegradable polymers which actually induces the decrease of mechanical properties. In addition, anti-oxidant (IRGANOX 1010, Ciba Specialty Chemical) of 0.3 parts per hundred of resin by weight (PHR) for each PLA/PBAT blend system was added. A laboratory-scale twin-screw extruder with a die length/die diameter (L/D) ratio of 40 was used to mix the PLA/PBAT/MWNT. The mixing temperature was varied from 160 °C to 190 °C and the screw speed was 250 rpm. Biodegradable polymer blend/MWNT nanocomposite was thus prepared with various compositions as shown in Table 1. Disk-shape of the sample was prepared using a hot press at 190 °C under 20 MPa pressure for 3 min.

Morphological and shear characterization

To investigate morphology of the polymer blend/MWNT nanocomposites, a scanning electron microscopy (SEM) was used. The prepared samples were fractured in liquid nitrogen for characterizing morphology via SEM (S-4300, Hitachi, Japan) which was operated at 10 kV accelerating voltage. TEM images were used to investigate the dispersion of MWNTs in the polymer blend matrix, in which a FE-TEM (JEM2100F/JEOL) images were obtained with a condition of acceleration voltage of 200 kV. Thermal gravimetric analysis (TGA) (STA 409 PC/NETZSCH) was carried out to examine thermal decomposition temperature. The sample was heated up to 800 °C under a nitrogen atmosphere at a heating rate of 10 °C/min. Rheological properties of the PLA/PBAT/MWNT nanocomposites were determined using a rotational rheometer (MCR300, Physica, Germany). Both steady and dynamic measurements were taken using a parallel-plate geometry (diameter: 25 mm) of 1 mm gap and at

Table 1 Compositions and sample code name of PLA/PBAT/MWNT nanocomposites

Sample code	PLA (wt%)	PBAT (wt%)	MWNT (wt%)	Anti-oxidant (PHR)
PL100PB0	100	0	2	0.3
PL90PB10	90	10	2	0.3
PL80PB20	80	20	2	0.3
PL70PB30	70	30	2	0.3
PL60PB40	60	40	2	0.3
PL50PB50	50	50	2	0.3
PL0PB100	0	100	2	0.3

a temperature of 170 °C. The steady shear test was performed as a function of shear rate in the range of 0.01–10 (1/s) while the angular frequency of the dynamic test was set from 0.5 to 100 (1/s) under a constant strain (0.1%). Prior to the dynamic measurements, an amplitude sweep test was carried out under a constant angular frequency of 10 (1/s) in order to find a linear viscoelastic region.

Results and discussion

Figure 1 shows morphology of the PLA/PBAT blend with various PBAT ratios at a fixed MWNT weight. Especially, Fig. 1a represents PLA/MWNT nanocomposites without any PBAT content, in which MWNTs were dispersed in the PLA phase but MWNT bundles were aggregated with each other and entangled due to a strong van der Waals interaction of the MWNT [21]. In addition, MWNT in Fig. 1a was well distributed in the PLA matrix but partially dispersed in the PBAT matrix as shown in Fig. 1b–d in which the continuous phase was PLA and the dispersed phase was PBAT. Figure 1b, c indicated that the PLA/PBAT blends were immiscible and MWNTs were dominantly dispersed in the PBAT rich phase. In addition, Fig. 1d

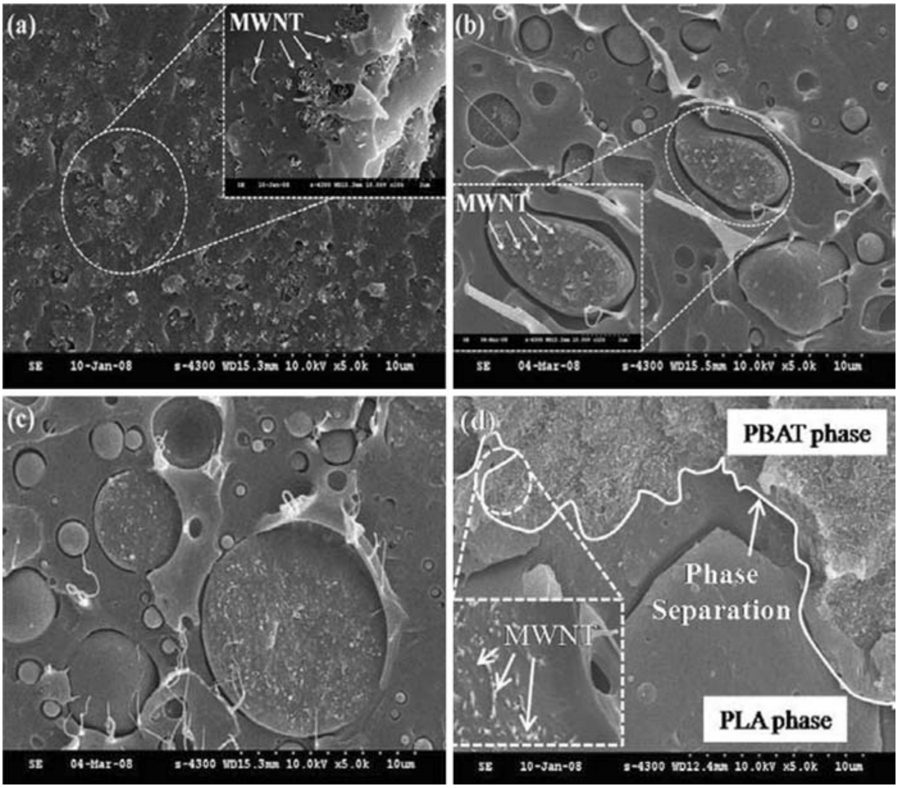

Fig. 1 SEM images of various PLA/PBAT compositions with a fixed MWNT ratio of 2 wt%: **a** PL100PB0, **b** PL80PB20, **c** PL60PB40, **d** PL50PB50

indicates distinctive phase separation in the two immiscible polymer blends and most MWNTs were found to be dispersed in PBAT phase rather than PLA phase which can be dispersed from the boundary region. Therefore it can be considered that in the immiscible polymer blend/MWNT nanocomposites, the MWNT possesses a preferential affinity into one phase and this phenomenon makes unique morphological properties of the nanocomposite system. Such a strong affinity of the MWNT to the PBAT phase might be related to chemical structure of the PBAT which possesses aromatic molecules in its main chain, as many groups reported that MWNT prefers aromatic molecules [22, 23].

TEM techniques are necessary to provide actual images of the MWNT for identifying physical properties of MWNT in the polymer blend matrix. Figure 2 clearly proved that MWNT prefers one phase affinity of their physical properties. Immiscible two polymers were being separated forming two different regions. MWNTs were dominantly dispersed in one phase, assuring that the MWNT possesses strong interaction with the PBAT phase rather than PLA phase. Since no direct chemical bonding between polymer and MWNT is reported, the interfacial interaction between polymers and MWNT [24] is dominantly being considered. In the immiscible blend system, carbon fillers are considered to control the interfacial tension between polymer and the carbon filler [25, 26]. Generally, MWNT prefers to be well dispersed in the polymer which has a lower interfacial tension. Therefore, we can predict that the PLA/MWNT interfacial tension is stronger than PBAT/MWNT interfacial tension. Besides, other characteristics, such as viscosity ratio of the blend compositions [26] and flexibility of the polymer chains [27] can also influence the dispersion of MWNT. Based on the results of Figs. 1 and 2, we can conclude that MWNT can be well dispersed in the PBAT matrix, in which serious aggregation of MWNT bundles was absent.

Figure 3 represents TGA data of the PLA/PBAT/MWNT nanocomposites which show two-step thermal degradation except PL100PB0 of PLA/PBAT/MWNT nanocomposites. This indicates that two different polymers in the blend are immiscible if we exclude the MWNT effect [28].

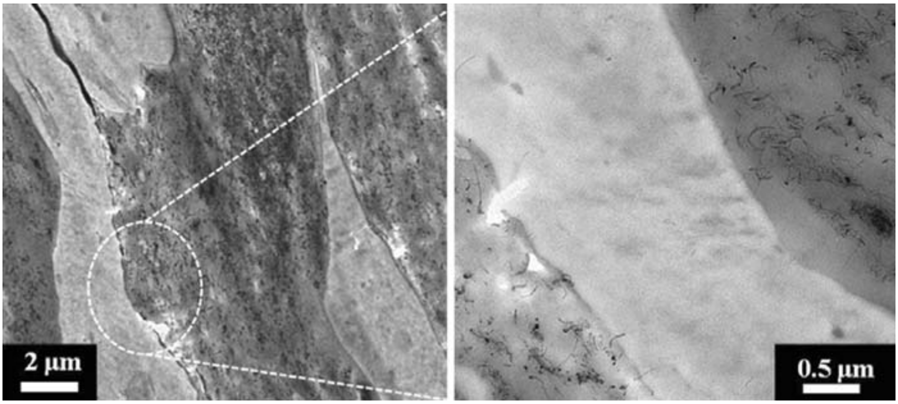

Fig. 2 TEM images of PL50PB50 nanocomposites (2 μm, 0.5 μm scales)

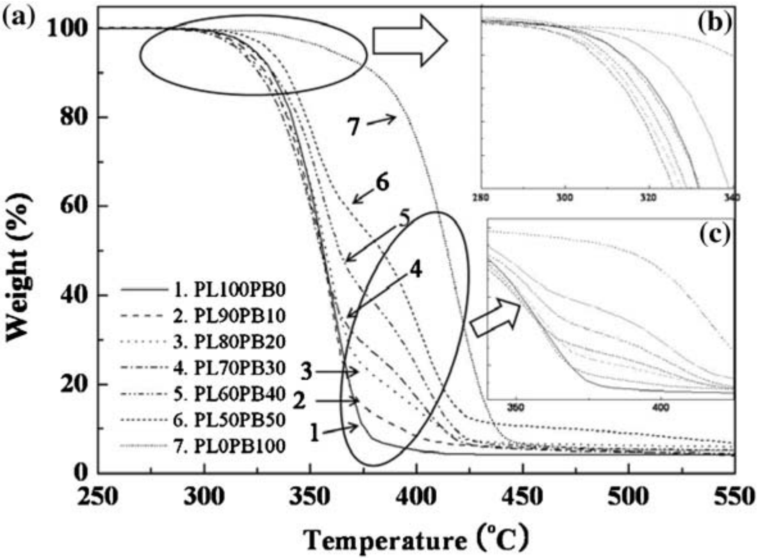

Fig. 3 TGA curves: **a** Temperature region from 250 °C to 550 °C, **b** Temperature region from 270 °C to 345 °C, **c** Temperature region 340 °C to 440 °C

Table 2 represents mass loss at two specific temperatures to analyze their thermal properties [29], in which we chose 325 °C and 380 °C because severe mass loss was observed at these temperature regions. This thermal degradation of the PLA/PBAT/MWNT nanocomposites started at around 325 °C. The PL70PB30 degraded first and PL50PB50 slowly degraded compared with other compositions. At this thermal degradation temperature, the PLA starts to degradation based on Fig. 3b graph and mass loss (325 °C) data of Table 2. The temperature at 380 °C revealed the second step degradation. This region is highly dependent on the PBAT matrix because the mass loss becomes higher with increasing the PBAT content. On the other hand, Fig. 3 also suggested that the MWNT has a good affinity to the PBAT region in the PLA/PBAT/MWNT nanocomposites, indicating that the MWNT was dominantly dispersed in the PBAT matrix. Therefore, the regions of MWNT were also increased with an increased PBAT content. As the MWNT region being increased, thermal properties of the PLA/PBAT/MWNT nanocomposites have been enhanced because the MWNT possesses good thermal properties. As a result, it can be concluded that the PBAT contents and the dispersed MWNTs regions in PBAT matrix mainly affect thermal properties of the nanocomposite.

Steady shear viscosity as a function of shear rate for the PLA/PBAT/MWNT nanocomposites is represented in Fig. 4, which shows their shear thinning behavior. It is well known that the presence of fillers in polymer melts not only increases their shear viscosity but also affects their shear rate dependency [30]. The extent of shear thinning behavior of PL50PB50 appears to be higher than that for other PLA/PBAT/MWNT nanocomposites. The extent of shear thinning for these nanocomposites having less than 50 wt% of PBAT is much less pronounced. However, as PBAT

Table 2 TGA data of mass loss at 325 °C and 380 °C

Sample code	Mass loss (%, 325 °C)	Mass loss (%, 380 °C)
PL100PB0	94.70	7.96
PL90PB10	92.92	13.65
PL80PB20	91.93	22.43
PL70PB30	91.01	27.79
PL60PB40	94.39	38.99
PL50PB50	97.22	52.91
PL0PB100	99.25	90.04

content is increased, the PBAT-MWNT region also increases. And the MWNT is expected to contribute to the high shear thinning behavior due to its alignment under external shear stresses. This is similar to fiber filled polymeric systems, in which the filler induces higher shear thinning behavior compared to the neat polymer [31]. Shear viscosity of the PL50PB50 became smaller than that of other compositions, when a shear rate of 0.9 (1/s) was reached.

Storage modulus (G′) of the PLA/PBAT/MWNT nanocomposites as a function of angular frequency is shown in Fig. 5. The PLA/PBAT/MWNT nanocomposites exhibit a cross-over point at an angular frequency of 6.5 (1/s). Three points of view [32] are presented here to interpret their demonstrated rheological properties. First, to compare the degree of dispersion, the MWNT of PL50PB50 was more dispersed in a broad region, thus the storage modulus is higher than other composition at a low angular frequency region. Second, regarding the filler structure of nanocomposites, MWNT bundles in PL100PB0 are highly aggregated but MWNT bundles in other compositions of the PLA/PBAT/MWNT nanocomposites are randomly presented.

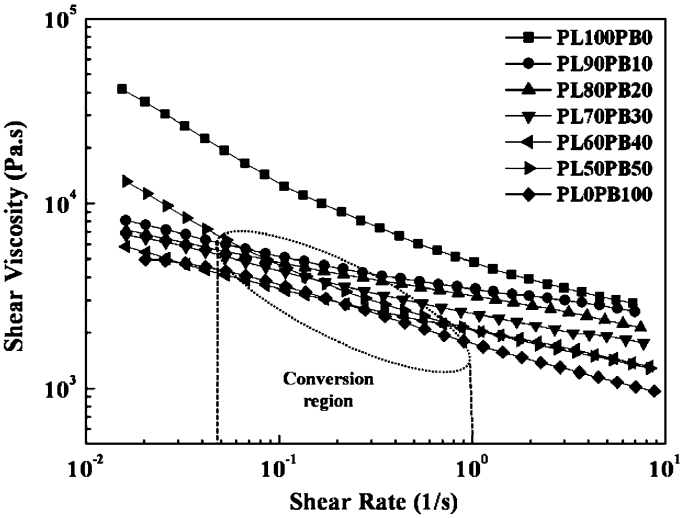

Fig. 4 Shear viscosity of PLA/PBAT/MWNT nanocomposites at 170 °C

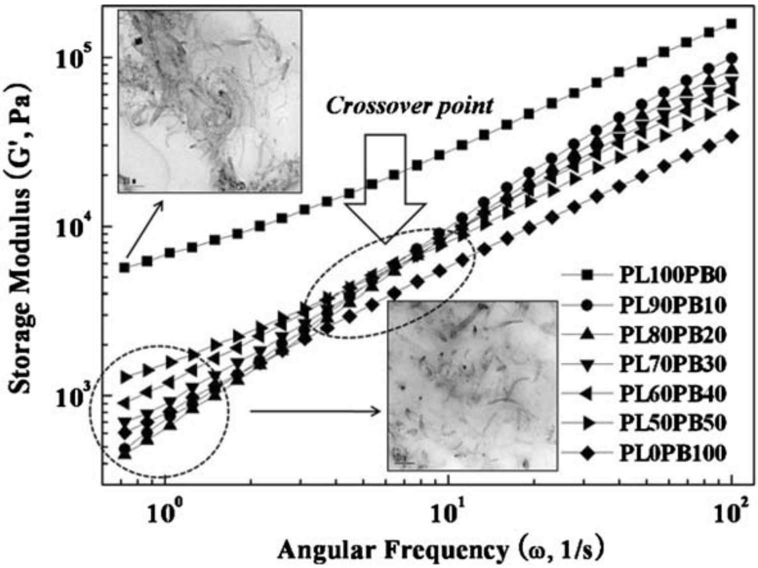

Fig. 5 Storage modulus (G′) of PLA/PBAT/MWNT nanocomposites at 170 °C

Highly aggregated MWNT has more elastic properties based on storage (G′) modulus below the crossover point. The last point of view is regarding the polymer–filler interactions. From Figs. 1 and 2, we assume that PBAT and MWNT have a better affinity, supporting the interaction between PBAT and MWNT. Thus, with increasing the content of PBAT, the storage modulus also increased.

Conclusion

Morphological, thermal, and rheological properties of one phase affinity of MWNT in the biodegradable PLA/PBAT blend system were investigated, in which the PLA/PBAT/MWNT nanocomposites were prepared for various compositions of PLA and PBAT with a fixed MWNT content. Experimental results showed that the PLA/PBAT blend is immiscible and MWNT has a good affinity to the PBAT phase due to an interfacial tension of polymer and MWNT. In addition, several factors such as viscosity of blend composition, flexibility of polymer chain and polymer chemical structure are found to be related to the selectively localized MWNT in the PBAT phase. The PLA/PBAT/MWNT nanocomposites showed two steps on TGA data, and the thermal properties of PLA/PBAT/MWNT nanocomposites increased with increased PBAT content. Network formation of MWNT in the PLA/PBAT matrix created unique shear thinning, elastic (G′) and viscous (G″) properties. These results indicated that filler–filler and polymer–filler interactions are important. Further study on the interaction between polymer and MWNT or the flexibility of polymer chain, can predict selective dispersion of MWNT in polymer matrix and their network formation in immiscible blend system, which induces the unique properties.

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