

Study of Carbon Black-Filled Poly(butylene succinate)/Polylactide Blend

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Received 18 August 2011; accepted 3 February 2012

DOI 10.1002/app.36944

Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: In this study, carbon black (CB) was used to control the conductivity and the compatibility of immiscible poly(butylene succinate)/polylactide (PBS/PLA) blend. It is shown that most of the CB particles are selectively dispersed in the matrix PBS phase because of the viscosity ratio of the blend components. The increasing viscosity of PBS phase prevents the coalescence of the dispersed PLA domain during the melt mixing. The domain sizes of PLA are refined when compared with that of blank PBS/PLA blend. The ternary composite shows an onset of the electrical conductivity at low filler loadings (1.5 wt %), which is attributed to a percolation of CB in

the insulating matrix polymer. Moreover, the composites exhibited remarkable improvement of rheological properties in the melt state when compared with that of blank PBS/PLA blend. According to the van Gurp-Palmen plot, the rheological percolation threshold for ternary systems is lower than 1.5 wt %. Furthermore, the ternary composites present improved mechanical properties and thermal stability even at very low loading levels of the CB. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: immiscible blends; biodegradable nanocomposites; conductive polymers; compatibilization

INTRODUCTION

Till date, polymer blends have received much attention because of their potential opportunities of combining the attractive features of each blend component and at the same time reducing their deficient characteristics. The performance of polymer blends is determined not only by the properties of the component polymers but also by the morphology formed.^{1–4} However, most of the polymer blends are immiscible because of high interfacial tension and poor adhesion, that is, simply mixing these polymer pairs cannot get practically useful materials. Therefore, the compatibilization is necessary for the immiscible polymer blends that can be obtained by introducing a third component named as compatibilizer into an immiscible blend. The function of a compatibilizer is to refine the droplet size of the dispersed minor phase, to stabilize it against coalescence during melt mixing, and to ensure strong interfacial adhesion between the phases. Additionally, the compatibilizer can also lower the interfacial tension, resulting in the suppression of coalescence in the dispersed phase.

A considerable number of research works have been published on introducing nanoscale fillers into

polymer blends.^{5–12} The addition of nanoscale fillers, such as organoclay, calcium carbonate, and silica particles, affects the dynamic phase behavior and the morphology of blends. The addition of carbon black (CB) to immiscible blends will increase the viscosity of the CB-localized phase, therefore slowing down coalescence and reducing the droplets size of dispersed phase. Similar effects were also reported for CB-filled immiscible blends such as polystyrene/polyethylene (PS/PE), acrylonitrile-butadiene-styrene/polyamide (ABS/PA6), and polypropylene/polystyrene (PP/PS).^{13–15} Moreover, the selective localization of CB in multiphase polymeric materials will also improve the conductivity at much lower filler contents for the more easily forming conductive network in the immiscible blends. The percolation in such blends is governed by the percolation of the CB-rich phase and the continuity of this phase in the blend. The selective localization of CB particles in multiphase polymeric materials provides a composite with lower filler loading. Sumita and coworkers¹⁶ have shown that for high density polyethylene/isotactic polypropylene (HDPE/iPP) blends, electrical conductivity can be observed at CB loadings of less than 1 phr. In addition to the improvement of conductivity, CB can also improve the modulus and strength of the composites as the reinforced filler.

In this study, CB is not only used as compatibilizer but also as conductive additive for the immiscible poly(butylene succinate)/polylactide (PBS/PLA)

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blend. PLA has excellent mechanical properties and good biocompatibility, but shows brittleness and difficulty in processability. On the contrary, PBS has high flexibility and excellent impact strength. Immiscible PBS/PLA blend becomes an interesting biomaterial and can be potentially useful as a packaging material because of their potential applications in the fields related to environmental protection and the maintenance of physical health.¹⁷ Various CB loadings were added to immiscible blend of PBS/PLA. Generally, viscosity ratio of the blend components is one of the main influencing factors for phase inversion. Filling of immiscible polymer blend with CB nanoparticles leads to an evident change of viscosity ratio because of its selective localization. As a result, the addition of CB nanoparticles into immiscible polymer blend has been found effective in extending phase co-continuity over a much larger composition range. Moreover, the percolation threshold of such blends is governed by the percolation of the CB-rich phase and the continuity of this phase in the blend. Thus, the weight ratio of PBS and PLA was fixed in the proportion of 60/40. It can be expected that the PLA phase appears to form elongated or fibrous structure more easily than PBS because of its high viscosity. Moreover, the percolation threshold will be attained at much lower filler contents if the conductive network is more easily formed in the immiscible blends. Adding CB nanoparticles into immiscible polymer blends has been found effective in extending phase co-continuity especially when the content of the minor component increases to a critical value. The distribution of CB particles and the immiscible morphology of the blend matrix were systematically investigated. The new ternary system of PBS/PLA/CB has been investigated, and a lower percolation load of CB was achieved. The aim of this work was to investigate the effects of preferential localization of CB on the morphology and compatibilization of the immiscible blends of PBS/PLA. Furthermore, the percolation of CB is described by measurements of the electrical conductivity and is compared with the results derived from rheological experiments. In addition, substantially improved mechanical properties and thermal stability of PBS/PLA/CB composites were also achieved.

EXPERIMENTAL

Materials and sample preparation

PBS (Bionolle#1010) was purchased from Showa Highpolymer, Japan. Its melt index (MI) is about 25 g/10 min (190°C/2.16 kg; ASTM D-1238). The weight-average molecular weight is 9.02×10^4 and a polydispersity of 1.88 (GPC analysis). PLA (2002D) is also a commercial product of Nature Works (USA),

which exhibits a weight-average molecular weight of 1.30×10^5 and a polydispersity of 1.83 (GPC analysis). Its MI is about 8 g/10 min (190°C/2.16 kg; ASTM D-1238). Conductive CB was purchased from Huaguang Chemical Plant, People's Republic of China. The particle diameter and surface area of the particle are 40 nm and 1000 m²/g, respectively.

All of the materials were dried in a vacuum oven at 50°C for at least 12 h before processing. Various CB loadings were added to immiscible blend of PBS/PLA, with weight ratio of PBS and PLA fixed in the proportion of 60/40. The PBS/PLA/CB ternary composites (PBS/PLA_x, where *x* denotes the weight of the CB per hundreds weight of the blend resin) with various CB loadings of 1.0, 1.5, and 2.0 wt % were prepared from direct melting process. Dried pellets of PLA and PBS were mixed with CB in a melt mixer (Rheomix 600p; Haake, Germany) at a fixed temperature of 180°C and a rotation speed of 60 rpm for 6 min. The sheet specimens for measurements were hot pressed at 190°C and 5 MPa with a thickness of about 1 mm, followed by quenching to room temperature. The binary PLA/CB nanocomposite with 1.5 wt % of CB and the binary PBS/CB nanocomposite with 1.5 wt % of CB were also prepared under the same processing conditions for the properties comparison.

Characterization

The dispersion of CB particles was observed using a transmission electron microscope (TEM) (JEOL JEM-1011, Japan). The nanocomposite specimen for TEM observations was about 50–70 nm in thickness, which was prepared by ultramicrotoming under cryogenic conditions using a Leica ultramicrotome (Ultracut R with FCS). The morphology of the blends was observed by field-emission scanning electron microscopy (XL30 ESEM FEG; FEI) at an accelerating voltage of 15 kV. The sample was broken into pieces in liquid nitrogen and coated with gold before examination.

Dynamic mechanical analysis (DMA) was carried out with a DMA/SDTA861e apparatus (Mettler-Toledo, Switzerland) in the tensile mode. All tests were conducted at a frequency of 1 Hz and a heating rate of 3°C/min as a function of temperature from –55 to 90°C. The volume resistance of sheet samples was measured by ZC36 high-resistance meter (Shanghai Precision and Scientific Company, People's Republic of China) at room temperature.

Rheological measurements were carried out on a rheometer (TA Series AR2000; TA Instrument, USA) using a parallel-plate geometry with 25-mm-diameter plates. The dynamic strain sweep was first carried out to determine a common linear region up to 100% strain at 10 rad/s. Then, the dynamic frequency sweep was carried out over a frequency range of 0.1–100 rad/s at a strain of 1.25%.

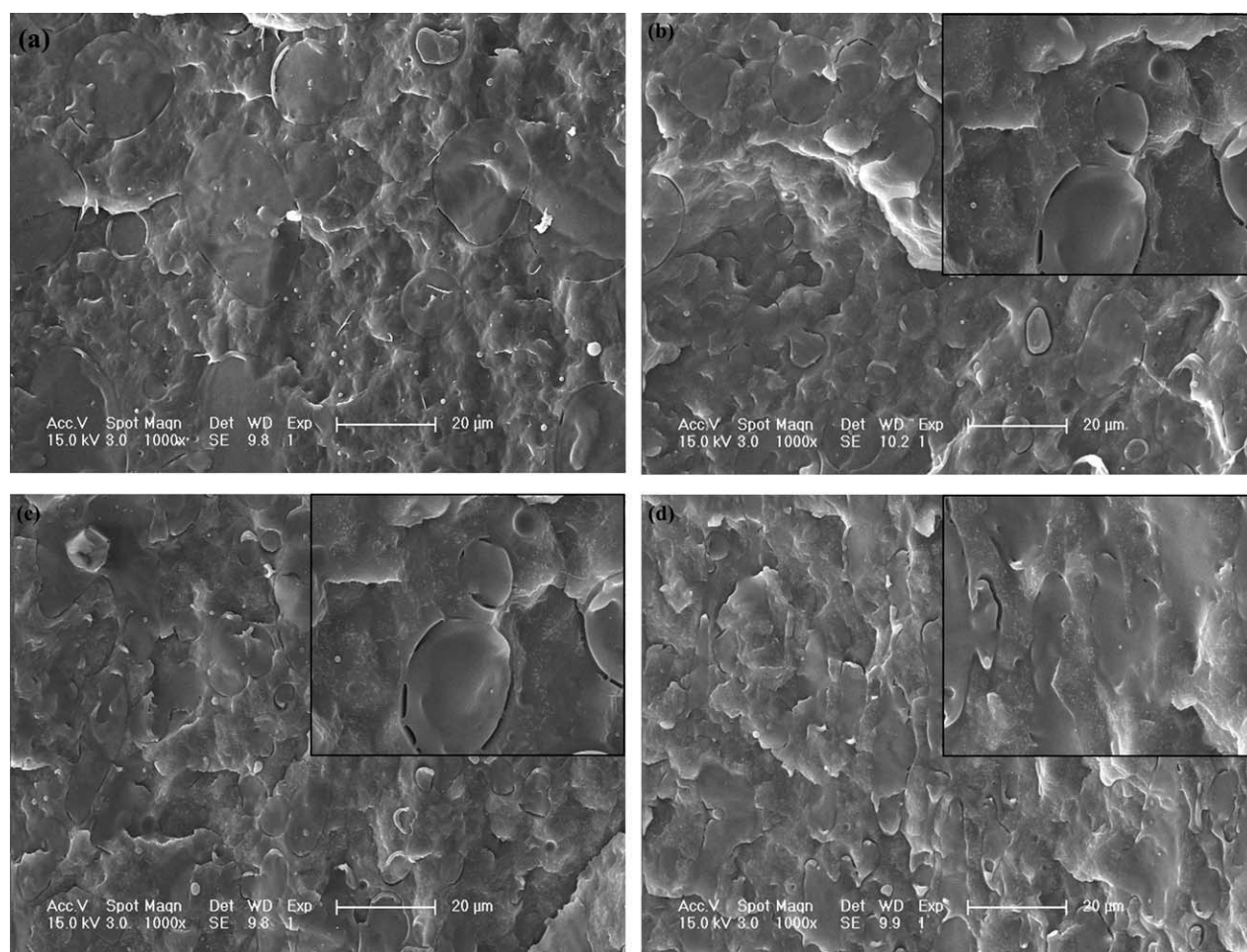


Figure 1 SEM images of the fractured (a) blank PBS/PLA sample and (b–d) PBS/PLA samples with various CB loadings of 1.0, 1.5, and 2.0 wt %.

The mechanical properties of the blends were measured using Instron 1121 tensile testing machine (Canton, MA) at a rate of 5 mm/min at room temperature. Oar-shaped specimens with 20-mm gauge length and 4.0 mm width were used for this test. All tests were carried out at room temperature. At least five samples of each type were drawn to fracture.

The thermal properties of the blends were investigated by differential scanning calorimetry (DSC; TA Instrument Q20, USA). All samples were heated to 175°C and kept isothermal for 2 min to erase previous thermal history. Then they were cooled to –50°C and subsequently scanned between –50 and 175°C at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA7 thermal analyzer (Wellesley, MA) from 25 to 600°C at a heating rate of 10°C/min in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Morphology

It is well known that the dispersion of CB in the polymer blend is the key factor influencing the

physical properties of the polymer blend. To reveal the distribution of CB, the surface of PBS/PLA/CB nanocomposites fractured in liquid nitrogen were examined by SEM. SEM micrographs depicted in Figure 1(a–d) shows the influence of CB addition on the morphology of PBS/PLA composites. Clearly, PBS/PLA blank sample shows typical two-phase structure, in which the discrete PLA domains are dispersed in the PBS matrix. On the amplified images in Figure 1(b–d), it is clearly seen that the CB particles are uniformly dispersed in the continuous PBS phase. The selective location of CB particles results in a refined domain size of dispersed PLA phase when compared with that of blank PBS/PLA blend. To further evaluate the effect of preferential localization of CB on the morphology, the specimen of the composite containing 1.5 wt % of CB was examined by TEM. Figure 2 shows TEM micrographs of a composite containing 1.5 wt % of CB particles. The typical two-phase structure can also be seen in Figure 2(a), in which the light and dark gray parts correspond to dispersed PLA and matrix PBS phase, respectively. On the amplified images of the

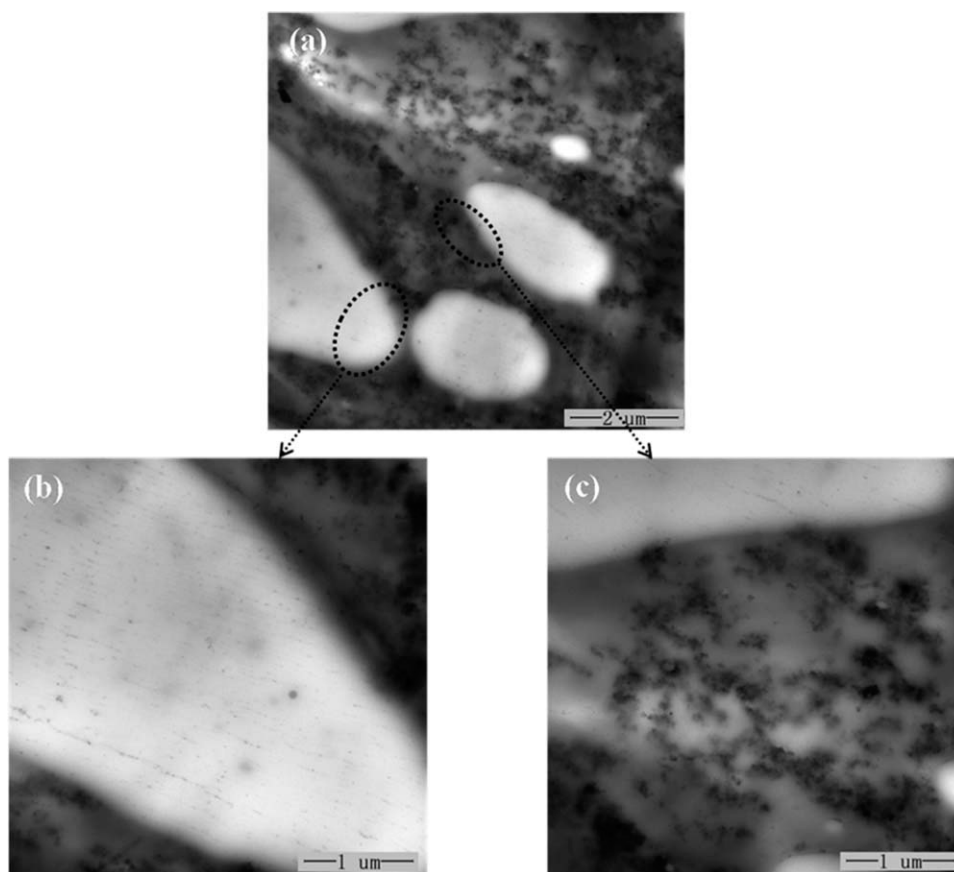


Figure 2 TEM images for the sample of PBS/PLA1.5. The parts indicated (a) are amplified and shown in (b) and (c).

parts marked in Figure 2(b,c), it is seen clearly that the CB is mainly dispersed in PBS phase, whereas small amount is located in PLA phase.

The effect of CB on the morphology and the compatibilization of the ternary blends should originate from the selective localization of CB in the PBS matrix. Thus, it is interesting to explore the mechanism of the morphological change with the addition of CB. The selective localization of CB in this work is attributed to the viscosity ratio of the blend components and the flexibility of the polymer chains. As shown in Figure 3, at the given temperature (180°C), the viscosity of PBS is much lower than that of PLA (PLA/PBS \approx 20), and therefore, the PBS chains can diffuse around and into CB aggregates more easily when compared with that of the PLA at the initial stage of melt mixing. As a result, CB prefers to be dispersed in the lower viscous PBS continuous phase rather than the discrete PLA phase. This selective localization not only changes the viscosity ratio of the two components but also prevents the coalescence of the dispersed PLA domains during the melt mixing, improving compatibility between two phases kinetically. Moreover, for the ternary systems in this work, CB particles are selectively localized in the matrix PBS, which has lower glass transition temperature (T_g) and viscosity when compared with

that of PLA. Both T_g and viscosity are generally related to a higher flexibility of chains and, thus, a low entropic loss for adsorption on the CB surface. As a result, it suggests that the entropy penalty may also play a decisive role in competitive adsorption of polymers on the surfaces of nanofillers. The preferential location of CB particles has also been observed on some ternary systems. In these cases, the viscosity ratio, the interfacial tension, and the chemical

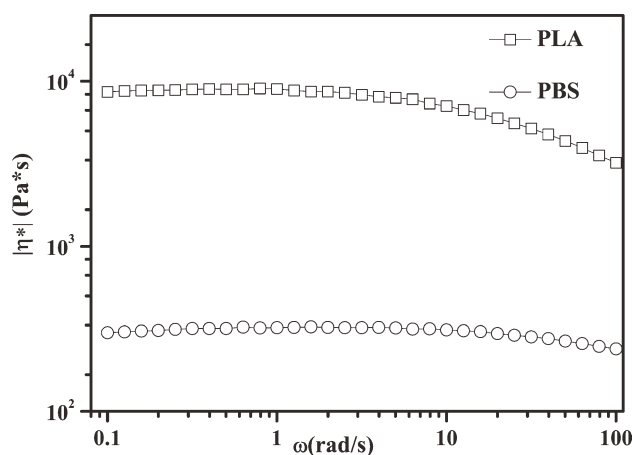


Figure 3 The complex viscosity ($|\eta^*|$) of neat PLA and neat PBS as a function of frequency.

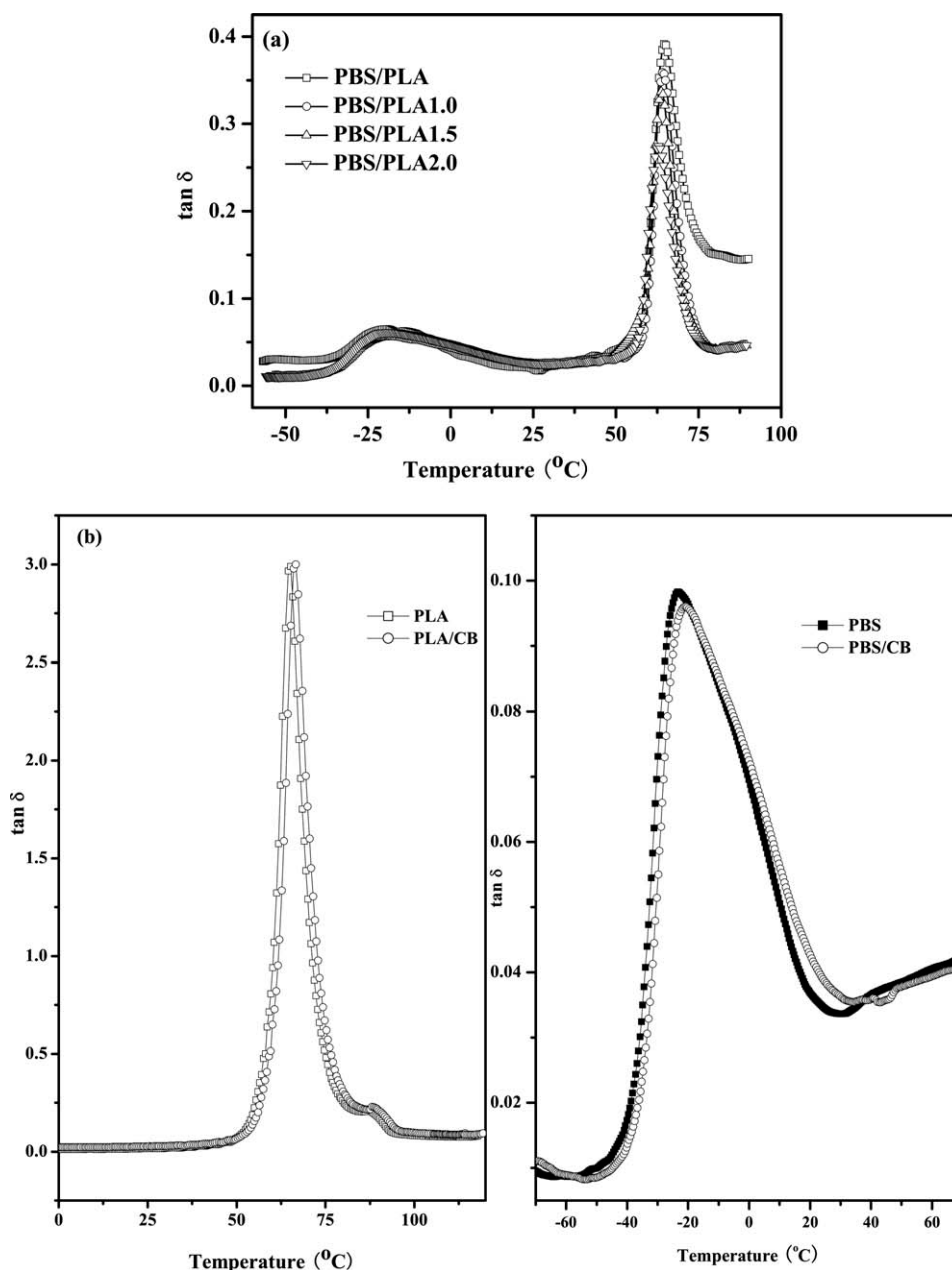


Figure 4 DMA thermogram for the samples with various CB loadings.

affinity are the key factors determining the location.^{13,14,18} Overall, the compatible effect of CB is good, indicating that kinetically driven compatibility is dominant in the melting process. The increasing viscosity of PBS matrix of the ternary systems, due to the preferential localization of CB, will slow down the kinetic conditions of phase separation and then improve the stability of the polymer morphology. With rapid reduction in the viscosity ratio between PBS and PLA polymers, the higher viscous PLA phase can be broken into smaller droplets more easily. However, when the content of CB particles increases to a point, the breakup of PLA phase may be inhibited or even suppressed that a co-continuous

structure is attained because of the existence of elongated and interconnected domains of PLA phase. The final morphology of the ternary composites is a result of the dynamic processes of breakup of large droplets and coalescence of the small ones during mixing.¹⁹ To further evaluate the compatible effect of CB on the PBS/PLA blend system, the dynamic thermal mechanical analysis was performed. Figure 4(a) shows the DMA curves for blank PBS/PLA and the ternary systems. Figure 4(b) shows the DMA curves for neat polymer and the binary systems. The T_g of PLA and PBS obtained from the curves are listed in Table I. It is seen that with the increase of CB loadings, T_g of the two-component polymers

TABLE I
 T_g s of Binary Blends and PBS/PLA/CBx Ternary Nanocomposites

Sample	T_{g-PLA} (°C)	T_{g-PBS} (°C)
PLA	65.14	
PLA/CB	66.64	
PBS		-23.22
PBS/CB		-21.09
PBS/PLA	64.53	-21.80
PBS/PLA1.0	64.10	-19.87
PBS/PLA1.5	63.67	-18.92
PBS/PLA2.0	62.93	-18.45

shift to each other gradually. This indicates that emulsification occurs at the phase interface in the presence of CB, leading to interface stabilization thermodynamically. However, in the ternary blend, both PBS and PLA still present evident glass transition behavior, and the shift degree of the two T_g is not notable, suggesting that thermodynamically driven compatibility by CB is not very remarkable.

Furthermore, the selective dispersion of the CB in the ternary systems, as displayed in the SEM micrographs, may reduce the conductive percolation threshold and enhance the composite conductivity. It suggests that the conductive network forms more easily in PBS matrix because of the selective localization of CB in the immiscible PBS/PLA blend. Conductive and rheological evidence for this phenomenon is given.

Conductivity and rheology

It is well known that nonlinear electrical properties of the polymeric composites filled with CB shows percolation behavior.^{3,18} Owing to the selective localization of the CB, polymer blending is one of the most promising methods to reduce the percolation

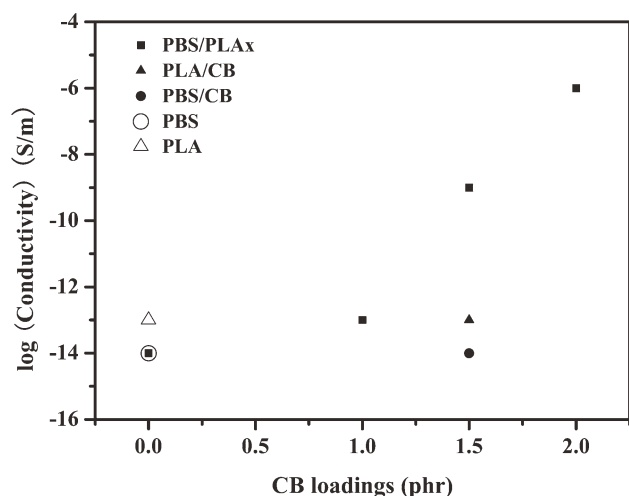


Figure 5 Plots of electrical conductivity versus weight fraction of the CB loadings.

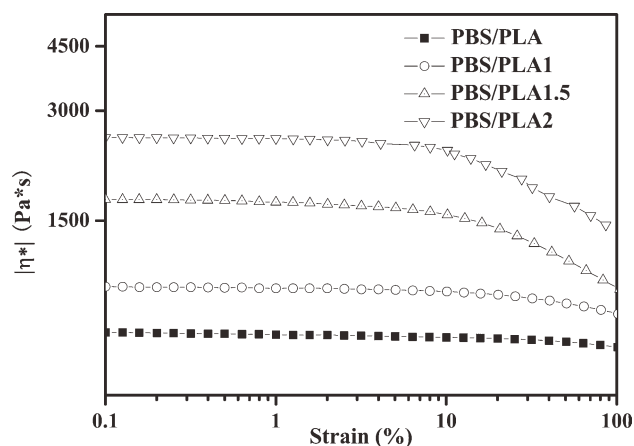


Figure 6 Evaluation of the linear viscoelastic response of blank PBS/PLA blend and the ternary composites.

threshold and to enhance the composite conductivity at low CB loading.¹⁸ It can be expected that the ternary systems may show lower conductive percolation threshold than that of the binary ones. Figure 5 shows the electrical conductivity as a function of CB content for the ternary composites. At identical CB loading of 1.5 wt %, the conductivity of the ternary composites is far higher than that of the CB-filled binary ones by 4–5 orders of magnitude. This indicates that the selective localization of CB particles makes the conductive network form more easily, even at relative lower loading levels. Thus, the ternary composites present higher conductivity and lower conductive percolation threshold than that of the binary ones.

Rheological experiment is a sensitive tool to investigate the percolation of filler in a viscoelastic fluid. To further explore the influence of CB on the melt rheological of the composites, preliminary studies were conducted on pure PBS/PLA blend and their composites to ensure that the dynamic properties were measured in the linear viscoelastic region. We focus on the storage modulus, as it is the most sensitive rheological function to the changes in the mesoscopic structure of the hybrids. It can be observed in Figure 6 that the limit of linearity of viscoelastic region tended toward low-strain amplitudes (%) with increasing content of CB. In quiescent state, with increasing CB loading, the filler–filler interaction becomes increasingly important and in fact dominates the long-time viscoelasticity of the nanocomposites. Additionally, because of the increasing filler–filler interaction, the filler agglomerates can be altered by flow more easily. Based on the above fact, it is not surprising that the expected strain-softening behavior is observed with the critical strain amplitude for the transition decreasing with increasing CB loading. Furthermore, the strain amplitude dependence of the storage modulus in the strain-softening regime increases with increasing CB loading.

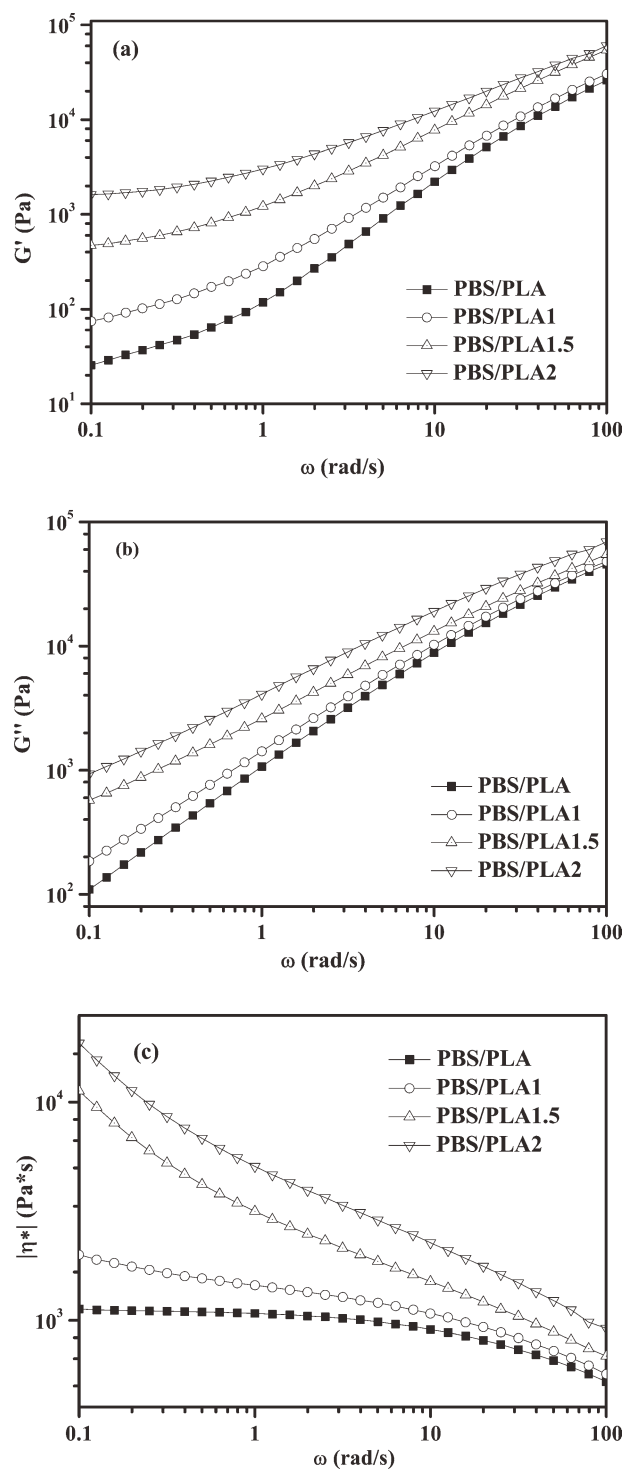


Figure 7 Plots of (a) dynamic storage modulus (G'), (b) loss modulus (G''), and (c) complex viscosity ($|\eta^*|$) versus frequency.

The subsequent dynamic frequency sweep tests were conducted at strain amplitudes within the linear viscoelastic region. The dynamic storage modulus (G') and loss modulus (G'') obtained from the dynamic frequency sweep are shown in Figure 7(a,b). The moduli of the composites increase with increasing CB concentration. At high frequencies, the quali-

tative behaviors of G' and G'' are essentially similar and not affected by the existence of CB particles. However, at low frequencies, G' and G'' increase monotonically with increasing CB loadings. As CB loadings increase up to 1.5 wt %, the slopes of the modulus curves of the composites change significantly. The dynamic storage modulus (G') is nearly independent of frequency, indicating that CB forms a pseudo-solid-like network in the matrix. Meanwhile, the frequency dependence of G'' also shows the same tendency as G' . Complex viscosities $|\eta^*|$ of PBS/PLA ternary systems are shown in Figure 6(c). It is clearly seen that the existence of CB has a dramatic effect on the complex viscosity of the composites. With CB loadings increasing up to 1.5 wt %, the viscosity curve of the ternary composite shows non-Newtonian shear thinning behavior, and no plateau regions is observed over the full frequency range. However, blank PBS/PLA blend shows the Newtonian plateaus at low frequencies. Under near-quiescent condition, the presence of pseudo-solid-like behavior is observed, which is indicative of a percolated filler network and strong filler–filler interaction. Evidently, the complex viscosity increases mainly at low frequency where the relaxation is due to the particle–particle interactions inside the percolation network of CB. Overall, both complex viscosity and storage moduli demonstrate gradual change from the liquid-like behavior to pseudo-solid-like behavior with the increasing concentration of CB.

In Figure 8, the phase angle δ is plotted versus the absolute value of the complex modulus ($|G^*|$) for the ternary composites. In the literature, this plot is known as the van Gorp-Palmen plot, which is usually used to detect the rheological percolation of the filled polymeric composites.¹² The low-frequency δ of the blank PBS/PLA and the PBS/PLA1.0 samples are

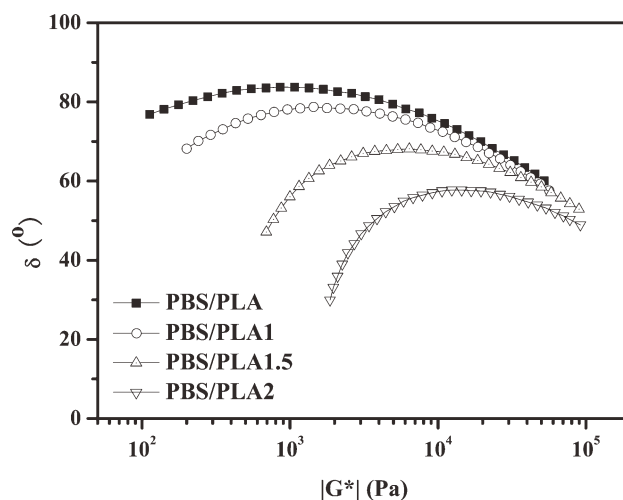


Figure 8 van Gorp-Palmen plots of phase angle (δ) versus complex modulus ($|G^*|$) of the samples with various CB loadings.

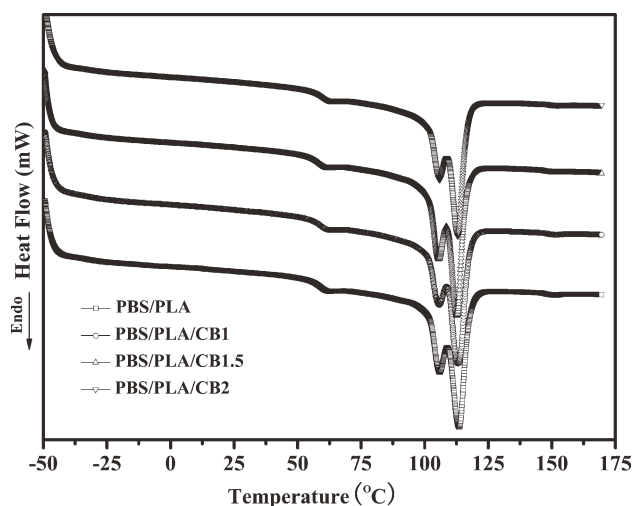


Figure 9 Thermal properties of the ternary blends.

close to 80° , which is indicative of a flow behavior presented by the viscoelastic fluid. In contrast, the ternary systems with high CB contents resemble the behavior of an elastic solid with a corresponding equilibrium modulus, which can be determined by extrapolating the curves to a phase angle of $\delta = 0^\circ$. The phenomenon of percolating filler in a viscoelastic fluid is rheologically equivalent to a fluid–solid transition. We can estimate the filler concentration at which a gel-like behavior is observed. It is in the range between 1.0 and 1.5 wt %. As the CB loadings increase to 1.5 wt %, the low-frequency δ decreases remarkably to lower than 45° , indicating a rheological fluid–solid transition in that ternary system. Accordingly, the rheological percolation threshold for ternary systems is lower than 1.5 wt %. This is due to the selective localization of CB consequentially. The self-assembly-like behavior of CB can enhance the particle–particle interactions more effectively in the ternary systems, promoting the formation of percolated CB network structure even at lower CB concentration. As a result, the PBS/PLA x ternary systems present very low percolation threshold.

Mechanical and thermal properties

The above results show that the performance of the ternary composites highly depends on the phase

TABLE II
Thermal Properties of Ternary Nanocomposites

Sample	$T_{m\text{-PBS}}$ ($^\circ\text{C}$)		$\Delta H_{m\text{-PBS}}$ (J/g)
	T_{m1}	T_{m2}	
PBS/PLA	105.77	113.03	47.57
PBS/PLA1	105.68	113.08	47.83
PBS/PLA1.5	105.46	112.80	47.57
PBS/PLA2	105.75	113.16	45.46

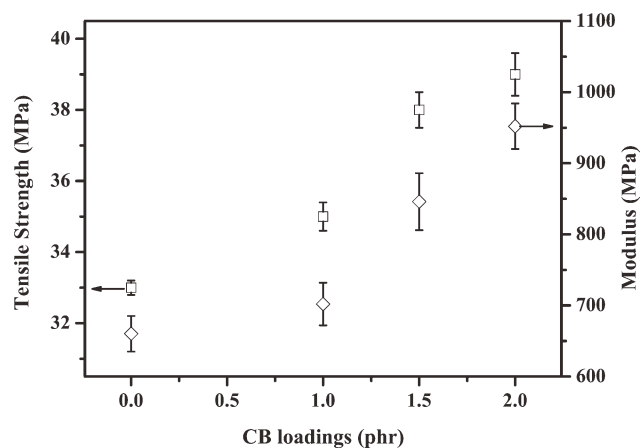


Figure 10 Tensile strength and modulus of the blend with different weight fractions of the CB loadings.

morphology of the blend matrix and the dispersion state of CB particles. As CB can also improve the modulus and strength of composites as reinforce filler, the enhancement in the mechanical properties is, therefore, foreseeable on those ternary composites owing to the unique localization of CB and the improvement of phase structure when compared with that of the blank PBS/PLA blend. Moreover, the variation of crystallinity of the PBS/PLA blend due to the presence of CB is also an important factor to change the mechanical properties of the matrix. Therefore, the thermal properties of the PBS/PLA x nanocomposites were analyzed by DSC as seen in Figure 9, and the data are listed in Table II. As shown in Figure 9, the very similar melting peaks and ΔH_m values for each sample (Table II) indicate that the addition of CB had little effect on crystallinity of the ternary composites when compared with that of blank PBS/PLA. The reinforcing effect is almost increased by adding CB particles. Small addition of CB particles, as expected, enhances the mechanical properties of the blend materials remarkably, and the strength of ternary composites increases monotonically with the increase of the CB loadings within experimental loading ranges, as seen in Figure 10. With increasing loading levels, those well-dispersed CB selectively in the matrix PBS phase and the dual-continuous morphology begin to play important role in bearing an extra load. As a result, the tensile yield strength of the

TABLE III
Thermal Decomposition Temperature (T_d s) of the Ternary Systems

Sample	T_{onset} ($^\circ\text{C}$)	$T_{\text{peak-PBS}}$ ($^\circ\text{C}$)	$T_{\text{peak-PLA}}$ ($^\circ\text{C}$)
PBS/PLA	322	341	389
PBS/PLA1.0	324	353	390
PBS/PLA1.5	330	357	393
PBS/PLA2.0	335	359	395

ternary composites further increases. Moreover, all investigated samples show an increased modulus with increasing filler content. This also confirms that the selective localization of CB and the resulting morphology of the ternary composites can bring reinforcing effect to an immiscible blend system.

CB is also a material with excellent thermal stability, which can always be used to improve the thermal properties in the field of composites. Table III shows the thermal decomposition temperature (T_d) of the ternary systems, indicating that the addition of CB increased T_d for the ternary composites. This is because the presence of CB retards organic combustion and acts as a gas barrier that prevents the permeation of volatile gas out of the ternary composites during the thermal decomposition. The T_d enhancement of the ternary systems was remarkable, and with the addition of 2 wt % of CB, the T_d was increased as much as 12°C.

CONCLUSION

The ternary composites with various CB loadings were prepared by direct melt mixing. The selective location of CB particles, resulting from the viscosity ratio, not only increases the viscosity of PBS matrix but also refines the domain size of dispersed PLA phase of the ternary blends. As the CB loading increases to 1.5 wt %, the conductivity of the ternary composites is far higher than that of the CB-filled binary composites. Moreover, the composites exhibited remarkable improvement of rheological properties in the melt state when compared with that of blank PBS/PLA blend. The transition from the liquid-like to the solid-like viscoelastic behaviors at low frequencies demonstrates that the long-range polymer chains motion is restrained by the CB network.

According to the van Gurp-Palmen plot, the rheological percolation threshold for ternary systems is lower than 1.5 wt %. Furthermore, the addition of CB causes significant increase in stiffness and thermal stability of the immiscible PBS/PLA blend. Overall, the ternary systems containing CB particles hence present high improvement of the performance in terms of rheological, conductive, and mechanical properties.

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