Deep insight into the key role of carbon black self-networking in the formation of co-continuous-like morphology in polylactide/poly(ether)urethane blends

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ABSTRACT

Polymer blending has been intensively investigated in recent decades because it is a simple way to achieve high-performance polymeric materials. It has been demonstrated that the properties of polymer blends are largely determined by its phase morphology. Recently, a change of sea-island morphology to a unique co-continuous-like structure was observed by adding a small amount of filler particles with self-networking capability in polymer blends. The formation of co-continuous-like structure can impart polymer blends with a good stiffness-toughness balance. However, the underlying mechanism for the formation and evolution of this structure is still not clear. In this work, three types of carbon black (CB) with different self-networking capabilities was used to tailor the phase morphology of polylactide (PLA)/poly(ether)urethane (PU) blend with fixed ratio (85/15 wt/wt). It was found that adding CB with high self-networking capability could lead to an easier formation of co-continuous-like structure compared with those with low self-networking capability, as confirmed by SEM observations. The CB induced co-continuous-like structure was further investigated by rheology time sweep tests. It was found that the formation process and stability of co-continuous-like structure is not only dependent on CB content and CB self-networking capability, but also on sweep temperature and frequency. This work gives a deep insight into the key role of the self-networking capability of fillers in controlling the phase morphology of immiscible polymer blends which can provide guidance for preparing high-performance polymeric materials.

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1. Introduction

Blending various polymers to develop new materials with desirable performance has been extensively investigated in recent decades [1–5]. Due to the immiscibility of most polymer pairs, polymer blends usually show heterogeneous structure and their performance mainly depends on the properties of the component polymers, the interfacial properties and more importantly, the phase morphology [6,7]. Two types of phase morphology, i.e., sea-island structure (one phase is dispersed as isolated droplets, rods or platelets in the matrix) and co-continuous structure (two phase interpenetrates each other in the form of network structure), are generally achieved in a binary polymer blend. Compared with sea-

island structure, the co-continuous one has gained more attention because it can better combine the performance of both components and the synergistic effects of different components may be achieved [8,9]. It has been reported that the co-continuous structure can promote the improvement of Young's modulus [10,11], impact toughness [12,13], shape memory properties [14,15] and even the electric conductivity if the continuous phase is filled by conductive fillers [16,17]. Hence, the key issue is how to control and achieve a co-continuous structure during processing. Generally, the co-continuous structure can be obtained within a composition region, i.e., phase inversion composition. According to the classical Paul−Barlow theory [18], the phase inversion condition for a binary polymer blend is shown as:

$$\phi_1/\phi_2 = \eta_1/\eta_2 \tag{1}$$

where ϕ_i and η_i is the volume fraction and melt viscosity of component i, respectively. That is to say that the increase in volume

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fraction or the decrease in melts viscosity of dispersed phase would increase its continuity in the matrix, thus forming a co-continuous structure. Besides, the stability of co-continuous structure is of significance in maintaining the properties during further shaping or using. When annealing a polymer blend with co-continuous structure in the molten state, structural coalescence and morphological change to sea-island structure will occur due to the requirement of minimizing the interfacial free energy [19], which leads to a deterioration in properties. It was found that low interfacial intension [20] and high viscosities of fillers-filled phase [19,21] can suppress the kinetics of this change and stabilize the obtained co-continuous structure.

Very interestingly, a morphological change from sea-island structure to co-continuous one was observed by adding small amounts of nanofillers, such as silica dioxide (SiO_2) [22,23], carbon black (CB) [24,25], clay [26,27], into polymer blends. This method was mainly applied in elastomer-toughen polymer blends [22,23]. First, the incorporation of rigid nanofillers can compensate the modulus and strength decrease induced by adding flexible elastomer. Second, the co-continuous structure can be formed even at low content of elastomer, which can largely improve the impact toughness of the blends. Third, the electric conductivity of the blends can be dramatically enhanced through the electric double percolation if a conductive filler is employed [24,25]. When adding the nanoparticles into a polymer blend, they are usually located in one of the two polymer phases due to the different affinity of the nanoparticles to each phase [28,29]. As for the situation that nanoparticles are dispersed in the matrix phase, the selective localization of nanoparticles in matrix phase usually lead a slight increase in the volume fraction but a large improvement in the melt viscosity of the matrix phase. The changed viscosity ratio between matrix and minor phase will lead to the formation of co-continuous structure based on Equation (1) [30]. However, the formation of co-continuous structure has also been observed when the fillers are selectively located in the minor phase where Paul—Barlow theory cannot explain. Some researchers proposed that the co-continuous structure can be kinetically trapped by the largely improved viscosity of minor phase during the coalescence process [31,32]. The filler-induced increase in viscosity of minor phase can significantly slow down the phase separation of the blend, thus arresting and obtaining the metastable phase morphology. Others argued that the co-continuous structure can be stabilized by the dramatically enhanced elasticity of minor phase [33,34]. The filler-induced increase in elasticity of minor phase can largely slow down the relaxation process and stabilize the elongated minor phase which connects with each other during melt blending finally leading to a co-continuous structure. It is accepted that the fillers are mobile and can self-assemble into different patterns (e.g. three-dimensional (3-D) networks (CB [35,36], SiO_2, clay) or separate clusters (TiO_2)) in polymer melts. Based on this observation, Wu et al. [37,38] first associated the self-assemble behavior of fillers with the morphological change of polymer blends and proposed that the self-assembly of fillers can direct the morphology evolution of immiscible polymer blends. In order to verify this viewpoint, the morphology evolution of annealing filler-filled polymer blend was examined by optical microscopy (OM) in real-time and evaluated by dynamic mechanical analysis (DMA). The morphology would be changed from sea-island to co-continuous structure if filler with the ability of self-assemble into 3-D network is employed. They attributed the thermodynamic unfavorable phenomenon to the self-networking effect of fillers. Filler with self-networking ability tends to form a continuous network in the polymer melts and lead the droplets of the minor phase fuse together into co-continuous structure.

In our recent works [39,40], a unique co-continuous-like structure (composed of discontinuous irregular PU domains) was first obtained by adding small contents of nanoparticles with strong self-working capability (e.g. SiO_2 or CB) into a polylactide(PLA)/poly(ether)urethane (PU) (85/15 by weight) blend with the sea-island structure. The formation of this special structure gives a great rise to the mechanical and electrical properties of PLA/PU blend. These results provide a new mean to obtain polymer/elastomer/fillers nanocomposites with a good stiffness-toughness balance and even an excellent electrical properties. It should be noted that the size of minor phase in 85PLA/15PU blend is only sub-even nano-scale which make it not suitable to be observed by optical microscopy. Thus the structure formation mechanism and the role of self-working of fillers in determining phase morphology are still not clear. Furthermore, the stability of co-continuous-like structure which is vital to the application of polymer blends with such structure has not been discussed before. In present work, we aim at to elucidate the formation reason and the stability of co-continuous-like structure of PLA/PU blends, focusing on the effect of fillers self-networking, by adding three CB with different self-networking capability, using rheological characterization. The rheology is adopted in this work as the following reasons. First, rheology is extremely sensitive to the phase morphology and its change of polymer blends without concerning whether the sample is optically transparent or not [41,42]. Second, rheology is a powerful tool in studying the formation and evolution of fillers network structure in polymer melts [43,44]. Third, qualitative parameters of self-networking of CB in polymer melts, e.g. kinetics and stability of formed network can been obtained by using rheology, which cannot be easily obtained by other methods. It is expected to establish the rheology-self-networking of fillers-phase morphology triadic correlation in fillers-filled polymer blends.

2. Experimental section

2.1. Materials

PLA (4032D, Nature Works) and PU (WHT-1570, Yantai Wanhua) was used in this study. Three types of Cabot CB, i.e., Printex 35, Vulcan XC-72, and Printex XE2B, with different parameters were purchased from Degussa Co. Ltd., Germany. For convenience, Printex 35, Vulcan XC-72, and Printex XE2B are called P35, V72, and PX for short in this work, respectively. The detailed parameters of three kinds of CB are listed in Table 1. All the CB particles have almost the same diameter of about 30 nm but the varied n-dibutylphthalate (DBP) adsorption number, v. The DBP adsorption number was often used for characterizing the CB aggregate structure [45,46]. It has been demonstrated a higher v value implies a stronger self-aggregate capability into a network structure and a lower percolation threshold in polymer matrix [37,38]. Hence, the self-networking capability should be PX > V72 > P35 according to Table 1.

2.2. Sample preparation

All the materials were dried under vacuum at 60 °C for at least 12 h before melt blending. Then, PLA/PU/CB ternary nanocomposites

Table 1
The detailed parameter of three kinds of CB.

Grade name	Diameter (nm)	DBP adsorption number (mL/100 g)
Printex 35	31	42
Vulcan XC-72	30	172
Printex XE2B	30	420