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Structural and phase separation characterization of poly(lactic acid)/poly(ethylene oxide)/carbon nanotube nanocomposites by rheological examinations

Yasser Zare[a], Hamid Garmabi[a], Kyong Yop Rhee[b,*]

[a] Department of Polymer Engineering and Color Technology, Amirkabir University of Technology, Tehran, Iran
[b] Department of Mechanical Engineering, College of Engineering, Kyung Hee University, Yongin 446-701, Republic of Korea

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ABSTRACT

The morphology and phase separation have significant impacts on the properties and applications of polymer blends and nanocomposites. In this study, poly(lactic acid) (PLA)/poly(ethylene oxide) (PEO) blends and PLA/PEO/carbon nanotube (CNT) nanocomposites are prepared by solution mixing and the rheological approach is applied to study the morphology and phase separation of the prepared samples. Scanning electron microscopy (SEM) is also used to study the morphology and structure of samples. Additionally, the miscibility or immiscibility between polymer blends was analyzed through Han plots. The results display the lower critical solution temperature (LCST) phase diagram for the prepared samples demonstrating that the enhancement of temperature promotes phase separation. Moreover, the addition of nanoparticles transfers the LCST diagram to high temperatures. The deformation relaxation of PEO droplets commonly diminishes the modulus at very low frequencies, while the formation of big CNT networks in nanocomposites containing high CNT content results in a constant modulus. Han plots also represent the immiscibility in the samples containing 60 and 75 wt% PLA and the nanocomposites including 90 wt% PLA show homogenous structures. The SEM images verify the outputs of rheological tests conducted for the morphology of samples.

1. Introduction

The ecological, biomedical and farming applications of biodegradable polymers have motivated much research in recent years because of the degradation of their hydrolysable bonds in a humid environment [1–10]. Poly(lactic acid) (PLA) being a derivative of polyester exhibits good stiffness along with biocompatibility and hence, commonly used in biomedical applications [11–15]. However, the low degradation rate of PLA has limited their applications in several biomedical fields. In order to accelerate the degradation of PLA in different media, polymers or nanoparticles can be mixed [16–19].

Poly(ethylene oxide) is a hydrophilic, biodegradable and semi-crystalline polymer with good biocompatibility and toughness [20,21], which is considered as a good candidate to be combined with PLA to produce a biodegradable and biocompatible polymer blend. Nakafuku and Sakoda [22] and Agari et al. [23] have reported a partial miscibility between PLA and PEO polymers. Since the morphology and phase separation of crystalline/crystalline blends significantly manipulate the properties and applications, the structure and phase behavior of PLA/PEO products deserve a deep investigation.

Carbon nanotubes (CNTs) can alter the crystallinity of polymers and thus govern the degradation [24–27]. Moreover, the formation of a super-conductive network of CNTs improves the conductivity of the reinforced composites above percolation threshold [28–35]. Undoubtedly, CNTs affect the morphology and phase behavior of PLA/PEO blends controlling their final properties. The conductive PLA/PEO/CNT products can be used in numerous biomedical applications such as prosthetic devices, sensors, actuators and drug delivery [36–40]. Therefore, the production and properties of PLA/PEO/CNT nanocomposites are valuable to study.

The insignificant mixing entropy of binary polymer blends cannot justify the whole miscibility and thus, the polymer blends are typically immiscible or partially miscible [41,42]. Moreover, the high viscosity of polymer blends causes a time-consuming procedure to touch the equilibrium state at the liquid–liquid phase transition [43]. The phase separation in polymer blends consisting of two semi-crystalline polymers depends on the relationship between the crystallization of components [42]. Therefore, the transitions of crystallization and liquid-liquid phase separation result in a complex morphology in these samples. Rheology is the most favorable and sensitive tool to determine the

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* Corresponding author.
E-mail address: rheeky@khu.ac.kr (K.Y. Rhee).

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phase separation temperature of polymer blends among the other common methods such as optical microscopy and light scattering [44–53]. Some studies have used different rheological procedures in the linear viscoelastic region to determine the phase diagrams [46,48]. In fact, the enhancement of elasticity due to the concentration fluctuation and the change of interfacial tension is a sign of phase separation during rheological investigations [43].

The time-temperature superposition (TTS) attitude, Cole–Cole plots and Han curves are regularly used to decide whether the blend is homogenous or heterogeneous [54,55]. TTS principle is proper in the miscible regions when the temperature is high enough above the glass transition temperature, while it fails at the temperatures near liquid–liquid phase transition [12]. The Cole–Cole plots, from plotting the imaginary component of complex viscosity versus its real component can differentiate the homogenous blends from heterogeneous ones [54,56]. The same results can be achieved from Han plots plotting the storage modulus versus loss [43,57,58]. It was reported that Cole-Cole and Han plots are more sensitive than TTS [59]. Furthermore, the temperature sweep can quantify the binodal and spinodal decomposition temperatures [43,60]. The storage modulus falls in the miscible region as a result of enhanced chain mobility, but an abrupt change in the slope of the storage modulus plot occurs due to the enhanced elasticity near the mixing-demixing temperatures [20,59]. This behavior is more evident in polymer blends showing strong dynamic asymmetry or large variance in viscoelasticity.

In this paper, PLA/PEO blends and PLA/PEO/CNT nanocomposites are prepared by solution mixing at different compositions and the rheological protocols are applied to study the phase separation temperature and the morphology of samples. In addition, scanning electron microscopy (SEM) is also conducted to analyze the structure of samples as well as to confirm the rheological outputs. The temperature sweep is performed to determine the liquid–liquid phase separation temperatures. In addition, the dynamic viscoelastic properties in the melt state are applied to observe the correlation of linear viscoelastic properties of samples to morphology. Finally, Han curves are obtained to study the miscibility or immiscibility between polymer blends in the blends and nanocomposites. This study properly highlights the role of CNTs in the phase separation temperature and morphology of PLA/PEO blends.

2. Experimental

2.1. Materials

PLA (biopolymer, ME346310), PEO (M_v = 200000 g/mol) and phosphate-buffered saline (PBS) powder were obtained from Sigma-Aldrich Chemical Co. Multi-walled carbon nanotubes (MWCNTs) (CM-95) were purchased from Hanhwa Nanotech CO., Korea. The length and diameter of MWCNTs were reported as 10 µm and 20 nm, respectively. In addition, chloroform was supplied from Shindo Co., Korea.

2.2. Sample preparation

PLA/PEO/CNT nanocomposites were produced by solution mixing in chloroform. The chosen amount of CNTs was dissolved in chloroform at a concentration of 1 mg/ml by stirring and sonication (at 300 W) for 8 h to obtain a homogeneous dispersion. Both PLA and PEO were completely dissolved in chloroform at a concentration of 100 mg/ml. The polymer solution was mixed with CNT suspension and stirred for 5 h to obtain a homogeneous solution. After sonication for 1 h, the solvent was evaporated at room temperature and the remaining PLA/PEO/CNT solution was poured on a Petri-plate to obtain a film. Finally, the film was obtained after drying the poured mixer in a vacuum oven at 45 °C for 12 h. The chosen weight concentration of PLA in blends and nanocomposites was 60, 75 and 90 wt % while the CNT content was 1 and 2 wt %. The samples are nominated as PLAx/PEOy/CNTz, where x, y and z represent the weight fraction of PLA, PEO and CNT, respectively.

2.3. Characterizations

The dynamic rheological properties were obtained by a Paar-Physica rheometerwith disk-type parallel plates whose diameter was 25 mm with 1-mm gap. All experiments were carried out under a continuous nitrogen atmosphere to prevent the sample degradation. An isochronal dynamic temperature sweep was carried out from 160 to 230 °C at a fixed frequency of 0.05 Hz, a certain strain of 1% and a uniform heating rate of 1 °C/min from homogeneous to the phase-separated regime to detect the onset of phase separation. Moreover, the isothermal dynamic frequency sweep was performed at 180 °C and strain of 1% covering the range of 0.01–628 rad/s to evaluate the linear viscoelastic properties including storage and loss modulus. The scanning electron microscopy (SEM) (XL30S) was also performed on gold-coated samples to investigate the structure of blend and the dispersion of CNTs in the matrix at the accelerating voltage of 10 kV.

3. Results and discussion

3.1. Determination of decomposition temperatures

The temperature sweep at a low frequency suggests that only the variation of morphology governs the changes in the viscoelastic properties. The methodology proposed by Ajji and Choplin [61] presents the decomposition temperatures for the prepared samples. Fredricson and Larson [62] expressed the influence of concentration fluctuation on the shear stress of block copolymers near the critical points by mean field theory. The following expressions for storage (G′) and loss modulus (G″) were given by:

$$G^{'}(\omega) = \frac{\mathrm{k_B} T\omega^2}{15\pi^2}\int_0^{k_0} \frac{\mathrm{k}^6 S_0^2(k)}{\omega^2 + 4\varpi(k)}\left[\frac{\partial S_0^{-1}(k)}{\partial k^2}\right]^2 dk \tag{1}$$

$$G^{''}(\omega) = \frac{2\mathrm{k_B} T\omega}{15\pi^2}\int_0^{k_0} \frac{\mathrm{k}^6 S_0^2(k)\varpi(k)}{\omega^2 + 4\varpi^2(k)}\left[\frac{\partial S_0^{-1}(k)}{\partial k_2}\right]^2 dk \tag{2}$$

$$\varpi(k) = \mathrm{k}^2 S_0^{-1}(k)\lambda(k) \tag{3}$$

where ω is angular frequency, T is temperature (Kelvin unit), k_B is the Boltzmann coefficient, k is wave factor, S_0 (k) is a static structure factor and λ (k) is Onsager coefficient. Ajji and Choplinextended the Fredrickson-Larson approach to binary polymer blends and suggested the following equation using the static structure factor calculated by de Gennes [63] as:

$$\frac{1}{S_0(k)} = \frac{1}{\varphi N_1 g_1(k)} + \frac{1}{(1-\varphi)N_2 g_2(k)} - 2\chi \tag{4}$$

where φ is the volume fraction of one of the polymers, N_i is the number of statistical segments, χ is the interaction parameter and g_i (k) is attributed to Debye function. The storage and loss modulus at a one-phase region near the order–disorder point can be calculated after some mathematical operations as:

$$G^{'}(\omega) = \frac{\mathrm{k_B} T\omega^2}{1920\pi}\left[\frac{1}{3}\left(\frac{R_{g1}^2(k)}{\varphi N_1} + \frac{R_{g2}^2}{(1-\varphi)N_2}\right)\right]^{1/2}\left[\frac{1}{\varphi a_1^2 W_1} + \frac{1}{(1-\varphi)a_2^2 W_2}\right]^2 [2(\chi_s - \chi)]^{-5/2} \tag{5}$$

$$G^{''}(\omega) = \frac{\mathrm{k_B} T\omega}{240\pi}\left[\frac{1}{3}\left(\frac{R_{g1}^2}{\varphi N_1} + \frac{R_{g2}^2}{(1-\varphi)N_2}\right)\right]^{-1/2}\left[\frac{1}{\varphi a_1^2 W_1} + \frac{1}{(1-\varphi)a_2^2 W_2}\right][2(\chi_s - \chi)]^{-1/2} \tag{6}$$