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Thermal and rheological properties of poly(ϵ -caprolactone) and polystyrene blends

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Abstract

The thermal and rheological properties of blends of poly(ϵ -caprolactone) (PCL) and polystyrene (PS) have been investigated by differential scanning calorimetry (DSC), scanning electron microscopy, and Advanced Rheometric Expansion System. Two different molecular weights of PS 1 ($M_w = 1000$) and PS 2 ($M_w = 69,000$) have been used in the PCL–PS blend. In the thermal analysis of the PCL–PS 1 blend by DSC, the T_c of PCL in the blend decreased by about 3–13 degrees with blend composition compared to the T_c of pure PCL. The decrease in T_c of PCL in the blend indicates that the crystallization of PCL in the PCL–PS 1 blend is deactivated by PS 1. The T_m of PCL in the blend decreased by about 2–6 degrees with blend composition compared to the T_m of pure PCL. From the results of T_c and T_m of PCL, it is suggested that the PCL–PS 1 blend is partially miscible. The T_c of PCL in the PCL–PS 2 blend increased by about 2–5 degrees in the PCL-rich compositions. The increase in T_c of PCL can be explained by the nucleating effect of PS 2 on the primary nucleation of PCL in the PCL–PS 2 blend. From the results of the rheological properties of the PCL–PS 2 blend, the storage modulus of the blend at low frequencies has a larger value than that of the simple mixing rule. The elasticity increase from the simple mixing rule is consistent with the emulsion model for a dispersed system. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Biodegradable polymer blends; Thermal properties; Rheological properties

1. Introduction

Poly(ϵ -caprolactone) (PCL), an aliphatic polyester made from the ring opening polymerization of ϵ -caprolactone, is known to be a biodegradable polymer. Recently in order to obtain less expensive degradable polymers, blends of PCL and several polymers such as poly(hydroxybutyrate-co-hydroxyvalerate) [1], polycarbonate [2], polyethylene, and polypropylene [3–5] have been studied.

For the blends of PCL and low molecular weight polystyrene (PS), Nojima et al. [6] have studied the crystallization and morphology of PCL–PS blends at various crystallization temperatures by using the X-ray scattering method. In the study of the phase behavior of PCL–PS blends, Li et al. [7] have reported that the PCL–PS blends are partially miscible and show an upper critical solution temperature behavior. From the dynamic mechanical tests and tensile properties of PCL–PS blends, Koleske [8] has

reported that the PCL–PS blends are incompatible, but have good mechanical properties. There are several studies about the phase behavior of blends of PCL and PS [6–10]. However, the rheological properties of the PCL–PS blend have not been reported yet. Also, the studies on the crystallization behavior of PCL in the PCL–PS blend are very limited.

We report here on the relationship between crystallization behavior and miscibility of the PCL–PS blends having two different molecular weights of PS. The morphology and rheological properties of the PCL–PS blends have been investigated by scanning electron microscopy and Advanced Rheometric Expansion System (ARES). From the ARES measurement, the results of rheology are interpreted in the context of the emulsion/dispersion model by Oldroyd and Palierne [11–13], which describes well the increase of elasticity of incompatible blends.

2. Experimental

2.1. Polymers

The polymers used in this study were obtained from

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Table 1
Characteristics of polymer samples used in the PCL–PS blend

	\bar{M}_w^a	\bar{M}_n^a	\bar{M}_w/\bar{M}_n^a	T_g (°C) ^b	T_m (°C) ^b	T_c (°C) ^b
PCL ^c	163,300	56,400	2.90	–60.8	57.0	20.0
PS 1 ^d	1000	800	1.23	57.8	–	–
PS 2 ^e	69,000	21,700	3.18	92.1	–	–

^a Measured in our laboratory by GPC.

^b Measured in our laboratory by DSC.

^c Supplied by Union Carbide Chemicals and Plastics Co.

^d Supplied by Polysciences, Inc.

^e Supplied by Miwon Petrochemical Co.

commercial sources. The characteristics and sources of the polymer samples used in this study are shown in Table 1. PCL was obtained from Union Carbide Co. under the trade name of Tone P-787. PS 1 ($\bar{M}_w = 1000$) and PS 2 ($\bar{M}_w = 69,000$) were supplied by Polysciences, Inc. and Miwon Petrochemical Co., respectively.

2.2. Blend preparations

For differential scanning calorimetry (DSC) measurements, the blends of PCL–PS 1 and PCL–PS 2 were prepared by solution casting. For solution casting, a total of 0.8 g of the PCL/PS mixture was dissolved in 20 ml of methylene chloride at room temperature (4.0% (w/v) solution) for at least 1 day. The blends were cast on glass plates, and all the film samples were dried under vacuum for 7 days at room temperature. For rheological measurements, the blend of PCL and PS 2 was prepared by screw extrusion. The length to diameter ratio (L/D) of the circular die was a 20.0 with a diameter of 2 mm. The polymer samples were dried under vacuum before use. Temperatures of the extru-

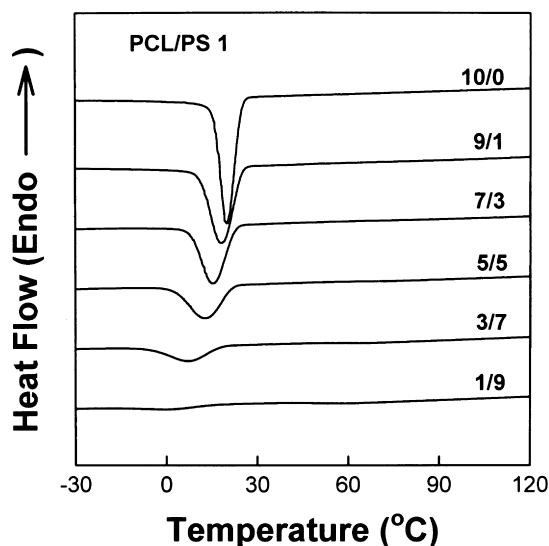


Fig. 1. DSC cooling thermograms of the PCL–PS 1 blend.

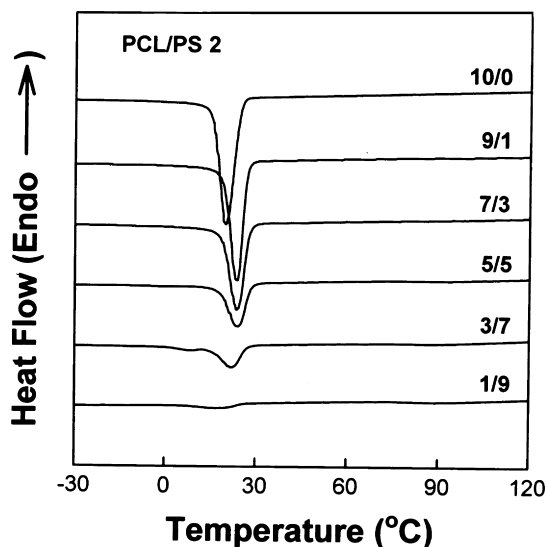


Fig. 2. DSC cooling thermograms of the PCL–PS 2 blend.

der were set at 180°C in the barrel zones and at 160°C in the die zone.

2.3. Differential scanning calorimetry

The thermal properties of all the samples were analyzed using a Perkin–Elmer DSC, Model DSC-7. Temperature calibration was performed using indium ($T_m = 156.6^\circ\text{C}$, $\Delta H_f = 28.5 \text{ J/g}$). In order to measure the melting and crystallization temperatures of the PCL–PS blend, samples of 5–15 mg were heated in a nitrogen atmosphere from -30 to 180°C at a heating rate of 20 K/min and then cooled to -30°C at a rate of 20 K/min.

2.4. Scanning electron microscopy (SEM)

The morphology of the cross-section of the extrudate was analyzed by scanning electron microscopy in a JEOL Model JSM-5200 microscope at 15 kV accelerating voltage after gold sputter-coating. The fractured surface of the extrudate was prepared by cryogenic fracturing.

2.5. Advanced rheometric expansion system (ARES)

The rheological measurements were carried out on a ARES in oscillatory shear at 10% strain in the cone-and-plate arrangement with 25 mm platens and a cone angle of 0.1 rad. To avoid thermal degradation, all the test samples were dried under vacuum and then fabricated into 25 mm disks by molding at 180°C . Dynamic experiments were performed under a continuous purge of dry nitrogen at 180°C . Before the rheological test, a linear viscoelasticity on frequency and thermal stability at the test temperature was checked.

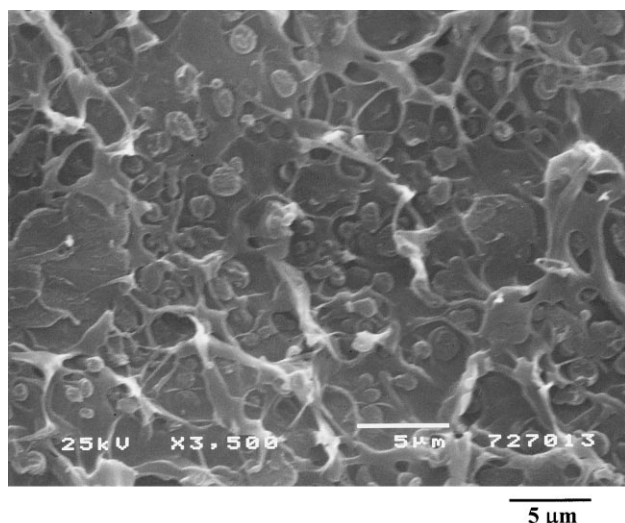


Fig. 3. Scanning electron micrograph of cryogenically fractured cross-sectional surface of 8:2 PCL–PS 2 blend.

3. Results and discussion

3.1. Thermal behavior of the PCL–PS blend

From the thermal analysis of the PCL–PS 1 blend by DSC, the crystallization temperature (T_c) of PCL in the PCL–PS 1 blend is shown in Fig. 1. From Fig. 1, we can see that the T_c of PCL in the blend decreases by about 3–13 degrees with blend composition compared to the T_c of pure PCL. The decrease in the T_c of PCL in the blend suggests that the crystallization of PCL in the PCL–PS 1 blend is suppressed by the addition of PS 1.

The melting point (T_m) of PCL in the blend has been examined and found to decrease by about 2–6 degrees with blend composition compared to the T_m of pure PCL. For the measurement of the glass transition temperature (T_g) of PS 1 in the PCL–PS 1 blend, the T_g appeared near the T_m of PCL; therefore, the T_g of PS 1 in the blend was not

detectable. The melting and crystallization temperature depressions are classically associated with miscibility [12]. From the above results, it is suggested that the PCL–PS 1 blend is partially miscible.

The T_c of PCL in the PCL–PS 2 blend is shown in Fig. 2. From Fig. 2, we can see that the T_c of PCL in the blend is shown to increase by about 2–5 degrees in the 9:1, 7:3, and 5:5 PCL–PS 2 blends. The increase in T_c of PCL in the blends suggests that PS 2 affects the crystallization of PCL in the PCL–PS 2 blend. For the immiscible blends, the effect of the second component on the crystallization behavior of the crystallizing component has been studied widely. In the blend of polypropylene (PP) and atactic PS, Bartczak et al. [14] have reported that the heterogeneous nuclei of PP increase with increasing the weight fraction of PS. Therefore, the increase in T_c of PCL in the PCL–PS 2 blend can be explained by the nucleating effect of PS 2 on the primary nucleation of PCL. For the T_m of PCL and T_g of PS 2 in the PCL–PS 2 blend, the values of T_m and T_g are shown to be almost unchanged compared to those of the pure polymers.

It is known that the presence of the second component in polymer blends has a great effect on the primary nucleation of the crystallizing component [15]. The influence of the second component in the blend on primary nucleation of the crystallizing component depends on the chemical structure of the polymer, miscibility and its ability to crystallize, blend composition, and conditions of the mixing process. When the polymer blends are miscible, the energy barrier for the formation of a critical nucleus in the blends is greater than that of the homopolymer [16]. Therefore, nucleation activity of heterogeneous nuclei in the blends generally decreases with increasing concentration of a second polymer in the blends. Therefore, the results of T_c of PCL shown in Fig. 1 suggest that the crystallization of PCL in the PCL–PS 1 blend is deactivated by PS 1. From the results of T_c and T_m of PCL, it is suggested that the PCL–PS 1 blend is partially miscible.

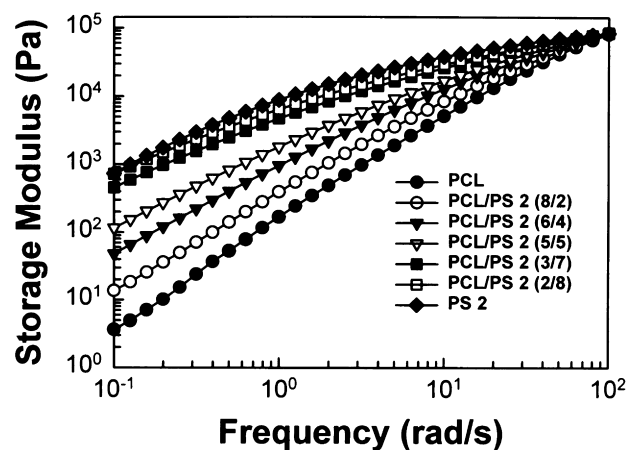


Fig. 4. Storage modulus (G') vs. frequency for the PCL–PS 2 blend at 180°C.

3.2. Morphology and rheology of the PCL–PS blend

The cross-sectional surface of the PCL–PS 2 blend was examined using SEM. The micrograph of 0.8 weight fraction of PCL in the PCL–PS 2 blend is shown in Fig. 3. Phase separation between PCL and PS 2 was observed for all the blend compositions. This result indicates that the PCL–PS 2 blend is immiscible under the mixing condition, and is consistent with the thermal analysis results of the PCL–PS 2 blend.

The rheological properties of the PCL–PS 2 blend were investigated using ARES. The frequency dependence of the storage modulus (G') of 0.0, 0.2, 0.3, 0.5, 0.6, 0.8, and 1.0 weight fraction PCL in the PCL–PS 2 blend is shown in Fig. 4. In Fig. 4, at all frequencies, the storage modulus of the PCL–PS 2 blend has larger values than that of the simple mixing rule.

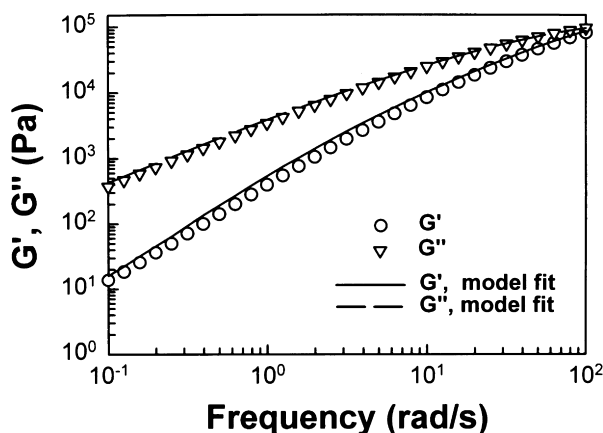


Fig. 5. Comparison of experimentally obtained storage modulus (G') and loss modulus (G'') vs. frequency with model prediction for the 8:2 PCL–PS 2 blend.

The increase in elasticity of incompatible polymer blends at low frequencies has been interpreted in the context of emulsion models [11–13]. We use the model developed by Oldroyd for an emulsion of two incompatible fluids in a flow in which the suspended particles are assumed to be monodisperse and depart only slightly from a spherical shape. This model is supported by a more recent development by Palierne [11] for the linear rheology of viscoelastic emulsion with interfacial tension. For an oscillatory shear flow the emulsion model leads to the following expression:

$$G^* = G_M^* \frac{1 + 3\phi H}{1 - 2\phi H} \quad (1)$$

with

$$H = \frac{4\gamma_{12}/R(2G_M^* + 5G_I^*) + (G_I^* - G_M^*)(16G_M^* + 19G_I^*)}{40\gamma_{12}/R(G_M^* + G_I^*) + (2G_I^* + 3G_M^*)(16G_M^* + 19G_I^*)} \quad (2)$$

where G^* is the complex modulus of the blend, G_M^* and G_I^* the complex moduli of matrix and inclusions (dispersed phase), respectively, ϕ the volume fraction of inclusions, γ_{12} the interfacial tension, and R the radius of the inclusions. The γ_{12} between PCL and PS 2 is estimated [17] and found to be 1.53 mN/m.

For the 8:2 PCL–PS 2 blend, experimentally obtained dynamic moduli (storage and loss modulus) and model predictions are shown in Fig. 5. For the diameter of the dispersed phase, an average value from the SEM micrograph was used and found to be 1.5 μm . The thermal analysis showed that the T_m and T_g values of the PCL–PS 2 blend are almost unchanged on annealing. If small but non-negligible changes of T_m and T_g are observed, PS and PCL in the blend are mixed to a non-negligible extent and the G^* of the PS and PCL phases are not identical to the G^* of the pure PS and PCL. The emulsion model utilized in Fig. 5 is for the systems containing dispersed droplets. Thus the model does not seem to be applicable to the PCL–PS blends with a

composition of around 5:5 where both PCL and PS would form continuous phases. Therefore, the increase of the elasticity of such blends cannot be explained from the simple emulsion model. Fig. 5 shows a quantitative agreement between experimental data and model predictions over the whole frequency range.

4. Conclusions

In the thermal analysis of the PCL–PS 1 blend by DSC, the T_c of PCL in the blend decreased by about 3–13 degrees with blend composition compared to the T_c of pure PCL. The T_m of PCL in the blend was found to decrease by about 2–6 degrees with blend composition compared to the T_m of pure PCL. The decrease in T_c of PCL in the blend indicates that the crystallization of PCL in the PCL–PS 1 blend is deactivated by PS 1. From the results of T_c and T_m of PCL, it is suggested that the PCL–PS 1 blend is partially miscible.

The T_c of PCL in the PCL–PS 2 blend increased by about 2–5 degrees in the PCL-rich compositions. The increase in T_c of PCL suggests the nucleating effect of PS 2 on the primary nucleation of PCL in the PCL–PS 2 blend. The values of T_m of PCL and the T_g of PS 2 in the blend did not change significantly compared to those of the pure polymers. From these results, it is indicated that the PCL–PS 2 blend is immiscible for the prepared blend compositions.

From the results of the rheological properties of the PCL–PS 2 blend, the storage modulus of the blends at low frequencies has a larger value than that of the simple mixing rule. The elasticity increase from the simple mixing rule is consistent with the emulsion model for a dispersed system.

Acknowledgements

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