The Effect of SEBS on Interfacial Tension and Rheological Properties of LDPE/PS Blend

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ABSTRACT: The effects of SEBS as a compatibilizer on the interfacial tension and rheological properties of LDPE/PS blend have been studied. Interfacial tension was measured by the breaking thread method. The measured interfacial tension of the LDPE/PS blend was 8.26 dyn/cm. It decreased rapidly with SEBS contents to 1 wt % and then leveled off to a saturation value, 3.6 dyn/cm. Dynamic oscillatory shear, elongational viscosity, and recovery after elongation were measured as the rheological properties. Storage modulus at low frequencies decreased with SEBS contents to 1 wt %. More addition of SEBS, however, increased the storage modulus at low frequencies. Similar behaviors could be observed in elongation viscosity and recovery after elongation. Hardening of elongational viscosity and recovery after elongation were reduced with 1 wt % SEBS, and they enhanced again with more SEBS contents. This means that there is a critical concentration of SEBS that acts as a compatibilizer and reduces the interfacial tension. More SEBS than the critical concentration saturates the interface and increases the elasticity of the LDPE/PS blend, while maintaining the interfacial tension between LDPE and PS constant. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 905–911, 2005

Key words: LDPE/PS blend; compatibilizer; interfacial tension; breaking thread method; rheological properties

INTRODUCTION

Interfacial characteristics of a polymer blend are closely related to the rheological properties, as well as the morphology and mechanical properties. Poor interfacial properties often limit the applications of blends having phase separated structure. Therefore, it is important to employ a proper compatibilizer for improving interfacial adhesion of a polymer blend.[1] A proper compatibilizer placed at the interface reduces interfacial tension, which plays an important role in the development and stabilization of blend morphology. The relationship between the interfacial tension and rheological properties of low density polyethylene (LDPE)/polystyrene (PS) blend has been investigated in this study. During several proposed methods, the breaking thread method was used to measure the interfacial tension of the blend.[2–11] This method has some merits over other methods, such as the pendant drop method or spinning drop method, from the fact that it requires shorter experimental time and simpler experimental apparatus.[12–14] It calculates the interfacial tension by measuring the evolution of a thread distortion amplitude versus time. Styrene-ethylene-butylene-styrene triblock copolymer (SEBS) was used as a compatibilizer, and the effects of the compatibilizer on the interfacial tension were studied.

Measurements of rheological properties are very effective in understanding the polymer blend. As for the rheological properties, dynamic modulus from oscillatory shear, melt elongational viscosities, and recovery behavior after elongation were measured. Dynamic modulus measured at small amplitude can be classified as linear viscoelastic properties. The common behavior of immiscible polymer melt is the increase of elasticity at low frequency range in the oscillatory test. This comes from the interfacial tension of the two phases. On the other hand, elongational viscosities and recovery after elongation can be classified as nonlinear viscoelasticity because samples experience large and rapid deformation. In the melt elongation test, LDPE exhibits a significant degree of strain hardening due to its highly branched structure, whereas PS exhibits less. In the recovery after elongation test, the deformed sample recovers and the morphology changes from needles to spheres. In this study, three rheological properties were measured, and the effects of SEBS on the rheological properties have been investigated.

EXPERIMENTAL

Materials

LDPE was from LG Chemical with T_m 107°C, MI 5.8g/10min (190°C, 2.16kg), and density 0.920g/cm³. PS

was also from LG Chemical with T_g 97°C, MI 3.3g/10min, and density 1.05g/cm^3. SEBS was Kraton G block-co-polymer from Shell Chemical Company with density 0.9g/cm^3, ethylene-butylene block 70%, and styrene block 30%.

Compounding

LDPE and PS were dried over 24 h at 80°C, and SEBS over 12 h at 60°C, in an air circulating oven before being compounded to prevent hydrolytic degradation during processing. The blend compositions of LDPE/PS were varied: 10/90, 20/80, and 30/70. The effect of the SEBS copolymer was studied with the 20/80 LDPE/PS blend. The copolymer compositions were varied 0.5, 1, 3, 5, and 7 wt % relative to the total weight of the blend.

Blending was carried out in a melt mixer (Haake Rheomix 600) with 60rpm at 210°C. Torque data and the morphology from a scanning electron microscope were stabilized after 10 min of mixing time.

Interfacial tension measurement

The breaking thread method was used to measure the interfacial tension between PS and LDPE containing various amounts of compatibilizer. It was developed as a dynamic method for measuring the interfacial tension between molten, high molecular weight polymers. For experiments, films of LDPE were pressed using a Carver laboratory press at 210°C. The 50–100μm diameter PS fibers were obtained by drawing melted pellets on a hot plate. This PS thread (15mm length) was embedded between two LDPE films (10mm × 10mm). To remove the voids and residual stresses between the thread and films, it was dried in a vacuum oven at 100°C for 24 h. Then, the sample was inserted between two glasses and placed on a hot plate (Mettler FR-2). Temperature was set to 210°C, and the sample was observed by an optical microscope (Nikkon) in transmission mode. Images were taken, and the changes of amplitude and wavelength of the thread were analyzed with time.

Rheological measurements

Rheometrics ARES was used to measure the dynamic modulus of the blends. The frequency range was 0.1 $\sim$ 100s^{-1}, and the temperature was 210°C. Measurements of dynamic mode were operated with a parallel plate type fixture (D = 25mm), gap distance of 1.5mm, and strain amplitude was kept 10% to ensure linear viscoelasticity. Time sweeps did not show any thermal degradation for time up to 30 min, which exceeded the time required to perform a complete experiment. To obtain the zero shear viscosity of each component, the rate sweep test was performed. The range of shear rate was 0.01 $\sim$ 1 s^{-1}, and the temperature was 210°C.

The melt elongation and recovery measurements were performed in a rotary clamp elongational rheometer. For elongational viscosity, the test temperature was 180°C and the elongation rates were varied 0.05, 0.1, and 0.25 s^{-1}. Rod-shaped samples with diameter of 3mm and length of 170mm were prepared using a capillary rheometer. Samples were stretched by one side of rotary clamps in a silicon oil bath, which is used both as a thermostat and to eliminate gravitational effects. During elongation, the strain rate was kept constant. The strain (Hencky strain) increases linearly with time and is related to the stretch (or stretch ratio) by

$$\varepsilon(t) = \dot{\epsilon}_0 t = \ln \lambda(t) \qquad (1)$$

Recovery after elongation was measured by cutting the stretched sample. After being cut, samples immediately shrank into small pieces due to the interfacial tension of the two polymers. The recovered stretch ratio is defined as follows

$$\lambda_r(t') = L_A/L(t') \qquad (2)$$

where L_A is the initial cut-off length and L(t') is the length of the sample cut-off after recovery time t'. The transient recovery was measured by taking photos of the cut-off at different instants during recovery. For this purpose, a digital-camera was installed on top of the rheometer housing. Samples were cut after being stretched for 20 s with a stretch ratio of 0.1. The initial cut-off length was 10cm.

RESULTS AND DISCUSSION

Interfacial tension

The breaking thread method calculates the interfacial tension by measuring the evolution of the thread distortion amplitude versus time. Temperature microgradients, which create amplitude differences in the Brownian motion, are the driving force for this sinusoidal distortion of the threads to break up into a number of smaller drops. Because this method is based on liquids that exhibit Newtonian behavior, it is applicable only when the polymers exhibit plateau viscosity at low shear rates and, therefore, the loss angle should be close to 90°. The thread and matrix polymer, PS and LDPE with SEBS from 0 to 7 wt %, showed plateau zero shear viscosity at low shear rate. The zero shear viscosities of PS and LDPE were 3.2 × 10^3 and 2.6 × 10^3 Pa.s, respectively.

The amplitude α grows exponentially with time with the growth rate q:

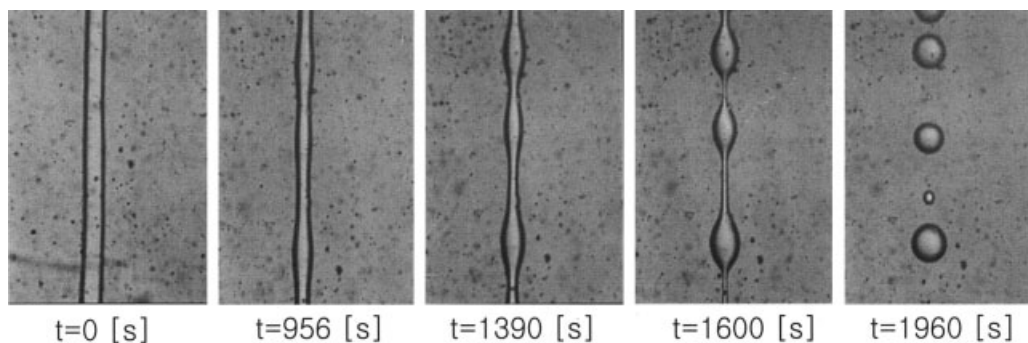$$\alpha = \alpha_0 \exp(qt), q = \frac{\sigma \Omega(\lambda, p)}{2\eta_c R_0} \qquad (3)$$

Figure 1 Sinusoidal distortions on a PS thread embedded in an LDPE matrix.

where α_o is the original amplitude, t is the time, σ is the interfacial tension, Ω is the tabulated function related to the viscosity ratio p, η_c is the continuous phase viscosity, and R_o is the initial radius of the thread. For a given p, there is a dominant wavelength λ_m at which the amplitude grows fastest. The distortion having this wavelength consequently causes the thread to break up into droplets. The dominant wavenumber χ_m ($=2\pi R_0/\lambda_m$) and Ω_m are tabulated as a function of viscosity ratio.[2] The application of the tabulated function $\Omega(\lambda,p)$ is possible only if the thread breakup is generated by a distortion having the dominant wavelength λ_m. Therefore, the comparison of the experimental wavelength to the theoretical one is essential whether both values are close to an accuracy of 10%.[5] In this study, all the interfacial tension measurements were made on the above 5 distortions and only the distortions having a wave number which lies ± 10% of the χ_m were taken.

Figure 1 shows the shape evolution of PS fiber in the LDPE matrix with time. The initial thread diameter is $80\mu m$ and the initial sinusoidal distortion appears after 16 min. It takes 33 min for the thread to break down and form into perfect spheres. To investigate the effect of SEBS, LDPE matrices containing various amounts of SEBS were examined. The natural logarithm of relative amplitude, $2\alpha/D_o$, versus time is represented in Figure 2 with various SEBS contents. The experimental points lie in straight lines, and the growth rate q can be calculated from the slope. The slope is stiff without SEBS, and decreased with the addition of SEBS. The growth rate q does not change with SEBS more than 3 wt %.

Interfacial tensions of LDPE/PS blend with different amounts of SEBS contents are shown in Figure 3. The interfacial tension of LDPE/PS is 8.26 dyn/cm. This value decreases rapidly with SEBS contents to 1 wt % and then levels off to the constant value of 3.6 dyn/cm after SEBS 3 wt %. This is probably due to the strong affinity of SEBS for both LDPE and PS. The styrene block of SEBS will have a strong affinity with the PS, and the ethylene-butylene block likely has an affinity with the LDPE.

Dynamic shear oscillation

In the LDPE/PS blend, a secondary plateau of storage modulus at low frequency is observed as the LDPE contents increase. This is due to the change of the total area in the interface and, as a result, increases the interfacial energy.[6] The effects of SEBS on the storage modulus of the LDPE/PS blend, by changing the interfacial tension and interfacial energy, are represented in Figure 4. It shows the storage modulus of LDPE/PS = 20/80 with various SEBS contents as a function of frequency. When the SEBS contents are 0.5 and 1 wt %, there are significant drops of storage modulus at low frequency ranges. This is coincident with the previous interfacial tension result, at which the interfacial tension decreased rapidly to 1 wt % of SEBS and then leveled off. It is clear that SEBS reduces the interfacial energy and suppresses coalescence. As SEBS contents increase over 3 wt %, however, there is
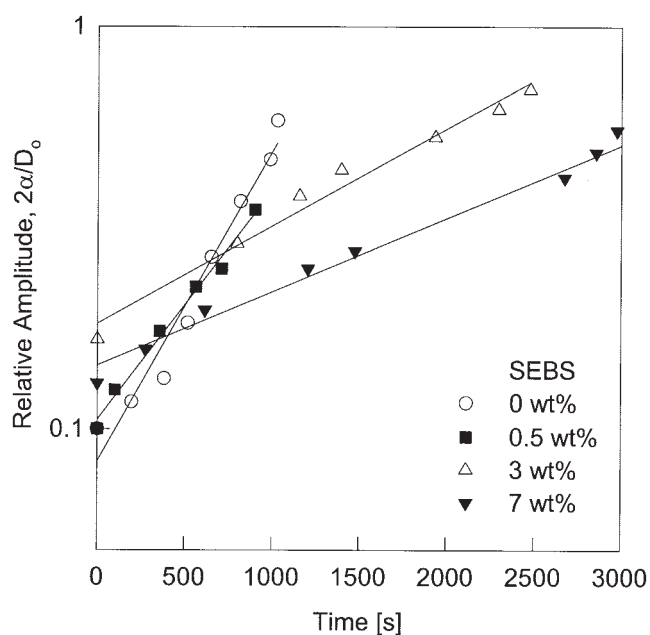

Figure 2 Relative amplitudes versus time of PS thread embedded in an LDPE matrix with various SEBS contents.
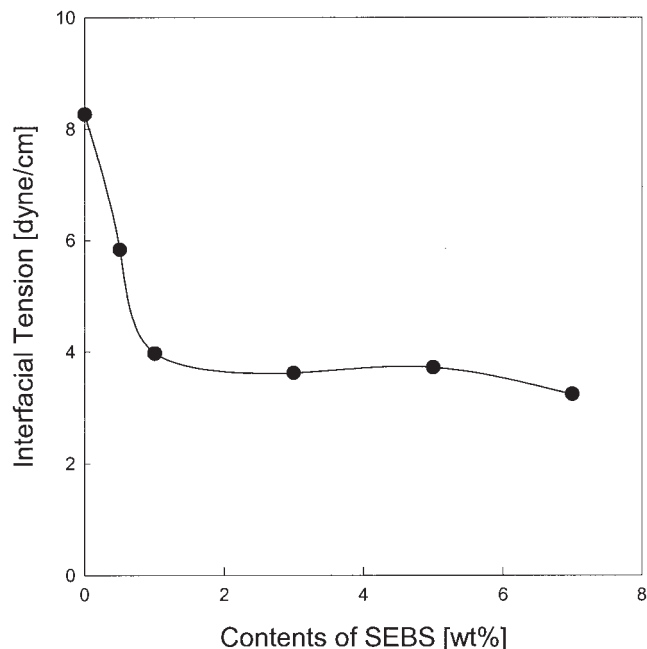
Figure 3 Changes of interfacial tension with SEBS contents in an LDPE matrix.

Figure 5 Elongational viscosities of LDPE/PS blends for various elongation rates.

an increase of storage modulus. This explains that there is a critical SEBS concentration over which SEBS is saturated and is dispersed either in both phases or in one of the phases. In the case of PE/PS blends, the copolymer is known to disperse preferentially in the PE phase.[15] The excess SEBS forms a micelle, and it is believed to be the reason to increase the elasticity of the blend in Figure 4.[16]

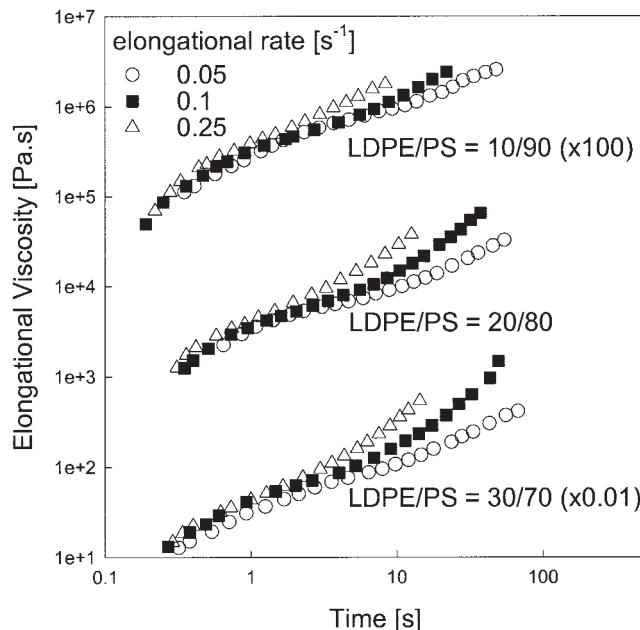**Figure 4** Storage modulus versus frequency of LDPE/PS = 20/80 with various SEBS contents.

Melt elongation

The transient elongational viscosities of LDPE/PS blends for different elongational rates are represented in Figure 5. The elongational rates are 0.05, 0.1, and 0.25 s^{-1}, respectively. In the low elongational rate, viscosities show weak extension thickening behavior. The higher the elongational rate, the shorter is the time when the strain hardening happens. The strain hardening can be defined as an elongational viscosity upturn above the linear viscoelastic start-up viscosity. As LDPE contents increase, strain hardening is enhanced noticeably. This is due to the presence of long chain branches in LDPE, which increases deformation and leads to more chain stretching. On the other hand, PS is radically polymerized and is free of long chain branching. Therefore, PS shows far less strain hardening behavior and is less sensitive to the elongational rates than LDPE.[17]

Figure 6 shows the effect of SEBS contents on the elongation properties for LDPE/PS = 20/80 blend. When the content of SEBS is 0.5 or 1 wt %, by acting as a compatibilizer and reducing the interfacial tension, it reduces the strain hardening. Though the interfacial tension is kept constant, more addition of SEBS than 3 wt % saturates the interface and increases the elasticity and strain hardening, which is similar to the result of the shear oscillation test.

Melt recovery

Figure 7 shows the sequence of the recovery of LDPE/PS = 20/80 after elongation with a strain rate
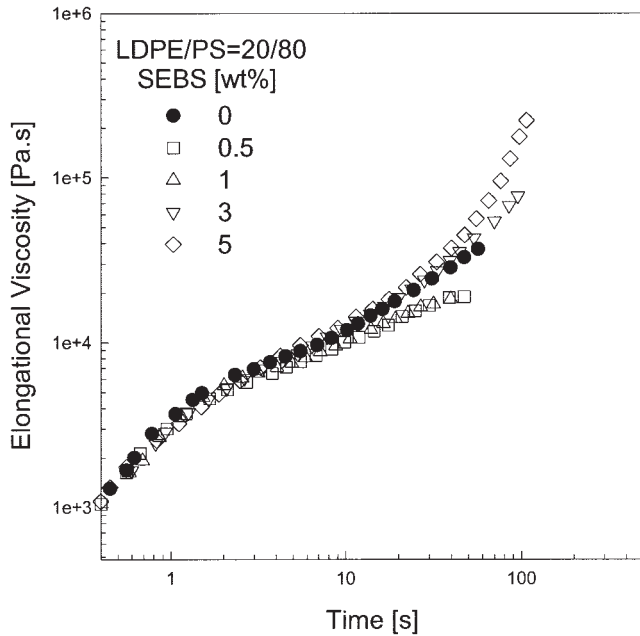
Figure 6 Elongational viscosities of LDPE/PS = 20/80 for various SEBS contents. Elongational rate is $0.05s^{-1}$.
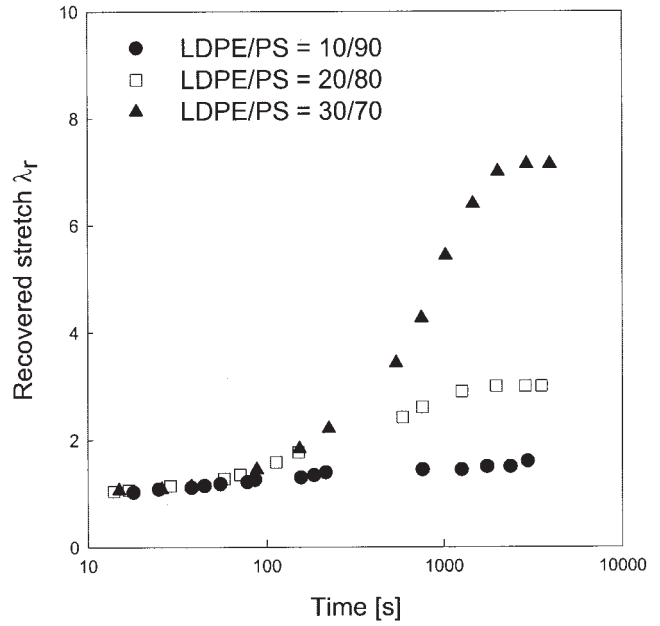

Figure 8 Recovered stretch ratios of various LDPE/PS blends.

of $0.1s^{-1}$ for 20 s at a temperature of 180°C. After 3000 s, there were no more recoveries. Recovered stretch ratios of various LDPE/PS compositions with time are represented in Figure 8. Recovering behavior was measured during 1 h. In the case of LDPE/PS

= 30/70, its final ratio reaches to 7.1. The ratio decreases as LDPE decreases, and becomes 1.6 with LDPE/PS = 10/90. Because the recovered stretch behavior depends on the LDPE/PS compositions, it is assumed that the interfacial tension between LDPE
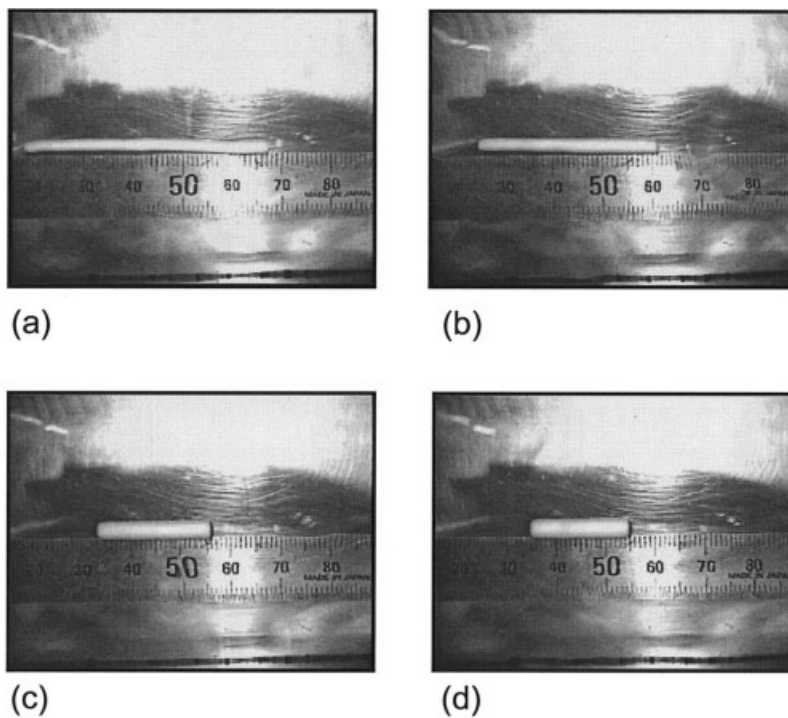

Figure 7 Recovery after a cut-off of LDPE/PS = 20/80 after elongation for 20 s with an elongational rate of $0.1s^{-1}$. Temperature is 180°C. (a) t = 0, (b) t = 50, (c) t = 500, (d) t = 3000 s.
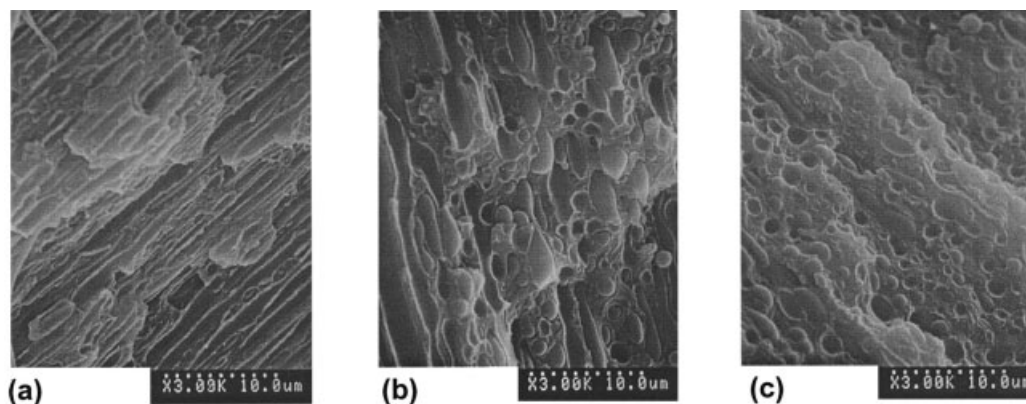
Figure 9 Morphological changes of sample after a cut-off of LDPE/PS = 20/80 with time. (a) t = 0, (b) t = 500, (c) t = 3000 s.

and PS is the driving force for creating such a different recovery. Meissner et al. also reported this melt recovery is due to the interfacial tension from their result that PS/PMMA = 16/84 and PS/PMMA = 84/16 showed the same total recovery.[18] Figure 9 shows the morphological changes of the cut-off recovery with time. During the recovery process, the elongated sample gradually recovers from long needles to complete spherical shapes.

The recovered stretch ratios of LDPE/PS = 20/80 with various SEBS contents are represented in Figure 10 with time. The final recovered ratio of LDPE/PS = 20/80 is 3. When 1 wt % of SEBS is added, it reduced to 2.5. As the SEBS content increased to 5 wt %, the final recovered stretch ratio increased to 3.5 again. Saturation of SEBS increases the elasticity and,
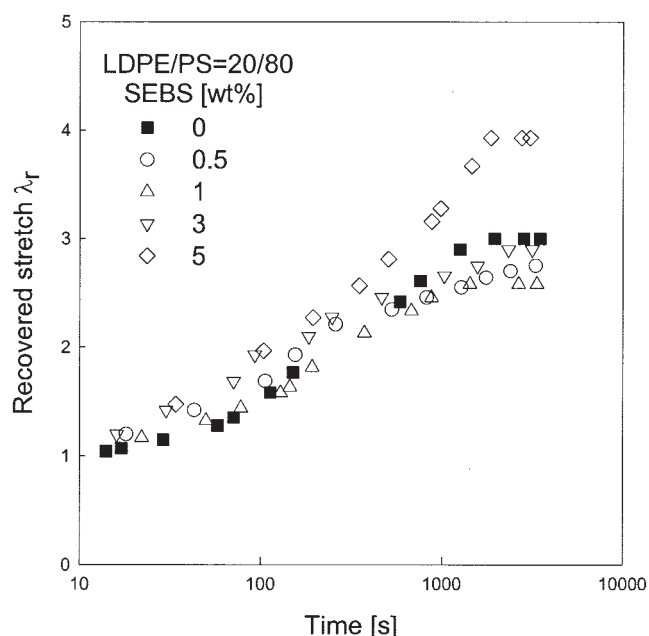
as a result, increases the melt recovery. From these results, the critical concentration of SEBS as a compatibilizer in LDPE/PS blends is believed to be around 3 wt %.

CONCLUSIONS

The effects of compatibilizer SEBS on the interfacial tension and rheological properties of LDPE/PS blends have been investigated. The interfacial tension was measured by the breaking thread method. The measured interfacial tension of LDPE/PS blends decreased rapidly with SEBS contents to 1 wt %, and then leveled off to a saturation value. The storage modulus of LDPE/PS blends showed that there is a critical concentration of SEBS. Up to 1 wt %, SEBS lowered the storage modulus at low frequencies by reducing the interfacial energy. Over 3 wt % of SEBS, however, increased the storage modulus. This is due to the saturation of SEBS between the phases. Similar results were obtained from the elongation viscosity and recovery tests. With 1 wt % of SEBS, strain hardening and recovery after elongation were relieved in the LDPE/PS = 20/80 blend. More addition of SEBS increased the strain hardening and recovered stretch ratio. As a result, it is concluded that the critical concentration of SEBS in LDPE/PS blends is around 3 wt % over which, the elasticity increases though the interfacial tension is constant.

Figure 10 Recovered stretch ratios of various SEBS contents of LDPE/PS = 20/80.

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