The effect of SEBS on Interfacial Tension and Rheological Properties of LDPE/PS Blends

H. S. Yang, G. J. Nam*, H. S. Kim**, J. W. Lee

Department of Chemical Engineering, Sogang University
*R&D Center for Chemical Technology, Hyosung Corp.
** Department of Chemical Engineering, Dankook University

LDPE/PS 블렌드계의 계면장력과 유변물성에 미치는 SEBS의 영향

양현석, 남기준*, 김형수**, 이재욱

서강대학교 화학공학과
*(주)효성 화학연구소
**단국대학교 화학공학과

Introduction

The morphology of the immiscible polymer blend system, which significantly influences the rheological and mechanical properties, is closely related to the interfacial characteristics. It is quite important, therefore, to elucidate the relationship between rheological properties, morphology, and interfacial tension. The common rheological behavior of immiscible polymer melt is the increase of elasticity at low frequency range in the oscillatory test. This behavior is related to the interfacial tension of two phases. Several methods have been proposed to measure the interfacial tension. They are pendant drop method(1), spinning drop method(2), and breaking thread method(3), etc. Recently, imbedded fiber retraction (IFR) method was used(4,5) and other methods have been introduced which are using the shear oscillation test.

In this study, breaking thread method was used to measure the interfacial tension between PS and LDPE, or that between PS and LDPE containing various amount of SEBS as a compatibilizer. Also, the effects of compatibilizer on the morphology and rheological properties have been investigated.

Experimental

LDPE(Tm 107.43°C, MI 3.0 g/10min, density 0.920 g/cm^3), PS(Tg 97.11°C, MI 3.3 g/10min, density 1.05 g/cm^3), and SEBS(density 0.9 g/cm^3, MI 65 g/10min, EB block 70%, Styrene block 30%) were used in this study. The effect of block copolymer SEBS as a compatibilizer was studied with 20/80 LDPE/PS blends. The copolymer compositions were 1, 2, 3, 5, 7, 10wt% relative to the total weight of the blend. Prior to mixing operation, LDPE and PS were dried over 24 hours at 80°C, and SEBS over 12 hours at 60°C in an air circulating oven before being compounded to prevent the hydrolytic degradation during processing. Blending was carried out in a melt mixer(Rheomix600-roller blade, Haake) with 60rpm at 210℃ for 10 minutes. Morphology of blend was observed from scanning electron microscope (HITACHI S-2500).

Measurement of interfacial tension was performed in the following procedure. Films of LDPE/SEBS were pressed using a Carver laboratory hot press at 210℃, and PS threads were obtained by drawing melted pellets on a hot plate. The PS thread(50~100μm diameter, 15mm length) was embedded in two LDPE/SEBS films(10mm×10mm). Samples were dried in an vacuum oven at 100℃ for 24 hours to remove the voids and residual stress between the thread and films. Optical microscope(Nikon Optiphot 2-pol) was used to observe the shape changes of sample. Hot stage(Mettler FP82HT) and controller(Mettler FP90 central processor) were used to control temperature to 210°C. Images were taken pictures and the amplitudes and wavelength of the thread were analyzed as time.

Plate-plate rheometer (ARES, Rheometrics Scientific) was used to measure the dynamic modulus and zero shear viscosity. Experiments were carried out with 25mm plate diameter, 1.5mm gap distance, 10% strain rate, and 0.1~100rad/sec frequency ranges.

Result and Discussion

Figure 1 shows the typical pictures of PS thread distortion changes as time. The initial sinusoidal distortion appears after 33 minutes, and it breaks up into perfect spheres after 87 minutes. Distortion growth rate were calculated from the slope of Fig. 2, and the measured interfacial tension of LDPE/PS system is 5.52dyne/cm. The changes of interfacial tension as SEBS contents are represented in Figure 3. It decreases rapidly with SEBS contents to 1wt% and then level off to a saturation value of 3.1dyne/cm. These results could be related to the change of morphology.

Figure 4 shows the SEM morphology of LDPE/SEBS/PS blends for SEBS contents from 0wt% to 5wt%. When the SEBS content is 1wt% (Fig. 4(b), x5,000), the overall size of the dispersed phase decreased than that of LDPE/PS:20/80 (Fig. 4(a), x1,000). SEBS acts as a compatibilizer, reduces the interfacial energy, and consequently reduces the size of the dispersed phase. When SEBS content is 5wt% (Fig. 4(c), x5,000), the size of the dispersed phase is similar to that of 1wt% SEBS. It is consistent in a quantitative sense with the interfacial tension results. Large amount of micelles can be observed at the LDPE/PS interfaces in Fig. 4(c), which are due to the saturation of the interface between the LDPE and PS phases.

The storage modulus result is represented in Fig. 5. The LDPE/PS composition was set to 20/80 and SEBS contents were varied as 1, 2, 3, 5, 7, 10wt%. The results obtained with 3wt% compatibilizer were the same as those obtained with 2wt% and are not presented here for the shake of clarity. When the SEBS content is 1wt%, there is a slight drop of storage modulus at low frequency ranges. As the SEBS contents increase over 3wt%, however, there is a dramatic increase of storage modulus. This is somewhat controversial to the result of interfacial tension, and is due to the saturation of the interface and micelle formation.

Conclusion

The relationships between interfacial tension and rheological properties have been investigated for LDPE/PS blend system. SEBS was used as a compatibilizer. The interfacial tension of LDPE/PS blend, which was measured by breaking thread method, was decreased rapidly with SEBS contents to 1 wt% and then level off to a saturation value. Also, there was a slight drop of storage modulus of LDPE/PS at low frequency ranges when 1wt% of SEBS was added. As SEBS contents increased over 3wt%, there was a dramatic increase of storage modulus. It was because of the saturation of the interfacial and micelle formation. The micelles were observed by SEM photograph.

The elongational viscosity behaviors of LDPE/PS with SEBS contents will also be mentioned in the presentation.

Acknowledgement

This study was supported by the research grants from the Korea Science and Engineering Foundation (KOSEF) through the Applied Rheology Center (ARC).

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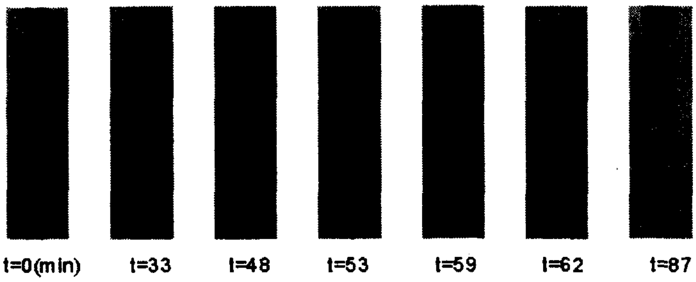


Fig. 1. Sinusoidal distortions on a PS thread embedded in a LDPE matrix.

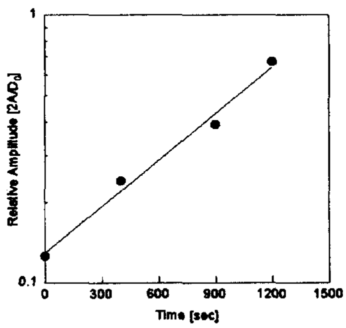


Fig. 2. Relative amplitude vs. time for LDPE/PS blend.

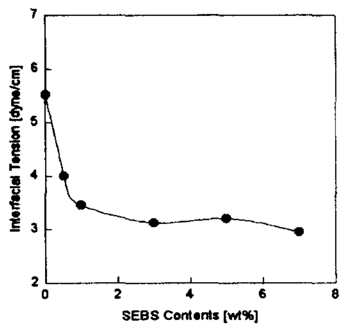
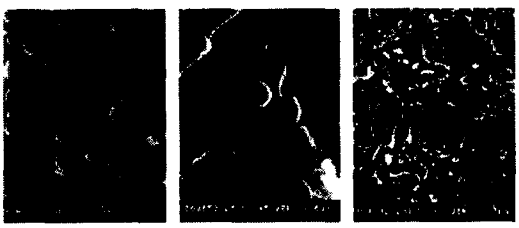


Fig. 3. Changes of interfacial tension with SEBS contents in LDPE matrix.



(a) x1,000 (b) x5,000 (c) x5,000

Fig. 4. Morphology of the LDPE/SEBS/PS blends with 20 wt% LDPE ; (a)SEBS 0 wt%, (b)SEBS 1wt%, (c)SEBS 5 wt%.

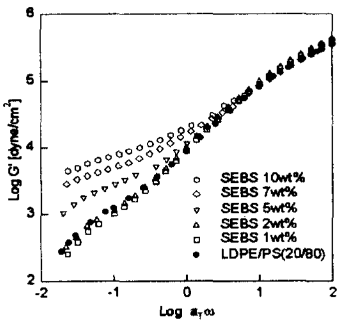


Fig 5.Storage modulus vs. frequency with LDPE/SEBS/PS blends with SEBS contents.