

Effect of Diblock Copolymers on Morphology and Mechanical Properties for Syndiotactic Polystyrene/Ethylene-Propylene Copolymer Blends

Won Mook Choi,¹ O Ok Park,¹ Jae-Gon Lim²

¹Center for Advanced Functional Polymers, Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 373-1, Gusong-Dong, Yuseong-Gu, Daejeon 305-701, South Korea

²Polyolefin Development III Project, R&D Center, Samsung ATOFINA Co. Ltd., San 411-1 Dokgod-Ri, Daesan-Up, Seosan, Chung Nam, 356-711, Republic of Korea

Received 18 June 2003; accepted 18 September 2003

ABSTRACT: Interfacial agents are often used to compatibilize immiscible polymer blends. They are known to reduce the interfacial tension, homogenize the morphology, and improve adhesion between phases. In this study, two diblock copolymers of styrene/ethylene-propylene (SEP), which have different molecular weights, were used to compatibilize a blend of syndiotactic polystyrene (sPS) 75% and ethylene-propylene rubber (EPR) 25% so as to extend the applications of sPS as incoming thermoplastics. The morphological analysis and emulsification curve, which relates the average size of the dispersion particles to the concentration of diblock copolymers added, was used to investigate the efficiency of the interfacial agents on the blend morphol-

ogy. A notched izod impact test and a tensile test were also performed to determine the compatibilization effect of different molecular weight copolymers on the mechanical properties of the blends and to establish links between morphology and mechanical properties. Results suggest that the lower molecular weight diblock copolymer showed an effective emulsifying capacity for sPS/ERP immiscible blend in morphology and mechanical properties. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3618–3626, 2004

Key words: syndiotactic polystyrene; diblock copolymer; styrene/ethylene-propylene copolymer

INTRODUCTION

Syndiotactic polystyrene (sPS) was first synthesized by using homogeneous organometallic catalytic systems based on titanium compounds and methylaluminumoxane.¹ Its characterization has been of considerable interest. sPS is a new crystalline polymer with a high melting temperature (270°C) and its crystallization rate is very fast in comparison with that of isotactic polystyrene. sPS has some superior properties such as heat resistance, chemical resistance, water/steam-resistance, and so on. As such, it is recognized as a promising crystalline thermoplastic material for use in engineering applications. Although sPS has many desirable properties as an engineering thermoplastic, its main disadvantage is its low impact strength. Therefore, improvements in the impact strength are very

essential to the expansion of its various applications.^{2–4}

For this purpose, blending with a rubber component that can act as an impact modifier is an effective, low-cost strategy.^{5–7} However, the vast majority of polymer pairs is mutually immiscible and, when blended, display very poor mechanical properties, due to their coarse, heterogeneous morphology and weak adhesion. The effective way to solve this problem is to incorporate a third component, or interfacial agent, into the immiscible blend. Block copolymers have been shown to be effective interfacial agents for many incompatible blends of homopolymers. Each block of a diblock or multiblock copolymer is usually either miscible or has strong affinities, with one of the two homopolymer phases. Thus, block copolymers can act by migrating to the interface between the homopolymers. It is believed that each block then localizes itself in its respective phase, thus reducing interfacial tension and promoting adhesion between phases. Then, the average size of a dispersed phase and the relative effect of coalescence can be subsequently decreased. The efficiency of this copolymer in the immiscible blend strongly depends on its molecular architecture, molecular weight composition, and content.^{8–11} It is well known that block copolymer is found to be

Correspondence to: O. O. Park (ookpark@kaist.ac.kr).

Contract grant sponsor: Ministry of Commerce, Industry, and Energy.

Contract grant sponsor: Brain Korea 21 Project of the Ministry of Education (MOE) of Korea.

Contract grant sponsor: Center for Advanced Functional Polymers.

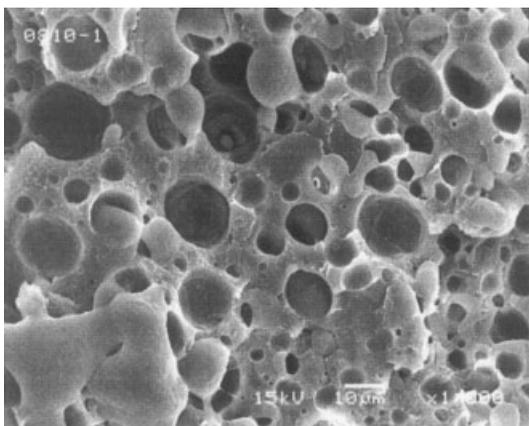


Figure 1 SEM of cryofractured and hexane-etched surface of sPS75/EPR25 without copolymer.

more efficient than graft, and when block copolymers are compared, the diblock copolymer is preferred to the triblock one.

Matos et al.¹² studied a system of 90% PS and 10% ethylene-propylene rubber (EPR) compatibilized by different triblock and star-shaped copolymer modifiers. It was found that the molecular weight of satu-

rated triblock copolymers of styrene/ethylene-butylene/styrene (SEBS) did not have a significant effect on their emulsification capacity for this blend. However, the efficiency of the modifier is strongly influenced by its chemical composition and molecular architecture. Thus, star-shaped copolymers did not perform as well as triblock copolymers of similar composition. Saturation of the middle block of the triblock copolymer also has an important effect: the SEBS copolymers were better emulsifiers than a copolymer of similar molecular weight but with a butadiene central block.

Cigana et al.¹³ used a series of diblock copolymers of styrene/ethylene-butylene (SEB) to modify an 80% PS and 20% EPR blend. An effect of modifier molecular weight on the critical concentration for emulsification was observed in this case (contrary to what was shown in the triblock work), but there was no effect on the equilibrium domain diameter. Also, symmetrical diblock copolymers containing 50 wt % styrene were shown to be more effective than asymmetrical copolymers containing 30 wt % styrene of similar molecular weight. Finally, inserting a taper between the blocks did not affect the emulsification capacity of the modifier.

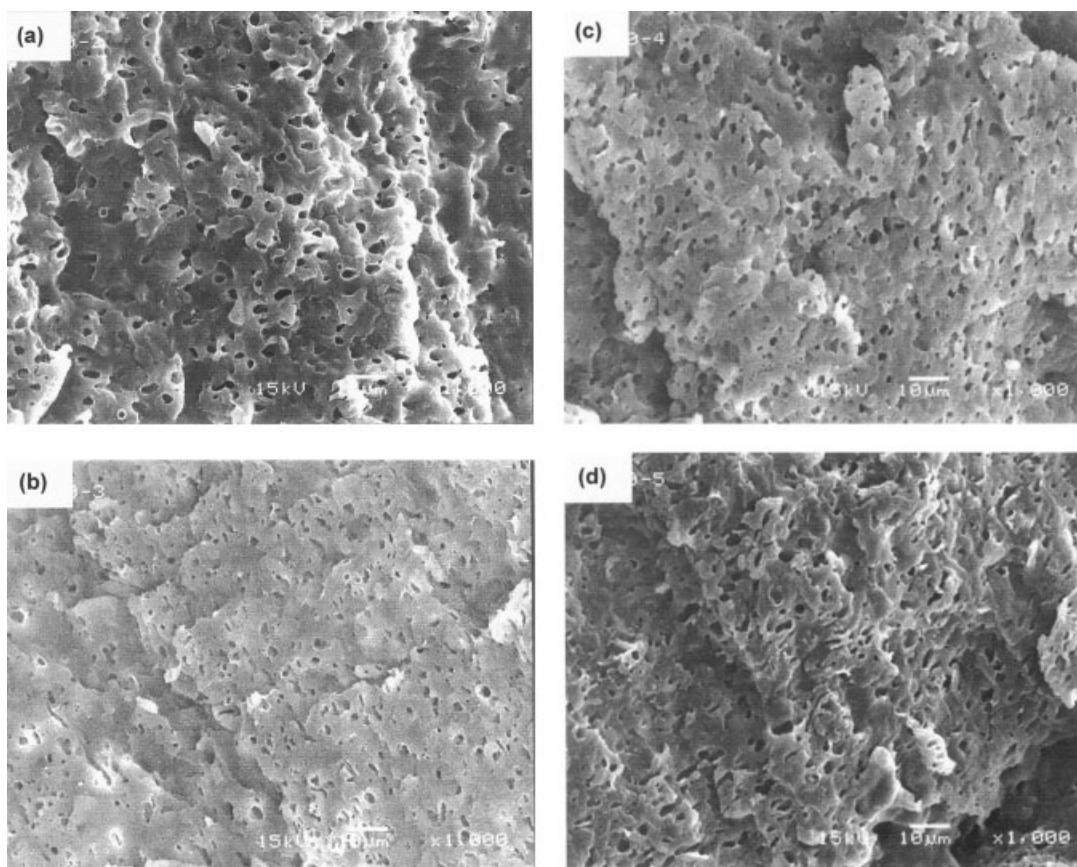


Figure 2 SEM of cryofractured and hexane-etched surface of sPS75/EPR25 blends with SEP (G1): (a) 3, (b) 5, (c) 7, and (d) 10 wt %.

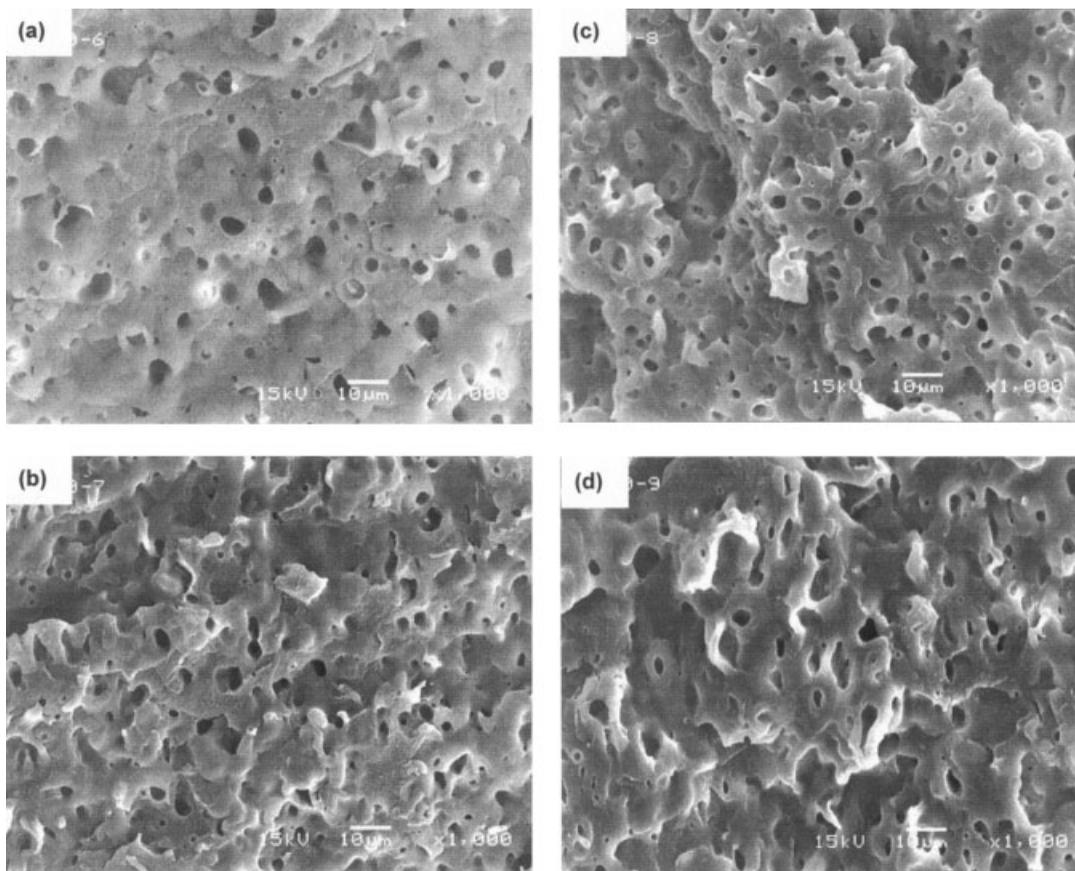


Figure 3 SEM of cryofractured and hexane-etched surface of sPS75/EPR25 blends with SEP (G2): (a) 3, (b) 5, (c) 7, and (d) 10 wt %.

This work will focus on the emulsification efficiency of diblock copolymers (SEP) with different molecular weights in sPS and EPR blend. We observed the rela-

tion of the morphology of compatibilized polymer blends and the resulting mechanical properties. Because the study of evaluation of the efficiency of dif-

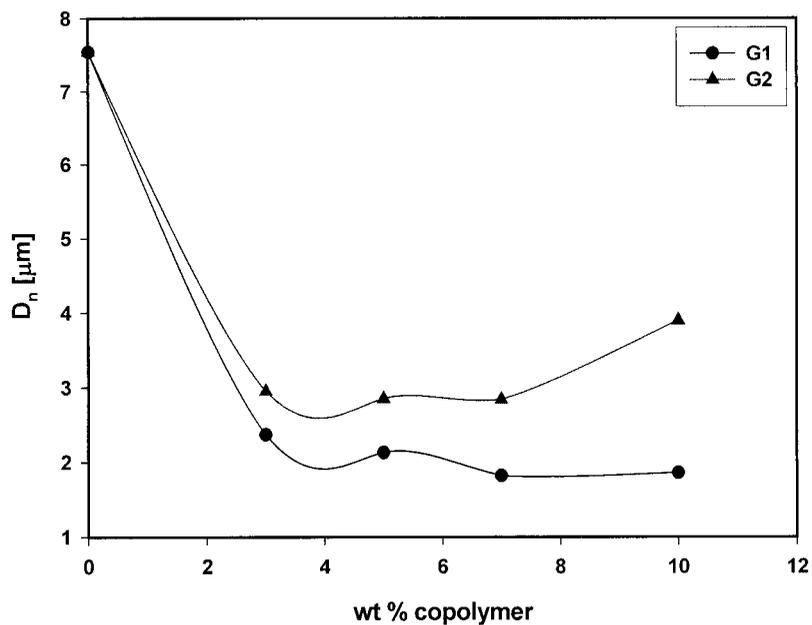


Figure 4 EPR particle diameter versus added copolymer.

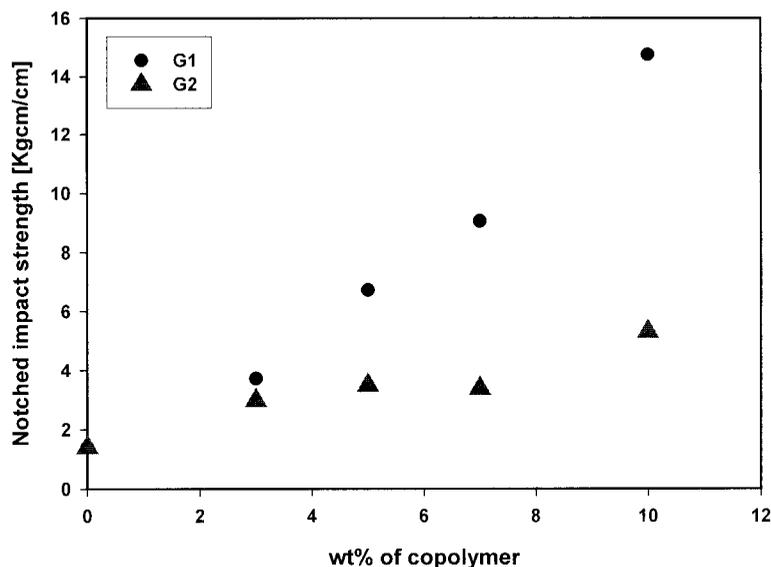


Figure 5 Notched impact strength versus added copolymer.

ferent types copolymers in immiscible sPS/EPR blends is rare, this study is important for the expansion of the applications of sPS as an incoming thermoplastic.

EXPERIMENTAL

Materials

The system used consists of a matrix of sPS with M_w of 375,000, supplied by Samsung General Chemicals Co. Ltd. (SGC, Korea), a minor phase of EPR with M_w of 244,500, and a random copolymer containing 68% ethylene, supplied by Kumho Polychem (070P, Korea). The interfacial agents were supplied by SGC. They consist of two SEP diblock copolymers, containing 31% styrene. Low molecular weight of SEP (G1) with M_n of 85,000 and high molecular weight of SEP (G2) with M_n of 130,000 were prepared in SGC, respectively.

Blends preparation

All materials were dried in a vacuum oven at 80°C for 24 h before use. Blending with constant rubber content (25 wt %) was carried out in a Haake Rheo Mixer 600 at 275°C for 6 min at a rotor speed of 50 rpm, and then the materials were cooled down in air. Blends were prepared with interfacial agent concentrations of 0, 3, 5, 7, and 10% based on the total weight of blends. Thus, the sample denoted as G1-3 has the following composition: 75 parts sPS, 25 parts EPR, and 3 parts of G1.

The blended samples were then molded into 3-mm-thick plates by using a compressing mold at 280°C for

mechanical characterization and morphological analysis.

Characterization of samples

Samples were held under -100°C with liquid nitrogen for 10 min to minimize surface deformation while cutting. Extraction of the minor phase was performed by immersion in *n*-hexane for 1 min. Morphological analysis of the fractured surfaces after an izod impact test was carried out without extraction of the minor phase.

The samples were then gold-coated prior to scanning electron microscopy (SEM). Micrographs were taken by using a JEOL scanning microscope. Diameters of the minor phase were determined from surface area measurements by using an image analysis pro-

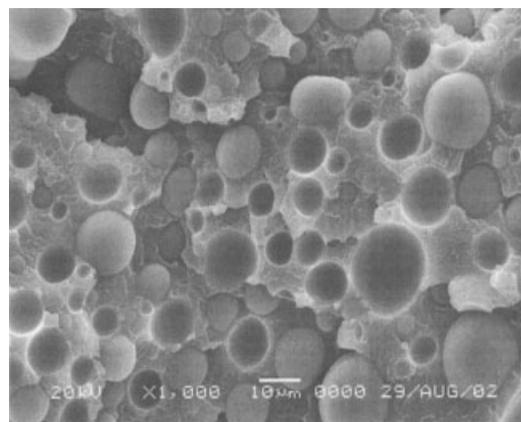


Figure 6 SEM of fractured surface after impact test of sPS75/EPR25 without copolymer.

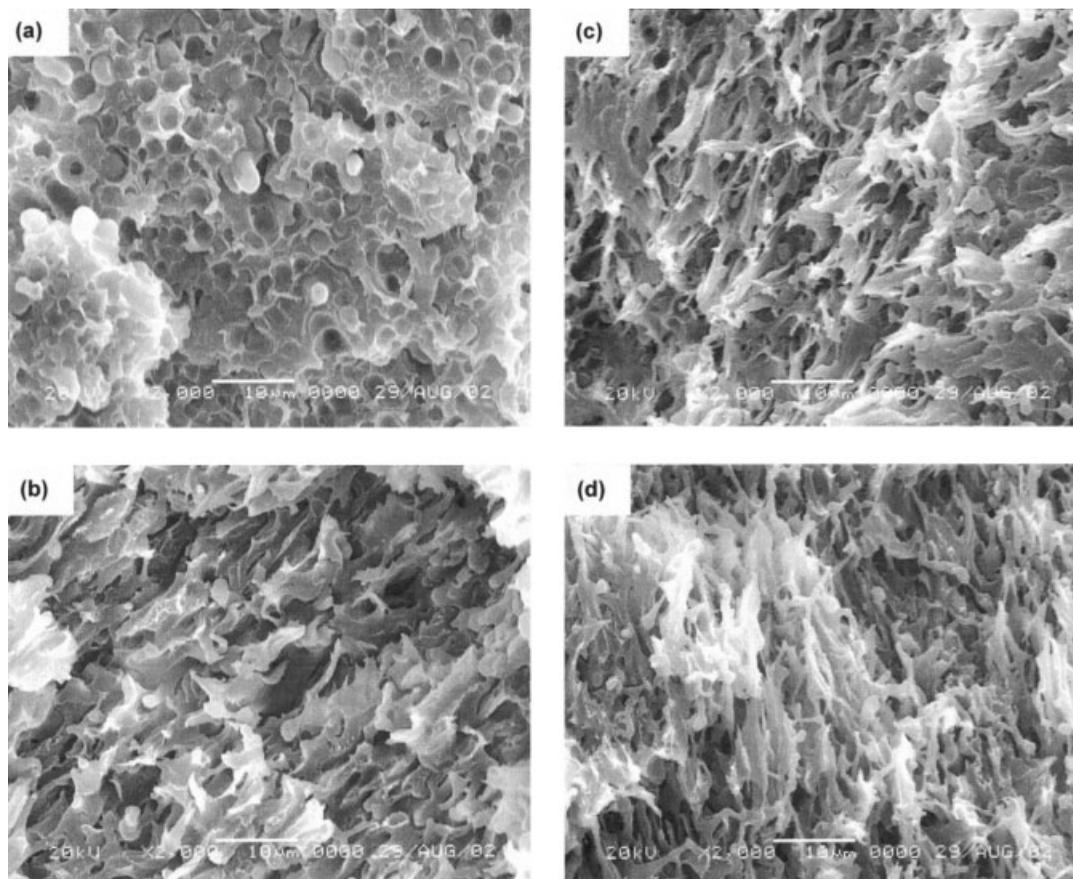


Figure 7 SEM of fractured surface after impact test of sPS75/EPR25 with SEP (G2): (a) 3, (b) 5, (c) 7, and (d) 10 wt %.

gram. To minimize the statistical errors, an average of 200–300 particles per sample was considered. More than one SEM micrograph per sample were usually analyzed. Because not all the particles observed were systematically cut through their equator, a correction was applied, as previously reported by Wu.¹⁴

The notched izod impact test of the rectangular specimen ($3 \times 13 \times 67$ mm) of samples was measured by Test Machine Inc. model 43-02 at 23°C according to the method described in ASTM D-256. Test specimens were cut from 3-mm-thick plates compression molded at 280°C and all data were taken as an average of five test runs.

Tensile properties (tensile strength and elongation at break) were measured with an Instron tensile tester at room temperature and at a crosshead speed of 10 mm/min. Test specimens were prepared by using a Mini-Max mold and reported values are the averages of five tests.

The dynamic melt viscosity was measured as a function of frequency by using an Advanced Rheological Expansion System (ARES, Rheometric Scientific Inc.) at a constant temperature of 280°C. Corn plate geometry was used. Disk-shaped specimens of 25 mm diameter were prepared from the molded 1-mm-thick sheets. Before measuring the rheological properties of

the samples, strain sweep tests at various frequencies were carried out to confirm that the applied strain does not exceed the limit of linear viscoelastic behavior. 10% strain was found to be suited to all samples in this study.

RESULTS AND DISCUSSION

Morphology

Figure 1 shows the morphology of the cryofracture surface of binary (noncompatibilized) sPS75/EPR25 blend. The SEM analysis reveals a typical morphology of an immiscible blend with the polydispersity of large and spherical EPR particles in the sPS matrix, which is the result of high interfacial tension and coalescence. Figures 2-3 show that the addition of SEP diblock copolymers with two different molecular weights changes the phase morphology of blends. These micrographs reveal clearly that by addition of a copolymer at any concentration, the EPR-dispersed particles exhibit significant size reduction. The particle size of the dispersed EPR phase in blends is decreased significantly with the addition of G1. Furthermore, when compared with the morphology of uncompatibilized blend in Figure 1, the blends used G1 to show a fine distribution of particles.

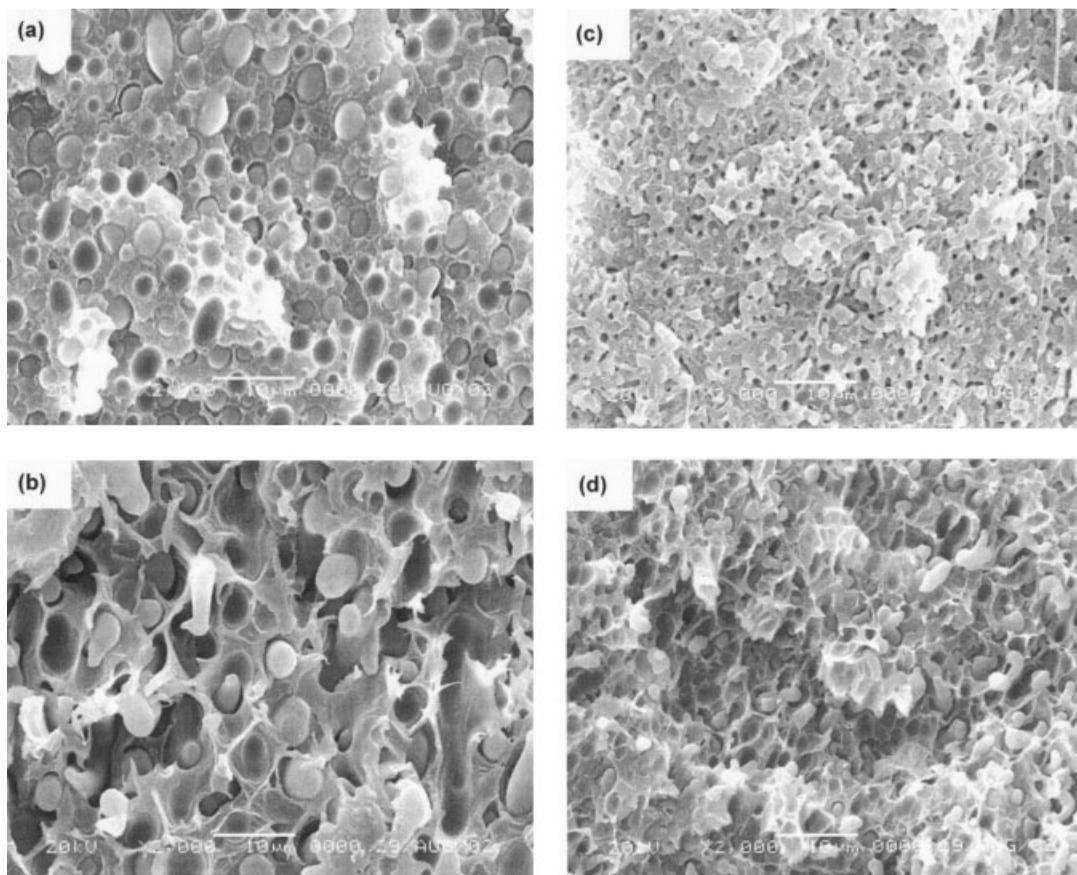


Figure 8 SEM of fractured surface after impact test of sPS75/EPR25 with SEP (G1): (a) 3, (b) 5, (c) 7, and (d) 10 wt %.

When the G2, a high molecular weight diblock copolymer, is used as a compatibilizer, a change in morphology of blends is shown, as in Figure 3. The particle size of the dispersed EPR phase is decreased with 3 wt % of G2, as shown in Figure 3(a). However, when compared with the corresponding blends used G1 in Figure 2, it reveals that the size of the dispersed EPR phase in blends using G2 is larger and more irregular, indicating that the added G1 acts as an effective compatibilizer to reduce the size of the dispersed EPR phase.

The computed size of the dispersed EPR in blends is plotted as a function of the added amount of copolymer in Figure 4. The emulsification curve for the blends added with the lower molecular weight copolymer, G1, clearly shows a better effect on reducing the size of dispersed phases. Only 3 wt % of G1 allows for a significant particle reduction to about $2.3 \mu\text{m}$ under these processing conditions, this size being threefold smaller compared with the uncompatibilized blend. When the G1 is added further, this equilibrium particle size of about $1.8 \mu\text{m}$ is observed and maintained steadily with as much as 10 wt % of G1. However, when the G2 is added in sPS/EPR immiscible blend, the equilibrium reaches about $2.8 \mu\text{m}$ at 7 wt %, and at 10 wt %, the particle size rather increases to $3.9 \mu\text{m}$ because of aggregation of the particles. G1, the lower

molecular weight diblock copolymer, is by far more efficient than G2 in reducing and stabilizing the EPR dispersion in the sPS matrix.

It is worth mentioning how sensitive the compatibilization is to the nature of the blend components and the molecular characteristics of the selected compatibilizing copolymer. Based on the present investigation, because the ability of low molecular weight SEP (G1) to migrate to the interface between sPS and EPR phases is superior to that of high molecular weight SEP (G2) due to its low viscosity, G1 has the better interfacial agent effect in sPS/EPR blends.

Impact strength

The impact strength of unmodified copolymer and the addition of two types of diblock copolymer (G1, G2) are reported in Figure 5. The impact strength of sPS/EPR blends with G1 added increases significantly about 10-fold higher than the unmodified blend, implying that G1 effectively improves the interfacial adhesion between sPS and EPR phases. When G2 is used, however, the impact strength of the blends increases marginally compared to G1. These results indicate that the high molecular

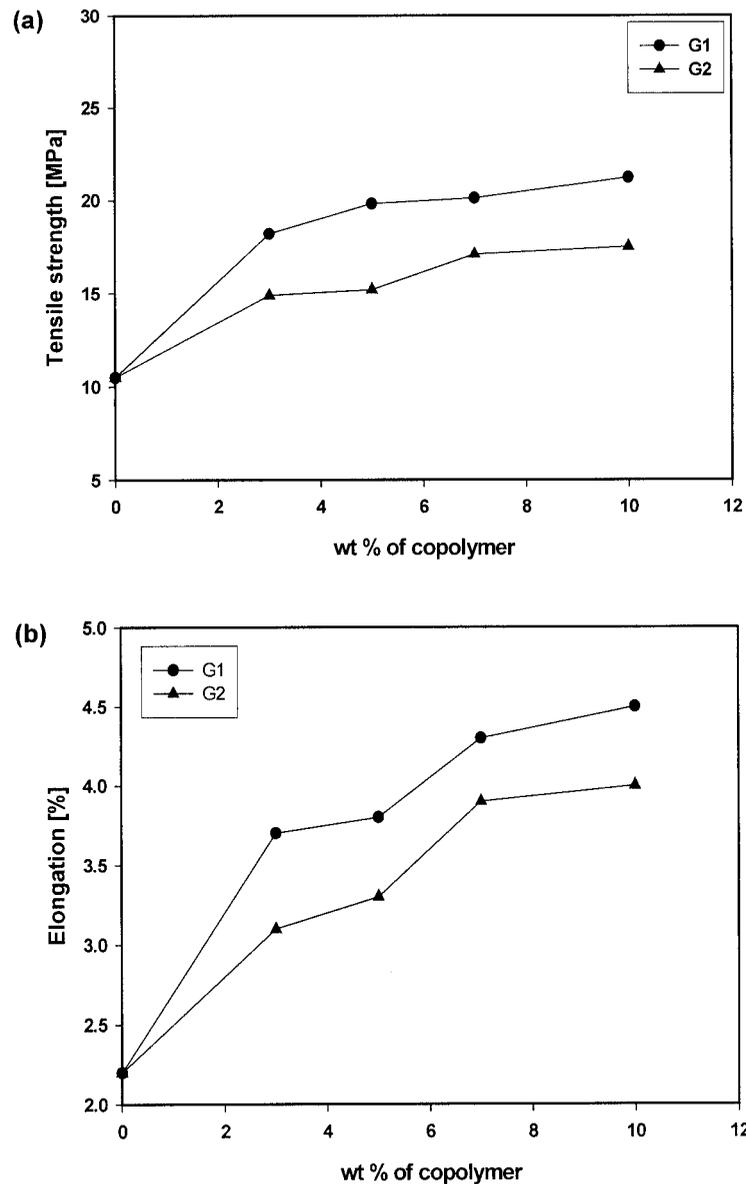


Figure 9 (a) Tensile strength and (b) elongation at break versus added copolymer.

weight diblock copolymer (G2) is not as effective in increasing the impact strength as the low molecular one, which easily migrates to the interface of two phases because of its low viscosity and reducing the interfacial tension.

We examined the morphology of the fractured surface of the unmodified sPS/EPR blend compatibilized with diblock copolymers after the notched impact test shown in Figures 6-8, respectively. The fractured surface morphology in Figure 6 of the uncompatibilized blends exhibits a typical morphology of blend with a brittle nature: the shape of particles is round and the particles are easily pulled out; thus, the interface of the dispersion is clear, implying a poor adhesion between sPS matrix and dispersed EPR phases. Figure 7 shows a variation in the morphology of fractured surfaces of the sPS/

EPR blends with G1 after the impact test as a function of diblock copolymer contents. As the amount of G1 in blends increases, the fractured surface of the blends becomes rougher, indicating the behavior of ductile blends. Moreover, the EPR particles seem to adhere strongly to the sPS matrix, resulting in a significant increase in the impact strength of compatibilized blends. In contrast to the G1 blends, the blends with G2 (Fig. 8) show that the shape of the EPR particles is still round and the particles are easily pulled out, and the deformation of EPR dispersion rarely occurs compared to the G1 blends, which implies a poor adhesion between the sPS matrix and EPR dispersion. This may be responsible for the low impact strength of the sPS/EPR blends with G2 in comparison with the G1 blends.

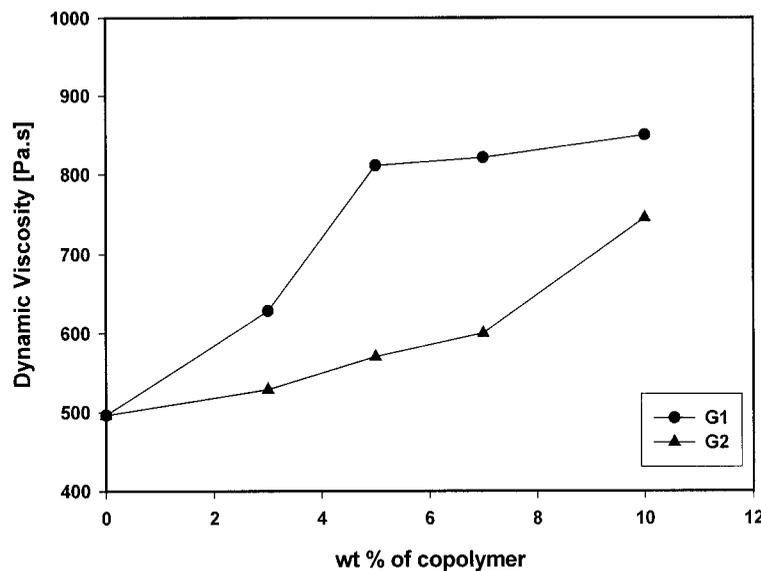


Figure 10 Dynamic viscosity (determined at 1.0×10^{-1}) versus added copolymer.

Tensile properties

The tensile strength and elongation at break of the sPS/EPR blends, unmodified and added with the various contents of each type of copolymer, are shown in Figure 9(a, b). For the unmodified sPS75/EPR25 blend, a tensile strength of 10.5 MPa and an elongation at the break of 2.2% are clear indications of the poor mechanical properties. The addition of the SEP diblock copolymers improves this brittle behavior. For instance, the low molecular weight G1 increases greatly tensile strength and elongation at the break, 21 MPa and 4.5% at 10 wt % of G1, respectively. However, the high molecular weight G2 imparts a little improvement of tensile properties, when compared with the G1. The effect of the copolymer molecular weight on the tensile properties is similar to that observed for the morphology analysis and impact strength: the low molecular weight G1 shows a better interfacial agent effect in the tensile properties compared with the relatively high molecular weight G2. The tensile properties are sensitive to interfacial adhesion, implying that G1 effectively strengthens the interfacial adhesion between the sPS matrix and EPR dispersion.

Dynamic viscosity

The interfacial interaction that the copolymers should induce in the blend is expected to also modify its viscous behavior at low frequencies. Indeed, the rheological properties such as viscosity and storage modulus at the melt state were previously used to elucidate the interfacial activity of block and graft copolymers in immiscible polymer blends. Brahim et al.¹⁵

showed that an important increase in the low-frequency viscosity of high-density polyethylene (HDPE80)/high impact polystyrene (HIPS20) was observed when the concentration of hydrogenated polybutadiene-*co*-polystyrene (PB-*co*-PS) diblock copolymers added to these blends was increased.

In Figure 10, the dynamic viscosity of the blends is plotted as a function of the amount of the added copolymer at a constant frequency of 1.0×10^{-1} rad/s. This figure is constructed from individual viscosity-frequency plots obtained for each copolymer modified blend.

It is observed that the magnitude of dynamic viscosity of the G1-added blends increases significantly with an increase in the amount of G1 in blends. This is probably due to a coupling effect of the block copolymer—when the G1 is added to the sPS/EPR blend, it gives better interfacial adhesion between the sPS matrix and dispersed EPR phase, as the PS and EP blocks in G1 penetrate into the sPS matrix and the EPR phase, respectively. When G2 is added to the blend, the magnitude of dynamic viscosity increases slightly, unlike the G1-added blends, although the G2 has higher viscosity. From these results, it is suggested that the coupling effect of the low molecular weight G1 is greater than that of the high molecular weight G2. This is in good agreement with the morphological and mechanical properties results.

CONCLUSION

The effect of molecular weight of SEP diblock copolymer on the morphology, the mechanical properties approach, and rheological property was in-

vestigated. The reported morphological analysis results revealed clearly that the low molecular weight diblock copolymer (G1) exhibited good efficiency to reduce the size of the EPR dispersed phase. For blends compatibilized by the low molecular weight copolymer G1, the notched izod impact strength increased 10-fold at 10 wt % of G1, whereas the impact strength of the G2-added blend is slightly increased by an increase in the amount of G2. The morphology after impact test also showed the same trend for those samples, and it indicates that the addition of G1 gives good adhesion between the sPS matrix and the EPR dispersions. The dynamic viscosity of the G1-added blends is higher than that of the G2-added blends, although the G1 has a lower viscosity, indicating that the coupling effect of G1 is greater than that of G2. These results show that the low molecular weight copolymer was an efficient interfacial agent, and it is believed that it migrates effectively to the interface and penetrates into each corresponding phase more easily; this explains its capacity to significantly improve the blend toughness.

The authors thank the Ministry of Commerce, Industry, and Energy (MOCIE) for supporting this research. This work is

also partially supported by the Brain Korea 21 Project of the Ministry of Education (MOE) of Korea and by the Center for Advanced Functional Polymers supported by KOSEF.

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