

Preparation and Characterization of Syndiotactic Polystyrene/Ethylene-Propylene Copolymer Blends

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ABSTRACT: The reactive compatibilization of syndiotactic polystyrene (sPS)/oxazoline-styrene copolymer (RPS)/maleic anhydride grafted ethylene-propylene copolymer (EPR-MA) blends is investigated in this study. First, the miscibility of sPS/RPS blends is examined by thermal analysis. The cold crystallization peak (T_{cc}) moved toward higher temperature with increased PRS, and, concerning enthalpy relaxation behaviors, only a single enthalpy relation peak was found in all aged samples. These results indicate that the sPS/RPS blend is miscible along the various compositions and RPS can be used in the reactive compatibilization of sPS/RPS/EPR-MA blends. The reactive compatibilized sPS/RPS/EPR-MA blends showed finer morphology than sPS/EPR-MA physical blends and higher storage modulus (G') and complex viscosity (η^*) when RPS contents were increased. Moreover, the impact strength of sPS/RPS/EPR-MA increased significantly compared to sPS/EPR-MA blend, and SEM micrographs after impact testing show that the sPS/RPS/EPR-MA blend has better adhesion between the sPS matrix and the dispersed EPR-MA phase. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2084–2091, 2002

Key words: syndiotactic polystyrene; ethylene-propylene copolymer; reactive compatibilization

INTRODUCTION

To increase the compatibility of immiscible polymer blends, a number of strategies have been employed. One of the most frequently used methods is to add a third component that is totally or partially miscible with both phases. The third component may be a suitable block or graft copolymer. It is well known that a block copolymer is an effective compatibilizer for immiscible polymer

blends.^{1,2} Another method is to use reactive interfacial agents that have reactivity with specific functional groups. The reactive interfacial agent has a specific functional group and it can generate *in situ* formation of block or graft copolymer at the interface during the blend preparation by the reaction of functional groups incorporated onto the blend components.^{3,4} The reactive compatibilization method has been proved to be effective for controlling morphology in a variety of blend systems. However, research promoting a detailed understanding of the enhancement of interfacial properties resulting from reactive compatibilization is very limited.^{5,6}

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Numerous papers of polymer blend systems for toughening have been reported using maleic anhydride (MA)-grafted polymers as a reactive modifier with various copolymers.⁷ One of the well-known examples is DuPont's super tough nylon, where MA is first grafted onto poly(ethylene-co-propylene-co-diene) (EPDM) rubbers and then reacted with the terminal amine groups of nylons. A number of other engineering thermoplastics have followed with similar compatibilization strategies. Another functionalized polymer recently used in reactive polystyrene blends is poly(styrene-co-vinyl oxazoline) (RPS). The introduction of RPS started an interesting period of research on the utilization of oxazoline functionality in the reactive compatibilization of polystyrene blends. Research efforts have also been made on the functionalization of polymers with oxazoline and their use in interfacial reaction with other functional polymers.⁸

Because syndiotactic polystyrene (sPS) with a very high degree of stereospecificity (>96%) has successfully been synthesized by stereospecific polymerization,⁹ characterization of this new material 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 disadvantage is its low impact strength. Therefore, an improvement in the impact property is essential to expand its various applications. However, research on this subject is still very limited.

Blending of sPS with other rubbers can be a convenient way to increase the impact strength of sPS.^{10,11} Because the melt-processing temperature of sPS is very high due to its melting temperature, the rubbers for blending with sPS should be stable at that high temperature range. For this reason, ethylene-propylene rubber (EPR), a random copolymer of ethylene and propylene, is chosen as a rubber component. However, sPS is immiscible with EPR because of lack of specific interaction between these two polymers. Hence, we would like to introduce reactive components to induce the reactive compatibilization during blending. The reactive components used are maleic anhydride (MA)-functionalized EPR (EPR-

MA) and styrene-oxazoline copolymer (RPS). The utilization of oxazoline has been of interest in the reactive compatibilization of polymer blends.^{5,12,13}

The focus of this work is to assess two important factors, the miscibility of the sPS/RPS blend for use as a third component in the reactive compatibilization of sPS/RPS/EPR-MA, and the effect of chemical reaction on the mechanical and rheological properties of blends when RPS is used as a reactive compatibilizer.

EXPERIMENTAL

Materials

sPS, with a molecular weight (M_w) of ~375,000, was supplied by Samsung General Chemicals (SGC) Company, Ltd. RPS containing 5 wt% oxazoline (Epocros RPS1005) was received from Nippon Schokubai Company, Ltd. ($M_w = 156,000$). EPR of commercial grade (070P) with 68% ethylene was supplied by Kumho Polychem (melt index at 230°C and 2.16 kg is 0.6, and M_w is 244,500). EPR-MA was prepared in our laboratory by adding dicumyl peroxide (DCP; 0.25 phr) and MA (5 phr) according to a reported method.¹⁴ The grafted MA contents, measured by Fourier transform infrared spectroscopy (FT-IR) was 1.24 wt%. MA and DCP were used as a powder from Aldrich Chemical Company, Ltd. without further purification.

Blend Preparation

To study the miscibility of sPS/RPS blends, melt blending proceeded at 280 °C for 6 min in a Mini-Max molder and cooled in air. For the reactive blending of sPS/RPS/EPR-MA, all components were completely dried in a vacuum oven for 24 h at 80 °C before use. Blending with constant rubber content (25 wt%) was carried out in a Haake Rheo Mixer 600, at 280 °C for 6 min at a rotor speed of 50 rpm, and then cooled in air. The samples are injection-molded with a Mini-Max molder for the mechanical and rheological characterizations.

Characterizations

A differential scanning calorimeter (DSC; TA instrument DSC-2010) was used for thermal analysis under a nitrogen atmosphere between 0 and 300 °C (RPS was analyzed up to only 200 °C). Samples were heated to 300 °C for 3 min to fully

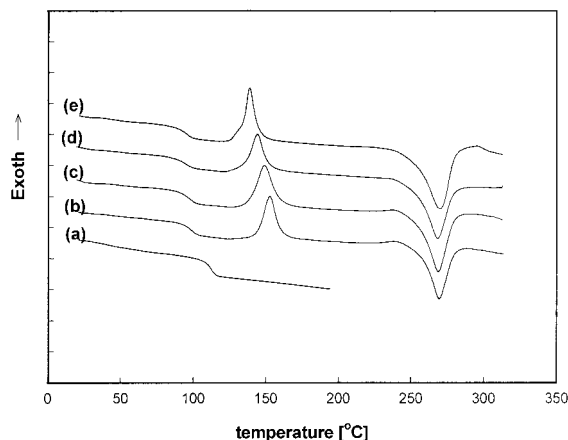


Figure 1 DSC thermograms of as-quenched sPS/RPS blends: (a) RPS; (b) sPS/RPS (70/30); (c) sPS/RPS (80/20); (d) sPS/RPS (90/10); (e) sPS at 20°C/min.

melt all crystals, quenched in liquid nitrogen, and then re-heated to that temperature at a scanning rate of 20 °C/min. Data were taken from the re-heating scan.

The rheological measurement was performed at 280 °C with a Rheometric Scientific Inc. advanced rheological expansion system (ARES) with a cone-plate fixture ($\varphi = 25$ mm) under a nitrogen atmosphere. The dynamic frequency sweep tests were carried out from 0.1 to 100 rad/s, and the strain used was 10%. Before measuring the rheological properties of samples, strain sweep tests at various frequencies were carried out to confirm that the applied strain did not exceed the limit of linear viscoelastic behavior.

The notched izod impact test of the rectangular specimen (3 × 13 × 67 mm) of sPS/RPS/EPR-MA blends was measured by Test Machine Inc. (model 43-02) at 23 °C according to the method describe in ASTM D-256. All specimens were injection molded and all data were taken as an average of five test runs.

The morphology of these samples was observed with a JEOL (JSM 5800LV) scanning electron microscope (SEM) at an accelerating voltage of 15 kV. The fracture surfaces of izod impact test samples were coated with gold to avoid charging.

RESULTS AND DISCUSSION

Miscibility of sPS/RPS Blends

In the ternary reactive blends of sPS/RPS/EPR-MA, one important point to consider is the misci-

bility between sPS and RPS. Some reports^{15,16} concluded that sPS/atactic polystyrene (aPS) blends are confirmed to be miscible by either crystallization kinetics or enthalpy relaxation. It is worthwhile to examine the miscibility of sPS/RPS blends in this study because RPS has a 5 wt% oxazoline functional group on the aPS main chain, which indicates RPS has different polarity from sPS.

All samples for glass transition temperature (T_g) characterization were initially heated to 300 °C to erase the thermal history of each sample, and then quenched from the melt state in liquid nitrogen before a second DSC scanning. The DSC thermograms of various compositions with one single clear T_g are shown in Figure 1. However, these results cannot be sufficient evidence of homogeneity because the appearance of a single T_g could arise from an overlapping of the T_g s of each polymer because of the small difference in T_g s of sPS and RPS. Therefore, further thermal analysis should be employed to determine the miscibility. The cold crystallization peak temperatures (T_{cc}) determined by DSC scanning are compared in Table I. The T_{cc} of neat sPS is the lowest; however, by increasing the fraction of RPS in the blends, the T_{cc} for the sPS segment increases steadily. This result suggests that the molecular segments of noncrystallizing RPS may intimately interact with the sPS segments. Intersegment interaction between sPS and RPS exists, and the noncrystalline nature of RPS might make it difficult for the sPS chains to crystallize. This segmental interaction results in the need for a higher T_{cc} for the sPS segment to be packed into a crystalline domain in the sPS/RPS blend than what would be needed for neat sPS.

The T_g transition breadth of sPS/RPS blends was also measured and compared. Although sPS and RPS have a small difference in T_g , the extents

Table I Thermal Transition Behavior of sPS/RPS Blend Samples

sPS/RPS	T_g (°C)	ΔT_g (°C) ^a	T_{cc} (°C) ^b
(100/0)	89.0	10.3	139.0
(90/10)	89.1	10.2	144.1
(80/20)	91.4	10.5	149.0
(70/30)	92.4	10.1	152.9
(0/100)	108.4	7.4	—

^a Transition breadth of T_g .

^b Cold crystallization temperature.

of T_g breadth may be used to determine whether or not there is overlapping of the T_g s of individual polymers. The transition breadth measured by TA instruments software remains quite constant ($\Delta = 8\text{--}10\text{ }^\circ\text{C}$) for various blend compositions, indicating the single T_g is not likely a partial superposition of two close T_g s but a single T_g of homogeneous mixture.

When the T_g s of polymers are very close to each other, another way to determine the miscibility between them is the enthalpy relaxation method, which occurs during physical aging and the subsequent enthalpy recovery in reheating. The use of enthalpy relaxation for determination of miscibility is based on the characteristic that relaxation of polymers at temperatures below the T_g results in decreases in many physical properties, such as enthalpy and density, that are recovered during reheating to above the T_g . This recovery is manifest as an endothermic peak in the heat capacity at a temperature ranging from well below the T_g to its upper edge. The position of this peak depends on the thermal treatment and on the structure of the material itself. Each polymer has its own individual aging behavior that is reflected in the position and magnitude of the recovery peak on heat through T_g .

The DSC thermograms of sPS, RPS, and sPS/RPS blends with various compositions (100/0, 90/10, 80/20, 70/30) after aging at $80\text{ }^\circ\text{C}$ for 6 h and thermograms of quenched samples are shown in Figure 2(i). As a result of physical aging, a peak of enthalpy relaxation is seen on the top of the T_g in each of the DSC curves, but for quenched samples, the enthalpy relaxation peak disappears. Apparently, there is only one identifiable enthalpy relaxation peak, suggesting that only one T_g transition is involved in each of the blend samples. The relatively sharp endothermic peak indicates that it is not possible that multiple T_g transition may be involved. Note that as a result of aging treatment, the T_g s of the blend samples are slightly elevated, but otherwise appeared to be a distinctly single transition. The result clearly revealed only one enthalpy relaxation peak, which more positively suggests only one T_g transition in each of the aged blend samples. Note that the RPS components again lead to increased T_{cc} of sPS in the aged sPS/RPS blends, which is in agreement with the cold crystallization behavior observed earlier. In Figure 2(ii), the thermograms of aged samples are collected to compare enthalpy relaxation peak change along the composition. Only one single enthalpy relaxation peak appears

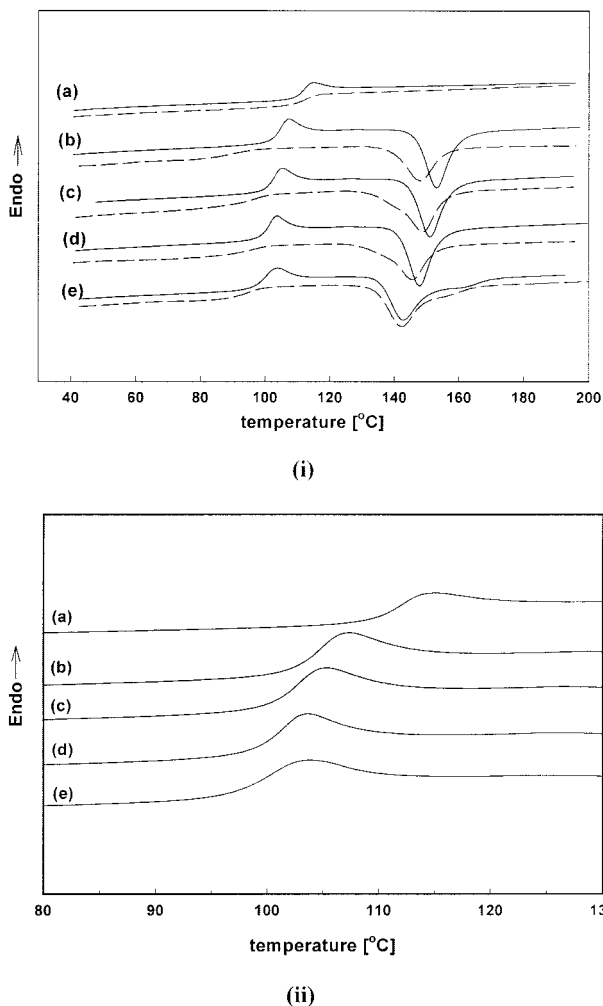


Figure 2 (i) DSC thermograms of aged (solid line) and quenched (dotted line) samples and (ii) a collection of thermograms of aged samples. Key: (a) RPS; (b) sPS/RPS (70/30); (c) sPS/RPS (80/20); (d) sPS/RPS (90/10); (e) sPS at $20^\circ\text{C}/\text{min}$.

between those of the two component polymers. This result suggests that the amorphous RPS is miscible with sPS, like aPS, although functional groups are attached on aPS chains.

sPS/RPS/EPR-MA Reactive Blends

Mechanical properties of a heterogeneous polymer blend are directly related to its microstructure, especially the size and shape of the dispersed phase. Incompatible polymer blends often have poor mechanical properties relative to their respective components because of their high interfacial tension, leading to poor control of morphology and stress transfer under loading in the

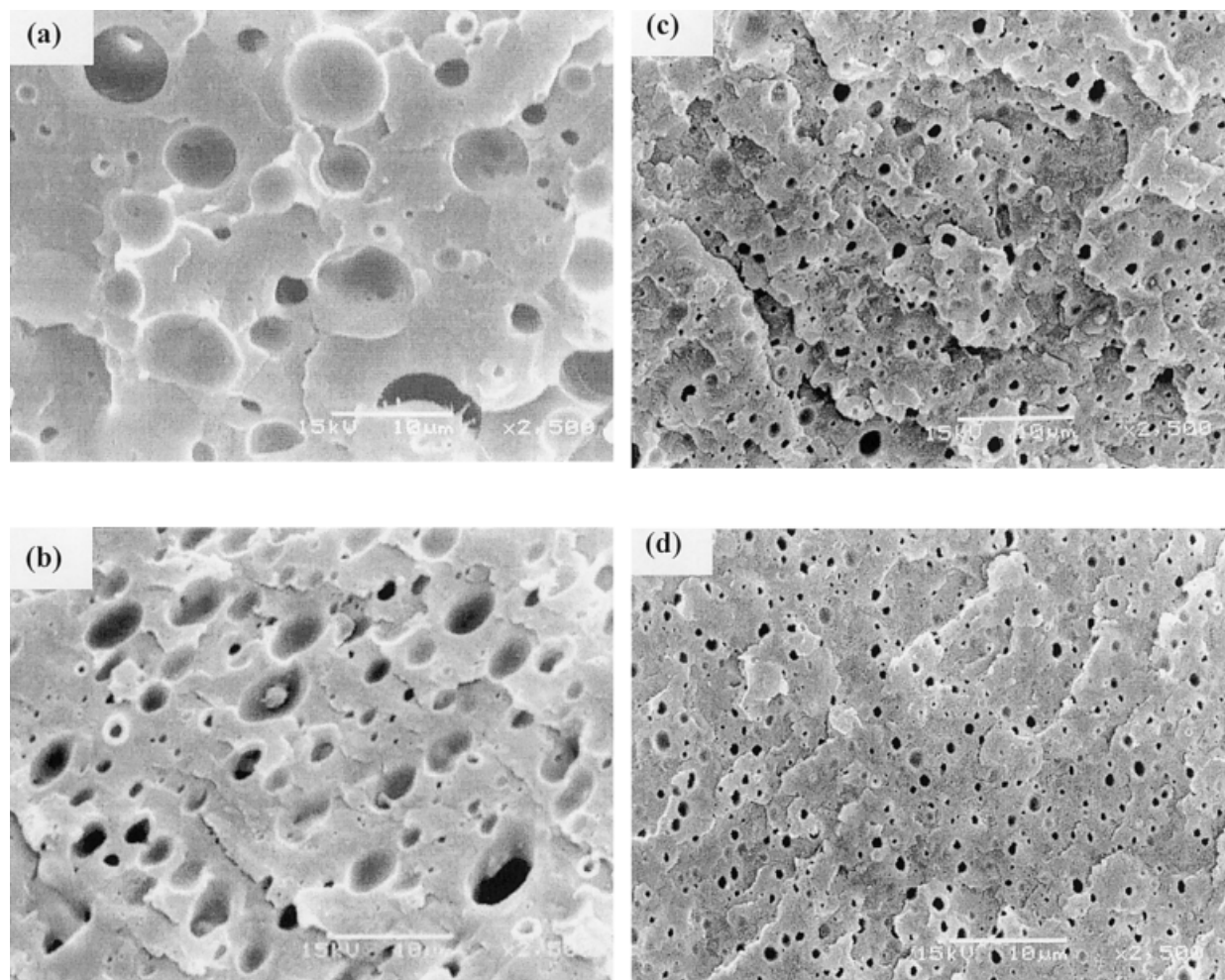


Figure 3 SEM micrographs of cryogenically fractured surfaces of (a) sPS/RPS (75/25), (b) sPS/RPS/EPR-MA (75/0/25), (c) sPS/RPS/EPR-MA (70/5/20), and (d) sPS/RPS/EPR-MA (65/10/25).

solid state. An efficient compatibilization in the blend can reduce the interfacial tension and enhance the interfacial adhesion between two incompatible polymers and thus improve its mechanical properties. A SEM micrograph of a cryogenically fractured surface etched with *n*-hexane is shown in Figure 3. The uncompatibilized sPS/EPR blend and sPS/EPR-MA (75/25) show a typical morphology of an immiscible blend nature. The large dispersed and spherical EPR or EPR-MA particles with different dimensions can be easily identified from this uncompatibilized blend because of the incompatibility between these two component polymers. The interface between sPS and EPR or EPR-MA is quite sharp, which is an indication of low interfacial adhesion. SEM micrographs of sPS/EPR-MA with added 5 and 10 wt% RPS components are shown in Figures 3c and 3d,

respectively. The general trend indicates that the dispersed EPR-MA particle size decreases with the addition of RPS. Size reduction of the EPR-MA phase domain in the blend can be attributed to the better compatibilization through the *in situ* formation RPS-co-EPR copolymer by the reactive blend system. RPS can react with EPR-MA simultaneously to produce the desired copolymers at the interface, and the compatibilizers formed *in situ* reduce the interfacial tension and result in a smaller domain size of dispersed phase particles.

To examine the reactive interfacial agents on the rheological properties of sPS/RPS/EPR-MA blends, the changes of storage modulus (G') and complex viscosity (η^*) against dynamic frequency were measured by ARES at 280 °C. The flow properties of polymer blends depend, among other factors, on the morphology and interfacial prop-

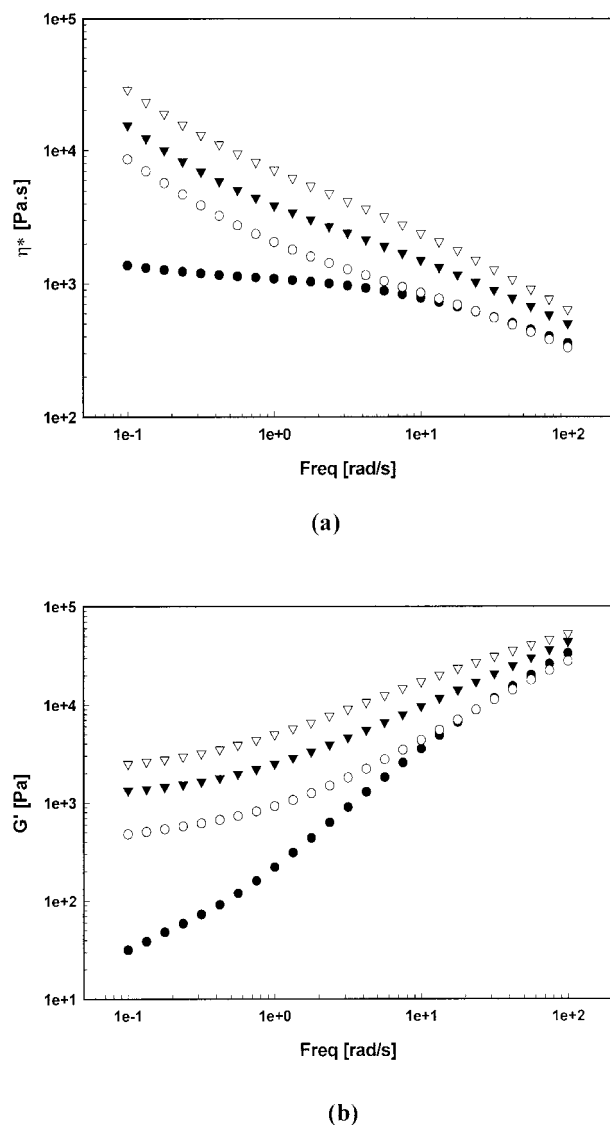


Figure 4 (a) Storage modulus (G') and complex viscosity (η^*) of (●) sPS; (○) sPS/RPS/EPR-MA (75/0/25); (▼) sPS/RPS/EPR-MA (70/5/25); and (▽) sPS/RPS/EPR-MA (65/10/25).

erties. A modification of morphology by added compatibilizers (e.g., reduction in particle size), can result in a change in flow properties of the blends. The rheological property (G' and η^*) changes of sPS/RPS/MA-EPR at 280 °C were plotted against frequency, as shown in Figure 4. As RPS increases, the values of η^* in Figure 4a, especially at low frequencies, increases significantly. The increase in complex viscosity with increase RPS content could be due to an increased interfacial adhesion as a result of copolymer formed *in situ* at the interface and to the fine rubber dispersion. The trends in the elastic be-

havior of blends, as indicated by G' , are similar to those for η^* . The increase in elasticity of the blends at low frequencies, which has frequently been reported for other systems,^{17,18} is usually attributed to the deformation of the dispersed particles and the recovery to their equilibrium shape due to interfacial tension. Both the complex viscosity and the storage modulus increase along the RPS contents; this result could be attributed to the interface interaction increase and the finer rubber domain by copolymer formed *in situ* during blending of polymer components.

The reactive compatibilization on the impact strength of sPS/RPS/EPR-MA blends is examined. As shown in Figure 5, the impact strength of the sPS/RPS/EPR-MA (65/10/25) blend increases about six times, and is three times higher than that of sPS and sPS/EPR-MA physical blend, which implies that the interfacial agent RPS effectively improved the interfacial adhesion between sPS and EPR phase and makes the dispersed EPR act as an effective stress transfer in sPS matrix. This effect of reactive compatibilization on the mechanical property of blends is also shown in the SEM micrographs (Figure 6) of the fractured surfaces after impact test. In the case of sPS/EPR-MA, the dispersed EPR domain maintained its round and large shape and easily pulled out at the impact test, implying a poor adhesion between the sPS matrix and dispersed EPR phase. With addition of the reactive compati-

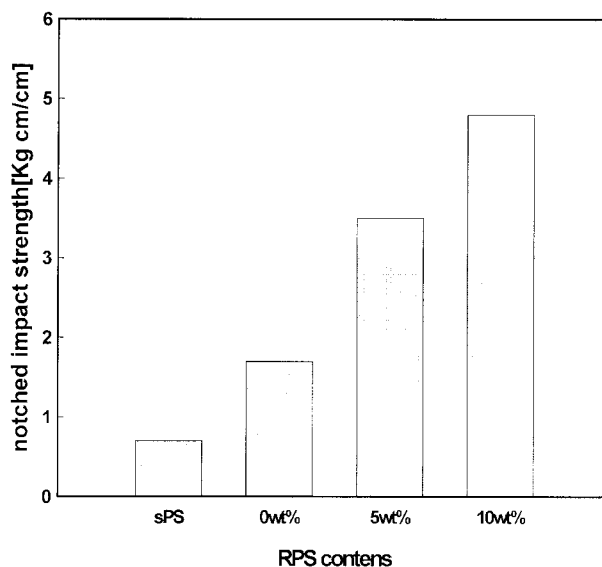


Figure 5 Change in notched izod impact strength of reactive blends (sPS/RPS/EPR-MA) with increasing amount of RPS.

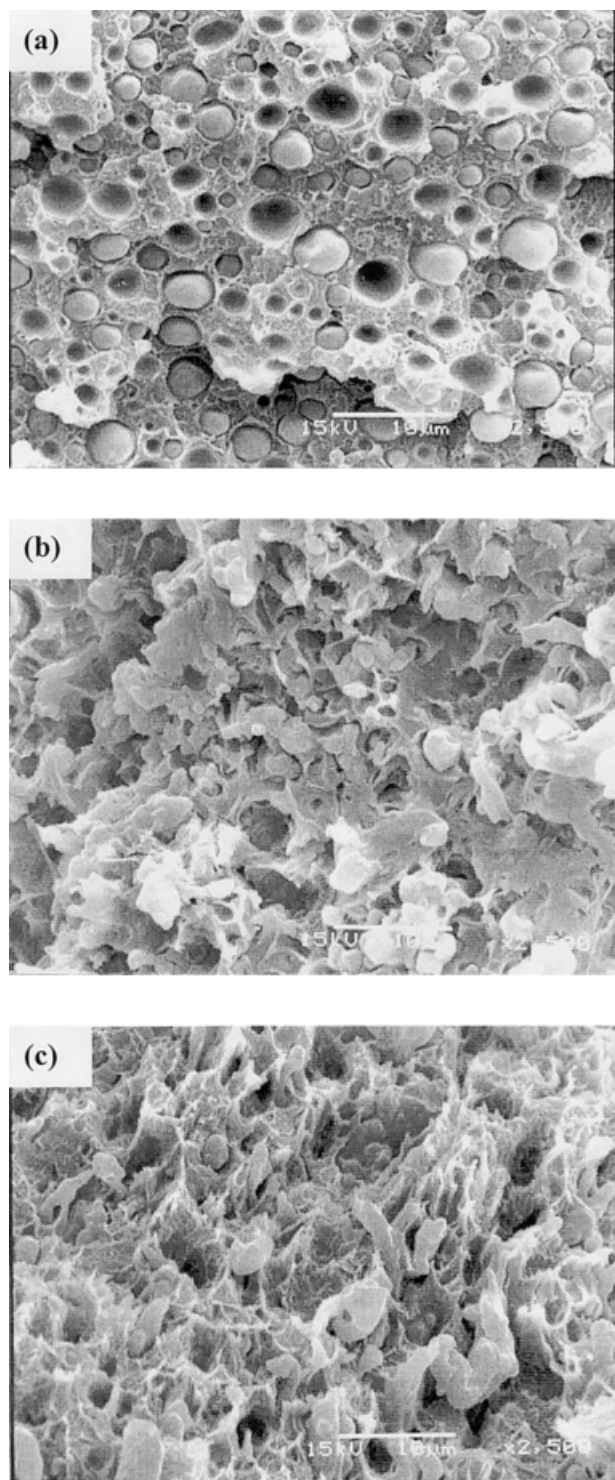


Figure 6 SEM micrographs of the fracture surface after an impact test at room temperature: (a) sPS/RPS/EPR-MA (75/0/25); (b) sPS/RPS/EPR-MA (70/5/25), and (c) sPS/RPS/EPR-MA (65/10/25).

lizer RPS, the fracture surface of the blend sample after the impact test becomes rougher and shows deformation of the rubber domain. Moreover, the EPR domains seem to be strongly adhered to the sPS matrix, resulting in improved impact strength by reactive compatibilized blends system.

CONCLUSIONS

sPS is an incoming engineering plastic for industrial and academic area and it is essential to increase its low impact strength, which is a critical defect, to widen its applications. To that goal, we prepared toughened sPS/EPR blends and characterized morphological, rheological, and mechanical properties of blends.

First, we observed glass transition behaviors and enthalpy relaxation to examine the miscibility of sPS/RPS. We found that sPS/RPS are truly miscible along the various compositions, even though they have different tacticity and functionality. The functional group in RPS, oxazoline, has reactivity with MA and other functional groups, which could be useful in blending other polymers with that functional group.

From this result, sPS/RPS/EPR-MA reactive blends were prepared. By introducing RPS, the size of the dispersed EPR domains was decreased and the distribution of the domains became uniform. Also, the impact strength of reactive compatibilized blends improved significantly compared with the uncompatibilized blend. The SEM micrographs after the impact test showed that the sPS/RPS/EPR-MA reactive blends have good adhesion between the sPS matrix and the dispersed EPR domains. Toughened sPS/RPS/EPR blends with improved morphological and mechanical properties were prepared in a cost-effective manner, without using high-cost polymers.

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