Toughening of Recycled Polystyrene Used for TV Backset

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ABSTRACT: The recycled polystyrene (rPS) was toughened with ethylene-octylene copolymer thermoplastic elastomer (POE) and high-density polyethylene (HDPE) with various melt flow index (MFI), compatibilized by styrene-butadiene-styrene copolymer (SBS) to enhance the toughness of rPS for use as TV backset. The rPS/POE binary blends exhibited an increased impact strength with 5–10 wt % POE content followed by a decrease with the POE content up to 20 wt %, which could be due to poor compatibility between POE and rPS. For rPS/POE/SBS ternary blends with 20 wt % of POE content, the impact strength increased dramatically and a sharp brittle-ductile transition was observed as the SBS content was around 3–5 wt %. Rheological study indicated a possible formation of network structure by adding of SBS, which could be a new mechanism for rPS toughening. In rPS/POE/HDPE/SBS (70/20/5/5) quaternary blends, a fibril-like structure was observed as the molecular weight of HDPE was higher (with lower MFI). The presence of HDPE fibers in the blends could not enhance the network structure, but could stop the crack propagation during fracture process, resulting in a further increase of the toughness. The prepared quaternary blend showed an impact strength of 9.3 kJ/m^2 and a tensile strength of 25 MPa, which can be well used for TV backset to substitute HIPS because this system is economical and environmental friendly. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3725–3732, 2008

Key words: fibril-like structure; network; recycled polystyrene; toughening

INTRODUCTION

Polystyrene (PS) is one of the widely used plastics with good properties such as high degree of hardness, excellent electrical properties, good clarity, low moisture absorption, and ease of fabrication. Because of its low cost, it is used for many products such as packagings, appliance housings, automobile interior parts, food containers, etc. However, PS plastic wastes are not degradable, piling them will pollute environment, nourish disease, cause fire and waste energy sources, so the large amount of disposable PS and expanded PS plastic wastes produced nowadays makes imperative about the search for recycling them.[1–3]

At present, the recycling ways mainly include the reuse of the original plastic waste, chemical recycling,[4] mechanical recycling,[5,6] and energy recovery.[7] Of these ways mechanical recycling is a good economical and environmental option, being used for the 51.5% of the total plastic waste recovered in Western Europe in the year 2002. This technique directly recovers clean plastics for reuse in the manufacturing of new plastic products. However, the recycled polystyrene (rPS) has the unsatisfactory mechanical properties of low impact strength because of the degradation during reprocessing. Blending rPS with other polymers will lead to good mechanical properties, combining the advantages of two or more polymers. Because most polymers are immiscible, the incompatibility between polymers is responsible for the poor mechanical properties. In such immiscible blends, a successful blending material is related to three factors: a proper interfacial tension to transfer stress, good dispersion, and phase morphology. Thus, a compatibilizer is needed to improve the interfacial tension and dispersion of the immiscible polymer blends. It is now well-known that copolymers, especially block copolymer such as styrene-butadiene-styrene (SBS),[8] styrene-acrylonitrile (SAN),[9] and styrene-etheylene-butylene-styrene (SEBS),[10,11] are effective for this purpose.

Blending rubber with PS is the most efficient way to improve the impact toughness of PS and extend its application range so far.[12–15] A large number of toughened polymers such as high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene compolymer (ABS) have been developed and widely employed as engineering materials.[16] Concerning the

TABLE I
Materials

Trade marked	Supplier	Characteristics	M_n
rPS	Changxin Corp., MianYang, China	MFI: 25.8 g/10 min (200°C, 5 kg)	
POE-DF610	MITSUI Japanese	MFI: 1.2 g/10 min	
HDPE-F600	Petrochemic Corp., Korea	MFI: 0.05 g/10 min	5.0×10^5
HDPE-5000s	Daqing Petrochemic Corp., China	MFI: 1.1 g/10 min	3.3×10^5
HDPE-2200J	Daqing Petrochemic Corp., China	MFI: 5.5 g/10 min	2.3×10^5
HDPE-8916	Maoming Petrochemic Corp., China	MFI: 10 g/10 min	1.3×10^5
HDPE-2911	Fushun Petrochemic Corp., China	MFI: 20 g/10 min	1.2×10^5
SBS-1401	Yanhua Petrochemic Corp., China	S/B (weight ratio) = 40/60, MFI: 0.5 g/10 min	

toughening mechanism, various conceptual models, including crazes,[17–19] shear deformation,[20] cavitations, etc,[21,22] have been proposed. In rubber toughened PS, crazing in the matrix is the main method to absorb the impact energy.[18] A large amount of energy is consumed in craze initiation and development. However, the addition of a low-modulus rubbery component generally leads to a sharp decrease in the tensile strength and modulus of the blends. The recently introduced rigid–rigid polymer toughening idea has provided a new route for improving the mechanical properties. According to this new idea, it is possible to improve the toughness of rPS by incorporating with a rigid polymer, such as polypropylene (PP),[23–25] polymethyl methacrylate (PMMA),[26] polyethylene (PE), and polyamide(PA).[27,28] There are many reports on blending PS with PE to increase its impact toughness without sacrificing too much of its tensile strength.[29–31] Recent investigation indicates that using two toughening agents instead of one has synergistic effect on the toughness of PS. Some systems such as PS/HDPE/SBS.[32] and HDPE/PS/CaCO$_3$/SEBS-g-MA[33] have been studied on their morphology, compatibility, and mechanical properties. The impact strength of PS was increased about 10-fold when it was toughened with high-density polyethylene (HDPE) and SBS.[32]

One goal of this work is to largely improve the toughness of rPS without decreasing much of its tensile property by using multicomponent toughening system. The mechanical properties of the prepared material should be good enough to substitute HIPS as TV backset. The other goal is to investigate the toughening mechanism of the polymer blends with more than one component, particularly the synergistic effect by adding two toughening agents. For this reason, we begin with rPS/POE binary system, then rPS/POE/SBS ternary system, finally rPS/POE/HDPE/SBS quaternary system. In this article, to achieve the good combination of mechanical properties, ethylene-octylene copolymer thermoplastic elastomer (POE) and HDPE are introduced as toughening agents for rPS. POE is used as the main toughen-

ing agent because of its popularity, better weather resistance, good processability, and flexible structure, leading to better toughening efficiency. To see the effect of molecular weight of HDPE on the toughness of the blends, various HDPE with different melt flow index (MFI) are chosen. SBS is used as the compatibilizer. The toughening mechanism is discussed based on (1) the possible formation of POE network, as indicated by rheological result, and (2) the formation of HDPE fibril structure when its molecular weight is higher (with lower MFI), as indicated by SEM observation.

EXPERIMENTAL PART

Materials

The materials used for the preparation of rPS/POE, rPS/POE/SBS, and rPS/POE/HDPE/SBS blends were listed in Table I. Recycled polystyrene (rPS), ethylene-octylene copolymer thermoplastic elastomer (POE), high-density polyethylene (HDPE), and styrene-butadiene-styrene (SBS) used in our study were commercially available.

Sample preparation

The blending was conducted in a two-screw extruder at 150–210°C, and then injection molded in a PS40E5ASE (Japan) injection-molding machine at 180–210°C to obtain standard specimen for mechanical properties tests.

Notched Izod impact tests

Notched Izod impact tests were performed using an I200XJU-2.75 impact tester according to GB/T 1834-1996 standard. The specimens were injection-molded rectangular bars with a milled single-edge 45° V-shaped notch (depth 2 mm). All the tests were performed five times at room temperature and the results were averaged.
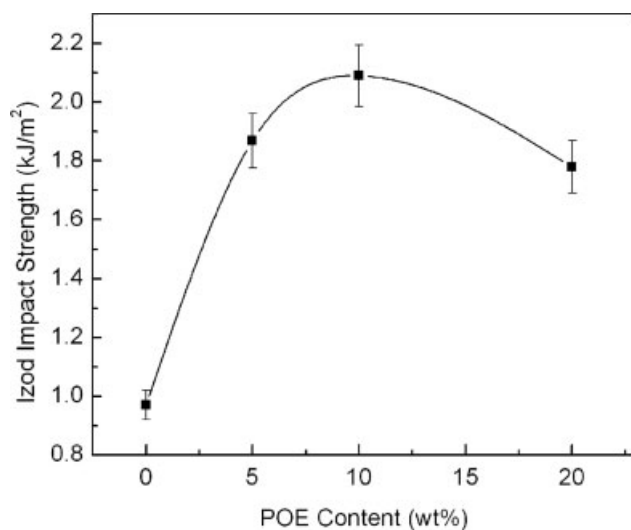
Figure 1 Impact strength of rPS/POE binary blends via POE content.

Testing

All rheological measurements were performed on a controlled stress rheometer (ARES rheometer, Rheometrics Scientific, NJ) with a torque transducer range of 0.2–2000 gfcm using 2.5 cm diameter parallel plates at 190°C. Testing sample disks with a thickness of 1.5 mm and a diameter of 2.5 mm were prepared by compression molding of the extruded pellets at 190°C for 5 min. Small-amplitude oscillatory shear measurements were conducted within a frequency range of 0.01–100 rad/s.

Scanning electron microscope

A JEOL JSM-5900LV scanning electron microscope (SEM) instrument was used to examine the morphology of the fractured surfaces and the dispersed particles in the matrix using an acceleration voltage of 20 kV. The samples were fractured in the direction perpendicular or parallel to flow direction in liquid nitrogen or achieved after impact test. The fractured surfaces of the specimens were sputter coated with a thin gold layer prior SEM examination.

RESULTS AND DISCUSSION

rPS/POE blends compatibilized by SBS

The Izod impact strength of rPS/POE binary blends is shown in Figure 1. It can be seen that the addition of POE to rPS matrix results in a better impact strength. For example, the impact strength increases from 0.97 kJ/m^2 of rPS to 2.09 kJ/m^2 when 10 wt % POE is used. However, the impact strength becomes to decrease with the further increasing of POE content up to 20 wt %, this is probably due to the poor

compatibility between POE and rPS matrix, as shown in Figure 2. The average domain size increases with increasing of POE content. In rPS/POE (90/10) blends [see Fig. 2(a)], the POE particles are well dispersed as spherical domains with about 0.5 μm in diameter in the rPS matrix. In rPS/POE (80/20) blends, the POE particles are irregular distributed in the rPS matrix and the domain size of POE is enlarged to about 2 μm [Fig. 2(b)]. The boundary between the phase domains of POE and rPS is more clear and sharper, and many POE particles are released from rPS matrix (the holes), particularly for blends with higher POE content, suggesting a poor compatibility between the two components.

However, as SBS is added into rPS/POE blends as a compatibilizer, an increase of impact strength is observed, as shown in Figure 3. For blends with 5 wt % and 10 wt % POE, one observes a limited increase of impact strength as increasing of SBS content up to 10 wt %. For blends with 20 wt %, however, the impact strength is dramatically increased by adding SBS, and a sharp brittle-ductile transition is seen when SBS content is around 3–5 wt %. Only a slight increase of toughness is observed by further
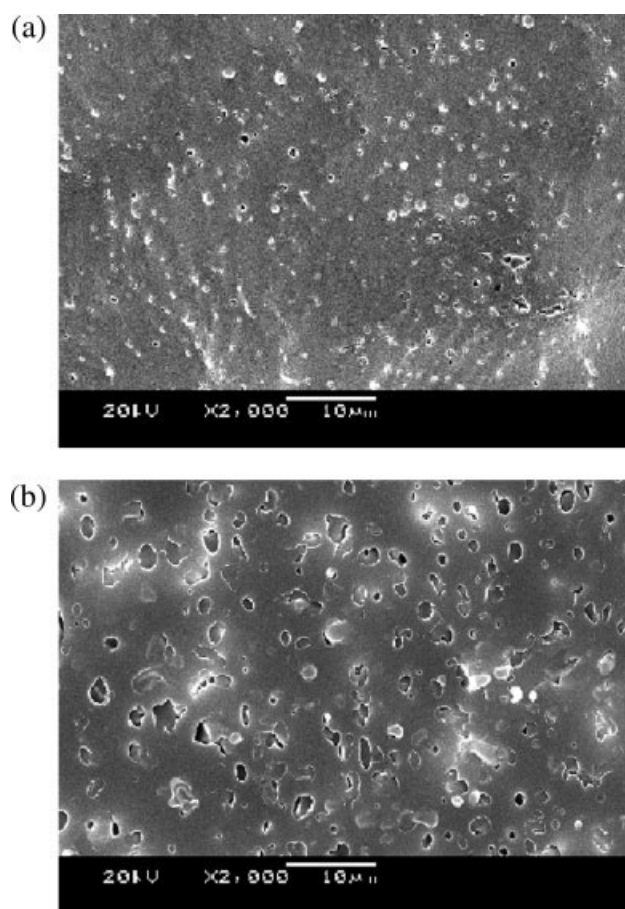

Figure 2 SEM micrograph of the rPS/POE binary blends. (a) 90/10 and (b) 80/20.
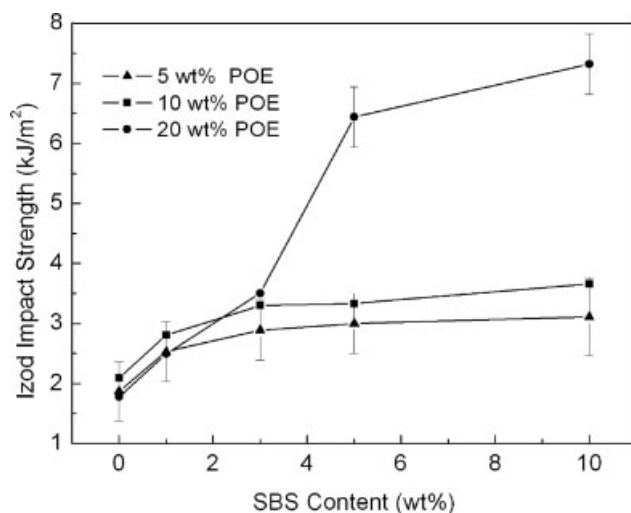
Figure 3 Impact strength of rPS/POE/SBS ternary blends via SBS content.

increasing of SBS content, indicating a saturation of SBS as a compatibilizer for rPS/POE blends. Because rPS/POE blends are expected to be immiscible, the improvement of the impact strength by adding SBS must be related to the improved compatibility between POE and rPS matrix, and one expects higher compatibilization efficiency for rPS/POE blends with addition of higher SBS content. SBS copolymer contains the styrene segments chemically identical to rPS and the butadiene segments which have relatively high affinity with the POE phase. Consequently, the incorporation of SBS can improve the compatibility of the rPS/POE blends as a bridge between POE phase and rPS matrix. ATR-FTIR has been used to verify the possible interaction by adding SBS, however, no obvious change of the characterization peaks were observed in the spectra (not shown here), which indicates that the enhanced compatibility by adding SBS is mainly due to a physical interaction, instead of chemical interaction in this blend. Figure 4 shows the SEM micrographs of the fractured surface of rPS/POE/SBS ternary blends. For rPS/POE/SBS (85/10/5) blends [see Fig. 4(a)], not much change of dispersed phase domain is seen, compared with that of rPS/POE (90/10) blends. For rPS/POE/SBS (75/20/5) blends, however, the particle size and the interparticle distance of the POE dispersed phase become smaller on addition of 5 wt % SBS, indicating an improved compatibility between POE particles and rPS matrix [see Fig. 4(b)]. The boundary between the phase domains of POE and rPS with SBS copolymers is obscure, and only few released POE particles are observed. The SBS phase is expected to be located in the interlayer between rPS matrix and POE phase which can not be seen by SEM because of its good miscibility with rPS matrix.
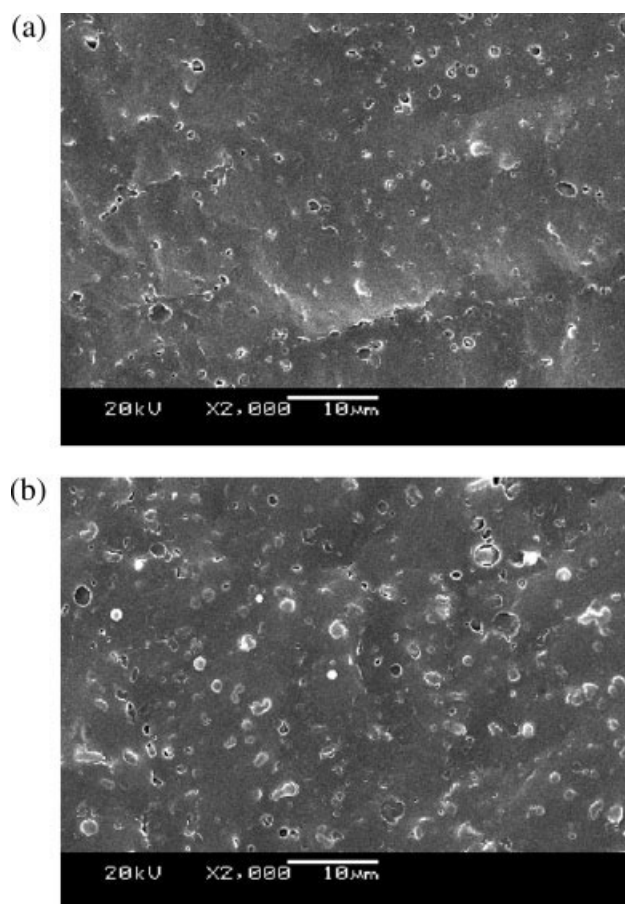
Figure 4 SEM micrograph of the rPS/POE/SBS ternary blends. (a) 85/10/5 and (b) 75/20/5.

Rheological property

To understand the toughening mechanism of rPS/POE blends by adding SBS, particularly, the brittle-
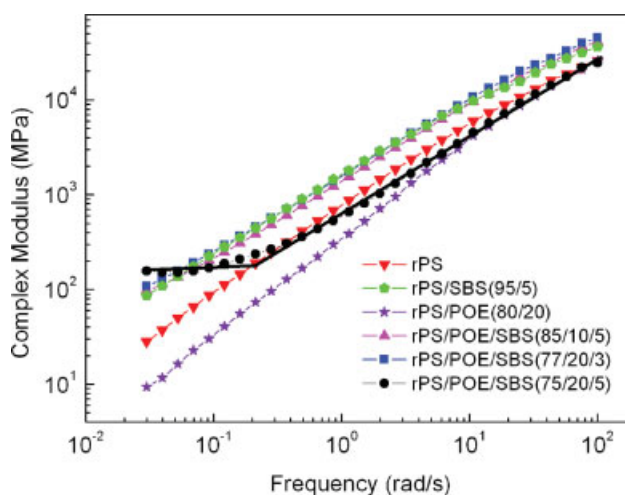

Figure 5 Complex modulus of rPS, rPS/POE, and rPS/POE/SBS blends versus frequency at 190°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
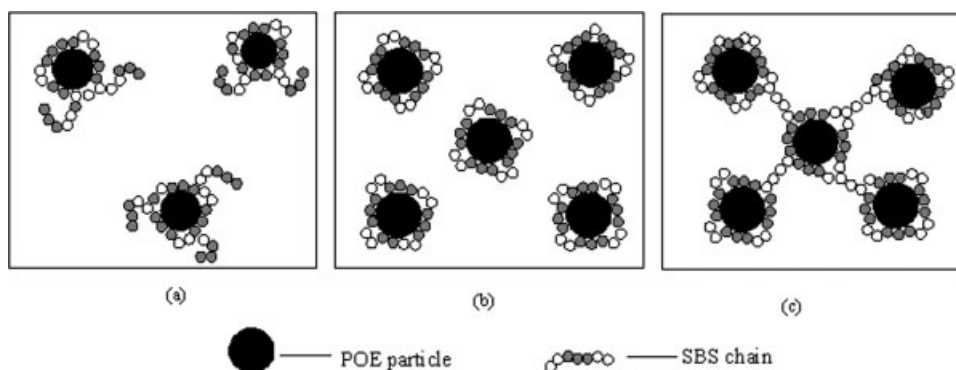
Figure 6 The schematic drawing of toughening mechanism of rPS/POE/SBS blends. (a) 85/10/5, (b) 77/20/3, and (c) 75/20/5.

ductile transition in rPS/POE (75/20) blends compatibilized by 5 wt % SBS, the rheological measurements are carried out, and the result is shown in Figure 5. In low frequency region, complex modulus of rPS and rPS/POE blends are lower than that of rPS/POE/SBS blends, indicating an increased interaction between rPS and POE on addition of SBS as compatibilizer. The rheological properties in low frequency region can be considered to reflect the relaxation and motion of the whole polymer chains. From the results of Figure 5, it can be seen that there exhibits a solid-like behavior for rPS/POE/SBS (75/20/5) blends. But such solid-like behavior is not observed in both rPS/POE (80/20) and rPS/SBS (95/5) blends. This result indicates a possible network structure in rPS/POE/SBS (75/20/5) blend. Meanwhile, it should be noted that the brittle-ductile transition occurs also in rPS/POE/SBS blends as the content of SBS is around 5 wt %. Namely, the network structure could efficiently improve the impact property and lead to brittle-ductile transition in rPS/POE/SBS blends. In rPS/POE/SBS (85/10/5) blends, the interparticle distance is too large to form an efficient network structure because of the less POE content. Moreover, there is not enough SBS to bridge POE phases together in PS/POE/SBS (77/20/3) blends to form the network structure. The schematic drawing of toughening mechanism of rPS/POE/SBS blends is given in Figure 6. The correlation between impact strength and the formation of dispersed particles network has not yet been reported and provides a new understanding of polymer toughening mechanism.

rPS/POE/HDPE/SBS quaternary blends

Because it is not possible to further increase the impact strength of rPS/POE/SBS blends by adding more SBS, the rPS/POE/HDPE/SBS quaternary system is considered. Here we want to investigate the synergistic toughening effect by using both POE and HDPE. To see the effect of molecular weight of HDPE on the toughness of the blends, HDPE with

various MFI (g/10 min) ranging from 0.05 to 20 are employed.

The Izod impact strength of rPS/POE/HDPE/SBS (70/20/5/5) blends is shown in Figure 7. It can be seen that the impact strength increases with increasing of HDPE molecular weight or decreased MFI. HDPE with higher molecular weight greatly improves the impact toughness; however, the HDPE with lower molecular weight makes the impact strength even poorer. For example, the impact strength is enhanced from 6.44 to 9.26 kJ/m^2 on addition of 5 wt % HDPE with MFI of 0.05 g/10 min, while it decreases from 6.44 to 3.6 kJ/m^2 on addition of 5 wt % HDPE with MFI of 20 g/10 min. Comparing the impact properties of rPS, rPS/POE, rPS/POE/SBS, rPS/POE/HDPE/SBS blends, and HIPS [see Figure 8], one observes a great improvement in impact strength of rPS toughened by POE, HDPE, and SBS, which has already exceeded the impact property of HIPS (9.0 kJ/m^2). Meanwhile, it has a tensile strength of 25 MPa which has been reached the tensile strength of HIPS (25MPa). The
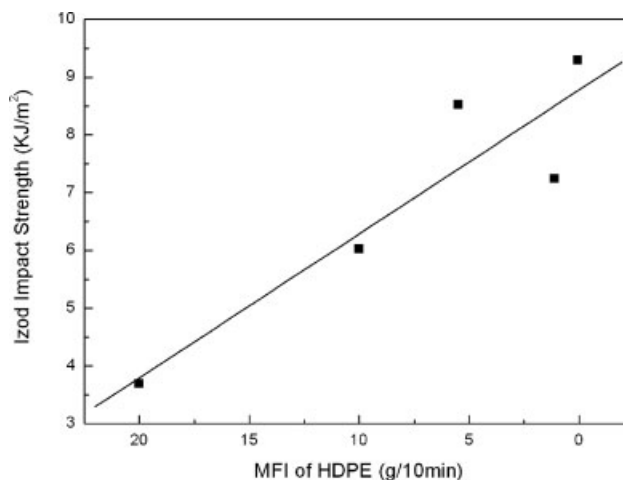

Figure 7 Impact strength of rPS/POE/HDPE/SBS (70/20/5/5) quaternary blends via different HDPE with various MFI.
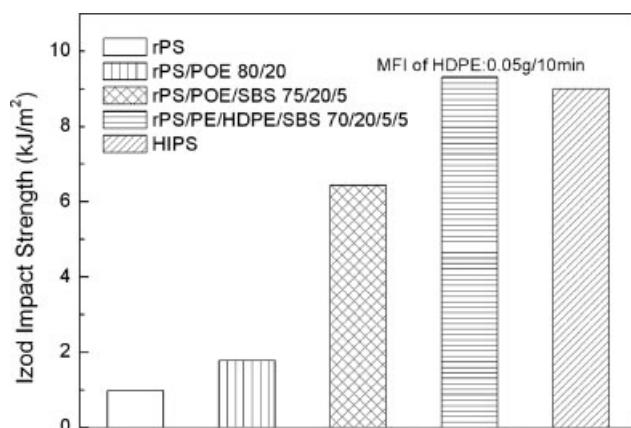
Figure 8 Impact strength of rPS, binary blends, ternary blends, quaternary blends, and HIPS.

mechanical property of the modified material is good enough to be used as TV backset to substitute HIPS.

Figure 9 shows the complex modulus of rPS/POE/SBS (75/20/5) blends and rPS/POE/HDPE/SBS (70/20/5/5) blends with various HDPE of different MFI versus frequency at 190°C. A solid-like behavior in low frequency region is observed for all the blends, which indicates the formation of the network structure in these blends. Not very much difference of the complex modulus is seen between quaternary blends and ternary blends, and between the quaternary blends with different MFI of HDPE, over a range of frequencies. This could be understood that the complex modulus of a blend depends mainly on the matrix, and all the blends have roughly the same rPS content. Thus, the formation of network structure could be a new toughening mech-
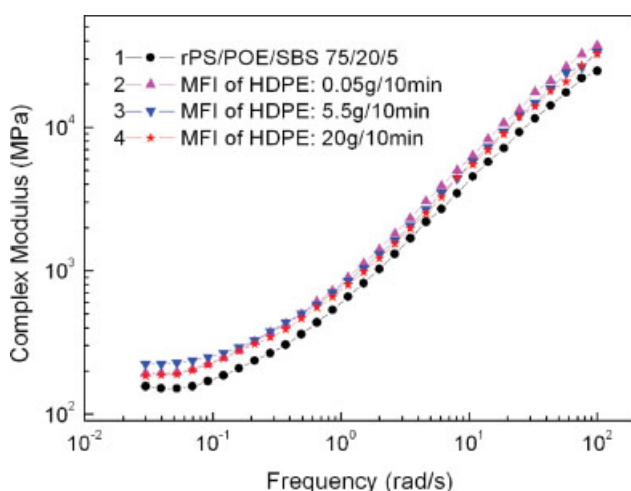

Figure 9 Complex modulus versus frequency (2′3′4-rPS/POE/HDPE/SBS 70/20/5/5). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
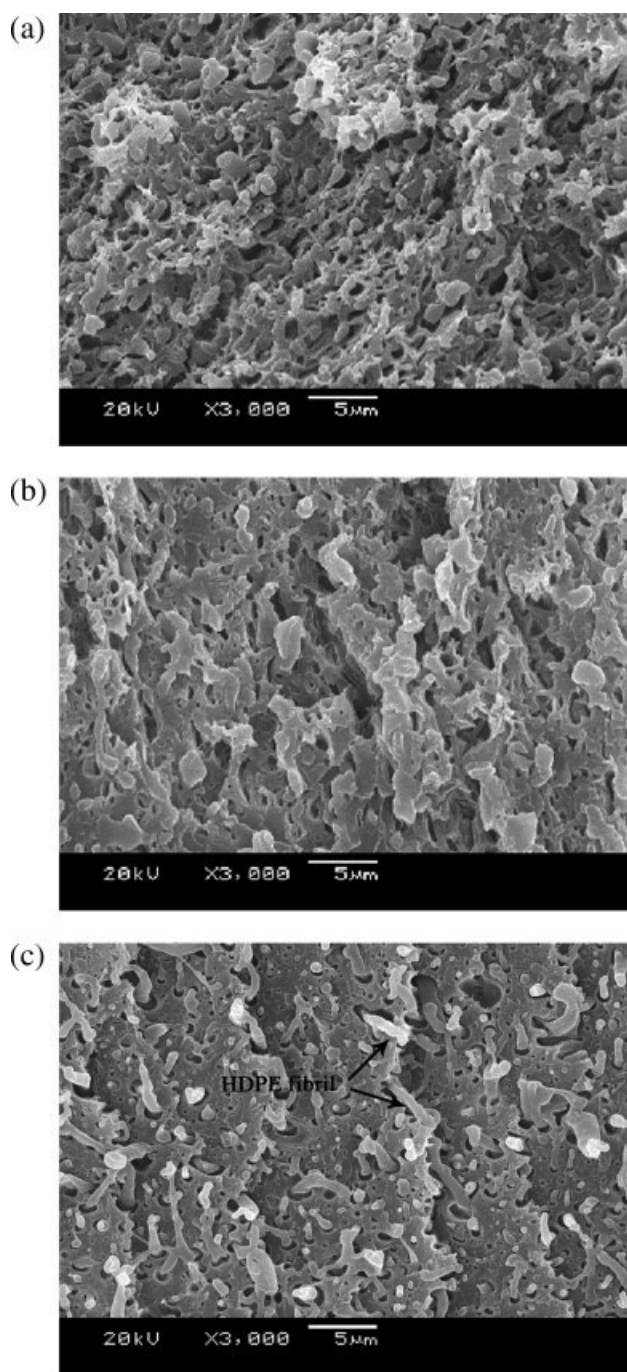
Figure 10 SEM morphology of the fractured surface of the PS/POE/HDPE/SBS (70/20/5/5) quaternary blends with HDPE of higher molecular weight. (a) Near the notch, (b) middle place, and (c) the end.

anism in rPS/POE/SBS blends, as mentioned earlier, but could not explain the additional increase of impact strength by adding HDPE with higher molecular weight. To understand the role of HDPE in the improvement of toughness of the quaternary blends, the morphology of the fractured surface is examined, and the result is shown in Figures 10 and 11. For blend with higher molecular weight HDPE (lower
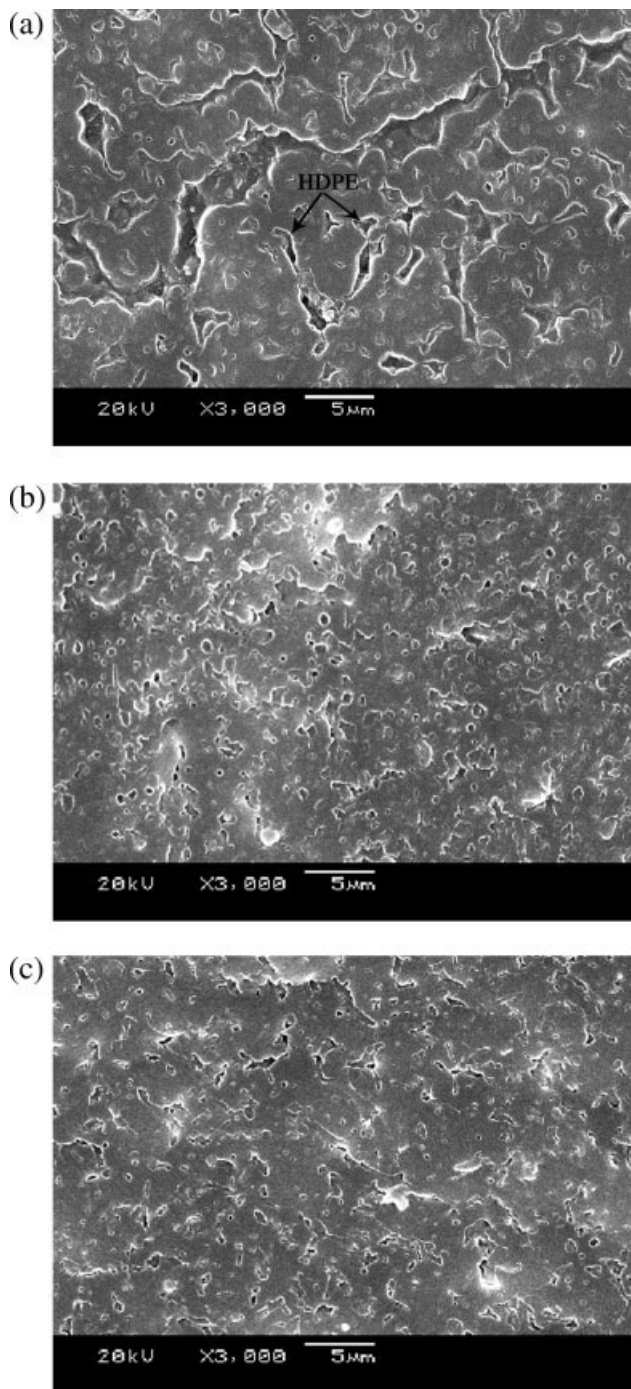
Figure 11 SEM morphology of the fractured surface of the PS/POE/HDPE/SBS (70/20/5/5) quaternary blends with HDPE of lower molecular weight. (a) Near the notch, (b) middle place, and (c) the end.

MFI), one observes many fibrils on the fractured surface (Fig. 10), which are pulled out during the impact testing. For blend with lower molecular weight HDPE (higher MFI), a smooth surface with dark holes and dispersed particles are observed (Fig. 11). No fibril-like structure is seen. This morphology is very similar to that observed in rPS/POE/SBS ternary blends. The morphological observation could

give us some idea to understand the change of impact strength with HDPE molecular weight. As for the decrease of impact strength by adding lower molecular weight HDPE, a temporary explanation could be due to its lower viscosity and better compatibilization with rPS matrix. HDPE with lower molecular weight could be better dispersed in rPS matrix as droplets with a smaller size. HDPE with small size could not be easily deformed to form fibril-like structure during processing, or it could be easily relaxed back once deformed due to its low viscosity and short relaxation time. The small size of HDPE could not stop the crack propagation, but induce a crack as a stress concentration, resulting in a decrease of toughness.

Synergistic toughening effect by both POE and HDPE

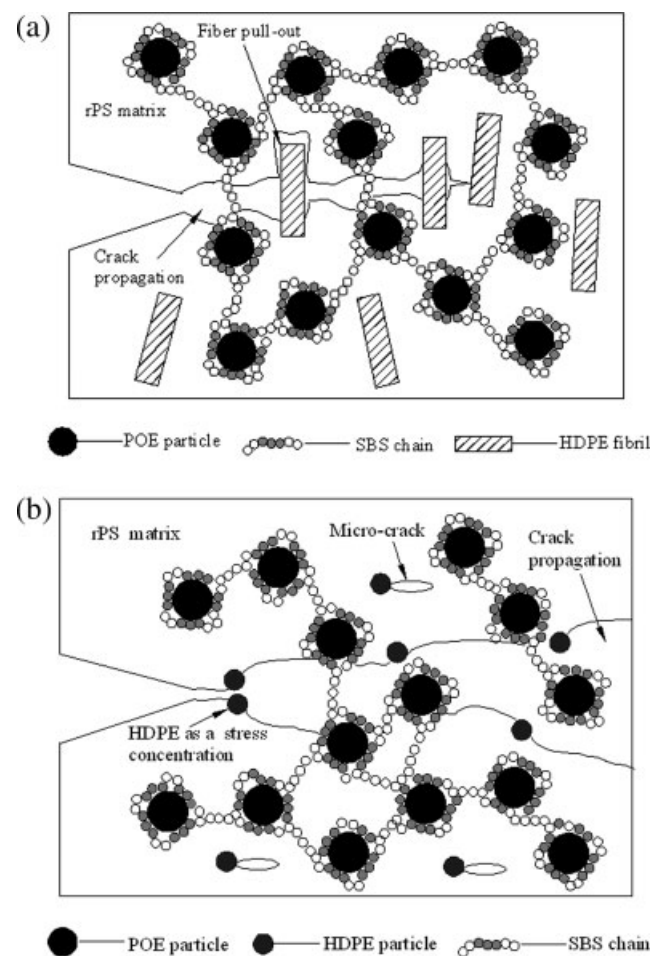By Combining the impact strength and the fractured surface together, it can be seen that the impact

Figure 12 Schematic drawing of toughening mechanism for PS/POE/HDPE/SBS (70/20/5/5) blends: (a) with higher molecular weight HDPE and (b) with lower molecular weight HDPE.

strength increases greatly on addition of 5 wt % HDPE with higher molecular weight. The HDPE forms a fibril structure and is pulled out during impact testing. The pullout of HDPE fiber during the fracture process will absorb more fracture energy. More importantly, these HDPE fibers could stop the crack propagation, which could cause a large increase of toughness. The rheological result shows that there still exists a network structure for rPS/POE/HDPE/SBS (70/20/5/5) blends with higher molecular HDPE. Thus, the toughening mechanism that works in rPS/POE/SBS blends also works in these blends. But due to the formation of HDPE (lower MFI) fibril structure, additional increase of impact strength is achieved (Fig. 10). HDPE with lower molecular weight could be better dispersed in rPS matrix as droplets with a smaller size. The small size of HDPE could not stop the crack propagation, but induce a crack as a stress concentration, resulting in a decrease of toughness (Fig. 11). The schematic drawing of toughening mechanism of rPS/POE/HDPE/SBS blends is shown in Figure 12.

CONCLUSIONS

The morphology, mechanical, and rheological properties of the rPS/POE binary blends, rPS/POE/SBS ternary blends, and rPS/POE/HDPE/SBS quaternary blends were studied. On the basis of the results of the work, the following conclusions could be drawn.

1. The rPS/POE binary blends exhibit an increased impact strength until the POE content up to 20 wt %, because of the poor compatibility between POE and rPS matrix.
2. For rPS/POE/SBS ternary blends with 20 wt % of POE content, impact strength is increased dramatically and a sharp brittle-ductile transition is observed as SBS content is around 3 wt % to 5 wt %. A possible formation of network structure by adding of SBS could be the main reason for the toughening.
3. In rPS/POE/HDPE/SBS (70/20/5/5) blends, a fibril-like structure is observed as the molecular weight of HDPE is higher (with lower MFI). The presence of HDPE fibers in the blends could not enhance the network structure, but could stop the crack propagation during fracture process, resulting in a further increase of the toughness.

4. A modified rPS material with impact strength of 9.3 kJ/m^2 and tensile strength of 25 MPa, could be well used for TV backset to substitute HIPS.

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