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Optimum toughening via a bicontinuous blending: toughening of PPO with SEBS and SEBS-*g*-maleic anhydride

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Abstract

The poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was toughened by melt extrusion through its blending with a styrene-*b*-ethylene/butadiene-*b*-styrene triblock copolymer (SEBS), or with maleic anhydride (MA) grafted SEBS (SEBS-*g*-MA). Their morphology, mechanical properties, and rheology have been investigated. Transmission electron microscopy revealed that both kinds of blends had an island–sea structure at low concentrations of SEBS or SEBS-*g*-MA and a bicontinuous one at sufficiently high concentrations. However, the percolation threshold was higher for SEBS than for the SEBS-*g*-MA. The Izod impact strength of PPO could be significantly improved through its blending with SEBS-*g*-MA, particularly in a blend with 20 wt% of SEBS-*g*-MA at which it had a maximum value. The rheological experiments indicated that the incorporation of SEBS increased and that of SEBS-*g*-MA decreased the melt viscosity of the system. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(2,6-dimethyl-1,4-phenylene oxide); Styrene-*b*-ethylene/butadiene-*b*-styrene triblock copolymer; Toughening

1. Introduction

One of the important procedures to modify and improve the properties of a polymer is its blending with one or several other polymers. Most commercial multi-component polymer systems are two-phase blends that provide advantages over the single-phase systems [1,2]. The toughening of a brittle plastic via blending with an elastomer constitutes a convincing example [3]. The amount, particle size and properties of the elastomer, as well as the interactions between phases determine the mechanical properties of the toughened plastics [4–8].

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) has maintained a key position within engineering plastics since the middle of 1960s [9], because it exhibits a high strength, an excellent heat resistance, and a good dimensional stability. However, deficiencies, such as brittleness, poor processability and solvent resistance prohibited its broader use [10]. The current research involving the PPO was mainly focused on its blending with polyamide 6 (PA 6), polystyrene (PS) and its derivatives. The properties of PPO and PA 6 suggested that their combination could provide a useful blend with improved solvent resistance and processability [11–15]. It is well-known that PPO is miscible in all proportions with PS due to the favorable interactions among their aromatic rings [16–18]. Mixtures of PPO and PS provided amorphous and segmentally miscible blends of commercial importance [19,20]. The blends of PPO with PS or its derivatives, such as the high-impact PS and the brominated PS, resulted in tough materials with good processability and flame retardance. Consequently, the investigation of the blends of PPO and polymers containing PS blocks is of both scientific and technological interest [21,22].

In this paper, a styrene-*b*-ethylene/butadiene-*b*-styrene triblock copolymer (SEBS) as well as the latter polymer grafted with maleic anhydride(MA) (SEBS-*g*-MA) were employed as impact modifiers. These modifiers have been selected because they contain blocks, which are miscible with PPO, as well as blocks, which are not miscible with PPO. As a result, a two-phase system with high toughness was expected to be generated. The grafting with MA increases the polarity of the ethylene/butadiene (E/B) blocks thus affecting the interactions with PPO and hence the characteristics of the second phase. The above block copolymers are thermoplastic elastomers that can flow at high temperatures and behave as a crosslinked rubber at low temperatures. Their use as impact modifier in a number of polymer blends was examined by Paul [23–26]. New blends with PPO will be investigated here by transmission

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electron microscopy (TEM), and melt rheology, and their mechanical properties will be determined.

2. Experimental

2.1. Materials

The PPO (646-111 grade) was purchased from the GE Plastics Company; it had an intrinsic viscosity of 0.43 dl/g determined in chloroform at 25°C. SEBS (Kraton G 1651) contained 29 wt% styrene, and had a number average molecular weight of 29,000 in the polystyrene blocks and 116,000 in the polyolefine blocks. SEBS-*g*-MA (Kraton FG 1901) contained 29 wt% styrene, and had a number average molecular weight of 7500 in the polystyrene blocks and 37,500 in the polyolefine blocks. The weight percent of MA grafted onto this elastomer was 1.7–2.0 wt%. SEBS and SEBS-*g*-MA were supplied by Shell Chemical Company.

2.2. Preparation of blends

The pellets of the materials were vacuum dried at 90°C overnight. The constituents of the blends were mixed in a ZSK 30 mm twin-screw extruder (Werner & Pfleidere Corp.) with the length to diameter ratio (*L*/*D*) of 35. The temperature along the barrel was increased from 210 to 320°C (the latter temperature being that of the die), and the rotation speed of the screw was 200 rpm. The blends were passed through a cooling water bath after which they were pelletized.

2.3. Mechanical properties tests

The tensile and impact bars were prepared using a reciprocating screw injection machine (M-20-55); the barrel temperature was 320°C and the mold temperature was 90°C. The tensile properties were determined with an Instron Universal Testing Machine (Model 1130) according to ASTM D638. The notched Izod impact strength was measured with a SUMITOMO impact tester according to ASTM D256. All the tests were conducted at room temperature and five measurements were carried out for each data point.

2.4. Transmission electron microscopy

The morphology was examined by TEM. The samples were cryogenically microtomed from fractured Izod impact bars perpendicular to the flow direction using a diamond knife; the cut direction is shown in Fig. 1. The samples of the skin, intermediate and core of the impact bars were all cut from a position near the fracture point. The micro-chips were stained with RuO_4 by soaking them in the vapor of a 2 wt% aqueous solution of RuO_4 for 30 min. A Hitachi H-800 transmission electron microscope was used to examine the samples.

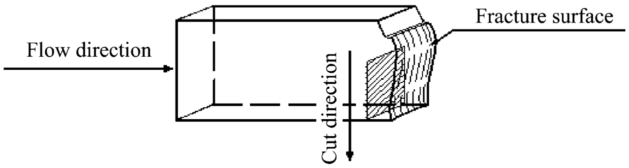

Fig. 1. The position and direction in which the TEM samples were taken.

2.5. The rheological measurements

The apparent viscosity at various shear rates was determined using an Instron capillary rheometer with a capillary diameter of 1.262 mm and an *L*/*D* ratio of 60.51. The experiments were carried out at 300°C under a shear rate ranging from 1 to $10^3\ s^{-1}$.

3. Results and discussion

3.1. Morphology

The morphologies of PPO/SEBS and PPO/SEBS-*g*-MA systems could be visualized with the aid of the RuO_4 staining. Although the PPO and the blocks of PS and ethylene/butylene (E/B) can be stained with RuO_4, the staining rates are very different. The staining rate of the PS blocks being faster [27], they appear in the micrographs as black regions.

Fig. 2(a) shows that SEBS itself has a two-phase structure. The PS blocks form elongated islands surrounded by E/B blocks. Because SEBS is a tri-block copolymer, the two kinds of blocks are chemically linked, and the regions near the islands are gray. The PS forms the islands and the E/B the sea. The solubility parameters of E/B and PS are 8.6 and 8.5 $(cal/cm^3)^{1/2}$ [28], respectively. Because their cohesive energies are comparable, the morphology of the phases should depend on the relative amounts of the components. The molecular weights of the polyolefin and PS being

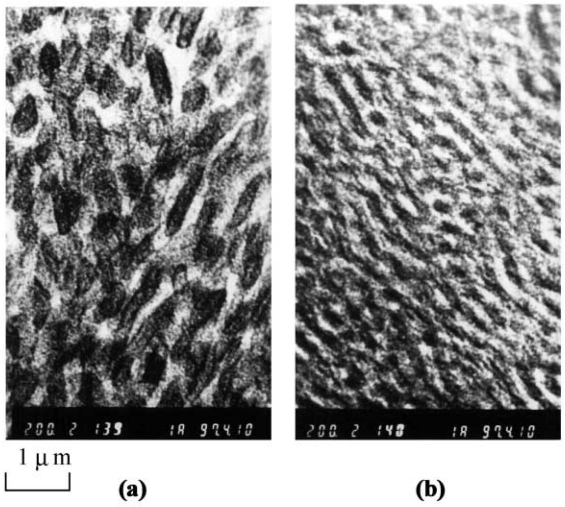

Fig. 2. TEM micrographs of (a) pure SEBS and (b) pure SEBS-*g*-MA.

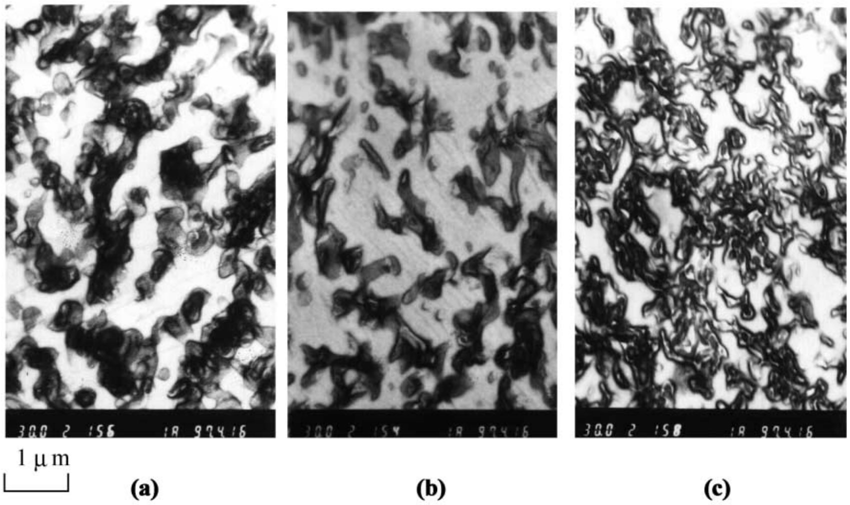

Fig. 3. TEM micrographs of PPO/SEBS blends (wt/wt): (a) 90/10, (b) 85/15, and (c) 80/20.

116,000 and 29,000, respectively, the former is in greater amount than the latter, and will constitute the continuous phase. For the same reason, SEBS-*g*-MA shown in Fig. 2(b) also has a sea–island structure. Since the molecular weight of SEBS-*g*-MA is much smaller than that of SEBS, its morphology is finer.

Fig. 3(a)–(c) are the micrographs of the PPO/SEBS blends. Because its amount is greater, the PPO is located in the sea. It is well-known that PPO and PS are fully miscible [16–20]. When SEBS was added to PPO, the PS segments could readily mix with those of PPO. However, since the blocks of E/B are not miscible with PPO, they impeded the free dispersion of the PS blocks in PPO. As a result, the PS segments could be only partly diluted with PPO chains. As shown by the figures, some of the slender PS islands became gray or even transparent with black edges because of their dilution with PPO. For an SEBS content greater than about 20 wt%, a percolation threshold was reached and a bicontinuous structure was generated.

When SEBS was grafted with MA, its E/B blocks became more polar and this increased the tendency for aggregation. Fig.4 shows the morphology of the intermediate regions of the impact bars near the fracture point. One may notice that the greater the amount of SEBS-*g*-MA introduced, the higher was the aggregation. When the amount of SEBS-*g*-MA became greater than about 15 wt%, a bicontinuous structure was generated. Although the black area represents the PS blocks, the grafted E/B blocks are sandwiched between the PS ones, and consequently one should consider that SEBS-*g*-MA rather than PS alone generated the continuous network.

However, the morphology changes slightly in different positions of the impact bar. Figs. 5 and 6 show the micrographs for samples taken from the skin, intermediate and core regions of the bar. One may notice that on the skin, the network of SEBS-*g*-MA is less complete, whereas in the intermediate and core regions, fully connected networks are generated.

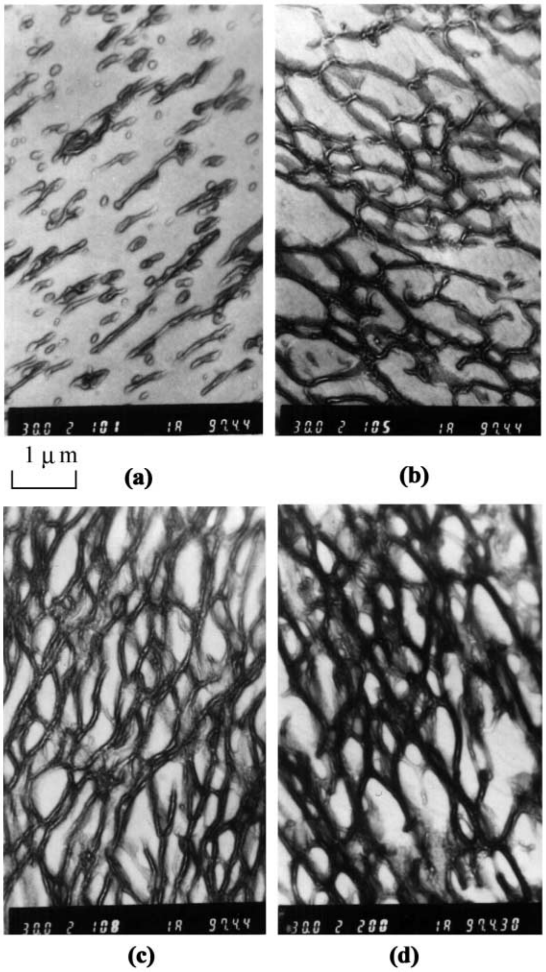

Fig. 4. TEM micrographs of PPO/SEBS-*g*-MA blends (wt/wt): (a) 90/10, (b) 85/15, (c) 80/20, and (d) 70/30.

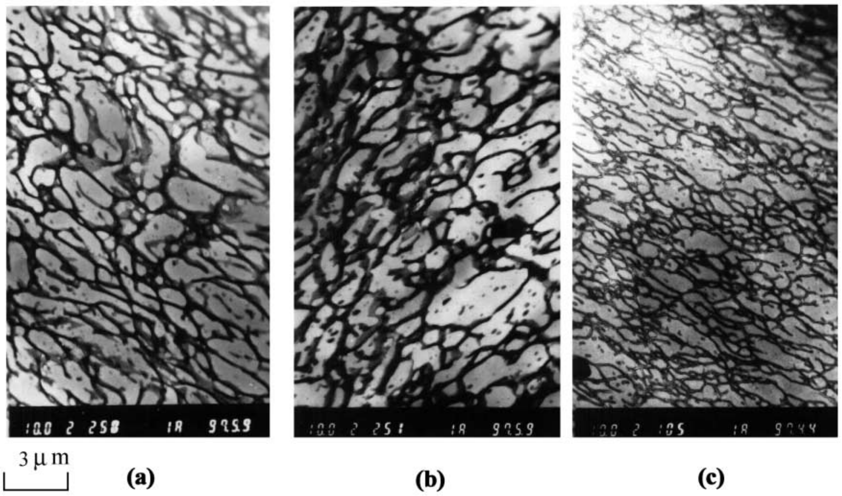

Fig. 5. TEM micrographs of PPO/SEBS-*g*-MA blend (90/10) at a position near the fracture point: 10,000: (a) skin, (b) intermediate, and (c) core regions.

3.2. Impact strength

The notched Izod impact strengths of the PPO/SEBS or PPO/SEBS-*g*-MA blends are plotted in Fig. 7, which shows that the grafting of MA had a major effect on the impact strength. While the impact strength of the blend increased with increasing SEBS content, it increased much more dramatically when the SEBS-*g*-MA was employed. While the impact strength decreased when the amount of SEBS-*g*-MA became too high, it remained still much higher than that of the corresponding PPO/SEBS blend. The MA graft can modify the blend in two ways. Firstly, by increasing the polarity of the E/B blocks. Because the solubility parameters of PPO and E/B are comparable, the difference between them is not large enough to result in a remarkable toughening. The MA graft imparts to the E/B blocks a higher polarity, and thus a greater difference in the solubility parameters of PPO and E/B-*g*-MA. As a result, a more effective toughening is achieved. Secondly, and perhaps more importantly, the MA graft generates a network structure of SEBS-*g*-MA in the matrix of PPO, which can be more effective than the individual particles in stopping the growth of cracks. Furthermore, the molecular weight of SEBS-*g*-MA used in this paper being much smaller than that of SEBS, it may act as a plasticizer, thus resulting in a more effective toughening. However, high concentrations of SEBS-*g*-MA caused a too high softening with a negative effect on toughness. As shown in Fig.7, when the amount of SEBS-*g*-MA exceeded 20 wt%, the impact strength started to drop.

3.3. Tensile properties

Fig. 8 presents the stress–strain curves of the neat PPO

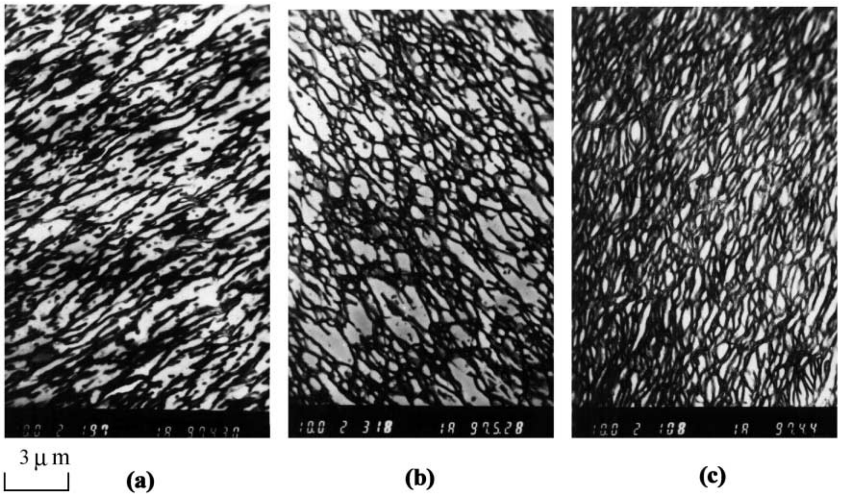

Fig. 6. TEM micrographs of PPO/SEBS-*g*-MA blend (70/30) at the position near the fracture point: 10,000: (a) skin, (b) intermediate, and (c) core regions.

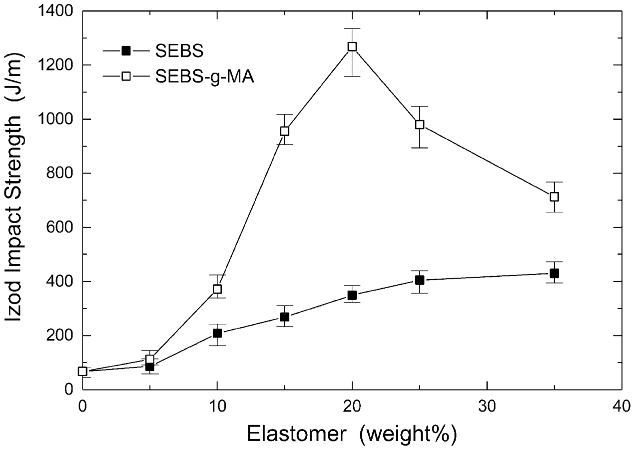

Fig. 7. The notched Izod Impact Strength of PPO/SEBS and PPO/SEBS-*g*-MA blends.

and its various blends. One can see that the shapes of the stress–strain curves are similar; as the strain increases, the stress passes through a maximum (the yield strength) and subsequently levels off. The neat PPO possesses the highest yield strength, but the lowest elongation at break. The chains of PPO are rigid because of their planar benzene rings and generate a compact, rigid structure due to the attractive interactions among the benzene rings. The presence of SEBS, neat or grafted with MA, weakens the interactions among the benzene rings. There are two kinds of blocks in the backbone of SEBS: namely, PS and E/B. The PS blocks, with benzene rings as lateral groups, are fully miscible with PPO. The E/B blocks are, however, immiscible with PPO and weaken the interactions among the benzene rings of both PPO and PS. For these reasons, the yield strength of the blends decreases with increasing SEBS content. For the SEBS grafted with MA, the drop in the yield strength is even greater. As already mentioned, the MA-grafting introduces a higher polarity into the blocks of E/B resulting in a higher incompatibility with the PPO segments. The small molecular weight of SEBS-*g*-MA also constitutes a reason for the low yield strength of its blends with PPO. Similar arguments can be also brought with regard to the tensile strength and modulus. As shown in Figs. 9 and 10, the addition of SEBS to PPO decreases the tensile strength and modulus. The tensile strength and modulus of the blends with MA-*g*-SEBS are even lower than those based on SEBS. The decreases of the yield and tensile strength shown in Fig. 11 are accompanied by an increase in the elongation at break. This occurs because the presence of the additives weakens the interaction among the benzene rings, and the chains can be more easily elongated.

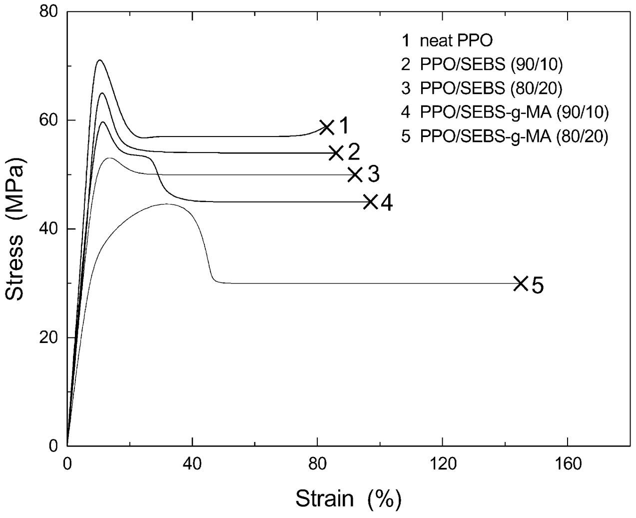

Fig. 8. The stress–strain curves of PPO and its blends.

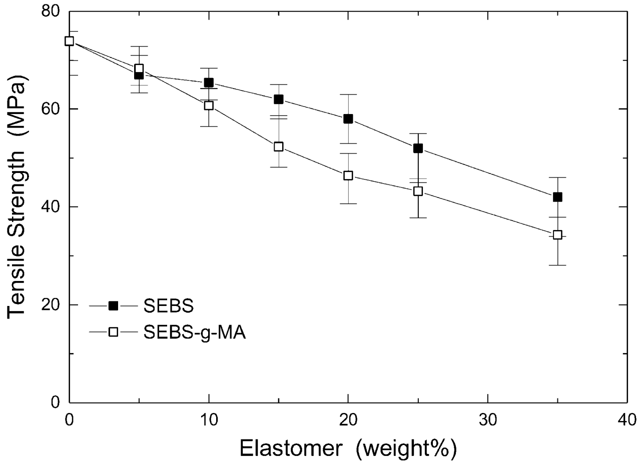

Fig. 9. The tensile strength of PPO/SEBS and PPO/SEBS-*g*-MA blends.

3.4. Rheology

In Fig. 12, the viscosity–shear rate curves of neat PPO and its blends with SEBS are plotted. It shows that SEBS increases the viscosity of the system; the higher the content of SEBS, the higher is the viscosity. The increase in viscosity is due to the entanglement caused particularly by the E/B blocks. Being flexible, the E/B blocks can entangle

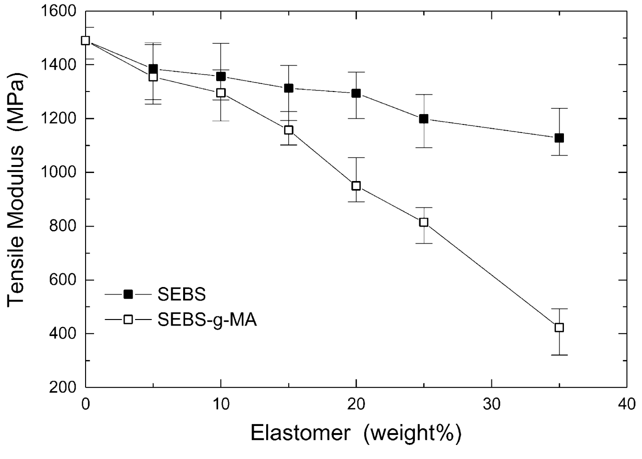

Fig. 10. The tensile modulus of PPO/SEBS and PPO/SEBS-*g*-MA blends.

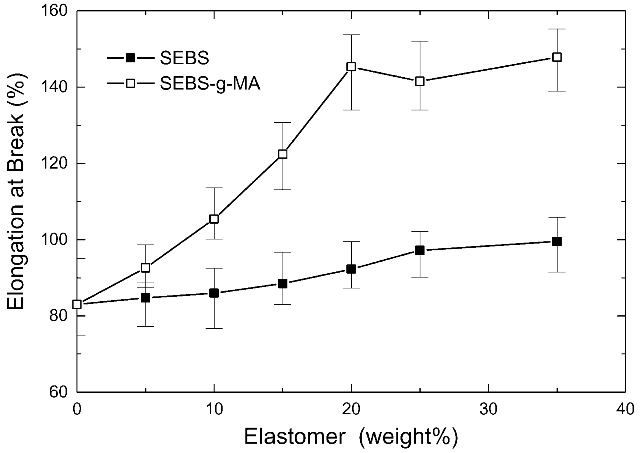

Fig. 11. The elongation at break of PPO/SEBS and PPO/SEBS-*g*-MA blends.

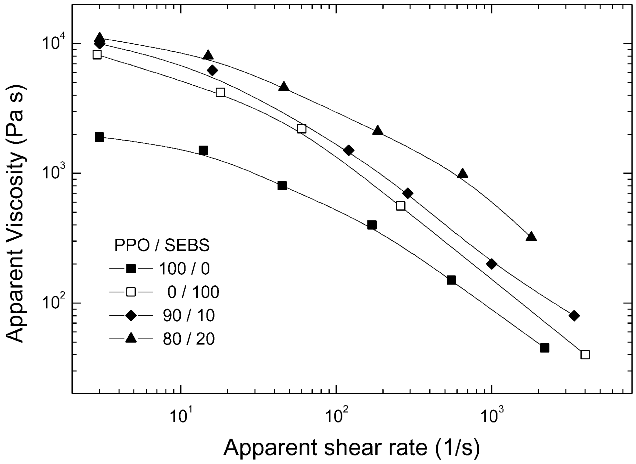

Fig. 12. Plots of apparent viscosity vs. apparent shear rate for PPO/SEBS blends.

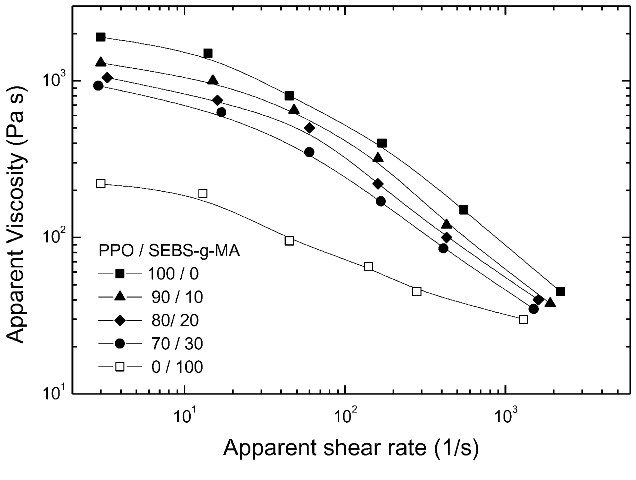

Fig. 13. Plots of apparent viscosity vs. apparent shear rate for PPO/SEBS-*g*-MA blends.

among themselves and also with the PS blocks and PPO chains. At low shear rates, the entanglement impedes severely the flow of the melt, and the viscosity is high. However, Fig. 12 shows that at high shear rates the viscosity decreases. This occurs most likely because the molecules are disentangled by high shear rates.

Fig. 13 presents the viscosity–shear rate curves of neat PPO and its blends with SEBS-*g*-MA. In contrast to the SEBS, the increase in the SEBS-*g*-MA content causes a decrease in viscosity. This occurs mainly because of the low molecular weight of SEBS-*g*-MA. In addition, as already mentioned, the grafting with MA increases the polarity of the E/B blocks. This increases the incompatibility with the PPO, and decreases the entanglement with other non-polar chains, the decrease being greater as the content of SEBS-*g*-MA increases.

4. Conclusion

SEBS and MA grafted SEBS (SEBS-*g*-MA) can be employed as impact modifiers for PPO. SEBS or SEBS-*g*-MA is distributed in the PPO matrix as discrete domains at low contents and as a continuous phase at high contents. The percolation threshold is lower for the SEBS-*g*-MA based blends. While SEBS-*g*-MA provides a high toughening of PPO (an optimum toughness higher than 1200 J/m was attained for a 20 wt% SEBS-*g*-MA content), the SEBS provides a more moderate one. The addition of SEBS-*g*-MA to PPO results in a dramatic reduction of the melt viscosity, thus improving the processability of PPO.

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