Novel Polyisobutylene Stars. XXIII. Thermal, Mechanical, and Processing Characteristics of Poly(phenylene ether)/ Polydivinylbenzene(polyisobutylene-*b*-polystyrene)$_{37}$ Blends

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ABSTRACT: The objective of these investigations was to increase the use temperature of novel star-block polymers consisting of a crosslinked polydivinylbenzene (PDVB) core from which radiate multiple poly(isobutylene-*b*-polystyrene) (PIB-*b*-PSt) arms, abbreviated by PDVB(PIB-*b*-PSt)$_n$. We achieved this objective by blending star-blocks with poly(phenylene oxide) (PPO) that is miscible with PSt. Thus, various PPO/PDVB(PIB-*b*-PSt)$_n$ blends were prepared, and their thermal, mechanical, and processing properties were investigated. The hard-phase glass-transition temperature of the blends could be controlled by the amount (wt %) of PPO. The blends displayed superior retention of tensile strengths at high temperatures as compared to star blocks. The melt viscosities of blends with low weight percentages of PPO were lower than those of star blocks. © 10928 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2866–2872, 2002

Key words: star-polymers; poly(phenylene oxide); blends

INTRODUCTION

The aim of this work was to increase the softening point of polydivinylbenzene[poly(isobutylene-*b*-poly-styrene)$_n$] [PDVB(PIB-*b*-PSt)$_n$] by blending with poly-(phenylene oxide) (PPO). Our incentive was to create easily processible thermoplastic elastomer (TPEs) with softening temperatures higher than those of polystyrene (PSt)-based TPEs. PPO [glass-transition temperature (T_g) ≈ 225°C] is miscible with PSt (T_g ≈ 100°C) in all proportions[1] and forms blends whose T_g's are between those of PSt and PPO and are determined by the relative proportions of PPO and PSt. Blends of PPO with PSt-*b*-poly(ethylene-butene)-*b*-PSt display a single hard phase,[2-4] and the T_g of the hard phase is dependent on the weight percentage of PPO in the blend.[3-5] The basis for the miscibility of PPO with PSt is the exothermic heat of mixing, which provides the driving force for miscibility on the molecular level.[6]

EXPERIMENTAL

Materials

Star-block syntheses have been described elsewhere.[7-9] The star block used in this study consisted of a crosslinked polydivinylbenzene (PDVB) core from which radiated 37 ± 5 poly(isobutylene-*b*-polysty-rene) (PIB-*b*-PSt) arms with number-average molecular weights (M_n's) of 14,300 (PSt) and 44,200 g/mol polyisobutylene (PIB). Thus, its overall composition was 22.5 wt % PSt, 70 wt % PIB, and 7.5 wt % PDVB; it contained about 25% diblock impurity.

Two PPOs were obtained from General Electric Company (Schenectady, NY): (1) $M_{n,PPO}$ = 10,500 g/mol, weight-average molecular weight (M_w)/M_n = 2.3, and T_g = 225°C and (2) $M_{n,PPO}$ = 3100 g/mol, M_w/M_n = 2.7, and T_g = 160°C.

We prepared the blends by dissolving a predetermined amount of PPO in a 50/50 (v/v) toluene/chloroform mixture and adding a measured quantity of star-block polymer at room temperature while stirring with a magnetic stirrer. A homogeneous solution was obtained. To prepare solvent cast films, we poured the solution into a 4 × 3 in. rectangular Teflon mold, covered with aluminum foil, and the solvent was evaporated slowly (2–3 weeks). Finally, the films were vacuum dried at room temperature for at least 2 weeks before testing. The films were clear (no entrapped bubbles) and were transparent.
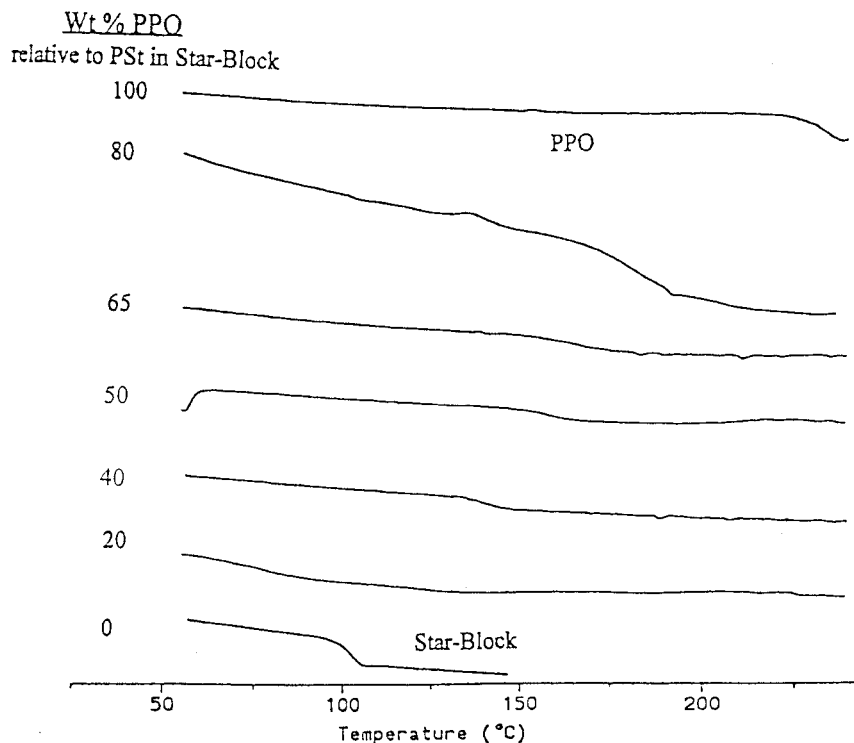
Figure 1 DSC thermograms of PPO (M_n = 10,500 g/mol)/PDVB(PIB/44-b-PSt/14)$_{37}$ blends.

Characterization

T_g's were determined by differential scanning calorimetry (DSC; Perkin-Elmer, DSC7). Thermograms were recorded by heating to 240°C at 10°C/min.

Stress–strain properties were measured by an Instron 5567 machine equipped with a video extensometer at room temperature. Tensile properties at elevated temperatures were measured by an Instron 1130 machine equipped with a temperature-controlled chamber with N_2 purging. The crosshead speed was 5 cm/min. The instruments were calibrated such that the full scale chart was 5, 10, or 20 kg. The chart speed and crosshead speed were the same.

Dynamic melt viscosities were investigated at 230°C with a rheometric mechanical spectrometer (Rheometrics, model 800) with a parallel plate arrangement. Circular samples (~2 mm thick, 2 cm in diameter) were cut from molded films. Dynamic viscosities were measured in the 0.01–100 rad/s range.

RESULTS AND DISCUSSION

Thermal properties

Figure 1 shows representative thermograms in the hard-phase transition region of PPO/star-block blends. The blends comprised various proportions of PDVB(PIB-b-PSt)$_{37}$ and a PPO of M_n = 10,500 g/mol. The horizontal axis is temperature (°C), and the vertical axis shows the weight percentage of PPO [W_{PPO}/

(W_{PPO} + W_{PSt}), where W is weight] relative to PSt in the star block. The T_g of the PSt phase of the star-block was about 100°C and that of the PPO was about 225°C. The thermograms between these two limits were for PPO/star-block blends. Evidently, the hard-phase T_g of the blends increased with the amount of PPO. In some cases (e.g., 20 wt % PPO), the transition was broad, however, visible. The breadth of the glass transition (ΔT_g) has been associated with the intimacy of aggregation of the two components in miscible blends[10] and may reflect compositional fluctuations of longer range concentration gradients. For the blends under investigation, ΔT_g was broader than expected and broader than for PPO/PSt blends.[11] According to the data in Figure 1, the blends exhibited one hard phase composed of the PSt blocks of the star block and PPO.

Figure 2 shows change in heat capacity (ΔC_p; based on the total hard-phase weight) of blends of star block with PPO (M_n = 10,500 g/mol, $T_g \simeq$ 225°C). The star block contained about 25% diblock impurity. The experimental data were close to the theoretical additive line; however, some deviation from the predicted[12] appeared at high weight percentages of PPO. This deviation may be significant as it may reflect the presence of a small pure PPO phase. Others have also noticed similar deviations from the theoretical with PPO/PSt-b-poly(ethylene-butene)-b-PSt blends and have found evidence by transmission electron microscopy for a small separate PPO phase at high PPO
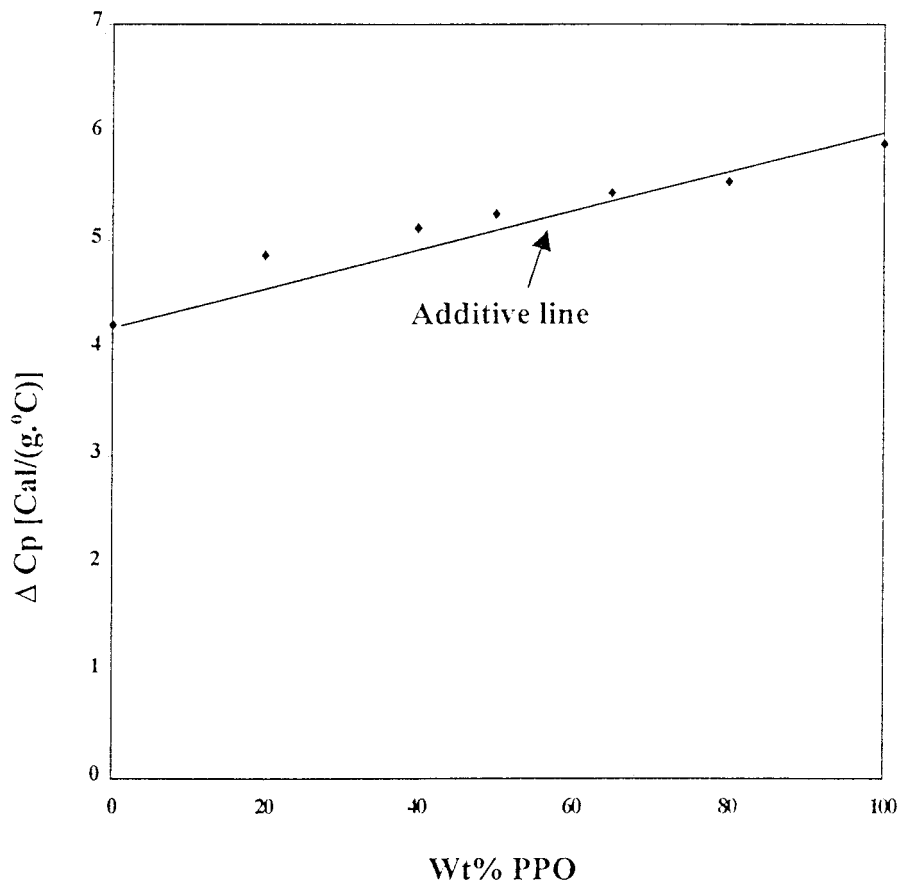
Figure 2 ΔC_p of PPO (M_n = 10,500 g/mol)/PDVB(PIB/44-b-PSt/14)$_{37}$ blends.

concentrations.[4] The polydispersity of the commercial PPO samples used in this research was broad (see the Experimental section), and the high-molecular-weight PPO fraction may have been of higher molecular weight than that of the PSt block in the star block (i.e., $M_{n,\text{PPO}} > M_{n,\text{PSt}}$). The high-molecular-weight PPO would have been immiscible with the PSt phase and would have caused ΔC_p to deviate from the theoretical.

Figure 3 summarizes the hard phase T_g's of two blends as a function of blend composition. The solid line connecting the T_g of the PSt phase in the star block with that of PPO was calculated by the Flory–Fox equation[12] and described the T_g of PPO/PSt blends. Blends of the low-molecular-weight PPO (M_n = 3100 g/mol, T_g = 160°C) showed one hard-phase T_g, which indicated a single PPO/PSt phase with an intermediate T_g. The T_g's of blends with the low-molecular-weight PPO followed the Flory–Fox prediction at all compositions.

The T_g's of blends with the high-molecular-weight PPO (M_n = 10,500 g/mol, $T_g \simeq$ 225°C) showed some deviation from the values predicted by the Flory–Fox equation, particularly at high PPO concentrations. Authors who have studied PPO/PSt-b-poly(ethylene-butene)-b-PSt blends[2,3] have also observed a similar

deviation between experimental and predicted T_g's and have attributed this discrepancy to the formation of PSt-rich and PPO-rich phases. The PPO-rich phases would have been expected to form in this research also due to the broad polydispersity of the PPO employed (M_w/M_n = 2.3). This PPO may have contained a PPO fraction whose molecular weight was higher than that of the PSt in the star block (i.e., $M_{n,\text{PPO}} > M_{n,\text{PSt}}$). Thus, the high-molecular-weight PPO fraction would have been immiscible with the PSt, and the PPO-rich phase so formed would have depressed the experimental T_g's relative to those predicted by theory.

An annealing study was made to determine how far these blends were from equilibrium. Figure 4 shows two DSC scans, one before and the other after a representative blend was annealed. To obtain the equilibrium morphology, we annealed a sample of the blend for 20 min at 160°C, which was just above the T_g of the hard phase. After annealing, the T_g of the mixed PPO + PSt phase increased and became sharper. Evidently, some material that affected the T_g before annealing no longer did so after annealing. Perhaps some PIB segments dispersed in the PPO + PSt phase may have redistributed into the PIB matrix as a result of annealing, which would have tended to increase the T_g of the hard phase. On annealing, the mixed PPO + PSt
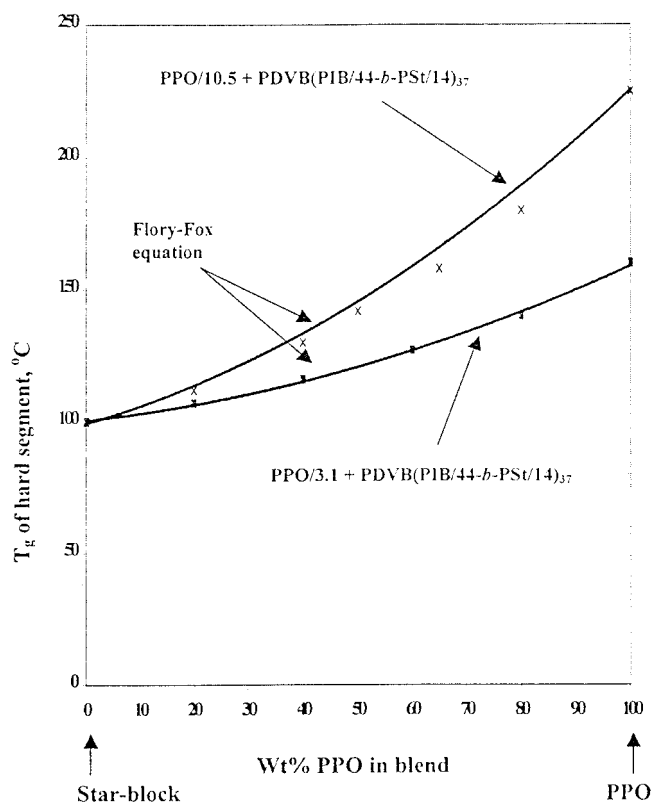
Figure 3 Hard-segment T_g's of PDVB(PIB/44-b-PSt/14)$_{37}$/PPO/10.5 and PPO/3.1 blends as a function of blend composition.

phases were expected to become more homogeneous, as evidenced by a sharpening of the T_g after annealing. The fact that the T_g did not change appreciably on annealing indicates that the system was nearly at equilibrium even before annealing.

Mechanical properties

The mechanical properties of star-block/PPO blends containing 20, 40, 50, and 80% PPO (M_n = 10,500 g/mol, T_g = 225°C) were investigated. Figure 5 shows stress–strain traces of the blends together with that of the star block at room temperature, and Table I summarizes the results for permanent set and hardness data.

The blends displayed higher moduli relative to those of the star block at all elongations. Elongations decreased with increasing amounts of PPO because the relative amounts of PIB decreased. The modulus and shore A hardness (see Table I) increased with increasing PPO weight percentage. Blends with 20 and 40 wt % PPO displayed conventional stress–strain profiles of thermoplastic elastomers (absence of yield points or no cold-draw regions). A dramatic difference in tensile behavior occurred with 80% PPO. The blend showed a prominent yield point with a short draw and about 150% elongation. A similar yield behavior with short necking (cold draw) was also seen for the blend with 50 wt % PPO, however, with 200% elongation.

Interest in triblock copolymers, such as poly(styrene-b-butadiene-b-styrene (PSt-b-PBD-b-PSt), is primarily due to their thermoplastic elastomer characteristics. A desirable feature of TPEs is a relatively temperature-independent modulus in the vicinity of use temperature, with the upper and lower limits being defined by the softening temperatures of the two phases. The absolute value of the modulus is governed by the relative proportions of the two phases and their spatial arrangement or morphology. As seen in the previous section, moduli can be affected by blending star blocks with varying amounts of PPO. An increase in hard-phase T_g (over that of the star block) of the blends has also been shown in the previous section. We investigated the tensile properties of the blend containing 20 wt % PPO at elevated temperatures. This blend was chosen because its stress–strain curve displayed characteristics of a thermoplastic elas-
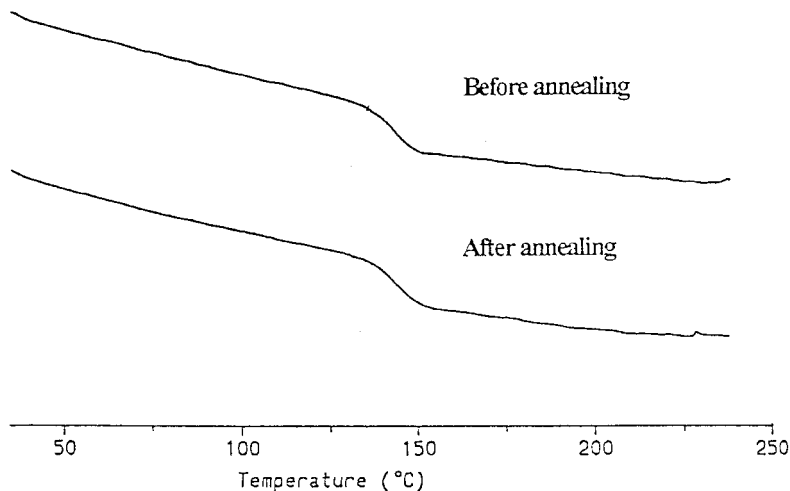

Figure 4 DSC thermograms of 70/40 (w/w) PDVB(PIB/44-b-PSt/14)$_{37}$/PPO/10.5 blends. Annealing was performed for 20 min at 160°C.
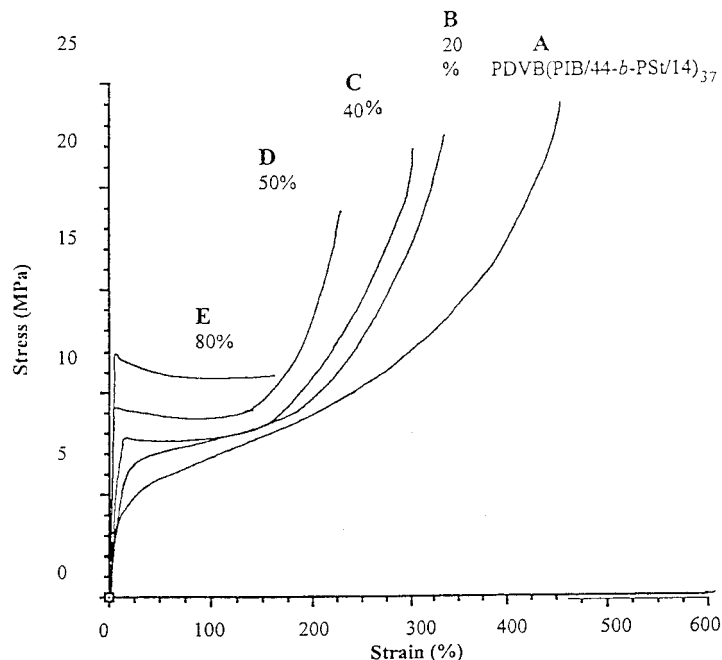
Figure 5   Stress–strain traces of PDVB(PIB/44-*b*-PSt/14)$_{37}$/PPO/10.5 blends.

tomer; it did not show yield, and its hard phase T_g was about 120°C.

Figure 6 shows stress–strain traces of the blends in the 25–90°C range. According to the data, tensile strengths, moduli, and elongations decreased with increasing temperatures. At 40°C, the elongation was still above 400%; in fact, it was slightly higher than that at room temperature. Elongations and moduli dramatically decreased with increasing temperature, indicating deformation of the hard PPO + PSt phases. The elongation at 90°C was only about 140% as compared to about 350% at room temperature. Evidently, the hard phases softened with increasing temperature, and their stress bearing ability diminished. Due to the increase in temperature, the hard domains underwent thermal swelling, and the energy needed for stress fracture decreased.

In summary, the rubbery phase was dominant in blends containing 20 and 40 wt % PPO, whereas the hard phase dominated tensile behavior in blends with 50 and 80 wt % PPO. The blend with 80 wt % PPO exhibited plastic-like behavior. PPO/star-block blends had higher moduli, lower elongations, and higher shore A hardness than those of star-block polymers.

Melt viscosity of star-block/PPO blends

We investigated the melt viscosity of star-block/PPO blends to gain insight into their processability. Figure
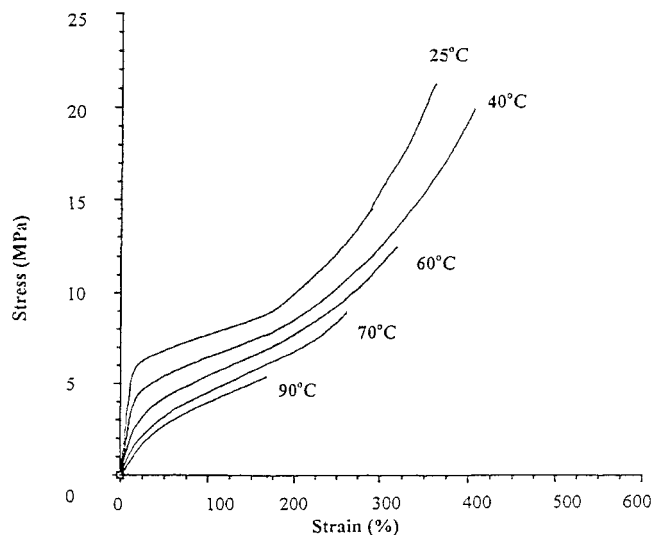
TABLE I
Hardness and Permanent Set of PDVB(PIB-*b*-PSt)$_{37}$/PPO Blends

Blend composition (% PPO)[a,b]	Shore A hardness	Permanent set (%)
0	62	14
20	66	17
40	74	22
50	78	27
80	86	36
100	96	Not applicable[c]

[a] Star block = PDVB(PIB/44-*b*-PSt/14)$_{37}$; the star block contained about 25 wt % prearm diblock impurity.
[b] $M_{n,\text{PPO}}$ = 10,500 g/mol.
[c] Material exhibited only 27% elongation.

Figure 6   Stress–strain traces of PDVB(PIB/44-*b*-PSt/14)$_{37}$/PPO/10.5 blends at various temperatures.
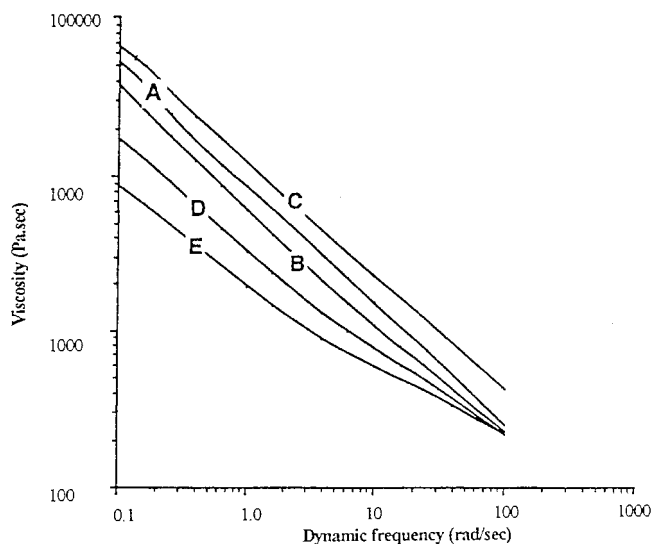
Figure 7 Dynamic melt viscosity of PDVB(PIB/44-*b*-PSt/14)$_{37}$/PPO/10.5 and PPO/3.1 blends: (A) star block, (B) star block + 20 wt % PPO/10.5, (C) star block + 40 wt % PPO/10.5, (D) star block + 20 wt % PPO/3.1, and (E) star block + 40 wt % PPO/3.1.

7 shows the melt viscosity of a star block and its blends with two kinds of PPOs ($M_{n,PPO}$ = 10,500 and 3100 g/mol). The melt viscosity of the blends showed non-Newtonian behavior and decreased with increasing frequency. In line with Storey et al.'s findings,[13] the samples were expected to be phase separated at the testing temperature (230°C). The reduction of melt viscosity with increasing frequencies was expected because phase segregation in the melt was progressively disrupted by increasing frequencies. At low frequencies, phase separation prevailed, whereas at increasing frequencies, it became increasingly disrupted. This kind of flow behavior was caused by phase separation. The viscosity of phase separated systems was high because energy was needed to overcome the resistance of high solubility-parameter PSt + PPO domains to flow through the low solubility-parameter PIB matrix (δ_{PPO} = 9.5,[14] δ_{PSt} = 9.4,[15] δ_{PIB} = 7.8[15]). Additionally, at low frequencies, the time was sufficient for the hard domains to reorganize in the melt. In contrast, at high frequencies hard phases could not form in the melt, and flow became controlled by chain entanglements in the PIB phase.

Both samples B and D contained 20 wt % PPO, but B contained a higher molecular weight PPO. It was evident that even at the same hard-phase content, the molecular weight of the PPO affected melt viscosity. In sample D, the low-molecular-weight ($M_{n,PPO}$ = 3100 g/mol) PPO may have exerted a plasticizing effect, which may have dramatically reduced the melt viscosity of the star block. Sample B contained the higher molecular weight PPO ($M_{n,PPO}$ = 10,500

g/mol), and although the melt viscosity of B was lower than that of the star block, this reduction in melt viscosity was lower than that for sample D. So, even at equal hard-phase contents, the blend with the higher molecular weight PPO displayed a higher melt viscosity. A similar explanation may hold for the difference in the melt viscosities of samples C and E.

Blends B and C contained the same PPO ($M_{n,PPO}$ = 10,500 g/mol) but different amounts of it (B contained 20 wt %, and C contained 40 wt %). The melt viscosity of sample C was higher than that of B, which suggests that the hard phase was larger in C than in B. A larger hard phase (as in C) would have required more energy (stress) input to flow at the same rate as a smaller hard phase (as in B) through the PIB matrix. These higher energy requirements (of C) would have appeared in the form of higher melt viscosity. A similar chain of thought could explain the difference in the melt viscosities between samples D and E.

Unexpectedly, the melt viscosity of sample C (40 wt % PPO, $M_{n,PPO}$ = 10,500 g/mol) was higher than that of the star block (sample A). This observation could be explained by considering that PPO may have crystallized at about 230°C.[16] The melting temperature of PPO crystals is about 265°C,[16] and at the testing temperature (230°C), the PPO-rich phase may have contained sufficient PPO for crystallization. Thus, sample C would have contained three phases: a PIB matrix, a PSt-rich phase, and a crystalline PPO phase. The crystalline PPO phase would have been solid at the testing temperature and would have increased the melt viscosity.

CONCLUSIONS

Blends of star blocks consisting of a crosslinked PDVB core and multiple PIB-*b*-PSt arms with PPO were prepared, and their thermal, mechanical, and rheological properties were tested. The hard-phase T_g of the blends could be increased over those of star blocks, and the T_g's could be controlled by variation of the amount of PPO in the blends. The $M_{n,PSt}/M_{n,PPO}$ ratio should have been greater than unity for obtaining a uniform single hard phase. The blends displayed higher tensile moduli, higher shore A hardness, lower elongations, and a lower melt viscosity than star blocks. The blends were easily processible thermoplastic elastomers.

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