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Blends of SBS Triblock Copolymer with Poly(2,6-dimethyl-1,4-phenylene oxide)/Polystyrene Mixture

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ABSTRACT: Blends of styrene–butadiene–styrene (SBS) or styrene–ethylene/1-butene–styrene (SEBS) triblock copolymers with a commercial mixture of polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) were prepared in the melt at different temperatures according to the chemical kind of the copolymer. Although solution-cast SBS/PPO and SBS/PS blends were already known in the literature, a general and systematic study of the miscibility of the PS/PPO blend with a styrene-based triblock copolymer in the melt was still missing. The thermal and mechanical behavior of SBS/(PPO/PS) blends was investigated by means of DSC and dynamic thermomechanical analysis (DMTA). The results were then compared to analogous SEBS/(PPO/PS) blends, for which the presence of a saturated olefinic block allowed processing at higher temperatures (220°C instead of 180°C). All the blends were further characterized by SEM and TGA to tentatively relate the observed properties with the blends' morphology and degradation temperature. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2698–2705, 2003

Key words: processing; blends; polyethers; polystyrene; thermal properties

INTRODUCTION

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is a very attractive material to be blended with other polymers because it displays a very high chemical resistance and high glass-transition temperature (T_g) at about 215°C.[1,2] In particular, the thermal stability[1] of PPO is quite interesting, given that the degradation mechanism is a function of testing atmosphere: thermal degradation temperatures and kinetic parameters seem to be higher in air than in nitrogen.

PPO and polystyrene (PS) were solution blended to evaluate the thermal and rheological behavior of the blend.[3,4] In particular, films of PS/PPO have been studied by DSC and thermooptical analysis (TOA).[3] Both the TOA transition temperature (T_{TOA}, the temperature at which birefringence disappears) and the T_g value of the blend increase monotonously by adding PPO to PS, suggesting a good compatibility between the two components. A more detailed characterization of PS/PPO blend properties was performed by evaluating the viscoelastic response.[4] The thermomechanical response of PPO/PS blends exhibits a single T_g and a single rubbery plateau that falls between the response of the individual components, thus confirming a strong compatibility between PPO and PS. Of course, the chemical modification of PS chains can strongly influence the compatibility with PPO.[5] Compatibility of random copolymers of *para*-chlorostyrene and *ortho*-chlorostyrene (PO copolymers) with PPO was studied by DSC analysis. On the basis of classical compatibility analysis (single T_g and optical clarity for compatibilized blends), it is possible to observe that PO copolymers are compatible with PPO for certain copolymer compositions, although they are not miscible with the two homopolymers.

Values of T_g and T_{TOA} were used to rationalize the properties of SBS/PPO blends.[6] TOA transition temperature of blends increases monotonously from SBS-rich blends to PPO-rich ones. Therefore, a good compatibility between the components has been suggested by assuming that the melt blending of SBS with PPO yields the complete incorporation of the latter into PS domains of the former. A more detailed characterization of solution-cast SBS/PPO blends was previously performed by DSC, TEM, and DMA analyses.[7] Both DSC and DMA data clearly suggest that PPO forms a single, mixed hard phase on the observation of a single glass-transition temperature and tan δ peak, which are intermediate between those of pure components. However, at high PPO content, TEM microscopy indicates the presence of an additional "hard" phase, which can be tentatively identified as pure PPO. Both DSC and DMA techniques are not able to detect such a new phase, whose formation is consistent with T_g depression of a PS-rich phase at high PPO content.

TABLE I
DSC Analysis of SBS/PPO and SEBS/PPO Blends

Run[a]	T_g^1 (°C)[b]	T_g^2 (°C)[c]
SBS	−84.8	80.4
SEBS[d]	—	81.8
PPO	—	114.4
SBS/PPO 90/10, 12 min	−86.1	87.8
SBS/PPO 80/20, 12 min	−85.2	93.1
SBS/PPO 70/30, 12 min	−86.9	97.5
SBS/PPO 90/10, 20 min	−85.8	90.4
SBS/PPO 80/20, 20 min	−86.3	92.6
SBS/PPO 70/30, 20 min	−86.3	95.9
SEBS/PPO 90/10	—	99.3
SEBS/PPO 80/20	—	105.0
SEBS/PPO 70/30	—	106.8

[a] Blends composition is expressed in weight ratios.
[b] Evaluated from first cooling curves.
[c] Evaluated from second heating curves.
[d] T_{g1} for SEBS copolymer and relative blends could not be correctly determined because of the superposition with the broad melting endotherm of EB block.

These results are in agreement to what was already reported in the literature about general blending of SBS triblock copolymer with polystyrene.[8,9] It is in fact possible to explain such results by assuming that when increasing the PPO amount, blend morphology moves toward macrophase separation, with worsening of dynamic and thermal behavior. Significantly, the tan δ peak for the soft phase shifts slightly to lower values by adding PPO, suggesting a rejection of PS chains from the PB phase upon mixing with a hard component. By taking into account some theoretical models and calculations,[10] a concentration gradient spanning the mixed phase, composed of copolymer end blocks and homopolymer, has been proposed. Concentration of PS end-block segments reaches its highest value at the interface, where concentration of PPO is minimized.

In this work a commercial PPO/PS mixture was used to combine the good solubility of both PPO and PS into the PS domains of the triblock copolymers SBS and SEBS with the synergism in thermal and mechanical properties previously observed for blends of SBS with PS-based materials.[8,9,11–13]

EXPERIMENTAL

Polymers

The PPO/PS blend (referred to as PPO, for simplicity in the text), Noryl PX-1766, was produced by GE Plastics (USA) (specific density, 1.04 g/cm³; elongation at break, 160–170%). The blend was characterized, as determined by ¹H-NMR, by a 1 : 1 M ratio between PPO and PS.

The block copolymer SBS (Calprene 501; Softer S.p.A, Forlì, Italy) was used without further purifica-

tion. It was characterized by a butadiene/styrene ratio of 69/31 (w/w), block average molecular weights 9300/41,400/9300 with $\overline{M_w}/\overline{M_n} = 1.5$, and vinyl units in the butadiene block of 10 wt % with respect to the total amount of butadiene units.

The block copolymer SEBS Kraton G-1650 (hereafter, SEBS) was supplied by Shell and used without further purification. This polymer contains 19 mol % styrene; $\overline{M_n} = 8.0 \times 10^4$; and $\overline{M_w}/\overline{M_n} = 1.2$–1.5.

Characterization

DSC analyses were performed on a Perkin–Elmer DSC-7 calorimeter (Perkin Elmer Cetus Instruments, Norwalk, CT) equipped with a CCA7 cooling device. Mercury (m.p. −38.4°C) and indium (m.p. 156.2°C) standards for low-temperature scans and indium and zinc (m.p. 419.5°C) for high-temperature scans were used for instrument calibration. Heating and cooling thermograms were carried out at standard rate of 20°C/min.

For thermogravimetric analysis, all TGA thermograms were recorded by a Mettler TC11 instrument equipped with a Mettler M3 balance, with an accuracy of 10^{-3} mg. Heating thermograms were carried out at a standard rate of 10°C/min under dry nitrogen atmosphere.

All SEM micrographs were recorded on samples of cryogenically fractured surfaces by a JEOL instrument (JSM model T-300; JEOL, Peabody, MA) at the Chemical Engineering Department of Pisa University.

Dynamic-mechanical thermograms (DMTA) were recorded by a Perkin–Elmer DMA-7e instrument (three-point bending geometry). Thermograms were carried out at a standard heating rate of 1°C/min.

Preparation of blends in the melt

Blends of SBS with PPO were prepared using different weight ratios (10, 20, and 30 wt % of PPO) between the components and also different mixing times (12 and 20 min) so that they are coded as "SBS/PPO wt/wt x min," with x corresponding to the mixing time. Blends with SEBS were prepared according to the same compositions but the mixing time was kept constant and equal to 12 min.

The blends were prepared in a Brabender plastograph mixer under nitrogen atmosphere by introduc-

TABLE II
Calculated Solubility Parameters of Blends Components

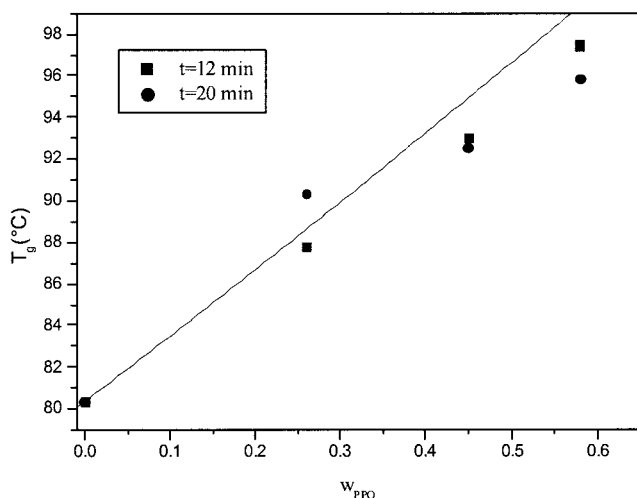| Sample	δ (cal/cm³)$^{0.5}$
PPO	9.6
PS	9.5
PB	8.0
P(EB)	7.8

Figure 1 T_g versus weight fraction of PPO with respect to PS blocks (w_{PPO}) at different mixing times.

ing the desired amounts of the components (for a total amount of 20 g) in the mixer at 180°C for SBS/PPO and at 220°C for SEBS/PPO, rotor speed 50 rpm. After the desired time, the mixing was stopped and the materials recovered from the Brabender mixing chamber.

RESULTS AND DISCUSSION

Blends of SBS or SEBS and PPO were prepared at different temperatures: 180°C for SBS and 220°C for SEBS. The reason for such a difference can be found in the different stabilities of the two triblock copolymers during melt processing. The chemical structure of SBS and SEBS is of course very similar and, most important, the PS blocks, which are demonstrated to directly interact with PPO and PS,[3,4,6] show the same chemical structure and very similar average length. To gain
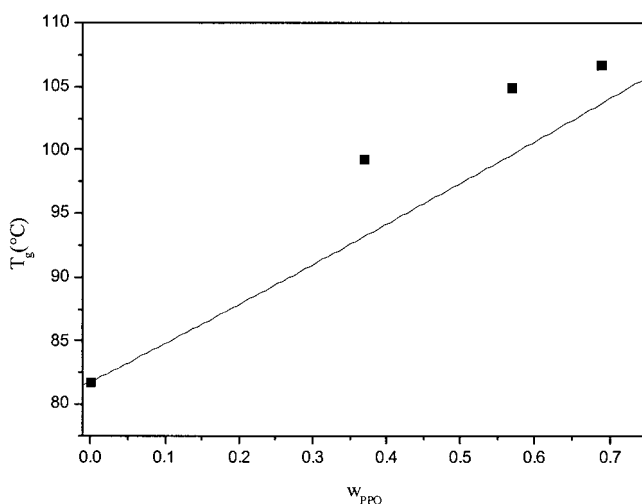

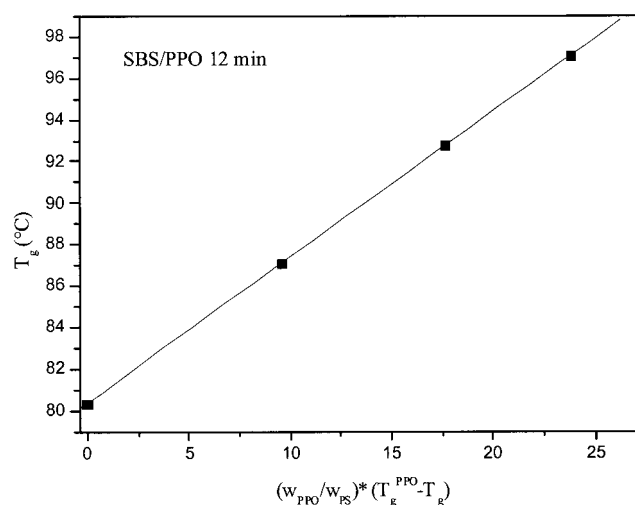**Figure 2** T_g versus weight fraction of PPO with respect to PS blocks (w_{PPO}).

Figure 3 Gordon–Taylor plot for SBS/PPO 12 min blends.

insight into the influence of the processing time on the product properties, blends of SBS and PPO were carried out for two different mixing times ($t = 12$ and 20 min).

All blends, as given in Table I, display the presence over room temperature of a single glass-transition temperature (T_g), intermediate between those of the neat components, confirming that PPO is completely compatible with the PS blocks of SBS and SEBS. For SBS/PPO blends, the T_g of the "soft" phase does not change appreciably upon mixing, showing that PPO interacts most exclusively with the "hard" phase of the triblock copolymer.[3,6,10] This result can be also supported from a more theoretical point of view. If one compares, as given in Table II, the calculated[14] solubility parameter (δ_x, where x denotes the polymer) of the PPO/PS blend with those of the blocks in SBS and SEBS copolymer, that is, PS and the two "soft" phases, the minimum difference is clearly observed when comparing δ_{PPO} with δ_{PS}. On the basis of this result, it can be stated that only the PS phase, for both SBS and SEBS copolymers, solubilizes PPO upon processing. For this reason, when trying to correlate the blends' thermal behavior with their composition, the weight fraction of PPO (w_{PPO}) was calculated with respect of the amount of PS blocks and not of the overall copolymer. Besides, the observed thermal behavior does not agree with the expected outcome on the basis of theoretical predictions of T_g for miscible blends. Figures 1

TABLE III
Gordon–Taylor Constants (k_{GT}) for Blends of SBS or SEBS with PPO

Sample	k_{GT}	R^2
SBS/PPO, 12 min	0.70 ± 0.01	0.99
SBS/PPO, 20 min	0.56 ± 0.14	0.91
SEBS/PPO	1.55 ± 0.26	0.96

(a) SBS/PPO 12min 90/10

(b) SBS/PPO 20min 90/10

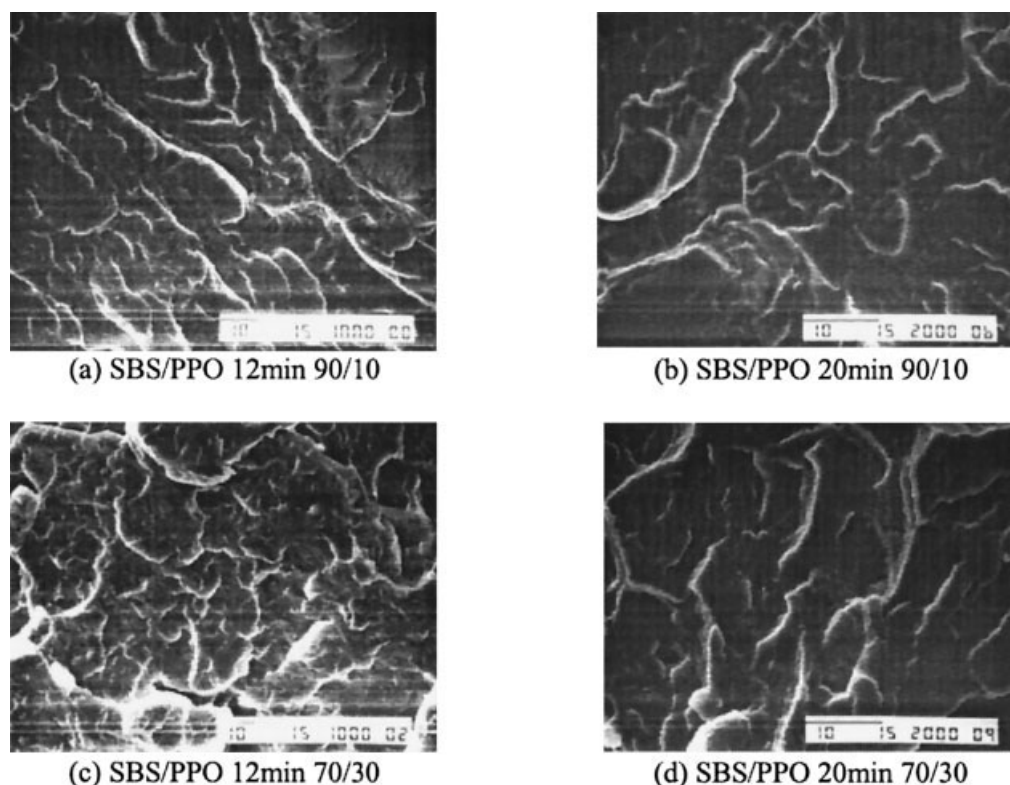(c) SBS/PPO 12min 70/30

(d) SBS/PPO 20min 70/30

Figure 4 SEM micrographs for SBS/PPO blends: (a) SBS/PPO 12 min 90/10; (b) SBS/PPO 20 min 90/10; (c) SBS/PPO 12 min 70/30; (d) SBS/PPO 20 min 70/30.

and 2 depict the comparison, as a function of the blends' composition, between the observed T_g values with those predicted by the Fox equation (continuous lines in Figs. 1 and 2):

$$\frac{1}{T_g} = \frac{w_{PPO}}{T_g^{PPO}} + \frac{w_{PS}}{T_g^{PS}}$$

where T_g is the glass-transition temperature of the blend, T_g^x is the glass transition of the neat component x, and w_x is the weight fraction of component x (only the PS block of the SBS copolymer was considered). Deviations of the experimental values from the theoretical trend are clearly detected. In particular, the

experimental T_g values for the SEBS/PPO blends are strongly and positively deviating from the expected values. However, it is clear that the Fox equation is not suitable to describe the blends' thermal properties over room temperature. For this reason, the Gordon–Taylor equation[15,16] was used:

$$T_g = \frac{w_{PS}/T_g^{PS} + k_{GT} * w_{PPO}/T_g^{PPO}}{w_{PS} + k_{GT} * w_{PPO}}$$

where T_g, T_g^x, and w_x have the above-mentioned meaning; and k_{GT}, the Gordon–Taylor constant, is a parameter that can be qualitatively related to the strength of the interaction between the two components in the
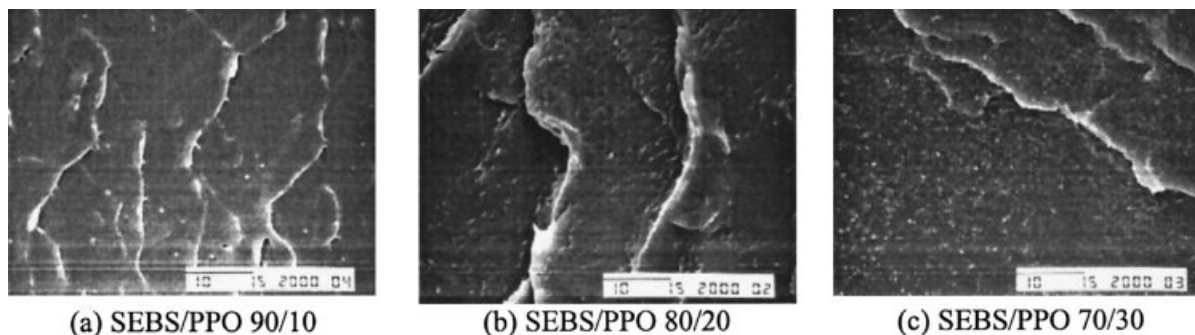

(a) SEBS/PPO 90/10

(b) SEBS/PPO 80/20

(c) SEBS/PPO 70/30

Figure 5 SEM micrographs for SEBS/PPO blends: (a) SEBS/PPO 90/10; (b) SEBS/PPO 80/20; (c) SEBS/PPO 70/30.

TABLE IV
TGA Analysis of SBS/PPO and SEBS/PPO Blends

Sample[a]	T_d (°C)[b]	$T_{10\%}$ (°C)[c]	$T_{20\%}$ (°C)[c]	$T_{30\%}$ (°C)[c]
SBS	446.8	380.6	404.8	417.8
PPO	446.7	352.2	400.3	419.1
SEBS	426.3	396.2	404.0	410.0
SBS/PPO 12m 90/10	449.0	265.6	318.1	388.3
SBS/PPO 12m 80/20	449.0	259.4	311.8	388.0
SBS/PPO 12m 70/30	451.3	273.1	339.5	402.7
SBS/PPO 20m 90/10	451.3	271.9	320.7	386.1
SBS/PPO 20m 80/20	451.3	258.5	313.8	392.5
SBS/PPO 20m 70/30	451.3	275.1	338.3	401.7
SEBS/PPO 90/10	389.0	367.0	373.7	378.8
SEBS/PPO 80/20	433.3	392.1	402.2	410.5
SEBS/PPO 70/30	433.3	393.5	404.5	412.7

[a] Blends composition is expressed by weight ratios.
[b] Determined as abscissa of the inflection point in the 1st-derivative TGA curves.
[c] $T_{x\%}$, loss mass temperature, is defined as the temperature at which $x\%$ of the initial mass is lost.

blends. The higher the k_{GT} value, the stronger the interaction between the two components. k_{GT} was determined, according to the literature,[15] by linear fit of data in plots (see, for example, Fig. 3) of T_g as a function of composition. The results, as given in Table III together with the values of the squared correlation coefficient (R^2) for the linear fit analysis, clearly address that reaction time has a slight but negative influence on the strength of interaction between components, whereas, on the other hand, the mixing temperature seems to have a positive influence, as demonstrated by the high k_{GT} value for SEBS/PPO blends.

The presence of the above differences in the interaction of PPO with PS blocks of SBS and SEBS, however, did not result in appreciable differences in the blends' morphology. SEM micrographs, as depicted in Figures 4 and 5, show in all cases the presence of a homogeneous morphology, strongly suggesting that a single "hard" phase, containing the PS blocks of the triblock copolymer and PPO, is formed upon mixing.

The blends' degradative behavior was a very important issue, especially to determine whether the high thermal stability of PPO could be observed even in its blends with the two copolymers. However, the differences in the mixing behavior as a function of time and temperature are not clearly reflected by the blends' degradative behavior. A simple TGA analysis, whose results are given in Table IV, clearly shows that both the degradation (T_d) and loss-mass ($T_{x\%}$) temperatures display an ill-defined dependency on the blends' composition. This result can, in the first instance, be explained by the fact that the degradation parameters for the neat components are too close to each other to promote appreciable differences in the blends. On the other hand, such similar degradative behavior of the blends' components suggested the use of a more accurate TGA model[17] to investigate the blends' behav-
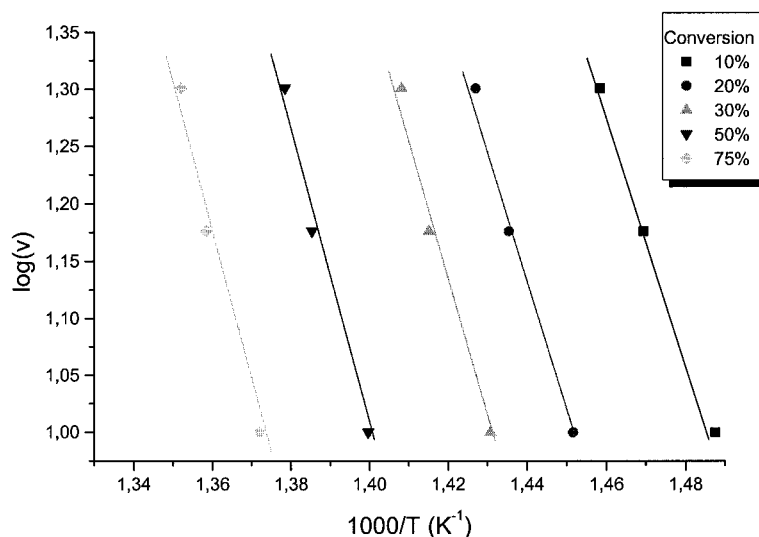

Figure 6 Arrhenius-type plot for SEBS/PPO 80/20 blend.

TABLE V
Activation Energy (E_a), as Derived from TGA Analysis, for Blends of PPO with SBS and SEBS

Sample[a]	E_a 50% (kJ/mol)[b]	R[c]
SBS/PPO 12m 90/10	128 ± 2	−0.99
SBS/PPO 12m 80/20	108 ± 5	−0.99
SBS/PPO 12m 70/30	117 ± 50	−0.98
SBS/PPO 20m 90/10	114 ± 1	−0.99
SBS/PPO 20m 80/20	118 ± 15	−0.99
SBS/PPO 20m 70/30	101 ± 1	−0.99
SEBS/PPO 90/10	111 ± 32	−0.96
SEBS/PPO 80/20	114 ± 12	−0.99
SEBS/PPO 70/30	64 ± 12	−0.98

[a] Blends composition is expressed in weight ratios.
[b] E_a x% = activation energy calculated at x% conversion (loss-mass).
[c] Correlation coefficient for the linear fit analysis.

ior. If one assumes that degradation follows a first-order kinetic, it is possible to plot experimental data according to an Arrhenius-type equation:

$$\log(v) = \log(z) - \frac{E_a}{RT}$$

where E_a is the activation energy, z is the preexponential factor, T is the absolute temperature, R is the perfect gas constant, and v is the heating rate of the TGA experiment. By carrying out, on every single blend, TGA runs at different values of v, it is then possible to plot $\log(v)$ against $1/T$, as given, for example, in Figure 6. By interpolating the data with a linear fit, it is possible to obtain $\log(z)$ as the intercept and E_a from the slope of the obtained straight lines. Given the assumption of first-order kinetics, the meaning of E_a is the same as that of pure kinetic activation energy[17]: the greater the E_a value, the more improved the thermal stability. Such an approach allows a choice of the level of conversion (i.e., of mass loss), and allows a comparison of E_a values for different samples at that conversion. The assumption of first-order kinetics,

which may not hold for the blends' degradative behavior, can be evaluated on the basis of the correlation coefficient (R) values for each linear-fit analysis. The results of the above-mentioned analysis on the SBS/PPO and SEBS/PPO blends, as given in Table V for a 50% loss-mass, demonstrate the decrease of the blends' thermal stability by increasing the amount of PPO. This trend is evident by comparing the E_a values of blends with 30 wt % of PPO with the others, but cannot be explained solely on the basis of the neat components' degradation behavior. Indeed, it must be stressed that more accurate conclusions could not be drawn from the data, whose difference often lies within experimental error.

DMTA data for all blends, as given in Table VI, resulted in some interesting considerations. All blends were in fact tougher than the corresponding SBS and SEBS components. Both T_g and tan δ peak values for the blends are shifted to higher temperatures with respect to the corresponding triblock copolymer, which also results in a well-defined dependency of the tan δ peak position on the PPO amount in the blends, as depicted, for example, in Figure 7. Also interesting is the relative decrease of the storage modulus ($\Delta E/E$), which represents the decrease of the storage modulus in the temperature range ΔT, the latter corresponding to the T_g of the "hard" phase. In all cases $\Delta E/E$ decreases drastically as a result of the mixing of PPO with SEBS or SBS, clearly confirming the toughening effect of PPO on both SBS and SEBS. The same considerations hold if one compares (as depicted, for example, in Fig. 8) the entire storage modulus (E') curves as a function of the temperature. A shift of the storage modulus and relative onset T_g points toward higher temperatures is clearly observed by increasing the PPO content in the blends.

Conclusions

Blends of PPO with SBS or SEBS triblock copolymers were prepared in the melt at different temperatures

TABLE VI
DMTA Analysis of SBS/PPO and SEBS/PPO Blends

Run[a]	T_g (°C)	tan δ (°C)	$\Delta E/E$ (%)[b]	ΔT (°C)[b]
SBS	64.6	78.2	82.8	50 ÷ 78
SEBS	83.1	93.3	67.5	50 ÷ 100
SBS/PPO 90/10, 12min	74.4	90.1	47.3	50 ÷ 80
SBS/PPO 80/20, 12min	79.9	95.6	36.0	50 ÷ 80
SBS/PPO 70/30, 12min	88.4	102.0	10.4	70 ÷ 80
SBS/PPO 90/10, 20min	77.0	92.0	53.7	50 ÷ 80
SBS/PPO 80/20, 20min	83.6	100.2	31.0	50 ÷ 80
SBS/PPO 70/30, 20min	86.3	104.2	19.6	50 ÷ 80
SEBS/PPO 90/10	86.5	146.7	37.7	50 ÷ 100
SEBS/PPO 80/20	102.5	148.7	23.2	50 ÷ 100
SEBS/PPO 70/30	105.4	146.7	34.6	50 ÷ 100

[a] Blends composition is expressed in weight ratios.
[b] Relative decrease of the storage modulus {$\Delta E/E = [(E_{T_1} - E_{T_2})/E_{T_1}) \times 100$]} calculated in ΔT ($T_1 ÷ T_2$) range.
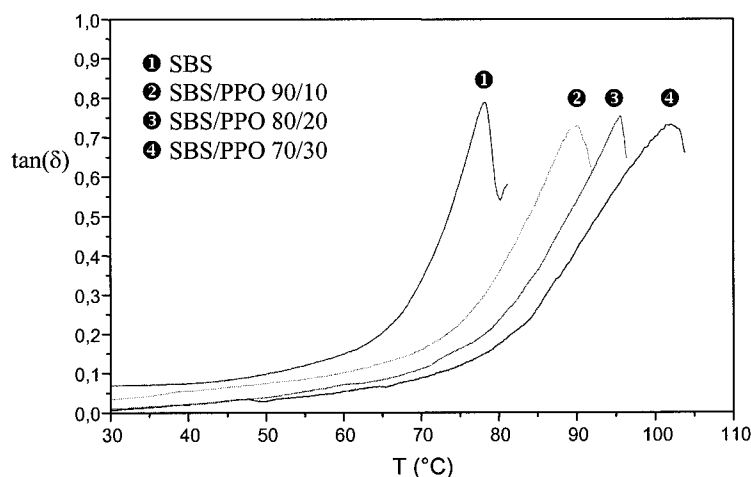
Figure 7   Tan δ curves for SBS/PPO 12m blends.

according to the chemical kind of the copolymer. In all cases both DSC and SEM analysis clearly demonstrated that PPO interacts preferably with the PS block of the copolymer and that a new single hard phase, containing PPO and PS chains, is formed upon mixing. The use of Fox and Gordon–Taylor equations for the interpretation of the blend T_g values established that the mixing time has only a slight influence on the blends' compatibility and in general on the interaction between the blends' components. On the other hand, SEBS seems to be more compatible than SBS with PPO, resulting in higher T_g values for the blends and more uniform morphology. These results can be explained on the basis of the different mixing temperatures (220°C for SEBS/PPO and 180°C for SBS/PPO blends) if one does not take into account, as already suggested by DSC analysis, the interaction of PPO with the "soft"

phases of the two copolymers. No synergism in the thermal properties was observed, given that the T_g value of the blends always lies between those of the neat components.

The degradation behavior of the blends, as investigated by TGA, shows an ill-defined dependency on the blend composition and does not establish any clear conclusion about the components' interaction. This is probably a result of the fact that the degradation behavior of the components is too similar to promote appreciable differences in their blends.

However, DMTA data address the fact that both triblock copolymers become tougher upon addition of PPO. The T_g value of the "hard" phase increases by as much as 40°C (SEBS/PPO 70/30 blend), whereas the relative decrease of the storage modulus clearly decreased with the amount of PPO in the blend.
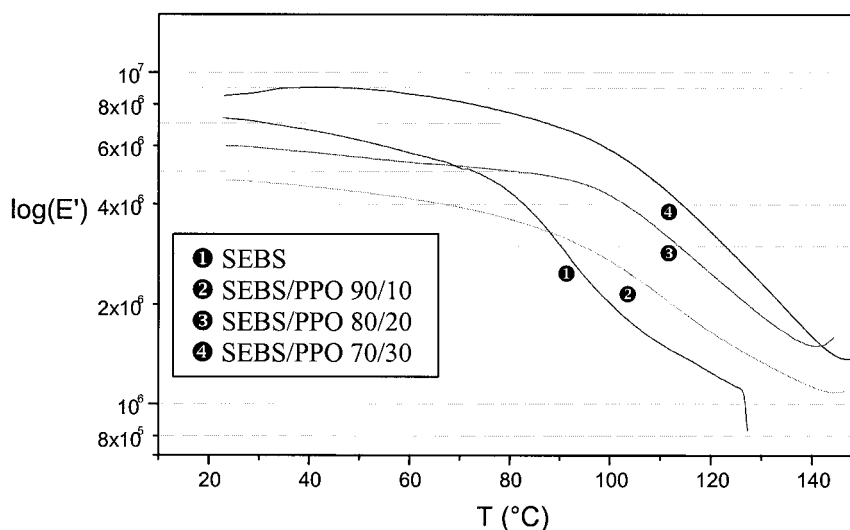

Figure 8   Storage modulus for SEBS/PPO blends.

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