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Full Paper: Blending of polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) triblock copolymers with syndiotactic polystyrene (PSsyn) has been performed in a Brabender mixer above the glass transition temperature of the triblock copolymer but below the melting point of PSsyn. The presence of a large excess of amorphous SBS (at least 70 wt.-%) as well as of the amorphous PSsyn phase (about 60 wt.-%, also above its T_g) allowed the easy mixing of the components. In contrast, the presence of unmelted PSsyn crystallites affects both the final morphology of the blend as well as its dynamic behavior. Indeed, according to the dynamic thermomechanical analysis (DMTA) data it is possible to suggest that such solid particles act to reinforce the overall blend structure (as in composite materials filled with inorganic solid particles). Similar behavior is also observed for the SBS copolymer alone below the T_g of the styrene blocks, T_g (PS). This conclusion is supported by both the compatibility of the blends, and the thermal and dynamic thermomechanical behavior at $T > T_g$ (PS) as investigated by means of Differential Scanning Calorimetry (DSC), Scanning Electron

Microscopy (SEM) and DMTA. The results obtained are tentatively compared with those of similar blends obtained from toluene solution.

SEM micrograph of a solution-cast SBS/PSsyn550k blend.

Blends of Syndiotactic Polystyrene with SBS Triblock Copolymers

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Introduction

Syndiotactic polystyrene (PSsyn) is a new semi-crystalline engineering polymer that has become available at an industrial scale recently due to the use of metallocene catalysts.^[1–3] This polymer has attractive characteristics such as high melting temperature (about 270 °C) and fast crystallization. In particular, the thermal and mechanical behavior of PSsyn is very interesting when compared with that of the atactic and isotactic analogues.^[4] The melting enthalpy ($\Delta H_m = 2050 \pm 100$ cal/unit) and entropy ($\Delta S_m = 3.8 \pm 0.2$ cal/K unit) of PSsyn, determined by melting point depression in the presence of diluents, show that the difference in melting enthalpy between PSsyn and isotactic PS (iPS) is within the experimental accuracy. However the two stereoisomers also display differences in their dynamic-mechanical behavior which have been tentatively explained on the basis of the different chain packing in iPS and PSsyn.^[5]

On the other hand, PSsyn also displays a polymorphic behavior^[6–8] that is strongly affected by several factors when cooling from the melt: the cooling rate, the crystalline form of the starting material, the maximum temperature of the melt, the time of residence at that temperature and finally the heating rate to reach the melting point. Of course the presence of several crystalline structures, which can be finely “tuned” according to the materials thermal history, makes PSsyn an even more attractive material from a strictly applications point of view.^[9–13] However the low solubility of PSsyn in common solvents, as well as its high melting point, have in the past limited the possibility for this material to be blended with other polymeric materials in order to achieve commercial composite materials. In particular blending with styrene block copolymers such SBS or styrene-ethylene/1-butene-styrene (SEBS) seems to represent an attractive route to combine the PSsyn properties, with those of rubbery

materials. Moreover, the solubility of the syndiotactic component into the atactic PS domains of the copolymers should be reasonably ensured by the demonstrated miscibility in solution of PSsyn with its atactic stereoisomer. In fact both modulated DSC^[14,15] and diffusion experiments^[16] clearly demonstrated for these blends the presence of a single T_g , that is also dependent on composition according to Fox equation.

On the other hand solution cast blends of SBS with atactic PS have recently been performed;^[17,18] it has been demonstrated that the key parameter governing the solubility of the PS homopolymer into the PS domains of SBS is the ratio between the molecular weight of the homopolymer ($\bar{M}_{n(ho)}$) and that of the PS blocks of the copolymer ($\bar{M}_{n(co)}$). When the two values are close enough to each other, their ratio being nearly unity, synergism in thermal and dynamic behavior has been observed,^[12] and explained on the basis of entanglement formation in the new PS phase of the copolymer.

Our previous studies^[19] demonstrated the possibility for PSsyn to be mixed in a Plastigraph Brabender-type mixer with SEBS triblock copolymer at 220 °C provided that the percentage and crystallinity of PSsyn was low.

Therefore, the objective of the present work was to study the miscibility of syndiotactic PS with the atactic PS blocks of SBS triblock copolymer as a function of the molecular weight ratio ($\bar{M}_{n(ho)}/\bar{M}_{n(co)}$) both in toluene solution and in the melt at 180 °C. Furthermore, attention has been devoted to the investigation of the blends properties, and in particular to the behavior at $T > T_g$ (PS).

Experimental Part

Polymers

Two samples of syndiotactic polystyrene were kindly supplied by Enichem Elastomeri (Ravenna, Italy). PSsyn59k was characterized by $\bar{M}_n = 5.9 \times 10^4$, $\bar{M}_w/\bar{M}_n = 2.4$ and a stereoregularity degree 98%. PSsyn550k was characterized by $\bar{M}_n = 5.5 \times 10^5$, $\bar{M}_w/\bar{M}_n = 2.2$, stereoregularity degree of 99.5% and no atactic fraction. Both homopolymers were used without further purification.

Atactic PS (Repsol; $\bar{M}_n = 5.2 \times 10^3$, $\bar{M}_w/\bar{M}_n = 2.5$) was used without purification.

The block copolymer SBS (Calprene 501, Softer S.p.A, Forlì, Italy) was employed without further purification. It had a butadiene/styrene ratio of 69/31 (wt./wt.), block average molecular weights of 9300–41400–9300 with $\bar{M}_w/\bar{M}_n = 1.5$ and vinyl units in the butadiene block of 10 wt.-% with respect to the total amount of butadiene units.

Characterization

Differential scanning calorimetry (DSC) analyses were performed using a Perkin Elmer DSC7 calorimeter 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-tem-

perature scans have been used for instrument calibration. Heating and cooling thermograms were carried out at a standard rate of 20 °C/min.

Thermogravimetric analyses (TGA) were recorded using 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 a dry nitrogen atmosphere.

Scanning electron microscopy (SEM) micrographs were recorded, from cryogenically fractured surfaces of samples, with a Jeol JSM T-300 instrument at the Chemical Engineering Department of Pisa University.

Dynamic-mechanical thermograms (DMTA) were recorded using a Perkin-Elmer DMA7e instrument (three-point bending geometry). Thermograms were carried out at a standard heating rate of 1 °C/min.

Preparation of Blends by Mechanical Mixing

The blends (SBS/PSsyn wt./wt.) were prepared in a Brabender plastograph mixer under a nitrogen atmosphere by introducing the desired amounts of the components in the mixer at 180 °C with a rotor speed of 50 rpm. After 10 min, the mixing was stopped and the materials recovered.

Preparation of Blends by Solution Casting

30 mL of toluene were introduced under a dry nitrogen atmosphere into a 100 mL two-necked flask equipped with a reflux condenser. Then the calculated amount of PS or SBS and PSsyn were added in order to obtain c.a. 0.5 g of blend. The mixture was stirred for 4 h at the boiling temperature of toluene, and then left to cool at room temperature. The solvent was evaporated under reduced pressure: first at $p = 20$ mmHg and then at $p = 1$ mmHg to constant weight.

Results and Discussion

Solution-Cast Blends

In order to get a preliminary insight into the compatibility of PSsyn with the styrene blocks of the SBS triblock copolymer, solution-cast blends containing 10, 20 and 30 wt.-% of the homopolymers have been prepared in toluene solution. For comparison PS/PSsyn blends with the same PSsyn contents have also been prepared.

DSC (Table 1) shows, for the PS/PSsyn blends, a single, nearly additive, glass transition temperature, intermediate between those of solution-cast components, thus confirming^[14–16] a good compatibility. However a deeper insight into the blends thermal behavior can be achieved by comparing the normalized melting and crystallization enthalpies per gram of PSsyn, ΔH_m and ΔH_c (J/g_{PSsyn}), of the blends with those of the solution-cast PSsyn samples. Experimental values for both melting and crystallization enthalpies agree with those expected on the basis of the behavior of the pure components. This suggests that, within the experimental accuracy, solution blending does not modify the thermal properties of PSsyn. However, the

Table 1. DSC analysis of solution-cast PS/PSsyn blends.

Sample ^{a)}	$T_g^{1\text{ b)}}$ °C	$T_g^{2\text{ b)}}$ °C	$T_m^{b)}$ °C	$\Delta H_m^{b)}$ J/g	$\Delta H_m^{b)}$ J/g _{PSsyn}	$T_c^{d)}$ °C	$\Delta H_c^{d)}$ J/g	$\Delta H_c^{d)}$ J/g _{PSsyn}
PS	—	81.7	—	—	—	—	—	—
PSsyn59k	—	95.1	258.4	25.7	25.7	218.8	25.8	25.8
PSsyn550k	—	96.5	270.9	24.5	24.5	255.8	24.1	24.1
PS/PSsyn59k (90/10)	—	83.4	249.7	0.9	9.0	n.d.	n.d.	n.d.
PS/PSsyn59k (80/20)	—	83.2	251.2	4.8	24.0	188.3	3.8	19.0
PS/PSsyn59k (70/30)	—	86.5	255.0	8.1	27.0	189.9	8.8	29.3
PS/PSsyn550k (90/10)	—	85.3	267.3	2.7	27.0	n.d.	n.d.	n.d.
PS/PSsyn550k (80/20)	—	87.1	270.0	5.3	26.5	216.7	3.9	19.5
PS/PSsyn550k (70/30)	—	86.3	270.0	7.4	24.7	216.7	6.0	20.0

a) Composition of blends is expressed in weight ratios.

b) Evaluated from 2nd-heating curve.

c) Calculated by dividing measured ΔH_m and ΔH_c values by corresponding PSsyn weight fractions.

d) Evaluated from 1st-cooling curve.

Table 2. DSC analysis of solution cast – SBS/PSsyn blends.

Sample ^{a)}	$T_g^{1\text{ b)}}$ °C	$T_g^{2\text{ b)}}$ °C	$T_m^{b)}$ °C	$\Delta H_m^{b)}$ J/g	$\Delta H_m^{b)}$ J/g _{PSsyn}	$T_c^{d)}$ °C	$\Delta H_c^{d)}$ J/g	$\Delta H_c^{d)}$ J/g _{PSsyn}
SBS	−85.0	80.6	—	—	—	—	—	—
PSsyn59k	—	95.1	258.4	25.7	25.7	218.8	25.8	25.8
PSsyn550k	—	96.5	270.9	24.5	24.5	255.8	24.1	24.1
SBS/PSsyn59k (90/10)	−85.2	89.5	256.8	2.9	29.0	206.1	2.7	27.0
SBS/PSsyn59k (80/20)	−85.1	88.8	255.8	4.7	23.5	211.1	4.4	22.0
SBS/PSsyn59k (70/30)	−85.1	89.6	256.7	6.9	23.0	212.1	7.2	24.0
SBS/PSsyn550k (90/10)	−85.1	90.6	269.0	1.4	14.0	230.0	0.5	5.0
SBS/PSsyn550k (80/20)	−85.8	93.4	269.7	3.8	19.0	228.3	2.4	12.0
SBS/PSsyn550k (70/30)	−85.3	94.6	269.3	6.5	21.7	217.8	6.6	22.0

a) Composition of blends is expressed in weight ratios.

b) Evaluated from 2nd-heating curve.

c) Calculated by dividing measured ΔH_m and ΔH_c values by corresponding PSsyn weight fractions.

d) Evaluated from 1st-cooling curve.

PS/PSsyn59k (90/10) blend shows a marked reduction in crystallinity ($\Delta H_m = 9.0 \text{ J/g}_{\text{PSsyn}}$ instead of 25.7). This blend is characterized by the most favorable conditions for mixing: low PSsyn content and with the lowest difference in molecular weight between polystyrene blocks in the copolymer and the homopolymer. The corresponding PS/PSsyn550k (90/10) blend, where the difference in molecular weight is higher, does not show the above effect, thus confirming^[17,18] that the molecular weight ratio between polystyrene chains of the components is an important parameter affecting the blends thermal properties.

Also solution-cast blends of SBS with the two samples of PSsyn display a single glass transition temperature for the PS phase (Table 2), intermediate between those of neat SBS and PS components. However, T_g does not vary with the composition for PSsyn59k, whereas the T_g of the PSsyn550k-based blends increases monotonously with PSsyn content. At the same time, the T_g of the butadiene phase does not change upon solution mixing of SBS with

PSsyn, thus suggesting a negligible interaction of the homopolymers with the PB blocks. More significant modifications can be observed for the SBS/PSsyn550k (90/10) blend. Indeed, normalized ΔH_m values are clearly lower than that of the pure component, indicating that the difference is decreasing with increasing content of PSsyn550k from 10 to 30 wt.-%. These results suggest that PSsyn550k is more compatible than PSsyn59k with the PS blocks of SBS, a fact that would not be expected on the basis of the lower $\bar{M}_{n(\text{ho})}/\bar{M}_{n(\text{co})}$ ratio for the SBS/PSsyn59k blend. This hypothesis has been tested by SEM analyses which show (Figure 1 and Figure 2) white domains dispersed in the dark matrix; the latter become more evident with increasing PSsyn59k content. When using higher molecular weight PSsyn, the morphology is slightly more homogeneous since only white line fractures over the surface are displayed. All these considerations agree with DSC data and indicate a better compatibility, for solution-cast blends, of PSsyn550k than PSsyn59k.

Figure 1. SEM micrographs of solution-cast SBS/PSsyn59k blends.

Blending in a Brabender Mixer

The moderate crystallinity (about 40 wt.-% as determined by DSC analysis) of the PSsyn used could allow bulk mixing with SBS below the PSsyn melting temperature but above the T_g (PS). Six blends (SBS/PSsyn), three for each PSsyn sample, have been prepared, using 10, 20 and 30 wt.-% of syndiotactic component, by mixing in the Brabender at 180 °C for 10 min.

In the blends, T_g values (Table 3) for the PB-rich phase are very similar to that of pure SBS, indicating the lack of strong interaction between PSsyn and the soft phase of the triblock copolymer. The PS phase shows only one T_g , intermediate between those of the pure components, which does not depend on composition and on PSsyn molecular weight. Indeed, all differences in measured values are within instrument experimental accuracy. For all blends it is possible to observe that T_m is very similar to that of neat PSsyn, except for the SBS/PSsyn550 (70/30) blend that displays a melting point depression of about 10 °C.

Figure 2. SEM micrographs of solution-cast SBS/PSsyn550k blends.

A more accurate evaluation of compatibility between the PS phase of SBS and PSsyn can be performed on the basis of the crystallization and melting behavior as already discussed for solution-cast blends. When normalizing for example, crystallization enthalpy values per gram of PSsyn, it is possible to compare experimental enthalpy values (plotted as a function of PSsyn weight fraction, w_{PSsyn}) with those expected on the basis of neat PSsyn thermal behavior (Figure 3). The strong deviations of experimental trends from the expected ones suggest that the blending procedure affects also the amorphous-crystalline interface of PSsyn. This hypothesis is confirmed, within every single DSC run, by the different values of the melting and crystallization enthalpies as determined respectively by the 1st-cool and 2nd-heating curves. The neat PSsyn homopolymers do not show, within the experimental accuracy, any detectable change in the melting and crystallization enthalpies, thus strongly suggesting that the chemical nature of the amorphous crystalline interface does not change during the DSC

Table 3. DSC analysis of SBS/PSsyn blends.

Run ^{a)}	$T_g^{1\text{ b)}}$ °C	$T_g^{2\text{ b)}}$ °C	$T_m^{b)}$ °C	$\Delta H_m^{b)}$ J/g	$T_c^{d)}$ °C	$\Delta H_c^{d)}$ J/g
SBS	-84.8	80.8	—	—	—	—
PSsyn59k	—	100.0	258.5	24.5	225.9	24.1
PSsyn550k	—	101.3	270.8	25.7	237.3	25.8
SBS/PSsyn59k (90/10)	-84.7	98.3	255.6	2.6	204.6	2.1
SBS/PSsyn59k (80/20)	-83.7	96.2	256.3	3.5	212.6	3.0
SBS/PSsyn59k (70/30)	-84.7	98.6	256.5	5.3	211.7	6.5
SBS/PSsyn550k (90/10)	-84.0	96.9	267.8	2.5	215.7	2.1
SBS/PSsyn550k (80/20)	-84.4	97.1	268.5	4.7	214.7	5.0
SBS/PSsyn550k (70/30)	-84.6	98.3	259.2	5.2	215.9	4.9

^{a)} Composition of blends is expressed in weight ratios.

^{b)} Evaluated for 2nd-heating curve.

^{c)} Evaluated from 1st-cooling curve.

Figure 3. Crystallization behavior of SBS/PSsyn blends.

Figure 4. SEM analysis of SBS/PSsyn59k blends.

measurement.^[20] In contrast, strong changes are detected when PSsyn is blended with SBS, even if the PSsyn crystallites remain unmelted during the process: this result clearly demonstrates the fact that interactions between the components occur upon mixing at 180 °C, and that these interactions are able to modify the thermal behavior of the PSsyn crystallites. In particular (Figure 3) the blends containing 20 wt.-% of PSsyn59k and 30 wt.-% of PSsyn550k display melting enthalpies that are well below those expected on the basis of PSsyn thermal behavior. This can be considered as indirect evidence that a synergistic effect occurs for these particular compositions, due to interactions between the triblock copolymer and the syndiotactic component. The nature of such synergistic effects can be explained on the basis of entanglement formation, in the hard phase, upon mixing.^[17,18] This occurrence, for certain PSsyn contents, is still unclear but represents quite a common phenomenon in polymer blends.^[21] SEM micrographs show (Figure 4 and Figure 5) the presence of large white domains, probably corresponding to PSsyn crystallites, dispersed in the dark

Figure 5. SEM analysis of SBS/PSsyn550k blends.

Table 4. E_a values for SBS/PSsyn blends at a conversion of 20%.

Sample ^{a)}	E_a kJ/mol
SBS/PSsyn59k (90/10)	98 ± 9
SBS/PSsyn59k (80/20)	183 ± 18
SBS/PSsyn59k (70/30)	94 ± 8
SBS/PSsyn550k (90/10)	82 ± 6
SBS/PSsyn550k (80/20)	78 ± 9
SBS/PSsyn550k (70/30)	114 ± 8

^{a)} Composition of blends is expressed in weight ratios.

matrix. However significant changes in the average crystallites size, as a function of the blends composition, could not be detected.

If one assumes that chain entanglement, whenever it occurs in the prepared blends upon mixing, creates in the system a physically crosslinked network, then TGA analysis can be tentatively used in order to verify the occurrence of a synergistic behavior.^[17,18] Each sample was subjected to three TGA runs^[22] at three different scanning rates. By plotting the logarithm of heating rate against the reciprocal of temperature in an Arrhenius-type plot it is possible to obtain values of activation energy (E_a) and pre-exponential factor (z). Changes in the slope of straight lines can be associated with the variation of degradation mechanism. Indeed, the slope is directly proportional to E_a values that can be related to thermal stability: the greater the E_a value the higher the stability. It appears that after loss of 10 wt.-% a change in degradation mechanism occurs so that it's worth comparing E_a for different blends only at conversion values higher than 10%. E_a values at 20% conversion are reported in Table 4. There is a clear dependence of E_a on the composition of the blends (trends are similar for other conversion values); in particular SBS/PSsyn59k (80/20) and SBS/

Table 5. DMTA analysis of SBS/PSsyn blends.

Run ^{a)}	T_g °C	$\Delta E/E$ ^{b)} %	ΔT ^{b)} °C
SBS	73	93	25–120
SBS/ PSsyn59k (90/10)	76	89	25–120
SBS/ PSsyn59k (80/20)	78	89	25–120
SBS/ PSsyn59k (70/30)	79	90	25–120
SBS/ PSsyn550k (90/10)	78	90	25–120
SBS/ PSsyn550k (80/20)	78	91	25–120
SBS/ PSsyn550k (70/30)	78	91	25–120

^{a)} Composition of blends is expressed in weight ratios.

^{b)} Relative decrease of the storage modulus ($\Delta E/E$) in the temperature range ΔT , expressed as a percentage ratio of E' values before and after the PS-domains glass transition temperature.

PSsyn550k (70/30) show a much higher thermal stability than the others, indicative of the presence of a synergistic effect. This evidence is in striking agreement with that already discussed for the DSC data, although a direct correlation between these two kinds of effects needs to be further investigated.

DMTA analysis of all the blends (Table 5) indicates a variation in T_g of the hard phase of about 3–6 °C with respect to pure SBS. These values seem to be rather independent of composition for blends with PSsyn550, while T_g increases with PSsyn59 content. The relative decrease of the storage modulus ($\Delta E/E$), calculated in correspondence of the hard phase T_g , is less upon mixing with PSsyn (with respect to the pure SBS).

Conclusion

The blends of SBS triblock copolymer with syndiotactic polystyrene samples of different molecular weight display different morphological and thermal behaviors, as a function of the average molecular weight of the PSsyn and of the method of blend preparation. In the case of solution-cast blends, DSC and SEM investigations suggest the occurrence of partial mixing of the PS of SBS with the amorphous phase of PSsyn; PSsyn550k seems more effective than PSsyn59k. In each case all blends display a single T_g (at high temperatures), thus confirming that the difference in tacticity does not appreciably affect the solubility of the syndiotactic chains into the atactic PS domains of the triblock copolymer. The crystallization behavior of the homopolymers is only slightly modified after mixing with SBS.

In the case of the blends prepared in the Brabender mixer, the presence of a composition-dependent synergistic effect for both kinds of PSsyn can be inferred based on the blends thermal behavior as investigated by DSC and TGA. SEM micrographs show the presence of a new morphology, with PSsyn crystallites widespread around a homogeneous matrix and displaying good adhesion with the latter. Dynamic behavior of such new morphological

structures is only slightly different from that of neat SBS: in each case, both T_g and loss-modulus values suggest that the triblock copolymer stiffens upon mixing with the syndiotactic component. An increase in T_g values, as determined by DMTA, is also displayed by SBS/atactic PS blends, but in this case the morphology is much more simple due to the lack of a crystalline phase. On the other hand such crystalline domains seem to have a small influence on loss-modulus values in contrast to what we previously reported on SEBS/PSsyn blends,^[19] where a new $\tan(\delta)$ peak arose at $T > T_g$ (PS). Such differences can be tentatively ascribed to the different processing temperatures: mixing at 220 °C (SEBS/PSsyn blends) allows a more intimate mixing between the components than blending at 180 °C (SBS/PSsyn blends).

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