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Blends of syndiotactic polystyrene with SEBS triblock copolymers

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Abstract

Blending of styrene-\textit{b-}(ethylene-co-\textit{1-butene})-\textit{b}-styrene (SEBS) triblock copolymers with syndiotactic polystyrene (PS\textsubscript{syn}) has been performed in a Brabender mixer above the higher glass transition temperature of the triblock copolymer but below the PS\textsubscript{syn} melting point. The large excess of the triblock copolymer over the homopolymer as well as the significant amount of plasticized amorphous PS\textsubscript{syn} phase allowed the easy processing under the used temperature conditions with good interface compatibility. The consequent interfacial adhesion between the amorphous PS phase and the unmelted PS\textsubscript{syn} crystallites affects both the final morphology of the blend as well as its dynamic behavior. Indeed, such solid particles act as reinforcing point of the overall blend structure, as evidenced by scanning electron microscopy. Moreover, they contribute to a $T_g$ increase in the order of 20 °C with respect to pure SEBS and to an appreciable conservation of mechanical properties at temperatures higher than the $T_g$ of the PS blocks of SEBS. The mechanical and thermal behavior of the synthesized blends has been studied and tentatively correlated to the molecular weight ratio between PS\textsubscript{syn} and the PS blocks of SEBS. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Blends; Styrene-\textit{b-}(ethylene-co-\textit{1-butene})-\textit{b}-styrene; Syndiotactic polystyrene

1. Introduction

Syndiotactic polystyrene (PS\textsubscript{syn}) is a new semi-crystalline engineering polymer that has became available up to an industrial scale recently by the introduction of metalloocene catalyst systems [1–3].

This polymer has attractive characteristics such as high melting temperature (about 270 °C) and high crystallization rate. In particular, the thermal and mechanical behavior of PS\textsubscript{syn} is very interesting if compared with that of atactic and isotactic analogs [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 PS\textsubscript{syn}, determined by melting point depression in the presence of diluents, show that the difference in melting enthalpy between PS\textsubscript{syn} and isotactic PS (iPS) is within the experimental accuracy. The differences in the two structures are then accounted for by different $\Delta S_m$ and $T_m$ values.

Differences between isotactic and syndiotactic PS are also observed in their dynamic behavior [5]. The modulus of isotactic-PS decreases with higher rate (derivative), whereas that of PS\textsubscript{syn} is still high near the melting point. Such a drastic difference between the two isomers cannot be ascribed to different behaviors of one amorphous phase, which must be substantially similar in the two systems. Instead, the difference can be attributed to the crystalline component: the zig-zag planar conformation of PS\textsubscript{syn} sample, with a dense packing of aromatic rings, can be responsible for such a high stiffness as compared with iPS. In the case of iPS chain the conformation is helicoidal, which probably gives rise to a more pronounced plastic behavior of the crystalline blocks [5].

Moreover, PS\textsubscript{syn} displays a polymorph behavior [6–8] that is strongly affected, when cooling from the melt, by 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. This suggests the possibility of PS\textsubscript{syn} properties to be finely tuned depending on processing conditions and on the characteristics of the starting material.

The influence on miscibility of different microtacticity has been investigated for solution cast PS/PS\textsubscript{syn} blends [9–11]. Blends of atactic and syndiotactic PS show a single glass transition temperature, its value depending on blend composition. However, this result does not confirm the complete miscibility because there is only a small difference in $T_g$ of the two neat polymers [9]. In order to get a deeper insight into the miscibility of the two homopolymers both diffusion [9] and modulated Differential scanning calorimetry (DSC) [10,11] experiments have been carried.
Table 1
Characteristics of the polymeric materials used in preparing SEBS/PSyn blends

<table>
<thead>
<tr>
<th>Blends</th>
<th>$M_n^{lo}$ (amu)</th>
<th>$M_n^{co}$ (amu)</th>
<th>$M_n^{lo}/M_n^{co}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEBS-1/PS</td>
<td>52,000</td>
<td>24,000</td>
<td>2.2</td>
</tr>
<tr>
<td>SEBS-1/PSyn59k</td>
<td>59,000</td>
<td>24,000</td>
<td>2.5</td>
</tr>
<tr>
<td>SEBS-1/PSyn550k</td>
<td>550,000</td>
<td>24,000</td>
<td>22.9</td>
</tr>
<tr>
<td>SEBS-2/PSyn59k</td>
<td>59,000</td>
<td>20,000</td>
<td>2.9</td>
</tr>
<tr>
<td>SEBS-2/PSyn550k</td>
<td>550,000</td>
<td>20,000</td>
<td>27.5</td>
</tr>
</tbody>
</table>

a Each series consists of three blends with 10, 20 and 30% by weight of added homopolymer.
b Number average molecular weight of the added homopolymer.
c Number average molecular weight of PS blocks of SEBS triblock copolymer.

out. All experimental results clearly demonstrated the presence, for these blends, of a single $T_g$ that is also dependent on composition according to Fox equation.

Up to now the high melting temperature of PSyn has limited the possibility of blending it by means of extrusion and melt processing techniques. However, evidences of compatibility of PSyn with atactic PS strongly suggest that the former should as well give partial miscibility with the PS domains of styrene-$b$-(ethylene-$co$-1-butene)-$b$-styrene (SEBS) triblock copolymer. On the other hand, for solution cast blends of styrene-butadiene-styrene triblock copolymers (SBS) with PS, it has been demonstrated [12,13] 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 ($M_n^{lo}$) and that of the PS blocks of the copolymer ($M_n^{co}$). When the two values are close enough to each other, their ratio being nearly unitary, synergism in thermal and dynamic behavior has been observed [12]. In particular a blend $T_g$ higher than those of the neat components could be detected. This result was tentatively explained on the basis of entanglement formation in the new PS phase of the copolymer between the styrene blocks belonging to PS and SBS.

Objective of the present work was therefore the study of the miscibility of syndiotactic PS with the atactic PS blocks of SEBS triblock copolymer as a function of the molecular weight ratio ($M_n^{lo}/M_n^{co}$). Furthermore attention has been also dedicated to the investigation of the blend properties and in particular to the behavior at temperature higher than the $T_g$ of polystyrene blocks in SBS. This work is part of a project aimed at the enlargement of the SBS ‘working window’ towards temperatures higher than the $T_g$ of the PS phase.

2. Experimental

2.1. Polymers

The two kinds of syndiotactic polystyrene were supplied by Enichem Elastomeri (Ravenna, Italy). PSyn59k was characterized by $M_n = 5.9 \times 10^4$, $M_n/M_n = 2.4$, stereoregularity degree of 98% and no atactic fraction. On the other hand PSyn550k was characterized by $M_n = 5.5 \times 10^5$, $M_n/M_n = 2.2$, stereoregularity degree of 99.5% and no atactic fraction. Both homopolymers were used without further purification.

The block copolymer SEBS Kraton G-1650 (SEBS-1) was supplied by Shell and was employed without further purification. This polymer contains 19% by mol of styrene, $M_n = 8.0 \times 10^5$ and $M_n/M_n = 1.2–1.5$ as determined by GPC.

The block copolymer SEBS Europrene Sol TH 212 (SEBS-2) was supplied by Enichem Elastomeri and was employed without further purification. This polymer contains 19% by mol of styrene units, 32.4% of 1,2 butadiene, 48.6% of 1,4 butadiene units: $M_n = 7.0 \times 10^5$ and $M_n/M_n = 1.03–1.11$ as determined by GPC.

Atactic PS (Respol) was characterized by $M_n = 5.2 \times 10^5$ and $M_n/M_n = 2.5$; it was used without purification.

2.2. Characterization

Differential scanning calorimetry: DSC analyses were performed by a ‘Perkin–Elmer DSC7’ calorimeter equipped with a CCA7 cooling device. The calibration was carried out by using 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 ones. Heating and cooling thermograms were carried out at standard rate of 20 °C/min.

Scanning electron microscopy analysis: all SEM micrographs were recorded on samples cryogenic fracture surfaces by a Jeol JSM model T-300 instrument at the Chemical Engineering Department of Pisa University.

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

2.3. Melt blending

All blends were prepared in a Brabender mixer under nitrogen atmosphere by introducing the desired amounts of the components in the mixer at 220 °C (SEBS/PSyn blends), rotor speed 50 rpm. According to the desired time of residence (10 min) the mixing was stopped and the materials recovered from the Brabender mixing camera.

3. Results and discussion

Blends of syndiotactic polystyrene with SEBS triblock copolymers (see Table 1) have been prepared at 220 °C in a Brabender mixer. Different blend compositions actually correspond to several different values of $M_n^{lo}/M_n^{co}$ ratio, i.e. to different number average molecular weight ratios between the added homopolymer ($M_n^{lo}$) and the PS blocks
Table 2
DSC analysis of SEBS/Psyn blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (°C)$^a$</th>
<th>$T_m$ (°C)$^b$</th>
<th>$\Delta H_m$ (J/g)$^b$</th>
<th>$T_c$ (°C)$^c$</th>
<th>$\Delta H_c$ (J/g)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEBS-1</td>
<td>81.8</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SEBS-2</td>
<td>84.1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PS</td>
<td>87.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PSyn59k</td>
<td>100.0</td>
<td>258.4</td>
<td>25.7</td>
<td>218.8</td>
<td>25.8</td>
</tr>
<tr>
<td>PSyn550k</td>
<td>101.3</td>
<td>270.9</td>
<td>24.5</td>
<td>255.8</td>
<td>24.1</td>
</tr>
<tr>
<td>SEBS-1/PSyn59k</td>
<td>100.3</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SEBS-1/PSyn59k</td>
<td>107.1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SEBS-1/PSyn59k</td>
<td>105.7</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SEBS-1/PSyn59k</td>
<td>96.2</td>
<td>255.2</td>
<td>0.4</td>
<td>201.8</td>
<td>0.3</td>
</tr>
<tr>
<td>SEBS-1/PSyn550k</td>
<td>97.3</td>
<td>254.7</td>
<td>2.5</td>
<td>200.5</td>
<td>1.7</td>
</tr>
<tr>
<td>SEBS-1/PSyn59k</td>
<td>95.8</td>
<td>254.8</td>
<td>4.7</td>
<td>200.4</td>
<td>3.3</td>
</tr>
<tr>
<td>SEBS-1/PSyn550k</td>
<td>91.9</td>
<td>270.6</td>
<td>1.7</td>
<td>213.1</td>
<td>1.3</td>
</tr>
<tr>
<td>SEBS-1/PSyn550k</td>
<td>97.9</td>
<td>267.4</td>
<td>5.3</td>
<td>217.9</td>
<td>5.1</td>
</tr>
<tr>
<td>SEBS-1/PSyn59k</td>
<td>99.1</td>
<td>269.0</td>
<td>5.7</td>
<td>214.4</td>
<td>7.0</td>
</tr>
<tr>
<td>SEBS-2/PSyn59k</td>
<td>109.1</td>
<td>254.3</td>
<td>1.4</td>
<td>199.5</td>
<td>1.5</td>
</tr>
<tr>
<td>SEBS-2/PSyn59k</td>
<td>101.5</td>
<td>258.1</td>
<td>2.2</td>
<td>200.7</td>
<td>2.3</td>
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<tr>
<td>SEBS-2/PSyn59k</td>
<td>100.9</td>
<td>259.1</td>
<td>4.4</td>
<td>203.0</td>
<td>4.4</td>
</tr>
<tr>
<td>SEBS-2/PSyn550k</td>
<td>n.d.</td>
<td>267.9</td>
<td>1.5</td>
<td>212.8</td>
<td>2.1</td>
</tr>
<tr>
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<td>97.5</td>
<td>268.3</td>
<td>3.5</td>
<td>217.9</td>
<td>4.3</td>
</tr>
<tr>
<td>SEBS-2/PSyn550k</td>
<td>102.2</td>
<td>269.1</td>
<td>4.5</td>
<td>213.4</td>
<td>4.7</td>
</tr>
</tbody>
</table>

$^a$ Blends composition is expressed in weight ratios.

$^b$ Evaluated from 2nd-heating curve.

$^c$ Evaluated from 1st-cooling curve.

of SEBS triblock copolymer ($M_n^{co}$). Blends of SEBS with atactic PS (SEBS-1/PS) were also prepared in order to study the influence of the homopolymer tacticity. Indeed, a different tacticity can in principle result in a different solubility of the homopolymer into the PS domains of SEBS and eventually [12] into different blend glass transition temperatures.

All blends show, as given in Table 2, a single glass transition temperature for the ‘hard phase’, thus suggesting a good compatibility between the homopolymer chains and those of the PS blocks of the copolymer. The value of this $T_g$ is generally larger than for pure SEBS and in some cases (SEBS-1/PS) significantly higher than those of the neat components. The larger increase in the glass transition temperature of the SEBS/PS blend strongly suggests that atactic PS is more soluble than Psyn in the SEBS polystyrene. Indeed, SEBS-1/PS and SEBS-1/Psyn59k blends have nearly the same $M_n^{co}/M_n^{ps}$ ratio (respectively, 2.2 and 2.5), but display a different thermal behavior, with synergism taking place only in the former case. On the other hand such effect can only be inferred on the basis of the $T_g$ values and not of the occurrence of a single transition, since also all SEBS-1/Psyn blends display one single $T_g$ value over room temperature. In fact, the good compatibility between Psyn and the hard phase of SEBS-1 is strongly supported also by melting and crystallization behaviors (Fig. 1), according to what already reported in the literature for solution cast blends of Psyn with poly(phenylene ether) [14] and atactic PS [15]. The comparison of the melting and crystallization enthalpies ($\Delta H_m$ and $\Delta H_c$, respectively) of Psyn both neat and in the blends, indicates that both crystallization and

Fig. 1. (a) Melting behavior of SEBS-1/Psyn blends. (b) Crystallization behavior of SEBS-1/Psyn blends.
melting behavior of PSyn are affected by the blending with SEBS-1. In particular, the compatibility in the amorphous PS phase between the copolymer atactic and the homopolymer syndiotactic PS chains, can reasonably affect the structure of the interface between the crystalline and amorphous PS domains. This interface modification can also be detected within every single DSC run by the differences in the melting and crystallization enthalpy [16] (Table 2), which are significantly absent in the neat PSyn homopolymers. Reduction in crystallinity for the blends with PSyn59k is more evident than in those with PSyn550k, thus suggesting that a significant modification of the crystalline–amorphous interface, with respect to the neat PSyn, has occurred upon mixing and might promote significant differences in the morphology and distribution of PSyn crystallites. Such hypothesis has been tested by SEM analysis (Fig. 2). The same sample (SEBS-1/PSyn59k 90/10), at larger magnification, displays the presence of small dispersed particles, which can be reasonably associated with PSyn crystallites, whose maximum average size is about 3–4 μm. Moreover, such ‘droplets’ seem to be well connected to the matrix and also show good adhesion to the latter. The situation is different when using PSyn550k (Fig. 2). Indeed, in the latter case average dispersed-particle dimensions are more than 10 μm and bigger than in SEBS-1/PSyn59k blends. Moreover, higher magnification shows low adhesion of the dispersed phase with the matrix. All these observations clearly suggest a better compatibility of SEBS-1 with PSyn59k than PSyn550k as already suggested by DSC analysis and according to the molecular weight values. Indeed, blends with PSyn550k show a higher $M_n^\text{vis} / M_n^\text{co}$ value (22.9) than those with PSyn59k (2.5) and this should correspond [12,13] to enhanced solubility of PSyn59k over PSyn550k in the PS blocks of the copolymer.

Blends of PSyn with another kind of triblock copolymer (SEBS-2), characterized by a lower average length of the PS blocks with respect to SEBS-1, were considered. DSC analysis (Table 2) strongly indicates, also in the case of SEBS-2/PSyn blends, the presence of good compatibility due to the presence of a single $T_g$ at high temperatures as well as of deviations in the blends melting and crystallization behaviors from those predicted on the basis of neat PSyn thermal properties (Fig. 3). Like in the case of SEBS-1/PS blends, synergism in the thermal behavior, i.e. a blend $T_g$ significantly higher than those of the neat components, is observed for SEBS-2/PSyn59k blends ($M_n^\text{vis} / M_n^\text{co} = 2.9$) but not for SEBS-2/PSyn550k ($M_n^\text{vis} / M_n^\text{co} = 27.5$). This result clearly addresses [12,13] the higher solubility of PSyn in the PS domains of SEBS for low (nearly unitary) $M_n^\text{vis} / M_n^\text{co}$ ratios. SEM micrographs (Fig. 4) of SEBS-2/PSyn59k blends show an inhomogeneous morphology characterized by an average size of crystallites of about 10 μm. This value slightly decreases
increasing the PSyn content even if it remains, at all compositions, higher than in the case of blends with SEBS-1. These results suggest that significant interactions are still occurring between SEBS-2 and PSyn, accounting for the modification of the amorphous–crystalline PS interface as revealed by the melting and crystallization behavior. The situation is quite different for SEBS-2/PSyn550k blends (Fig. 5) where the average domains size is more than 10 μm and independent of PSyn content.

DMTA analysis has been performed on all blends (Table 3). \( T_g \) values, as determined from storage modulus vs. temperature curves, clearly agree with those determined by DSC: the highest values are indeed displayed by the blend of SEBS-1 with PSyn. Furthermore, the relative decrease of the storage modulus (ΔE/E), calculated in correspondence of the hard phase \( T_g \), clearly demonstrates a strong toughening of the structure over that of pure SEBS: SEBS-1/PS blends show an average loss of about 20% during PS glass transition with respect to 67.5% observed for pure SEBS-1. The same consideration holds for PSyn blends even if, in all cases, a clear relationship between blends composition and such toughening effect could not be detected. Finally, the fact that unmelted PSyn crystallites can act as reinforcing points of the system at temperature higher than the \( T_g \) of the copolymer PS blocks, is strongly suggested by \( \tan(\delta) \) profiles for SEBS-1/PSyn55k blends (Fig. 6): a shoulder of the main \( \tan(\delta) \) relaxation peak is observed at relatively high temperature (about 135 °C) and may tentatively be explained on the basis of PSyn crystallites ‘filler effect’. Indeed this relaxation must be related to the presence of PSyn crystallites since it could not be detected in SEBS-1/PS blends, which show although the highest \( T_g \) among all blends. It may eventually be noted that SEBS-1/PSyn55k blends, which show the lowest \( M_{\text{copol}} / M_{\text{copol}}^0 \) ratio among all blends with PSyn, display in general high \( T_g \) values and are the only ones with two \( \tan(\delta) \) relaxation peaks over room temperature.

4. Conclusions

Blending SEBS triblock copolymers with syndiotactic PS could be easily performed at 220 °C, i.e. below the melting temperature of the PSyn crystallites, thanks to the large amount of PSyn amorphous phase (about 50 wt% of the entire PSyn amount) as well as to the large weight excess of the rubber component (at least 70 wt% of the entire blend amount).

Blends of SEBS-1 with atactic PS display the presence of a single \( T_g \) over room temperature, strongly suggesting that only one ‘hard’ phase is formed upon mixing. Moreover these blends, characterized by the lowest \( M_{\text{copol}} / M_{\text{copol}}^0 \) ratio (2.2), display synergy in the thermal and dynamic-mechanical properties.
Fig. 4. SEM micrographs of SEBS-2/PSyn59k blends.

Fig. 5. SEM micrographs of SEBS-2/PSyn550k blends.
The determined \( T_g \) values, by both DSC and DMTA analyses, clearly address the higher efficiency of PS over both kind of PSyn in enhancing the hard phase \( T_g \). However, blending SEBS with PSyn introduces a very interesting feature with respect to the use of atactic PS: the presence in the blends of unmelted PSyn crystallites. The crystallites cannot be considered as simply inert solid particles: DSC data clearly demonstrate that the amorphous–crystalline interface in the blends is modified with respect to the neat PSyn. Moreover, such modification influences the melting and crystallization behavior of PSyn crystallites but also their average size and distribution in the blend morphology. If favorable conditions for entanglement formation upon mixing, i.e. for \( \frac{M_n^\text{PSyn}}{M_n^\text{PS}} \) close to 1, are provided, the crystallites result strongly anchored to the PS amorphous phase and can consequently influence the blend mechanical properties. Indeed, the blends with the lowest \( \frac{M_n^\text{PSyn}}{M_n^\text{PS}} \) ratio (SEBS-1/PSyn59k) display an additional \( \tan(\delta) \) relaxation peak over room temperature, which can be tentatively ascribed to a ‘filler reinforcing effect’ of the PSyn crystallites.

The results described in the work disclose in our opinion a new route for processing syndiotactic polystyrene and the possibility to shift the upper-working temperature of SEBS copolymers, which is usually limited by the \( T_g \) of the PS blocks. The limitations and the possible technological impact of the studied systems are currently under evaluation.

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**References**