ELSEVIER

Polymer 43 (2002) 3323–3329

polymer

www.elsevier.com/locate/polymer

Blends of syndiotactic polystyrene with SEBS triblock copolymers

Francesco Picchioni[a,*], Mauro Aglietto[b], Elisa Passaglia[b], Francesco Ciardelli[b]

[a]*Department of Chemical Engineering, SKT, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
[b]*Department of Chemistry and Industrial Chemistry, University of Pisa, Via Risorgimento 35, 56126 Pisa, Italy*

Received 18 June 2001; received in revised form 23 January 2002; accepted 23 January 2002

Abstract

Blending of styrene-*b*-(ethylene-*co*-1-butene)-*b*-styrene (SEBS) triblock copolymers with syndiotactic polystyrene (PSsyn) has been performed in a Brabender mixer above the higher glass transition temperature of the triblock copolymer but below the PSsyn melting point. The large excess of the triblock copolymer over the homopolymer as well as the significant amount of plasticized amorphous PSsyn 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 PSsyn 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 PSsyn and the PS blocks of SEBS.

Keywords: Blends; Styrene-*b*-(ethylene-*co*-1-butene)-*b*-styrene; Syndiotactic polystyrene

---

1. Introduction

Syndiotactic polystyrene (PSsyn) is a new semi-crystalline engineering polymer that has became available up to an industrial scale recently by the introduction of metallocene 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 PSsyn 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 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. The differences in the two structures are then accounted for by different ΔS_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 PSsyn 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 PSsyn 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, PSsyn 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 PSsyn 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/PSsyn 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

---

* Corresponding author. Fax: +31-40-243-6999.
E-mail address: f.p.picchioni@tue.nl (F. Picchioni).

0032-3861/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(02)00103-9

Table 1
Characteristics of the polymeric materials used in preparing SEBS/PSsyn blends

Blends[a]	$\bar{M}_n^{ho}$ (amu)[b]	$\bar{M}_n^{co}$ (amu)[c]	$\bar{M}_n^{ho}/\bar{M}_n^{co}$
SEBS-1/PS	52,000	24,000	2.2
SEBS-1/PSsyn59k	59,000	24,000	2.5
SEBS-1/PSsyn550k	550,000	24,000	22.9
SEBS-2/PSsyn59k	59,000	20,000	2.9
SEBS-2/PSsyn550k	550,000	20,000	27.5

[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 PSsyn has limited the possibility of blending it by means of extrusion and melt processing techniques. However, evidences of compatibility of PSsyn 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 ($\bar{M}_n^{ho}$) 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 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 ($\bar{M}_n^{ho}/\bar{M}_n^{co}$). 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). PSsyn59k was characterized by $\bar{M}_n = 5.9\times10^4$, $\bar{M}_w/\bar{M}_n = 2.4$, stereoregularity degree of 98% and no atactic fraction. On the other hand PSsyn550k was characterized by $\bar{M}_n = 5.5\times10^5$, $\bar{M}_w/\bar{M}_n = 2.2$, stereoregularity degree of 99.5% and no atactic fraction. Both homopolymers were used without further purification.

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, $\bar{M}_n = 8.0\times10^4$ and $\bar{M}_w/\bar{M}_n = 1.2$–$1.5$ 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: $\bar{M}_w = 7.0\times10^4$ and $\bar{M}_w/\bar{M}_n = 1.03$–$1.11$ as determined by GPC.

Atactic PS (Repsol) was characterized by $\bar{M}_n = 5.2\times10^4$ and $\bar{M}_w/\bar{M}_n = 2.5$; 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 mod.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/PSsyn 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 $\bar{M}_n^{ho}/\bar{M}_n^{co}$ ratio, i.e. to different number average molecular weight ratios between the added homopolymer ($\bar{M}_n^{ho}$) and the PS blocks

Table 2
DSC analysis of SEBS/PSsyn blends

Sample[a]	T_g (°C)[b]	T_m (°C)[b]	ΔH_m (J/g)[b]	T_c (°C)[c]	ΔH_c (J/g)[c]
SEBS-1	81.8	–	–	–	–
SEBS-2	84.1	–	–	–	–
PS	87.5	–	–	–	–
PSsyn59k	100.0	258.4	25.7	218.8	25.8
PSsyn550k	101.3	270.9	24.5	255.8	24.1
SEBS-1/PS 90/10	100.3	–	–	–	–
SEBS-1/PS 80/20	107.1	–	–	–	–
SEBS-1/PS 70/30	105.7	–	–	–	–
SEBS-1/PSsyn59k 90/10	96.2	255.2	0.4	201.8	0.3
SEBS-1/PSsyn59k 80/20	97.3	254.7	2.5	200.5	1.7
SEBS-1/PSsyn59k 70/30	95.8	254.8	4.7	200.4	3.3
SEBS-1/PSsyn550k 90/10	91.9	270.6	1.7	213.1	1.3
SEBS-1/PSsyn550k 80/20	97.9	267.4	5.3	217.9	5.1
SEBS-1/PSsyn550k 70/30	99.1	269.0	5.7	214.4	7.0
SEBS-2/PSsyn59k 90/10	109.1	254.3	1.4	199.5	1.5
SEBS-2/PSsyn59k 80/20	101.5	258.1	2.2	200.7	2.3
SEBS-2/PSsyn59k 70/30	100.9	259.1	4.4	203.0	4.4
SEBS-2/PSsyn550k 90/10	n.d.	267.9	1.5	212.8	2.1
SEBS-2/PSsyn550k 80/20	97.5	268.3	3.5	217.9	4.3
SEBS-2/PSsyn550k 70/30	102.2	269.1	4.5	213.4	4.7

[a] Blends composition is expressed in weight ratios.

[b] Evaluated from 2nd-heating curve.

[c] Evaluated from 1st-cooling curve.

of SEBS triblock copolymer ($\bar{M}_n^{co}$). 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 PSsyn in the SEBS polystyrene. Indeed, SEBS-1/PS and SEBS-1/PSsyn59k blends have nearly the same $\bar{M}_n^{ho}/\bar{M}_n^{co}$ 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/PSsyn blends display one single T_g value over room temperature. In fact, the good compatibility between PSsyn 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 PSsyn with poly(phenylene ether) [14] and atactic PS [15]. The comparison of the melting and crystallization enthalpies (ΔH_m and ΔH_c, respectively) of PSsyn both neat and in the blends, indicates that both crystallization and

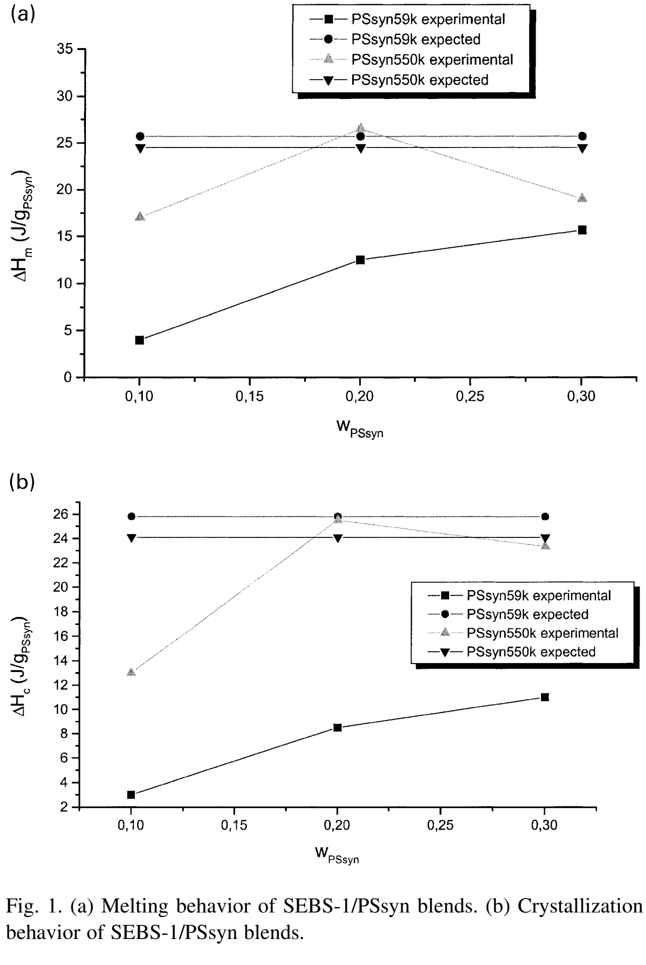
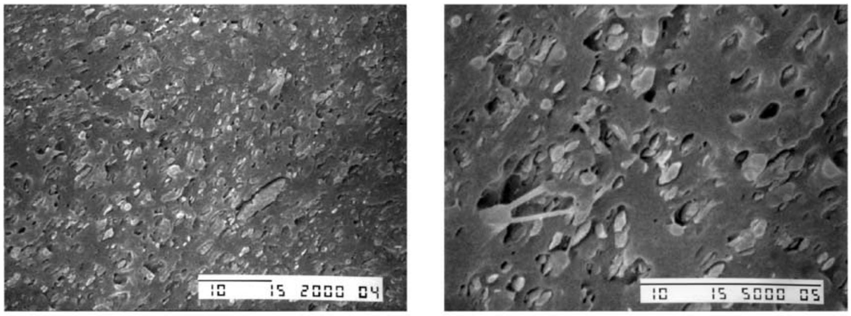
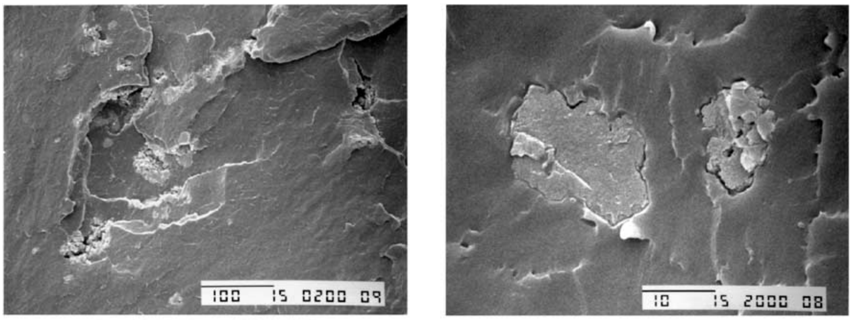


Fig. 1. (a) Melting behavior of SEBS-1/PSsyn blends. (b) Crystallization behavior of SEBS-1/PSsyn blends.



SEBS-1/PSsyn59k 90/10
(a)

SEBS-1/PSsyn59k 90/10
(b)



SEBS-1/PSsyn550k 90/10
(c)

SEBS-1/PSsyn550k 90/10
(d)

Fig. 2. SEM micrographs of SEBS-1/PSsyn blends.

melting behavior of PSsyn 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 PSsyn homopolymers. Reduction in crystallinity for the blends with PSsyn59k is more evident than in those with PSsyn550k, thus suggesting that a significant modification of the crystalline–amorphous interface, with respect to the neat PSsyn, has occurred upon mixing and might promote significant differences in the morphology and distribution of PSsyn crystallites. Such hypothesis has been tested by SEM analysis (Fig. 2). The same sample (SEBS-1/PSsyn59k 90/10), at larger magnification, displays the presence of small dispersed particles, which can be reasonably associated with PSsyn 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 PSsyn550k (Fig. 2). Indeed, in the latter case average dispersed-particle dimensions are more than 10 μm and bigger than in SEBS-1/PSsyn59k 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 PSsyn59k than PSsyn550k as already suggested by DSC analysis and according to the molecular weight values. Indeed, blends with PSsyn550k show a higher $\bar{M}_n^{ho}/\bar{M}_n^{co}$ value (22.9) than those with PSsyn59k (2.5) and this should correspond [12,13] to enhanced solubility of PSsyn59k over PSsyn550k in the PS blocks of the copolymer.

Blends of PSsyn 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/PSsyn 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 PSsyn 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/PSsyn59k blends ($\bar{M}_n^{ho}/\bar{M}_n^{co} = 2.9$) but not for SEBS-2/PSsyn550k ($\bar{M}_n^{ho}/\bar{M}_n^{co} = 27.5$). This result clearly addresses [12,13] the higher solubility of PSsyn in the PS domains of SEBS for low (nearly unitary) $\bar{M}_n^{ho}/\bar{M}_n^{co}$ ratios. SEM micrographs (Fig. 4) of SEBS-2/PSsyn59k blends show an inhomogeneous morphology characterized by an average size of crystallites of about 10 μm. This value slightly decreases

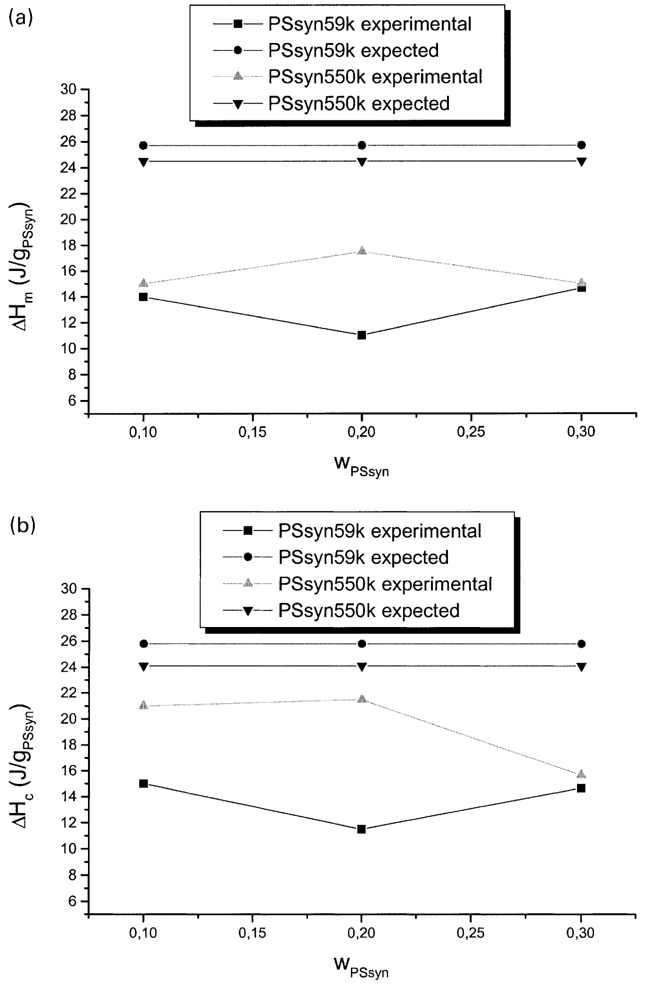


Fig. 3. (a) Melting behavior of SEBS-2/PSsyn blends. (b) Crystallization behavior of SEBS-2/PSsyn blends.

increasing the PSsyn 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 PSsyn, 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/PSsyn550k blends (Fig. 5) where the average domains size is more than 10 μm and independent of PSsyn 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 PS. Furthermore, the relative decrease of the storage modulus ($\Delta E/E$), 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 PSsyn 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 PSsyn 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(δ) profiles for SEBS-1/PSsyn59k blends (Fig. 6): a shoulder of the main tan(δ) relaxation peak is observed at relatively high temperature (about 135 °C) and may tentatively be explained on the basis of PSsyn crystallites ‘filler effect’. Indeed this relaxation must be related to the presence of PSsyn 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/PSsyn59k blends, which are characterized by the lowest $\bar{M}_n^{ho}/\bar{M}_n^{co}$ ratio among all blends with PSsyn, display in general high T_g values and are the only one with two tan(δ) relaxation peaks over room temperature.

Table 3
DMTA analysis of SEBS/PSsyn blends

Run[a]	T_g (°C)[b]	$\Delta E/E$ (%)[c]	ΔT (°C)[c]
SEBS	83.1	67.5	50–100
SEBS-1/PS 90/10	90.8	27.8	75–100
SEBS-1/PS 80/20	102.9	15.6	50–100
SEBS-1/PS 70/30	99.5	n.d.	n.d.
SEBS-1/PSsyn59k 90/10	88.4	53.3	50–100
SEBS-1/PSsyn59k 80/20	84.9	48.2	50–100
SEBS-1/PSsyn59k 70/30	78.5	52.0	60–100
SEBS-1/PSsyn550k 90/10	80.1	48.1	75–100
SEBS-1/PSsyn550k 80/20	80.7	59.4	50–100
SEBS-1/PSsyn550k 70/30	88.4	52.8	50–100
SEBS-2/PSsyn59k 90/10	81.8	57.7	50–100
SEBS-2/PSsyn59k 80/20	78.1	63.8	50–100
SEBS-2/PSsyn59k 70/30	90.3	60.1	50–100
SEBS-2/PSsyn550k 90/10	80.5	65.4	50–100
SEBS-2/PSsyn550k 80/20	78.5	68.4	50–100
SEBS-2/PSsyn550k 70/30	82.3	37.5	50–100

[a] Blends composition is expressed in weight ratios.

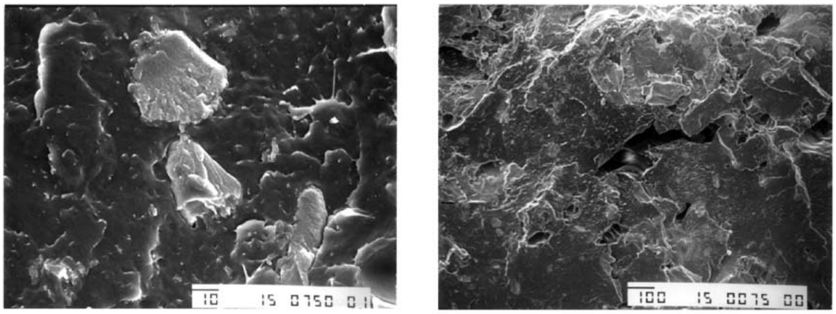
[b] Evaluated as onset of storage modulus/temperature curves.

[c] Relative decrease of the storage modulus ($\Delta E/E$) calculated in temperature range ΔT.

4. Conclusions

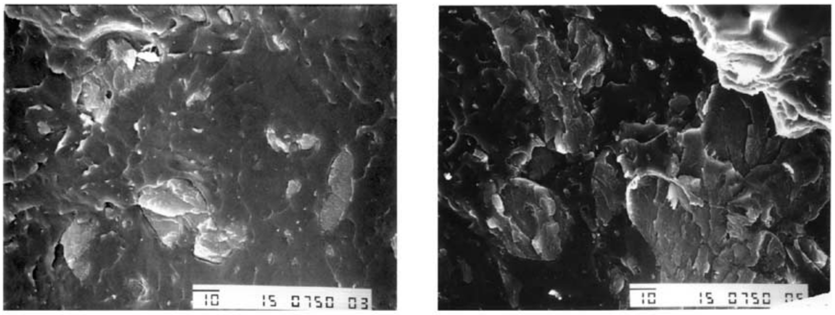
Blending SEBS triblock copolymers with syndiotactic PS could be easily performed at 220 °C, i.e. below the melting temperature of the PSsyn crystallites, thanks to the large amount of PSsyn amorphous phase (about 50 wt% of the entire PSsyn amount) as well as to the large weight excess of the rubber component (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 $\bar{M}_n^{ho}/\bar{M}_n^{co}$ ratio (2.2), display synergism in the thermal and dynamic-mechanical properties.



SEBS-2/PSsyn59 90/10 SEBS-2/PSsyn59 90/10

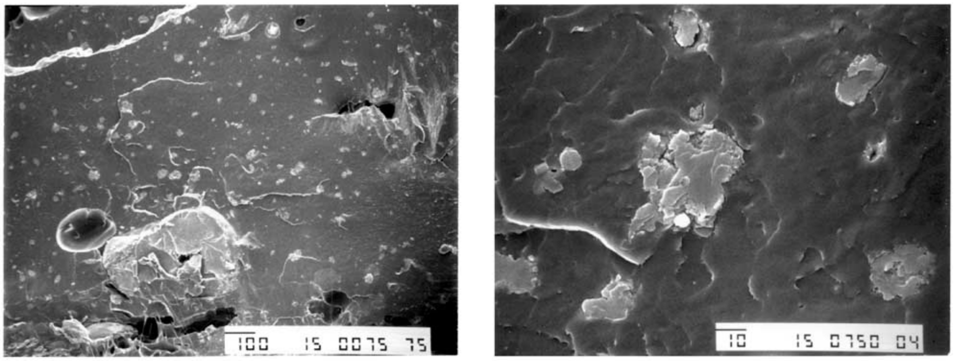
(a) (b)



SEBS-2/PSsyn59 80/20 SEBS-2/PSsyn59 70/30

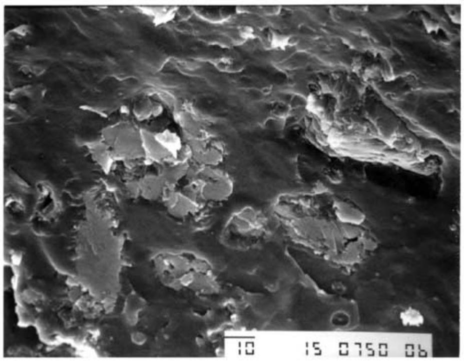
(c) (d)

Fig. 4. SEM micrographs of SEBS-2/PSsyn59k blends.



SEBS-2/PSsyn550k 90/10 SEBS-2/PSsyn550k 80/20

(a) (b)



SEBS-2/PSsyn550k 70/30

(c)

Fig. 5. SEM micrographs of SEBS-2/PSsyn550k blends.

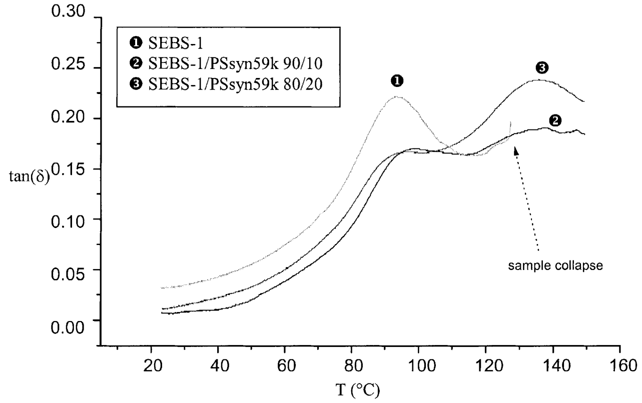


Fig. 6. Tan(δ) curves for SEBS-1/PSsyn59k blends.

The determined T_g values, by both DSC and DMTA analyses, clearly address the higher efficiency of PS over both kind of PSsyn in enhancing the hard phase T_g. However, blending SEBS with PSsyn introduces a very interesting feature with respect to the use of atactic PS: the presence in the blends of unmelted PSsyn 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 PSsyn. Moreover, such modification influences the melting and crystallization behavior of PSsyn crystallites but also their average size and distribution in the blend morphology. If favorable conditions for entanglement formation upon mixing, i.e. for $\bar{M}_n^{ho}/\bar{M}_n^{co}$ 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 $\bar{M}_n^{ho}/\bar{M}_n^{co}$ ratio (SEBS-1/PSsyn59k) display an additional tan(δ) relaxation peak over room temperature, which can be tentatively ascribed to a ‘filler reinforcing effect’ of the PSsyn 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.

Acknowledgements

Dr G. Ruggeri (University of Pisa) and Dr A. Zazzetta (Softer S.p.A.) are acknowledged for helpful discussions.

References

[1] Ishihara N, Seimiya T, Uoi M. Macromolecules 1986;19:2464–5.
[2] Zambelli A, Longo P, Pellecchia C, Grassi A. Macromolecules 1987;20:2035–7.
[3] Zambelli A, Oliva L, Pellecchia C. Macromolecules 1989;22:2129–30.
[4] Gianotti G, Valvassori A. Polymer 1990;31:473–5.
[5] De Candia F, Russo R, Vittoria V. J Polym Sci, Part C: Polym Lett 1990;28:47–51.
[6] Nyquist RA. Appl Spectrosc 1989;43:440–2.
[7] Guerra G, Vitagliano VM, De Rosa C, Petraccone V, Corradini P. Macromolecules 1990;23:1539–44.
[8] Guerra G, Musto P, Karasz FE, MacKnight WJ. Makromol Chem 1990;191:2111–9.
[9] Ermer H, Thomann R, Kressler J, Brenn R. Macromol Chem Phys 1997;198:3639–45.
[10] Bonnet M, Buhk M, Trögner G, Rogausch K, Petermann J. Acta Polym 1998;49:174–7.
[11] Woo EM, Lee ML, Sun Y. Polymer 2000;41:883–90.
[12] Feng H, Feng Z, Shen L. Macromolecules 1994;27:7835–9.
[13] Xie R, Li G, Jiang B. Macromolecules 1996;29:4895–903.
[14] Duff S, Tsuyama S, Iwamoto T, Fujibayashi F, Birkinshaw C. Polymer 2001;42:991–1000.
[15] Park JY, Kwon MH, Park OO. J Polym Sci, Part B: Polym Phys 2000;38:3001–8.
[16] Garcia-Martinez JM, Laguna O, Areso S, Collar EP. J Polym Sci, Part B: Polym Phys 2000;38:1564–74.