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In this work the compatibility of aromatic copolycarbonates containing bisphenol A (BPA) and tetramethyl bisphenol A (TMBPA) with polystyrene (PS) was investigated. Miscibility prediction data were used to select copolycarbonates of potential interest for developing highly compatible blends. Statistical copolycarbonates (CPCs) containing different BPA/TMBPA molar ratios were synthesized by polycondensation reaction and the effect of copolymer composition on the PS/CPC miscibility was studied. The blends were prepared by casting from chloroform solutions and/or melt mixing. The compatibility was evaluated by optical microscopy (OM), calorimetric (DSC), and dynamic-mechanical thermal (DMTA) analyses. Two glass transition temperatures were found for all the prepared PS/CPC blends, but an improvement of compatibility was obtained increasing TMBPA content in CPC copolymer.

On the other hand, blends of polycarbonate of bisphenol A (PCPA) and CPCs were characterized by a single glass transition temperature and transesterification reaction was noticed. Finally, a compatibilization effect of CPCs and polycarbonate of tetramethyl-bisphenol A (PCTMP) was highlighted in PS/PCPA/CPCs and PS/PCPA/PCTMP three components blends.

Keywords: blend, compatibility, copolymer, polycarbonate, polystyrene

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INTRODUCTION

Blends based on polystyrene (PS) and polycarbonate of bisphenol A (PCPA) are of potential interest in many application fields [1–4]. In particular, properties of polystyrene such as heat distortion temperature (HDT), impact strength, and optical properties (birefringence-free material) could be improved by blending with PCPA [5]. Unfortunately, when a high incompatibility exists between polymers, blends having poor physical and mechanical properties are often obtained [6–8]. For this reason considerable efforts in blend research are aimed to overcome such limitative factors [9]. Generally, two main ways are followed for decreasing the interfacial energy of incompatible blends: the addition of a compatibilizer agent or a chemical modification of one of the components. The final goal is to increase the inter-phase interactions, which is the necessary condition for obtaining materials with higher performance than the starting polymers.

Although graft or diblock copolymers are often used with success, random copolymer have showed in many instances good compatibilizing effect as well [10–12]. Although in case of diblock and graft copolymers the compatibilizing effect is attributed to a sort of “stitching” resulting from the mixing of each block with the more miscible phase, in case of random and alternating copolymer the compatibilization is often still effective but the mechanisms are not so clear. Hypotheses were proposed suggesting that, when the copolymer is at least partially miscible with both phases, individual polymer chains may make multiple crossings at the interface, in this way enhancing interactions between phases [13–15].

In this connection, it is well known that PCPA and PS are completely immiscible, whereas polycarbonate of tetramethyl-bisphenol A (PCTMP) is miscible both with PS and PCPA [7,16–18]. PCTMP is a very brittle material and shows a glass transition temperature (T_g) remarkably higher than PCPA; on the other hand it is expected that copolymerization of BPA with TMBPA should produce materials with controlled thermal properties and that can be usefully employed in blends with PS and PCPA.

A first objective of this work was to evaluate the effect of statistical copolycarbonates (CPC) composition on the compatibility of PS/CPC blends. To foresee this effect, miscibility of various blends was estimated according to a simple prediction scheme based on the Flory-Huggins theory and developed by Sonja Krause [16,19–20]. The computed results were used as a guideline for synthesizing, by stepwise polymerization, statistical CPC copolymers with suitable composition [21]. Secondly, the miscibility in PCPA/CPC blends and

the compatibilization ability of the prepared CPC copolymers and of PCTMP itself in PS/PCPA blends was experimentally evaluated by morphological, calorimetric, and dynamic-mechanical thermal analyses.

The importance of different blending procedures (in solution or in the melt) over the obtained materials was also considered. The possibility of a transesterification reaction between CPCs and PCPA in ternary blends cast from melt was highlighted by calorimetric data, gel permeation chromatography (GPC), and viscosity measurements.

EXPERIMENTAL

Instruments

The infrared spectra were recorded by a 5300 Jasco FT-IR spectrophotometer from films obtained by casting from solvent or by compression molding. $^1\text{H-NMR}$ spectra were run in deuterated chloroform with a 60 MHz Varian 360 A spectrometer, using TMS as internal reference.

The viscometry measurements were performed in chloroform at 32°C with a Schott Geräte mod AVS 310 semiautomatic viscometer.

The gel permeation chromatography (GPC) experiments were run on an Erma instrument, using Shodex KF columns. Chloroform as eluent, flow rate 1 ml/min, and a Knauer RI detector were used. Calibration curves were obtained using polystyrene standards purchased from Polymer Laboratories, Shropshire (U.K.).

The differential scanning calorimetry (DSC) analyses were carried out using a TA Instruments Q100 DSC. A sample weight of about 10 mg and a heating rate of 10°C/min in the range of 50–280°C or 50–320°C, under nitrogen flow (50 ml/min), were used.

Dynamic-mechanical thermal analyses (DMTA) were performed with Polymer Laboratories DMTA. The data were obtained at frequency of 1 Hz, using a heating rate of 0.8°C/min.

Optical microscopy (OM) was performed using a Nikon Labophot-2 (Nikon Corporation) microscopy equipped with a Sony color video camera DXC-950P (Sony Corporation). A discontinuous mixer (Brabender) equipped with a 60 ml chamber was used to prepare melt mixed blends.

Methods

All polymeric materials were dried under vacuum at 60°C for 48 h before blending.

Blends by casting. Binary and ternary blends were prepared via solution casting from chloroform (b.p. 61°C) at level of 10 wt% of solids.

The casting solutions were dried at 25°C and 760 mmHg for two days, at 60°C and 1 mmHg for 7 days, and at 235°C and 1 mmHg for 5 min. The resulting films were further dried in a vacuum oven (1 mmHg) at 280°C and then at 320°C both for 30 s.

Blends by melt. Ternary blends were also prepared by melt mixing at 240°C and 60 rpm, with a mixing time of 2 and 4 min. Some materials were then compression molded in a hot press at 230°C for 5 min.

Starting Materials

PS having $M_n = 132000$ g/mol and $M_w = 189600$ g/mol ($T_g = 99.6^\circ\text{C}$), PCPA having $M_n = 20100$ g/mol and $M_w = 37400$ g/mol ($T_g = 144.8^\circ\text{C}$), BPA and TMBPA were purchased from Aldrich Co. (Milan, Italy) and used as received.

N-ethyldiisopropylamine (EDIPA) (99 wt% purity) was purchased from Aldrich Co. (Milan, Italy) and dried over calcium hydride for 48 hours.

4-Dimethylaminopyridine (DMP) (99 wt% purity) and Phosgene solution (20 wt% in toluene) were purchased from Aldrich Co. (Milan, Italy) and used as received.

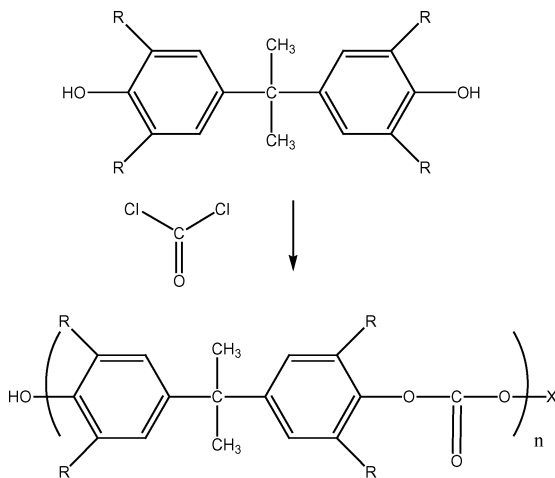
Chloroform was a high-grade commercial product purchased from various sources, not containing ethanol as stabilizer. It was allowed to remain some hours over calcium hydride before use.

All other reagents were high-grade commercial products and were used without further purification.

Synthesis of PCTMP and CPC Copolymers

Procedure

74 ml (0.14 mol) 20 wt% toluene solution of phosgene were placed, under nitrogen atmosphere, in a flask equipped with a stirrer, a gas inlet that can be lifted at several levels, a gas outlet connected with a sodium hydroxide trap, and a dropping funnel with pressure-equalizing side arm, into which a global mixture of 0.14 mol of BPA and TMBPA, 49 ml (0.28 mol) of EDIPA, 8.55 g (0.07 mol) of DMP in THF (88 ml) had been charged. The flask was cooled by means of an external bath at 5°C and the solution in the funnel was added dropwise to the phosgene solution under stirring. After the addition, the reaction mixture was maintained at 5°C for 8 h under stirring, and then for further 10 h while rising to room temperature. After this time, the solvent was eliminated by evaporating under vacuum the synthesis is schematically described in Scheme 1. The final product was then dissolved in chloroform, precipitated with an excess of isopropanol, and



where R= H and/or CH₃

SCHEME 1 Synthesis of Polycarbonates.

immediately washed with ether. The product was dried at room temperature and 1 mmHg. The composition and molecular characteristics of all synthesized products were determined by FT-IR, ¹H-NMR, viscosimetric analysis and GPC. All data are reported in Table 1.

RESULTS AND DISCUSSION

Prediction of Miscibility

The miscibility as function of composition and molecular weight of copolycarbonates was estimated using a simple miscibility prediction scheme, based on the solubility parameters developed by Sonja Krause [19–20]. According to this scheme, which is based on the Flory-Huggins theory, polymers A and B are miscible if $[\chi_{AB} - (\chi_{AB})_{cr}] < 0$,

TABLE 1 Molecular and Thermal Properties of Synthesized Polycarbonates

Sample	TMBPA ^a mol-%	η dl/g	$M_n \cdot 10^{-3}$ g/mol	$M_w \cdot 10^{-3}$ g/mol	T_g °C	T_m °C
PCTMP	100	0.217	9.1	18.8	192	316
CPC50	50	0.248	8.4	23.8	156	—
CPC5	5	0.245	8.3	20.1	136	—

^aTetra methyl bisphenol A (TMBPA) molar fraction.

being χ_{AB} the Flory's interaction parameter. The χ_{AB} and $(\chi_{AB})_{cr}$ values were calculated through the following equations:

$$\chi_{AB} = [(\delta_A - \delta_B)^2]/6$$

$$(\chi_{AB})_{cr} = 1/2 \left(1/x_A^{1/2} + 1/x_B^{1/2} \right)^2$$

where δ_A and δ_B are the Hildebrand solubility parameters of the two polymers and x_A and x_B are the corresponding degrees of polymerization. A good approximation is to let $x_A = M_A/100$ and $x_B = M_B/100$, where M_A and M_B are the molecular weights of polymers. It is necessary to know the approximate molecular weight of polymers of interest in order to predict whether they will be compatible or not.

According to Sonja Krause and co-workers [22] the Hildebrand solubility parameters of a statistical copolymer turn out to be:

$$\delta_c = \sum \delta_i \phi_i$$

where δ_i is the solubility parameter of the homopolymer that corresponds to the monomer i in the copolymer and ϕ_i is the corresponding volume fraction. The summation is taken over all the different repeat units in the copolymer.

The solubility parameters of PS, PCPA, and PCTMP were evaluated using the group molar attraction constants according to Small's, Van Krevelen's, and Hoy's tables [23] (see Table 2). The predicted compatibility curves of PS/PCPA, PS/PCTMP, and PCPA/PCTMP, binary blends are shown, respectively, in Figure 1(a), 1(b), and 1(c). Notwithstanding the limited differences between the estimated δ from different sources, it should be noted that, concerning the miscibility of PS/PCTMP and PCPA/PCTMP [8,16–18] and the immiscibility of PS/PCPA [24], only the Hoy's curves are in complete accordance with what is known from literature. In fact, Small's table predicts, erroneously, miscibility of PS/PCPA and partial miscibility of

TABLE 2 Solubility Parameters (δ) Evaluated by Group Contributions According to Various Authors at 298 K

Material	δ (cal ^{1/2} /cm ^{3/2})		
	VanKrevelen	Hoy	Small
PS	9.7	9.2	9.2
PCPA	9.9	10.2	9.6
PCTMP	10.1	9.5	10.0

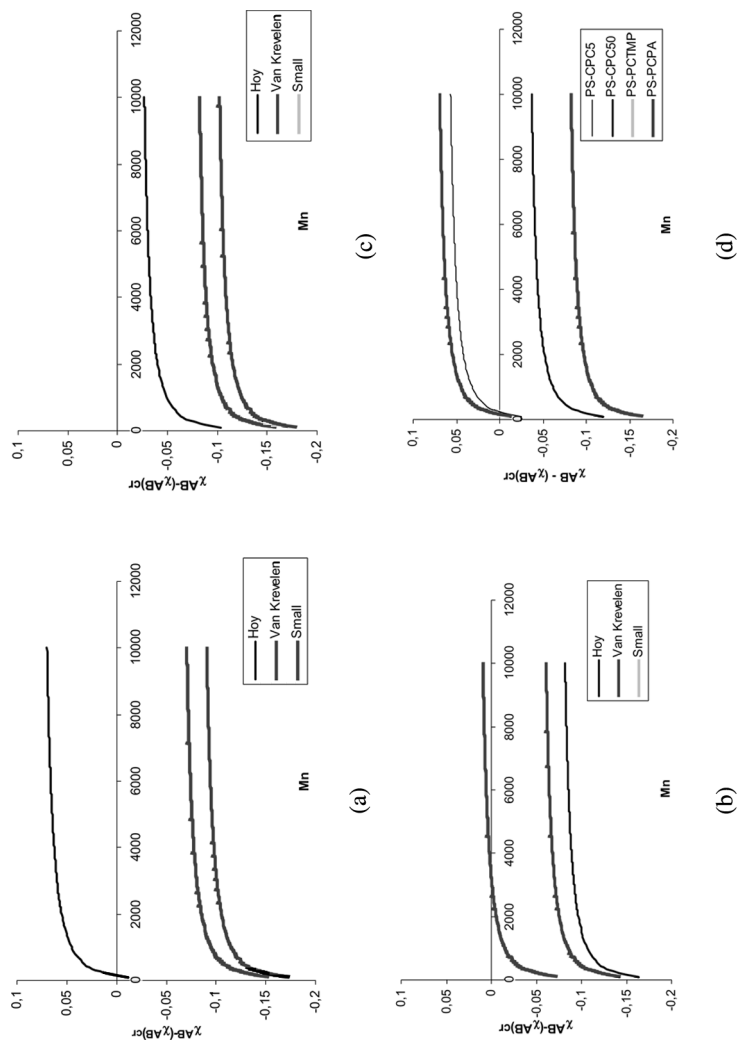


FIGURE 1 Miscibility prediction curves at 298 K calculated using Hoy's, Small's and Van Krevelen's tables for: (a) PS/PCPA, (b) PS/PCTMP, (c) PCPA/PCTMP, and (d) PS/CPCs curves obtained with Hoy's data.

PS/PCTMP, whereas Van Krevelen's table gets a wrong prediction of PS/PCPA miscibility. This suggests that the evaluation is quite sensitive to actual δ values. Hoy's table was, however, assumed to evaluate the effects of copolymer composition and of copolymer average molecular weight in PS/CPC blends. The resulting predictive curves are reported in Figure 1(d). The trends of $[\chi_{AB} - (\chi_{AB})_{cr}]$ vs. \bar{M}_n of CPC having different TMBPA/BPA ratios foresee that the miscibility remarkably increases with the TMBPA content. An interesting result should be expected if a 50:50 copolymer is employed, where χ_{AB} becomes lower than $(\chi_{AB})_{cr}$ and a marked improvement of miscibility is expected. This same composition was found in some instances to give the optimum compatibilizing effect [12].

Synthesis of PCTMP and CPCs Polymers

Statistical copolycarbonates containing different TMBPA/BPA molar ratio were synthesized by polycondensation reaction between a mixture of the two bisphenols and phosgene (see Scheme 1). The molecular structure of all copolymers was detected by $^1\text{H-NMR}$ and FT-IR spectroscopy, while the molecular mass was detected by GPC and viscosity measurements.

The composition data and molecular characteristics of the polymers are summarized in Table 1. It should be observed that the selected reaction conditions produce polymers having comparable molecular weights ($\bar{M}_n \approx 8000$); this is essential if the composition effect on the miscibility is studied.

The calorimetric properties of the products were also investigated with differential scanning calorimeter (DSC) (Table 1). It should be noticed that the two synthesized copolymers are amorphous materials (some crystallinity could be induced by slow chloroform evaporation) and the corresponding T_g increases with TMBPA content. On the contrary, PCTMP was obtained in a semi-crystalline state with high melting point ($T_m = 316^\circ\text{C}$).

PS/PCTMP and PS/CPC Binary Blends

PS/CPC and PS/PCTMP blends (50/50 wt%) were prepared by casting from chloroform solutions. For comparison purpose, a blend of PS and a typical commercial polycarbonate (PCPA) was also prepared. The solvent was removed first at room temperature and then under vacuum, with a multistep thermal treatment as described in the Experimental section. The last high temperature step was carried

TABLE 3 Thermal Properties of Binary Blends (50/50 wt%) and Starting Materials all Cast from Chloroform Solutions

Material	Low T_g °C	ΔT^c Low T_g	High T_g °C	ΔT^c High T_g
PS ^a /CPC5	101.7	2.1	131.8	-4.6
PS ^a /CPC50	103.2	3.6	152.7	-3.5
PS ^a /PCTMP	108.3	8.7	168.9	-23.4
PS ^a /PCPA ^b	100.0	0.4	143.7	-0.8
PCPA ^b /CPC5	136.7	—	—	—
PCPA ^b /CPC50	148.6	—	—	—
PCPA ^b /PCTMP	163.0	—	—	—
CPC5	—	—	136.4	—
CPC50	—	—	156.2	—
PCTMP	—	—	192.3	—
PS ^a	99.6	—	—	—
PCPA ^b	—	—	144.5	—

^aCommercial PS: $M_n = 132000$ g/mol and $M_w = 189600$ g/mol.

^bCommercial PCPA: $M_n = 20100$ g/mol and $M_w = 37400$ g/mol.

^c $\Delta T = T_g(\text{blend}) - T_g(\text{starting material})$.

out to erase the crystallinity of the polycarbonate phase resulting from slow chloroform evaporation. In fact, some crystalline regions were clearly highlighted (i.e., $T_m = 234^\circ\text{C}$ for PS/PCPA). These phenomena were observed in all blends. Information on compatibility was obtained using DSC and OM analyses. The calorimetric data of blends, and of starting materials, are summarized in Table 3. For PS/PCPA, PS/CPC5, and PS/CPC50 blends two glass transition temperatures were observed. These results can be considered in limited accordance with Hoy's predictions curves. In fact, although complete miscibility was not observed in any blend, it should be noted that the T_g values are shifted with respect to the T_g of starting materials and the shift increases with TMBPA content in CPC, indicating partial miscibility.

For PS/PCTMP blend two glass transition temperatures were also observed. Even though a marked shift of T_g s and the absence of crystallinity clearly suggest high compatibility, this result seems to be in contrast with literature data. In fact, complete miscibility of polystyrene and tetramethyl bisphenol A polycarbonate, at all compositions and temperatures up to their low critical solution temperature (LCST), is reported. In particular, as reported, LCST strongly depends on average molecular weight of two components (i.e., LCST goes from 240°C to 285°C for a 50/50 PS/PCTMP ($M_w = 54700$ g/mol) blend, respectively, with PS $M_w = 198800$ g/mol and $M_w = 20000$ g/mol) [17,23,25]. In this connection, it should be considered that the PCTMP molecular weight used in this work is $M_w = 18800$ g/mol, however

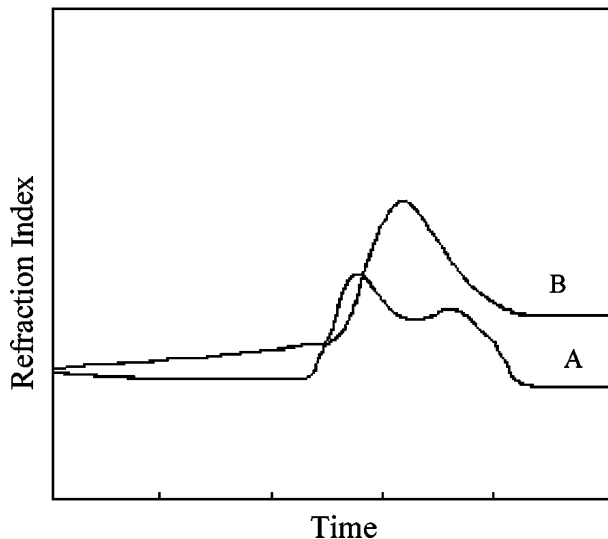


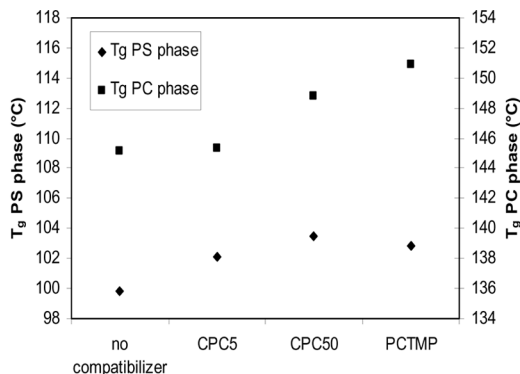
FIGURE 2 GPC curves of PC/PCTMP 50/50 blend (A) without thermal treatment and (B) after thermal treatment.

the thermal treatments carried out to allow a complete solvent evaporation and to erase the crystallinity of polycarbonate, probably overcame the LCST of the authors' system, causing phase separation. Also in this case the estimations based on Hoy's data remain questionable. Morphological analyses confirm the calorimetric data: all materials reveal some heterogeneousness and less evident phase separation is observed upon increasing TMBPA content.

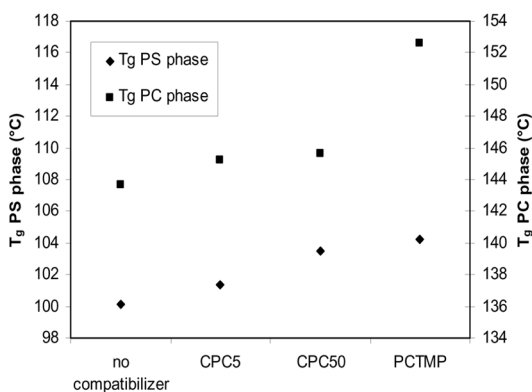
PCPA/PCTMP and PCPA/CPC Binary Blends

PCPA/CPC and PCPA/PCTMP blends (50/50 wt%) were prepared by solution casting following the procedure described in the methods section. The corresponding calorimetric data are summarized in Table 3. It should be noticed that a single T_g is always observed for all analyzed samples. In particular, T_g values of 136.7, 148.6, and 163.0°C were detected for blends containing CPC5, CPC50, and PCTMP, respectively. The morphological analyses performed by optical microscopy showed homogeneous samples.

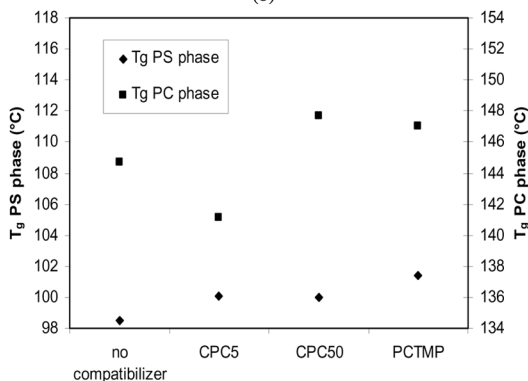
In this case, the results are in good agreement with the prediction curves reported in Figure 1(c) and with literature data [18]. Moreover a transesterification reaction taking place between the two components



(a)



(b)



(c)

FIGURE 3 T_g values vs. compatibilizer composition of three ternary blends obtained adding 5% by weight of compatibilizer, respectively, to (a) PS/PCPA 25/75, (b) PS/PCPA 50/50, and (c) PS/PCPA 75/25. All blends were prepared by casting from chloroform solutions.

was highlighted. In Figure 2 are reported the GPC traces performed on a PCPA/PCTMP 50/50 mixture before (curve A) and after thermal treatment (curve B). It should be noted that curve A shows two peaks related, respectively, to PCPA, at lower elution times (which means higher molecular weights), and to PCTMP, at higher elution times (which means lower molecular weights). On the other hand, curve B shows only one peak, which position is intermediate with respect to the curve A. In general it means that after the thermal treatment the molecular weight of PCPA is lowered but the decrement of the long elution time fraction is consistent with the occurrence of the transesterification reaction.

This interesting result suggests that PCTMP and CPCs could possibly be used as macromolecular reagents for compatibilizing PS/PCPA blends by reactive processes.

Three Components Blend

Ternary blends were prepared via casting from three PS/PCPA (25/75, 50/50, 75/25 wt%) chloroform solutions adding 5% by weight of total polymer mass of CPC5, CPC50, and PCTMP, respectively. The casting solutions were dried following the multistep thermal treatment described in the methods section. The resulting films were characterized with DSC and OM. Calorimetric data are summarized in Figure 3 where the effect of the type of compatibilizer is reported for PS/PCPA PCPA 25/75, 50/50, and 75/25 wt%, respectively, in Figure 3(a), 3(b), and 3(c). It should be noted that the addition of CPC5, CPC50, and PCTMP in order, acts on the T_g s of PS and PCPA phases increasing

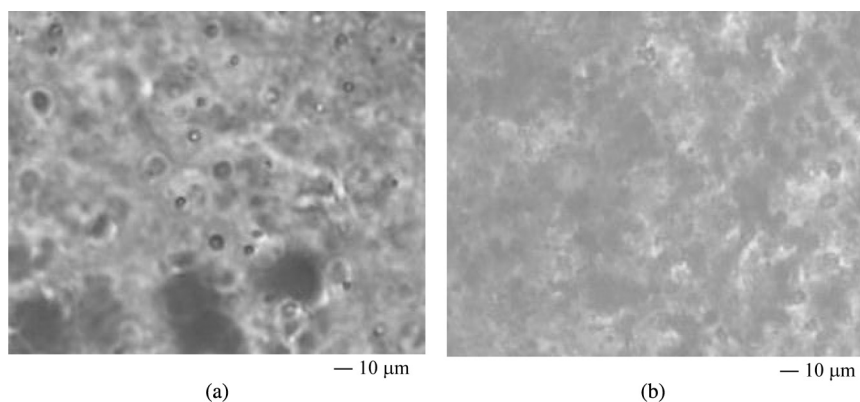


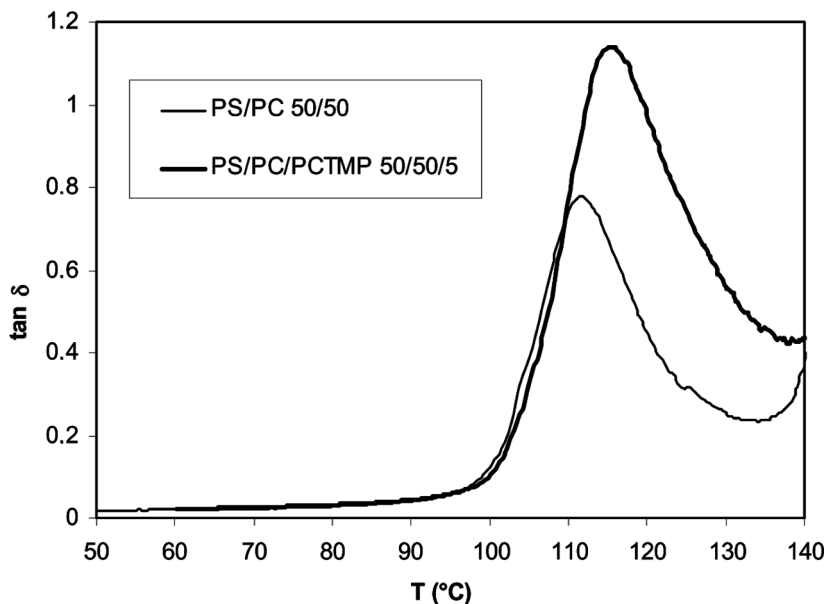
FIGURE 4 Optical micrographs of 50/50 PS/PCPA blends (a) without compatibilizer and (b) with 5% by weight of CPC50.

TABLE 4 Thermal Properties of 50/50 PS/PCPA Blends with Different Content of PCTMP Cast from Melt and then Molded

Sample	PCTMP %	2 min in Brabender		Molded ^a	
		Low T _g °C	High T _g °C	Low T _g °C	High T _g °C
PS/PCPA	—	101.4	142.1	101.4	143.5
PS/PCPA/PCTMP05	0.5	101.1	141.4	101.4	139.3
PS/PCPA/PCTMP1	1	101.8	140.7	101.8	140.4
PS/PCPA/PCTMP2	2	102.5	144.6	102.1	139.3
PS/PCPA/PCTMP2-A ^b	2	101.1	137.5	101.1	134.0
PS/PCPA/PCTMP5	5	103.7	144.7	102.1	136.9

^a5 min at 230°C.^bIn Brabender for 4 min.

them for all the ternary blends. In Figure 4(a) and 4(b) the optical micrographs, respectively, of 50/50 PS/PCPA and 50/50 PS/PCPA with 5% by weight of CPC50 are shown. Microscopy observations show a reduction of dispersed phase particles dimensions suggesting that the

**FIGURE 5** DMTA curves of 50/50 PS/PCPA blends without compatibilizer and with 5% by weight of PCTMP.

phases compatibility is increased when the CPC copolymer is added. These results are in agreement with the expected miscibility of PCTMP both with PS and PCPA, so that the increase of TMBPA content means some compatibility improvement in the ternary blend.

Ternary blends were also prepared melt mixing 50/50 PS/PCPA blend and different amount of PCTMP, as compatibilizer. All samples were worked in Brabender mixer at 240°C for 2 min and then were molded at 230°C for 5 min; in both cases DSC analyses were carried out and the results are reported in Table 4. The DSC data after 2 min of mixing confirm the previous conclusions concerning the low T_g : it increases with PCTMP content although the variations remain quite small. Better evidence of such T_g variation is obtained by DMTA analysis, as shown in Figure 5. The limited low T_g shift may result from the fact that PCTMP shows better miscibility with PCPA, so that the actual PCTMP content in PS remains lower than in PCPA. Even in this case however effective interfacial interactions remain possible. On the other hand, the high T_g values are not in accordance with the data obtained for solution cast ternary blends. The discrepancy is more evident for molded samples: in fact the high T_g decreases with the increment of PCTMP content in the blend. This decrement is reasonable due to the transesterification reaction between the two

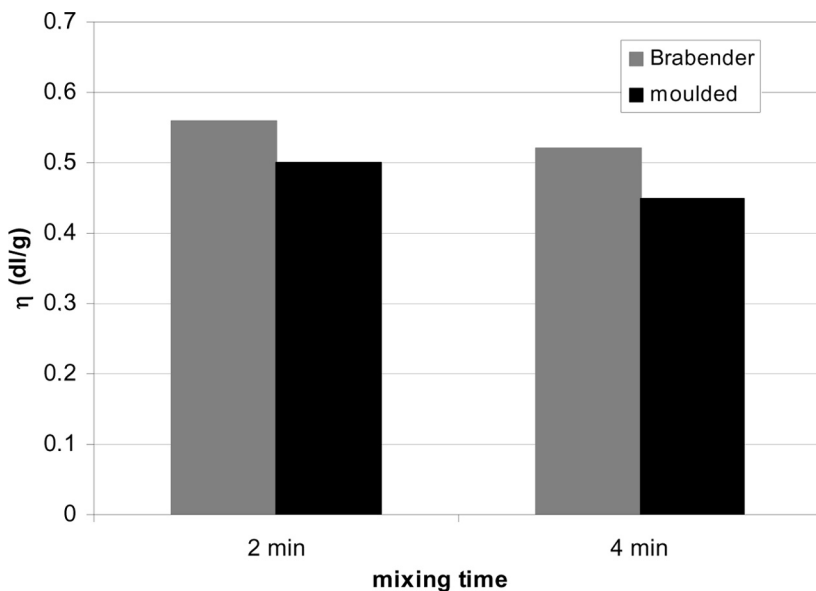


FIGURE 6 Viscosity of PS/PCPA/PCTMP2-A ternary blend as a function of the mixing time in Brabender and subsequent moulding at 230°C for 5 min.

polycarbonates that leads to a molecular weight lowering of the polycarbonate phase. The occurrence of such reaction depends on the residence time at high temperature. In fact, the PS/PCPA/PCTMP2-A sample presented a decrement of high T_g from 144.6°C to 137.5°C, increasing the mixing from 2 min to 4 min. The thermal treatment due to molding, that means additional 5 min at 230°C, acts in the same direction. No such variations were presented by uncompatibilized PS/PCPA blend. Viscosity measurements, summarized in Figure 6, confirmed a marked molecular weight reduction with increasing high temperature exposure time.

CONCLUSIONS

Binary blends based on polystyrene and aromatic polycarbonates with improved compatibility can be obtained using random copolymers of BPA and TMBPA. The simple prediction scheme developed by Sonja Krause is employed to evaluate the effects of copolymers composition and molecular weight on compatibility with PS. According to different authors, three data tables are used to calculate the solubility parameters and the corresponding prediction curves are compared. Only Hoy's data give results consistent with what is known from literature, predicting that PS/CPCs miscibility increases with increasing TMBPA content. The DSC analyses of PS/CPCs and PS/PCTMP blends showed always two T_g but the respective values are shifted with respect to pure polymers in the direction of an increased compatibility if TMBPA rises in the copolymer. The optical microscopy analyses confirm these results.

In agreement with the prediction of miscibility curves, only one T_g is observed in PCPA/CPC and PCPA/PCTMP binary blends. On the other hand, the occurrence of a transesterification reaction between the polycarbonates is evidenced from GPC analysis. This is a very interesting result because, in principle, PCTMP and CPCs could be used as macromolecular reagents to compatibilize PS and PCPA by reactive process.

Finally, CPC and PCTMP are used as compatibilizers in PS/PCPA blends. Also in this case, the increase of PCTMP content means some compatibility increment in ternary blends. The raise of low T_g value, more evident from DMTA curves, takes place both for cast and melt mixed blends. On the other hand, high T_g turns out to be very sensitive to the mixing time and the molding. In fact a decrease of high T_g is observed going from 2 to 4 min of mixing time and, additionally, after the molding process. Once more, this is due to the occurrence of

a transesterification reaction between polycarbonates confirmed by viscosity measurements.

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