Macromol. Symp. **2004**, *218,* 183-190

Blends Based on Polystyrene and Statistical Aromatic Copolycarbonates

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Summary: The compatibility of polystyrene (PS) with aromatic copolycarbonates containing bisphenol A (BPA) and tetramethyl bisphenol A (TMBPA) was investigated. The simple prevision scheme developed by Sonja Krause was employed to evaluate the effect of the copolymer molecular structure on the miscibility with polystyrene. These prevision data were used to select copolycarbonates of potential interest. Statistical copolycarbonates (CPC) containing different BPA/TMBPA molar ratios were synthesised by polycondensation reaction between a mixture of the two monomers and phosgene. PS/polycarbonates blends, prepared by casting from chloroform solution, were studied with differential scanning calorimetry and optical microscopy to evaluate the components compatibility, which increases with the TMBPA copolymer content.

Keywords: blend; compatibility; copolymer; polycarbonate; polystyrene

Introduction

Polymer blending is a simple and efficient method for designing and controlling the performance of polymeric materials. Unfortunately, a high incompatibility is often shown between the components, and blends having poor properties are obtained. For this reason, considerable efforts in the blends science are aimed to overcome this limitative factor [1]. In general, two main ways are followed for decreasing the interfacial energy of incompatible blends: the addition of a compatibilizer agent or the chemical modification of one of the components. Therefore, the final goal is to increase phase adhesion, which is a necessary condition for obtaining materials with high performance in comparison with starting

DOI: 10.1002/masy.200451419

polymers. This paper studies the effect of the molecular characteristics of statistical aromatic polycarbonates on the compatibility with polystyrene.

Many application fields show a potential interest in binary blends based on polystyrene (PS) and polycarbonate of bisphenol A (PCPA) [2-5]. In particular, polystyrene properties such as thermal stability (HDT), impact strength and optical properties (birefringence-free material) have been increased by blending PS and PCPA [6]. Unfortunately, high incompatibility exists between these polymers [7-9]. On the other hand, it is well-known that PS and polycarbonate of tetramethyl bisphenol A (PCTMP) exhibit good compatibility [10]. PCTMP has a higher glass transition temperature (Tg) than PCPA but is very brittle and thus it is not useful to improve the PS impact strength. Aim of this work is to study the composition effect of statistical copolycarbonates (CPC) containing BPA and TMBPA units on the compatibility of PS/CPC blends. The experimental results were compared with data obtained with a simple prevision scheme based on the Flory-Huggins theory [11]. Miscibility was the criterion used to foresee polymer compatibility.

Experimental

1. Instruments

The infrared spectra were recorded by a 5300 Jasco FT-IR spectrophotometer on films obtained by casting from solvent. ^{1}H-NMR spectra were run in deuterared chloroform on a 60 MHz Varian 360 A spectrometer, using TMS as internal reference. Viscometric measurements were performed with a Schott Geräte mod AVS 310 semiautomatic viscometer. The GPC experiments were run on an Erma instrument, using Shodex KF columns, operating with chloroform as eluent, flow rate 1 ml/min and a Knauer RI detector. Calibration curves were obtained by polystyrene standards purchased from Polymer Laboratories, Shropshire (U.K.). The DSC analysis was carried out using a Mettler TC11 Thermal Analyser Processor equipped with a Low Temperature Cell DSC30. The DSC curves were obtained by heating a sample of about 10 mg from 50 to 280°C (or 50 to 320 °C) at 10°C/min, under nitrogen flow (10 ml/min).

2. Methods

Blend preparation: binary blends were prepared from 10 weight % chloroform (b.p. 61°C) solutions. The solvent was first evaporated at 25°C and 760 mmHg for two days, then the film was subjected to the following thermal treatments at 1 mmHg: 7 days at 60°C, 5 minutes at 200°C, 0.5 minutes at 280°C and, finally, 0.5 minutes at 320°C.

3. Starting materials

PS having $\overline{M}_n$ =132000 was purchased from Aldrich Co. (Tg = 99.6°C).

Polycarbonate (PCPA) having $\overline{M}_n$ =20100 was purchased from Aldrich Co. (Tg = 144.5°C).

BPA and TMBPA were purchased from Aldrich Co.

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

4-Dimethylaminopyridine (99 wt.-% purity) was purchased from Aldrich Co. 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.

4. Synthesis of PCTMP and CPC copolymers

Typical procedure: 74 ml (0.14 mol) 20 wt.-% toluene solution of phosgene was placed, under nitrogen atmosphere, in a flask equipped with a stirrer, a gas inlet which 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 N-ethyldiisopropylamine (EDIPA), 8.55 g (0.07 mol) of 4-dimethyl aminopyridine (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 drop wise 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 final product was then dissolved in chloroform, precipitated with an excess of isopropanol and immediately washed with ether. The precipitate was dried at room temperature and 1 mmHg.

Results and discussion

1. Prevision of miscibility

The composition and molecular weight of copolycarbonates were selected using a simple miscibility prediction scheme developed by Sonja Krause [11,12]. According to this scheme, which is based on the Flory-Huggins theory, polymers A and B are miscible if $[\chi_{AB} - (\chi_{AB})_{cr}] < 0$, χ_{AB} being the Flory's interaction parameter. The χ_{AB} and $(\chi_{AB})_{cr}$ values were calculated through the following equations:

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

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

where δ is the Hildebrand solubility parameter and x is the number-average degree of polymerization. The solubility parameters of the homopolymers were evaluated using the group molar attraction constants according to Hoy [13], while the copolymer parameters δ_c were calculated from:

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

where δ_i and ϕ_i are the solubility parameter and the volume fraction, respectively, of the homopolymer that corresponds to monomer i.

Values of $[\chi_{AB} - (\chi_{AB})_{cr}]$ versus the $\overline{M}_n$ of copolymer having different composition for blends with PS ($\overline{M}_n$=132000) are shown in Figure 1. It should be observed that a negative value of this parameter is always obtained for the PCTMP homopolymer. Our prevision agrees with literature works where some miscibility is reported. Furthermore, it foresees that the miscibility of PS and CPC increases with the TMBPA content. Interestingly, in spite of the large amount of PCPA units present in CPC50, a miscibility similar to that of PCTM is predicted for this copolymer.

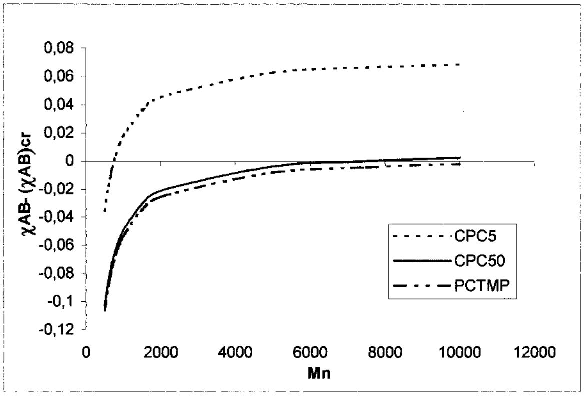

Figure 1. Miscibility prevision curves for 5, 50 and 100 TMBPA mol-% copolymers (CPC5, CPC50 and PCTMP polycarbonates).

2. Synthesis and thermal properties of polycarbonates

Statistical copolycarbonates containing different BPA/TMBPA molar ratios were synthesized by polycondensation reaction between a mixture of the two bisphenols and phosgene. The composition of all copolymers was evaluated by ^{1}H-NMR and FT-IR spectroscopy while gel permeation chromatography (GPC) and viscosity measurements were employed to determine the molecular mass.

Table 1. Molecular and thermal properties of synthesized polycarbonates.

Sample	TMBPA[a] mol-%	$\overline{M}_n \cdot 10^{-3}$	$\overline{M}_w \cdot 10^{-3}$	Tg °C	Tm °C
CPC50	50	8.4	23.8	156.2	-
CPC5	5	8.3	20.1	136.4	-
PCTMP	100	9.1	18.8	192.3	287.4
PS	-	132.3	189.6	99.6	-

[a] Tetramethyl bisphenol A.

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

The calorimetric properties of the products were investigated by differential scanning calorimetry (DSC) (Table 1). It should be noticed that both CPC5 and CPC50 copolymers are amorphous materials and their Tg increases with the TMBPA content. On the contrary, PCTMP is a high melting point semicrystalline material with Tm=287.4°C.

3. PS/polycarbonate blends

Polystyrene/polycarbonate blends were prepared by casting from chloroform solution. The solvent was removed first at room temperature, then under vacuum with a multi-step thermal treatment (see experimental section). A high temperature step was carried out to destroy the crystallinity of the polycarbonate phase produced during the evaporation of chloroform. In Figure 2 an optical micrography of a commercial polycarbonate (PCPA) film obtained by the casting process is shown. The presence of crystalline regions (Tm = 234 °C) can be recognized. In general, some crystallinity was observed in all polycarbonate samples obtained by solvent evaporation.

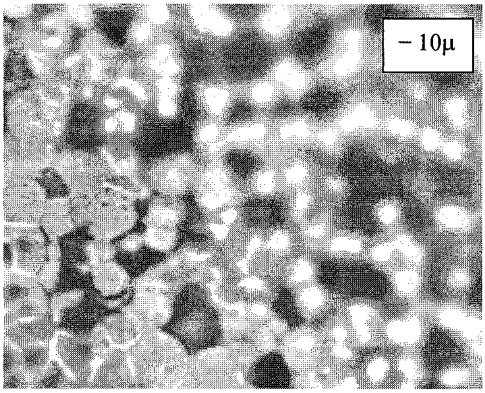

Figure 2. Crystallinity in PCPA films obtained by casting.

Blend compatibility was evaluated using DSC and optical microscopy. The calorimetric data of 50:50 weight-% PS/polycarbonate blends are summarized in Table 2. For comparison, data relative to a blend with commercial PCPA and to films of pure polymers prepared under the same conditions as the blends are also reported.

Table 2. Thermal properties of 50/50 wt-% blends and of neat components.[a]

Materials	Low Tg (°C)	ΔT^c (°C) low Tg	High Tg (°C)	ΔT^c (°C) high Tg
PS/CPC5	101.7	2.1	131.8	-4.6
PS/CPC50	103.2	3.6	152.7	-3.5
PS/PCTMP	108.3	8.7	168.9	-23.4
PS/PCPA[b]	100.0	0.4	143.7	-0.8
CPC5	-	-	136.4	-
CPC50	-	-	156.2	-
PCTMP	-	-	192.3	-
PS	99.6	-	-	-
PCPA	-	-	144.5	-

a) Film

b) commercial PCPA with $\overline{M}_n$ =20100; $\overline{M}_w$ =37400

c) $\Delta T = T_{g\,(blend)} - T_{g\,(starting\ material)}$

In all blends two glass transition temperatures are observed whose values are shifted compared to neat polymers. In particular, it is interesting to observe that some phase separation is present also in PS/PCTMP, even if no appreciable crystallinity is observed. This result agrees with literature data because a considerable shift of the Tg and the absence of crystallinity clearly suggest high compatibility. Compatibility decreases with increasing the bis-phenol A content. Even if larger Tg shifts are obtained using the 50:50 copolymer (CPC50), also the PS/CPC5 data are interesting because they evidence that only a slight chemical modification of "typical" polycarbonate produces a fair improvement of compatibility.

The morphological analysis confirms the calorimetric results. In Figure 3.a and 3.b the micrographs of PS/PCTMP and PS/CPC50 are shown. Both materials reveal some heterogeneity but phase separation is more evident in the PS/CPC50 blend.

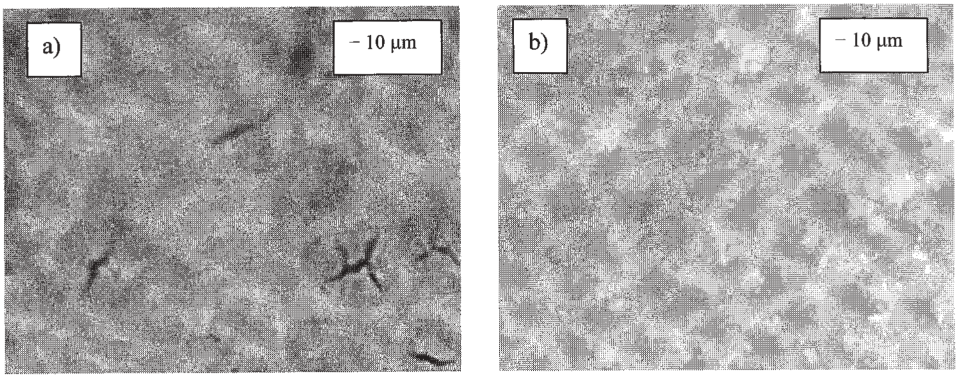

Figure 3. Morphology of 50:50 PS blends: a) PCTMP and b) CPC50.

Conclusions

Compatible binary blends based on polystyrene and aromatic polycarbonates can be obtained using random copolymers of BPA and TMBPA. The simple prevision scheme of Sonja Krause can be employed to design the copolymer molecular structure for specific applications.

The experimental data are consistent with these prevision results showing that PS has higher compatibility with the copolymers richer in TMBPA.

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