

Miscibility of Blends of Bisphenol-A-Polycarbonate and Poly(styrene-*co*-acrylonitrile-*co*-hydroxystyrene) Terpolymer

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ABSTRACT: The miscibility of blends of bisphenol-A-polycarbonate (BAPC) with the terpolymer poly(hydroxystyrene-*co*-acrylonitrile-*co*-styrene) (OHS-AN-S) and the copolymer poly(hydroxystyrene-*co*-acrylonitrile) (OHS-AN) was investigated. BAPC was found to be miscible with terpolymers incorporating 25–80 mol % hydroxystyrene. The introduction of the acrylonitrile monomer (AN) into poly(styrene-*co*-hydroxystyrene) (PSHS) produces a wider “miscibility window” with BAPC compared with that of blends of BAPC with PSHS i.e. a miscible blend is obtained at relatively lower levels of hydroxyl groups in the terpolymer. However, the miscibility range in terpolymer/BAPC blends is affected by the amount of AN monomer incorporated into the terpolymer. This is probably a consequence of the influence of the AN monomer on the closer spatial correlation

between the terpolymer and BAPC chains. BAPC is also found to be miscible with the OHS-AN copolymer within the composition range 12–50 AN mol % in the copolymer. A triangular phase diagram for binary blends of terpolymer/homopolymer ($A_xB_yC_z/D$) is suggested, to determine the miscible region of the terpolymer compositions in the blends. A model used for predicting the miscibility of binary blends consisting of a homopolymer and a terpolymer was also proposed on the basis of the mean-field theory, and tested with the experimental results obtained in this work. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 944–949, 2007

Key words: miscibility; polymer blends; terpolymer; bisphenol-A-polycarbonate; poly(hydroxystyrene-*co*-acrylonitrile-*co*-styrene)

INTRODUCTION

Intermolecular attractive interactions, the so-called specific interactions, and intramolecular repulsive interactions have been extensively used to promote miscibility in homopolymer and copolymer blends.^{1–8} Early studies of polymer blends relied on the use of intermolecular specific interactions such as hydrogen-bonding,¹ Lewis acid and base interactions etc.^{7,8} to enhance the miscibility among the polymeric components. More recently, the “intramolecular repulsive” effect^{2–4} has been shown to be effective in promoting miscibility in blends containing copolymers.^{2–6,9} A large number of studies have therefore focused on the miscibility of copolymer blends. Although terpolymers such as ABS and EPDM have long been playing a significant role in commercial applications, there is a limited number

of publications on the miscibility of blends containing a terpolymer.¹⁰ In this article, we report a study of miscibility of blends of bisphenol-A-polycarbonate (BAPC) and a terpolymer poly(hydroxystyrene-*co*-acrylonitrile-*co*-styrene) (OHS-AN-S).

While BAPC and polystyrene (PS) are immiscible, compatibility between these two components can be significantly improved by introducing a given amount of acrylonitrile (AN) monomer into the PS chains.^{11,12} An “optimum window” of AN composition in the SAN copolymer exists within which the interfacial thickness was found to be several times that of BAPC/PS blends, resulting in the excellent mechanical strength of the blends.^{12,13}

In our previous study of BAPC/poly(styrene-*co*-hydroxystyrene) (PSHS) blends, we demonstrated¹⁴ that BAPC is miscible with PSHS for certain amounts of hydroxyl groups in the copolymer. The driving force for miscibility to occur was attributed to the combined action of intermolecular attractive forces related to H-bonding between the hydroxyl groups and aromatic rings of BAPC, and the intramolecular repulsive forces resulting from the juxtaposition of the vinyl phenol and styrene groups within the copolymer.

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In the present article, we extend previous work and investigate the miscibility of blends of BAPC and the terpolymer poly(styrene-*co*-acrylonitrile-*co*-hydroxystyrene) (OHS-AN-S). It is well known that blend miscibility relies not only on the existence of intermolecular specific interactions between the components but also on a close contact between a donor group on a chain and an acceptor group on the second polymer molecule.¹⁵ The fact that improved compatibility between BAPC and SAN was achieved compared to BAPC/PS blends^{11–13} indicates that in BAPC/SAN blends a closer contact between the two polymeric species can be established. It is therefore expected that the introduction of AN units in PSHS should favor interactions between the —OH groups of the terpolymer OHS-AN-S with the aromatic ring sections of BAPC in the blends. Accordingly, miscibility between BAPC and OHS-AN-S may be obtained at a lower —OH content compared with BAPC/PSHS copolymer blends. In other words, a wider miscible window is expected for the BAPC/terpolymer system. However, since AN influences the contact between the two different components in the blend, the miscibility range should be affected by the amount of AN monomer used. A two-dimensional “miscibility map” for determining the misci-

ble region of the three compositions of terpolymer was suggested in this article that describes the influence of these monomers in the terpolymer on the blend miscibility. Following the same strategy used for predicting miscibility in blends containing copolymers, a model based on the mean-field theory is proposed here to predict miscibility of terpolymer/homopolymer binary blends. The model is tested experimentally using the results reported in this work.

EXPERIMENTAL

The polymers used in this study are listed in Table I. BAPC was supplied by GEC; poly(4-hydroxystyrene) was purchased from Polysciences. The monomers styrene, acrylonitrile and 4-acetoxystyrene, from Sigma Aldrich, were purified by distillation prior to use, after removal of the inhibitor. The terpolymer poly(styrene-*co*-acrylonitrile-*co*-hydroxystyrene) (OHS-AN-S) was synthesized by polymerization of the styrene, acrylonitrile and 4-acetoxystyrene monomers, followed by hydrolysis of the acetoxy groups. Free radical solution polymerization was carried out at 338 K, using toluene as solvent and α , α' -azobisi-

TABLE I
Characteristics of Polymers used in this Work

| Polymer | Composition | M_w (g mol ⁻¹) ^a | T_g (K) |
|--------------|-------------------------------|---|-----------|
| BAPC | | 57,200 | 433 |
| PHS | | 30,000 | 429 |
| Terpolymer | | | |
| OHS76-AN4-S | 4.3 mol % AN, 76.0 mol % —OH | 29,000 | 395 |
| OHS64-AN8-S | 8.0 mol % AN, 64.4 mol % —OH | 69,400 | 395 |
| OHS13-AN12-S | 12.0 mol % AN, 3.0 mol % —OH | 52,000 | 380 |
| OHS54-AN12-S | 12.2 mol % AN, 54.2 mol % —OH | 57,000 | 385 |
| OHS20-AN21-S | 21.9 mol % AN, 20.3 mol % —OH | 42,000 | 395 |
| OHS47-AN27-S | 27.3 mol % AN, 47.5 mol % —OH | 30,000 | 368 |
| OHS30-AN34-S | 34.0 mol % AN, 30.0 mol % —OH | 65,300 | 386 |
| OHS18-AN35-S | 35.0 mol % AN, 18.0 mol % —OH | 58,300 | 385 |
| OHS26-AN40-S | 40.0 mol % AN, 26.0 mol % —OH | 46,000 | 388 |
| OHS39-AN41-S | 41.3 mol % AN, 39.1 mol % —OH | 29,000 | 383 |
| OHS19-AN45-S | 45.3 mol % AN, 19.3 mol % —OH | 82,000 | 390 |
| OHS21-AN51-S | 51.5 mol % AN, 21.7 mol % —OH | 71,000 | 398 |
| OHS12-AN59-S | 59.3 mol % AN, 12.6 mol % —OH | 80,000 | 395 |
| OHS14-AN69-S | 69.1 mol % AN, 14.0 mol % —OH | 65,000 | 400 |
| Copolymer | | | |
| OHS-AN12 | 12.3 mol % AN | 62,000 | 401 |
| OHS-AN20 | 20.0 mol % AN | 57,000 | 381 |
| OHS-AN24 | 24.6 mol % AN | 57,000 | 401 |
| OHS-AN30 | 30.1 mol % AN | 62,000 | 401 |
| OHS-AN38 | 38.4 mol % AN | 54,000 | 376 |
| OHS-AN39 | 39.2 mol % AN | 72,000 | 381 |
| OHS-AN42 | 42.4 mol % AN | 43,300 | 393 |
| OHS-AN49 | 49.5 mol % AN | 55,900 | 376 |
| OHS-AN54 | 54.5 mol % AN | 64,000 | 398 |
| OHS-AN73 | 72.9 mol % AN | 54,000 | 391 |
| OHS-AN91 | 91.4 mol % AN | 33,000 | 383 |

^a Polystyrene equivalents.

TABLE II
Miscibility of Blends of BAPC with OHS-AN-S
Terpolymer and OHS-AN Copolymer

| Blends (50 : 50 w/w) | Miscibility |
|----------------------------|-------------|
| OHS12-AN59-S | Immiscible |
| OHS13-AN12-S | Immiscible |
| OHS14-AN69-S | Immiscible |
| OHS18-AN35-S | Immiscible |
| OHS19-AN45-S | Immiscible |
| OHS20-AN21-S | Immiscible |
| OHS21-AN51-S | Immiscible |
| OHS26-AN40-S | Miscible |
| OHS30-AN34-S | Miscible |
| OHS39-AN41-S | Miscible |
| OHS47-AN27-S | Miscible |
| OHS54-AN12-S | Miscible |
| OHS64-AN8-S | Miscible |
| OHS76-AN4-S | Miscible |
| Poly(hydroxystyrene) (PHS) | Immiscible |
| OHS-AN12 | Miscible |
| OHS-AN20 | Miscible |
| OHS-AN24 | Miscible |
| OHS-AN30 | Miscible |
| OHS-AN38 | Miscible |
| OHS-AN39 | Miscible |
| OHS-AN42 | Miscible |
| OHS-AN49 | Miscible |
| OHS-AN54 | Immiscible |
| OHS-AN73 | Immiscible |
| OHS-AN91 | Immiscible |

sobutyronitrile (AIBN) as initiator. The reaction was terminated by precipitation of the reaction products into methanol. The product was purified by using THF as solvent, and then dried in a vacuum oven at 335 K for 24 h. The hydrolysis reaction was carried out in 1,4-dioxane using hydrazine hydrate as hydrolytic agent^{14,16,17} at room temperature. The reaction was stopped after 20 h by precipitation into petroleum ether. The samples obtained were purified twice using THF as solvent and then dried in a vacuum oven at 335 K for 48 h. The completion of the deprotection of the acetoxy groups was followed by IR spectroscopy using a Perkin-Elmer FTIR 1720 spectrometer (resolution = 4 cm⁻¹) and was indicated by the disappearance of the carbonyl group band at 1765 cm⁻¹ and the appearance of a strong broad band due to the hydroxyl groups at 3600–3200 cm⁻¹.^{14,17} The copolymers poly(hydroxystyrene-co-acrylonitrile) (OHS-AN) were synthesized by copolymerization of acrylonitrile and 4-acetoxystyrene monomers followed by hydrolysis of the acetoxy group. The reaction conditions were similar to those used for the terpolymers.

Gel permeation chromatography was used to estimate the molecular weights of the synthesized polymers (polystyrene was employed as the calibration standard). The gel permeation chromatography used consisted of a Waters 590 programmable HPLC pump, a Waters 410 differential refractometer and a

Waters 745B data module. Gel permeation chromatography measurements were carried out with a Polymer Laboratories gel 5 μ mixed-C column using THF as solvent, pumped at a rate of 1 mL/min at 30°C.

The terpolymer and copolymer compositions were determined by ¹H-NMR using a Bruker 400 MHz spectrometer and by element analysis using a Perkin-Elmer 2400 elemental analyzer.

Blends were prepared by codissolution of the polymers into dioxane followed by coprecipitation into petroleum ether. All blends prepared contained equal amounts of the two components (50 : 50 weight ratio). The samples were dried under vacuum at 335 K for 48 h.

Glass transition temperatures (T_g) were determined using a Perkin-Elmer DSC-4 differential scanning calorimeter at a heating rate 20 K min⁻¹. Each sample was first heated at a rate of 20 K min⁻¹ to 15–20 K above its T_g and then kept to this temperature for a few minutes before quenching to room temperature. Blend miscibility was assessed using the criterion that a miscible blend exhibits a single T_g whereas an immiscible system shows multiple glass transitions corresponding to the T_g s of its components.

RESULTS AND DISCUSSION

The miscibility of BAPC blended with the terpolymers of OHS-AN-S and the copolymers of OHS-AN, containing different amounts of hydroxyl groups respectively, was studied and the results are listed in Table II. It is evident that for BAPC/OHS-AN-S blends miscibility occurs in the range of 25–80 mol % hydroxystyrene in the terpolymer. This corresponds to a wider “miscibility window” compared with that observed for BAPC/PSHS copolymer blends¹⁴ (Table III). This “miscibility window” was found to be affected by the AN content in the terpolymer.

TABLE III
Miscibility of Blends of BAPC with OHS-AN-S
and Comparison with Miscibility Behavior of
BAPC/OHS-AN and BAPC/PSHS^a

| Blend (50 : 50 w/w) | Miscibility |
|---------------------|-------------|
| BAPC/PSHS26 | Immiscible |
| BAPC/OHS26-AN40-S | Miscible |
| BAPC/PSHS44 | Immiscible |
| BAPC/OHS47-AN27-S | Miscible |
| BAPC/PSHS54 | Miscible |
| BAPC/OHS54-AN12-S | Miscible |
| BAPC/PSHS63 | Miscible |
| BAPC/S-AN8-OHS64 | Miscible |
| BAPC/PSHS77 | Immiscible |
| BAPC/OHS76-AN4-S | Miscible |

^a See Ref. 14.

Inspection of the data in Table III shows that whereas the blend of BAPC and PSHS containing 77 mol % —OH group, which is beyond its original “miscible window” with BAPC, is immiscible, miscibility can be achieved by simply incorporating as small an amount as 4 mol % AN monomer into the copolymer. The content of —OH groups in the terpolymer, required for maintaining its miscibility with BAPC, may reduce further down to about 26 mol %, reaching its lower limit of the “miscible region”, if the AN monomer in the terpolymer increases to about 40–45 mol %, that corresponds to a weight percentage of 25–29 wt % AN monomer in the copolymer. It is known that the most favorable interaction occurs between BAPC and SAN molecules in the mixture when the AN monomer content in the SAN copolymer falls within the range of 25–28 wt %, ¹⁸ as the interaction energy density (B_{blend}) of BAPC/SAN blend would reach its minimum at this stage resulting in a maximum mixing (closer contact) between BAPC and SAN molecules. Accordingly this effect should favor the effective interaction of the —OH groups in the terpolymers with the BAPC chains, leading to miscibility at relatively lower levels of the —OH groups in the terpolymer compared to those required for blends of BAPC with the PSHS copolymer.¹⁴ As shown in Table II this is also true for BAPC/OHS-AN blends which are miscible when the OHS-AN copolymer contains 12–50 mol % acrylonitrile units. However, the details of the mechanism of the miscibility for the blends of BAPC and OHS-AN will be discussed elsewhere separately.

The FTIR technique was employed to investigate the possibility of hydrogen-bonding interactions between the carbonyl groups of BAPC and the hydroxyl groups of the OHS-AN-S terpolymers. As reported previously for BAPC/PSHS copolymer blends,¹⁴ no visible shift of the band associated with the carbonyl group of BAPC (at 1774 cm^{-1}) was observed after blending with OHS-AN-S. However, in the spectral region associated with the stretching of the hydroxyl groups ($3200\text{--}3600\text{ cm}^{-1}$), a peak shift from 3369 cm^{-1} for immiscible blends to 3339 cm^{-1} for miscible systems was observed. This implies that an intermolecular attractive interaction may exist between the hydroxyl groups of OHS-AN-S and the π electrons of the aromatic rings of BAPC. As discussed in our previous paper,¹⁴ π bases such as aromatic hydrocarbons are known to have proton-accepting ability similar to ethers or amines. Interactions have been observed to occur between hydroxyl groups and the π electrons of aromatic rings and have been documented in the literature.¹⁸ We conclude that, as observed before for the PSHS system, the carbonyl groups are rather inert in this case.¹⁴

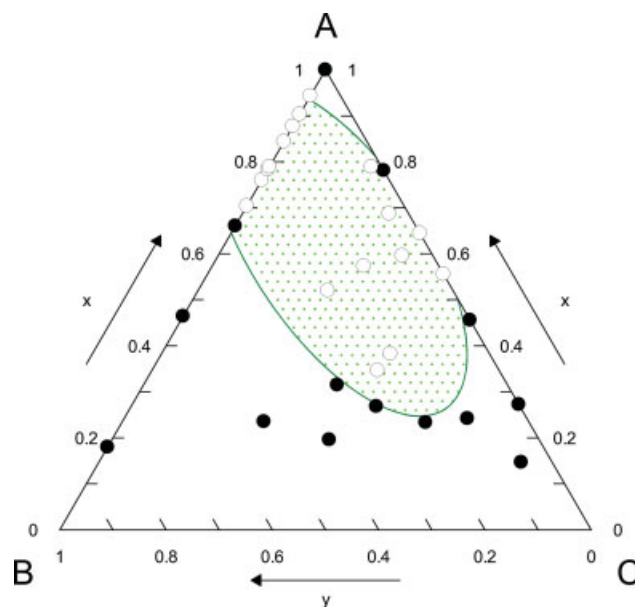


Figure 1 Phase diagram of BAPC/OHS-AN-S terpolymer blends. For all samples a 50 : 50 wt % blending ratio was used. In the diagram: A corresponds to OHS, B to AN, and C to S units. Symbols represent experimental data: (○) miscible and (●) immiscible blends. Data relative to BAPC/PSHS blends (reported on the x-axis) have been taken from our previous work reported in Ref. 14. All composition data are here expressed as volume fractions. The ellipsoidal curve drawn in the Figure defines the miscibility area calculated using eq. (1) in this article. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

For a blend of a terpolymer with a homopolymer, i.e. an $A_xB_yC_z$ (where A corresponds to OHS, B to AN, and C to S units)/D type blend, a miscibility area of the terpolymer compositions can be defined by plotting the experimental data on a two-dimensional “phase map” of the X-Y composition plane of the $A_xB_yC_z$ terpolymer as shown in Figure 1. This diagram only covers a triangular area because the volume fractions relative to the three units in the terpolymer need to obey the relationship $x + y + z = 1$. The three sides of the triangle give the three copolymer compositions, separately. In particular, the data on the AB axis in Figure 1 represent the compositions of OHS-AN blended with BAPC. The influence of the AN and hydroxystyrene monomers on the terpolymer/BAPC blend miscibility is evident in so far as no miscible blends would be formed if the content of hydroxystyrene in the terpolymer is less than 20 mol %. The same is true for AN monomers if its amount in the terpolymer is more than 50–55 mol %. The whole miscible region of the three compositions of terpolymer in the blends can be clearly profiled by taking this method.

To predict the miscibility region of compositions of a binary blend consisting of a terpolymer (compo-

TABLE IV
Interaction Parameters used for Calculations of the Miscibility Map for Blends of BAPC and OHS-AN-S or AN-OHS

| Pairwise | χ_{ij} | B_{ij} (cal/cm ³) | Resources |
|----------|--------------------|---------------------------------|-------------|
| BAPC-S | 0.11 | 0.61 | Ref. 18 |
| BAPC-AN | 0.63 | 3.80 | Ref. 18 |
| BAPC-OHS | 0.031 ^a | | Refs. 20,21 |
| S-AN | 0.92 | 5.45 | Ref. 18 |
| S-OHS | 0.25 | | Ref. 19 |
| AN-OHS | 1.03 ^a | | Ref. 20,21 |

^a Calculated by solubility parameter method as discussed in the text.

nent 1) blended with a homopolymer (component 2) i.e. of type $A_xB_yC_z/D$, on the two-dimensional "phase map," a formula on the basis of the mean-field theory was derived. The assumptions used are the standard ones viz $\chi_{\text{blend}} = \chi_{\text{crit}}$, the volume fractions of the two blend components ϕ_1 and ϕ_2 are 0.5, and $\chi_{\text{crit}} = 0.5 \times (1/\sqrt{m_1} + 1/\sqrt{m_2})^2$ where m_1 and m_2 are the degrees of polymerization of the two components.

The interaction parameter of the binary system χ_{blend} is then given by:

$$\chi_{\text{blend}} = x\chi_{AD} + y\chi_{BD} + (1-x-y)\chi_{CD} - xy\chi_{AB} - x(1-x-y)\chi_{AC} - y(1-x-y)\chi_{BC} \quad (1)$$

here the three letters A, B, and C represent the three monomer units of the terpolymer while D indicates the homopolymer; the x , y , and z are the volume fraction of each of corresponding monomers in the terpolymer; χ_{ij} s represent the segment interaction parameters between the component i and j .

While there are six segment interaction parameters required for the calculation, only four of them for the blends of BAPC and OHS-AN-S ($\chi_{\text{BAPC-S}}$, $\chi_{\text{BAPC-AN}}$, $\chi_{\text{S-AN}}$, and $\chi_{\text{S-OHS}}$) are available so far from experimental data (Table IV).^{19,20} For the other two interaction parameters i.e. $\chi_{\text{AN-OHS}}$ and $\chi_{\text{BAPC-OHS}}$, the solubility parameter approach was adopted^{21,22}:

$$\chi = \frac{(\delta_1 - \delta_2)^2 V_{\text{ref}}}{RT} \quad (2)$$

where δ_i is the solubility parameter of component i , V_{ref} is the reference volume (100 cm³ mol⁻¹), R is the gas constant and T is the temperature in Kelvin. To calculate $\chi_{\text{AN-OHS}}$, the experimental δ of acrylonitrile (13.36 cal^{1/2} cm^{3/2}) was used, whereas for OHS a calculated value was obtained (10.89 cal^{1/2} cm^{3/2}) from Hoy's group contribution method.²² The latter approach could not be used for the determination of the solubility parameter of BAPC and OHS and

hence $\chi_{\text{BAPC-OHS}}$. This is because Hoy's group contribution method does not consider the influence of intermolecular specific interactions such as hydrogen bonding. Hence, an indirect method was employed to calculate $\chi_{\text{BAPC-OHS}}$ based on a knowledge of the experimental values of $\chi_{\text{St-OHS}}$ (0.25), $\chi_{\text{BAPC-St}}$ (0.103),^{19,20} and the literature value of the solubility parameter of styrene (8.92 cal^{1/2} cm^{3/2}).²² For BAPC and OHS δ values were obtained from eq. (2) and found to be 9.7 and 10.13 cal^{1/2} cm^{3/2}, respectively. Finally, $\chi_{\text{BAPC-OHS}}$ was obtained (0.031).

Using all these parameters, the predicted region of miscibility for BAPC/OHS-AN-S blends has an ellipsoidal shape (Fig. 1) which is in very good agreement with the experimental data.

CONCLUSIONS

The miscibility of blends of OHS-AN-S/BAPC blend was investigated in this work. It was found that BAPC is miscible with the terpolymer when the hydroxystyrene content varies between 25 and 80 mol %. The introduction of a third monomer (AN) into PSHS indeed extends the "miscibility window," i.e. for the terpolymer blend, miscibility is achieved at lower —OH group content than for BAPC/PSHS copolymer blends. The miscible region is affected by the amount of AN monomer incorporated into the terpolymer and it is suggested that the presence of AN units lead to closer spatial correlation between terpolymer and BAPC chains. The minimum amount of hydroxystyrene required for maintaining blend miscibility is 26 mol % when the AN content is in the range 40–45 mol %. This corresponds to the "optimum window" in the SAN copolymers blended with BAPC, within which improved compatibility has been previously observed. It is believed that this effect should also play a role in blends of BAPC and OHS-AN-S terpolymer. A closer contact between the two components is expected in these conditions, leading to enhanced miscibility at relatively low levels of —OH groups compared with the BAPC/PSHS system. A triangular phase diagram for the binary terpolymer/homopolymer ($A_xB_yC_z/D$) blend system was developed, to determine the miscible region in the blends. The miscibility area, predicted on the basis of the mean-field theory, is in excellent agreement with the experimental data presented in this work.

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