Miscibility Studies on a Copolyester of Bisphenol-A with Terephthalic and Isophthalic Acids/Bisphenol-A Polycarbonate Blends

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ABSTRACT: The miscibility behavior of the blends of a copolyester of bisphenol-A with terephthalic and isophthalic acids (PAr) and a bisphenol-A polycarbonate (PC) was studied in dilute chloroform solutions at 25°C. The intrinsic viscosity and Huggins' parameter of the binary mixtures were determined from the intercept and slope of the linear straight line between specific viscosity and the overall polymer concentration at the studied compositions. From experimental results of the intrinsic viscosities of the mixtures, some miscibility parameters Δb, $\Delta b'$, $(\Delta b)^G$, $\Delta[\eta]$, α, and β were obtained by applying the criteria proposed by the research groups Krigbaum and Wall, Catsiff and Hewett, Garcia et al., Sun et al. and Jiang and Han, respectively. The miscibility of mixtures was also studied by using differential scanning calorimetry and fourier transform infrared spectroscopy. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 309–314, 2010

Key words: bisphenol-a polycarbonate; Polyarylate; blends; miscibility; viscosity

INTRODUCTION

Blending of polymers has given a new direction for developing novel materials. The manifestation of the superior properties of polymer blends depends upon the miscibility of its components at the molecular scale.[1] The most commonly used techniques for investigation of polymer–polymer miscibility are thermal analysis,[2,3] electron microscopy,[4,5] and spectroscopy. These techniques are very powerful for such applications, but they are somewhat expensive for most of the researchers. Therefore, other methods on investigation of polymer–polymer miscibility were proposed either using alternative properties or low cost equipment. Among them, viscometry is a very promising technique. Several works on polymer–polymer miscibility via viscometry have been done in recent years.[6–13]

The polycarbonates are well known high performance, engineering molding plastics. Bisphenol-A polycarbonate (PC) is a transparent high performance thermoplastic having good physical properties such as toughness, dimensional stability, good impact strength, high heat and electrical resistance. Because of these attributes, polycarbonate is used in a wide variety of common products including digital media (e.g., CDs, DVDs), electrical and electronic equipment, automobiles, sports safety equipment, reusable food and drink containers, and many other products.[14,15] On the other hand, polyarylate (PAr) is a kind of aromatic polyester of bisphenol-A with terephthalic and isophthalic acids (50/50) that combine clarity, high heat deflection temperature, high impact strength and good electric properties with inherent ultraviolet stability and flame resistance.[16] Attempts can be made to blend these polymers to get composites with a high performance molding plastic with good ultraviolet stability and flame resistance. Chemical structures of PC and PAr were given in Scheme 1.

In this study, the miscibility of PAr and PC was evaluated by several techniques such as viscometry, differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR). Viscometric analysis of polymer–polymer miscibility in dilute solution is based on the Huggins' equation which reflects the relationship between specific viscosity and polymer concentration. DSC is used to investigate the miscibility of the polymer blends using the single glass transition criterion in the binary mixtures.[3] FTIR is used to seek specific interactions between components of the mixture depending on shift of the characteristic peaks.

THEORETICAL BACKGROUND

For the ternary mixture of polymer 1, polymer 2, and a common solvent, at constant weight ratio of
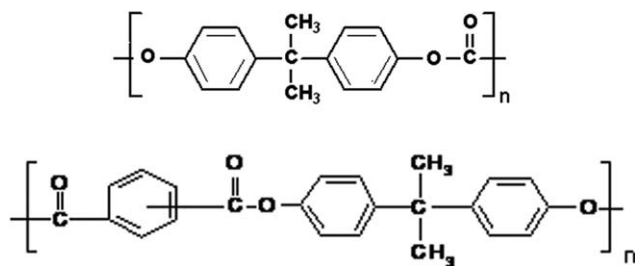
Scheme 1 Chemical structures of PC (a) and PAr (b).

polymer 1 to 2 for a given composition, m, the classical Huggins' equation is written as[17]

$$(\eta_{sp})_m/c_m = [\eta]_m + b_m c_m \tag{1}$$

where c, $(\eta_{sp})/c$, $[\eta]$, and b are concentration, reduced viscosity, intrinsic viscosity and viscometric interaction parameter of the polymer in the solution, respectively, while subscript "m" denotes "mixture".

Parameter b_m, which reflects the binary interactions between polymer segments is related to the Huggins' coefficient, k_H

$$b_m = k_H[\eta]^2 \tag{2}$$

The miscibility of the polymer 1 and 2 is estimated by comparison of the experimental and ideal values of b_m and $[\eta]_m$. The experimental values (b_m^{exp} and $[\eta]_m^{exp}$) are determined from the slope and intercept of the linear straight line plotted according to eq. (1) for solutions containing one of the polymer in binary mixtures or both of them at a given ratio in ternary mixtures in a solvent.

Krigbaum and Wall[18] have defined the ideal value of the interaction parameter b_m^{id} as

$$b_m^{id} = b_{11}w_1^2 + b_{22}w_2^2 + 2b_{12}^{id}w_1w_2 \tag{3}$$

and the b_{12}^{id} as a geometric mean

$$b_{12}^{id} = b_{11}^{1/2}b_{22}^{1/2} \tag{4}$$

The miscibility criterion Δb was described by Krigbaum and Wall: if $\Delta b = b_m^{exp} - b_m^{id} > 0$, polymer blend is miscible since attractive molecular interactions are present while if $\Delta b < 0$, polymer blend is immiscible since repulsive molecular interactions are considered. In the case of $\Delta b = 0$, neither attractive nor repulsive molecular interactions are present between polymers.

Catsiff and Hewett[19] have defined the ideal value of the interaction parameter, $b_{12}^{id'}$ as an arithmetic mean

$$b_{12}^{id'} = \left(\frac{b_{11} + b_{22}}{2}\right) \tag{5}$$

This is useful for the systems in which the individual b_{11} or b_{22} values are negative since geometric

mean is meaningless in this case. The miscibility criterion $\Delta b'$ was proposed by Catsiff and Hewett in which positive sign shows miscibility and negative one indicates immiscibility.

On the other hand, Garcia et al.[20] have proposed another definition for ideal value of the interaction parameter, b_m^{id} in the eq. (3), symbolized by $(b_m^{id})^G$ as

$$(b_m^{id})^G = b_{11}w_1^2 + b_{22}w_2^2 \tag{6}$$

Furthermore, Garcia et al. have also proposed another miscibility criterion based on the difference between experimental and ideal values of $[\eta]_m$ assuming that the intrinsic viscosity can be treated as an excess property. The value of $[\eta]_m^{id}$ has been defined as

$$[\eta]_m^{id} = [\eta]_1 w_1 + [\eta]_2 w_2 \tag{7}$$

where $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities of corresponding polymers. Garcia et al. described the miscibility criteria as $(\Delta b)^G = b_m^{exp} - (b_m^{id})^G > 0$ and $\Delta[\eta] = ([\eta]_m^{exp} - [\eta]_m^{id}) < 0$ if the blend is miscible or viceversa.

Sun et al.[21] have proposed another miscibility criterion, α for polymer–polymer miscibility defined as

$$\alpha = k_m - \frac{k_1 w_1^2[\eta]_1^2 + 2(k_1 k_2)^{1/2}w_1 w_2[\eta]_1[\eta]_2 + k_2 w_2^2[\eta]_2^2}{(w_1[\eta]_1 + w_2[\eta]_2)^2} \tag{8}$$

where

$$k_1 = b_1/[\eta]_1^2; \quad k_2 = b_2/[\eta]_2^2; \quad k_m = b_m/[\eta]_m^2;$$
$$k_{12} = \frac{b_{12}}{[\eta]_1[\eta]_2} \tag{9}$$

With the weighted additive rule as shown in eq. (7), an expression of k_m can be concluded as

$$k_m = \frac{k_1 w_1^2[\eta]_1^2 + 2k_{12}w_1 w_2[\eta]_1[\eta]_2 + k_2 w_2^2[\eta]_2^2}{(w_1[\eta]_1 + w_2[\eta]_2)^2} \tag{10}$$

Later, Jiang and Han[22] derived an improved criterion by substituting eq. (10) to (8) and parameter α was replaced with β

$$\beta = \frac{2w_1 w_2[\eta]_1[\eta]_2}{(w_1[\eta]_1 + w_2[\eta]_2)^2} \Delta k \tag{11}$$

where

$$\Delta k = k_{12} - \sqrt{k_1 k_2} \tag{12}$$

Sun et al. and Jiang and Han have proposed that the positive signs of α and β indicated miscibility of

Figure 1 The photo of the equipment which is the home-made modified Ubbelohde-type capillary viscometer in a constant temperature bath. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

the blend, respectively, i.e. $\alpha > 0$ and $\beta > 0$ if miscibility exist, $\alpha < 0$ and $\beta < 0$ if immiscibility exist between polymers in the blend.

EXPERIMENTAL

PAr ($\rho = 1.21$ g/cm^3) and PC ($\rho = 1.20$ g/cm^3) were provided as pellets by Amoco and General Electric Corp. The number average molecular weights of the polymers were determined as 14,500 and 31,000 g/mol[1] for PAr and PC, respectively, by gel permeation chromatography. Chloroform was supplied from Merck AG Inc. GPC measurements were performed with an Agielent model 1100 instrument consisting of pump and refractive-index and UV detectors and three Waters Styragel columns (HR4, HR3, and HR2). Both of the polymers were purified by being dissolved in chloroform as a dilute solution and precipitated in a large amount of methanol. DSC measure-

ments were performed on about 7 mg samples with a Perkin Elmer Pyris DSC 6 Series. The DSC curves were recorded at a heating and cooling rate of 10°C min^{-1} in two scans between 323 and 523 K. The second scans were reported in the paper.

FTIR spectra were collected using a Perkin Elmer Spectrum One FTIR spectrometer with a diamond micro-ATR accessory. The individual polymer samples were placed onto the ATR crystal and the anvil was hand-tightened to apply pressure. FTIR spectra of 64 scans at 4 cm^{-1} resolution were added and averaged to obtain the single-beam background and sample spectra.

All viscosity measurements were performed at 25°C using a home-made modified Ubbelohde-type capillary viscometer in a constant temperature bath controlled with $\pm$ 0.02°C by a Huber type electronically controlled thermostat (Fig. 1). Stock solutions of the binary and ternary systems were freshly prepared by dissolving appropriate amount of polymers in chloroform into a concentration of 0.125 g/25 cm^3 solutions. For each measurement, 7 cm^3 stock solution was loaded into the viscosimeter and diluted by adding 2 cm^3 chloroform to yield five lower concentrations. The elution time of each solution was taken as an average of four readings agreed to within $\pm$0.5%.

RESULTS AND DISCUSSION

Reduced viscosities in different compositions of PAr/PC: 0/100, 20/80, 40/60, 60/40, 80/20, 100/0 were measured at 25°C. Figure 2 shows the Huggins' plots for the pure components and their blends
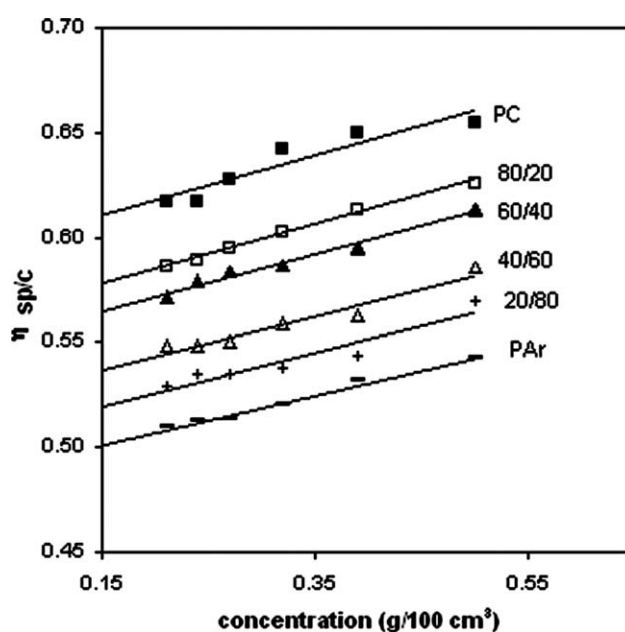

Figure 2 Huggins' plots for pure PAr, PC and their blends in compositions of PAr/PC: 0/100, 20/80, 40/60, 60/40, 80/20, 100/0 at 25°C.

TABLE I
Experimental Dilute Solution Viscosity Data of the
Blends and Constituent Polymers at 25°C

PAr/PC	b_m^{exp} (cm⁶/g²)	$[\eta^{exp}]$ (cm³/g)	k_H	r^2
100/0	0.1182	0.4836	0.5054	0.985
80/20	0.1295	0.4997	0.5186	0.908
60/40	0.1291	0.5171	0.4828	0.944
40/60	0.1363	0.5444	0.4599	0.982
20/80	0.1419	0.5567	0.4579	0.993
0/100	0.1430	0.5892	0.4119	0.885

Figure 3 Variation of interaction parameters α and β with weight fraction of PAr in the blends.

at 25°C. The linear relationships were observed for the polymers and their blends studied.

The b_m^{exp} and k_H were found from slopes of the experimental lines in Figure 2 using eqs. (1) and (2). The values of b_m^{exp} and the Huggins' coefficient k_H were given in Table I.

Theoretically, k_H of a flexible polymer is around 0.5 and 0.3 for theta and good solvents, respectively. However, k_H of a rigid polymer varies around 0.88 and 0.69 for theta and good solvents, respectively.[23]

The Huggins' coefficients of all blends and constituent polymers suggest that the shapes of PAr, PC and their blends in the solution under the studied conditions were semi rigid because the values of k_H take part between 0.4 and 0.5 in chloroform which is a good solvent.

The miscibility criteria proposed by Krigbaum and Wall, Catsiff and Hewett and Garcia et al. were given in Table II. The signs of the miscibility criteria, i.e. $\Delta b > 0$, $\Delta b' > 0$, $(\Delta b)^G > 0$, and $\Delta[\eta] < 0$, shows that PAr/PC are miscible and attractive intermolecular interactions are present in the blends.

The plots of the interaction parameters, α and β, which are calculated using eqs. (8)–(12) against composition of the blends, were illustrated in Figure 3.

It can be concluded that from the figure that PAr/PC blends are miscible for all of the studied compositions since the values of the parameters α and β are positive. It should be noted that the values of α are lower at compositions close to 50/50 than other compositions.

The FTIR/ATR spectra of PC, PAr and their blends in the compositions of 80/20, 60/40, 40/60, 20/80 were presented in Figure 4.
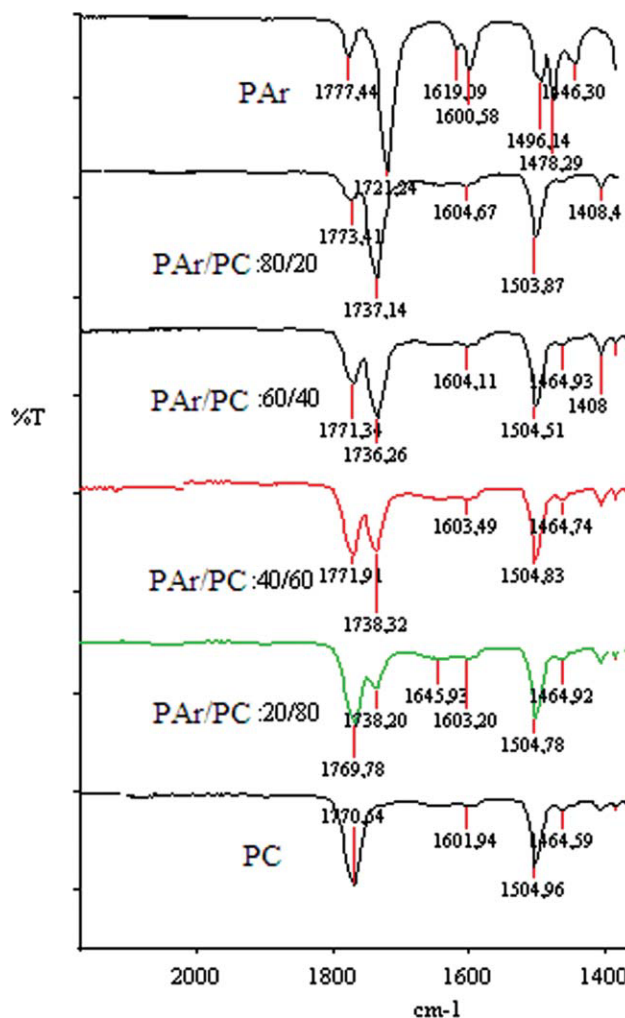

Figure 4 FT/IR ATR spectra of PAr, PC, and PAr/PC blend in compositions at 80/20, 60/40, 40/60, 20/80. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
The Miscibility Criteria of PAr/PC blends: Krigbaum
and Wall (Δb), Catsiff and Hewett ($\Delta b'$), Garcia et al.
(($\Delta b)^G$ and $\Delta[\eta]$)

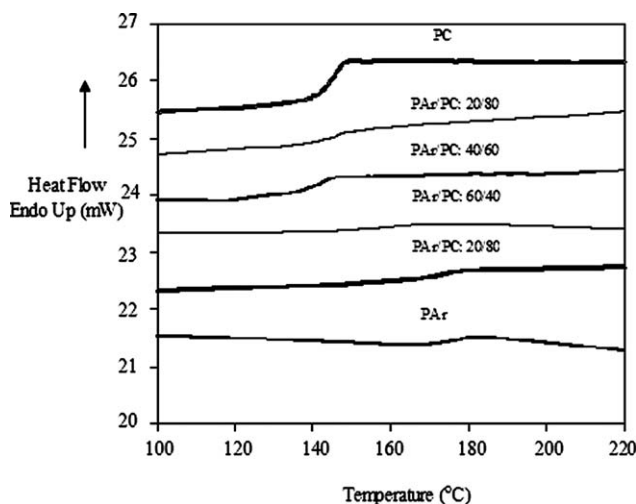| PAr/PC	Δb (cm⁶/g²)	$\Delta b'$ (cm⁶/g²)	$(\Delta b)^G$ (cm⁶/g²)	$\Delta[\eta]$ (cm³/g)	Miscibility
80/20	0.0065	0.0063	0.0481	−0.0050	Miscible
60/40	0.0013	0.0010	0.0637	−0.0087	Miscible
40/60	0.0035	0.0032	0.0659	−0.0026	Miscible
20/80	0.0040	0.0039	0.0456	−0.0114	Miscible

Figure 5 DSC thermograms of PAr, PC, and PAr/PC blend compositions at 80/20, 60/40, 40/60, 20/80.

As can be seen from Figure 4, the typical peaks of FTIR/ATR spectra of the films are centered at about 1777 and 1721 cm^{-1} ($\nu_{C=O}$), 1600 cm^{-1} ($\nu_{C=C}$) and 1496 cm^{-1} ($\nu_{C=C}$) for PAr; 1770 cm^{-1} ($\nu_{C=O}$) and 1505 cm^{-1} ($\nu_{C=C}$) for PC. It is easier to detect the changes in carbonyl absorption band of PAr and PC. Figure 4 shows a progressive shift up to 8 cm^{-1} and 17 cm^{-1} in the peak positions of the carbonyl stretching frequency of PAr by increasing concentration. This suggests that attractive forces are present between constituents of the blend.

To confirm the correct nature of the blend under consideration, DSC analysis also was carried out. DSC thermograms of the polymers and their blends are shown in Figure 5.

The glass transition temperatures of PAr, PAr/PC blends in compositions at 80/20, 60/40, 40/60, 20/80 and PC were found as 177, 173, 153, 147, 146 and 145 in °C, respectively. It was seen that the blends studied exhibit single T_gs which are between those of PAr and PC, indicating the miscibility of the blends. A lot of hypothetical equations were suggested in literature by many authors to envisage the T_g of a miscible blend in a certain composition. Among them, the equations of Gordon-Taylor[24–26]

$$T_g = \left[\frac{w_1 T_{g1} + K w_2 T_{g2}}{w_1 + K w_2} \right]; \quad K = \left(\frac{\rho_1 T_{g1}}{\rho_2 T_{g2}} \right) \quad (13)$$

and Couchman[27]

$$\ln T_g = \left(\frac{w_1 \Delta c_{p1} \ln T_{g1} + w_2 \Delta c_{p2} \ln T_{g2}}{w_1 \Delta c_{p1} + w_2 \Delta c_{p2}} \right) \quad (14)$$

are plotted in Figure 6 together with the experimental T_g values.

Where T_{gi}, w_i, ρ_i, and ΔC_p are the glass transition temperature, weight fraction, density and specific heat capacity difference between glass and rubber states of the component i in the blend, respectively. The ΔC_p value of PAr was given as 0.115 J/gK by Robeson and that of PC was derived as 0.519 J/gK from Figure 6.

The experimental T_g values of the blends exhibited a significant negative deviation than of the Gordon-Taylor's prediction however in agreement with the Couchman's equation. This was attributed to the low value of specific heat difference between the glass and rubber states of PAr as noted by Robeson to be a major factor in the Couchman's T_g versus composition relationship.

No studies are encountered in literature on determination of miscibility of PAr and PC by viscometry although a few ones are present based on DSC experiments with samples prepared by melt mixing or/and solution casting. In these studies, the authors focused on the existence of ester-exchange reactions in the blends. In Robeson's study, a PAr/PC : 50/50 mixture extruded at 265–270°C was compression molded at temperatures 260, 320, and 350°C. A reasonably complete phase separation was encountered in samples molded at 260°C, whereas at 320°C, a partial miscibility was observed as evidenced by two T_g intermediate between the component values. Howevester-exchangeer, a miscibility was observed based on a single T_g at 350°C. Robeson explained his results by formation of a copolymer due to ester-exchange reactions above 350°C.[28] Eguiazabal et al.[29]
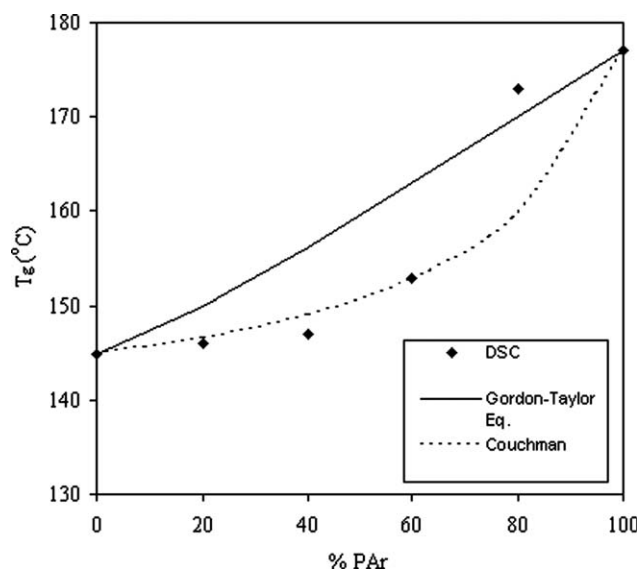

Figure 6 Glass transition temperature (T_g) versus composition of PAr/PC blends: solid and dotted lines are produced from the equations proposed by Gordon-Taylor [eq. (13)] and Couchman [eq. (14)], respectively, the points are experimental data obtained by DSC.

and Mondragon et al.[30] concluded that PAr and PC were miscible. Eguiazabal et al. determined a single T_g for their 50/50 blend sample prepared by solution casting from chloroform and heating at 277°C for 20 min. Mondragon et al. were determined single T_gs and transparent films for the samples prepared by both melt mixing and solution casting from chloroform and annealed at 300°C for 10 min. Robeson stated that PAr and PC are basically immiscible at ordinary conditions but become miscible as a result of ester-exchange reactions if samples are exposed to high temperatures for a long time, therefore, Eguiazabal et al. and Mondragon et al. observed single T_g as the time–temperature exposure conditions of both studies were significantly higher than the minimum condition in his study.[30]

In this study, a single T_g was observed at each composition by DSC measurements of the samples heated up to 250°C for a short time. In viscosity measurements, the samples are not exposed to any heating process. It seems that the miscibility of PAr and PC depends on the preparation conditions of the sample.

CONCLUSION

The miscibility of PAr/PC blends was investigated by viscometry, FTIR, and DSC. FTIR/ATR spectra show that PAr interacts with PC through their carbonyl units in solid state. The single T_gs of the blends obtained by DSC indicate that the blends are miscible in the solid state at the studied compositions. According to the miscibility criteria proposed by Krigbaum and Wall (Δb), Catsiff and Hewett ($\Delta b'$), Garcia et al., {$(\Delta b)^G$ and $\Delta[\eta]$}, Sun et al. (α) and Jiang et al. (β), PAr/PC blends are miscible in the compositions studied in chloroform solution. All miscibility criteria obtained by viscosity experiments indicate miscibility. However, the presence of an interaction observed by FTIR spectra implies that the values of the miscibility criteria should not be very close to zero. Thus, the results suggests that the criteria $(\Delta b)^G$ and α should be more certain since their values are higher than others. On the other hand, it is known that the miscibility of a component in a blend generally increases as its amount decreases. Therefore, it seems that α is more reasonable since its values are higher at compositions of PAr/PC: 20/80 and 80/20 than others.

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