Dynamic Mechanical Properties of Polycarbonate and Acrylonitrile–Butadiene–Styrene Copolymer Blends

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ABSTRACT: Blends of polycarbonate (PC) and poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS) with different compositions are characterized by means of dynamic mechanical measurements. The samples show phase separation. The shift in the temperatures of the main dynamic mechanical relaxation shown by the blend with respect to those of the pure components is attributed to the migration of oligomers present in the ABS toward the PC in the melt blending process. A comparison with other techniques (dielectric and calorimetric analysis) and the application of the Takayanagi three block model confirm this hypothesis. In all the studied blend compositions (ABS weight up to 28.6%) the PC appears as the matrix where a disperse phase of ABS is present. The scanning and transmission electron microscopy micrographs show that the size of the ABS particles increases when the proportion of ABS in the blend increases. The FTIR results indicate that the interaction between both components are nonpolar in nature and can be enhanced by the preparation procedure. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1507–1516, 2002

Key words: polycarbonate; acrylonitrile–butadiene–styrene; polymer blends; dynamic mechanical properties

INTRODUCTION

In the last few decades great attention has been paid to the development of polymer blends. Blends offer the possibility of combining the properties of available materials to produce new materials with better properties.

Polycarbonate (PC) is an amorphous polymer with good mechanical properties, but it can result in brittle failure, depending on the environmental factors.[1] On the other hand acrylonitrile–butadiene–styrene (ABS) is widely used as a thermoplastic with good physical properties, but the overall mechanical properties of ABS are lower than those of other engineering plastics. PC and ABS can be blended to improve their applications[2]; these blends have been reported to have a useful balance of toughness, heat resistance, and ease of processing. Nevertheless, the properties of

this blend could be affected if commercial polymers contain low molecular weight species such as monomers, oligomers, and others additives that accumulate at the interface. These effects can be reflected in changes in their calorimetric, mechanical, or dielectric properties.

PC and ABS are inmiscible, and the blend presents phase separation.[3,4] Two glass-transition and two main dynamic mechanical relaxation processes appear in the blend.

ABS is a copolymer containing a block of polybutadiene to which styrene–acrylonitrile (SAN) random copolymer has been grafted. Thus, in the PC/ABS blend the interface between the two phases present is in fact a PC/SAN, which has also been reported to be immiscible.[3,5]

Shifts in the glass transitions are shown by both the PC/ABS and PC/SAN blends. These shifts have been ascribed to partial miscibility[3,4] and to the migration of SAN oligomers to the PC phase during the blending process.[1,5–8]

This work studies the properties of various compositions of PC/ABS systems. Thermal, dynamic mechanical, and dielectric measurements during melt blending were analyzed. IR spectrometry was carried out on melted, solid mixtures of powdered components and samples prepared from solution. The morphology of the blends was studied by transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials and Methods

In order to study the interactions between the components, blends of bisphenol-A PC (Lexan 920-A, General Electric), PC, and ABS (Novodur P2MC, 25% AN and 5% butadiene) were prepared in three different ways:

1. Samples were prepared by injection molding in a Meteor 440/90 machine. The weight fractions of ABS in the samples were 0, 4.8, 9.1, 16.7, 28.6, and 100%.
2. A solid mixture of powdered components in the same proportion of PC and ABS as the melted samples was prepared.
3. The same compositions were produced in film form by casting from the solution of the pure materials in *N,N*-dimethylformamide.

Series 2 and 3 were used only for the sake of comparison in the IR spectroscopy analysis.

Thermal Properties

The thermal properties were measured in a Perkin–Elmer DSC4 calorimeter. Samples prepared by injection molding were encapsulated in aluminum pans and kept at 180°C for 10 min to insure that the sample is in equilibrium and erase the effect of a previous thermal history. The sample was then cooled to 70°C at a rate of 40°C/min. The measuring scan was conducted on heating between 70 and 180°C at a heating rate of 10°C/min. The glass-transition temperature was determined as the midpoint of the rise of the heat capacity at constant pressure in the transition from the heat capacity curves as calculated from the heat flow output of the DSC4.

Dynamic Mechanical Measurements

Dynamic mechanical spectroscopy was performed in a Polymer Labs DMTA II in the double cantilever configuration at a frequency of 1 Hz with a heating rate of 1°C/min between 30 and 170°C. This apparatus gives the logarithm of the storage modulus ($\log E'$) and the loss tangent ($\tan \delta$) of the material sample. To avoid the uncertainty due to the geometry of the sample the results of $\log E'$ are normalized and are given as $\log(E'/E'_0)$, where E'_0 is the corresponding value of E' at 30°C (glass modulus). Samples prepared by injection molding were studied with this technique.

Dielectric Measurements

Dielectric experiments were performed in a General Radio 1689M apparatus. The measurements were conducted from 70 to 200°C during a heating scan at 0.1°C/min. The capacity and loss tangent measurements in the frequency range from 12 to 10^5 Hz took place in less than 1 min, so we consider them as isothermal measurements. The samples studied were prepared by injection molding, had 1-mm thickness, and were vacuum dried before analysis.

IR Spectroscopy

For the sake of characterization of the interactions between the PC and ABS phases, FTIR spectra were performed on each composition for the three types of samples in a Nicolet 510 FTIR spectrophotometer apparatus.

Table I   Glass-Transition Temperatures of Samples

	ABS (%)					
	0	4.8	9.1	16.7	28.6	100
$T_{g\mathrm{PC}}$ (°C)	142.5	139.5	138.5	135	130	
$T_{g\mathrm{ABS}}$ (°C)		107	107	106	103	100
$T_{\alpha\mathrm{PC}}$ (°C)	150	144	143	140	134	
$T_{m\mathrm{PC}}$ (°C)	171.5	166	166	163		
$T_{m\mathrm{ABS}}$ (°C)					142.5	141.4	137
β			0.41	0.39	0.37	0.33

$T_{g\mathrm{PC}}$, $T_{g\mathrm{ABS}}$, temperatures of the calorimetric glass transition corresponding to PC and ABS, respectively; $T_{\alpha\mathrm{PC}}$, temperature of the mechanical α relaxation corresponding to the PC; $T_{m\mathrm{PC}}$, $T_{m\mathrm{ABS}}$, temperatures of the maximum of the tan δ for PC and ABS, respectively, corresponding to the main dielectric relaxation measured at 10 kHz; β, parameter as a function of the ABS proportion in the blend.

Morphology

The morphology of the blends obtained by injection molding was characterized by SEM using a Jeol JSM 6400 apparatus and by TEM using a Hitachi H800 apparatus. For the SEM observations the specimen fracture surfaces were obtained at liquid nitrogen temperature and coated with gold. For the TEM observations sample slices were obtained with a cryogenic Riechert–Jung FC4E ultramicrotome at around 173 K. These slices were mounted on a copper grid and stained by exposure to vapors of a 1% aqueous solution of osmium tetroxide for 8 h.

RESULTS

Thermal Properties

Table I shows the glass-transition temperatures (T_g) of the samples. The results show two glass transitions, each one associated with one of the pure components. The low temperature transition appears at a temperature slightly higher than the T_g of the pure ABS and increases with the PC content of the blend. This is called the glass transition of the ABS phase of the blend ($T_{g\mathrm{ABS}}$). The high temperature transition in the blend ($T_{g\mathrm{PC}}$) appears at a temperature slightly lower than the T_g of the pure PC and decreases as the ABS content in the blend increases.

Dynamic Mechanical Measurements

Dynamic mechanical measurements were performed on all the samples prepared by injection

molding. The temperature dependence of the loss tangent is shown in Figure 1. Pure PC shows a broad secondary relaxation in the temperature interval between 50 and 105°C (β relaxation) followed by the main dynamic mechanical relaxation at 150°C (α relaxation).[9] Pure ABS shows a secondary relaxation that appears as a shoulder in the low temperature side of the main α relaxation whose maximum appears at 105°C. The relaxation spectrum of the blends clearly shows the relaxation corresponding to the PC and ABS phases. If we focus on the transition corresponding to the ABS phase (the lower temperature peak), we can distinguish two facts: its temperature does not change appreciably from one sample to another and its intensity increases when the content of ABS in the sample increases. On the
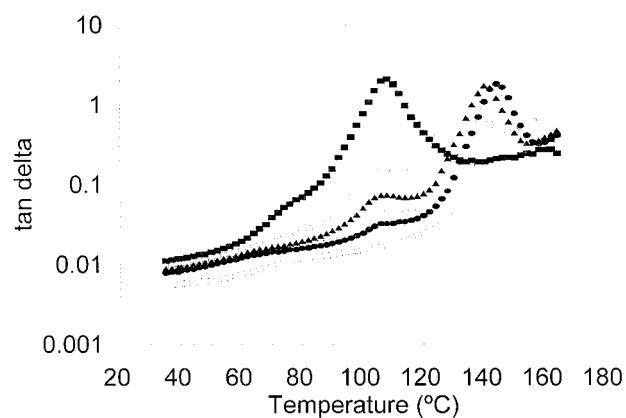

Figure 1   The temperature spectra of tan δ at 1 Hz of pure components and blends: (■) pure ABS, (○) 28.6% ABS, (▲) 16.7% ABS, (▽) 9.1% ABS, (●) 4.8% ABS, and (□) pure PC.
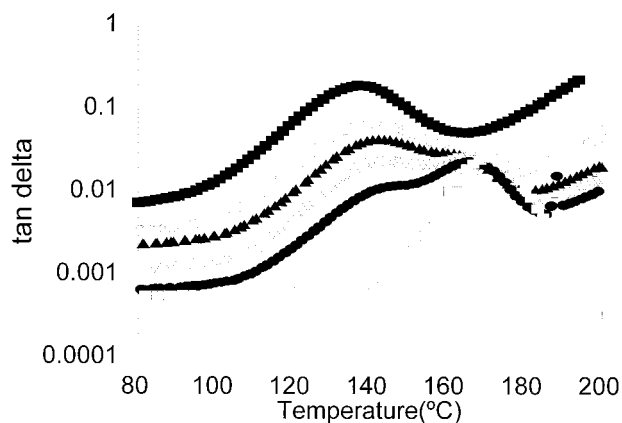
Figure 2 The loss tangent of the dielectric modulus as a function of temperature for a frequency of 10 kHz for (■) pure ABS, (○) 28.6% ABS, (▲) 16.7% ABS, (▽) 9.1% ABS, (●) 4.8% ABS, and (□) pure PC.

other hand, the transition corresponding to PC has an intensity that is more or less the same in all the samples, and its position moves toward lower temperatures when the content of ABS increases. Table I shows the temperature corresponding to the PC peak for each sample ($T_{\alpha PC}$)

Dielectric Measurements

The dielectric permittivity was measured for all the samples prepared by injection molding.

For the sake of comparison of the mechanical and dielectric measurements, we calculate the dielectric modulus (M^*) from the permittivity values, similar to the dynamic mechanical modulus (E^*). The dielectric modulus can be obtained from the complex permitivity by

$$M^* = M' + i \cdot M'' = \frac{1}{\varepsilon^*} \begin{cases} M' = \dfrac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} \\ M'' = \dfrac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \\ \tan \delta = \dfrac{M''}{M'} \end{cases} \quad (1)$$

where $i = -1$.

Figure 2 shows the loss tangent of the dielectric modulus measured at 10 kHz as a function of temperature.

The two peaks corresponding to each component move toward each other in the blends (see Table I), as occurs in the dynamic mechanical tests.

The dielectric relaxation spectrum of the pure components shows only the main dielectric relaxation. The spectrum of all the blends corresponds to the presence of two overlapped relaxation processes, although only the blend containing 16.7% ABS is resolved in two maxima. Samples with higher ABS content present a peak at a temperature slightly higher than pure ABS and increasing with the PC content in the sample and a shoulder in the high temperature side of the peak. Samples with ABS content lower than 16.7% show a peak at a temperature lower than pure PC, which decreases with ABS content, and a shoulder in the lower temperature side of the relaxation. Table I shows the temperature of the maximum (T_{mPC} and T_{mABS}) as a function of the composition of the blend at the frequency of 10 kHz.

From the isothermal dielectric modulus we made the master curves by a horizontal shift of the isothermal curves for each sample; the results for the pure components and the blends are shown in Figure 3. The master curves were fitted to the Kohlrausch–Williams–Watts equation.[10] The result for the ABS transition gives β parameter values from 0.33 ± 0.02 to 0.41 ± 0.02 when the PC proportion increases, as we can see in Table I; the corresponding value for the pure PC transition is 0.42 ± 0.02.

IR Spectroscopy

In addition to the injection molded samples studied in this work, a series of blends were prepared: a solid blend in which no interaction is expected between the blend components, and the film cast from the solution of the components in a common solvent. This procedure is expected to enhance the dispersion of the phase domains and thus increase the interfacial surface.

The three type of samples, injected, solid blend, and film cast from the solution, were analyzed and compared.

The absorption maximum at 2237 cm^{-1} that characterizes the nitrile group does not have any change (Fig. 4). We also did not observe any appreciable change in the position of the absorption maximum of the PC carbonile group (C=O) at 1775 cm^{-1}.

On the other hand, differences among the three kinds of samples studied were measured in the relative intensity of the absorption maximum of the benzenic rings (1507 cm^{-1} in the PC and 1495 cm^{-1} in the ABS, Fig. 5). The same differences
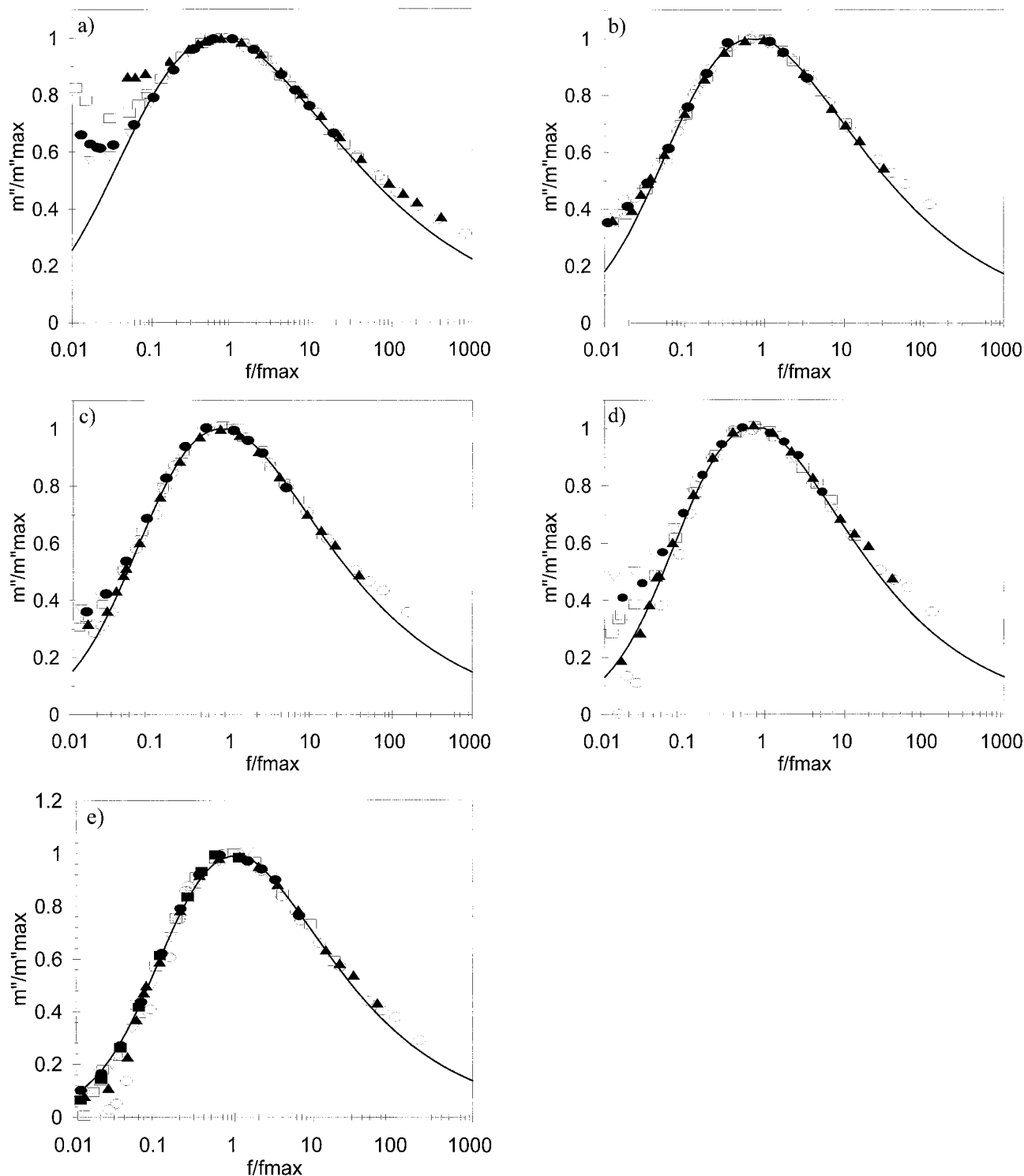
Figure 3 Master curves for the imaginary dielectric modulus for (a) pure ABS at (○) 116.1, (▲) 120.6, (□) 125.1, (●) 129.7, and (▽) 134.1°C, and (—) the Kohlrausch–Williams–Watts (KWW) fit with β = 0.33; (b) 28.6% ABS at (○) 127.5, (▲) 132, (□) 136.7, (●) 141.4, and (▽) 145.6°C, and (—) the KWW fit with β = 0.37; (c) 16.7% ABS at (○) 128.8, (▲) 133.7, (□) 137.8, (●) 142.5, and (▽) 147°C, and (—) the KWW fit with β = 0.39; (d) 9.1% ABS at (○) 130.2, (▲) 134.6, (□) 139.3, (●) 143.6, and (▽) 148.1°C, and (—) the KWW fit with β = 0.41; (e) pure PC made by superposition of the isotherms at (○) 162.5, (▲) 165.4, (□) 168.6, (●) 171.5, (▽) 174.5, (■) 177.5, and (△) 180.4°C, and (—) the KWW fit with β = 0.42.
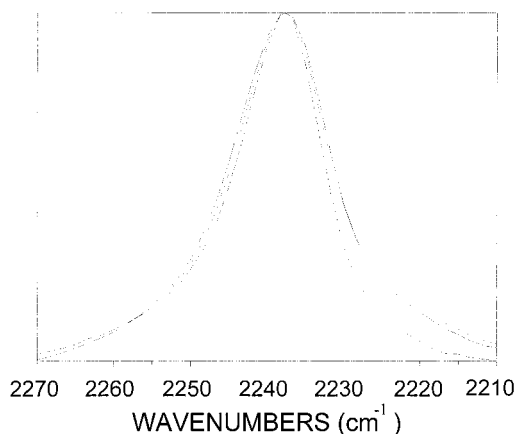
Figure 4   The absorption maximum corresponding to the C=N bond for the blend with 28.6% ABS: (- - -) the injected sample, (– –) the film sample, and (—) the solid sample.

were observed for the C—H bond in the benzenic ring (829, 1015, 1080, 3028, and 3040 cm^{-1}) and the hydrocarbonate chain (2933 and 2969 cm^{-1}). The characteristic interactions of polybutadiene are masked by the polystyrene signal, but we also detect some small change.

Morphology

Figure 6 shows the results obtained by TEM for all the blends. During the staining process, osmium tetroxide fixes only the butadiene's double bonds of ABS [black spots in Fig. 6(a–e)]. In Figure 6(e) we can see the ABS particles; their size ranges from 0.3 μm for the smaller units to 4 μm
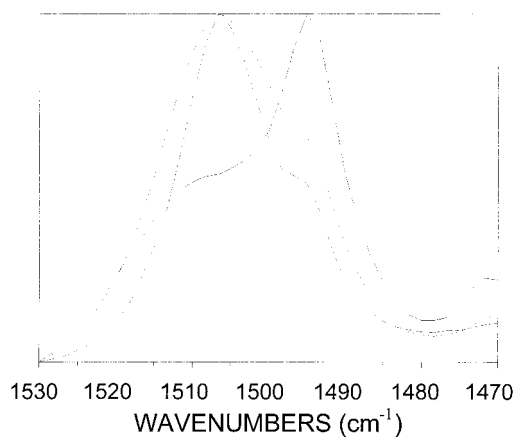

Figure 5   The absorption maximum corresponding to the benzenic ring for the blend with 28.6% ABS: (- - -) the injected sample, (– –) the film sample, and (—) the solid sample.
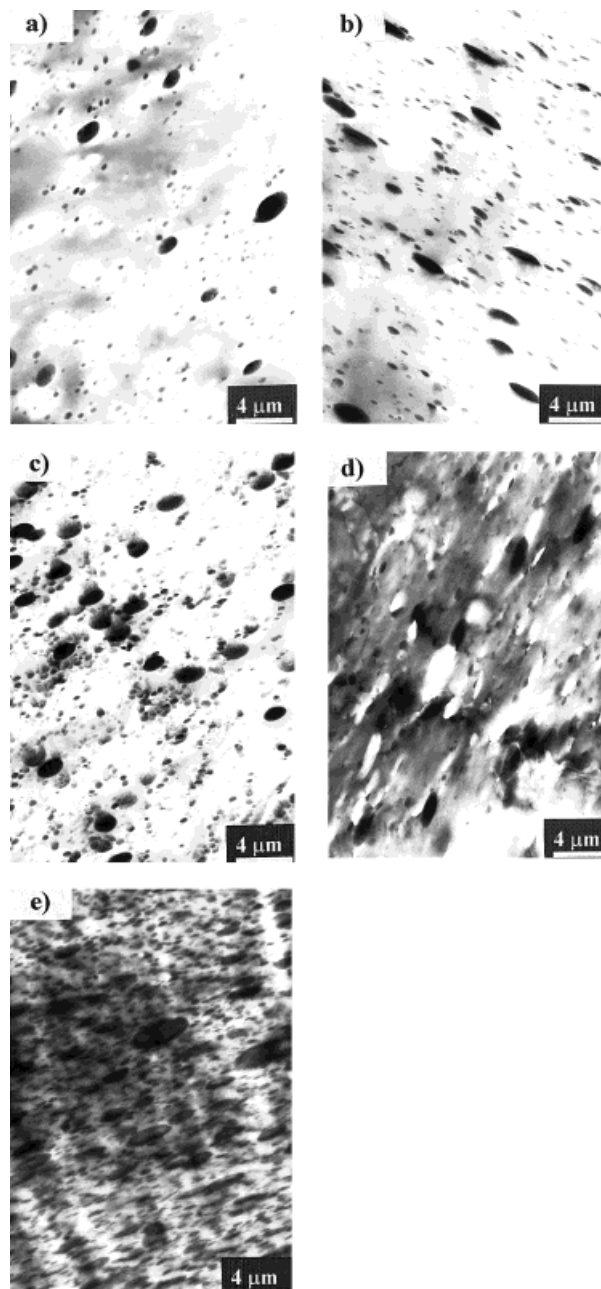

Figure 6   TEM micrographs of PC/ABS blends: (a) 4.8% ABS, (b) 9.1% ABS, (c) 16.7% ABS, (d) 28.6% ABS, and (e) pure ABS.

for the bigger ones. Figure 6(a) shows the dispersion of the ABS in the PC matrix. When the proportion of ABS increases, the material makes aggregates of bigger size inside the PC matrix. This is clear for ABS contents of 16.7% [Fig. 6(c)] and higher.

The size of the particles observed by TEM corresponds with that observed by SEM. The SEM
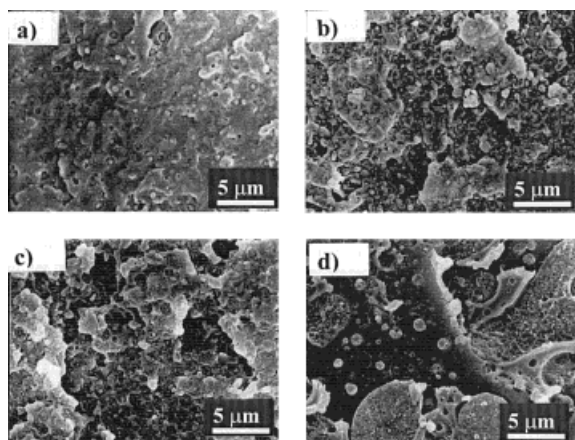
Figure 7 SEM micrographs from cryogenically fractured cross-sectional surfaces of PC/ABS blends: (a) 4.8% ABS, (b) 9.1% ABS, (c) 16.7% ABS, and (d) 28.6% ABS.

micrographs show the presence of two phases [Fig. 7(a–d)]. The ABS corresponds to the small particles whose size is between approximately 0.5 and 1.0 μm [Fig. 7(a)]. Some ABS particles show a dark contour, which might be an indication of slits between the particle and the matrix, implying bad adhesion.

Figures 6(d) and 7(d) show the photomicrographs for the blend of the highest ABS contents (28.6%). The distribution of polybutadiene points out that even the aggregates of ABS can reach sizes higher than 5 μm, but the ABS seems to always be the disperse phase in the PC matrix. There is no evidence of cocontinuity between both phases.

DISCUSSION

The TEM and SEM show that the blends consist of two phases. The fact that the T_g and the temperature of the main dielectric and dynamic mechanical relaxation processes of these two phases are closer to each other in the blend than those of the pure components can be explained by partial miscibility (i.e., the dilution of some ABS in the high T_g phase and some PC in the low T_g phase of the blend) and by the migration of oligomers from the ABS to the PC during the melt blending along the screw of the injection machine. The results of a number of studies[1,5–8] are conclusive in the sense that the latter phenomenon occurs, and thus partial miscibility is only a possibility that is very difficult to reach with our techniques.

There are important experimental data supporting this assumption. Dielectric spectroscopy is useful in this blend to differentiate the miscibility of both components in the blend because the permanent dipolar moment of the AN units of ABS is much higher than that of PC and, in spite of the low AN content of ABS, the main relaxation process of ABS has greater strength than PC. Thus, the changes of the ABS proportion in the blend with respect to the pure ABS can be well characterized in the blends.

It is clear that the main relaxation of the ABS phase becomes narrower (higher β value) as the ABS content in the blend decreases. If some of the PC chains are diluted in the ABS phase in the blend, the opposite behavior would be expected. If the ABS contains oligomers acting as a plastifier, its main relaxation process is broader than in the pure ABS; thus, as some oligomers leave the ABS during melt blending, the distribution of dielectric relaxation times becomes narrower at the same time that the peak shifts toward higher temperatures (or lower frequencies).

If the hypothesis of migration of oligomers is true, the shift of the glass-transition temperatures should be revealed by both dynamic mechanical and dielectric measurements. In the dynamic mechanical measurements there is a change in the temperature corresponding to the PC peak, but there is only a small change in the temperature corresponding to the ABS transition. This fact can be explained by supposing the components are immiscible and if two contrary effects are present: shifts of the ABS peak toward higher temperatures when the proportion of PC increases, which is due to the oligomer migration; and mechanical interaction between both components that produces variations of the peak temperature as suggested by other authors.[11]

To prove that the mechanical association of PC and ABS can produce variations in the transition, we applied a mechanical block model proposed by Takayanagi[12] in which two blocks in parallel model the continuous and disperse phases and a block in series models a fraction of the continuous phase. The model reproduces the properties of the blend from the properties of the pure components. The volume fraction of the continuous phase acting in series is represented by λ. This model was applied to different systems like poly(ethyl methacrylate)/ Kevlar,[13] poly(methyl methacrylate)/Kevlar,[14] and styrene–butadiene–styrene/ethylene vinyl acetate.[15] From the fit parameters it is possible to characterize the mechanical behavior of the blend
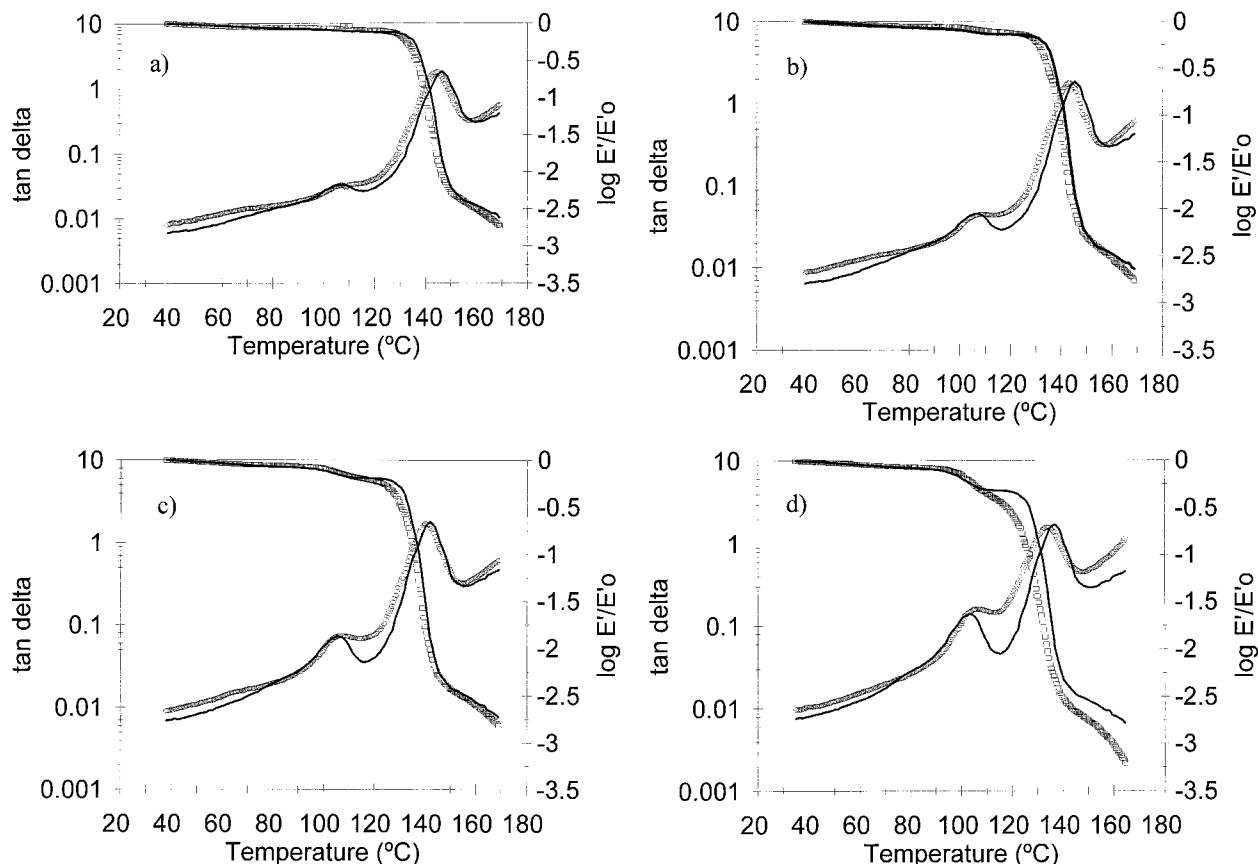
Figure 8 The temperature spectra of the loss tangent (tan δ) and storage modulus (E') at 1 Hz for PC/ABS blends: ($\bigcirc$) experimental data of tan δ, ($\square$) experimental data of $\log(E'/E'_0)$, and (—) model calculations with PC as the continuous phase; (a) 4.8% ABS, $\lambda = 0.9$; (b) 9.1% ABS, $\lambda = 0.8$; (c) 16.7% ABS, $\lambda = 0.7$; and (d) 28.6% ABS, $\beta = 0.7$.

and analyze the effects of the interphase. It is also possible to know which component acts as the matrix and establish the composition for the phase inversion if it is present. The experimental results of the E' and the tan δ of the loss angle are compared with the model's prediction.

If there is oligomer migration from one component to the other in the blends, the individual phases in the blend are not the same as the pure components. Having this in mind, we assume the spectra of pure materials to be those corresponding to the pure material but shifted in temperature by the same interval as the displacement of the T_g of the calorimetric measurement for the corresponding blend.

Figure 8 shows the result of the fit assuming a perfect adhesion between both components and taking λ as a fit parameter. In all the cases the results are better if the PC is considered as a matrix component. This is illustrated in Figure 9, which represents the application of the model assuming ABS as a matrix component.
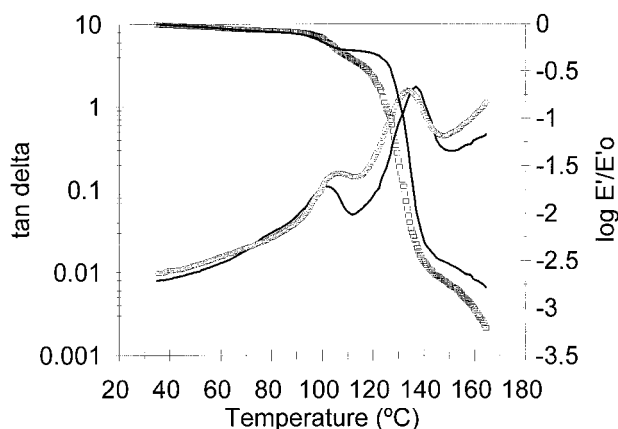

Figure 9 The temperature spectra of the loss tangent (tan δ) and storage modulus (E') at 1 Hz for the PC/ABS blend with 28.6% ABS: ($\bigcirc$) experimental data of tan δ, ($\square$) experimental data of $\log(E'/E'_0)$, and (—) model calculations with ABS as the continuous phase.

The model reproduces the position and the intensity of both relaxations. The λ parameter decreases when the proportion of ABS in the blend increases. This is normal because when the ABS proportion increases, the component that acts in series (i.e., PC) decreases. The results for the ABS transition show that. although the calorimetric transition moves toward higher temperatures, the mechanical interaction causes the position of the α peak to suffer only small changes when the composition of the blend changes.

In the PC relaxation there is a small discrepancy in the peak position. In all cases the experimental temperatures are lower than those expected from the model, especially with a higher ABS content. The reason for the discrepancy could be the shift of the peak taken from the calorimetric results, which could be different for the corresponding T_α of the mechanical measurements that depend on the frequency.

The results point out that the shift of the transition peaks could be caused by the oligomer migration, but the partial miscibility must not be discarded.

A relevant discrepancy between the fit of the Takayanagi model and the experimental results is present in the region between both transitions. The experimental mechanical modulus is always lower than that corresponding to the model. The discrepancy is higher when the ABS proportion increases. This was observed in other systems[15] and can be explained by bad adhesion between both components, which produces additional friction and thus a higher energy dissipation. This effect is amplified by the difference in the expansion coefficient of both components.[16] For this temperature interval the ABS is in the rubber state and the PC is in the glass state. This hypothesis is confirmed by the SEM results. As we commented before, a slit can be observed around the ABS particles, suggesting bad adhesion between the ABS and PC components. This result was reported by other authors.[17]

Some authors[17,18] observe a cocontinuity between the ABS and PC phases for samples with 30 wt % ABS. However, others[4] present PC/ABS blends with 40 wt % ABS where the PC acts as the matrix component. Our SEM results confirm the fact observed by the fit of the mechanical model that the PC acts as the matrix component and the ABS as the disperse phase for all the compositions lying between 4.8 and 28.6% ABS.

The IR technique was used to ascertain if the interactions between the molecules of PC and ABS (secondary forces) are of the van der Waals (polars) or London forces (nonpolars) types. Neither the nitrile (CN) polar group in the ABS nor the carbonyl group (C=O) in the PC show appreciable differences between the results of the three types of samples (solid blend, injected, and film). This indicates that the interaction between both components is not of the van der Waals type.

The shift measured in the absorption maximum of the PC ether group (C—O—C) at 1192 cm^{-1} can be interpreted as a structural adjustment due to the new interactions of the benzenic rings. This fact could justify the presence of small changes in the carbonyl group of the PC.

In every case the measured shifting depends on the proportion of each polymer and the injected samples always show the position of the absorption maximum between those of the solid and the film samples. This points out that its interaction and behavior are intermediate between the other two. The results indicate that the interaction forces between the blended polymers are London forces and they take place via the benzenic rings and the hydrocarbonate chain. There is no evidence of the presence of secondary polars forces (van der Waals type) between both components.

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