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# Polycarbonate/acrylonitrile-butadiene-styrene blends: miscibility and interfacial adhesion

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## Summary

By DSC measurements it has been determined that blends of Polycarbonate (PC) and a ABS "core-shell" terpolymer with 24 %-wt of Acrylonitrile and 6 %-wt of Butadiene seems to show limited miscibility due to the partitioning of the oligomers contained on each raw material. Like in other PC blends systems, the composition of the conjugated interphase is not constant but depends on the ratio of components in the blend. In all the compositions studied the apparent solubility of ABS (actually the SAN phase) in the PC-rich phase increase with decreasing volume fraction of PC in blends reaching a maximum at 10 %-wt of ABS. Yield Stress of the blends follows the rule of mixture almost until 10 %-wt of ABS, indicating that interfacial adhesion is strong enough to ensure stress transfer between phases in the course of yielding and drawing. Applying the Puckánszky et al. model, it was observed that over 15 % wt of ABS, the effectiveness in stress transfer depends on the morphologic gradient generated during the mixing and specimens' moulding.

## Introduction

Dealing with polymer blends its important to remind that the solubility degree between the parent components determines the morphological situation, and the stress transfer effectiveness between the phases generated after the "thermo-mechanical" mixing (1). Both aspects could be more difficult to analyse in Bisphenol A Polycarbonate/Acrylonitrile-Butadiene-Styrene (PC/ABS) systems if we consider the actual constitution of ABS terpolymer. ABS is produced by the grafting copolymerisation of Styrene (St) and Acrylonitrile (AN) into Polybutadiene (PB) latex, resulting in a mixture of PB, PB grafted with AN and St, and Styrene-Acrylonitrile (SAN) copolymer (2).

Based on previous reports on PC/SAN blends (3), and being the ABS a heterogeneous system itself, it is expected that the content and composition of the SAN phase could affect the miscibility degree between PC and ABS.

By "Lap Shear Strength" tests it has been determined that the interfacial adhesion between PC and SAN passes trough a maximum at 25-27 %-wt of AN, which may correspond to the interval of the highest miscibility, as was confirmed later by Callaghan et al. (4). At this AN proportion the energy interaction (both Flory-Huggins and Sánchez-Lacombe) between PC and SAN reach the minimum value. Stress-strain measurements

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indicates that interfacial adhesion at 25-32 %-wt of AN is sufficient for stress transfer at yielding, but is poor at 0-13 %-wt of AN in SAN (3).

Some aspects must be considered with the use of Tg variations on blend's miscibility studies. It is accepted that a unique Tg value indicates total miscibility of the components. Considering that the glass transition correspond to the "co-ordinated" motion of chain segments (almost 100 C atoms), the correct interpretation of a unique Tg should be that there are domains between 2 and 15 nm in diameter, indicating a very fine dispersion (5). For systems suspected to be partially or not miscible with less than 10 to 20 %-vol of one of the components, its difficult to obtain very "sharp" and well spaced Tg signals when the difference between those of the parents polymers are lower than 20 °C, taking this difference as a limiting factor to make an acceptable study (6)

The results reported and discussed in this paper are the initial stage on a brief study of PC/ABS blends in the PC rich range composition (until 40 %-wt of ABS) that account for the morphology, fracture and mechanical behaviour analysis at different strain rates. Here the suspected miscibility degree and the possible interphase composition were determined by DSC measurements following the Kolarik et al. procedure (7) and the effectiveness degree of stress transfer between the phases was studied by tensile tests.

## Experimental

The blends were prepared employing a Bisfenol A Polycarbonate (PC) (MFI = 12,35 g/10 min at 300°C/1,2 kg) and a Acrylonitrile-Butadiene-Styrene (ABS) "Core Shell" terpolymer (MFI = 22,25 g/10 min at 220°C/10 kg) containing 25 %-wt of Styrene-Acrylonitrile copolymer (SAN) and 5 %-wt of Butadiene. After melt mixing on a co-rotating twin screw at 280 °C and 100 rpm, the blends were injection moulded into prismatic bars (6 x 13 x 120 mm) and normalised dumbbell specimens, at the same mixing temperature.

The nominal ABS contents were varied from 5 to 40 %-wt as showed in Table 1. The actual composition expressed in volume fraction was calculated with the parents and blend's density determined at room temperature ($\rho_{PC}$, $\rho_{ABS}$, $\rho_b$) (Eq.1):

$$v_{ABS} = (\rho_b - \rho_{PC})/(\rho_{ABS} - \rho_{PC}) \qquad \text{(Eq. 1)}$$

With 10 to 15 mg of the prismatic bars' central section DSC measurements were made at 10 °C/min from 25 to 200 °C using a PERKIN-ELMER DSC 7. Prior to the scan, each sample was heated up to 170°C (260°C for PC), annealed at this temperature (3 min.) and cooled at 200°C/min (nominal) in order to ensure identical thermal history to all tested samples. From thermograms the Tg midpoint for each phase values were determined. The mean values of 5 samples by each composition were reported.

In order to study the mechanical effectiveness of the interphase generated, almost 10 specimen by blend composition were subjected to tensile tests following the ASTM D638 procedure with Type I dumbbell geometry in an universal testing machine (ADAMEL DY30) at room temperature and cross head rates of 1 and 500 mm/min.

## Results and discussion

### *Calorimetric analysis:*

DSC analysis of the blends reveals two glass transitions (Table 2), which prove the two-phase structure of the blends. The Tg values reported for each phase are not identical to the parents polymers (144 °C for PC and 100 °C for the SAN phase in the ABS) but they are somewhat shifted toward each other depending on the blend composition, indicating some degree of miscibility. From the variation of Tg's conjugated phase (Figure 1) it could be stated that the Tg-PC rich phase (Tg') seems to be more sensitive to the ABS phase than the ABS to the PC phase presence.

Calorimetric properties depend on volume relation between the phase and the interphase. Thus, the existence of an interphase affects in a higher degree the Tg of the minor phase increases the relative error on the ΔCp's minor phase determinations.

Nevertheless, the ΔCp values determined could be used to estimate the weight fraction of each parent polymer rich-phase ($w_{ABS}$ and $w_{PC}$) (neglecting PB's signal). Composition of conjugated phases can be calculated from its Tg (in K degree) and parent polymer's Tg as Fox stated (8):

$$w'_{ABS} = v'_{ABS}\rho_{ABS} = \frac{Tg_{ABS}\left(Tg_{PC} - Tg'\right)}{Tg'\left(Tg_{PC} - Tg_{ABS}\right)} \; ; \; w''_{PC} = v''_{PC}\rho_{PC} = \frac{Tg_{PC}\left(Tg'' - Tg_{ABS}\right)}{Tg''\left(Tg_{PC} - Tg_{ABS}\right)} \qquad \text{(Eqs. 2)}$$

where the super-symbols ('and ") refers to the PC and ABS-rich conjugated phases. Kolarik et al. (7) stated that $v_{PC}$' or $v_{ABS}$", determined by calorimetric analysis, could be considered as better miscibility indicators of the components than the interaction parameters $\chi_{21}$ or $\chi_{12}$ derived by Kim and Burns (9).

Table 1.- Actual blend density ($\rho_b$) and second phase contents expressed in weight (nominal) ($\%w_{ABS}$) and volume ($\%v_{ABS}$) basis

| Blend | $\%w_{ABS}$ | $\%v_{ABS}$ | $\rho_b$ (g/cm$^3$) |
|---|---|---|---|
| PC | 0 | 0 | 1,208 |
| PC-5 | 5 | 6,79 | 1,197 |
| PC-10 | 10 | 11,1 | 1,190 |
| PC-15 | 15 | 16,1 | 1,182 |
| PC-20 | 20 | 21,6 | 1,173 |
| PC-40 | 40 | 35,8 | 1,150 |
| ABS | 100 | 100 | 1,046 |

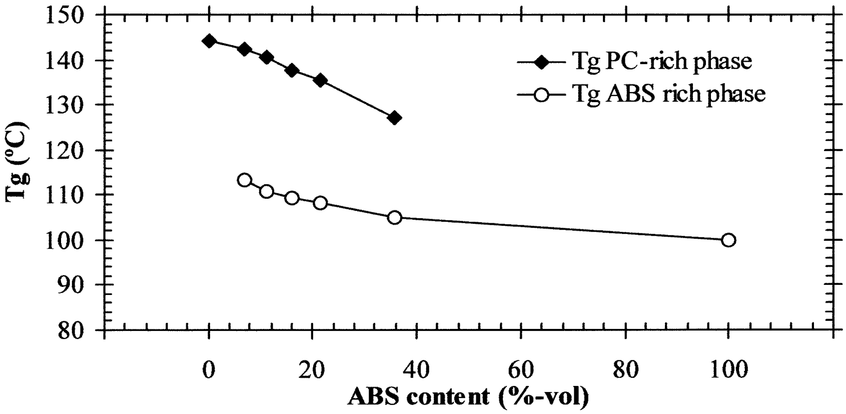

Figure 1.- Tg variation of the phases with blend's composition.

In order to quantify the participation degree of each component in the conjugated phase, it was calculated an "efficiency factor" (e) considering the ΔCp's phases -i.e. $w_{ABS}$ and $w_{PC}$-:

$$e_{ABS} = \frac{w'_{ABS} * w_{PC}}{\left(w'_{ABS} * w_{PC}\right) + \left[\left(1 - w''_{PC}\right) * w_{ABS}\right]} * 100 \qquad \text{(Eq. 3)}$$

The interphase composition is not constant but depends on the ratio of components in blend (Table 2). In all series, the apparent solubility of ABS (actually of the SAN phase) in the PC-rich phase increase with decreasing volume fraction of PC in blends reaching a maximum at 10 %-wt of ABS.

The existence of the conjugated phases and its interaction could be justified, in a first sight, considering the difference between the parent's polymers solubility parameters ($\delta_{PC}$ and $\delta_{ABS}$). As is well known, when dealing with amorphous polymers, one component will be soluble in other one when the difference between its δ's is lower than 2 (8). Estimating the $\delta_s$ for the ABS employed it was found a value of 21.2 MPa$^{1/2}$ against 19.4 MPa$^{1/2}$ for PC giving a difference of 1.8. The higher ABS solubility in the PC phase could be attributed to the major probability of interactions that present the former due to its higher active sites proportion (9).

Those observations seem to be correct when the molecular weight of the involved systems are low. For higher molecular weight, the Flory-Huggins interaction energies (B) estimated from the solubility parameters seems to be overestimated as was demonstrated by Callaghan et al. on PC/SAN blends, where a critical molecular weight analysis was applied (4). Thus, extrapolating the Callaghan et al. results to the PC/ABS system, the oligomer (from PC and ABS) partitioning between the phases generated during the mixing seems to have great influence on their Tg shifting.

As those authors reported, using the interaction energies determined by the critical molecular weight analysis, the maximum predicted Tg shift in the PC-rich phase was of about 1.6 °C while for the SAN-rich phase was only 0.15°C. By the other side, when the interaction energies reported by Kim and Paul were used, maximum shifts of 11 °C and 3 °C were predicted for the PC- and SAN-rich phases, respectively.

Comparing those predictions with the values obtained in the present work, it can be seen that shift of 17 °C and 13 °C for the PC- and ABS-rich phases are observed. Thus, we think that those oligomers could act as "binders" between the phases, promoting higher level of interaction.

**Table 2. Calorimetric properties, interphase composition and "ABS participation effectiveness degree on the PC-rich phase" ($e_{ABS}$) of the analysed blends.**

| Blend | Tg' (°C) | Tg" (°C) | $\Delta C_p'$ (J/g.°C) | $\Delta C_p''$ (J/g.°C) | $w'_{ABS}$ | $w''_{PC}$ | $v'_{ABS}$ | $v''_{PC}$ | $e_{ABS}$ (%) |
|---|---|---|---|---|---|---|---|---|---|
| PC | 144.3 | ---- | 0.2778 | ---- | ---- | ---- | ---- | ---- | ---- |
| PC-5 | 142.3 | 113.2 | 0.2608 | 0.0127 | 0.0399 | 0.3220 | 0.0461 | 0.2789 | 54.4 |
| PC-10 | 140.4 | 110.9 | 0.2625 | 0.0223 | 0.0788 | 0.2667 | 0.0910 | 0.2309 | 55.7 |
| PC-15 | 137.5 | 109.3 | 0.2432 | 0.0401 | 0.1388 | 0.2300 | 0.1603 | 0.1992 | 52.1 |
| PC-20 | 135.5 | 108.4 | 0.2035 | 0.0493 | 0.1820 | 0.2076 | 0.2100 | 0.1780 | 48.7 |
| PC-40 | 127.0 | 105.0 | 0.1629 | 0.0878 | 0.3652 | 0.1248 | 0.4218 | 0.1081 | 43.6 |
| ABS | ---- | 100.0 | ---- | 0.2840 | ---- | ---- | ---- | ---- | ---- |

*Tensile properties (interfacial adhesion):*

It is well known that this kind of interaction in polymers blends report an enhancement of the interfacial interaction between the conjugated phases. The interfacial adhesion and its dependence on blend composition can be evaluated studying the yield stress ($\sigma_y$) and compared with theoretical predictions based on different assumptions as far as the interfacial adhesion is concerned.

The simplest one is the “Rule of Mixtures” (Eq. 4) which assumes a strong enough interfacial adhesion to ensure the stress transfer between the phases and that both phases are submitted to the same deformation conditions, thus, the system responses will be determined by each phase volumetric proportion (8).

$$\sigma_{yb} = \sigma_{yPC}\left(1 - v_{ABS}\right) + \sigma_{yABS} v_{ABS} \qquad \text{(Eq. 4)}$$

Figure 2 shows the experimental data (Table 3) fitting to the model. It seems to be valid for low ABS contents, with a positive deviation (that increase at higher strain rate) from 15 %-wt of ABS and forward.

It must be kept in mind the modifications on interphase’s composition and geometry with the second phase proportion added as a consequence of the intensive mixing process.

**Table 3. Yield Stress ($\sigma_y$) values at 1 and 500 mm/min obtained from tensile tests.**

| Blend | $\sigma_y$ (MPa) 1 mm/min | $\sigma_y$ (MPa) 500 mm/min |
|---|---|---|
| PC | 57.5 ± 0.3 | 64.4 ± 0.3 |
| PC-5 | 55.6 ± 0.1 | 63.1 ± 0.1 |
| PC-10 | 55.2 ± 0.2 | 62.4 ± 0.4 |
| PC-15 | 54.9 ± 0.1 | 63.1 ± 0.1 |
| PC-20 | 52.4 ± 0.2 | 60.4 ± 0.2 |
| PC-40 | 49.6 ± 0.1 | 58.2 ± 0.4 |
| ABS | 34.2 ± 0.1 | 41.8 ± 0.2 |

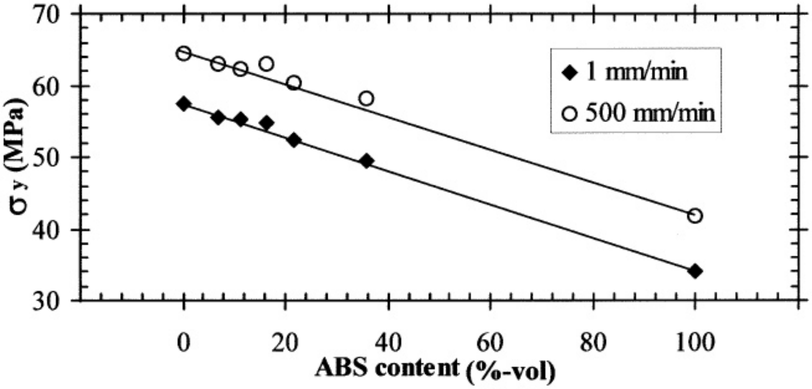

Figure 2. $\sigma_y$ variation with blend composition. Solid line represents the Rule of Mixture.

Making a SEM analysis of cryogenic fracture surfaces from the prismatic bars, a morphologic gradient dependent on blend composition was observed (10). It was characterised by a central region of dispersed spherical domains (relatively uniform) and a “superficial” layer with elongated domains like a “bead-string” structure oriented with the melt’s flow direction at the moulding cavity. This situation was so evident for PC-15 and PC-20 systems (Figures 3a and 3b).

For PC-40 system stratified and coarsened domains constituted the morphology gradient with different orientation degrees along the specimen cross section. Figures 3c and 3d show the morphology situation for this composition at two sites located at different distance from the specimen surface, in the flow direction on the moulding cavity.

These morphologic modifications result in important variations in the mechanical behaviour of the interphase affecting the stress transmission effectiveness between the phases. Adding a second phase reduce the load bearing cross-section of the matrix in a specimen thus the role of an optimal interfacial adhesion reach importance.

Pukànsky et al. (11) have proposed a model that consider, in a quantitative way, the effect of the interfacial interaction between the second phase particles and the matrix and its dependence on second phase proportion ($v_{ABS}$).

$$\sigma_{yb} = \sigma_{yPC}\left[(1 - v_{ABS})/(1 + 2{,}5v_{ABS})\right]\exp[\beta v_{ABS}] \qquad \text{(Eq. 5)}$$

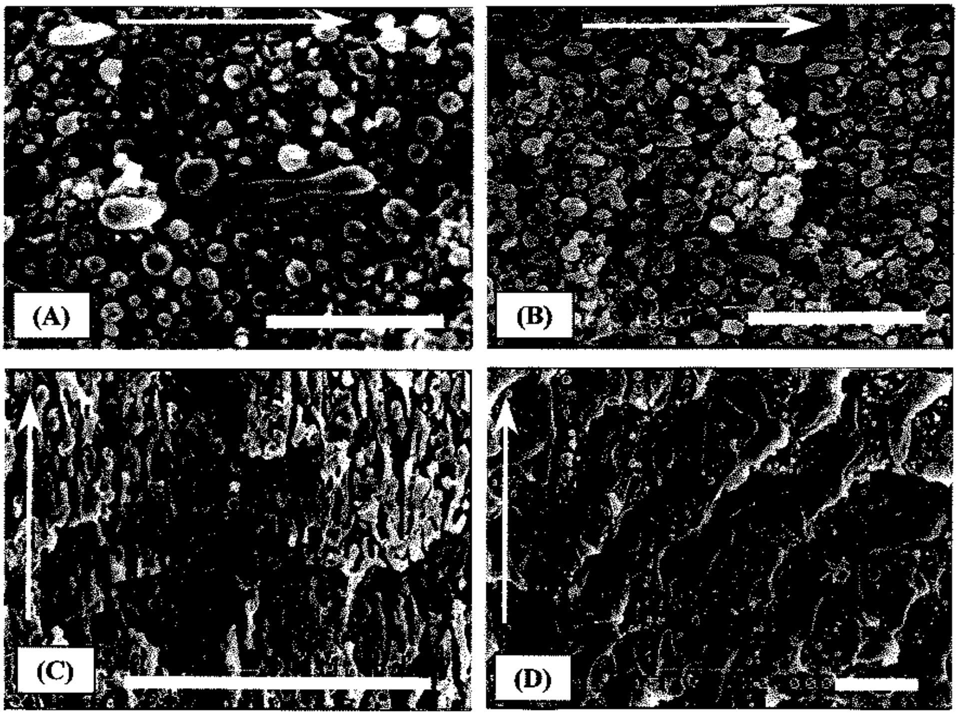

Figure 3.- SEM Micrographs of the cryogenic fracture surface parallel to flow direction at 0,3 mm from the edge for (A) PC-15 at 2 mm; (B) PC-20 at 2 mm; (C) PC-40 at 2 mm and (D) PC-40 at 0,5 mm, from the surface in contact with the moulding cavity. Flow direction indicated by the arrow. Scales bars: 10 μm

β is related to the relative capacity of the components to transfer the load and seems to vary with the thickness (i) and strength ($\sigma_{yi}$) of the interphase (12):

$$\beta = (1 + A_{ABS}\rho_{ABS} i) Ln(\sigma_i / \sigma_{yb}) \qquad \text{(Eq. 6)}$$

where $A_{ABS}$ and $\rho_{ABS}$ are the ABS phase specific cross section area and ABS density, respectively; $\sigma_b$ the blend's yield stress.

Figure 4 shows the experimental data's fitting to this model for two strain rates. It seems that the model predicts the behaviour until 15 %-wt (16,1 %-vol), from here an slope decrease is obtained, that could indicate important variations in the interphase geometry characteristics –i.e. decrease on AABS as a consequence of the greater size of phase- magnified by higher morphologic gradient. The increase on β-factor value with the strain rate applied could reflect an increase of the interphase strength as a consequence or its viscoelastic nature.

## Conclusion

The PC/ABS blends seem to show "partial miscibility" almost for the composition range and raw materials employed in this study. This behaviour can be attributed to the oligomers partitioning between the phases, phenomenon that was set for this kind of system.

It seems that ABS has a higher interaction and intermixing effectiveness on the interphase generated than PC, reaching a maximum at 10 %-wt of this component in the blend.

As the tensile tests results indicate, partial miscibility of the components seems account for interfacial adhesion sufficient strong to ensure stress transfer between phases in the course of plastic deformation (i.e. yielding), almost for lower ABS contents on the blend. From 15 %-wt of ABS and forward, morphological effects in the stress transfer between the phases reach importance, and could be explained by the increase on the specific cross section area of the second phase magnified by the morphologic gradient that the blends showed.

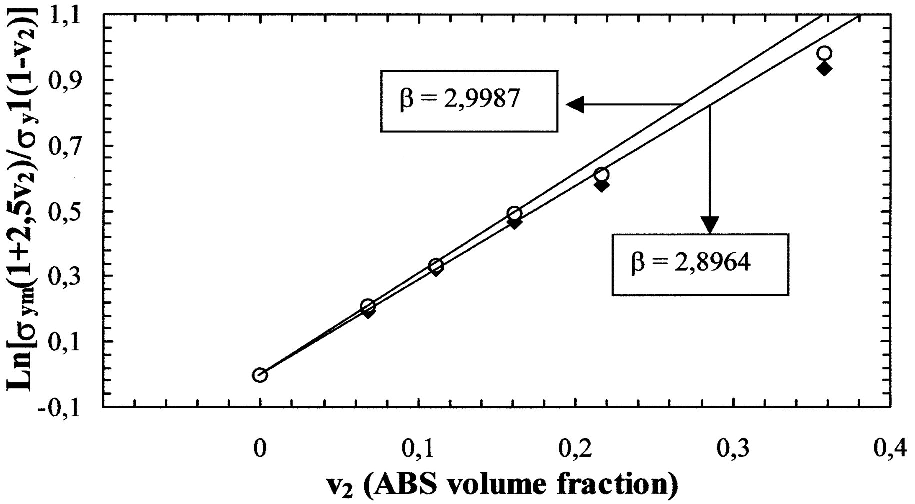

Figure 4.- Experimental data fitting to Puckánszky's model.

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