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# Polyarylate/polyamide 6 blends: A calorimetric study

**J. I. Eguiazábal and J. J. Iruin***

Departamento de Ciencia y Tecnología de Polímeros, Facultad de Ciencias Químicas,
P.O. Box 1072, San Sebastian, Spain

## Summary

A calorimetric study has been done of the miscibility of blends composed of polyarylate (PAr) and poly(ε–caprolactam) (polyamide 6, nylon 6). The thermal transitions of blends subjected to two different thermal treatments have been determined. Two glass transitions have been observed in the blends irrespective of the thermal history. These glass transitions indicate the existence of two amorphous phases in the blends, a practically pure nylon phase and a mixed PAr/nylon 6 phase. The variation of the melting temperature of nylon with the blend composition is in good agreement with the existence of phase separation in the blends. However, the melting heat shows a slightly positive deviation from linearity when it is represented against the blend composition.

## Introduction

Blending polymers is a good way for the obtention of new polymeric materials. This type of mixed materials provides the possibility of combining the useful properties of the components in order to obtain the desired properties in the blends.

Between the different polymeric materials which can be used as blend components, those which are called "engineering polymers" are of great importance, because of the good properties of these polymers. Blending different engineering polymers is thus an interesting field of research. Engineering polymers include polyesters as poly(ethylene terephthalate), poly(butylene terephthalate) and polyarylates; polycarbonates and also the different polyamides or nylon polymers (1).

Blends composed of a crystalline polymer and an amorphous one are an important type of polymer blends. In this case, blending provides the possibility of regulate the degree of crystallinity and the crystalline morphology of the crystallizable component, and hence the properties of the blends.

Poly(ε-caprolactam), nylon 6, is a readily crystallizable polymer whose blends with other polymers have been studied in the literature. Among the second components of the blends, other polyamides, polyolefines, rubbers and different types of copolymers have been the subject of a number of research works. Nylon 6 has been also mixed with poly(ethylene terephthalate) (2), poly(ether-esters) (3) and bisphenol A polycarbonate (4-9). The blends have been studied from different points of view, including miscibility, interchange reactions, mechanical properties, etc.

In this work, we have studied the miscibility of blends composed of an amorphous polymer very similar to polycarbonate, the polyarylate obtained from bisphenol A and 50/50 isophthalic/terephthalic acids (PAr), and poly(ε-caprolactam). The effect of the blend composition and of the thermal treatment on the different thermal transitions of the blends has been studied by Differential Scanning Calorimetry (DSC).

## Experimental

The polymers used in this work were commercial products. Polyarylate (Arilef U-100) was

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*To whom offprint requests should be sent kindly supplied by Solvay. Its average molecular weights were determined by GPC in THF. They are $M_w$=51,400 and $M_n$=21,500. Poly($\varepsilon$-caprolactam) was Duretan B-30S from BASF. The molecular weight of this polymer was $M_v$=29,000, determined at 25°C in aqueous formic acid (85%).

The PAr/nylon 6 blends were prepared by solution/precipitation in hot phenol/methanol, as has been reported in other previous works (10-11). These blends were dried in vacuo at 100°C for five days before calorimetric analysis.

DSC measurements were performed with a DuPont DSC cell equipped with a DuPont 2000 Thermal Analyst System. A heating rate of 20°C/min was used, and a nitrogen flow was maintained through the DSC cell. The temperature and the enthalpy were calibrated with reference to indium and tin standards.

The DSC scans on PAr/nylon 6 blends were carried out after two different thermal treatments. In the first case, the samples were quickly heated from room temperature to 250°C in a hot stage. After that, they were maintained at 250°C for five minutes to allow the melting of nylon 6 and finally quenched in liquid nitrogen. These quenched samples were then heated in the calorimeter from 0°C to 250°C. In this scan, the different thermal transitions were determined.

In the second case, the samples were rapidly heated to 250°C in the calorimeter, maintained at that temperature for five minutes and slowly cooled to 0°C. The calorimetric scan to determine the thermal transitions was carried out from 0°C to 250°C as in the first treatment. The different parameters related to the thermal transitions (glass transition temperature, $T_g$; crystallization temperature, $T_c$; crystallization heat, $\Delta H_c$; melting temperature, $T_m$ and melting heat, $\Delta H_m$) were determined in the usual way.

## Results and Discussion

As we have mentioned in the Experimental section, we have studied quenched and slowly cooled PAr/nylon 6 blends.

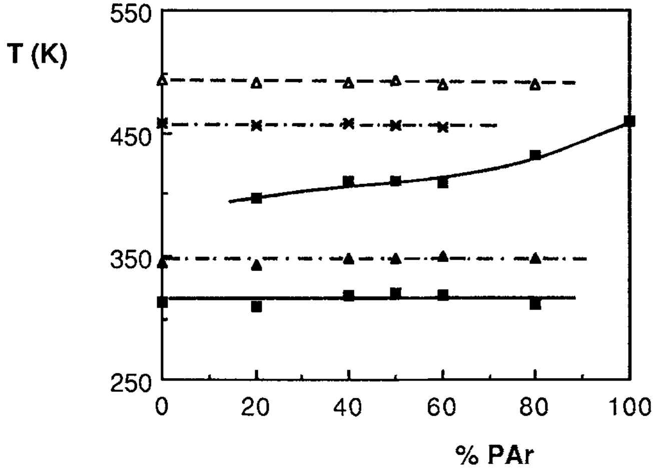

**Figure 1.-** Thermal transitions of quenched PAr/nylon 6 blends. (■): glass transition temperature, (▲): crystallization temperature, (✱): minimum of the premelting exotherm, (△): melting temperature.

In Figure 1, we show the different thermal transitions of quenched blends. As it is observed, two glass transitions are observed in all compositions. The lower transition corresponds to an amorphous phase which should be composed of practically pure nylon irrespective of the overall blend composition, given the $T_g$ values for such phase, very similar to that obtained for the pure polymer. The small differences observed may be attributed to the error inherent to the determination of $T_g$, which is more important in the case of semicrystalline polymers. The second $T_g$, which appears at higher temperatures, shows a clear variation with the blend composition. This $T_g$ decreases as the nylon content in the blend increases. This indicates that a second amorphous phase is present in the blends. This phase is composed of polyarylate and nylon, and has a higher content of the first polymer. Given the variation observed in the $T_g$-composition relationship, it appears that the PAr-rich phase absorbs more nylon when the overall content of this polymer in the blends increases.

The above explained calorimetric results indicate a partial miscibility of the PAr/nylon 6 system, a result which is very similar to that obtained in PC/nylon 6 blends (5). Other authors (7, 8) have interpreted the $T_g$-composition relationship in PC/nylon 6 blends on the basis of PC degradation during melt mixing. The blending method used in this work should avoid decomposition reactions, so that the results obtained for PAr/nylon 6 blends may be clearly due to partial miscibility.

From the $T_g$ values obtained for the two amorphous phases, we may calculate their composition assuming that the Fox equation (12) reproduces the $T_g$-composition relationship for this blend. Other $T_g$-composition equations cannot be used because of the need of adjustable parameters or additional parameters related to the glass transition, such as the heat-capacity increase at $T_g$. Thus, the Fox equation:

$$1/T_g = w_{ny}/T_{g,ny} + (1-w_{ny})/T_{g,PAr}$$

may be rearranged:

$$w_{ny} = (T_{g,ny}(T_{g,PAr} - T_g))/(T_g(T_{g,PAr} - T_{g,ny}))$$

where $T_g$ is the measured glass transition temperature, $T_{g,ny}$ and $T_{g,PAr}$ are the glass transition temperatures for pure nylon 6 and polyarylate respectively and $w_{ny}$ the weight fraction of nylon in the phase with glass transition temperature $T_g$. This equation has not been applied to the nylon-rich phase due to the problems mentioned above with respect to the errors inherent to $T_g$ measurements. Another reason is that the PAr content in the nylon-rich phase should be very small in all cases, as judged by the very small variation of $T_g$ with respect to that of pure nylon.

In Table 1 we show the weight fractions of nylon 6 in the PAr-rich phase of quenched blends for the different overall compositions.

TABLE 1

Weight fraction of nylon 6 in the PAr-rich phase of quenched PAr/nylon 6 blends

| Composition (PAr/nylon 6) | $T_g$ | $w_{ny}$ in the PAr-rich phase |
|---|---|---|
| 100/0 | 463 | 0 |
| 80/20 | 432 | 0.15 |
| 60/40 | 409 | 0.28 |
| 50/50 | 412 | 0.26 |
| 40/60 | 412 | 0.26 |
| 20/80 | 398 | 0.34 |

As expected from the $T_g$ values, the nylon content increases in the PAr-rich phase as the overall nylon content in the blends increases. The maximum solubility of nylon in PAr approaches 35%.

After the lower $T_g$, the calorimetric scans on quenched samples show a crystallization exotherm, which $T_c$ value is shown in Figure 1 as a function of composition. As it is observed, these $T_c$ values are practically independent of the blend composition. This could be expected taking into account the constancy of the low $T_g$ with the blend composition, and indicates that nylon 6 crystallizes from the almost pure nylon phase.

The heat of crystallization depends on the blend composition, as is observed in Figure 2. Values higher than those corresponding to the linear extrapolation between the values of the pure components are obtained in all compositions except for high PAr contents. From these $\Delta H_c$ values, it may be concluded that PAr affects the crystallization of nylon 6 and favours it. We think that this may be due to a nucleating effect of polyarylate during crystallization. On the other hand, the heat of crystallization is lower than the heat of melting, indicating that a fraction of nylon 6 crystallizes during quenching.

The melting behaviour of quenched PAr/nylon 6 blends as well as that of the pure crystalline polymer are somewhat complicated as we shall see.

In all compositions, except the 80/20 PAr/nylon 6, a very small exothermic peak is observed before the melting endotherm. The position of the minimum of this exotherm is practically independent of the blend composition as is shown in Figure 1, whereas the heat related with the exotherm is very small in all compositions and undergoes a slight variation with the blend composition (Figure 2). The exothermic peak seems to be indicative of the existence of reorganization processes in the crystalline phase of nylon 6 during the DSC scans. The existence of these reorganization processes in nylon 6 has been mentioned in the literature (13). On the other hand, exothermic peaks similar to those observed in this work seem to be present in PC/nylon 6 blends studied by Gattiglia et al. (7), although the authors do not comment about these exotherms. The observation that no exotherms are present in PAr/nylon 6 (80/20) blends may be attributed to the fact that at so high PAr concentration, this polymer makes difficult the reorganization processes.

The melting temperatures of quenched PAr/nylon 6 blends decrease slightly with the increase of the PAr content in the blend. This decrease should be due to morphological effects, as thermodynamical effects should be practically inexistent as a consequence of the phase separation which has been already commented.

Finally, the melting heats of nylon 6, as measured with respect to the overall blend mass, generally show a positive deviation with respect to the linear relation corresponding to the additivity between the values of the pure components, as it is observed in Figure 2. This result is similar to that obtained in other partially miscible blends composed of polyarylate and poly(ethylene terephthalate) (14) and may be explained on the basis of the already mentioned nucleating effect of polyarylate in accord with the explanation given by Porter et al. (15).

The second set of PAr/nylon 6 samples was studied after melting the blends 5 minutes at 250°C and slow cooling from the melt, in order to allow the nylon crystallization and to study the effect of crystallization on the phase behaviour of the blends. In Figure 3 we show the thermal transitions obtained for these slowly-crystallized samples.

As it is seen, two glass transitions are observed once again for the blends. The lower glass transition is somewhat higher for these blends than for quenched ones, possibly due to the higher crystallinity of nylon after slow cooling. This higher crystallinity restricts the molecular motion. The lower $T_g$ seems to increase slightly when the overall PAr content in the blend increases, although this increase cannot be considered as representative, due to the difficulties in adequately drawing the $T_g$'s because of the nylon crystallinity. This may be also the reason why the lower glass transition is not observed in the PAr/nylon 6 (60/40) and (80/20) compositions. In consequence it cannot be clearly concluded whether the slight increase observed in the $T_g$ of the nylon-rich phase is a consequence of an increase of the PAr content in this phase.

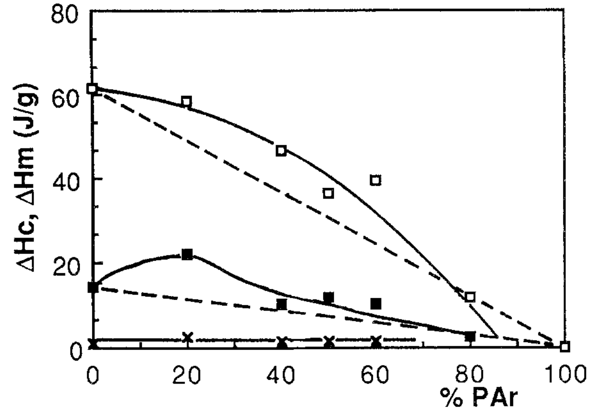

**Figure 2.**- Crystallization and melting heats of quenched PAr/nylon 6 blends. ( ■ ): crystallization heat, (□): melting heat, (×): heat related with the premelting exotherm.

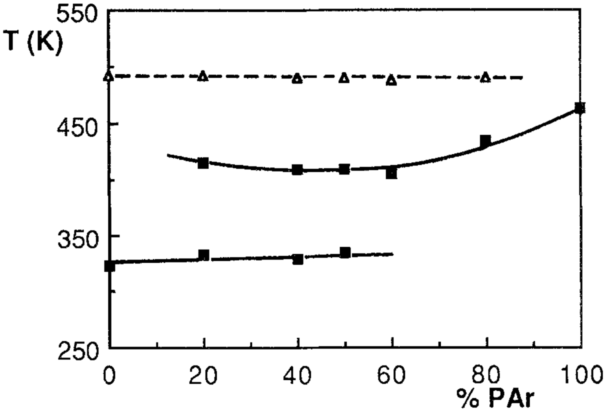

**Figure 3.**- Thermal transitions of slowly cooled PAr/nylon 6 blends. (■): glass transition temperature, (▲): melting temperature.

As far as the second glass transition of the blends is concerned, it appears at temperatures very similar to those found in the quenched blends, except in the PAr/nylon 6 (20/80) blend. For this composition, a higher $T_g$ value is obtained in the case of slowly cooled samples. The observed behaviour for the high $T_g$-composition relationship indicates that the nylon crystallization does not affect the composition of the PAr-rich phase, except at high nylon content. If the nylon content of the PAr-rich phase is calculated from the Fox equation, as above, the results reported in Table 2 are obtained.

As expected from the $T_g$ values, quenched and slowly cooled blends, except for the PAr/nylon 6 (20/80) composition, show approximately the same nylon content in the PAr-rich phase. In the overall composition mentioned, and during slow cooling, nylon is able to crystallize from the PAr-rich phase, and the content of this crystallizable polymer decreases as indicated by the experimental $T_g$ values.

TABLE 2

Weight fraction of nylon 6 in the PAr-rich phase of slowly cooled PAr/nylon 6 blends

| Composition (PAr/nylon 6) | $T_g$ | $w_{ny}$ in the PAr-rich phase |
|---|---|---|
| 100/0 | 463 | 0 |
| 80/20 | 435 | 0.14 |
| 60/40 | 406 | 0.30 |
| 50/50 | 409 | 0.28 |
| 40/60 | 409 | 0.28 |
| 20/80 | 416 | 0.24 |

Slowly cooled PAr/nylon 6 blends do not show any crystallization peak, giving an indication of a complete nylon crystallization during cooling.

Finally, the melting behaviour of these slowly cooled blends is somewhat different from that of the quenched samples. In slowly cooled samples no exotherms are observed before the melting endotherm, seeming to indicate that the crystals obtained during slow cooling are more perfect than those obtained in quenched samples, and thus reorganization is not observed during the calorimetric scan. However, the melting points of nylon are practically identical in both quenched and slowly cooled blends, indicating that similar crystalline perfection is finally obtained irrespective of the thermal treatment applied.

The melting heats of nylon in the slowly cooled blends, which are showed in Figure 4, follow a very similar trend to that observed in the quenched ones. Once again, a positive deviation from linearity is observed, indicating the positive effect of polyarylate in the nylon crystallization.

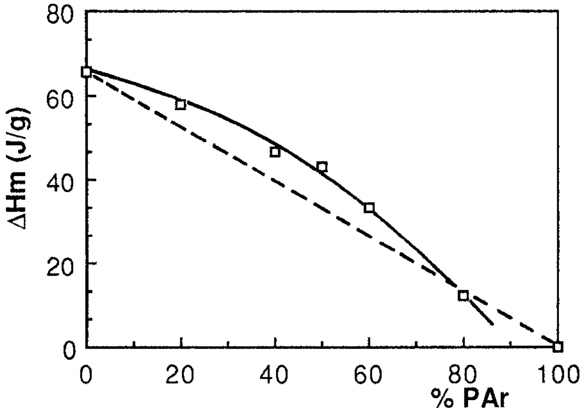

**Figure 4.-** Melting heat of slowly cooled PAr/nylon 6 blends.

## Conclusions

PAr/nylon 6 blends are partially miscible. The blends are separated in two amorphous phases, one of them composed of practically pure nylon 6 and the other composed of a mixture of PAr as major component and nylon 6. This phase absorbs more nylon as the overall content of this polymer in the blends increases.

The composition of both phases of the blends is practically unaffected by the thermal treatment, except at the higher nylon contents. In this case, the nylon crystallization during slow cooling causes a decrease of the nylon content in the PAr-rich phase.

From the melting behaviour of quenched and slowly cooled blends, it may be concluded that PAr favours the nylon crystallization from the blends. On the other hand, some different melting behaviours are observed depending on the thermal treatment applied to the blends.

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