Miscibility of Poly(ether imide) and Poly(ethylene terephthalate)

INTRODUCTION

Polymer blends containing engineering polymers are an attractive route for the development of new polymeric materials with good performance characteristics. Poly(ether imide) (PEI) is a thermally resistant engineering polymer that has received much attention for several years due to its good combination of properties. Blends of PEI with polymers containing carbonyl groups in the main chain, such as poly(ether ketones),[1,2] bisphenol A polycarbonate,[3] and polyarylate[4,5] have been studied recently. In these studies, a good level of properties in the blends has been observed. Thus, it is of great interest to study other blends containing PEI and other polymers with carbonyl groups in the main chain.

One of the possible partners for blending is poly(ethylene terephthalate) (PET). In the case of the PEI/PET blends and with respect to PET-rich blends, for instance, the presence of PEI should both decrease the crystallization ability of PET and also increase its glass transition temperature if the polymers are miscible. Both of these effects are positive in some of the applications of PET, such as bottle production, because they give rise to increased "melt strength" and also reduce crystallization tendency. These are the reasons why in this work we report preliminary calorimetric results concerning the miscibility of blends composed of PEI and PET.

EXPERIMENTAL

The PEI used in this work was Ultem 1000 (General Electric Plastics) and was supplied by Novoquimia S. A., Barcelona, Spain. It has a relative viscosity of 0.5 dL/g as measured at 0.2% and 25°C in chloroform.[1] PET was supplied by Brilen S. A., Barbastro, Spain, and had a molecular weight of $M_n = 25,000$, determined by viscometry in o-chlorophenol at 35°C. PEI/PET blends in the whole compositional range were prepared by melt mixing in a Brabender Plasticorder at 300°C and at a mixing blade speed of 30 rpm. The blends were compression-molded at 300°C and quenched in a water/ice mixture to obtain the lowest possible crystallinity level. To analyze the possible influence of degradation of PET during processing on the results obtained, some compositions were also prepared by a solution/precipitation process in phenol/methanol.

Calorimetric analysis was carried out with a DuPont DSC cell equipped with a DuPont 2000 Thermal Analysis System. The heating rate was 20°C/min and a nitrogen flow was maintained through the sample and reference chambers. The enthalpy and the temperature were calibrated with reference to an indium standard. The thermal transitions (glass transition temperature, T_g, crystallization temperature, T_c, and melting temperature, T_m) were determined in the usual way. In the case of the solution-mixed samples, the calorimetric scans were performed after heating of the samples in the calorimeter up to 300°C followed by rapid cooling to room temperature.

RESULTS AND DISCUSSION

The PEI/PET blends quenched from the melt state showed, during the DSC scan, a single glass transition. Figure 1 shows the T_g values determined at the onset of the transitions, as well as T_c and T_m values, all of them as a function of the blend composition. As can be seen, the single T_g values increase monotonically as the PEI content in the blends increases. These results indicate the miscibility of the PEI/PET blends.

Although from these T_g results blend miscibility exists, some heterogeneity seems to appear if we study the variation of the width of the glass transition with the blend composition (Fig. 2). As can be seen, in all cases, the glass transition is wider for the blends than for the pure components. The maximum width is found for the 50/50 composition. This indicates, in agreement with results obtained in other studies,[6] that some heterogeneity exists in the blends and that it is a maximum at intermediate compositions.

With respect to the crystallization behavior, PEI/PET blends, with PET contents equal to or higher than 50%, show, after the glass transition, a crystallization exotherm, whose crystallization temperature is shown in Figure 1 as a function of blend composition.

As the PEI content in the blend increases, the width of the exotherm increases, and at the same time, the T_c, measured at the minimum of the exotherm, increases. This indicates that PEI hinders the crystallization of PET from the glassy state, as could be expected taking into account the miscibility of the blend. This effect is also shown in
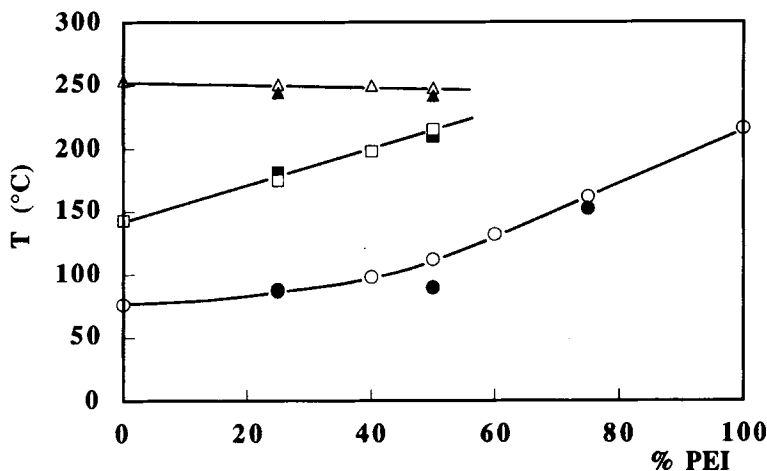
Figure 1 Thermal transitions of PEI/PET blends: (●) T_g; (■) T_c; (▲) T_m. Open symbols: melt-mixed blends. Solid symbols: solution-mixed blends.

Figure 3, in which the crystallization heats of the blends appear to be generally lower than the linear extrapolation between the values of the neat blend components. This indicates once again the difficulties for the PET crystallization during the scan due to the presence of PEI. At PEI contents higher than 50%, no crystallization exotherms appear, indicating that PET is unable to crystallize during the scan.

Finally, calorimetric scans carried out on blends with PET contents equal to or higher than 50% show a melting endotherm of PET. The temperature at the maximum of the endotherm decreases as the PEI content increases, as observed in Figure 1. Although morphological effects also may influence the melting point decrease, this is another indication of the miscibility of the PEI/PET system, as the decrease of the T_m of a crystallizable polymer in polymer blends is attributed generally to the thermodynamic interaction between the components.[7]

The calorimetric results obtained from the solution-mixed samples after quenching were practically identical to those obtained for the melt-mixed samples, as can be observed in Figures 1–3. The small differences observed may be attributed to the somewhat different thermal treatments applied to both types of samples. This similarity in the calorimetric results indicates that the possible degradation of PET during melt mixing does not affect the observed miscibility of the blends.

The interaction parameter between PET and PEI has been estimated in a first approximation, neglecting the morphological effects, by means of the equation proposed by Nishi and Wang[8]:

$$1/T_m - 1/T_m^0 = (RV_{2u})/(\Delta H_m V_{1u}) \, \phi_1^2 \chi_{12}$$

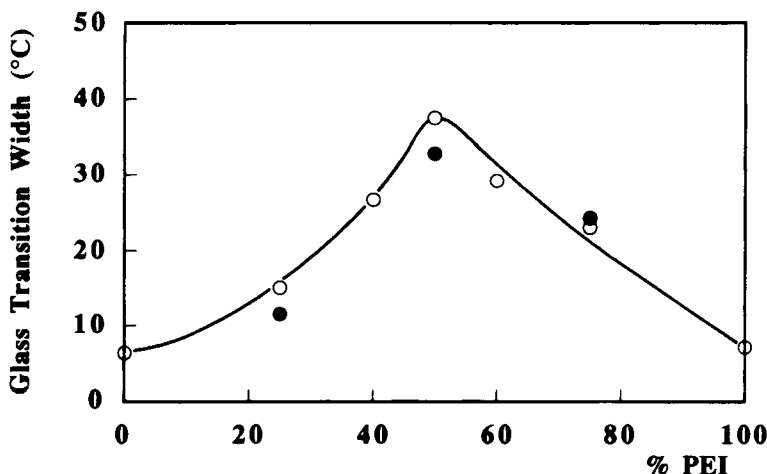where T_m^0 is the melting temperature of the pure crystal-

Figure 2 Glass transition width of melt-mixed (○) and solution-mixed (●) PEI/PET blends.
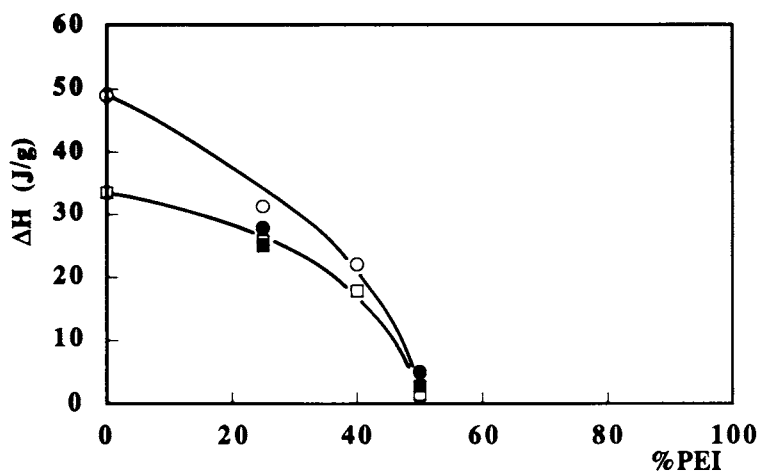
Figure 3   Crystallization (■) and melting (●) heats of PEI/PET blends. Open symbols: melt-mixed blends. Solid symbols: solution-mixed blends.

line polymer and T_m, the melting temperature of this polymer in the blend; R, the gas constant; V_{1u} and V_{2u}, the molar volumes of the repeating units of the amorphous and crystalline polymers, respectively; ϕ_1, the volume fraction of the amorphous polymer in the blend; and ΔH_m, the enthalpy of fusion per mole of repeating units. χ_{12} is the interaction parameter.

From the slope of the plot of $(1/T_m - 1/T_m^0)$ vs. ϕ_1^2, and using $V_{1u} = 475.3$ cm^3/mol, $V_{2u} = 160.8$ cm^3/mol and $\Delta H_m = 26.9$ KJ/mol,[9] a value of $\chi_{12} = -0.66$ is obtained. This negative value is in good agreement with the observed miscibility of the blends.

In Figure 3, we also show the variation of the melting heat of PET with the blend composition. A clear decrease is observed for ΔH_m when the PEI content in the blends increases and, moreover, the ΔH_m values are in all cases lower than expected on the basis of a linear relationship between the values of the pure components. These observations indicate, in good agreement with previous results in this work, the hindrance of PET crystallization imposed by PEI.

Another interesting observation is that the melting heat is, in all compositions, higher than the crystallization heat of PET. This indicates that some PET crystallizes during cooling after the molding process. The difference $\Delta H_m - \Delta H_c$ is smaller the higher is the PEI content; this indicates that the PET fraction, which undergoes crystallization during cooling, is also smaller. This provides additional evidence of the difficulties for PET crystallization imposed by PEI.

The results reported in this work show the miscibility of blends composed of PEI and PET and the strong influence that the PEI presence has on the crystallization-melting characteristics of PET in the blend. The properties of these blends, which may be of practical interest, are being studied at the present time.

Basque Government for the award of a grant for the development of this work.

References

1. J. E. Harris and L. M. Robeson, *J. Appl. Polym. Sci.*, **35**, 1877 (1988).
2. M. Amano, Y. Goto, T. Takahashi, and T. Tsutsumi, Jpn. Kokai Tokyo Koho JP01, 188,555 (89,188,55) (1989).
3. E. N. Peters and J. A. Rock, Eur. Pat. Appl. EP 325,719 (1989).
4. L. M. Robeson, M. Matzner, and L. M. Maresca, U.S. Pat. 4,250,279 (1981).
5. F. F. Holub and W. R. Schlich, U.S. Pat. 4,908,419 (1990).
6. J. R. Fried, F. E. Karasz, and W. J. MacKnight, *Macromolecules*, **11**, 150 (1978).
7. B. S. Morra and R. S. Stein, *J. Polym. Sci. Polym. Phys. Ed.*, **20**, 2243 (1982).
8. T. Nishi and T. T. Wang, *Macromolecules*, **8**, 909 (1975).
9. J. Brandrup and H. Immergut, Eds., *Polymer Handbook*, Wiley, New York, 1989.

J. M. Martínez
J. I. Eguiazábal
J. Nazábal
Dpto. de Ciencia y Tecnología de Polímeros
Facultad de Química, UPV/EHU
P.O. Box 1072
San Sebastian, Spain