STUDY OF PMMA/PNVK BLENDS BY DTA

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ABSTRACT

The glass transition temperature, T_G, of different PMMA/PNVK blends has been measured by DTA. The influence of molecular weight, keeping the ratio of both molecular weights approximately constant has been also evaluated.

It has been found that PMMA and PNVK are not miscible polymers, except in the outline of the composition range.

The C_P–blend composition plot seems to be a very good way to prove the existence of miscibility in the system.

INTRODUCTION

Nowadays, the study of polymer blends has experienced an unexpected development due to recent advances in the thermodynamic theory [1] and to the commercialization of new miscible polymer blends unknown so far.

This new field of polymer science presents a great interest for the polymer researcher and the Industry. For the former, because it is such a new field that it offers a lot of possibilities for empirical and theoretical investigation. For the latter, because polymer blends have important commercial properties, the most important one being their versatility: with a specific miscible polymer blend, the number of possible variations of the usual polymer properties is as large as the number of possible changes in the composition of the system.

In general terms, we can consider a blend as miscible if it has similar properties to those expected for a material which shows only one phase. The most frequently used macroscopic property for the determination of the behaviour of a polymer blend is the glass transition temperature, T_G, that is, the temperature for which characteristic properties of a material, such as, the thermal expansion coefficient, specific volume, refractive index, compressibility, calorific capacity, etc., experience a sharp change. We shall say, then, that a blend is miscible if it presents only one T_G and immiscible if it shows two values, corresponding to each polymer.

This criterion, though used often [2–4], is not accepted as universally valid due to the existence of certain microscopic questions for which there are no answers. The basic question is which molecular blend is required in a miscible blend to produce only one T_G value. Although a lot of studies have tried to answer this question [5–10], the solution of this problem is complex, especially so when the experimental results obtained from electronic microscopy [11] and small-angle neutron scattering [12] are different. Meanwhile, this debate continues: the glass transition behaviour of a blend is a characteristic of a system which can be used to evaluate, qualitatively, miscibility levels.

In this paper, we present the experimental results obtained in the study of the polymer blend: poly(methyl methacrylate)/poly(N-vinyl carbazole) (PMMA/PNVK). We have used as a criterion the formerly described glass transition temperature and, as an experimental method, differential thermal analysis (DTA).

EXPERIMENTAL

The PMMA samples used (S10275 and PMMA 9 of $\overline{M}_w = 150\,000$ and 7100 g mol^{-1}, respectively) were available in our laboratory. Poly(N-vinyl carbazole) was synthesized by free radical polymerization, fractionated by solubility and characterized by laser light scattering and liquid chromatography (GPC). We obtained seven fractions from which we used those of $\overline{M}_w = 140\,000$ and 10 000 g mol^{-1} (PNVK2 and PNVK7, respectively).

Polymer blends were prepared by dissolving the required quantities of both polymers in benzene and allowing the solvent to evaporate at room temperature. This process produces a polymer film of small thickness. These polymer films are later introduced into the aluminium crucibles used in differential calorimetry.

In this way, we have prepared two systems:
  (i) System A: PMMA (S10275)/PNVK (PNVK2);
  (ii) System B: PMMA (PMMA 9)/PNVK (PNVK7),
in order to show the influence of molecular weight in the miscibility level of the polymer blends.

The glass transition temperature, T_G, has been determined using a Mettler TA 2000 differential thermal analyser. Formerly, for the realization of any measurement, we calibrated the DTA using indium as standard. In order to minimize the effects of sample packing in the crucible and to eliminate any trace of solvent, we heated all the samples to 450 K and later quenched to measure the beginning temperature.

We also determined the specific heat at constant pressure, C_P, as a function of temperature (Fig. 1) using the following expression that relates
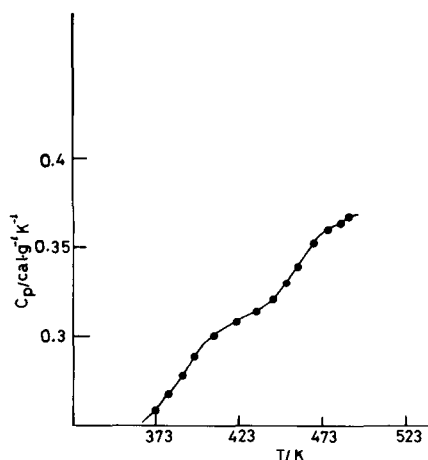
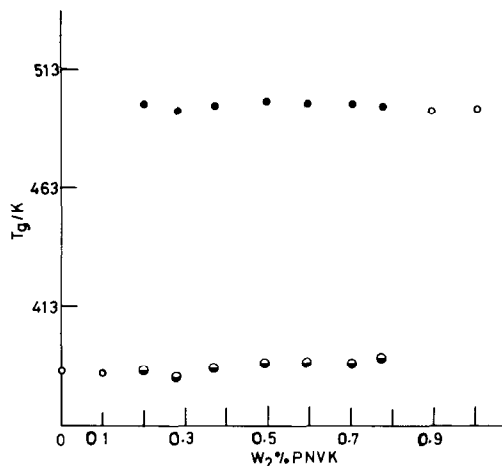Fig. 1. Plot of specific heat versus temperature for PMMA (7100)/PNVK (10000) system at W2% PNVK = 0.6.

Fig. 2. Plot of glass transition temperature, T_G, versus W2% PNVK for system A (PMMA (150000 g mol^{-1})/PNVK (140000 g mol^{-1})) cast from benzene.

this magnitude with system variables:

$$C_P = 3D_S S / \left[E_{rel} E_{in} (dT/dt) M \right] - C_{P(Al)} (M_{CM} - M_{CV}) / M$$

where D_S is the distance between vacuum and sample test, S the calorimetric sensibility, E_{rel} the relative sensibility, which depends on temperature, E_{in} the calibrated constant, M the sample weight (between 8 and 30 mg), M_{CV} the vacuum crucible weight, M_{CM} the crucible weight which contains the sample, $C_{P(Al)}$ the specific heat at constant pressure of aluminium and dT/dt the scan speed.

RESULTS AND DISCUSSION

The glass transition temperature, T_G, is a useful property for proving the existence of miscibility between two polymers. If a polymer blend shows only one glass transition temperature we can consider that miscibility between both polymers exists. Otherwise, if we find two different T_G values, then we say that the blend shows a two-phase behaviour. Figures 2 and 3 show the T_G values obtained by DTA as a function of PNVK composition. As it can be seen in Fig. 2, system A always shows two different T_G values except in the PNVK composition ranges 0–0.1 and 0.9–1.0. This implies that in the 0.1–0.9 PNVK composition range both polymers show a two-phase behaviour. In the outmost composition range it is possible to find the existence of a certain miscibility in this system, though it has been suggested
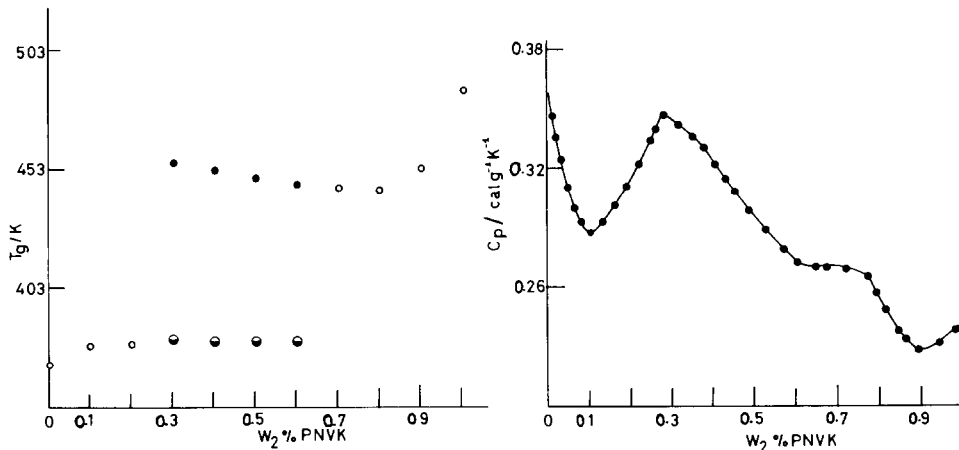
Fig. 3. Plot of glass transition temperature, T_G, against W2% PNVK for system B (PMMA (7100 g mol^{-1})/PNVK (10000 g mol^{-1})) cast from benzene.

Fig. 4. Specific heat, C_P, versus W2% PNVK at 368 K for system A.

[2] that the determination of T_G values of the minor components of a polymer blend is very complex. Hence, the results obtained in this composition range must be treated with caution. On the other hand, it can be seen in the same figure that the experimental T_G values obtained are nearly equal to those corresponding to both pure components. The PNVK and the PMMA T_G values are in good agreement with the literature values [13–17].

The effect of lowering the molecular weight of both polymers is illustrated in Fig. 3 corresponding to system B. In this system, the miscibility increases with respect to the other system. The differences observed in T_G values in both systems may be the consequence of a slight tendency of PNVK to be diluted by PMMA. At any rate, this effect must be small.

The molecular dimensions of both polymers are very similar, while there is a great difference in the backbone rigidity. This fact suggests a hindrance to the interpenetration of the macromolecular coils. This phenomenon is more significant when the molecular weight increases. We think that the use of good solvents for both polymers may minimize this hindrance and, thus, the interpenetration phenomenon is favoured. It is thus possible to increase the miscibility of two polymers slightly using a good solvent for them both. In this way, both macromolecular coils are swollen and the entanglement is, then, favoured. We have used benzene, which is a good solvent for PMMA and a moderate solvent for PNVK. Thus, the former is swollen in solution while the latter is not, which is another hindrance to the interpenetration phenomenon.

In Figs. 4 and 5, we show the specific heat at constant pressure, C_P, as a function of PNVK composition at constant temperature (368 K). As it can
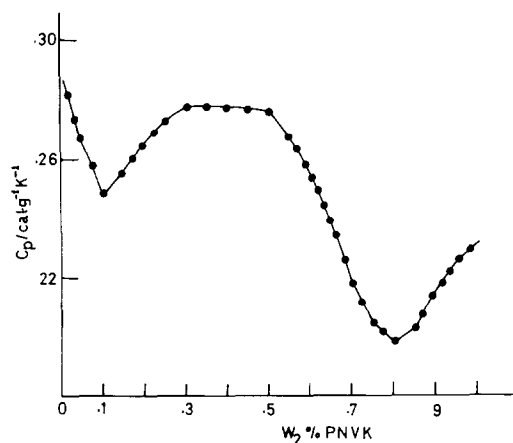
Fig. 5. Specific heat, C_P, versus W2% PNVK at 368 K for system B.

be seen, this plot is very useful for determining miscibility ranges because the minimum of the C_P–composition plot is located at the same composition miscibility ranges as those obtained from a T_G–composition plot. This behaviour may be due to a decrease in the degree of freedom when the two polymers are mutually miscible. As the C_P parameter is directly related to the degrees of freedom of the system, when the latter decreases, so does the former.

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