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DSC ANALYSIS OF COMPATIBILITY OF POLY(PHENYL METHACRYLATE) AND SOME POLY(XYLENYL METHACRYLATES)

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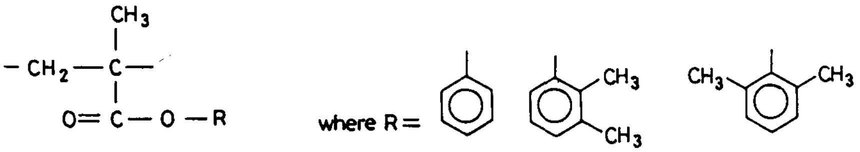
Glass transition temperatures of blends of (1) poly-(phenyl methacrylate) and poly(2,3-xylenyl methacrylate), (2) poly-(phenyl methacrylate) and poly(2,6-xylenyl methacrylates and (3) poly-(2,3-xylenyl-) and poly(2,6-xylenyl methacrylate) were measured. The data obtained suggest the existance of compatibility for blends of poly(xylenyl methacrylates) mentioned and incompatibility for both poly(phenyl methacrylate)/poly(xylenyl methacrylate) systems.

Keywords: alkylphenyl methacrylates, DSC, glass transition temperatures, kinetics of polymerization

Introduction

Previous papers have described the kinetics of polymerization of alkylphenyl methacrylates and dilute solution properties of their polymers [1–3]. The present investigation refers to the compatibility of poly(phenylmethacrylate) (PPhMA) with poly(2,3-xylenyl methacrylate) (P2,3XMA) and poly(2,6-xylenyl methacrylate) (P2,6XMA), as well as to the mutual compatibility of P2,3XMA/P2,6XMA. The formulae of the repeat units of the investigated polymers are as follows:



PhMA 2.3XMA 2.6XMA

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The phase behaviour of a polymer blend is most conveniently determined by calorimetric measurement using the well known single glass transition (T_g) criterion. The thermal analysis performed by differential scanning calorimetry (DSC) reveals either one or two discontinuities in the heat capacity, depending on whether or not phase separation has occured. This separated procedure works only if the T_g values of the pure components are sufficiently separated. This happened to be the case for the examined polymers (PPhMA 383 K; P2,3XMA 398 K; P2,6XMA 440 K) [4].

The experimental T_g values of compatible blends were compared to those calculated according to Fox [5] and a fair agreement was obtained.

Experimental

The monomers were synthethized by reacting methacryloyl chloride with the corresponding phenols at 5°C [6], and their purity chequed by elemental analysis and IR spectroscopy. The polymers, obtained by AIBN initiated polymerization in bulk [1], were used as unfractionated samples. Some of their properties are listed in Table 1.

Table 1 Data on polymers investigated

Polymer	$M_w \cdot 10^{-3}$	d /g·cm^{-3}	T_g / K	δ / MPa$^{1/2}$
PPhMA		1.204	383 (381)	19.2
P2,3XMA	≈ 100	1.156	398 (388)	18.8
P2,6XMA		1.146	440 (435)	18.9

Polymer blends were prepared by coprecipitation from dilute tetrahydrofuran solutions (1% w/v), using methanol in large excess and drying in vaccuo at 40°C for several days. The white powdery samples were obtained.

A Perkin-Elmer DSC 2 thermoanalyser, calibrated by measuring the heat of fusion of indium, was used for T_g measurements. DSC scans were taken from 313–473 K, the sample weight was 12–15 mg and the heating rate 20 deg·min^{-1}.

Result and discussion

Figure 1 shows the thermograms of PPhMA, P2,6XMA and of their 50:50 (w:w) blend. Similar thermograms for other PPhMA/P2,6XMA blends, as well as for PPhMA/P2,3XMA system were obtained.

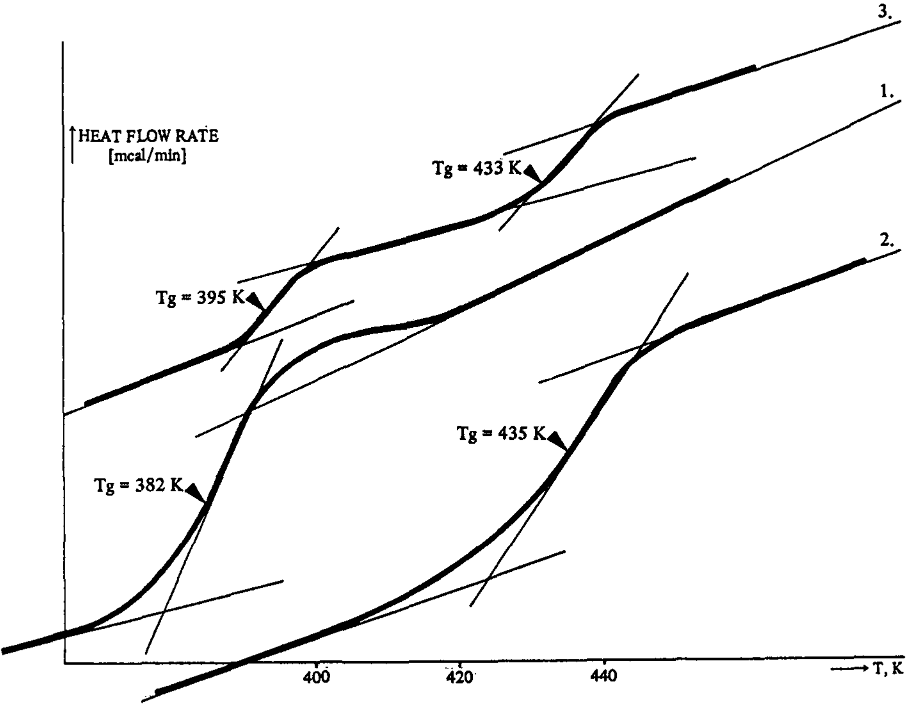

Fig. 1 DSC curves for PPhMA (1), P2, 6XMA (2) and their 50:50 blend (3)

P2,6XMA sample is characterized by a rather high T_g value (435 K) compared to other poly(xylenyl methacrylates) [4]. This was due to the highly restricted rotation of phenyl ring, substituted in both available o-positions. The T_g values of PPhMA and P2,3XMA with bulky side groups, were about 50 K lower.

Two incremental changes in heat capacity of PPhMA/P2,6XMA 50:50 blend were due to two different phases, with two T_g values between the T_g's of the individual polymers. The similar results, obtained for PPhMA/P2,3XMA system, unambiguously confirmed that both PPhMA/PXMA systems were incompatible over the whole composition range.

In Fig. 2 the DSC curves for P2,6XMA/P2,3XMA system are given. One single intermediate T_g was visible in all the scans of the blends examined (17:82; 33:67; 50:50; 67:33; 83:17; w:w). The change in configuration, caused by shifting the second methyl from position 3 to position 6 does not cause polymer segregation. The T_g's of P2,6XMA/P2,3XMA blends were shifted to the higher values with increasing P2,6XMA content (Fig. 3).

The most unambiguous criterion for polymer miscibility is the detection of a single glass transition temperature intermediate between those corresponding to the pure components. It can be concluded that poly(2,6-xylenyl methacrylate) and poly(2,3-xylenyl methacrylate) are compatible over the whole composition range.

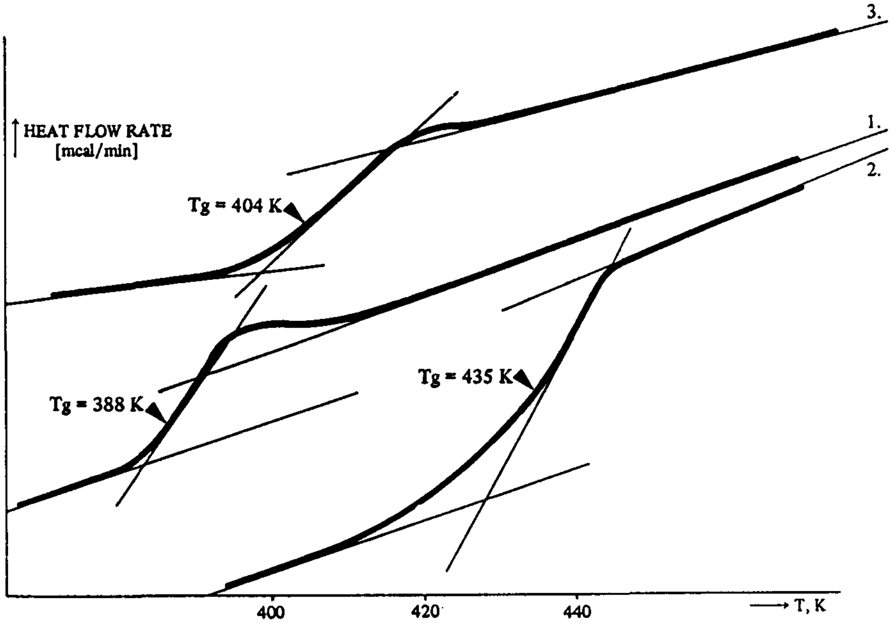

Fig. 2 DSC curves for P2,3XMA (1), P2,6XMA (2) and their 50:50 blend (3)

Several equations have been proposed to relate the T_g of polymer-plasticizer mixtures and of random copolymers to T_g's of the homopolymers. The same relations are frequently used for polymer mixtures. One of the simplest, proposed by Fox [5] is

$$1/T_g = W_1/T_{gl} + W_2/T_{g2} \tag{2}$$

where: $T_{g1,2}$ = glass temperature (K) of the mixture and components, respectively
$W_{1,2}$ = weight fraction

$$\text{Since } W_2 = 1 - W_1 \tag{2}$$

$$1/T_g = W_1(T_{g2} - T_{g1})/T_{g2}T_{g1} + 1/T_{g2} \tag{3}$$

The experimental T_g values for P2,6XMA/P2,3XMA blends were subjected to linear regression (Eq. 3) and a correlation coefficient r = -0.982 was obtained. This result indicates a high correlation between the experimental and calculated

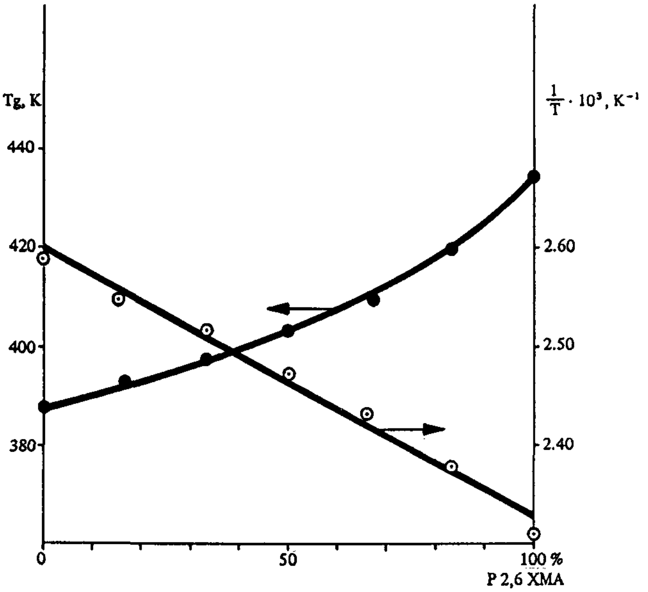

Fig.3 Relationship between T_g and weight fraction of P2,6XMAfor P2,3XMA/ P2,6XMA bleds

data (Eq. 3), confirming the dependence of T_g^1 on weight fraction of component polymers.

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Zusammenfassung — Es wurden die Glasumwandlungspunkte von Gemischen aus (1) Poly-(phenylmethacrylat) und Poly(2,3-xylolylmethacrylat), (2) Poly-(phenylmethacrylat und Poly(2,6-xylolylmethacrylaten) und (3) Poly-(2,3-xylolyl-) und Poly(2,6-xylolylmethacrylat) vermessen. Die erhaltenen Angaben weisen auf Kompatibilität für die Gemische aus den genannten Poly-(xylolylmethacrylaten) sowie auf Inkompatibilität für Poly(phenylmethacrylat)/Poly(xylolylmethacrylat)-Systemen hin.