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MISCIBILITY OF POLY(ACETONYL METHACRYLATE) AND POLY(n-PROPYL METHACRYLATE) WITH POLY(VINYLIDENE FLUORIDE)

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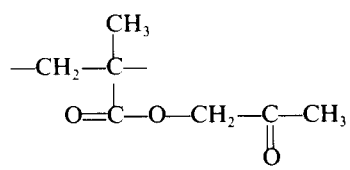
Abstract—Poly(vinylidene fluoride) (PVDF) is immiscible with poly(n-propyl methacrylate) but miscible with poly(acetonyl methacrylate) (PACMA), indicating the importance of the additional carbonyl group in PACMA in achieving miscibility. Based on the melting point depression of PVDF in the blends, the interaction parameter B was found to vary between -43.5 and -5.0 J/cm^3, depending on the composition.

INTRODUCTION

Many polymer blends containing poly(vinylidene fluoride) (PVDF) have been studied; the PVDF/poly(methyl methacrylate) (PMMA) system is the best known example of a miscible blend containing a crystallizable component [1–6]. PVDF is also miscible with poly(ethyl methacrylate) (PEMA) [4, 7–12] but it is immiscible with higher members of the polymethacrylate series, such as poly(isopropyl methacrylate) (PiPMA) and poly(isobutyl methacrylate) (PiBMA) [13]. Bernstein *et al.* [14] reported that PVDF is miscible with poly(vinyl methyl ketone) (PVMK) but immiscible with poly(vinyl methyl ether) (PVME), and concluded that PVDF interacts with the carbonyl group rather than the whole ester group. Furthermore, they also reported that PVDF is miscible with poly(vinyl acetate) (PVAC) [15] and suggested that placement of the carbonyl further from the main chain was responsible for the stronger interaction of PVAC with PVDF than that of poly(methyl acrylate) (PMA) [13]. The immiscibility of PVDF with PiPMA and PiBMA appears to be the result of the interference of the bulky alkyl groups on the interaction between PVDF and the carbonyl group. We now report the miscibility of PACMA with PVDF. It is of interest to know how the presence of an additional carbonyl group in the pendant alkyl group affects the miscibility behaviour of the polymethacrylate.



(PACMA)

EXPERIMENTAL PROCEDURES

Both PVDF and PnPMA ($\bar{M}_w$ = 175,000) were obtained from Scientific Polymer Products, Inc. The intrinsic viscosity of PVDF was 0.88 dl/g in dimethylformamide (DMF) at 30°. Acetonyl methacrylate (ACMA) was prepared by the method reported by Ueda *et al.* [16]; it was polymerized in 2-butanone at reflux temperature for 6 hr, using 0.25% by weight of α,α′-azobis (isobutyronitrile) as initiator. The polymer was obtained by precipitation of the solution in excess of methanol. The intrinsic viscosity of PACMA was found to be 0.099 dl/g in 2-butanone at 30°.

PACMA/PVDF and PnPMA/PVDF blends were prepared by solution casting using DMF as solvent. Solvent was first allowed to evaporate at 100° on a hot plate. The blends were then dried *in vacuo* at 90° for at least 48 hr.

The melting points (T_m) and heats of fusion (ΔH_f) of samples were measured with a Perkin–Elmer DSC-4 differential scanning calorimeter. Each sample was first heated to 170° using a heating rate of 20°/min and kept at that temperature for 5 min before being cooled to room temperature to ensure all samples had the same thermal history. The sample was re-scanned 24 hr later. The peak of the melting endotherm was recorded as T_m of the sample. The glass transition temperatures (T_g) of samples were measured with a Du Pont 910 differential scanning calorimeter. Each sample was scanned between $-80°$ and $+80°$, using a heating rate of 20°/min. The initial onset of the change of slope in the heat capacity plot was taken as T_g. Duplicate runs were made for each blend sample to ensure the reproducibility of the T_m and T_g values.

RESULTS AND DISCUSSION

PACMA was found to be miscible with PVDF, each blend showing a single T_g intermediate between those of PVDF and PACMA. The T_g of the blend is a linear function of the composition as shown in Fig. 1. The heat of fusion of the blend is also a linear function of the composition as shown in Fig. 2. This results means that PVDF crystallizes to the same extent in the blend as in the pure state. Similar behaviour has also been observed for PVDF/PMMA blends [1].

For a miscible blend containing a crystallizable component such as PVDF, the melting point depression of the crystalline polymer by the miscible diluent is used to calculate the intermolecular interaction parameter B using the equation [1, 7]

$$T_m = T_m^0 + B(V_{2u}/\Delta H_{2u})T_m^0\phi_1^2$$

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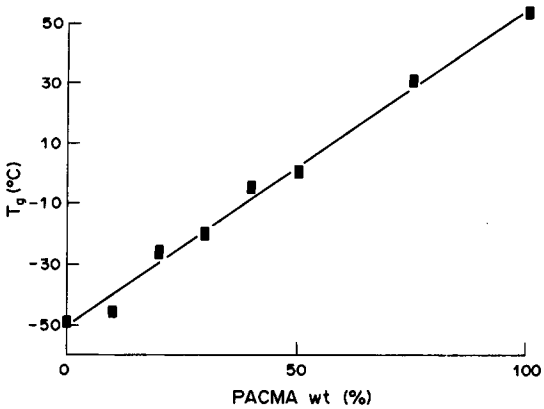

Fig. 1. T_g-composition curve for PACMA/PVDF blends.

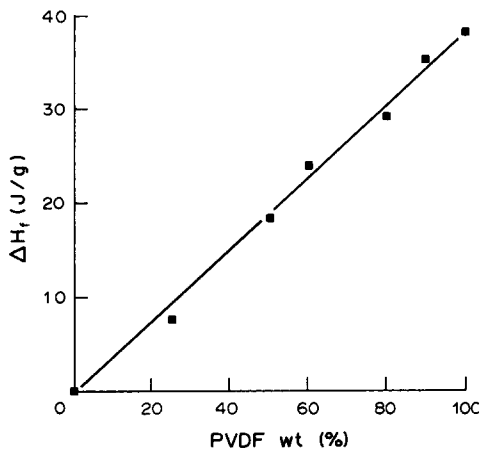

Fig. 2. ΔH_f for PACMA/PVDF blends.

where T_m^0 and T_m are the melting points of pure PVDF and PVDF in the blends respectively, $\Delta H_{2u}/V_{2u}$ is the heat of fusion per unit volume of repeating unit for PVDF [184.1 J/cm^3] [1] and ϕ_1 is the volume fraction of the non-crystallizable polymer in the blend. B is obtained from a plot of T_m against ϕ_1^2.

The T_m of PVDF was found to be depressed substantially by the addition of PACMA. A plot of T_m against ϕ_1^2 is shown in Fig. 3. The non-linearity of the plot indicates that B is composition dependent. The calculated B values as a function of the

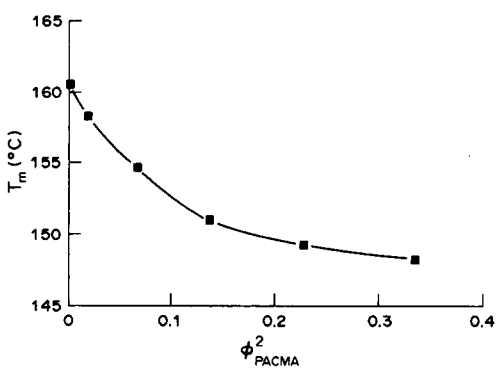

Fig. 3. Melting point depression plot for PACMA/PVDF blends.

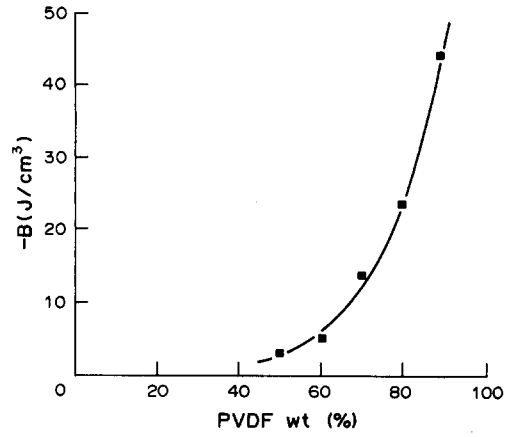

Fig. 4. Interaction energy density of PACMA/PVDF blends as a function of weight % of PVDF.

composition of the blend is shown in Fig. 4. It ranges from -43.5 J/cm^3 at high PVDF content to -5.0 J/cm^3 for a blend containing 50% by wt of PVDF. Many studies on the melting point depression in PVDF/PMMA blends reported a linear relationship between T_m and ϕ_1^2 indicating that B is composition-independent. However, Morra and Stein [5] reported that the B values for PVDF/PMMA blend ranged between -29.6 and -5.4 J/cm^3 which is of the same order of magnitude for the PACMA/PVDF system. In the present and other studies [1, 2, 4, 7, 8, 19], PVDF is crystallized with large undercooling and the measured melting point is not the thermodynamic equilibrium value. The use of non-equilibrium melting point may result in an underestimate of the interaction parameter [20]. Nevertheless, the negative B value obtained for PACMA/PVDF blends clearly indicates a favourable enthalpic interaction between the two polymers in the blend.

As mentioned earlier, PVDF is immiscible with PiPMA and PiBMA. However, to our knowledge there is no report on the miscibility of PVDF with PnPMA. As expected, PnPMA/PVDF blends show optical cloudiness and two T_gs, characteristics of an immiscible mixture as shown in Fig. 5. The present study shows that PnPMA is not miscible with PVDF yet PACMA is miscible. This difference suggests that

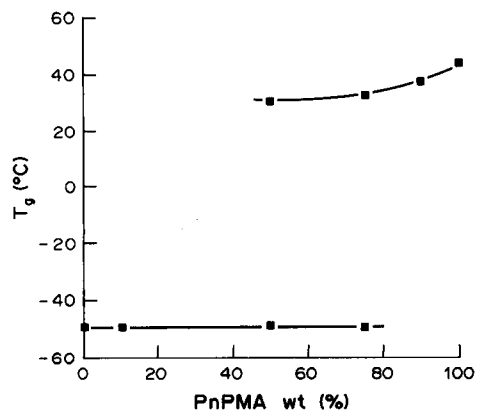

Fig. 5. T_g-composition curve for PnPMA/PVDF blends.

the presence of an additional carbonyl group in the structural unit influences the miscibility behaviour. By replacing the methylene groups in the pendant groups of PnPMA with carbonyl groups, the resulting PACMA becomes miscible with PVDF.

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