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Miscibility of poly(methoxymethyl methacrylate) and poly(methylthiomethyl methacrylate) with poly(vinylidene fluoride)

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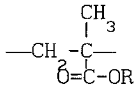
Summary

The miscibility behaviour of poly(methoxymethyl methacrylate) (PMOMA) and poly(methylthiomethyl methacrylate) (PMTMA) with poly(vinylidene fluoride) (PVDF) was examined by differential scanning calorimetry. PMOMA/PVDF blend system was judged to be miscible on the bases of the presence of a single, composition-dependent glass transition for the blend and a pronounced melting point depression of the PVDF component. Furthermore, lower critical solution temperature (LCST) behaviour was observed for all PMOMA/PVDF blends. PMTMA/PVDF blends were found to be immiscible. Based on the melting point depression of PVDF in PMOMA/PVDF blends, the interaction parameter *B* was found to be -14.5 J/cm^3.

Introduction

The miscibility of poly(vinylidene fluoride) (PVDF) with various polyacrylates and polymethacrylates has been widely studied. PVDF is miscible with poly(methyl methacrylate) (PMMA) (1-6) and poly(ethyl methacrylate) (PEMA) (4, 7-12), but it is immiscible with higher members of the polymethacrylate series, such as poly(n-propyl methacrylate) (PnPMA) (13), poly(isopropyl methacrylate) (PiPMA) and poly(isobutyl methacrylate) (PiBMA) (14). Bernstein *et al.* (15) 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. In an earlier study (13), we have noted that PnPMA is not miscible with PVDF yet poly(acetonyl methacrylate) (PACMA) is miscible. This difference suggests that the presence of an additional carbonyl group in the structural unit influences the miscibility behaviour. Besides carbonyl group, it is of interest to study how the presence of other functional moieties, for examples, ether oxygen and sulfur atoms, in the alkyl pendent group affects the miscibility behaviour of the polymethacrylate with PVDF. We have recently reported that PMMA is miscible with poly(methoxymethyl methacrylate) (PMOMA) but not poly(methylthiomethyl methacrylate) (PMTMA) (16). However, both PMOMA and PMTMA are miscible with poly(α-methylstyrene-co-acrylonitrile) (αMSAN) containing 30 wt % of acrylonitrile (17,18).



$$-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle O=C-OR}{C}}-$$

R = $-CH_2OCH_3$ (PMOMA)
$-CH_2SCH_3$ (PMTMA)

Experimental

The monomers of PMOMA and PMTMA were prepared following the procedures reported by Ueda *et al.* (19, 20). PMOMA and PMTMA were prepared by solution polymerization as described elsewhere (16). The $\bar{M}_n$ of PMOMA and the $\bar{M}_w$ of PMTMA are 17,000 and 48,000 respectively, as determined by intrinsic viscosity measurements, using the appropriate Mark-Houwink equations (19, 20). PVDF, with an intrinsic viscosity of 0.88 dl/g in dimethylformamide (DMF) at 30°C, was obtained from Scientific Polymer Products, Inc.

All blends were prepared by solution casting using DMF as solvent. Solvent was first allowed to evaporate at 100°C on a hot plate. The blends were then dried *in vacuo* at 90°C for at least 48 h. 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°C using a heating rate of 20°C/min and kept at that temperature for 5 minutes before being cooled to room temperature to ensure all samples had the same thermal history. The sample was re-scanned 24 h later. The peak of the melting endotherm was recorded as T_m of the sample. Duplicate runs were made for each blend sample to ensure the reproducibility of the T_m values. The glass transition temperatures (T_gs) of all samples were measured with the Perkin-Elmer DSC-4 differential scanning calorimeter equipped with an INTRACOOLER II. A cyclic heating and cooling procedure between the limits of -60 and 190°C was used. T_g was taken as the initial onset of the change of slope in the DSC curve. The reported T_g is the average value based on the second and subsequent runs.

All blends were examined for the existence of lower critical solution temperature (LCST) behaviour. The film was sandwiched between two microscopic cover glasses and heated in a Fisher-Johns melting point apparatus with a heating rate of about 10°C/min. The optical appearance of the film was observed with a magnifying glass attached to the apparatus. A transparent film which turns cloudy upon heating indicates the existence of LCST. The temperature at which the film first showed cloudiness was taken as the cloud point.

Results and Discussion

PMOMA/PVDF blends

PMOMA is miscible with PVDF in the amorphous phase as each blend showed a single, composition-dependent T_g intermediate between those of PVDF and PMOMA as shown in Fig. 1(a). All blends turned clear when heated above the T_m of PVDF and exhibited LCST behaviour upon heating to higher temperatures. It is known that PMMA/PVDF and PEMA/PVDF blend systems also show LCST behaviour (4,12). The cloud point curve for PMOMA/PVDF blends is shown in Fig. 1(b)

The presence of PMOMA greatly suppresses the crystallization of PVDF and also lowers its melting point as shown in Fig. 2. The extent of this depression is approximately 10°C in a blend containing 50 wt % of PVDF. No melting peak was observed for a blend containing 25 wt % of PVDF. This type of crystallization behaviour has proved to be quite common for miscible blends involving PVDF (4,15).

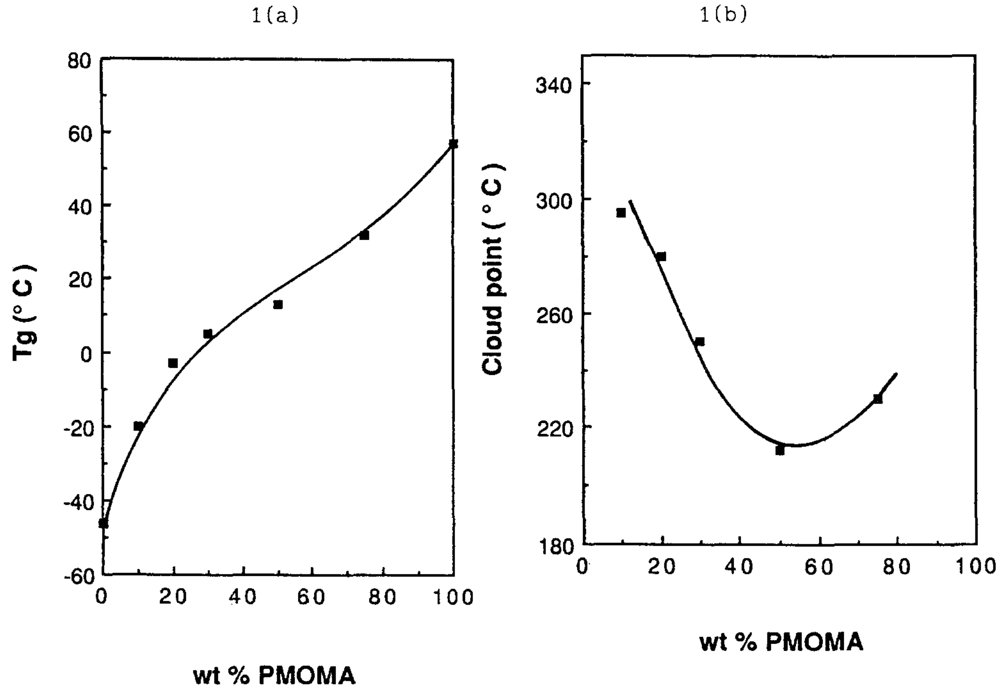


Fig. 1(a) *Tg*-comoposition curve for PMOMA/PVDF blends.
Fig. 1(b) The cloud point curve for PMOMA/PVDF blends.

The intermolecular interaction parameter *B* for blends of PMOMA with PVDF can be estimated from the melting point depression of PVDF in blends by using the equation (1,7,15)

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

where T_m^{o} and T_m are the melting points of pure PVDF and PVDF in the blend respectively, $\Delta H_{2u}/V_{2u}$ is the heat of fusion per unit volume of repeating unit for PVDF and its value is 184.1 J/cm^3 (1). ϕ_1 is the volume fraction of the non-crystallizable polymer in blends. *B* is obtained from a plot of T_m against ϕ_1^2 as shown in Fig. 3. The *B* value obtained is -14.5 J/cm^3.

In the present and other studies (1,2,4,7,8,13,22), 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 (23). Nevertheless, the negative *B* value obtained for PMOMA/PVDF blends clearly indicates a favourable enthalpic interaction between the two polymers in the blend.

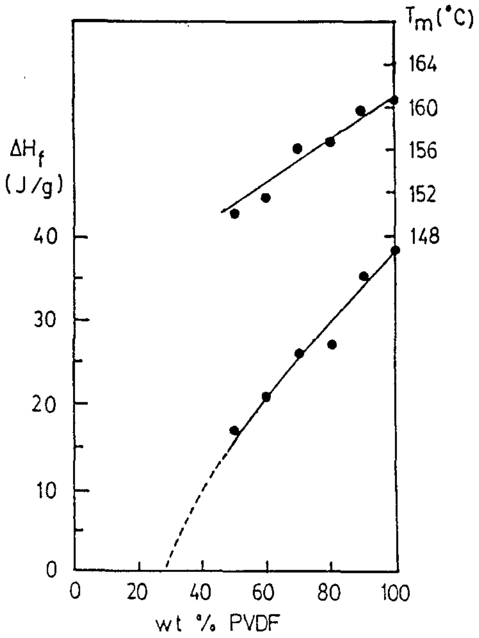


Fig. 2. Melting behaviour of PMOMA/PVDF blends

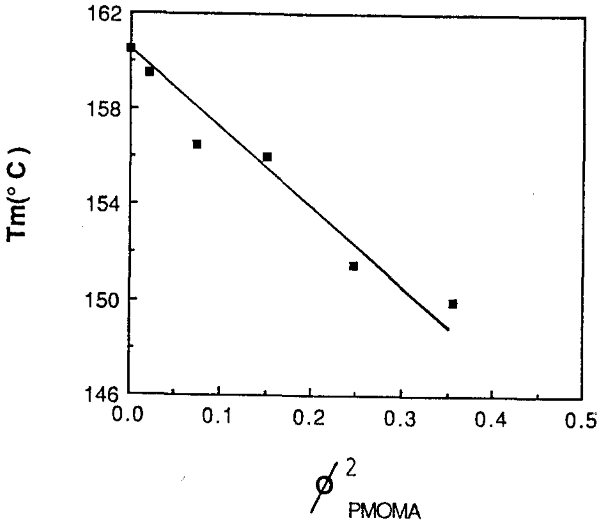


Fig. 3. Melting point depression plot for PMOMA/PVDF blends

PMTMA/PVDF blends

All blends remained cloudy even being heated above the melting temperature of PVDF and each blend showed two glass transitions, characteristic of an immiscible blend as shown in Fig. 4. The two *Tg* values are independent of blend composition and are almost the same as those of pure PMTMA and PVDF. The melting point of PVDF is depressed by increasing PMTMA content, but the depression is quite small and insignificant as shown in Fig. 5. It has been suggested that this type of depression may be attributed to the morphological effects (4). The heat of fusion of PMOMA/PVDF blend system is a linear function of the composition as shown in Fig. 5. This result means that PVDF crystallizes to the same extent in the blend as in the pure state. This crystallization behaviour has been observed for both miscible and immiscible blend systems (14,15,24,25).

Miscibility behaviour

The present study shows that PMOMA is miscible with PVDF yet PMTMA is immsicible. This result agrees well with the fact that the miscibility of polymethacrylate with PVDF decreases as the alkyl pendent group becomes bulkier. Since sulfur atom is larger than oxygen atom, PMTMA has bulkier pendent groups than PMOMA. Hence, it is expected to have poorer miscibility behaviour than PMOMA. Moreover, oxygen is more electronegative than sulfur and this may also account for the difference in miscibility behaviour of PMOMA and PMTMA.

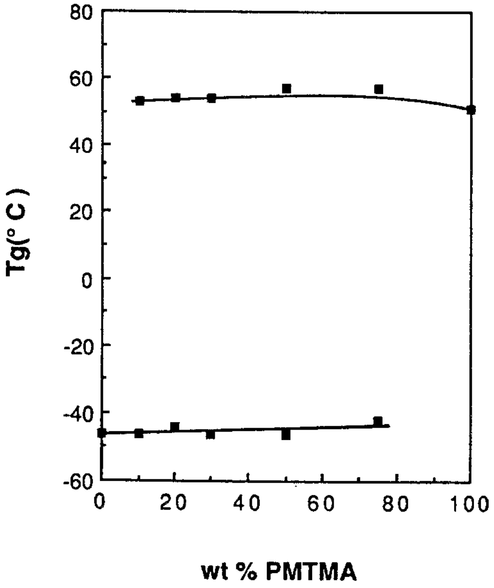


Fig. 4. *Tg*-composition curve for PMTMA/PVDF blends

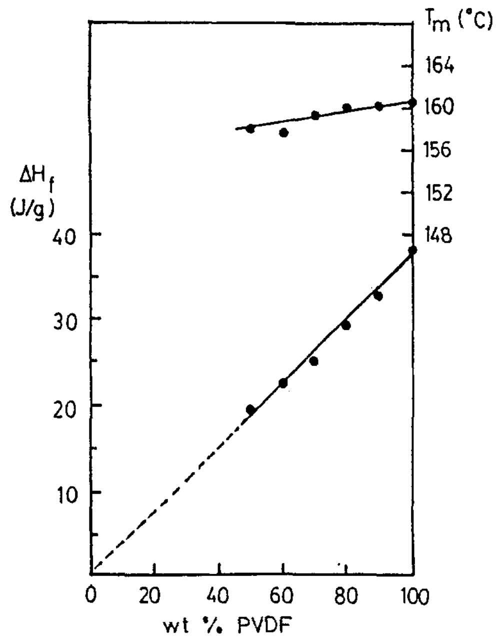


Fig. 5. Melting behaviour of PMTMA/PVDF blends

Table 1 summaries the *B* values estimated from the melting point depression of PVDF in blends with PMMA, PEMA and PMOMA. It is interesting to note that the magnitude of *B* is in the following order: PMMA > PMOMA > PEMA. The result suggests that the addition of ether oxygen atom in the the alkyl pendent group of PEMA improves the miscibility of the polymethacrylate with PVDF. Furthermore, the alkyl pendent groups of PMOMA and PnPMA are of similar sizes, yet PnPMA is immsicible with PVDF (13). By replacing the methylene groups in the pendent groups of PnPMA with ether oxygen instead of carbonyl group, the resulting PMOMA is still miscible with PVDF.

Acknowledgement

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Table 1. Interaction parameters for blend containing PVDF

Polymer	*B* (J/cm^3)	Reference
PMMA	-18.5	22
	-16.1	4
PEMA	-11.1	22
	-11.9	4
PMOMA	-14.5	This work

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