

Miscibility of C₆₀-Containing Poly(methyl methacrylate)/Poly(vinylidene fluoride) Blends

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ABSTRACT: The miscibility of C₆₀-containing poly(methyl methacrylate) (PMMA-C₆₀) with poly(vinylidene fluoride) (PVDF) was studied. Two PMMA-C₆₀ samples containing 2.6 and 7.4 wt % C₆₀ were found to be miscible with PVDF based on single glass transition temperature criterion and melting point depression of PVDF. However, the interaction parameters of the two blend systems are less negative than that of the PMMA/PVDF blend system, showing that the incorporation of C₆₀ reduces the ability of carbonyl groups of PMMA to interact with PVDF. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1393–1396, 2000

Key words: miscibility; melting point depression; C₆₀-containing poly(methyl methacrylate); poly(vinylidene fluoride)

INTRODUCTION

Blending of two or more polymers is an important method of making new materials. The properties of polymer blends depend strongly on the miscibility of the component polymers. Miscibility occurs when there are specific interactions, such as hydrogen bonding, ionic, charge-transfer complexes, acid–base type interactions, etc., between the two polymers.

Recently, the syntheses of many types of C₆₀-containing polymers have been reported.^{1–4} The possibility of producing novel materials that combine the unusual properties of C₆₀ and those of polymers has attracted the attention of many researchers. However, with the exception of our previous work,⁵ the miscibility behavior of blends of C₆₀-containing polymers has not been studied. In fact, the mixing of a C₆₀-containing polymer with other polymers is also a route of producing

novel materials. We have reported the effect of C₆₀ on the miscibility of two typical miscible amorphous/amorphous polymer blends.⁵ C₆₀-containing polystyrene with C₆₀ content up to 13.6 wt % is still miscible with poly(2,6-dimethyl-1,4-phenylene oxide), but it is partially miscible with poly(vinyl methyl ether). We have chosen a typical miscible amorphous/crystalline polymer blend system, poly(methyl methacrylate) (PMMA)/poly(vinylidene fluoride) (PVDF), to study the effect of C₆₀ on miscibility. It has been well established that PVDF and PMMA are miscible in the melt, and PVDF in the blend can crystallize upon cooling when the blend contains more than 60 wt % PVDF.^{6–20} In recent years, the dielectric relaxation of PVDF/PMMA blends has been extensively studied.^{16–20}

EXPERIMENTAL

PVDF was obtained from Scientific Polymer Products, Inc. Two poly(methyl methacrylate-co-2-bromoethyl methacrylate) samples were prepared by free radical copolymerization. The bromine groups in the copolymers were converted to azide

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Table I Characteristics of Polymers

	C_{60} Content (wt %)	10^{-3} M_n	10^{-3} M_w	T_g (°C)
PVDF		28	40	-43
PMMA- C_{60} -2.6	2.6	32.3	118.5	132
PMMA- C_{60} -7.4	7.4	41.2	160.9	148

groups followed by reaction with C_{60} to afford C_{60} -containing PMMA (PMMA- C_{60}). Details of the synthesis of PMMA- C_{60} were reported previously.²³ Table I lists the main characteristics of these polymers.

The blends were prepared by solution casting using dimethylformamide as solvent. Solvent was first allowed to evaporate at 110°C. The blends were then dried *in vacuo* at 90°C for 2 weeks.

The glass transition temperatures (T_g s) were measured using a TA Instruments (Model 2920; Newcastle, DE) differential scanning calorimeter (DSC) with a heating rate of 20°C/min. Samples were first heated to 180°C and kept at that temperature for 5 min before being cooled to -100°C. The quenched samples were then rescanned to 180°C. The initial onset of the change of slope in the DSC curve was taken as T_g .

The equilibrium melting point of PVDF was determined using the Hoffman-Weeks method.²⁴ Isothermal crystallization experiments were carried out in a Perkin-Elmer DSC (Model DSC-4; Norwalk, CT). Each sample was kept at 200°C for 10 min and then allowed to crystallize at the desired crystallization temperature (T_c) for 72 h. After crystallization the sample was cooled to room temperature. The melting point (T_m) was then measured using the TA Instruments 2920 differential scanning calorimeter with a heating rate of 5°C/min. The peak of the melting endotherm was recorded as T_m of the sample. The optical clarity of the amorphous blends at 200°C was examined using an Olympus BH2-UMA polarizing optical microscope equipped with a Leitz-Wetzlar (Wetzlar, Germany) hot stage.

RESULTS AND DISCUSSION

All PMMA- C_{60} -2.6/PVDF and PMMA- C_{60} -7.4/PVDF blends were brownish in color, and the color became deeper with increasing PMMA- C_{60} content in the blend. Nevertheless, all the blends

were optically clear when examined under the microscope at 200°C.

The DSC curves of various PMMA- C_{60} -2.6/PVDF blends are shown in Figure 1. Although PMMA- C_{60} -2.6 showed a distinct glass transition at 132°C, PVDF showed a weak glass transition at -43°C. Blend containing 25, 40, or 50 wt % PVDF also showed a single glass transition. The transition became broader and the T_g value moved to a lower temperature with increasing PVDF content in the blend. Thus, the optical clarity of the melt and the existence of a single glass transition show that these blends are miscible. Blends containing 60 and 75 wt % PVDF are semicrystalline as shown by the appearance of melting endotherms in the DSC curves. The melting point of PVDF in the two blends are significantly lower than that of PVDF. However, the glass transitions of the two semicrystalline blends were difficult to detect. Nevertheless, the optical clarity of the melt and the melting depression of PVDF by PMMA- C_{60} -2.6 also suggest that the two polymers are miscible in the melt.

The DSC curves of various PMMA- C_{60} -7.4/PVDF blends are shown in Figure 2. The features of these DSC curves are similar to those of the PMMA- C_{60} -7.4/PVDF blends. As compared to PMMA- C_{60} -2.6, the glass transition temperature of PMMA- C_{60} -7.4 is higher, but the glass transition is broader. PMMA- C_{60} -7.4/PVDF blends containing 25, 40, and 50 wt % PVDF each showed a broad glass transition, and the T_g value decreased with increasing PVDF content in the blend. Blends containing 60 and 75 wt % of PVDF are semicrystalline, and the melting point of PVDF in the blends also are depressed. Therefore, the

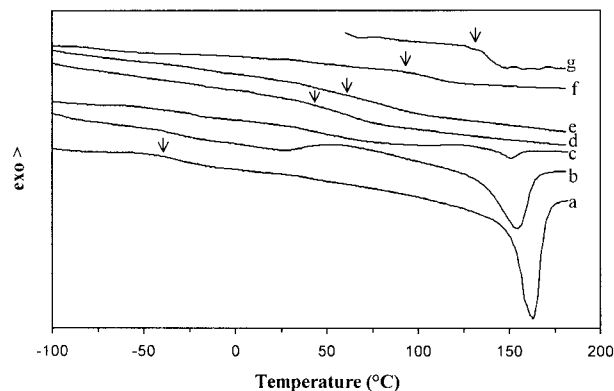


Figure 1 DSC curves of PMMA- C_{60} -2.6/PVDF blends: (a) 100, (b) 75, (c) 60, (d) 50, (e) 40, (f) 25, and (g) 0 wt % PVDF.

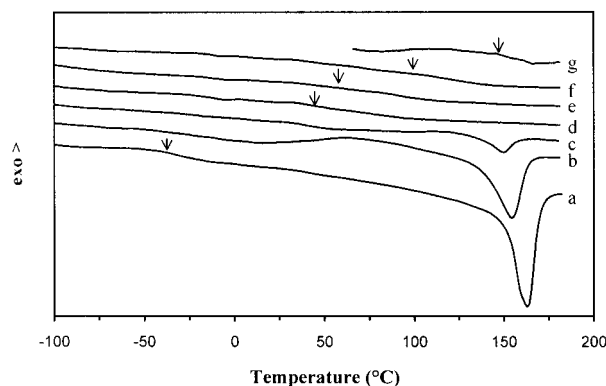


Figure 2 DSC curves of PMMA-C₆₀-7.4/PVDF blends: (a) 100, (b) 75, (c) 60, (d) 50, (e) 40, (f) 25, and (g) 0 wt % PVDF.

PMMA-C₆₀-7.4/PVDF blends also are judged to be miscible.

For a miscible crystalline/amorphous polymer blend system, the melting point depression of the crystalline polymer by the amorphous polymer can be used to calculate polymer-polymer interaction parameter χ .⁷ For polymers with sufficiently high molecular weights, χ can be calculated using the expression:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_{2u}}{\Delta H_{2u}V_{1u}} \chi \phi_1^2$$

where T_m^0 and T_m are the equilibrium melting temperatures of PVDF in the pure state and in the blend, respectively; V_{1u} and V_{2u} are the molar volumes of the repeating units of PMMA-C₆₀ and PVDF, respectively; ΔH_{2u} is the molar melting enthalpy of PVDF and ϕ_1 is the volume fraction of PMMA-C₆₀ in the blend. A plot of $(1/T_m - 1/T_m^0)$ against ϕ_1^2 enables the calculation of χ from the slope of the straight line. To remove the morphological effect on melting temperature, T_m and T_m^0 are commonly determined using the Hoffman-Weeks method, which involves the crystallization of a sample at various crystallization temperatures (T_C s). Extrapolation of the experimental T_m versus T_C line to the $T_m = T_C$ line gives the equilibrium melting temperature.

The Hoffman-Weeks plots of the two blend systems are shown in Figures 3 and 4, and the melting point depression plots are shown in Figure 5. The densities of the two PMMA-C₆₀ samples are assumed to be the same as that of PMMA (1.20 g/cm³).⁷ Using $\Delta H_{2u} = 1.6$ kcal/mol²⁵ and $V_{2u} = 36.4$ cm³/mol,²⁶ the χ values were found to

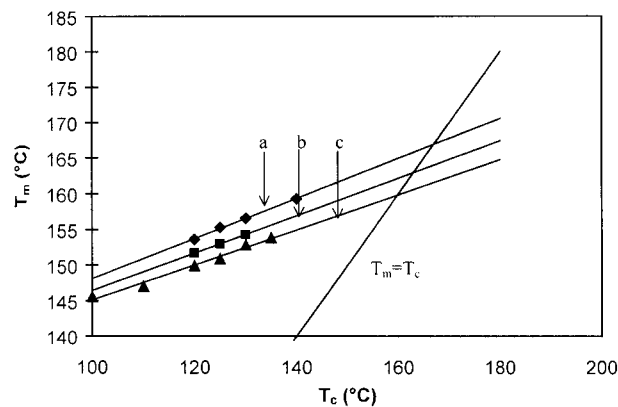


Figure 3 Hoffman-Weeks plots of PMMA-C₆₀-2.6/PVDF blends: (a) 100, (b) 75, and (c) 60 wt % PVDF.

be -0.25 and -0.16 for PMMA-C₆₀-2.6/PVDF and PMMA-C₆₀-7.4/PVDF, respectively. The lack of PMMA-C₆₀ samples precluded the inclusion of additional points in Figure 5. Therefore, the χ values provide only a rough estimation on polymer-polymer interaction between PVDF and PMMA-C₆₀. Nevertheless the χ values are substantially less negative than the reported χ values (-0.295 ⁷) or interaction energy densities (-2.98 cal/cm³,⁷ -2.93 cal/cm³,²⁷ -17 J/cm³²⁸), determined by the melting point depression for the PMMA/PVDF system. It appears that the interaction between PVDF and PMMA-C₆₀ is weaker than that that between PVDF and PMMA. The miscibility of the PVDF/PMMA blends arises from specific interaction involving the carbonyl groups of PMMA and PVDF.¹³⁻¹⁵ It is reasonable to conclude that the incorporation of C₆₀ onto PMMA must have reduced the ability of the carbonyl groups to interact with PVDF.

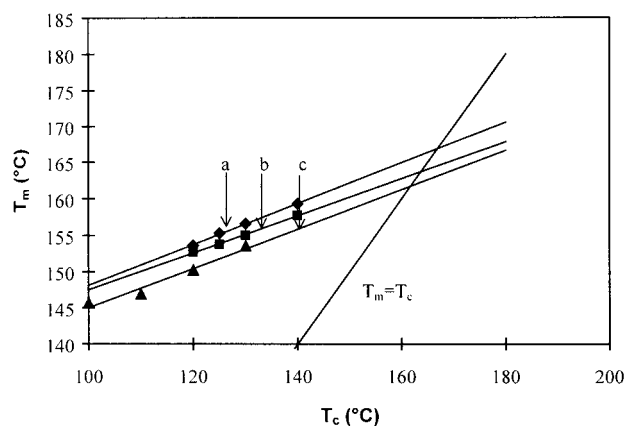


Figure 4 Hoffman-Weeks plots of PMMA-C₆₀-7.4/PVDF blends: (a) 100, (b) 75, and (c) 60 wt % PVDF.

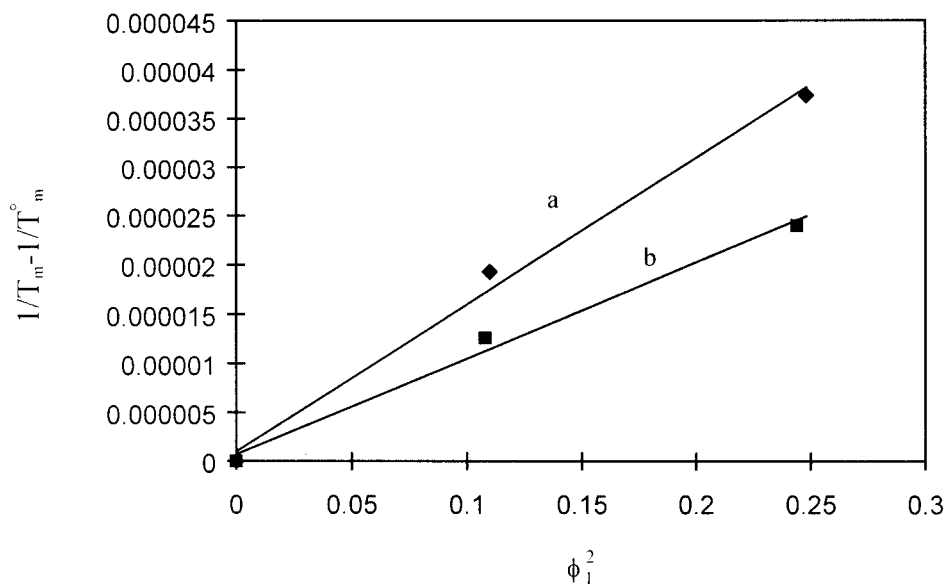


Figure 5 Plot of $(1/T_m - 1/T_m^0)$, as a function of ϕ_1^2 for (a) PVDF/PMMA-C₆₀-2.6, (b) PVDF/PMMA-C₆₀-7.4.

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