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Melting and crystallization behaviour of the poly(vinylidene fluoride)/poly(monobenzyl itaconate) blends

Issa A. Katime*, José R. Quintana, Luis C. Cesteros, and María C. Peleteiro

Departamento de Química Física, Grupo de Nuevos Materiales, Facultad de Ciencias,
Universidad del País Vasco, Apartato 644, Bilbao, España

SUMMARY

Melting and crystallization behaviour of blends of poly(vinylidene fluoride)(PVF_2) and poly(monobenzyl itaconate) (PMBzI) have been analyzed as a function of the composition in the range 100-40% PVF_2. Using the Hoffman-Week plot we have not found an equilibrium melting point depression in all the blends studied. However, the addition of PMBzI to pure PVF_2 leads to an increase in its crystallization rate. The results suggest that both polymers are incompatible and that PMBzI acts as nucleating agent in the PVF_2 crystallization.

INTRODUCTION

Poly(vinylidene fluoride) (PVF_2) is a very interesting polymer due to its extraordinary piezoelectric (KAWAI 1969) and pyroelectric properties (BERGMAN et al. 1971; NAKAMURA, WADA 1971). On the other hand, PVF_2 shows a very useful combina-tion of processability, mechanical resistance. Therefore the study of blends with others polymers is of great importance both from the scientific and practical point of view.

A large number of polymer blends containing PVF_2, both miscible and inmiscible have been studied. The compatible PVF_2/PMMA system has received the widest attention (NISHI, WANG 1975 and 1977; MORRA, STEIN 1982; WENDORFF 1980; NOLAN et al. 1971). Poly (vinylidene fluoride) is miscible with PMMA(NISHI, WANG, 1975) and PEMA (NOLAN et al. 1971; PAUL et al. 1978; KWEI et al. 1976; IMKEN et al. 1976) but not with higher poly(alkyl methacrylate) (NOLAN et al. 1971; PAUL et al. 1978; IMKEN et al. 1976). Poly(methyl acrylate) and poly(ethyl acrylate) are compatible with PVF2, however poly(isopropyl acrylate) and higher homologues are inmiscible (WAHRMUND et al. 1978). Likewise, PVF_2 has shown compatibility with poly(vinyl acetate), but not with propionate or butyrate (BERNSTEIN et al. 1978). On the other hand, poly(vinyl methyl ketone) is miscible with PVF_2, whereas poly(vinyl methyl ether) and polycaprolactone are not (SCHNEIDER et al. 1971).

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*To whom offprint requests should be sent

In this paper we have studied the miscibility of PVF_2 with poly(monobenzyl itaconate) by analyzing a possible influence of the amorphous polymer on the melting temperature and the crystallization kinetics of PVF_2.

EXPERIMENTAL PART

Poly(vinylidene fluoride) (PVF_2) was a commercial product supplied by Janssen Chimica. Monobenzyl itaconate (MBzI) was prepared by esterification of itaconic acid (1 mol) with benzyl alcohol (3-4 mol), using acetyl chloride as catalyst. The pure monomer was obtained by recrystallization from benzene (m.p. = 357.7-358.1 K, yield: 71%). The purity was confirmed by NMR and IR spectroscopy. Free radical polymerization of MBzI was carried out, in bulk between 360 and 323 K in N_2 using 2,2'-azobisiso(butyronitrile) (AIBN) as initiator. The sample was fractionated by solubility (THF/petroleum ether). The weight-average molecular weight, Mw, of the chosen fraction was 120,000.

Polymer blends were prepared by dissolving both polymers in N,N'-dimethylacetamide and blending the solutions in the desired proportion being the total polymer concentration of 2 g/dL. After a strong stiring the blend solution was precipitated in ethyl ether. The precipitate was centrifuged and washed with ethyl ether and again centrifuged. Finally, it was dried in vacuum for 48 hours at room temperature to complete removal of solvents.

Differential thermal analysis (DTA) was carried out using a Mettler TA-2000 differential calorimeter after previous calibration with Indium. Crystallization was realized isothermally by quenching the samples abruptly to the crystallization temperature from the temperature of 453 K at which the samples were annealed for 10 min. The heating rate applied to register the melting was 5 K/min up to 453 K.

RESULTS AND DISCUSSION

The miscibility of the blends was studied by analyzing a possible influence of the amorphous polymer on the melting temperature and the crystallization kinetics of PVF_2.

In the case of compatible polymers the presence of the amorphous component leads to a decrease in the chemical po-tential of the crystallizable polymer in the melt which is a function of the blend composition and is related to the polymer-polymer interaction parameter X. On the other hand, this chemical potential decrease raises a decrease in the melting temperatures of the blend, which was evaluated by Nishi and Wang (1975), using the Scott tretatment, and it is given by the equation:

$$\frac{1}{T_M} - \frac{1}{T_M^{\circ}} = - \frac{RV_C}{\Delta H_F^{\circ} V_A} \Phi_A^{2} X \qquad (1)$$

where T_M° and T_M are the melting temperatures of the crystallizable polymer in the pure state and in the blend, R is the gas constant, ΔH_F° is the perfect crystal heat of fusion of the crystallizable polymer, V_C and V_A are the molar volumes of the repeating unit of the crystallizable and amorphous polymers, respectively, and Φ_A is the volume fraction of amorphous polymer.

Equation (1) does not take into account the entropy contributions because its influence in the melting point depression is considered negligible. On the other hand, the melting point depression observed in the blends is a result of kinetic and thermodynamic factors. As in any polymer, the kinetic effects arise because crystals are formed at temperatures below the equilibrium melting temperature. The perfect extended chain crystals can only grow at the equilibrium melting temperature, but would take infinitely long to do so. At lower temperatures thinner lamellae develop which, therefore, melt below the equilibrium melting temperature. In order to measure the amount of enthalpic interaction, the kinetic factors first must be removed. This is done by using only the equilibrium melting temperatures for each composition, determined from the Hoffman-Weeks equation (1962):

$$T_M' = T_M^{\circ}\left(1 - \frac{1}{\mu}\right) + \frac{T_C}{\mu} \qquad (2)$$

where T_M' is the observed melting temperature for a sample crystallized at the temperature T_C and T_M° is the equilibrium melting temperature; μ is a morphological factor which is given by the ratio of the initial and final lamellar thickness. Plots of T_M' against T_C are linear with slope $1/\mu$ and will cut the line $T_M = T_C$ at T_M°.

As it is know, crystallized PVF_2 samples exhibit complicated melting endotherms. There are three types of crystals formed at low undercooling, each melting at differents temperatures. Morphological studies have shown these to comprise two crystal forms. The species melting first is the α phase. The species melting second and third were designed γ and γ', respectively, since they are both composed of γ-form crystals.

In our study, we have used large undercooling, and therefore we have obtained only α-form crystals. Figure 1 shows some melting endotherms obtained for pure PVF_2 and different blends at 415 K as crystallization temperature. The shoulder at temperatures below the peak are due to crystals formed during quenching, and recrystallization of these during melting.

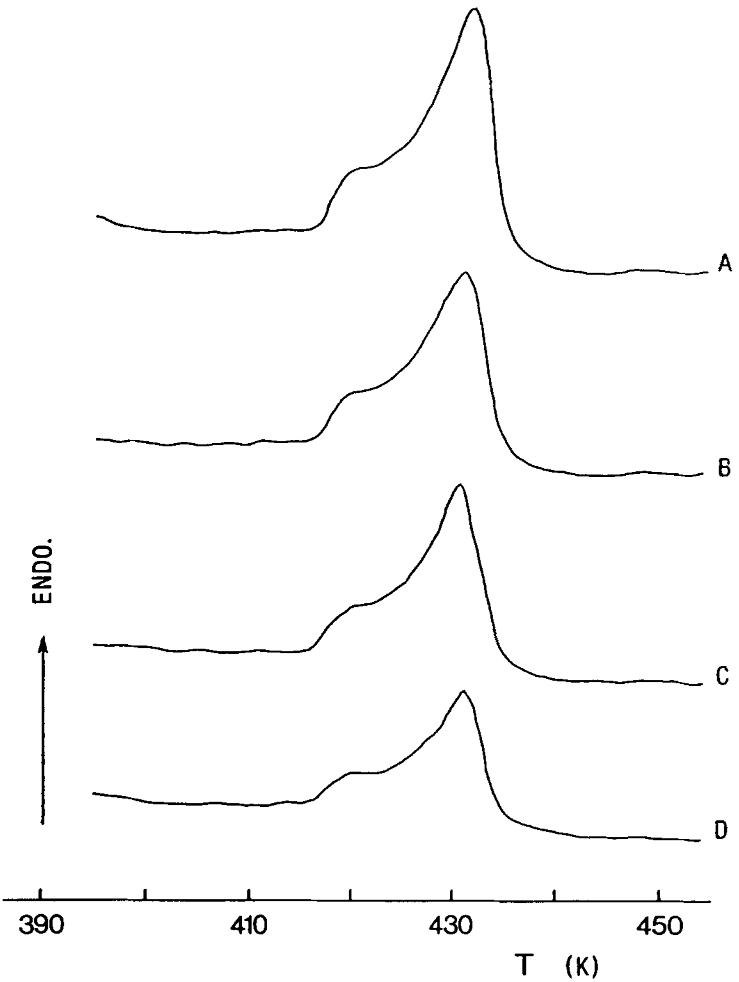

Figure 1. DTA melting curves of PVF2/PMBzI blends crystallized at 415 K. (A) 100/0; (B) 80/20; (C) 60/20 and (D) 40/60.

Figure 2 shows Hoffman-Weeks plots of the observed melting temperature, T_M, against crystallization temperature, T_c, for pure PVF_2 and PVF_2/PMBzI blends. In this case we chose for TM the temperature corresponding to the peak maximum. The melting temperatures increases linearly with the crystallization temperature at high undercooling. The values of the equilibrium melting temperatures obtained from the condition $T_M = T_c$ and the values of the morphological factor μ are given in Table 1.

Table 1. Equilibrium melting temperatures, TM, and morphological parameters, μ, calculated from Hoffman-Weeks plots for different PVF2 weight percentages.

% PVF2	TM/K	μ
100	435	5.29
80	434.7	4.74
60	434.3	4.91
40	434.8	4.35

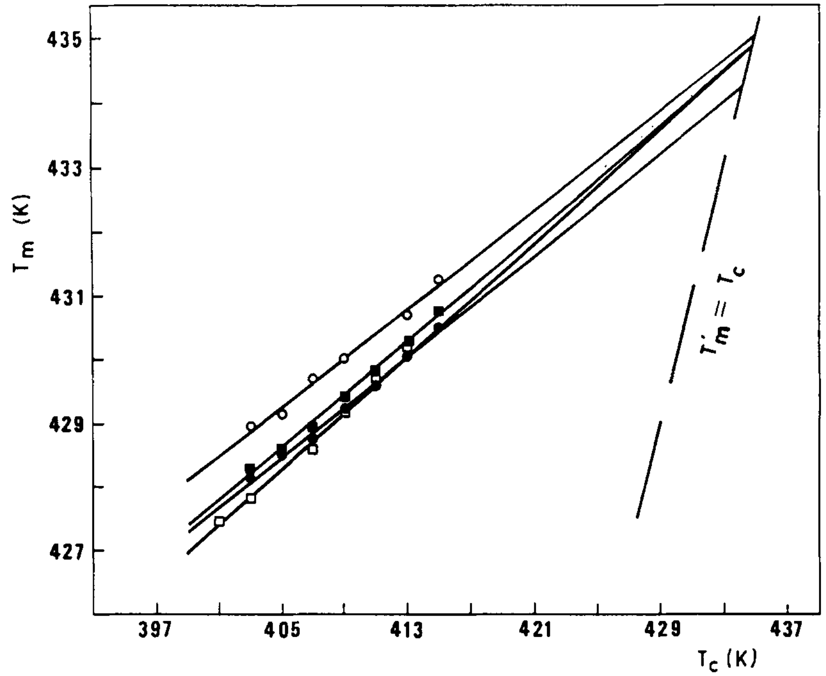

Figure 2. Hoffman-Weeks plots for PVF_2 and its blends with PMBzI: (O) PVF_2 pure; (■) PVF_2/PMBzI (80/20); (●) PVF_2/PMBzI (60/40) and (□) PVF_2/PMBzI (40/60).

It can be seen in Table 1, the addition of PMBzI to pure PVF_2 does not raise a melting point depression. The differences between the temperatures cannot be considered significant and are within the indetermination attributable to the extrapolation method. Considering Eq.(1), we can consider that the interaction parameter between both polymers is practically null. On the other hand the PMBzI content does not influence on the morphological factor μ either. These results seem to suggest that both polymers are incompatible. Although the equilibrium melting temperatures for the crystal form has been extrapolated only from low crystallization temperatures, we consider that it is enough to detect a melting point depression. So Morra and Stein (1982) shown a melting point depression corresponding to this extrapolation in PVF_2/PMMA blends.

The crystallization kinetics have been analyzed from the variation of the fraction of material crystallized, X_t, with time. Thus, for a time t, this fraction was determined by the relation:

$$X_t = \int_0^t (dH_t/dt)dt / \int_0^\infty (dH_t/dt)dt \qquad (3)$$

where the first integral is the heat generated at time t and the second is the total heat of crystallization.

The kinetics of isothermal crystallization as a function of the blend composition and crystallization temperature, were analyzed by means of the Avrami equation (1938):

$$(1 - X_t) = \exp(-Kt^n) \qquad (4)$$

where n is the Avrami exponent, a numerical value, which can provide information on the kind of nucleation and on the geometry of growing crystals; K is the rate constant which also can be calculated from the half crystallization time, $t_{\frac{1}{2}}$, defined as the time taken for half of the crystallinity to develop, and the exponent n, since:

$$K = \frac{\ln 2}{t_{\frac{1}{2}}} = \frac{0.693}{t_{\frac{1}{2}}} \qquad (5)$$

Both K and n are diagnostic of the crystallization mechanism. Plotting the quantity $\log[-\ln(-X_t)]$ against log t for the studied blends, linear trends have been observed, indicating that for all the temperatures investigated, the crystallization kinetics of these blends follow the Avrami exponent obtained from the slope of the straight lines, are very close to 2, showing that the Avrami exponent is not influenced by the addition of the amorphous component.

The half crystallization time is plotted against the PMBzI content for different crystallization temperatures in

Figure 3. The addition of PMBzI to pure PVF_2 leads to an increase in its crystallization rate. However, an increment in the PMBzI content does not influence the magnitude of this increase. Therefore, we think that the PMBzI acts as a nucleating agent causing an increase of the overall crystallization rate HAY et al. 1969; BANKS and SHARPLES 1963).

Taking into account that the exceptional compatibility of PVF_2 with oxygen containing polymers can be due, in many case, to strong dipolar interactions which involve carbonyl groups; the incompatibility of PVF_2 with PMBzI suggest that the benzyl groups hinder the accessibility of the carbonyl groups to dipolar influences of PVF_2.

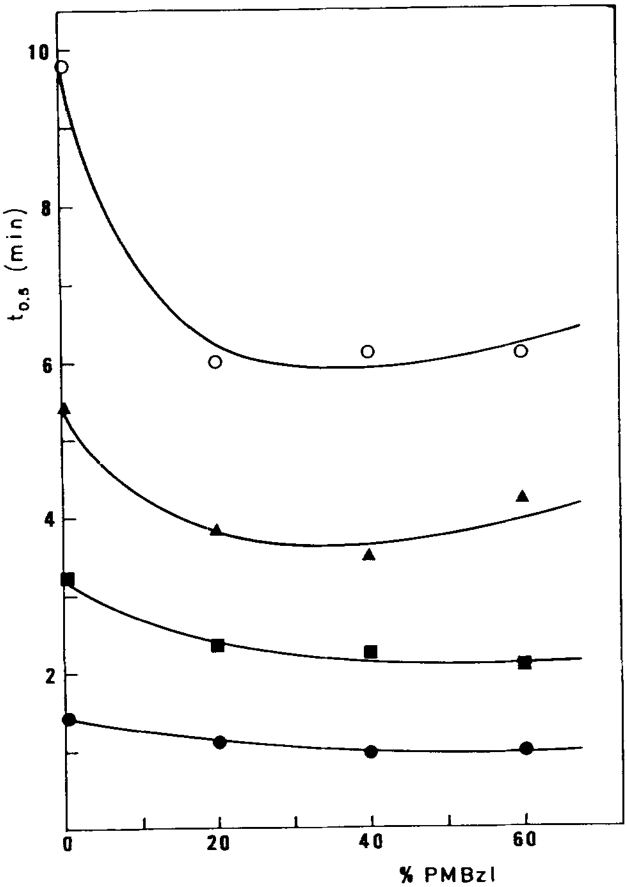

Figure 3. Plots of half crystallization time, $t_{½}$, against PVF2 composition at different crystallization temperatures: (○) 415 K; (▲) 413 K; (■) 411 K and (●) 407 K.

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