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On the melting behaviour of polymer single crystals in a mixture with a compatible polymer: 1. Poly(vinylidene fluoride)/poly(methyl methacrylate) blends

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Melting point depression techniques are used to test the compatibilty of poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA). The novelty of the experimental approach lies in the morphology of the melting lamellae, which is kept constant by using identical single crystals in various mixtures with PMMA. The values obtained for the Flory–Huggins interaction parameter are critically compared with those existing in the literature. Besides that, the effect of PMMA upon the kinetics of melting of PVDF is described.

(Keywords: polymer compatibility; melting point depression; PVDF/PMMA blends)

INTRODUCTION

The crystallization and melting behaviour of semi-crystalline polymers is known to be profoundly affected by the presence of a second compatible polymer[1]. In fact, the observed depression of the melting temperature of the crystal has been largely used as a way of assessing the degree of compatibility of the polymers around the melting temperature[2]. The basic understanding of the method still relies on the simple idea of Nishi and Wang[3] of setting the free energy of melting of the crystals equal to the free energy of mixing ΔF_{mix} of the two components as derived from the classical lattice model theory of Flory and Huggins for polymer/solvent systems[4,5]. Here the non-combinatorial term of ΔF_{mix} is expressed through a single empirical parameter χ_{12}, the so-called Flory–Huggins interaction parameter. This parameter, which was first envisaged only to account for enthalpic effects associated with the mixing of dissimilar segments, is known to contain additional information on specific interactions as well as a variety of entropic excess[6–8] not considered in its original ideal formulation. However, it is far from the scope of the present work to persist with the current argument about the physical meanings of the χ_{12} parameter, particularly when the melting point depression method provides only a global approximation to segmental polymer compatibility. Consequently, it seems more adequate to describe the melting depression through a single constant parameter rather than considering a set of additional constants in response to other physical effects that cannot be detected by this technique. Thus, in what follows the χ_{12} parameter has to be cautiously considered as a purely empirical constant. Nonetheless, the simplifying concept adopted here for the χ_{12} parameter is currently accepted in the literature and it is indeed used to quantify the strength of the molecular interaction[2]. The main criticism of the equation derived by Nishi and Wang is that it predicts the melting point depression of infinite crystals in equilibrium with the mixture. This is, of course, a major limitation of the method and the main criticism for its applicability since most of the available data on crystal melting points are obtained under conditions far from equilibrium. One might be tempted to use Hoffman–Weeks plots[9] (T_m against T_c) and to extrapolate to $T_m = T_c$, but then crystallization effects which in turn depend on blend concentration would be overlapping the subsequent melting, mainly through the generation of different morphologies. In view of the foregoing limitations, we have developed an experimental alternative which tries to minimize the above factors by melting identical crystals of the first component in a medium of the second component. This method has already been successfully applied to blends of linear and branched polyethylene (PE)[10,11], yielding for the first time a limiting value for the degree of molecular branching to be compatible with linear segments. The current work has two aims: first, to test the validity of the Nishi–Wang approach by extending this method to the study of the melting of lamellar crystals in more conventional compatible polymers; and secondly, to obtain reliable data on the melting point of poly(vinylidene fluoride) (PVDF) crystals in the presence of poly(methyl methacrylate) (PMMA). The first aim has also been treated in recent work where the combinatorial term was tested in the PE/paraffins system[12]. In both cases the polymers are well known and there exists a significant amount of experimental evidence proving the segmental interaction between them.

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Melting point equation

In what follows, polymer 2 will be the crystalline component which melts in the amorphous component, polymer 1. The partial free energy difference per mole of polymer 2 between a crystal of infinite thickness and the supercooled liquid is given by the standard approximation

$$\Delta F_{\text{melt}} = \Delta H - T\Delta S = \Delta H(1 - T_{\text{m}}/T_{\text{m}}^{\circ}) \qquad (1)$$

where ΔH and ΔS are respectively the enthalpy and entropy of fusion per mole of repeat unit and $\Delta H/\Delta S$ is assumed to be independent of temperature and equal to the equilibrium melting temperature T_{m}°. On the other hand, the difference in free energy per mole of polymer 2 between the pure melt and the mixture is

$$\Delta F_{\text{mix}} = RT\frac{V_2}{V_1}\left[\frac{\ln\phi_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1}\right)(1-\phi_2) + \chi_{12}(1-\phi_2)^2\right] \qquad (2)$$

where V_i and m_i are the molar volume and the degree of polymerization, respectively, of polymer i and χ_{12} is the polymer/polymer interaction parameter. At the melting point $\Delta F = \Delta F_{\text{melt}} + \Delta F_{\text{mix}} = 0$, and from equations (1) and (2) one obtains

$$\frac{1}{T_{\text{m}}^{\circ}(\phi_2)} - \frac{1}{T_{\text{m}}^{\circ}} = -\frac{RV_2}{\Delta H V_1}\left[\frac{\ln\phi_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1}\right)(1-\phi_2) + \chi_{12}(1-\phi_2)^2\right] \qquad (3)$$

For m_2, $m_1 \gg 1$ the combinatorial term in equation (3) can be neglected and the equation reduces to

$$\frac{1}{T_{\text{m}}^{\circ}(\phi_2)} - \frac{1}{T_{\text{m}}^{\circ}} = -\frac{RV_2}{\Delta H V_1}\chi_{12}(1-\phi_2)^2 \qquad (4)$$

In this expression T_{m}° and $T_{\text{m}}^{\circ}(\phi_2)$ represent the melting temperatures of an infinite crystal in equilibrium with the pure melt and with a mixture of concentration ϕ_2, respectively. In real cases polymer crystals grow and melt under non-equilibrium conditions and the corrected temperature for a crystal of thickness l is given by the well known Thompson–Gibbs equation

$$T_{\text{m}}(l) = T_{\text{m}}^{\circ}\left(1 - \frac{2\sigma_{\text{e}}}{\Delta H l}\right) \qquad (5)$$

where σ_{e} is the surface energy of the folded crystal. Now, if one assumes that $T_{\text{m}}^{\circ}(\phi_2)$ is depressed by the factor given in equation (5), one can rewrite equation (4) as

$$\left(1 - \frac{2\sigma_{\text{e}}}{\Delta H l}\right)\frac{1}{T_{\text{m}}(\phi_2)} = \frac{1}{T_{\text{m}}^{\circ}} - \frac{RV_2}{\Delta H V_1}\chi_{12}(1-\phi_2)^2 \qquad (6)$$

This assumption can be supported by the fact that σ_{e} is mainly determined by the work of chain folding[13] and it is not expected to be substantially modified by the presence of the second polymer. A similar equation correcting the thickness effect upon melting has been previously proposed by Chow[14].

General aspects of the PVDF/PMMA system

PVDF is known to crystallize in different crystallographic forms[15]. The conditions of growth and stability of these phases seem to depend on a number of factors such as the type of resin (mainly H-H and T-T defects), the nature and purity of the solvent, the application of external fields, the nucleation and growth temperatures[16] and blends with other polymers[16,17]. A good description of this polymorphism can be found, for instance, in the excellent review given by Lovinger[15]. Besides this polymorphism, PVDF also exhibits solid/solid phase transformations[15]. Among these phases we are concerned here with the α and γ phases. The α phase is described as the most common one and it is obtained under normal crystallization conditions either from the melt or from most solvents. The γ phase, which forms at high crystallization temperatures, is also named the γ' phase when it is obtained from transformation of the α phase on heating.

PVDF and PMMA are compatible polymers over the whole range of composition in the melt[18] below the lower critical solution temperature at 330°C[19]. The molecular compatibility between these two polymers can be better understood by the negative value of the enthalpy of mixing due to specific interactions involving the carbonyl group of PMMA and the CH_2 group of PVDF[20,21]. Since the first determination of the χ_{12} parameter by Nishi and Wang by melting point depression there have been a number of publications[6,22–30] related to the value of the χ_{12} parameter with various figures ranging from -0.7 to -0.03. A summary of the literature data is given in *Table 1*. In this table the PVDF grade, the molecular weights of the components (where reported by the authors) and the temperature of determination of χ_{12} are given. As a comparison, data obtained by techniques other than melting point depression are also included. Although it is not the purpose of this work to analyse in detail the peculiarities of each experimental determination, some general comments on these will help us to discuss our own results. At a first glance one can easily observe that apart from the highest values of -0.7 obtained by dilatometry[30], most of the χ_{12} values are distributed around -0.2. Furthermore, techniques capable of detecting local concentration fluctuations such as small angle X-ray scattering (SAXS)[27] and small angle neutral scattering (SANS)[28] give the lowest values ($\chi_{12} \approx -0.05$ for $\phi = 0.5$) which also show concentration dependence. Concerning the melting point depression data, it seems to be a slight tendency of χ_{12} to increase with increasing molecular weight. The highest value[25] reported is -0.42 and the minimum[22] -0.10. Although Wendorff[24] has found a slight dependence of χ_{12} on concentration using this technique (see the values in *Table 1*), most of the reported works do not consider this dependence. Kwei and Frisch[31] and Chow[14] have pointed out the important role of the morphology on the melting values and they have derived correction factors to account for crystallization effects on crystal thickness. Unfortunately, these factors introduce new variables which mask the true effect of PMMA on the melting behaviour of PVDF.

EXPERIMENTAL

The samples used in this work were PVDF Dyflor 2000

Table 1

PVDF sample	10^{-3} M_w (g mol^{-1})		χ_{12}	Technique	Ref.
	PVDF	PMMA			
Kynar 821	404.3	91.5	−0.295 (160°C)	ΔT_m	3
Kureha Chemical Industries	–	80	−0.10 (177°C)	ΔT_m	22
–	–	–	−0.375 (165°C)	ΔT_m	23
Solef X 8N	100	120	−0.10/−0.20 (160°C) −0.12 for $w_2=50$	ΔT_m	24[a]
Kynar 881	555	91.5	−0.2 (170°C)	ΔT_m	9
Scientific Polymer Products	–	–	−0.42	ΔT_m	25
–	215.8	36.6	−0.11 (170°C)	ΔT_m	26
Solef X 8N	100	120	−0.03/−0.16 −0.07 for $w_2=50$	SAXS	27[a]
Du Pont	555	102	−0.059/−0.226	SANS	28
Kynar 881	555	91.5	0.19/−0.58 (200°C) −0.03 for $w_2=50$	Inverse chromatography	29[b]
–	555[c]	500[c]	−0.6/−0.7 (220°C)	Dilatometry	30

[a]The values of χ_{12} are a function of the PVDF weight fraction w_2

[b]The values of χ_{12} are a function of both PVDF concentration and solvent. The quoted values of χ_{12} are averaged for different solvents

[c]M_n values

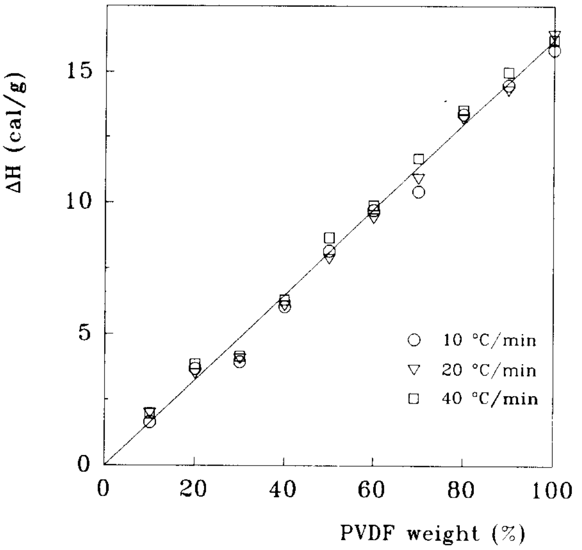

Figure 1 Experimental enthalpies of fusion of PVDF single crystals in different mixtures with PMMA

Figure 2 Transmission electron micrograph of part of an agglomerate of PVDF single crystals

from Atochem ($M_w=1.2\times10^5$ g mol^{-1}) and atactic PMMA ($M_w=8.7\times10^4$ g mol^{-1}, $M_n=5.3\times10^4$ g mol^{-1}) synthesized by Madruga and San Román[32] at the Institute of Science and Technology of Polymers in Madrid. PVDF single crystals were grown from a 0.1% (w/w) solution of PVDF in a 3/7 (v/v) mixture of cyclohexanone and bromobenzene. After dissolving the polymer at 130°C, the solution was transferred to a silicone oil bath at 125°C and the polymer was allowed to crystallize for 24 h. The single crystals were then separated from the solvent by centrifugation at 3500 rev min^{-1} over 5 min and washed several times in acetone to effect total removal of the original solvent. Finally, the samples were dried in a vacuum oven at 50°C to constant weight. PVDF single crystals were then dispersed in a hot solution of PMMA in acetone using an ultrasonic bath. Several mixtures ranging from 10 to 90% PVDF were prepared. On cooling, the PMMA precipitated and homogeneous mixtures of the two components were obtained. As a last step, the slurry mixtures were placed into aluminium differential scanning calorimetry (d.s.c.) pans and fully dried by evaporation of the acetone in a vacuum oven at 50°C.

Thermograms of the various investigated samples were obtained from a Perkin-Elmer DSC-4 using scanning rates of 10, 20 and 40°C min^{-1}. Indium was used as a calibration standard. For crystal identification in the electron microscope a drop of acetone containing crystals in suspension was deposited onto carbon-coated grids, and after drying the grids were shadowed with additional carbon at an angle of 60°. The samples were studied using a Siemens electron microscope.

RESULTS AND DISCUSSION

In *Figure 1* the experimental heats of fusion of the lamellar crystals are plotted against the PVDF concentration in the mixture. The good linear correlation confirms that the method of mixing preserves the right proportion of the components in the mixture. Morphological details of the PVDF single crystals are shown in *Figure 2*. In this electron micrograph, part of an agglomerate of single crystals can be seen. Electron diffraction patterns indicate the presence of the α phase, in good agreement with the results of Sakaoku *et al.*[33] and Grubb and Choi[34]. The

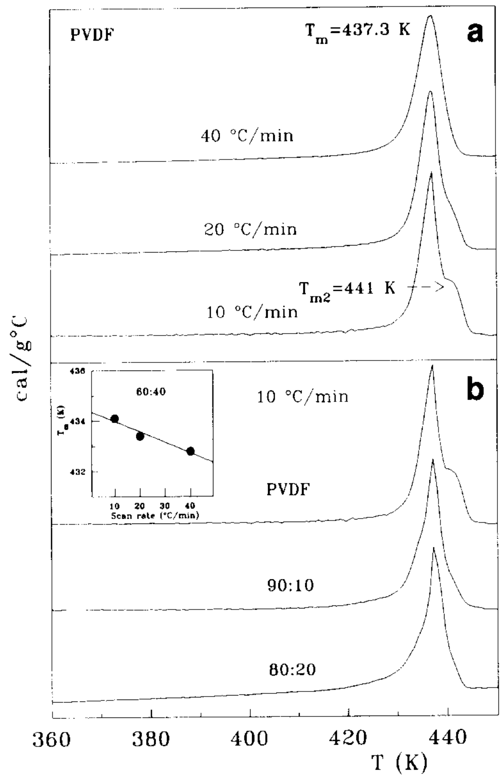

Figure 3 D.s.c. traces of PVDF single crystals at different heating rates (a) and in mixtures with 10 and 20% PMMA (b). The inset in (b) shows the variation of the melting temperature with heating rate for the 60/40 sample

habit of the lamellar single crystal is also comparable to that shown by Grubb and Choi[34], with mean values of 0.36 μm and 0.13 μm for the long axis and short axis, respectively. The thickness of the crystals as measured from the shadow length turns out to be of the order of 3 nm.

In *Figure 3a* the melting endotherms of the PVDF single crystals are shown as a function of heating rate. The measured melting points taken at the maxima are included in the figure. At the lower heating rates a high temperature shoulder is observed. The intensity of this maximum decreases with heating rate and it is practically absent for the run at 40°C min^{-1}. This second peak might be due to thickening effects during heating or to a true transformation to the high temperature γ' phase[35]. Reorganization of the crystals during heating at moderate rates is quite a common effect in semicrystalline flexible polymers[36], and it is particularly relevant for thin crystals like those formed by PVDF. The melting kinetics of PVDF are deeply modified by the presence of PMMA at the interphase. In *Figure 3b* it can be observed that the high temperature peak diminishes when 10% PMMA is added, indicating that the PMMA molecules are surrounding the PVDF crystals and are in close contact with them. The peak further diminishes in the mixture with 20% PMMA and it finally vanishes for a PMMA content greater than 30%. For higher contents of PMMA the melting curves shift to lower temperatures with increasing heating rate, showing a linear dependence with a constant slope for all the mixtures depicted in the inset of *Figure 3b*. This effect supports the idea that the crystals anneal in the mixtures in a similar way during the heating runs irrespective of the PMMA concentration. So, one might conclude that the PVDF crystals undergo two different transformations during the process of heating: one is related to the continuous thickening of the unstable thin crystals, and the other is a final transformation from the α to the γ' phase which is only observable at heating rates lower than 20°C min^{-1}. For higher heat fluxes the γ' phase is either suppressed or masked within the overall melting of the α phase. In order to evaluate the effect of PMMA and avoid at the same time the undesirable effect of the γ phase, we used the highest acceptable heating rate of 40°C min^{-1}. Undesirable overheating effects were minimized by reducing the sample weight down to 1 mg. From the experimental melting point measured at the maximum of the curve and by applying equation (5) one can get an estimate for the value of T_m° in our PVDF resin. Taking the widely accepted values of 2×10^8 J m^{-3} for the enthalpy of fusion of the α phase and 15.6×10^{-3} J m^{-2} for the surface free energy as quoted by Grubb and Choi[34], one obtains for T_m° a value of 458 K. Thus the actual melting of the crystal occurs more than 20 K below the equilibrium temperature.

The continuous effect of adding PMMA upon the melting of PVDF crystals is illustrated in *Figure 4*. The corresponding endotherms shift towards lower temperatures with increasing PMMA content as expected. It is worth mentioning that for concentrations of PMMA higher than 50%, the melting curves show increased broadening which makes it extremely difficult to define unambiguously a maximum. So, we alternatively defined the melting temperature as the mean value of the melting distribution which for a higher concentration of PVDF coincides with the maximum of the peak. The melting temperature of the PVDF crystals decreases almost continuously with increasing PMMA content at an average rate of 1.2 K per 10% additional PMMA. The $1/T_m$ data are plotted in *Figure 5* as a function of the square of the PMMA volume fraction ϕ_1. It can be seen that a well defined linear relationship is obtained in accordance with previous results[3]. Application of equation (6) allows one to determine the χ_{12} parameter from the slope of the line in *Figure 5*. Using the values of 84.5 cm^3 mol^{-1} and 34.6 cm^3 mol^{-1} for V_1 and C_2 and

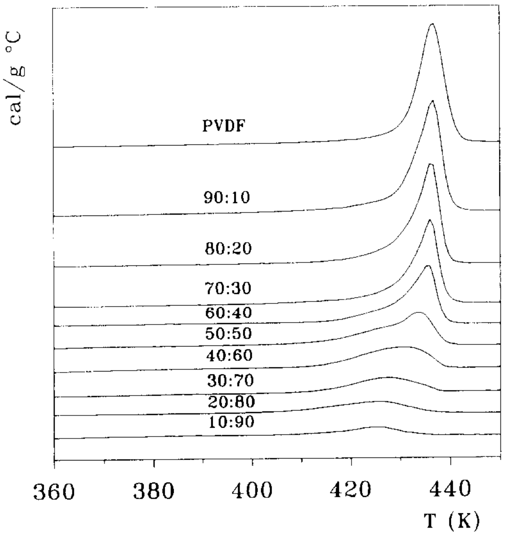

Figure 4 Melting endotherms of PVDF single crystals in different mixtures with PMMA

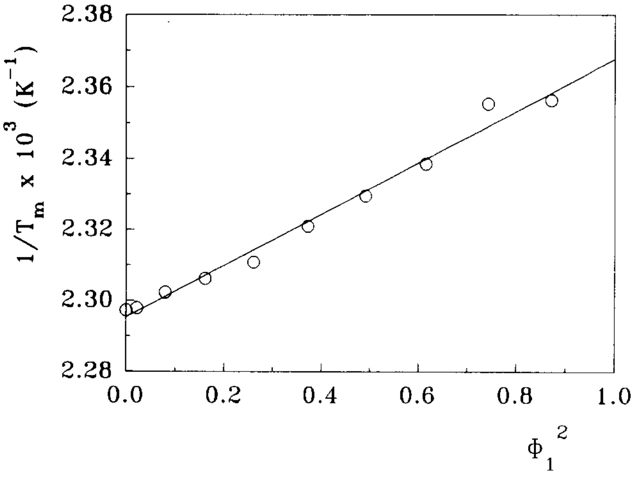

Figure 5 Variation of the reciprocal melting point of PVDF as a function of the square of the PMMA volume fraction ϕ_1

1536 cal mol^{-1} (1 cal = 4.2 J) for ΔH, the interaction parameter takes a value of -0.14. Similar plots derived from T_m at lower heating rates yield identical values for χ_{12} in the interval $0.3 < \phi_1 < 0.9$. The value found here is about half of that first published by Nishi and Wang[3] and close to the values reported by Jo Kwon[26] and Wendorff[24], although we did not observe any concentration dependence. Nevertheless, we did detect a certain levelling off for $\phi_1 > 0.8$, irrespective of the heating run used.

CONCLUSIONS

In summary, from the results shown above one can draw the following conclusions.

1. The use of PVDF single crystals in a mixture with PMMA is an elegant and effective method of studying the melting behaviour of the crystals. Besides the important point of avoiding morphological factors which could mask the true effect of PMMA upon melting, the method allows one to extend the range of experimental observations of melting down to a crystal concentration of 0.1%.
2. The PVDF single crystals in the α form, with an estimated thickness of 3 nm, reorganize during heating in the d.s.c. run and finally transform into the γ' phase. This transformation tends to decrease with increasing rate of heat flow. From the lowest melting point detected at a scanning rate of 40°C min^{-1} and using the widely accepted values of 2×10^8 J m^{-3} and 15.6×10^{-3} J m^{-2} for the enthalpy and surface free energy of melting, one can derive a value of 458 K for the equilibrium melting temperature of the α phase.
3. The presence of small amounts of PMMA at the interphase with the PVDF crystals inhibits the α to γ' transformation. However, the annealing behaviour of the crystals is not altered.
4. The melting temperature of the crystals decreases at a rate of 1.2 K per 10% additional PMMA.
5. By applying the approximation given by the classical Flory–Huggins theory one can obtain a value of -0.14 for the χ_{12} parameter. This value is independent of the heating rate used.

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