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Intermolecular interactions in poly(vinylidene fluoride) and ε-caprolactam mixtures

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Mixtures of poly(vinylidene fluoride) (PVDF) and ε-caprolactam (CPL) have been investigated as models for possible cross-interactions between vinylidene fluoride and amide structural units, that might account for the very fine phase morphology previously observed in PVDF/polyamide 6 blends. Over the entire composition range, the PVDF/CPL mixtures are monophase above the PVDF melting temperature. From the depression of the PVDF melting point, a negative interaction energy density, B, has been calculated that, however, depends on both temperature and CPL concentration. Mutual solubility of PVDF and CPL and negative B values are consistent with specific intermolecular interactions whose nature is discussed. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(vinylidene fluoride); melting point depression; intermolecular interactions; ε-caprolactam)

Introduction

Miscibility of 'unlike' polymers is driven by cross-intermolecular interactions. The stronger these interactions are, the greater is the tendency to miscibility. Conversely, a polymer pair is immiscible when the intermolecular interactions are much stronger in one of the blended polymers than in the second one. This situation would prevail in poly(vinylidene fluoride) (PVDF)/polyamide 6 (PA6) blends as a result of much stronger H bonding in the constitutive polyamide. This effect could explain the immiscibility of these two polymers, which has been observed by a set of techniques such as dynamic mechanical analysis, differential scanning calorimetry and scanning electron microscopy[1]. Nevertheless, a very fine phase morphology is currently observed, since the average size of the dispersed phases is in the range of 1.0 to 0.5 μm when PA6 is the continuous phase and 0.2 to 1 μm in the reverse situation[1]. When PVDF is substituted by polypropylene (PP), the dispersed PP phases in PA6 are larger than 4 μm[2,3]. The same observation is reported for dispersions of PP, Noryl and poly-(α-methylstyrene) in PVDF, since the average size of the dispersed phases exceeds 5 μm[4-6]. The average particle sizes in the PVDF/PA6 blends are thus much smaller than values reported for binary blends containing either PVDF or PA6 as a constitutive component.

Size of dispersed phases is controlled by a series of experimental parameters, such as chain structure, blend composition, relative polymer melt viscosities and processing conditions. Furthermore, all the other conditions being the same, the average particle size decreases with the interfacial tension[7,8]. Accordingly, the interfacial tension between PVDF and PA6 in the melt could be small enough to promote a very fine phase morphology as a result of some favourable cross-interactions. Due to experimental problems in the measurement of interfacial tension, the PVDF/PA6 intermolecular interactions have been tentatively estimated by substituting ε-caprolactam (CPL) for PA6 and investigating the parent PVDF/CPL model mixtures. This general strategy has been commonly reported in the scientific literature[9-11]. The PVDF/CPL mixtures have been analysed by differential scanning calorimetry and, since they have proved to be homogeneous above the melting temperature of PVDF (which is higher than the CPL melting temperature), depression of the melting point of PVDF has been measured as a function of the CPL concentration. The experimental data have been plotted against the mixture composition according to different relationships, as usually reported in the scientific literature[12], i.e. plot of the melting temperature (T_m) *versus* composition and plot of the melting point depression ($\Delta T_m/v_1$) *versus* v_1/T_m, where v_1 is the volume fraction of the diluent in the mixture.

Experimental

Poly(vinylidene fluoride) (Solef 1008) was kindly supplied by Solvay. ε-caprolactam (CPL) was a commercial product from Merck-Schuchardt. Since the viscosity of the melted PVDF/CPL mixtures was changing dramatically with composition, the experimental conditions of mixing were accordingly changed in such a way that the thermal properties of the final blends were independent of these mixing conditions, as ascertained by differential scanning calorimetry. Blends containing less than 80 wt% PVDF were mixed under magnetic stirring in tight glass vessels at either 150°C for 1 h (PVDF content less than 50 wt% PVDF) or 200°C for 30 min (PVDF content between 50 and 80 wt%). Mixtures containing less than 20% CPL were prepared in a Brabender internal mixer at 170°C for 30 min. In that case, the final composition was calculated from the initial composition and the CPL weight loss estimated by

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preliminary thermogravimetric analysis (t.g.a.) under the same temperature and time conditions.

Differential scanning calorimetry (d.s.c.) was performed with the DuPont 910 Thermal Analyzer at a heating rate of 20°C min^{-1}. T.g.a. was carried out with the thermogravimetric analyzer TGA51 from Du Pont.

Results and discussion

The melting point of a crystalline polymer is lowered by the addition of a soluble low molecular weight compound. Flory[13] proposed a relationship between the melting point depression and the polymer–diluent interaction parameter, χ:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{RV_u}{\Delta H_u V_l}(v_l - \chi v_l^2) \qquad (1)$$

where T_m is the melting point of the diluted polymer, T_m^0 the equilibrium melting point of the pure polymer, ΔH_u the heat of fusion, R the gas constant, V_u and V_l the molar volumes of the polymer repeat unit and the diluent, respectively, and v_l the volume fraction of the diluent.

If χ is independent of temperature and concentration, then a plot of $(1/T_m - 1/T_m^0)1/v_l$ *versus* v_l is linear, with a slope proportional to χ. However, χ, which is a function of the energy of mixing per unit volume, is inversely proportional to temperature and frequently expressed by[14,15]:

$$\chi = \frac{BV_l}{RT} \qquad (2)$$

where B is the difference between the geometric and arithmetic means of the cohesive energy densities of the polymer and diluent. Combination of equations (1) and (2) yields:

$$\left(\frac{1}{T_m} - \frac{1}{T_m^0}\right)\frac{1}{v_l} = \frac{RV_u}{\Delta H_u V_l} - B\frac{V_u}{\Delta H_u}\cdot\frac{v_l}{T_m} \qquad (3)$$

Thus, the left-hand side of equation (3) linearly depends on v_l/T_m with a slope proportional to B since $V_u/\Delta H_u$ is a constant. The melting temperature of PVDF/CPL mixtures of various compositions has been measured by differential scanning calorimetry. D.s.c. thermograms for eleven samples are shown in *Figure* 1. The melting temperature (T_m) of PVDF (177°C) is observed to decrease upon the addition of increasing amounts of CPL, whose T_m is 74°C. The melting endotherm of PVDF increasingly overlaps the melting peak of CPL as the PVDF content is decreased, particularly beyond 20 wt%. The two endotherms also overlap when the CPL content falls below 15 wt%.

Figure 2 shows a linear dependence for the PVDF melting point on the CPL content. The experimental data fit a straight line within the limits of experimental errors. Depression is as high as 60°C when 80 wt% CPL is added. This effect is so large that it reflects strong cross-interactions that deeply perturb the PVDF crystallization and not merely a change in the PVDF crystal morphology, which usually results in a T_m decrease not exceeding 15°C[16].

The application of equation (3) requires the knowledge of T_m^0 and ΔH_u. It is known that pure PVDF can exist in a variety of crystal forms that melt at different temperatures[17–21]. Since the β crystal is formed under elongation[22,23], this form may be precluded in this work. The α, γ and γ' crystals grow under different crystallization conditions, and they melt at ca. 177°C, 185°C and 192°C, respectively. Large supercooling favours formation of α crystals, in contrast to γ and γ' crystals that are formed under isothermal conditions[18–21]. This type of dependence of the melting point on the crystallization conditions has been confirmed in this study. α crystals are indeed essentially formed when solutions of PVDF in liquid CPL (monophase region in the phase diagram) are supercooled down to room temperature, which agrees with the known formation of α crystals by solution crystallization[23–27].

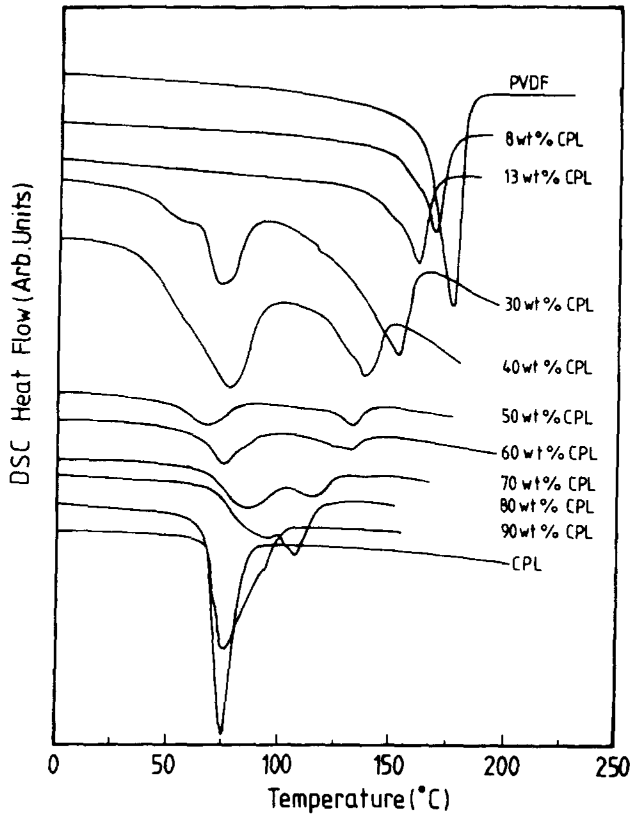

Figure 1 Differential scanning calorimetry (d.s.c.) thermograms for PVDF/CPL mixtures

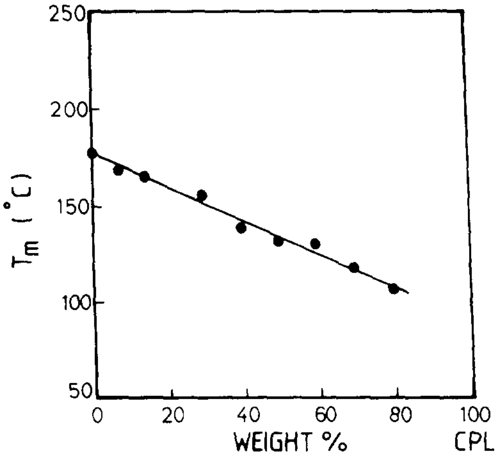

Figure 2 Dependence of PVDF melting point on CPL content

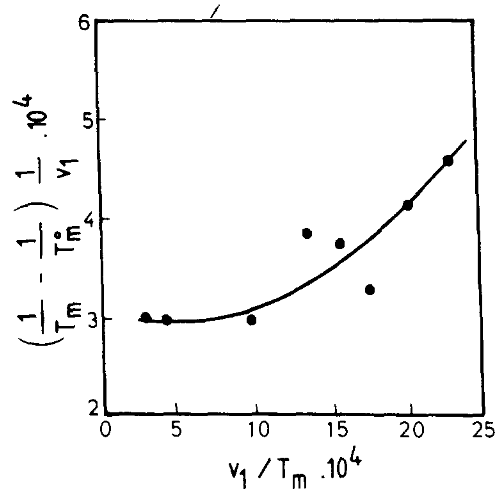

Figure 3 Dependence of melting point depression function (equation (3)) upon v_1/T_m ratio (the line is a guide to the eye)

The left-hand side of equation (3) has thus been plotted against v_1/T_m (*Figure 3*) by using values characteristic of α crystals, i.e. $T_m^0 = 177°C$, $\Delta H_u = 5965 \, J \, mol^{-1}$ (ref. 27), $V_u = 36.4 \, cm^2 \, mol^{-1}$ (ref. 28). v_1 has been calculated from the actual weight composition and the densities of PVDF ($1.78 \, g \, cm^{-3}$) (ref. 29) and CPL ($1.02 \, g \, cm^{-3}$) (ref. 30).

A nonlinear dependence is clearly observed, which more likely reflects the strong dependence of χ on concentration. For polymer–solvent systems, Welch and Miller[27] also used the Flory treatment (equations (1) and (2)) to calculate the Flory–Huggins interaction parameter (χ) for PVDF/dimethylacetamide (DMAC) mixtures. They observed the same type of plot as in *Figure 3*, and proposed that the concentration dependence of χ is responsible for this effect. Wendorff[31] used the X-ray scattering technique to study PVDF/PMMA blends. He concluded that χ was dependent on both temperature and concentration. Morra and Stein[25] extracted the interaction energy density (B) from PVDF melting point depression for PVDF/PMMA blends. They obtained negative but concentration-dependent B values.

It appears from *Figure 3* that B may not be positive at the PVDF melting temperature, which suggests the occurrence of complex specific interactions between PVDF and CPL. In this regard, Bottino *et al.*[32] calculated the solubility parameters for PVDF from solubility tests and concluded that hydrogen bonding ($\delta_{h,P} = 9.2 \, MPa^{1/2}$) was significantly contributing to the total solubility parameter ($\delta_{t,P} = 23.2 \, MPa^{1/2}$). Cangelosi and Shaw[10] suggested that hydrogen bonding in PVDF mixtures should involve the β-hydrogen atom of the repeating VDF units. According to Bernstein *et al.*[33], the specific interactions between PVDF and PMMA would imply the carbonyl groups in PMMA. Therefore, it seems reasonable that the specific interactions prevailing in PVDF/CPL mixtures are hydrogen bonds between the carbonyl part of the CPL amide groups and the β-hydrogen atoms of PVDF. They would account for the complete solubility of PVDF in CPL over the entire concentration range above the PVDF melting temperature.

Conclusions

CPL is a solvent for PVDF above the polymer melting temperature. Phase separation takes place upon cooling due to the propensity of each component to crystallize. The PVDF melting point is significantly depressed upon CPL addition. The Flory relationship for the dependence of the melting point depression on the binary mixture composition was rewritten by expressing the temperature dependence of the interaction parameter (χ) (equation (3)). A nonlinear relationship was observed for the PVDF/CPL mixtures, which emphasizes the so far neglected concentration dependence of χ. However, the interaction energy density (B) at the PVDF melting temperature may not be positive, which is indicative of specific intermolecular interactions between PVDF and the amide group of CPL.

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