Melting and crystallization of poly(vinylidene fluoride) blended with polyamide 6

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Abstract

Melting and crystallization of poly(vinylidene fluoride) (PVDF) blended with polyamide 6 (PA6) has been studied by differential scanning calorimetry. The melting of PVDF and PA6 is observed over a small temperature range, i.e. 174 to 181°C and 220 to 230°C, respectively, over the whole blend composition. This observation indicates that PVDF and PA6 are immiscible and do not co-crystallize, although evidence for intermolecular interactions between PVDF and PA6 has been previously reported. Crystallinity of PVDF seems to decrease on addition of the first 30 wt% PA6, although this effect is not so different from the experimental errors. Kinetics of non-isothermal crystallization of pure PVDF and PVDF blends containing 20 and 40 wt% PA6 has been investigated. The crystallization rate of PVDF is not influenced by PA6 in the temperature range 138.5—145°C. At lower temperatures, it is, however, adversely affected by addition of PA6. The non-isothermal crystallization data for PVDF are fitted by the Ozawa equation in the temperature range 131-141°C. The Ozawa index, or Avrami exponent, for pure PVDF decreases from 3 to 1 on decreasing temperature. This observation agrees with the nucleation of PVDF crystals which is heterogeneous, and a decrease from 3 to 1 in the growth dimension. The main effect of PA6 is to restrict the decrease of the Avrami exponent from 3 to 2 on decreasing temperature, more likely due to a slower decrease in the growth dimension. PA6 does not contribute to nucleation although it is phase separated.

Keywords: crystallization; poly(vinylidene fluoride); poly amide 6

INTRODUCTION

It is well known that the physico-mechanical properties of semi-crystalline polymers, such as poly(vinylidene fluoride) (PVDF), are strongly influenced by the extent and structure of the crystalline phase[1-4]. A recent study of PVDF modified by minor amounts of polyamide 6 (PA6) has shown that the mechanical properties of these immiscible PVDF/PA6 blends are superior to those of pure PVDF[5], particularly when the elongation at break is concerned. This observation is unusual for blends of two immiscible rigid polymers and might be associated with a change in crystallization of the continuous PVDF phase. The effect of a miscible amorphous polymer, i.e. poly(methyl methacrylate) (PMMA)[6], on the PVDF crystallization has been reported in the scientific literature. The melting temperature of PVDF is depressed by PMMA[2,7,8], and the radial growth rate of PVDF spherulites is decreased by as much as two orders of magnitude when the PMMA concentration is increased from zero to 50%[9]. It has also been reported that the nucleation mechanism is changed from multiple nucleation to single nucleation upon increasing the PMMA content[10]. Finally, the crystal form of PVDF can be altered by the addition of PMMA, depending on the experimental conditions[11,12].

Limited attention has been paid until now to the crystallization of PVDF in the presence of an immiscible component. Ambrosino and Sixou[13,14] have shown that the immiscible hydroxypropyl cellulose (HPC) reduces the Avrami exponent and changes the nucleation mechanism of PVDF. In a separate paper[5], we have shown that PVDF and PA6 are immiscible in spite of some specific intermolecular interactions. Since PA6 can crystallize in the PVDF/PA6 blends, it is worth investigating the crystallization behaviour of PVDF in the presence of crystallizable PA6.

The Avrami equation is widely used in the study of polymer crystallization, because the Avrami exponent provides information on the nucleation and growth of crystals[15,16]. However, isothermal crystallization experiments are time consuming, in contrast to non-isothermal experiments that are the most common conditions in polymer processing. Furthermore, the Ozawa equation[17] is quite useful in the analysis of non-isothermal polymer crystallization.

The purpose of this work is to examine: (i) the phase behaviour and possibility of cocrystallization in PVDF/ PA6 blends, (ii) the validity of the Ozawa equation for the non-isothermal crystallization of PVDF, and (iii) the effect of PA6 crystals on the PVDF crystallization mechanism.

EXPERIMENTAL

PVDF (Solef 1008) and PA6 (Ultramid B4) were supplied by Solvay Co. and BASF Co., respectively.
PA6 was dried in a vacuum oven at 125°C for two days before blending. PVDF and PA6 were mixed in a Brabender internal mixer at 240°C and 30revmin^{-1} for 15min. The entire PVDF/PA6 blend composition (wt/wt) was covered, i.e. 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90 and 0/100.
Melting temperature and heat of fusion were measured by differential scanning calorimetry (d.s.c.) (DuPont 910 Thermal Analyzer). Samples (ca 15mg) were heated from room temperature to 240°C at a rate of 20°Cmin^{-1} under nitrogen atmosphere. In order to erase the thermal history of the samples, a second run was carried out after the melted sample was rapidly cooled by capping the cell with a metal cooling can filled with water at 20°C.
The kinetics of non-isothermal crystallization of pure PVDF, 80/20 PVDF/PA6 and 60/40 PVDF/PA6 blends was measured with samples previously dried as explained before. The samples were heated in the d.s.c, cell (DuPont 910), under nitrogen, from room temperature up to 240°C, then held at this temperature for 10min, and cooled down to ca 80°C at various constant cooling rates: 5, 10, 15, 20, 30 and 40°Cmin^{-1}.

RESULTS AND DISCUSSION

Melting behaviour of PVDF and PA6 PVDF/PA6 blends were dried at 125°C in a vacuum oven for two days before being analysed by d.s.c, under nitrogen atmosphere. Although treatment at 125°C was necessary for drying PA6, the PVDF component was actually annealed on that occasion, which resulted in the observation of a shoulder on the low temperature side of the PVDF melting endotherm. In order to erase this annealing effect, the sample was heated in the d.s.c, cell up to 240°C and then rapidly cooled down by capping the cell with a metal can filled with water at 20°C. A second d.s.c, run was then recorded as shown in Figure 1. The melting of PVDF and PA6 is clearly observed, which is symptomatic of a lack of co-crystallization that, however, occurred when PVDF was blended with poly(vinyl fluoride) (PVF)[18]. A single melting point was indeed observed for those blends over the entire composition range, at a temperature halfway between the melting of PVDF and PVF, respectively.
Figure 1 shows that the melting temperature of each semi-crystalline polymer is essentially independent of the PVDF/PA6 polyblend composition, which is indicative of polymer immiscibility. The melting behaviour of PVDF in PVDF/PA6 blends is quite different from the behaviour reported for the PVDF/PMMA blends, although specific intermolecular interactions occur in these two types of binary blends[5,6]. Upon cooling of the melted PVDF/PMMA monophase blends, PVDF crystallizes only when its content is larger than ca 50 wt%[2,3,19,20]. This is typically the consequence of blend miscibility[1]. In contrast to the PVDF/PMMA blends, PVDF and PA6 are immiscible as a result of strong hydrogen bonds in PA6 and the propensity of this polymer to crystallization.
The dependence of the heat of fusion for PVDF and PA6 is shown in Figure 2 for PVDF/PA6 blends of various compositions. The heat of fusion of PVDF seems to decrease by ca 25% upon addition of the first 30wt% PA6, although this effect is not so different from the experimental error, which may be estimated at ca 5 J g^{-1}.
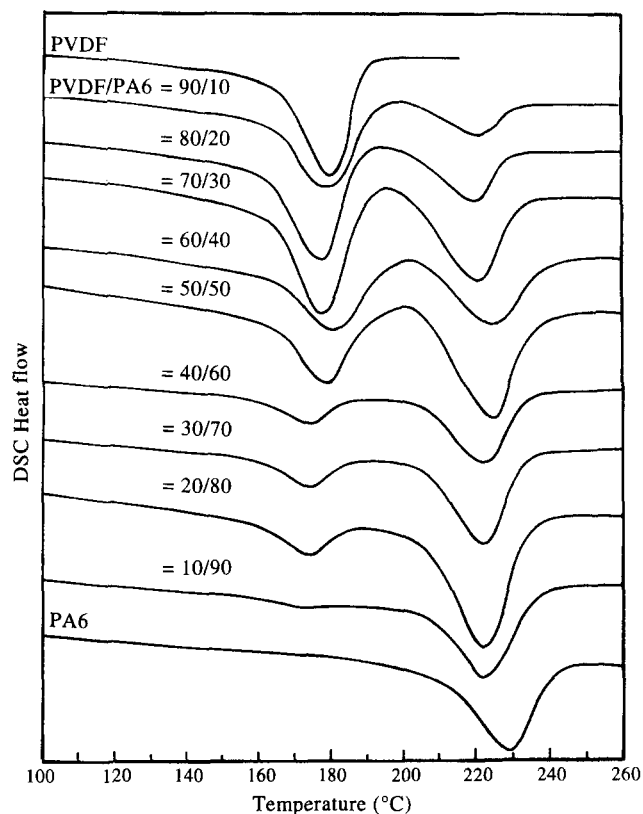
Figure 1   D.s.c. melting traces for PVDF/PA6 blends (heating rate: 20°Cmin^{-1})

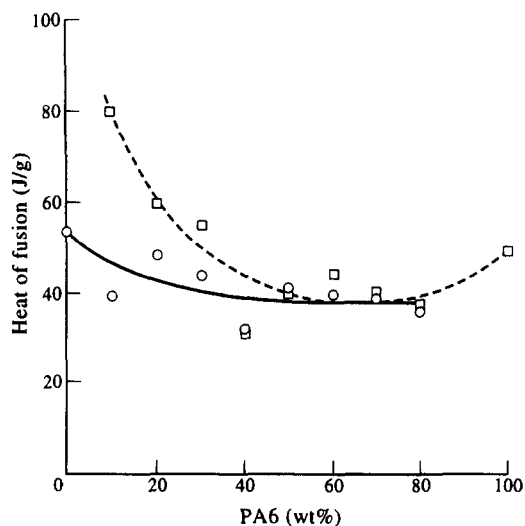*Figure 2 Heat of fusion for PVDF and PA6 versus composition for PVDF/PA6 blends: (o) PVDF; (□) PA6*

Dependence of the heat of fusion of PA6 goes through aminimum at ca 70wt% PA6. In the composition range 10-30 wt% PA6, this heat of fusion is larger than the value characteristic of pure PA6. The reverse situation is observed in the remaining composition range 30-100 wt% PA6. Since the thermal treatment of each blend is the same before recording the (second) d.s.c, scan, it appears that crystallization of one polymer is not deeply perturbed by the second one, and vice versa, except for the crystallization of PA6 in the presence of large amounts of PVDF.

Kinetics of non-isothermal PVDF crystallization Ozawa[17] has extended the Avrami equation, originally valid for isothermal crystallization, to non-isothermal conditions by assuming that the sample is cooled at a constant rate and that the mathematical analysis proposed by Evans[21] is appropriate. Accordingly, the relative crystallinity X(T), at temperature T and cooling rate γ is given by[t7]

$$1 - X_{(T)} = \exp[-k_{(T)}/\gamma^n] \qquad (1)$$

where $k_{(T)}$ is the cooling function of non-isothermal crystallization at temperature T, and n is the Ozawa index or Avrami exponent, which has a value in the range 1-4, depending on the nucleation mechanism and the growth dimension. Equation (1) can be rewritten as follows:

$$\ln[-\ln(1 - X_{(T)})] = \ln k_{(T)} + n \ln \gamma^{-1} \qquad (2)$$

In the case of a linear dependence of the left-hand side of equation (2) on $\ln \gamma^{-1}$, n and $\ln k_{(T)}$ are easily determined from the slope and the intercept of that relationship.

Figure 3 shows the crystallization exotherms for some PVDF/PA6 blends compared to pure PVDF and pure PA6, respectively (cooling rate: 10°Cmin^{-1}). Crystallization of PA6 occurs much earlier than that of PVDF upon cooling. Whether or not the PVDF crystallization is affected by the preformed PA6 crystals is one of the main questions addressed in this work.

Figure 4 shows the d.s.c, exotherms for the 60/40 PVDF/PA6 blend at various cooling rates. Quite comparable data have been collected for pure PVDF and the 80/20 PVDF/PA6 blend. The crystallization temperature is clearly shifted to lower temperatures as the cooling rate is increased.

Khanna[22] has introduced the crystallization rate coefficient (CRC), which allows for the comparison of the crystallization rate of various polymers. The CRC is calculated from the slope of the cooling rate versus crystallization temperature plot. The larger the CRC value, the faster the crystallization rate. Figure 5 shows the cooling rate-crystallization temperature relationship for PVDF in the PVDF/PA6 blends.
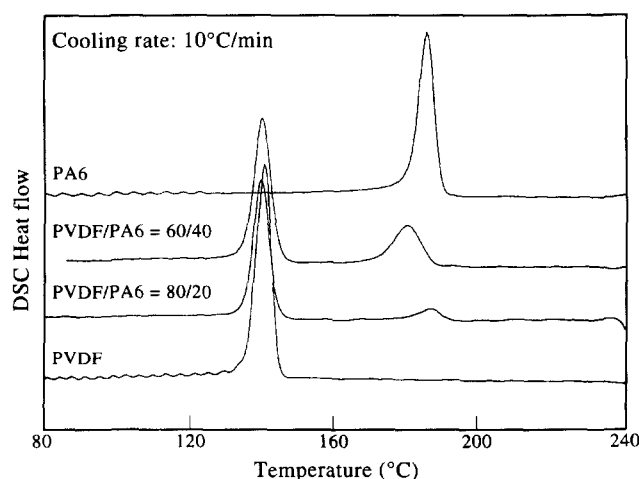

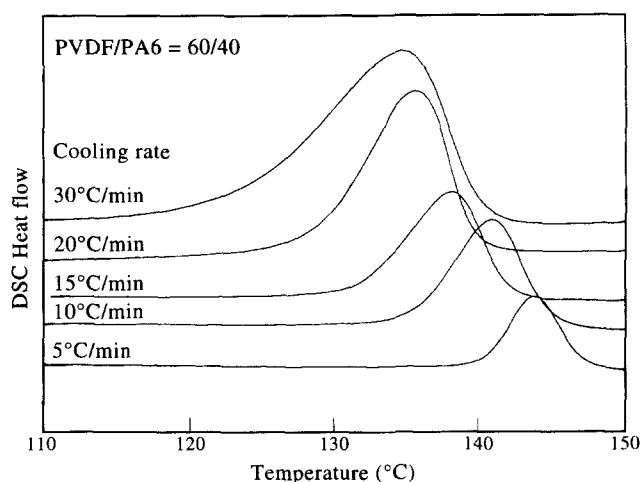*Figure 3   D.s.c. crystallization traces for PVDF/PA6 blends (10°C min^{-1})*

Figure 4   D.s.c. crystallization traces for PVDF in the 60/40 PVDF/ PA6 blend at various cooling rates
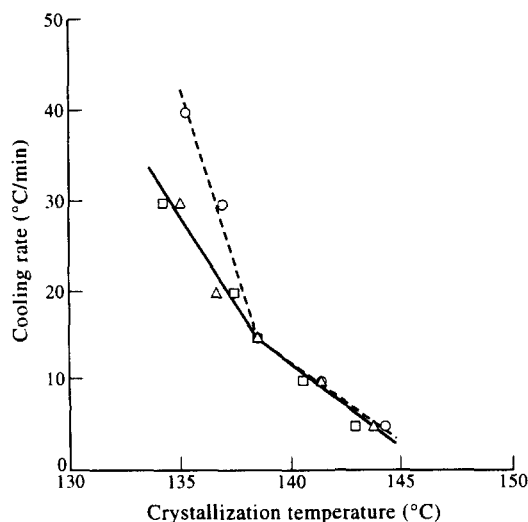
Figure 5 Cooling rate versus crystallization temperature for PVDF and PVDF/PA6 blends: (o) PVDF; (□) PVDF/PA6 (80/20); (Δ) PVDF/PA6 (60/40)

The CRC for the three samples under consideration is the same in the temperature range 138.5-145°C, i.e. 124h[-1]. Thus, the addition of PA6 does not change the overall crystallization rate of PVDF in the above temperature range. However, at lower temperatures (134—138.5°C), the CRC is different for PVDF (498 h^{-1}) and the two PVDF/PA6 blends (average CRC: 215 h^{-1}). It is usually observed that the crystallization rate increases, goes through a maximum and then decreases when the crystallization temperature is lowered from the melting point down to the glass transition. The glass transition temperature and melting temperature of PVDF are -37°C[23] and 179°C, respectively. Thus, an increase in the CRC values of PVDF in the temperature range 145-134°C in not surprising at all. The important observation is that the addition of PA6 slows down the increase in the overall crystallization rate of PVDF when the crystallization temperature is below 138.5°C. It must be noted that this effect would be amplified by corrections for thermal lag in the d.s.c. Furthermore, this effect, which is not very different for PVDF/PA6 blends containing 80 and 60wt% PVDF, might give some consistency to the small apparent decrease in the heat of fusion of PVDF when blended with PA6 (Figure 2).

The heat flow versus temperature relationship can be used to calculate the relative crystallinity $X_{(T)}$[24,25]:

$$X_{(T)} = \int_{T_0}^{T} \left(\frac{dH}{dt}\right)dt / \int_{T_0}^{T_\infty} \left(\frac{dH}{dt}\right)dt \qquad (3)$$

where T_0 and T_∞ are the lower and the upper crystallization temperatures, respectively. The relative PVDF crystallinity in the three investigated samples has been plotted against temperature, as examplified in Figure 6 in the case of the 60/40 PVDF/PA6 blend.

The calculated $X_{(T)}$ values have been analysed according to equation (2). The left-hand side of equation (2) has been plotted for a given temperature versus ln γ^{-1}, as illustrated for the 60/40 PVDF/PA6 blend in Figure 7. Since a linear relationship is usually a good approximation, the Ozawa equation[17] is applicable to the non-isothermal crystallization of the three samples, and the Avrami exponent, n, has been calculated from the slope of these straight lines.

Figure 8 shows how the Avrami exponent depends on temperature. At 141°C, the value of n is close to 3, whatever the investigated samples, which suggests that nucleation is heterogeneous, the growth of spherulites is tridimensional and the crystallization mechanism of PVDF is not affected by PA6.
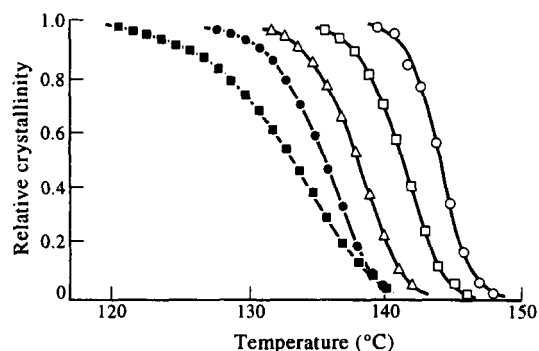
Figure 6 Relative crystallinity of PVDF versus temperature for the 60/40 PVDF/PA6 blend at various cooling rates ($^\circ Cmin^{-1}$): (o) 5; (□) 10; (Δ) 15; (●) 20; (■) 30
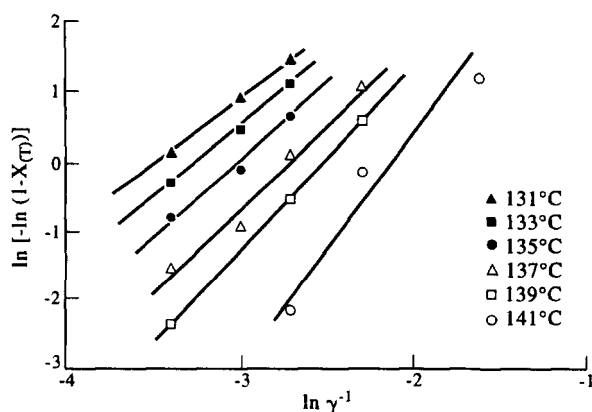

Figure 7   Plot of In[- ln[1 - $X_{(T)}$]] as a function of ln γ^{-1} for PVDF in the 60/40 PVDF/PA6 blend at various temperatures
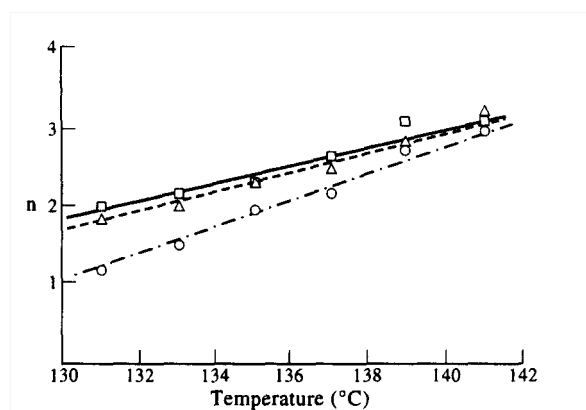

Figure 8 Avrami exponent (n) versus temperature for PVDF in PVDF/PA6 blends: (O) PVDF; (□) PVDF/PA6 (80/20); (Δ) PVDF/ PA6 (60/40)

Since n decreases with temperature, fractional values of n are observed, which is not unusual for polymer crystall!zation, e.g. for PVDF[26], polyethylene[27,28], polypropylene[29], PA6[30], poly(ethyleneoxide)[31,32], poly(p-phenylene sulfide)[33], poly(ethylene terephthalate)[34] and poly(ether ether ketone)[35].
Fractional values of n have been explained by the crystallization dependence on the nucleation and growth mechanisms[27-35]. At a constant growth dimension, n is decreased by 1 when nucleation is heterogeneous rather than homogeneous. For the same nucleation mechanism, n increases with the growth dimension, e.g. from 1 for rods, to 2 for discs and finally to 3 for spheres in the case of heterogeneous nucleation. Heterogeneous nucleation has been suggested to be responsible for fractional n values[27-35], although a decrease in the growth dimension could also be part of the explanation[27,33]. It has been proposed that spherulites start to grow as rods[36], which indeed happens in the

case of PVDF. Moreover, Nandi[37] has observed that the crystal morphology of PVDF was increasingly more disordered as the crystallization temperature was decreased. Therefore, a decrease in growth dimension with temperature seems to be a reasonable explanation for the data reported in Figure 8.

Nucleation of PVDF crystals in the miscible PVDF/ PMMA blends is usually multiple[38], indicating that PMMA is an additional nucleating agent. HPC also contributes to the nucleation of PVDF crystals although HPC and PVDF are immiscible[13,14]. The n values for PA6 containing PVDF decrease more slowly compared to those of pure PVDF upon decreasing the temperature, in agreement with Figure 5, which shows that the CRC of PVDF is not increased upon addition of PA6. This observation, which would not be qualitatively changed by corrections for thermal lag in the d.s.c., suggests that PA6 has no nucleating action. Conversely, the PA6 microdomains slow down the decrease in the growth dimension of the PVDF crystals as the temperature is decreased.

CONCLUSIONS

PVDF and PA6 do not cocrystallize over the entire composition range. The melting behaviour of PVDF and PA6 indicates that they are immiscible, in agreement with the morphology observed by transmission electron microscopy TEM[5]. The crystallinity of PVDF is not very significantly changed by the PA6 addition, although the crystallinity of PA6 goes through a minimum when the PVDF content is increased.

The overall crystallization rate of PVDF is independent of added PA6 in the temperature range 138.5-145°C, the CRC being 124 h^{-1}. However, at lower temperatures (138.5-134°C) the CRC becomes higher, although the effect is less pronounced when PA6 is added. This might explain a small apparent decrease in the PVDF crystallinity.

The Ozawa equation[17] is applicable to the non-isothermal crystallization of PVDF. The crystallization mechanism of PVDF is independent of composition at the temperature of 141°C. The nucleation of PVDF crystals is then heterogeneous and the growth dimension is 3. These characteristics are, however, dependent on composition when the temperature is decreased from 141 to 131°C. The phase separated PA6 does not contribute to nucleation, so that everything happens as the growth dimension decreases with temperature, although more slowly in the presence of PA6.

ACKNOWLEDGEMENT

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