Crystallization Studies of Polymer Blends of Nylon-11/Poly(vinylidene fluoride)

Qiong GAO[†,††] and Jerry SCHEINBEIM

Polymer Electroprocessing Laboratory, Department of Chemical and Biochemical Engineering,
School of Engineering, Rutgers University, Piscataway, NJ 08854–0909, U.S.A.

ABSTRACT: The crystallization of blends of two semi-crystalline polymers nylon-11 and poly(vinylidene fluoride) (PVF$_2$) was studied. The existence of separate melting and crystallization temperatures over the whole composition range showed that these two polymers did not co-crystallize. However, blending affected the crystallization behavior of each component. Adding nylon-11 decreased the crystallization temperature (T_c) of PVF$_2$, but increased its crystallization rate. On the other hand, the T_c of nylon-11 decreased, and its crystallization rate decreased as well when blended with PVF$_2$. The crystallization mechanism of both nylon-11 and PVF$_2$ changed in the blends compared to that in the pure states. The Ozawa index, or Avrami exponent, of PVF$_2$ in the blend decreased from 3 to 1 as the crystallization temperature decreased from 137 °C to 131 °C, compared with a decrease from 2.5 to 1.3 observed in pure PVF$_2$ at the temperature range from 145 °C to 135 °C. The Avrami exponent of nylon-11 in the blend decreased from 2 to 1 as the crystallization temperature decreased from 159 °C to 153 °C, compared with a decrease from 2.5 to 0.75 observed in pure nylon-11 at the same temperature range.

KEY WORDS   Nylon-11 / Poly(vinylidene fluoride) / Non-Isothermal / Crystallization / Ozawa's Theory / Intermolecular Interactions / Polymer Blends /

Nylon-11 and PVF$_2$ are both semi-crystalline polymers. Besides their excellent mechanical properties and chemical resistance, when uniaxially drawn, they also exhibit unique electroactive properties: high ferroelectric, piezoelectric and pyroelectric response.[1] In previous studies, we found large enhancements in ferroelectric,[2] and piezoelectric properties[3] produced by powder blending PVF$_2$ with nylon-11. The drawing behavior of PVF$_2$ was also significantly improved by blending with nylon-11. All the improvement of properties should be closely related to the structural development, especially the crystalline structure development in the blends. In this paper, we present a study of the crystallization behavior of the undrawn nylon-11/PVF$_2$ blend compared with that of the pure polymers which provide a base for establishing a structure-property relationship of this new ferroelectric polymer composite system. Nylon-11 is ferroelectric in the undrawn state while PVF$_2$ is not.

It is well known that these two polymers contain strong polar groups: CONH in nylon-11 and CF$_2$ in PVF$_2$, which, depending on their crystal structures, allows them to be ferroelectric and piezoelectric polymers. It is also known that the smaller the dipole moment difference, the more compatible the polymers. The dipole moment of the CONH group in nylon is 6.4×10^{-30} cm, while that of the CF$_2$ group in PVF$_2$ is 6.3×10^{-30} cm. For the mechanically mixed fine powder blends, the intra- and intermolecular interactions should contribute to the crystallization kinetics, crystallinity and even the polymorphic crystal form, which are all closely related to the processing and properties of these blends.

In this work, we studied the melting and crystallization behavior of these undrawn blends, comparing each components behavior with that of the homopolymers. The crystallization rates and crystallinity of each component were investigated as a function of blend composition. The crystallization mechanism of the 50/50 blend was studied using Ozawa's theory of non-isothermal crystallization.

Ozawa's Theory of Non-Isothermal Crystallization

Ozawa's model[4] of the non-isothermal kinetics of nucleation and crystal growth was derived by extending Avrami's equation[5] and Evan's approach[6] for isothermal crystallization. A constant cooling or heating rate was assumed. Crystallization is supposed to originate from a random distribution of nuclei and then expand as spheres for three dimensional growth, as discs for two dimension growth and as rods for one dimension growth.

The relative crystallinity $X(T)$ at temperature T and cooling rate γ is given by,

$$1 - X(T) = \exp[-k(T)/\gamma^n], \qquad (1)$$

where $k(T)$ is the cooling crystallization function and n is the Ozawa index or Avrami exponent, which depends on the nucleation mechanism and growth dimension.[4,7]

[†]To whom correspondence should be addressed (Tel: +1-516-801-9318, Fax: +1-516-484-7795, E-mail: Joan⎽Gao@Pall.com).
[††]Present Address: Pall Corporation, 25 Harbor Park Drive, Port Washington, NY 11050.

To obtain n and $k(T)$, eq 1 is rewritten as:

$$\ln\left[-\ln\left(1 - X(T)\right)\right] = \ln\left(k(T)\right) + n\ln\gamma^{-1}. \quad (2)$$

Plotting $\ln\left[-\ln\left(1 - X(T)\right)\right]$ versus $\ln\gamma^{-1}$ at a given temperature, T, a straight line may be obtained: n and $\ln\left(k(T)\right)$ can be estimated from the slope and intercept of the line.

This model of non-isothermal crystallization has been applied to numerous polymer systems including pure polymers, polymer blends, and polymer composite systems, such as polypropylene,[8] nylon-6,[9] poly(ethylene terephthalate),[4] poly (*p*-phenylene sulphide) (PPS),[10] *n*-paraffins,[11] polyethylene,[12] PPS/poly(ester amide) (Vectra-B950) blends,[13] and polypropylene(isotactic) in dotriacontare.[14] It has been proven to be a convenient way to study polymer crystallization and compare the crystallization behavior of different polymer systems.

EXPERIMENTAL

Fine powders of nylon-11 and PVF$_2$ (~1 μm) were mechanically mixed as described in our previous study.[2] Films of both pure polymers and blends were melt pressed and then stored in a dessicator before and after packing in differential scanning calorimetry (DSC) aluminum sample pans. All measurements were carried out using a PerkinElemer DSC-4 under a dry nitrogen atmosphere. To remove their thermal history, all film samples were first heated at $10\,°\mathrm{C\,min^{-1}}$ to $210\,°\mathrm{C}$ which is above the melting temperature of nylon-11 ($195\,°\mathrm{C}$) and PVF$_2$ ($175\,°\mathrm{C}$), and kept at $210\,°\mathrm{C}$ for 10 min. Samples were then cooled down to room temperature at different cooling rates varying from $2\,°\mathrm{C\,min^{-1}}$ to $40\,°\mathrm{C\,min^{-1}}$, to investigate the crystallization behavior, which include crystallization temperature and crystallization enthalpy changes with composition, cooling rate versus crystallization temperature and the crystallization kinetics of the 50/50 blends. For comparison, the blends and pure polymers underwent exactly the same thermo-mechanical history.

RESULTS AND DISCUSSIONS

Melting and Crystallization

Samples were first heated in the DSC cell up to $210\,°\mathrm{C}$ and kept there for 10 min to remove thermal history, then cooled to $0\,°\mathrm{C}$ at the maximum cooling rate of about $50\,°\mathrm{C\,min^{-1}}$. A second run at $10\,°\mathrm{C\,min^{-1}}$ heating rate was recorded as shown in Figure 1. The melting points of PVF$_2$ and nylon-11 were clearly observed which is symptomatic of a lack of co-crystallization. The lack of co-crystallization of these two polymers
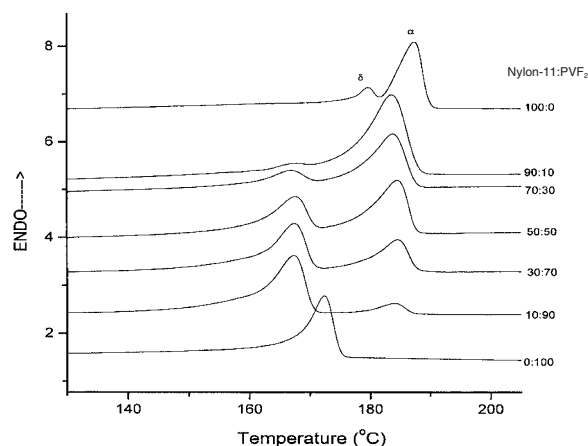

Figure 1. DSC heating traces ($10\,°\mathrm{C\,min^{-1}}$) for melt-quenched blends with different compositions after melted at $210\,°\mathrm{C}$ for 10 min and then rapidly cooled to room temperature in DSC cell.
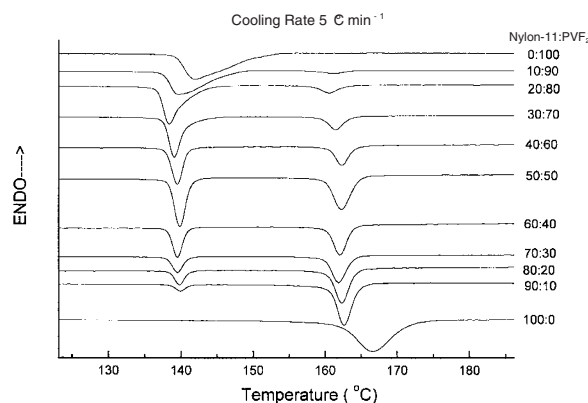

Figure 2. DSC cooling traces ($5\,°\mathrm{C\,min^{-1}}$) for melt-quenched blends with different compositions after melted at $210\,°\mathrm{C}$ for 10 min in DSC cell.

could result from the strong intermolecular hydrogen bonding in nylon-11 and the rapid crystallization of both polymers as well as the difference in their crystal structures (unit cell parameters). However, we found a significant decrease of melting points in the blends compared to their pure components. This melting point depression may indicate the existence of specific intermolecular interactions between the two polymers which should also affect both nylon-11 and PVF$_2$ crystallization behavior in the blends. Two melting peaks at $178\,°\mathrm{C}$ and $188\,°\mathrm{C}$ were observed in pure nylon-11 which correspond to the δ and α crystal forms respectively, which were also observed by Zhang *et al.*[15]

Figure 2 shows the DSC cooling traces for the blends, including those of pure nylon-11 and PVF$_2$, using a $5\,°\mathrm{C\,min^{-1}}$ cooling rate. Similar to the melting point decrease observed above, we found that both polymers in the blends also crystallize at lower temperatures compared to the pure phases. The composition dependence of the crystallization temperature is plotted in Figure 3 for nylon-11 and PVF$_2$. The crystal-
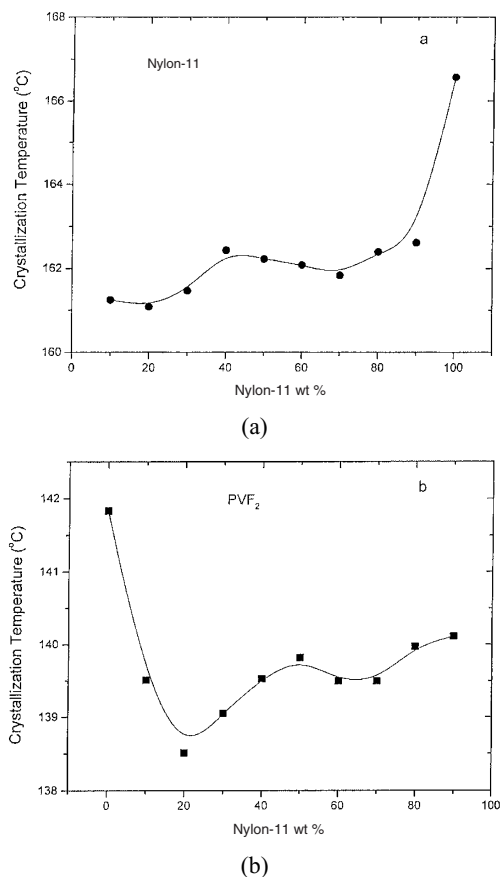
(a)

(b)

Figure 3. The composition dependence of the crystallization temperature of nylon-11 and PVF$_2$ from Figure 2.

Figure 4. The composition dependence of the crystallization enthalpy of nylon-11 and PVF$_2$ crystallized at a $5\,^\circ$C min^{-1} cooling rate.

lization temperature of nylon-11 dropped rapidly with the addition of small percentages of PVF$_2$ in the blend, then decreased more as additional PVF$_2$ was added. The crystallization temperature of PVF$_2$ also dropped rapidly with the addition of small amounts of nylon-11 in the blends, then increased as additional nylon-11 was added. We also notice that the crystallization temperature exhibited a small peak near the 40–50% composition range for both nylon-11 and PVF$_2$.

Crystallinity

We plotted the crystallization enthalpy versus composition for samples crystallizing at a $5\,^\circ$C min^{-1} cooling rate in Figure 4. We assumed that the melt or crystallization enthalpies for the different crystal phases of PVF$_2$ are approximately the same if more than one crystal phases developed in blends with different compositions. The same assumption is applied to the case of nylon-11. We can then discuss crystallinity based on crystallization enthalpy. From Figure 4c, we see that nylon-11 crystallinity decreases significantly as it became the minor phase in the blends. In contrast, PVF$_2$ crystallinity increased at that composition range. For example, in the 10:90 (10% nylon-11 by wt) blend, crystallinity increased 20% from that of pure PVF$_2$. We
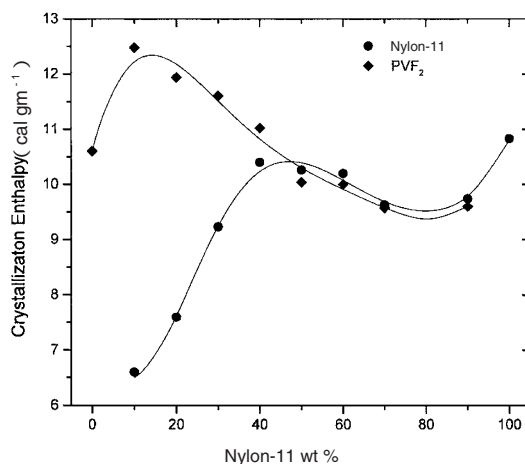
also noticed that at high and low nylon concentrations, the crystallinity of both nylon-11 and PVF$_2$ changed. The changes are much less significant when the two components are present in equal amounts. We interpret this as increased phase separation behavior. In the phase separation study of mixtures of PVF$_2$ and hydroxypropyl cellulose (HPC), Amobrosino *et al.*[16] found that the size of the dispersed phases was larger when the two polymers were in equal proportions, and decreased when one component dominated. The HPC polymer contained OH and C=O groups which should interact in a similar way as the NH and C=O moieties in nylon-11 with the PVF$_2$ polar CF$_2$ groups. For our system, in the middle of the nylon-11 concentration region, the size of each phase may also become bigger due to increased phase separation in the blends. So the crystallization behavior of each of the component phases changed less. However, this would reduce the interfacial region believed responsible for the enhancement of the remanent polarization in this concentration region.[9]

Crystallization Rate

In Figure 2, we can also see that the PVF$_2$ crystallization peak became much narrower after blending with nylon, with the change primarily on the high temperature side. Beck[17] suggested that the smaller the difference between the onset and peak temperatures, the faster the overall crystallization rate. The onset temperature indicates the beginning of the crystallization process, while the maximum of the exothermal peak indicates the occurrence of spherulite impingement if we assume that the spherulites impinge before the maximum spherulite growth rate is achieved.[18] The free expansion of the spherulites occurs between the onset and the peak temperatures. Figure 5 shows the difference between the onset and peak temperatures, ΔT_c,
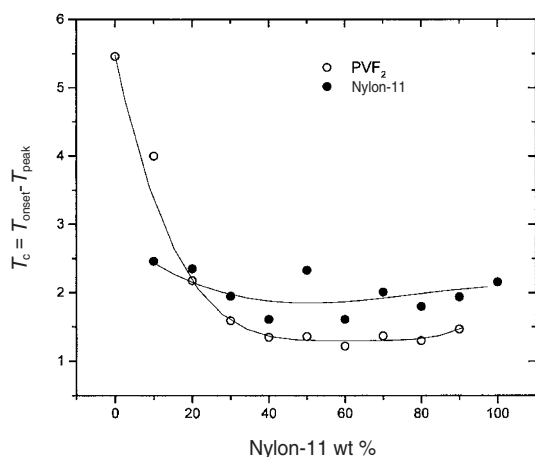
Figure 5. The difference between the onset and peak temperatures, ΔT_c, for nylon-11 and PVF$_2$ in blends with different compositions.

for nylon-11 and PVF$_2$ in blends with different compositions. From it, we see that the overall crystallization rate for PVF$_2$ in the blends is much faster than it is in the pure state. The change in nylon crystallization rate is not very obvious. This can be related to the observation in nylon-11/PECH blends[15] that the amorphous phase of nylon-11 changed less after blending with PECH. CCl groups in PECH are similar to the CF$_2$ groups in PVF$_2$ in terms of their interactions with the polar groups in nylon-11. Therefore, the crystallization kinetics of nylon in the blends is expected to change less, which is consistent with our current observations. The increase in crystallization rate of PVF$_2$ in the blend should be due to the increase of nucleation density of PVF$_2$ caused by adding nylon-11, a higher melting point polymer, to the system.

The crystallization rate can also be characterized by the crystallization rate coefficient (CRC) parameter proposed by Khanna.[19] The CRC is the slope of the plot of cooling rate versus crystallization temperature, which represents the change in cooling rate required to bring about a 1 °C change in the supercooling of the polymer melt. The larger the CRC value, the faster the crystallization rate. The CRC method allows a direct comparison of the crystallization rates of various polymers on a single scale.

Figure 6a–6c shows the crystallization of PVF$_2$, nylon-11 and a 50/50 blend at different cooling rate from 2 °C min^{-1} to 40 °C min^{-1}. Figure 7a is the plot of cooling rate versus crystallization temperature for pure PVF$_2$ and PVF$_2$ in the 50/50 blend, derived from Figures 6a and 6c. The CRC value of PVF$_2$ increased over the temperature range of 137–145 °C, which implies that the addition of nylon-11 increased the overall crystallization rate of PVF$_2$ over that temperature range. At lower temperatures, from 134 °C to 137 °C, the CRC
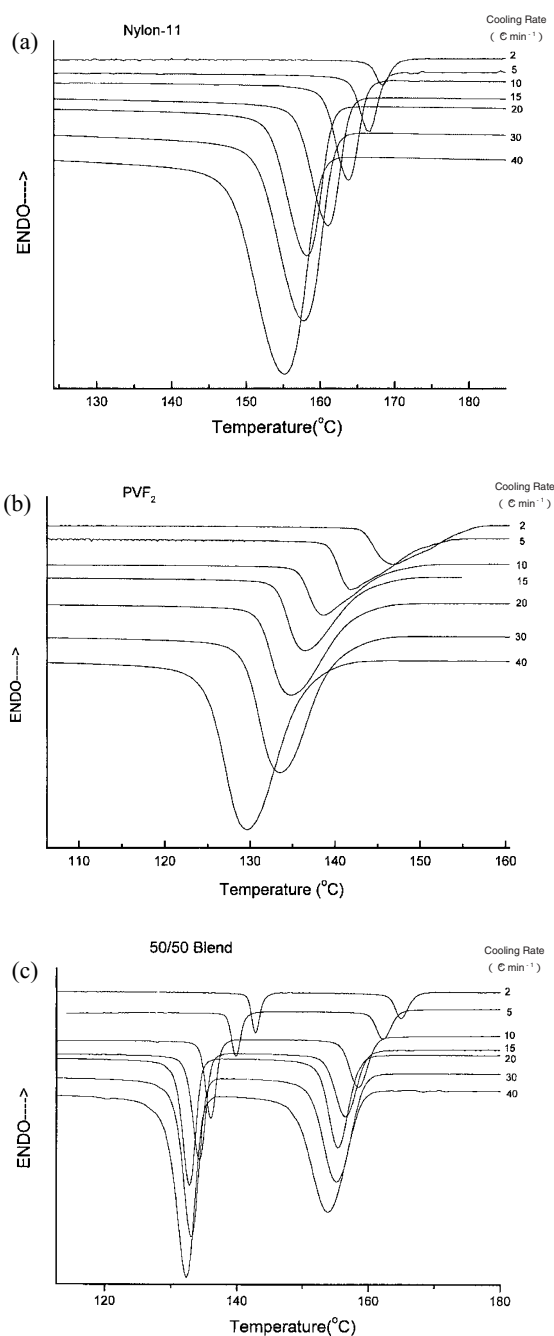

Figure 6. The effect of cooling rate on the crystallization of (a) nylon-11, (b) PVF$_2$, and (c) 50/50 blend.

of PVF$_2$ in the blend is significantly larger than that in pure PVF$_2$, which also indicates that blending with nylon-11 increases significantly the crystallization rate of PVF$_2$ over this temperature regime. Figure 7b is a plot of cooling rate versus crystallization temperature for pure nylon-11 and nylon-11 in the 50/50 blend taken from Figure 6b and 6c. We see here that the CRC value of nylon-11 decreased in the blends over the temperature range of 158–169 °C, indicating that its crystallization rate decreased. This result can be understood as the diluting effect of PVF$_2$ on nylon crystallization, be-
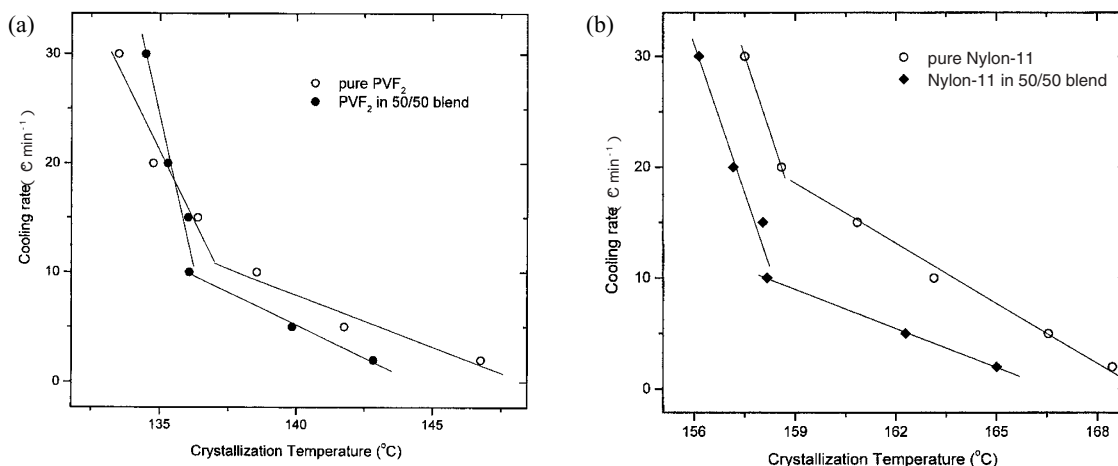
Figure 7. The plots of cooling rate versus crystallization temperature for (a) pure PVF$_2$ and PVF$_2$ in 50/50 blend from Figure 6a and 6c, (b) pure nylon-11 and nylon-11 in 50/50 blend from Figure 6b and 6c: the slope is the crystallization rate coefficient (CRC).

cause the studied temperature range is above the melting point of PVF$_2$. Correspondingly, we can attribute the increase of crystallization rate of PVF$_2$ to an increase in nucleation density resulting from the higher melting point nylon-11, acting as extra nucleation sites for PVF$_2$ crystallization.

In Figure 7a and 7b, we also observed that the CRC values increased as temperature decreased over the temperature region we investigated. It is generally recognized that the crystallization rate increases, goes through a maximum and then decreases when the crystallization temperature decreases from the melting point down to the glass transition temperature. The temperature region we investigated is located in the region that is far above the glass transition of both components, therefore the crystallization rate continuously increased as crystallization temperature decreased.

From the above study, we conclude that the crystallization rate of PVF$_2$ in the blends increased over the investigated crystallization temperature range at all compositions of the blends we studied. The crystallization rate of nylon-11 decreased with the addition of PVF$_2$ at relatively higher crystallization temperatures, from 158 to 169 °C, especially when nylon was the minor phase, which is consistent with the crystallization enthalpy decreases observed in Figure 4.

We can also see that the CRC method is more easily used for overall crystallization rate changes with temperature, and that the ΔT_c method is more easily used for the investigation of the overall crystallization rate change with composition. The combination of these two methods offers more comprehensive information on the crystallization in the blends.

Crystallization Mechanism
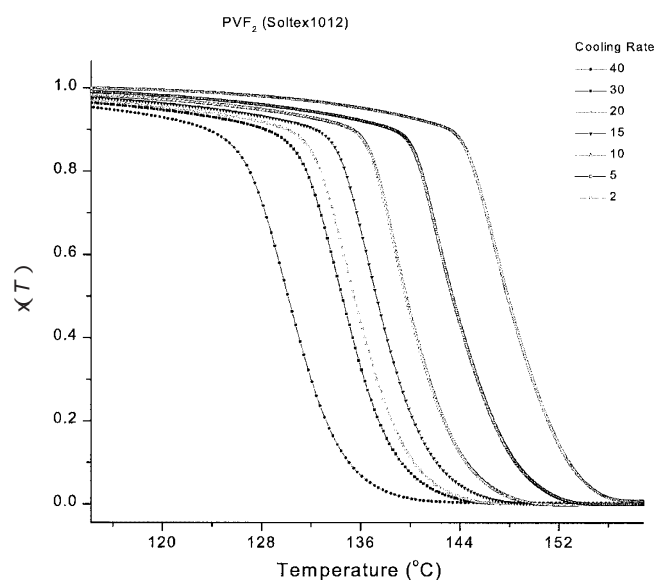
We employed Ozawa's model to analyze the non-

Figure 8. The relative crystallinity $X(T)$ change with temperature at different cooling rates for pure PVF$_2$.

isothermal crystallization curves shown in Figure 6a–6c for pure nylon-11, pure PVF$_2$, and the 50/50 blend. The relative crystallinity, $X(T)$, is calculated from the heat flow versus temperature plot as:

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

where T_0 and T are the lower and upper crystallization temperatures, respectively. Figure 8 shows how the relative crystallinity of pure PVF$_2$ changed with temperature at different cooling rates.

We plot $\ln\left[-\ln\left(1-X(T)\right)\right]$ *vs.* $\ln \gamma^{-1}$ in Figure 9a–9d for pure PVF$_2$, PVF$_2$ in the 50/50 blend, pure nylon-11, and nylon-11 in the 50/50 blend, respectively. A linear relationship is assumed, despite the scattering of the pure nylon-11 data. The Avrami exponent, or Ozawa index, n is obtained by the slope of these straight lines
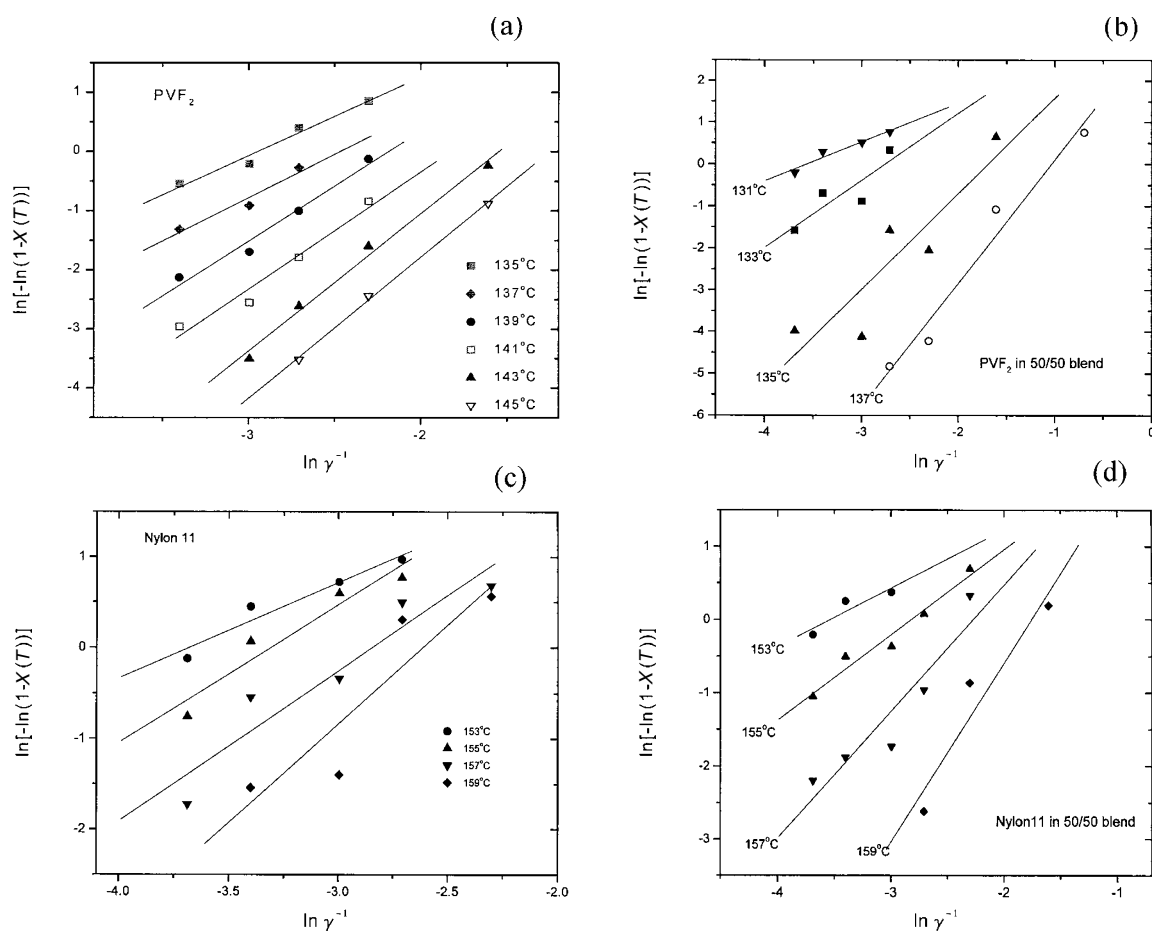
Figure 9. Plots of $\ln\left[-\ln\left(1-X(T)\right)\right]$ *vs.* $\ln\gamma^{-1}$ for (a) pure PVF$_2$, (b) PVF$_2$ in 50/50 blend, (c) pure nylon-11, and (d) nylon-11 in 50/50 blend.
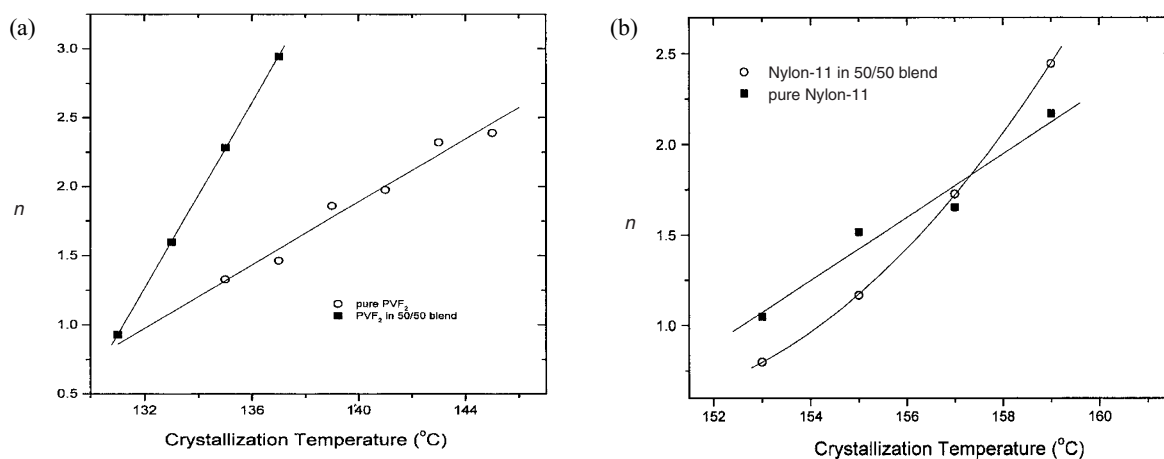

Figure 10. Ozawa's index, n, versus crystallization temperature for (a) pure PVF$_2$ and PVF$_2$ in 50/50 blend, (b) pure nylon-11 and nylon-11 in 50/50 blend.

shown in Figures 10a and 10b.

In Figures 10a and 10b, we see the decrease of n with decreasing temperature. The value of n is dependent on the nucleation and crystal growth mechanism. 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

growth dimension, *e.g.*, 1 for rods, 2 for discs, and 3 for spheres in the case of heterogeneous nucleation[7]. It was also proposed that spherulites start to grow as rods, which indeed is the case for PVF$_2$ and nylon-11.[20] It was also observed that the crystallization morphology of PVF$_2$ became increasingly more disordered as the crystallization temperature decreased.[21] Therefore, it is

expected that n decreased with decreasing crystallization temperature.

Figure 10a shows the n values of PVF_2. It is seen that n of pure PVF_2 increased from 1.2 to 2.5 as the crystallization temperature increased from 130°C to 145°C, in agreement with the common view that the growth dimension of PVF_2 increases with increasing crystallization temperature. For PVF_2 in the 50/50 blend, n increased from 1 to 3 as T_c increased from 131°C to 137°C. At crystallization temperatures lower than 131°C, n is about the same, 0.8 (not shown in Figure 10a), for both pure PVF_2 and PVF_2 in the blend, indicating that the crystallization mechanism may be the same in both systems over that crystallization temperature region. When the crystallization temperature increased, a large difference in n was observed. After considering the crystallization temperature decrease by blending, we still see that n of PVF_2 in the blends is much larger than it is in the pure state. If we expected an increase in nucleation density for PVF_2 caused by the presence of nylon-11 solid in the blends changing nucleation from more homogeneous to more heterogeneous, which however decreased n, then the growth dimension of PVF_2 in the blend must be much larger than that in the pure state. For example, at $T_c = 137°C$, $n = 3$ in the blend suggests that PVF_2 crystallization proceeds *via* three-dimensional growth with heterogeneous nucleation. While at that same temperature, for pure PVF_2, $n = 1.5$, which means that the crystal growth dimension is much more constrained in the pure state than that in the blend state.

In Figure 10b we see that for pure nylon-11, n increased from 1 to 2.2 when the crystallization temperature increased from 153°C to 159°C. For nylon-11 in the 50/50 blend, n increased from 0.75 to 2.5 over the same temperature region. At lower temperatures, n of nylon-11 in the blend is slightly smaller than that in the pure state. As the crystallization temperature increased, n became larger for nylon-11 in the blend compared to that of pure nylon-11. This is due to the presence of the lower melting point PVF_2 when nylon-11 crystallized in the blends. In general, the change in n for nylon-11 produced by blending with PVF_2 is less than that for PVF_2 produced by blending with nylon-11.

From the above study, we see that Ozawa's non-isothermal crystallization model is a convenient method to compare crystallization mechanism changes over a range of crystallization temperatures. If the crystalline components have close crystal morphology and crystallization temperatures as in the case of nylon-11 and PVF_2, it is difficult to use isothermal crystallization methods. The above non-isothermal crystallization results demonstrated that the crystallization mechanism

of PVF_2 was profoundly modified by the presence of nylon-11 at crystallization T_c higher than 131°C. The crystallization mechanism of nylon-11 exhibited smaller changes because it is the higher melting point component in the blend

CONCLUSIONS

In this new ferroelectric polymer blend, both component polymers, nylon-11 and PVF_2, are capable of crystallizing separately over a wide range of composition and crystallization temperatures. However the crystallinity of both components changes as a function of blend composition. Nylon-11 crystallinity decreased with decreasing concentration, and decreased significantly when its concentration became less than 40%. PVF_2 crystallinity increased when small amounts of nylon-11 were added, but PVF_2 crystallinity decreased when its concentration was lower than 40%. Both the melting and crystallization temperature of nylon-11 are depressed by the blending which is attributed to intermolecular interactions between the polar moieties of the two polymers.[3] The crystallization rate of PVF_2 increased in the presence of nylon-11; the nylon-11 crystallization rate decreased slightly when blended with PVF_2 which has lower melting point. The non-isothermal crystallization kinetics analysis based on Ozawa's theory revealed the change of crystallization mechanism. The crystallization mechanism of PVF_2 is profoundly modified by the presence of nylon-11, as indicated by the change of the Avrami exponent. The Avrami exponent, n, of PVF_2 in the 50/50 blend is larger than that of pure PVF_2 over the range of crystallization temperatures studied. The Avrami exponent of nylon-11 in the 50/50 blend decreased when temperature was lower than 157°C, which agrees with that its crystallization rate decrease compared with that of pure nylon-11. It was suggested that PVF_2 acted as a diluent when nylon-11 crystallized while nylon-11 acted as a nucleation agent.

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