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Crystalline Homopolymer–Copolymer Blends: Poly(tetrafluoroethylene)–Poly(tetrafluoroethylene-*co*-perfluoroalkylvinyl ether)

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ABSTRACT: In the present paper we focus on the miscibility and crystallization behavior of mixtures of poly(tetrafluoroethylene) (PTFE) and poly(tetrafluoroethylene-*co*-perfluoroalkylvinyl ether) (PFA). PFA is a random copolymer of tetrafluoroethylene and a small amount of perfluoropropylvinyl ether. Although miscibility is difficult to assess directly due to the uncertain origin of the mechanical α-transition, the crystallization and melting behavior of the blends points to significant mixing. Under most crystallization conditions investigated, PTFE and PFA were found to crystallize in distinguishable crystalline regions, with PTFE acting as an effective nucleant for at least a portion of the PFA. Under very rapid crystallization conditions, DSC data indicate that PTFE and PFA cocrystallize, lending further support to the idea that the polymers are well mixed in the melt.

1. Introduction

Mixtures of engineering polymers have been under intensive investigation in industrial and academic laboratories for many years. Such blends are frequently multiphase, and as a result, much emphasis has been placed on developing interfacial agents (e.g., block or graft copolymers) to provide the required dispersion and interfacial characteristics for suitable mechanical performance. Relatively strong intermolecular interactions are often required to attain melt miscibility although there are a number of cases where the components' chemical structures are sufficiently similar so that, although small, the combinatorial entropy is apparently sufficient to overcome unfavorable dispersive forces. Some examples of this situation are blends of polyethylenes,[1,2] poly(vinyl fluoride–trifluoroethylene) copolymers,[3] and homopolyester-segmented block copoly(ester–ether) blends.[4,5] In addition, in each of these cases the component polymers are both crystallizable and the unit cell structures and crystal compositions are very similar or identical, providing the opportunity for cocrystallization.

In the present paper we explore the miscibility and crystallization behavior of blends of two crystalline fluoropolymers that have similar chemical structures: poly(tetrafluoroethylene) (PTFE) and a random copolymer of tetrafluoroethylene (TFE) and a small amount (~1–2 mol %) of perfluoropropylvinyl ether (PFA). The addition of the perfluoroalkoxy, even at such low concentration, renders the copolymer melt-processable, lowers the melting point by some 20 °C, and slightly reduces the material's thermal stability. To our knowledge, this paper is the first to address the subject of TFE-based fluoropolymer–fluoropolymer blends outside of the patent literature.

2. Experimental Section

A. Materials. PTFE and PFA were obtained from E. I. duPont de Nemours & Co. in the form of stabilized dispersions in water. The specific products were designated as Teflon 3170 and Teflon PFA 335, respectively. The dispersions contained 60 ± 2% and 59 ± 4% polymer, respectively (average particle size is reported to be ~0.1–0.2 μm). The perfluoroalkoxy content in PFA has been reported to be 1–2 mol % (e.g., ref 6). Using the correlation developed by Suwa et al. between M_n and the heat of crystallization (ΔH_c) for PTFE,[7] we estimate M_n for the PTFE used in our experiments (based on the ΔH_c in Table 1) to be ~3.6×10^5. The molecular weight for Teflon PFA has been reported to be $(2–4.5) \times 10^5$.[8]

Dispersions were mixed in the proportions 75/25, 50/50, and 25/75. These mixtures, as well as the neat polymer dispersions, were precipitated into acetone, air dried, and then dried overnight in a vacuum oven at 100 °C. The presence of wetting agent (octyl- or nonylphenoxypoly(ethoxyethanol)) imparted a yellowish tinge to the resulting powders, and they were repeatedly extracted with acetone (about six or seven times) until this color disappeared. Thermogravimetric analysis (TGA) experiments confirmed that no detectable surfactant remained after these extractions. Consolidation of the powders was performed in a Smart Press. The powders were sandwiched between Kapton sheets and heated at 20 °C/min and 3000 lbs of pressure to 400 °C (typical for PTFE and PFA [e.g. ref 6]), where they were held for 15 min. Maintaining the force, samples were cooled to 40 °C at a rate of 40 °C/min. As will be described, other preparation conditions were also used. Film thicknesses were 0.2–0.3 mm for all samples except for neat PFA which, as expected from its higher fluidity, was ca. 0.1 mm.

B. Characterization. Storage and loss moduli were measured (at 1 Hz) for all samples from −100 to 200 °C using a Polymer Laboratories dynamic mechanical analyzer (DMA) in the tensile mode. The heating rate in these experiments was maintained at 2 °C/min. Melting and crystallization behavior was studied using a Perkin Elmer DSC-7. Temperatures and transition enthalpies were obtained by calibration with an indium standard. Sample sizes were generally ca. 5 mg, unless otherwise noted. The heats associated with the melting and crystallization processes were generally defined by a baseline constructed from 250 °C to a temperature above which no melting or crystallization was observed. Weight loss at the processing temperature for the neat polymers and blends was determined using a Perkin-Elmer TGS-2.

A limited number of small-angle X-ray scattering (SAXS) experiments was conducted on the "as-prepared" neat polymers and blends at Oak Ridge National Laboratory. Details of the

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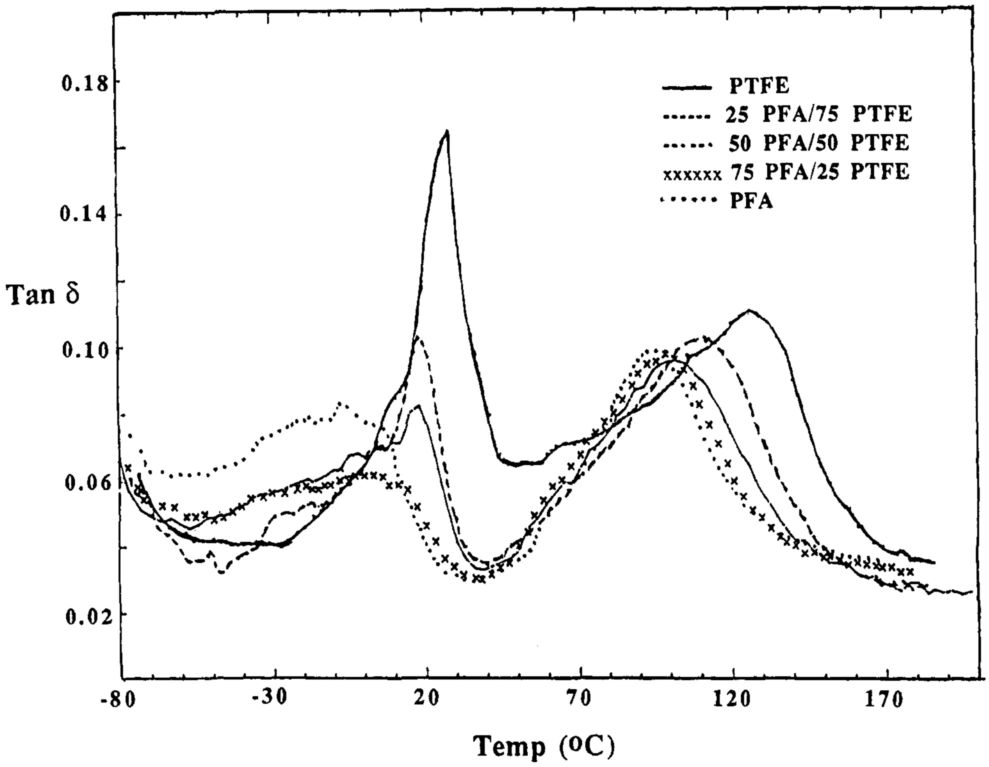

Figure 1. tan δ vs temperature (at 1 Hz) for as-prepared PTFE, PFA, and three blends.

ORNL 10-m SAXS instrument[9] and corrections to the scattering data and subsequent analysis[5] have been described in previous publications. As derived from the correlation function,[10] the as-prepared PFA exhibits a long period (L) of 28.6 nm and a linear crystallinity of 27% ($l_c = 7.6$ nm and $l_a = 21.0$ nm), in good agreement with the bulk crystallinity derived from DSC as described later in the paper. No scattering peak was observed for PTFE presumably as a result of a very large long period (e.g. ref 11). Of the blends, only the 25/75 and 50/50 PFA/PTFE mixtures exhibited a discernable scattering maximum, but the proximity to the primary radiation (i.e., they occur at low scattering vector (q)) prevented detailed analysis. However, it is clear that the peak position moves to lower q with increasing PTFE content in the blends (i.e., the average L increases from 28.6 nm to approximately 37.3 and 55.3 nm for the 25% and 50% PFA blends, respectively). Although there are a number of possible origins for this behavior, it is clear that the microstructure of the blends is not a simple combination of those of neat PFA and PTFE.

3. Results and Discussion

A. Dynamic Mechanical Behavior. Figure 1 summarizes the mechanical loss from −80 to 200 °C for as-prepared films of PTFE, PFA, and the three blends. Two transitions are clearly observed for the neat polymers. Following the nomenclature of Starkweather,[12] we refer to the high and lower temperature processes as the α- and β−transitions, respectively. It is well established that the PTFE β-process involves oscillations of chain segments within the crystalline phase and is associated with the first-order crystal disordering transitions seen near room temperature in DSC experiments.[12,13] The crystal disordering transition for PFA (as well as other PTFE copolymers) has been found to move to somewhat lower temperatures,[11,14,15] and this is consistent with the relaxation behavior seen in Figure 1. The α-relaxation of PTFE and copolymers has often been associated with cooperative, segmental (i.e. T_g-like) motion (e.g. refs 13 and 16), but this assignment remains controversial.[17]

We observe two β-processes for the as-prepared PTFE/PFA blends and, although there is some decrease in temperature of the higher temperature β-transition, the character of the parent polymers is largely retained (modified by the blend composition). As will be shown in section 3C, similar behavior is observed in DSC experiments for blends prepared under all conditions except very rapid cooling. This behavior suggests separate PTFE and PFA crystalline regions. We observe a single α-transition for the blends, which is close to that of PFA or intermediate to that of the neat polymer transitions. *If* the assignment of the α-process as that associated with segmental motion is correct, this would indicate a single amorphous environment and imply miscibility in the melt.

Since consolidation of the powdered blends was performed at high temperature, even though PTFE and PFA are considered to be relatively stable, we must be concerned with the role that degradation or interchain chemistry (through the end groups or PFA side chains) would have on the observed behavior. Isothermal weight loss of PTFE, PFA, and their physical mixtures was evaluated in air at 400 °C. Weight loss in 1 h (considerably longer than the experimental processing time) was found to be 0.09% and 0.64% for the neat PTFE and PFA powders, respectively, in good agreement with that reported recently for similar materials.[6] Weight loss for a 50/50 mixture was 0.21% in 1 h. Although the weight loss for the blend is more like that of PTFE than PFA, this in itself does not provide information on the possibility of interchain chemistry. The existence of separate PTFE and PFA crystals does, however, effectively rule out significant randomization of the repeat unit structures at high temperatures.

B. Crystallization and Melting Behavior. In an initial series of experiments, samples of the as-prepared films were heated in the DSC from ambient to 400 °C at 20 °C/min, held at 400 °C for 1 min, cooled to 100 °C at 20 °C/min, and then reheated at 20 °C/min. There

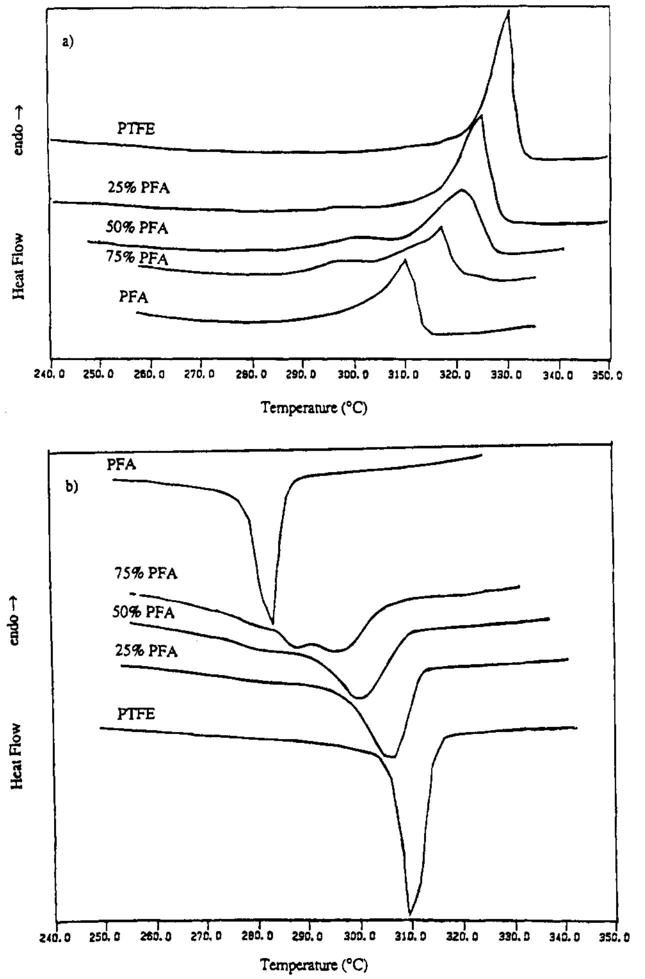

Figure 2. (a) Melting behavior of as-prepared PTFE, PFA, and blends at 20 °C/min. (b) Crystallization behavior (cooling at 20 °C/min) after 1 min of residence time in the melt at 400 °C.

Table 1. Heats of Transition and Melting Temperatures

PFA/PTFE	ΔH_f (J/g)[a]	ΔH_c (J/g)[b]	T_m (°C) main	T_m (°C) sub
0/100	40	35	329	
25/75	38	32	324	300
50/50	36	30	321	301
75/25	34	28	317	300
100/0	26	23	309	

[a] ΔH_f = heat of fusion of as-prepared materials. [b] ΔH_c = heat of crystallization on cooling at 20 °C/min (from 400 °C).

is little difference in the behavior from the first to the second run, so we will concentrate our discussion on the melting behavior of the as-prepared materials (Figure 2a) and the subsequent crystallization behavior (Figure 2b). Melting and crystallization temperatures, as well as heats of transition are summarized in Table 1. Degrees of crystallinity, based on a perfect crystal heat of fusion of 82 J/gm,[14] range from ~30 to 50%. The dominant melting endotherm for the blends is seen at an intermediate temperature compared to that of the neat polymers, although there is evidence of a second small endotherm located at a temperature below that of the PFA melting peak (but at a temperature that corresponds to the lower temperature portion of the PFA endotherm). Likewise, there is one dominant crystallization exotherm and also indication (most clearly seen for the 75/25 PFA/PTFE blend) of a lower temperature crystallization process in the blends.

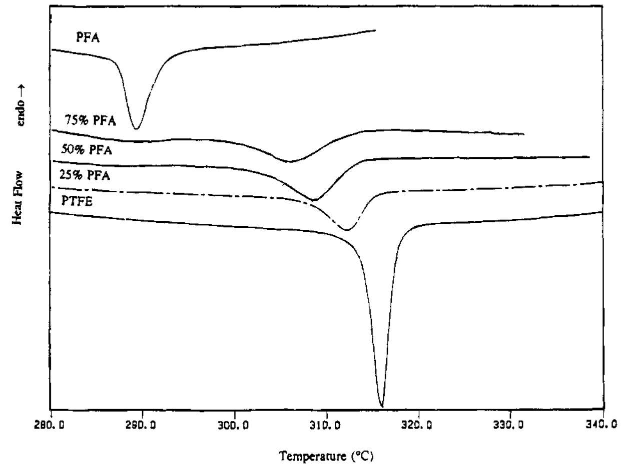

Figure 3. Crystallization behavior (cooling at 2 °C/min) after 1 min in the melt at 400 °C.

The significant influence of PTFE on the crystallization of PFA is seen particularly well in Figure 3 where the blends and neat polymers are crystallized at 2 °C/min. This behavior is reminiscent of that observed previously for polyester/segmented block copolyester blends.[5] Although not apparent in Figure 3 because of the difference in sample weights and the relative breadths of the exotherms, the heats of crystallization of all blends fall between those of the neat polymers, with the overall heat of crystallization decreasing with increasing PFA content in the blend. Further analysis shows that the "dominant" crystallization process becomes a progressively smaller portion of the total heat (e.g., roughly $^2/_3$ of the total for 25/75 PFA/PTFE). Taking as an example the 50/50 blend, it is seen that much (but not all) of the PFA in the mixture has concluded crystallization (inferred from the intermediate ΔH_c) at a temperature well above the onset of crystallization of PFA in the unblended state. Although the dominant crystallization process in the blends occurs at a lower temperature than neat PTFE (i.e., PFA inhibits the crystallization of the PTFE chains), the behavior shown in Figure 3 illustrates the role of PTFE in nucleating the crystallization of a rather significant portion of the PFA. The observation of one T_m from the primary crystallization process would seem at first to indicate cocrystallization of PTFE with a portion of the PFA (two significant melting endotherms are generally expected if PTFE simply nucleated PFA crystals) although the behavior of the crystal–crystal transitions (to be discussed shortly) strongly supports the existence of *separate crystal populations*, except for blends that are very rapidly crystallized.

As consolidation of the powders was originally conducted well above the T_m's of the neat polymers, we were curious if such a high melt temperature (and relatively long times) is required to obtain this behavior. Samples of the powder mixtures (that is, not hot pressed) were heated to 360 °C in the DSC (at 20 °C/min) and then immediately cooled at 20 °C/min. The resulting crystallization behavior is the same as that depicted in Figure 2b, and the subsequent melting behavior is essentially identical to that seen in Figure 2a. This is illustrated in Figure 4 for a 50/50 blend where curve a represents the melting of the physically-mixed powders; curve b crystallization at 20 °C/min after heating to 360 °C (no dwell time); and curve c, remelting at 20 °C/min. As seen in Figure 4, the magnitude of the lower temperature melting peak observed after consolidation in the

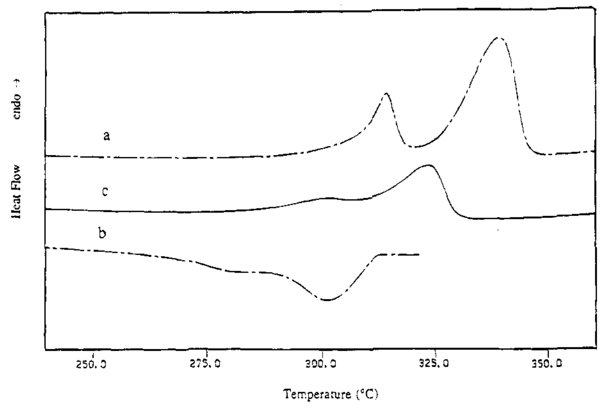

Figure 4. DSC therograms for a 50/50 mixture: (a) melting of physically mixed powders at 20 °C/min: (b) crystallization on cooling from 360 °C (no dwell time); (c) remelting at 20 °C/min.

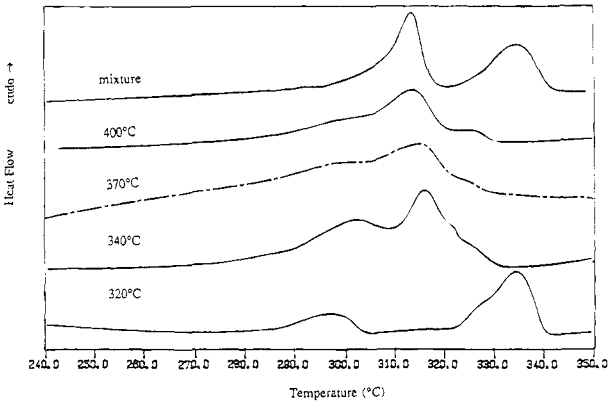

Figure 5. Melting behavior (20 °/min) of 25/75 PTFE/PFA blends hot pressed at different temperatures. Also shown is the behavior of a physical mixture.

melt (either at 400 °C or lower temperatures like 360 °C) corresponds to that of the lower temperature crystallization exotherm. Considering this, as well as the results of heating rate experiments to be presented shortly, we associate the lower temperature melting peak with the crystals formed in the lower temperature crystallization process. However, why then would the average T_m of these crystals be lower than that of neat PFA, especially considering that they have crystallized at temperatures comparable to neat PFA? Perhaps these crystals are formed from chains having a higher than average comonomer concentration (that are rejected at the growth front at higher T_c) and/or that they are of restricted thickness due to "secondary" crystallization within existing lamellar stacks. One thing is clear however—crystallization of PTFE and PFA is *not* completely separate in these mixtures.

In addition to the above experiments, 25/75 PTFE/PFA powder was hot pressed at 370, 340, and 320 °C for 15 min. DMA experiments indicate a single α-transition, even for the 320 °C melt temperature. The melting behavior of the resulting films is compared to that obtained after heating to 400 °C and for a physically mixed powder in Figure 5. The behavior of the sample melted at 370 °C is essentially identical to that obtained for the film prepared at 400 °C. The melting behavior of the sample prepared at 340 °C (i.e., just above the T_m of PTFE) is also similar to that of samples prepared at higher temperatures, although the lower temperature melting endotherm is more pronounced.

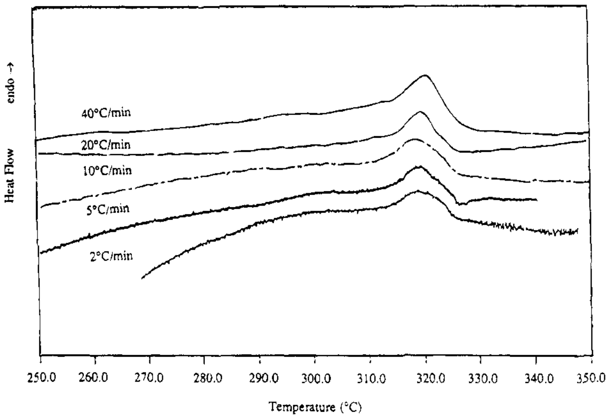

Figure 6. Heating rate dependence of the melting behavior of the 50/50 blend.

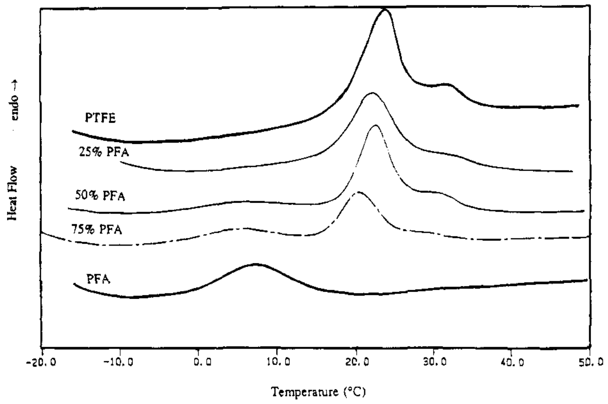

Figure 7. Thermograms of the neat polymers and blends after hot pressing at 400 °C in the region of the crystal–crystal transformations.

Figure 6 illustrates the heating rate dependence of the melting behavior of the 50/50 blend (400 °C melt temperature). These and similar experiments on other blend compositions were conducted with small sample sizes (ca. 1 mg) to minimize complications arising from low polymer thermal conductivity. It is important first to note that the negligible heating rate dependence indicates that the lower and dominant melting endotherms do not result from a melting and reorganization process during the DSC scan but arise from separate crystal populations. With respect to the dominant endotherm itself, however, there is a hint of a shoulder at higher temperatures at low heating rates, suggesting that the crystals responsible for this endotherm are capable of reorganization (thickening) during the DSC experiment.

C. Crystal Disordering Transitions. Figure 7 shows the thermograms of the as-prepared films (from the 400 °C melt temperature) upon heating from −50 to 70 °C. PTFE exhibits two well known transitions in this temperature range: one near 20 °C and another at about 32 °C. These have been assigned to solid-solid phase transformations and result in an increase of crystalline disorder.[18-20] PFA exhibits one crystalline transition in this temperature range, consistent with previous observations.[14,15] The blends, on either heating or cooling (the cooling curves are not shown), all exhibit multiple transitions—the behavior appears to be a weighted average of the thermograms of the components. This is in agreement with the DMA results presented earlier, although the additive-type behavior is in distinct contrast to the melting and crystallization behavior. The character of the thermograms of the as-

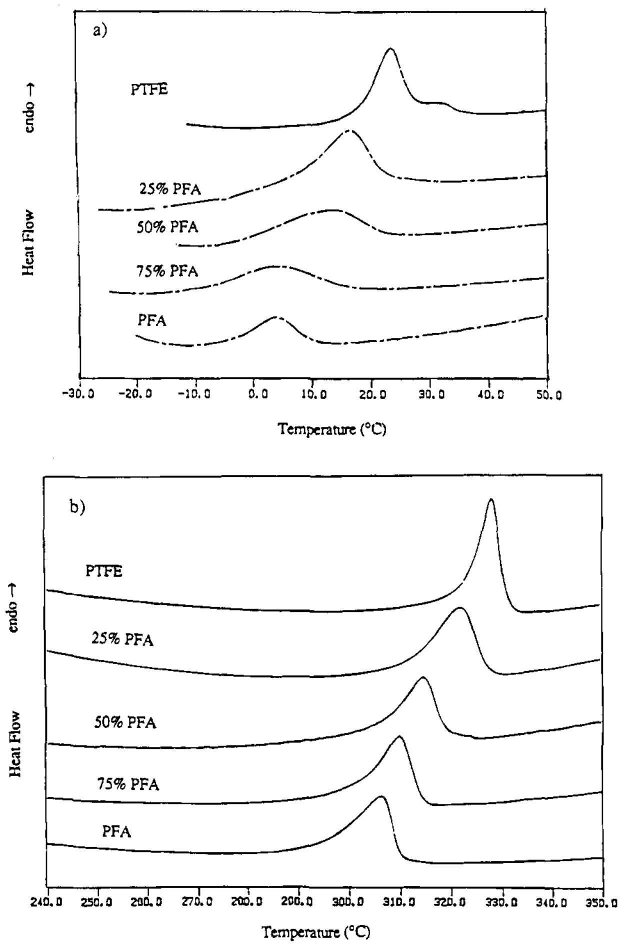

Figure 8. (a) Crystal–crystal transitions after quenching into liquid N_2 from 380 °C (20 °C/min heating rate); (b) subsequent melting behavior (at 20 °C/min).

prepared blends in this temperature interval is consistent with the idea that there are sufficiently large spatial regions of crystalline PFA and crystalline PTFE so that separate crystalline transitions are observed. Yet these regions must melt at similar temperatures as only one dominant T_m is observed.

There are crystallization conditions under which a single, intermediate-temperature transition is observed. Figure 8a shows the thermograms of the blends in the low temperature region after rapid cooling from the melt (from 380 °C) into liquid nitrogen. One intermediate transition is seen, which moves to higher temperatures with increasing PTFE content. In addition, a single melting endotherm is observed for these rapidly cooled samples (Figure 8b). Cocrystallization is well known to be favored under rapid crystallization conditions (e.g., ref 21), and we speculate that this is the origin of the behavior observed here—that is, PFA and PTFE chains are well mixed on the local level in the crystals.

4. Summary

The question of amorphous miscibility of PTFE and PFA is not easily addressed from analysis of the number and location of relaxations associated with segmental motion due to the uncertain origin of the α-transition. However, although largely circumstantial, the DSC results, including those conducted on physically mixed powders directly in the DSC, point to a significant degree of mixing of PTFE and PFA in the temperature range of interest. Upon cooling from the melt at various, relatively slow, rates (only the behavior at 20 °C/min was shown) blends of the fluoropolymers appear to crystallize as distiguishable populations, with PTFE behaving as a nucleant for crystallization of PFA chains. Finally, evidence derived from the behavior of the solid-solid phase transitions points to cocrystal formation upon very rapid solidification.

Since only dispersive forces are expected between PTFE and PFA, treatment of their miscibility using a Flory–Huggins formalism and estimating the interaction parameter (χ_{ab}) from the component solubility parameters appears to be a reasonable approach[22] and has been found to work well for other homopolymer–copolymer blends that do not exhibit strong intermolecular interactions (e.g., ref 5). χ_{ab} can be estimated using the relationship:[23]

$$\chi_{ab} = (V_r/RT)(\delta_a - \delta_b)^2 \qquad (1)$$

where V_r is the reference volume [taken as 100 cm^3/mol in our case; roughly midway between the computed[22] reference volumes of PTFE and poly(perfluoropropylvinyl ether) (PFPVE)] and δ_a and δ_b are the solubility parameters of the two polymers. Solubility parameters for PTFE and PFA were calculated using recently reported molar attraction constants.[24] The solubility parameters for TFE copolymers with perfluoropropylvinyl ether were determined by the volume fraction average of the solubility parameters of the constituents. δ_{PTFE} was found to be 5.0 (cal/cm^3)$^{0.5}$, while that of the homopolymer analogue of the FPVE comonomer was calculated to be 6.5 (cal/cm^3)$^{0.5}$. χ_{ab} for blends of PTFE and PFA with various copolymer compositions was estimated using eq 1, but it should be noted that δ's obtained by the group contribution approach are expected to only be accurate to ±0.4 (cal/cm^3)$^{0.5}$, and the corresponding variance in the calculated χ_{ab} is therefore significant.[24]

Using the Flory–Huggins expression for the free energy of mixing, the critical value of the interaction parameter (χ_{cr}) above which phase separation is predicted can be written as:

$$\chi_{cr} = (1/2)[(1/N_a^{0.5}) + (1/N_b^{0.5})]^2 \qquad (2)$$

where N_a and N_b are the degrees of polymerization of the component polymers. Assuming that the molecular weight of each polymer is 3.5×10^5 (i.e., $N \sim 3500$) leads to $\chi_{cr} = 5.7 \times 10^{-4}$. If the PTFE molecular weight was 10^6, this would lead to a somewhat smaller χ_{cr} of 3.6×10^{-4}. Considering the calculated χ_{ab}'s for these blends (assuming $T = 25$ °C), this leads to the prediction that relatively high molecular weight PFA and PTFE would be expected to be miscible when PFA contains about 4–5 wt % (~2 mol %) or less FPVE. The experimental results presented in the previous sections are consistent with the fact that the PFA used in our study is very close to or within this composition window.

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