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# Miscibility and cocrystallization behavior of two melt-processable random copolymers of tetrafluoroethylene and perfluoroalkylvinylether

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## Abstract

Miscibility, crystallization behavior, and mechanical properties of blends made from melt-processable perfluoropolymers of poly(tetrafluoroethylene-*co*-perfluoropropylvinylether) (PFA) and poly(tetrafluoroethylene-*co*-perfluoroethylvinylether) (EFA) have been examined by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). PFA and EFA (PEVE comonomer:5.7 wt%) blends cocrystallize regardless of crystallization speed and blending method. On the other hand, PFA/EFA blends that contain EFA with high PEVE comonomer content (PEVE:13.3 wt%) formed segregated crystals. However, these blends [PFA/EFA (PEVE:13.3%)] showed a composition dependent single α-relaxation temperature which suggests that they are miscible in the amorphous phase. Therefore, it is concluded that PFA/EFA blends are miscible in the amorphous or molten state, they form segregated crystals during crystallization. In contrast, EFA containing low PEVE content form cocrystals with PFA from the melt. Measuring the flex life (folding endurance) of the blends revealed that only 20% EFA (PEVE: 13.3%) is required to increase the flex life of neat PFA by four times.

*Keywords*: Cocrystallization; Crystalline polymer blend; Perfluoropolymer

## 1. Introduction

Miscibility between two amorphous polymers has been studied intensively by many researchers, especially in relation to phase separation dynamics. Miscibility between crystalline and amorphous polymers has also been examined, and a number of miscible blends are known. On the other hand, few studies have been reported on the miscibility and crystallization behavior of polymer blends between two crystalline polymers. A miscible crystalline/crystalline polymer blend is a rare phenomenon and only a few pairs have been reported to form miscible system. Although such binary blends of crystalline polymers are rare, these blends can be divided into three main categories. These are: (i) polymer/low molecular weight diluents, such as poly($\varepsilon$-caprolactone) (PCL)/Trioxane mixture [1]; (ii) two polymers of chemically different structures, such as PCL/poly(vinylidene chloride) (PVDF) [2,3], poly(3-hydroxybutyrate)/poly (ethylene oxide) [4], poly(butylene adipate)/PVDF [5–8], poly(butylene succinate) (PBSU)/PVDF [9], and PBSU/poly(vinylidene chloride-*co*-vinyl chloride) [10]; (iii) blends of chemically similar species, such as blends of two poly(aryl ether ketones) [11], blends of two polyethylenes [12], homopolymer/segmented block copolymer [13], copolymers of vinylidene fluoride/trifluoroethylene [14], poly(vinylidene fluoride)/poly(vinylidene fluoride-*co*-tetrafluoroethylene) [15], copolymers of vinylidene fluoride/tetrafluoroethylene [16], poly(tetrafluoroethylene-*co*-vinylidene fluoride)/poly(vinylidene fluoride-*co*-hexafluoroacetone) [17], poly(tetrafluoroethylene) (PTFE)/poly(tetrafluoroethylene-*co*-perfluoropropylvinylether) (PFA) [18], poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP)/poly(tetrafluoroethylene-*co*-perfluoromethylvinylether) (MFA) [19].

Recent studies of the blends in category (ii) showed that segregated crystals are formed and kinetic factors of the crystallization are important in crystallization behavior and morphology of two crystalline polymer blends [9,10]. On the other hand, there is a possibility of cocrystallization in the blends of category (iii).

Although general requirements for the cocrystallization of polymers are known: (a) close unit cell structures, (b) similar crystallization kinetics, and (c) rapid crystallization conditions, the nature of cocrystallization is still a controversy and difficult to resolve. However, the cocrystallization behavior of two crystalline polymers has been frequently observed in fluoropolymer blends [14–19]. Most recently, cocrystallization, under moderate cooling conditions, of several melt blended FEP/MFA compositions was reported by Pucciarello and Angioletti [19]. This result implies that

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blends of two melt-processable perfluoropolymers are useful systems for obtaining further insights about the cocrystallization behavior of two crystalline polymers.

In this study, the blend of PFA and poly(tetrafluoroethylene-*co*-perfluoroethylvinylether) (EFA) will serve as a melt-processable perfluoropolymer blend model to investigate the miscibility and cocrystallization behavior of two crystalline polymers. Each polymer is a random tetrafluoroethylene (TFE) copolymer with perfluoro propyl vinyl ether (PPVE) and perfluoro ethyl vinyl ether (PEVE) for PFA and EFA, respectively. The above mentioned melt processable perfluoropolymer pair was chosen because: (a) the individual components have similar chemical structures and (b) during crystallization of either the pure PFA or pure EFA it is believed that the segments containing comonomer are excluded from the PTFE crystalline unit [20]. This implies that the two blend components have similar crystalline unit cells and crystallization kinetics, fulfilling the above mentioned requirements for cocrystallization.

Additionally, if PFA/EFA blends are miscible and show cocrystallization behavior, properties of the two pure components could be improved by blending PFA and EFA. For example, since EFA shows much higher flex life than that of PFA, flex life of PFA could be improved by blending EFA. Although the flex life of EFA is improved significantly with increasing PEVE content, the melting temperature of EFA decreases with the increase of PEVE comonomer contents as in the case of other random copolymers. For example, $T_m$ of EFA containing 13.3% PEVE comonomer is 254°C, while $T_m$ of PFA is 308°C. The low $T_m$ of EFA is one of the problems that limits the utilization of EFA. However, if the blend forms cocrystals, the $T_m$ of the blend locates between the $T_m$ of the two constituent crystalline polymers, which results in the rise of $T_m$ of EFA (or lower melting component). Therefore, from an engineering point of view, the PFA/EFA blend is a useful blend pair if it forms cocrystals (i.e. rise of $T_m$ of EFA due to cocrystallization). Furthermore, a blend of PFA/EFA can improve mechanical properties (especially, flex life) of PFA (or lower flex life resin).

In this article, the results from the investigation of miscibility and crystallization behavior of PFA/EFA blends using dynamic mechanical analyzer (DMA) and differential scanning calorimeter (DSC) are reported. In particular, the effect of crystallization conditions on cocrystallization behavior of the blends was analyzed under various crystallization speeds. It was determined that PFA/EFA blends are miscible in the amorphous region because a single composition dependent α-relaxation temperatures was observed for the blends. In addition, PFA/EFA blends containing EFA with 5.7% PEVE showed very stable cocrystallization behavior regardless of crystallization conditions. Mechanical properties, such as flex life, were improved by blending. For example, blending only 20% of EFA with PFA increased the flex life of PFA by more than four times. To our knowledge, this article is the first to examine the effect of crystallization conditions on the cocrystallization behavior and to report data that supports that stable cocrystallization behavior is observed regardless of crystallization conditions. Additionally, the relationship between the miscibility, cocrystallization behavior of the blends, and the mechanical properties of the two crystalline polymer blends was discussed for the first time in this article.

## 2. Experimental

### 2.1. Materials

PFA (Teflon PFA 345J, Du Pont-Mitsui Fluorochemicals) and EFA (Du Pont-Mitsui Fluorochemicals) in the form of aqueous dispersion polymerized were used. Solid content of PFA dispersion was 25.5%. EFA having two extreme perfluoroethylvinylether (PEVE) comonomer contents (i.e. 5.7 wt% and 13.3 wt% for EFA-A and EFA-B, respectively) were used. Solid contents of EFA-A and EFA-B were 20.5% and 28.7%. Average primary particle size of EFA in aqueous dispersion was ca. 0.1 μm. A list of polymers and their characteristics are listed in Table 1.

### 2.2. Blending

Since there are no molecular interaction to promote intimate mixing of the two polymers in the melt state, we mixed aqueous raw dispersion of PFA and EFA (average primary

Table 1
Codes and characteristics of the polymers

| Polymer | Code | Comonomer (wt%) | MFR[a] (g/10 min) | $T_m$ (°C) | $T_c$ (°C) | $T_\alpha$[b] (°C) |
|---|---|---|---|---|---|---|
| PFA 345 | PFA | 3.5 (PPVE)[c] | 5.0 | 309 | 284 | 82.0 |
| PFA 340 | PFA 340[d] | 3.9 (PPVE) | 13.0 | 308 | 281 | – |
| EFA | EFA-A | 5.7 (PEVE)[e] | 23.0 | 297 | 270 | 79.9 |
| EFA | EFA-B | 13.3 (PEVE) | 9.7 | 252 | 238 | 61.7 |

[a] Melt flow rate.

[b] α-relaxation temperature.

[c] Perfluoro propyl vinyl ether.

[d] Used for the evaluation of flex life of the blend.

[e] Perfluoro ethyl vinyl ether.

particle size of each component was ca. 0.1 μm). Dispersions were mixed using a speed controlled agitator for 20 min. Sufficiently mixed dispersion were mechanically coagulated at a speed of 400 rpm using $HNO_3$ (20 g $HNO_3$/1500 g dispersion). Coagulated blends were dried at 150°C for 24 h. Melt blending was also performed using a twin rotor mixer (TOYOSEIKI R-60) in order to compare the effect of mixing method on the crystallization behavior of the blends. The pellets of PFA and EFA were mixed (40:60 blend) at 370°C at a rotor speed of 50 rpm and the mixing time was 15 min.

### 2.3. Differential scanning calorimetry (DSC)

Crystallization and melting behavior of the blends were studied using a Perkin–Elmer DSC 7 with a TAC 7/7 Controller. Since it was expected that the cocrystallization of the blend would be dependent upon the mixing method (i.e. raw dispersion mixing of primary particles is preferable), DSC measurements were performed mainly on raw dispersion mixed samples. Samples were dried at 150°C for 6 h before DSC measurements. To investigate the effect of crystallization conditions on the cocrystallization behavior, we maintained the blends at 400°C for 3 min to promote complete melting of crystalline phase and intimate molecular mixing and then crystallized the melts under various cooling conditions. Unless otherwise specified, the heating runs were performed at 10°C/min.

In order to compare the effect of mixing methods, a melt blended 40:60 blend was investigated. The value of $T_m$ or $T_c$ was determined from the DSC peak temperature.

### 2.4. Dynamic mechanical analysis (DMA)

Dynamic mechanical properties were measured at 1 Hz using Perkin–Elmer DMA 7e. Samples were mixed as raw dispersions. The blended samples were hot pressed at 360°C and then naturally cooled to room temperature. The sample (8 mm long, 3 mm wide, and 1.5 mm thick) was mounted on three-point bending mode plate and tan $\delta$ was measured from 15 to 160°C at a heating rate of 5°C/min. During this heating scan, $\alpha$-relaxation temperatures of the pure components or the blends were measured. $\alpha$-relaxation temperature was determined as the peak temperature of tan $\delta$ curve.

### 2.5. Mechanical properties

Tensile properties of the melt blended samples were tested using a Tensilon (Orientech Co.) at room temperature. Thickness of the melt blended samples were ca. 1.5 mm. A gauge length of 22.5 mm and a cross head speed of 50 mm/min were used. To evaluate the stress cracking resistance of the blends, MIT flex life of the blends were tested using a YASUDA No.307 MIT Folding Endurance Tester at room temperature. The hot pressed film samples (0.2 mm thick, 15 mm wide and 110 mm long) were mounted on a Folding Endurance tester according to the specification of ASTM-2176 so as to fold under a load of 1 kg from left and right to an angle of 135° at a rate of 175 cycle/min. The number of oscillating folds made until the test pieces ruptured (the average from three test pieces) was defined as the flex life (or MIT folding endurance). Since the flex life of perfluoropolymer is a function of molecular weight, we used PFA 340 (Du Pont-Mitsui Fluorochemicals) having similar melt flow rate (MFR) to EFA-B.

## 3. Results and discussion

### 3.1. Crystallization and melting behavior

Fig. 1 shows DSC melting curves of raw dispersion mixed PFA/EFA-A blends. In these blends the EFA-A contains 5.7 wt% PEVE comonomer. Since the PFA/EFA-A blends were only mechanically mixed at the primary particle level (ca. 0.1 μm), two melting peaks appear corresponding to the two pure components. Therefore, each crystalline component formed segregated crystals. Fig. 2 shows DSC crystallization curves of PFA/EFA-A blends, containing 5.7 wt% PEVE comonomer, on cooling 70°C/min. A single composition dependent crystallization peak appeared between the crystallization peaks of the two pure components. The composition dependent single crystallization peaks clearly indicate the occurrence of cocrystallization during cooling from the melt. Subsequent heating scans of the blends are

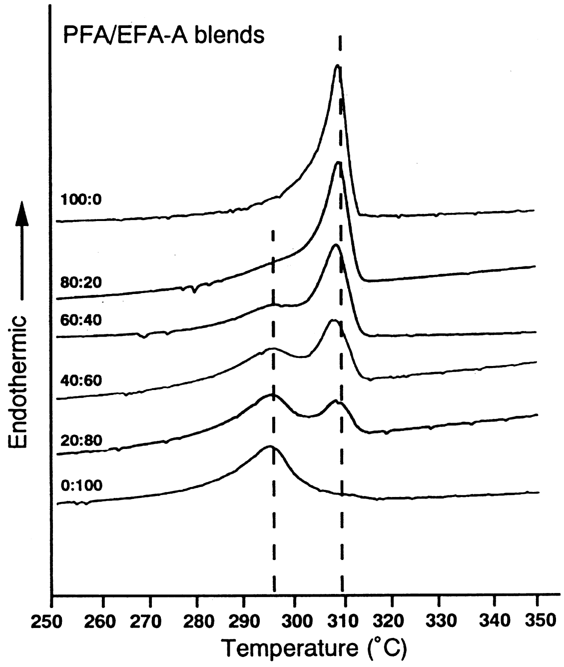

Fig. 1. DSC melting curves of raw dispersion mixed PFA/EFA-A blends. EFA-A contains 5.7 wt% PEVE comonomer. Each crystalline component formed segregated crystals. Scan rate was 10°C/min.

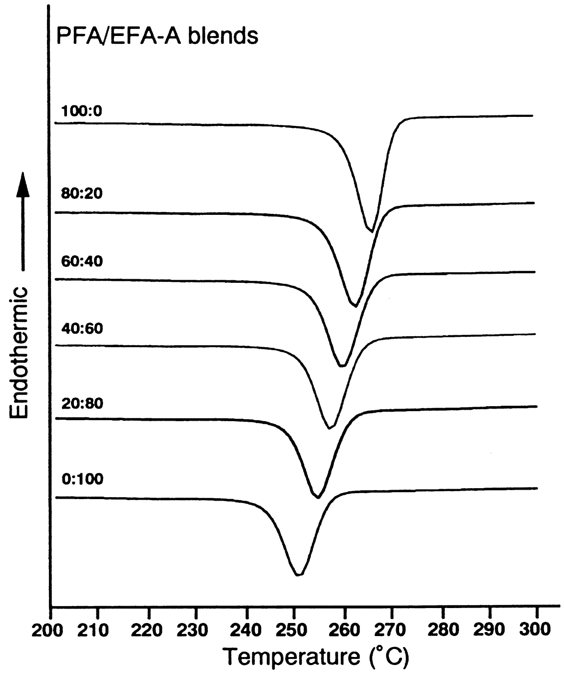

Fig. 2. DSC crystallization curves of PFA/EFA-A blends on cooling 70°C/min. Samples were heated at 400°C for 3 min before crystallization. Single composition dependent crystallization peak clearly indicates the occurrence of cocrystallization.

shown in Fig. 3. During the second heating scan, after cooling at 70°C/min, both the blends and neat PFA showed two melting peaks. This double melting peak is frequently found in the melt crystallized PFA. However, melt crystallized EFA-A showed only one melting peak. It is thought that the lower main-melting peak of the blend or neat PFA is attributed to the melting of thinner lamellar crystals and the higher sub-melting peak is related to the melting of thicker lamellar crystals having longer TFE segments (i.e. PFA has a distribution of PPVE comonomer in TFE segments and the lamellar thickness is limited by the distance between PPVE comonomers excluded from the lamellar crystals). Hereafter, the lower temperature main-melting peak is reported as the melting temperature of the blend and neat PFA. Heating scans of melt crystallized PFA/EFA-A blends also show single composition dependent main-melting peaks as shown in Fig. 3. Results obtained from Figs. 2 and 3 are summarized in Table 2. In Table 2, it is noticeable that by comparing the melting temperatures of PFA/EFA-A blends and neat EFA-A, blending of PFA in EFA-A raises the melting temperature of the blends. For example, melting temperature of PFA/EFA-A (40:60) blend is 7°C higher than that of neat EFA-A. This means that if the blends form cocrystals, then the melting temperature of lower-melting component (EFA) can be raised by blending.

Since the cocrystallization behavior of the two crystalline polymers is strongly dependent upon the crystallization speed (i.e. cooling speed from the melt) [11,18], the effect of cooling rates on the crystallization behavior of the PFA/EFA-A blend was investigated. The PFA/EFA-A (40:60) blends were crystallized at various cooling rates from the melt prior to the heating scan and the results are shown in Fig. 4. Cooling rates were varied from 5 to 70°C/min. Sham et al. reported that rapid crystallized (ca. 100°C/min) blends of two poly(aryl ether ketones) show single composition dependent melting peaks, while moderate cooling conditions (2.5, 10, and 40°C/min) show two melting peaks [11]. Runt et al. also reported similar result for the PTFE/PFA blends [18]. However, all PFA/EFA-A (40:60) blends showed a single main-melting peak, intermediate between the two pure components, regardless of cooling speeds. Therefore, we can conclude that PFA/EFA-A blends form cocrystal regardless of cooling speed. The melting temperature of the 40:60 blend slightly decreased as crystallization

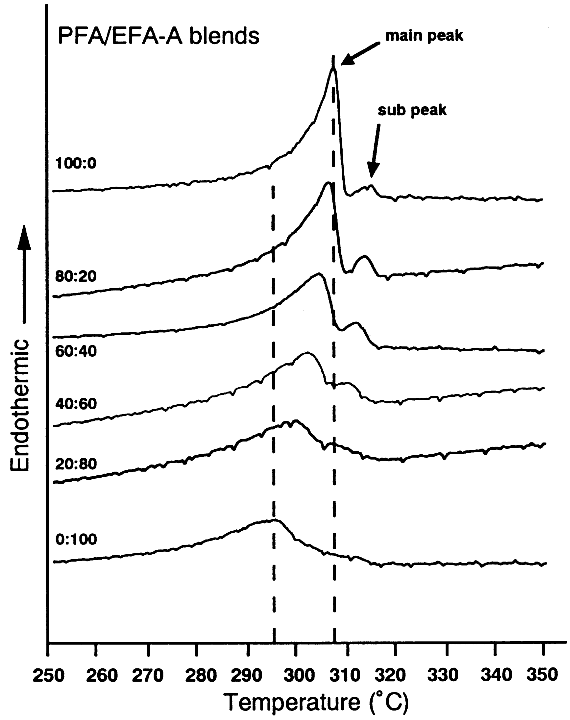

Fig. 3. DSC melting curves of PFA/EFA-A blends crystallized on cooling at 70°C/min. Scan rate was 10°C/min. Main melting peaks and sub melting peaks are attributed to the melting of cocrystal and PTFE-like segments in PFA, respectively. Single composition dependent main melting peak clearly indicates the melting of cocrystals.

Table 2
Crystallization temperatures $T_c$, heats of crystallization $\Delta H_c$, temperatures of melting peaks $T_m$, and heats of melting $\Delta H_m$ of PFA/EFA-A blends

| PFA/EFA-A | $T_c$ (°C) | $\Delta H_c$ (J/g) | $T_m$ (°C) | $\Delta H_m$ (J/g) |
|---|---|---|---|---|
| 100:0 | 266.8 | 23.5 | 308.1 | 25.6 |
| 80:20 | 263.2 | 22.5 | 306.8 | 24.2 |
| 60:40 | 259.7 | 21.6 | 305.0 | 23.9 |
| 40:60 | 257.4 | 20.2 | 302.8 | 22.8 |
| 20:80 | 255.1 | 19.7 | 299.9 | 22.4 |
| 0:100 | 250.4 | 19.0 | 295.6 | 20.8 |

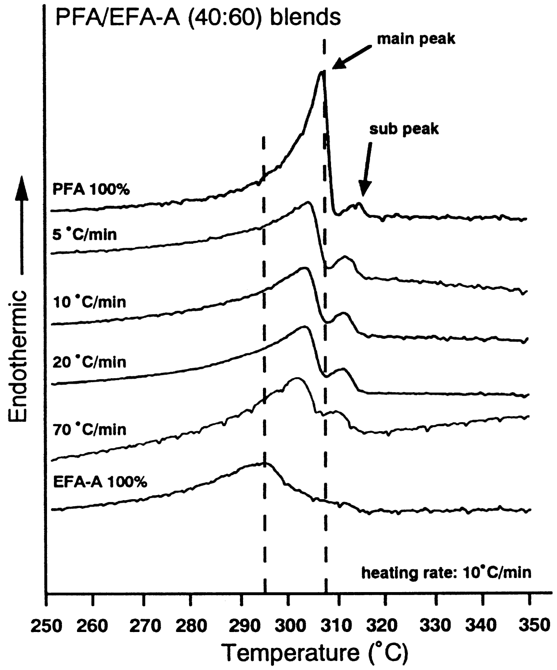

Fig. 4. DSC melting curves of PFA/EFA-A (40:60) blends. Scan rate was 10°C/min. PFA/EFA-A (40:60) blends were crystallized at various cooling rates (5, 10, 20, and 70°C/min) from the melt prior to the heating scan. PFA/EFA-A blends formed cocrystals regardless of crystallization speed (cooling speed).

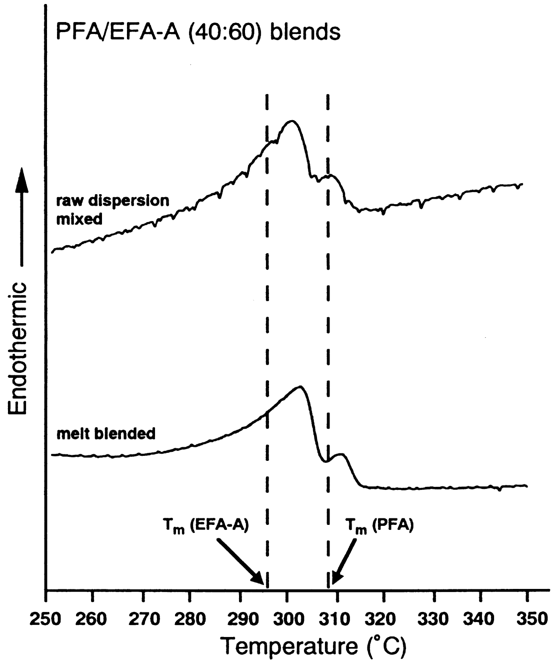

Fig. 5. DSC melting curves of aqueous raw dispersion mixed and melt blended PFA/EFA-A (40:60) blend. Samples were heated at 360°C for 5 min and then cooled to 200°C at 10°C/min before recording the second heating scan. Scan rate was 10°C/min. Two samples showed almost the same melting behavior and single main melting peak appeared between the two pure components. Therefore, PFA/EFA-A blend form cocrystals regardless of blending method.

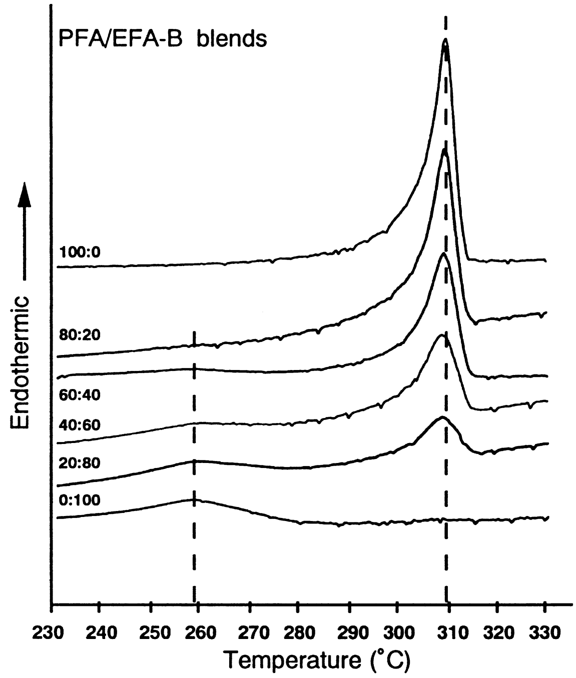

Fig. 6. DSC melting curves of raw dispersion mixed PFA/EFA-B blends. EFA-B contains 13.3 wt% PEVE comonomer. Each crystalline component formed segregated crystals. EFA-B showed a broader melting curve and lower degree of crystallinity than EFA-A. Scan rate was 10°C/min.

speed increased because crystallization occurs at lower temperature with the increased cooling rate.

It is known that the cocrystallization behavior of the blend is affected by the blending or mixing method of two crystalline polymers. For example, the mixing of the aqueous raw dispersions components promotes more intimate mixing than simple melt blending [19]. We prepared two PFA/EFA-A (40:60) blends using two different mixing methods and compared the effect of mixing method on the cocrystallization behavior of the blend. Fig. 5 shows DSC melting curves of aqueous raw dispersion mixed and melt blended samples. Each sample was heated at 360°C for 5 min and then cooled to 200°C at 10°C/min before recording the second heating scan. The two samples showed almost the same melting behavior, including a single main-melting peak that appeared between the two pure components. Therefore, Fig. 5 indicates that PFA/EFA-A blends form cocrystals regardless of the blending method.

However, PFA and EFA blends having a higher PEVE content EFA showed fundamentally different crystallization and melting behavior. Fig. 6 shows melting endotherms of raw dispersion mixed PFA/EFA-B blends that contain EFA with 13.3 wt% PEVE comonomer. As in the case of PFA/EFA-A blends, the raw dispersion blend of PFA/EFA-B showed two melting peaks which correspond to the two pure components (see Fig. 1). However, EFA-B showed a broader melting curve and lower degree of crystallinity than EFA-A. After heating at 400°C for 3 min, the subsequent

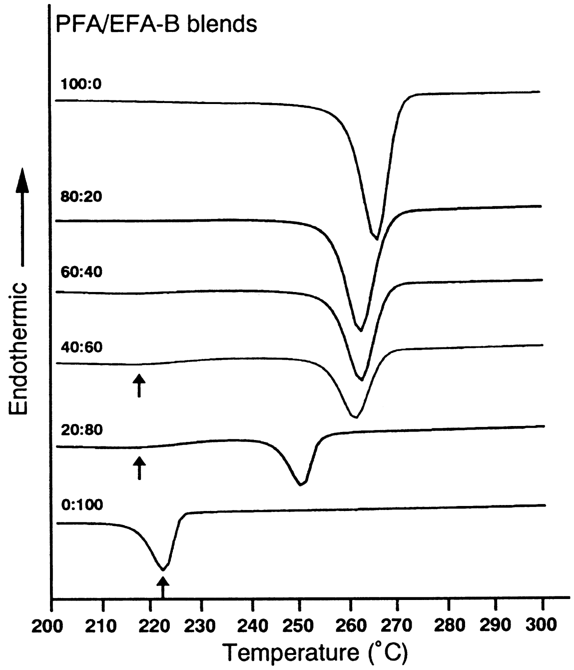

Fig. 7. DSC crystallization curves of PFA/EFA-B blends on cooling 70°C/min. EFA-B contains 13.3 wt% PEVE comonomer. Samples were heated at 400°C for 3 min before crystallization. Two crystallization peaks appeared for each blend and high-$T_m$ component (PFA) governed the overall cyrstallization process of the blends.

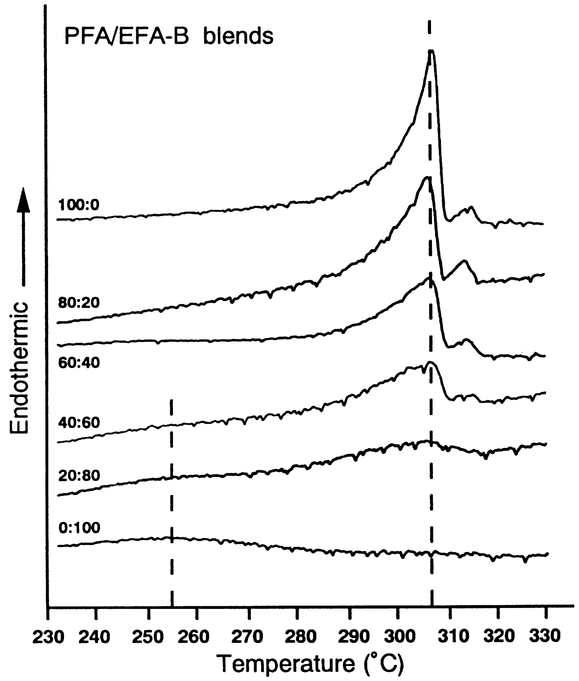

Fig. 8. DSC melting curves of PFA/EFA-B blends after cooling at 70°C/min. Two melting peaks appeared corresponding to the two pure components. PFA/EFA-B blends formed segregated crystals and blends are immiscible in crystalline region. The solid line is drawn as a guide.

cooling scans at 70°C/min to 200°C are shown in Fig. 7. During the cooling scan, two crystallization peaks appeared for each blend. In addition, the high-$T_m$ component (PFA) governed the overall crystallization process of the blends. Therefore, by blending only 20% of PFA to EFA-B as shown in the 20:80 blend, crystallization peak of EFA-B becomes substantially undetectable. This means that already crystallized PFA crystals hinder the crystallization of the lower melting component (EFA-B). The same observations were reported for other crystalline polymer blends and are characteristics of these type of blends [9,10]. The subsequent heating scans after cooling at 70°C/min to 200°C are shown in Fig. 8. As in the case of first heating scan, two melting peaks appeared independent of the blend ratio (Fig. 6). Figs. 6–8 indicate that PFA/EFA-B blends form segregated crystals and these blends are immiscible in the crystalline region. To investigate the miscibility of the blends in the amorphous region, we measured α-relaxation temperatures of the blends and the results will be shown in the next section.

As described above, the blends of PFA/EFA-A show almost perfect cocrystallization in the lamellar crystal. Additionally, since the melting temperature and the crystallization temperature of the PFA/EFA-A blend change coutinuously with the blend ratio, it seems that the lamellar thickness (or crystallite size) changes continuously with the blend ratio. We assume that the PFA containing less comonomer (or longer TFE segments) form more regularly packed thick crystal structure compared with EFA-A of the higher comonomer component having thinner and decreased regularity of crystal structure. Therefore, for the PFA/EFA-A blends, it seems like that the regularity of the crystalline structure and the lamellar thickness decrease gradually as the higher comonomer component EFA-A chains are introduced into the PFA crystals. To confirm this, X-ray diffraction measurements of PFA/EFA-A and PFA/EFA-B blends are in progress.

### 3.2. Dynamic mechanical behavior

It is known that the α-relaxation temperature of perfluoropolymers are associated with the cooperative segmental motion of long segments in the amorphous state [21]. In order to confirm whether the α-relaxation temperature is associated with the molecular motion of PFA or EFA in the amorphous region, we measured α-relaxation temperatures of EFAs having different comonomer contents. Fig. 9 shows the dependence of the α-relaxation temperature of EFA on comonomer (PEVE) content. As the PEVE content increases, the α-relaxation temperature of EFA decreases linearly. The composition dependent single α-relaxation temperature of EFA reflects molecular motion in the amorphous region and is a good measure of the miscibility of PFA/EFA blends in the amorphous region. For PFA/EFA-A blends, the α-relaxation temperatures of the two components were nearly the same (α-relaxation temperature of PFA and EFA-A are 82.0°C and 79.9°C, respectively). As a result, separation of the two tan $\delta$ peaks of the blends was

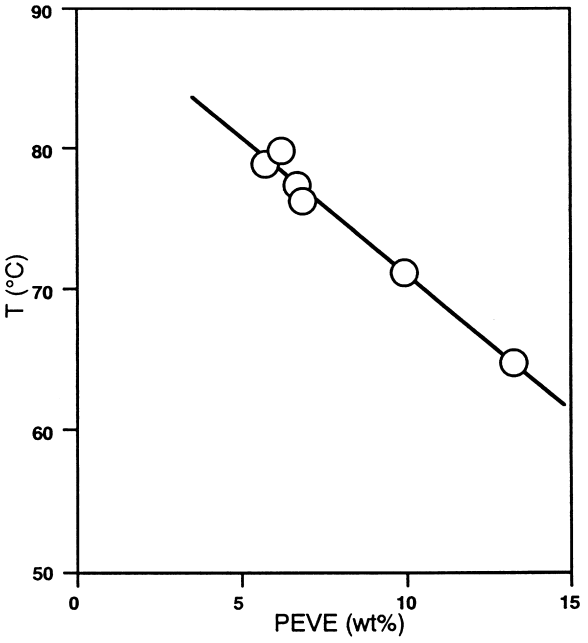

Fig. 9. Dependence of α-relaxation temperature of EFA on PEVE comonomer contents. α-relaxation temperature of EFA decreased linearly with the increase of PEVE comonomer content.

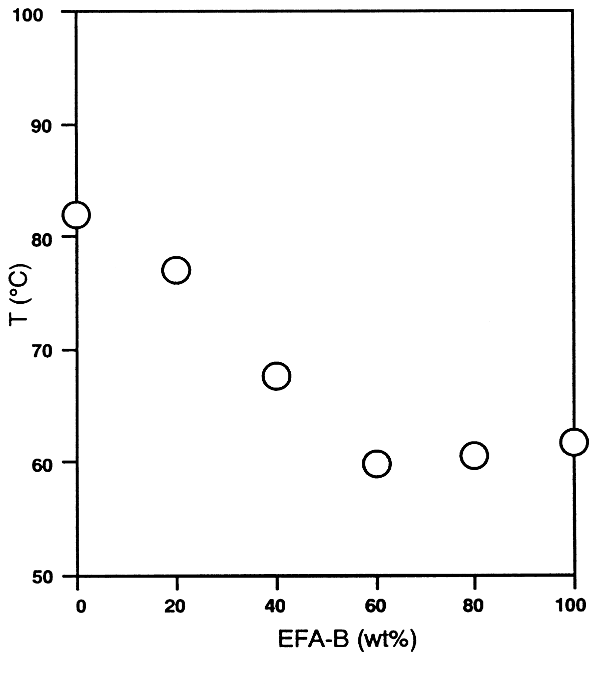

Fig. 10. Dependence of α-relaxation temperature of PFA/EFA-B blends on the weight fraction of EFA-B. EFA-B contains 13.3 wt% PEVE comonomer.

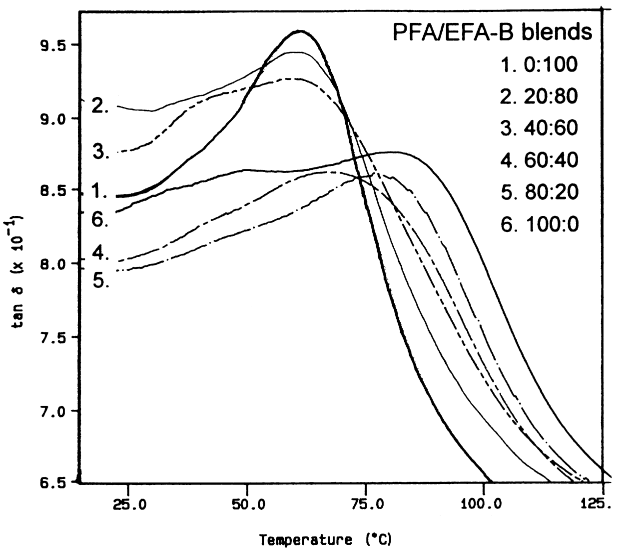

Fig. 11. tan $\delta$ vs temperature (at 1 Hz) for PFA/EFA-B blends. EFA-B contains 13.3 wt% PEVE comonomer.

unsuccessful. However, for PFA/EFA-B blends shown in Fig. 10, all the blends showed single α-relaxation temperature between the two pure components (tan $\delta$ curves are shown in Fig. 11). Up to 60% of EFA-B blend ratio the α-relaxation temperature of the blends decreases linearly with the increase of EFA-B blend ratio. Therefore, PFA/EFA-B blends are miscible in the amorphous region. However, it is not clear why the α-relaxation temperatures of the blends remain almost constant in EFA-B rich blends. Combining the results obtained from DSC and DMA for PFA/EFA-B blends, it is proposed that PFA/EFA-B blends are miscible in molten state before crystallization. However, during the crystallization process, the low degree of crystallinity of EFA-B and large differences in melting temperatures of the components of the PFA/EFA-B blends hinder the occurrence of the cocrystallization. This in turn results in segregated crystals in the crystalline region (i.e. two melting peaks), but single α-relaxation temperatures of the blends reveal that they are still miscible in the interlamellar amorphous region. On the other hand, PFA/EFA-A blends are miscible in the crystalline region because the blends form cocrystals. Although we cannot verify the misciblity in the amorphous region by DMA, PFA/EFA-A blends are also supposed to be miscible in the interlamellar amorphous region since blends are miscible in the molten state before crystallization.

### *3.3. Mechanical properties*

Since PFA/EFA blends are miscible in the amorphous region and blends containing lower PEVE content EFA (PFA/EFA-A blend) form cocrystals, it is proposed that mechanical properties of PFA or EFA could be improved by blending the two. To confirm this, various mechanical properties of the blends, such as, tensile properties, flex life and specific gravity were measured. While a synergistic effect on these properties was expected by blending PFA and EFA, all the examined properties of the blends showed a simple additive rule, no synergistic effect was observed. Since the mechanical properties of PFA and EFA-A are similar, all the mechanical properties of the PFA/EFA-A

Table 3
Modulus, yield strength, elongation and specific gravity of PFA/EFA-B blends

| PFA/EFA-B | Modulus (MPa) | Yield strength (MPa) | Elongation (%) | Specific gravity |
|---|---|---|---|---|
| 100:0 | 538.3 | 14.6 | 414 | 2.152 |
| 80:20 | 500.8 | 14.4 | 331 | 2.146 |
| 60:40 | 510.4 | 14.4 | 340 | 2.137 |
| 20:80 | 489.9 | 13.9 | 294 | 2.123 |
| 0:100 | 462.2 | 13.8 | 291 | 2.117 |

Table 4
Effect of EFA-B blend ratio on flex life of PFA 340/EFA-B blends

| PFA 340/EFA-B | Flex life (cycle) |
|---|---|
| 100:0 | 29,000 |
| 90:10 | 76,000 |
| 80:20 | 120,000 |

blends were located between the properties of the two pure components. Therefore, there was no noticeable benefit by blending PFA and EFA-A, except for the rise of $T_m$ for EFA-A (i.e. cocrystallization). On the other hand, PFA/EFA-B blends showed a benefit in flex life. Since the differences in the properties of PFA and EFA-B are relatively larger compared PFA and EFA-A. Therefore, in this section only the results obtained from PFA/EFA-B blends will be discussed. Modulus, yield strength, elongation, and specific gravity of PFA/EFA-B blends are summarized in Table 3. Although these properties showed a simple additive rule, flex life of the blends showed a benefit. The effect of EFA-B blend ratio on the flex life of PFA/EFA-B blends is shown in Table 4. Since flex life of perfluoropolymer is strongly dependent upon molecular weight (i.e. MFR), we used PFA 340 instead of PFA 345 (see Table 1). As can be seen in Table 4, by blending only 20% of EFA-B in PFA 340, the flex life of the PFA/EFA-B (80:20) blend becomes more than four times that of neat PFA. Since the flex life of the PFA/EFA-B blends change according to a simple additive rule, the flex life of the blends can be controlled by a simple physical mixing of PFA and EFA, not by additional polymerization. Caution should be exercised as these PFA/EFA-B blends are miscible in the amorphous region, but, immiscible in the crystalline region because segregated crystals are formed. Therefore, this outstanding improvement of the flex life of PFA by blending small amount of EFA-B is related to the intimate molecular mixing in the amorphous region of the blend, not related to the cocrystallization.

## 4. Conclusions

The results obtained from DSC, DMA, and flex life of the blends indicate that PFA/EFA blends are miscible in the amorphous region, regardless of the PEVE comonomer content of the EFA within the range investigated. Blends containing a low PEVE content EFA (PFA/EFA-A blend) form very stable cocrystals regardless of crystallization conditions. It is probable that this stable cocrystallization behavior originates from the similarity in chain conformation and crystalline lattice symmetry. For blends that form cocrystals, the $T_m$ of the lower-melting component (EFA-A) can be raised by blending with the higher-melting component (PFA). However, blends containing a higher PEVE content EFA (PFA/EFA-B blend) form segragated crystals because of the low degree of crystallinity of EFA-B and have different crystallization kinetics. However, PFA/EFA-B blends are miscible in the amorphous region since the blends show a single composition dependent α-relaxation temperature. Intimate molecular mixing of these blends in the amorphous region is closely related to the significant improvement of flex life of PFA by blending relatively small amount of EFA-B. To our knowledge, this study is the first finding that two crystalline polymers form such stable cocrystals regardless of crystallization conditions. Additionally, the relationship between miscibility and crystallization behavior to mechanical properties of two crystalline polymer blends is discussed for the first time in this article.

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