

Miscibility and Morphology of Poly(vinylidene fluoride)/Poly[(vinylidene fluoride)-*ran*-trifluoroethylene] Blends

RINALDO GREGORIO JR., MATHEUS RIGOBELLO CHAUD, WILSON NUNES DOS SANTOS,
JOÃO BAPTISTA BALDO

Department of Materials Engineering, Universidade Federal de São Carlos, CP 676, CEP 13.565-905, São Carlos, São Paulo, Brazil

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ABSTRACT: This study presents an investigation of the effect of the different crystalline phases of each blend component on miscibility when blending poly(vinylidene fluoride) (PVDF) and its copolymer poly[(vinylidene fluoride)-*ran*-trifluoroethylene] [P(VDF-TrFE)] containing 72 mol % of VDF. It was found that, when both components crystallized in their ferroelectric phase, the PVDF showed a strong effect on the crystallinity and phase-transition temperature of the copolymer, indicating partial miscibility in the crystalline state. On the other hand, immiscibility was observed when both components, after melting, were crystallized in their paraelectric phase. In this case, however, a decrease in crystallization temperatures suggested a strong interaction between monomers in the liquid state. Blend morphologies indicated that, in spite of the lack of miscibility in the crystalline state, there is at least miscibility between PVDF and P(VDF-TrFE) in the liquid state, and that a very intimate mixture of the two phases on the lamellar level can be maintained upon crystallization. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1362–1369, 2002

Key words: PVDF/P(VDF-TrFE) blends; crystallization; miscibility; morphology

INTRODUCTION

During the last decade much attention has been focused on the development and investigation of binary polymer blends. These blends allow the combination of desirable properties of different polymers, with exceptional advantages over the development of novel polymers. Several blends with interesting properties have been custom designed; however, little attention has been given to the morphological and structural characterization of these systems. Techniques such as thermal

analysis (DSC) and dynamic mechanical thermal measurements (DMTA), in addition to verifying blend miscibility, offer interesting possibilities to obtain additional information on blend structure and possible phase transitions that may occur. Optical and electron microscopy also allow verification of the morphology of these blends and, in the case of immiscibility, the degree of phase separation. Most blends investigated consist of either two amorphous polymers or just one semicrystalline component. Systems in which both components are semicrystalline are more complex, yet they may be of considerable technological interest, as well as offer the possibility of investigating crystallization and morphological behavior related to blend miscibility. Even in immiscible systems it is possible to determine how the crystallinity of one component affects the crystallization

Correspondence to: R. Gregorio Jr. (gregorio@power.fscar.br).

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process of the other. From a scientific point of view the study of these complex systems also allows verification of whether current knowledge of polymer blends would apply to such systems.

Recently, several blends containing the semicrystalline polymer poly(vinylidene fluoride) (PVDF) were studied. In most of the systems investigated, the second component of the blend was represented by an amorphous polymer, such as poly(methyl methacrylate) (PMMA),¹⁻⁴ poly(ethyl acrylate) (PEA),⁵ or poly(*o*-methoxyaniline) (POMA).⁶ However, less attention has been directed to mixtures of PVDF and another semicrystalline polymer. Liu et al.⁷ studied intermolecular interactions in PVDF/ ϵ -caprolactam (CPL) blends as well as crystallization, interfacial adhesion, morphology, and mechanical properties of PVDF/polyamide 6 blends.^{8,9} Their results showed that, despite the immiscibility of the components, a specific intermolecular interaction occurs between the two polymers, resulting in a strong interfacial adhesion. St. John Manley et al.¹⁰⁻¹² reported studies of the miscibility, crystallization, morphology, and mechanical properties of PVDF/poly(1,4-butylene adipate) (PBA) blends. They verified that these polymers are thermodynamically miscible, and the resulting blends display a morphology in which the two distinct crystalline phases coexist with an intimately mixed amorphous phase. During the crystallization, from the melt to room temperature, PVDF spherulites reject some PBA molecules to spherulitic boundaries, exhibiting an irregular texture at the interstitial region of the spherulites. Other PBA molecules are trapped in the interfibrillar domains of the spherulites.

Of particular interest are the blends with both semicrystalline components and where cocrystallization may occur, resulting in complete miscibility in the solid state. This is the case of blends formed by the ferroelectric copolymers poly[(vinylidene fluoride)-*ran*-trifluoroethylene] [P(VDF-TrFE)]. Employing thermal analyses (DSC) and wide-angle X-ray spectroscopy (WAXS), Tanaka et al.¹³ investigated the miscibility and cocrystallization of P(VDF-TrFE) copolymer blends containing 52, 65, and 73 mol % VDF and at different compositions. When in the ferroelectric phase, the (52/48)/(65/35) and (65/35)/(73/27) blends proved to be miscible and were characterized by isomorphic cocrystallization, whereas (73/27)/(52/48) blends were partially miscible. The authors state that blends of PVDF homopolymer with P(VDF-TrFE) copolymers are immiscible in the melt and are characterized by phase separation.

The scope of the current work was to investigate the effect of the crystalline phase of PVDF/P(VDF-TrFE) blend components on their miscibility. The morphology presented by the 50/50 blend crystallized from the melt was also verified by scanning electron and polarized light optical microscopy.

EXPERIMENTAL

Blends were prepared by dissolving the PVDF homopolymer (Forafion F4000; Atochem) and the random copolymer P(VDF-TrFE) (Solvay) containing 72 mol % VDF, in dimethylformamide (DMF) at the following PVDF/P(VDF-TrFE) wt % compositions: 100/0, 70/30, 50/50, 30/70, and 0/100. Films with thickness between 6 and 8 μm were obtained by spreading a solution with an initial concentration of 0.2 g/mL on a glass substrate maintained at 65°C for 1 h, which is the time necessary for complete evaporation of the solvent. The entire setup was maintained in a closed fume hood with exhaustion. Crystallization of PVDF at 65°C resulted in the formation of its ferroelectric β -phase exclusively.¹⁴ Because this temperature is below the Curie transition temperature of the copolymer, its crystallization also occurs exclusively in the ferroelectric phase. Hence, in the blends crystallized at 65°C both components crystallize in their ferroelectric phases. The phases present in each sample were verified by means of infrared spectroscopy. Thermal analyses were carried out in a DSC 2920 (TA Instruments, New Castle, DE), under nitrogen atmosphere and using indium as standard. The sample mass varied between 7 and 9 mg and both the heating and the cooling rate were 10°C/min. The dynamic mechanical analyses were performed in a Rheometric Scientific DMTA IV (PL-Thermal Science Equipment), at a heating rate of 3°C/min and frequency of 1.0 Hz. The film samples used in this analysis were 25 to 30 μm thick. In the morphological investigation controlled crystallization of the samples was carried out in a THMS 600 Linkan hotstage, connected to automatic temperature and heating rate. Micrographs were obtained at room temperature from a model DMRXP (Leica, Wetzlar, Germany) polarized light optical microscope and XL30 (Philips, The Netherlands) transmission electron microscope.

RESULTS AND DISCUSSION

Figure 1 shows the variation of $\tan \delta$ as a function of temperature for PVDF, the copolymer, and the

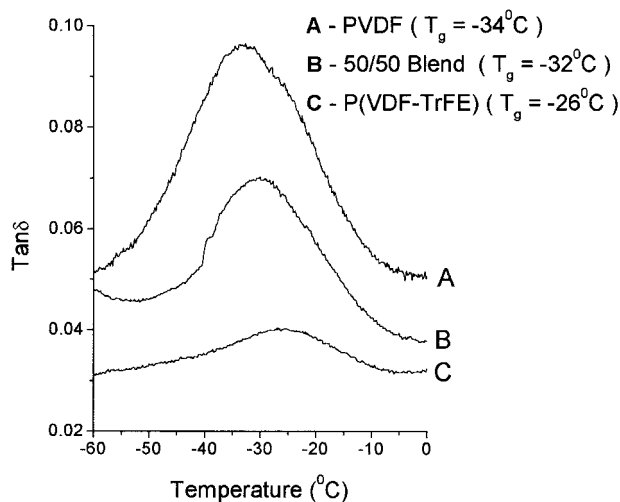


Figure 1 DMTA curves, showing the variation of $\tan \delta$ as a function of temperature for PVDF (A), the 50/50 blend (B), and the copolymer (C).

50/50 blend. Considering the maximum of these curves as the glass-transition temperature (T_g) of the material, these are for PVDF, the copolymer, and the 50/50 blend, -34 , -26 , and -32°C , respectively. The appearance of a single peak in the blend indicates miscibility of the components in the amorphous phase. However, proximity of the T_g 's of PVDF and of the copolymer makes this analysis difficult, not allowing such a conclusion. At first glance, the low $\tan \delta$ value in the T_g region presented by the copolymer when compared to that of PVDF suggests higher crystallinity. However, it is known that crystallization occurs in random copolymers only with great difficulty and, when it does occur, small imperfect crystals are formed. These crystals homogeneously dispersed in the amorphous region will restrain movement of this region, resulting in the strong reduction in the maximum $\tan \delta$ value.

Figure 2 shows the DSC curves, on heating, of the blends with different compositions crystallized at 65°C from solution. It can be seen from the figure that PVDF presented a single endotherm, with a peak at 169°C , corresponding to fusion of the crystallites (T_{fp}). The 72/28 copolymer presented two endotherms with peaks at 136 and 148°C , corresponding to the ferro-paraelectric phase transition (T_{tfp}) and fusion of the crystallites (T_{fc}). The blends presented three endotherms, corresponding in order of increasing temperature to T_{tfp} , T_{fc} , and T_{fp} , showing that the components are immiscible in the crystalline phase. Yet, a moderate reduction in T_{fc} can be

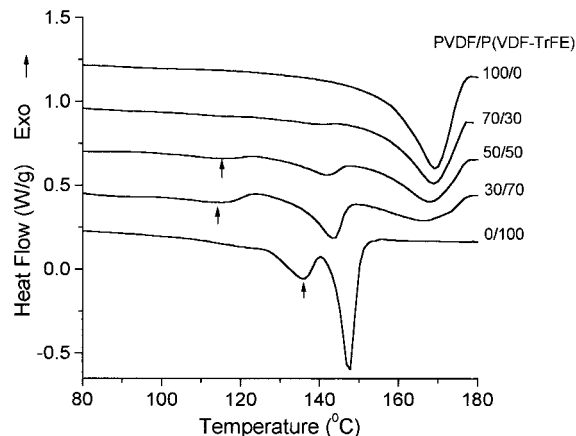


Figure 2 DSC curves, on heating, of the blends crystallized at 65°C from solution.

observed with an increase in wt % PVDF, and a strong reduction in T_{tfp} (see arrows in Fig. 2), as shown in Figure 3. These results indicate that the ferroelectric phase of the copolymer was formed in a more disorderly way, with less perfect and less stable crystals, attributed to the presence of PVDF. As a consequence, the resulting paraelectric phase also presented less perfect crystals, causing reduction in T_{fc} . The value of T_{fp} , on the other hand, practically did not vary with the inclusion of the copolymer, yet widening of the endotherms suggests an increase in the distribution of crystalline perfectness.

Figure 4 shows the variation in melt enthalpies of PVDF (ΔH_{fp}) and of the copolymer (ΔH_{fc}) as

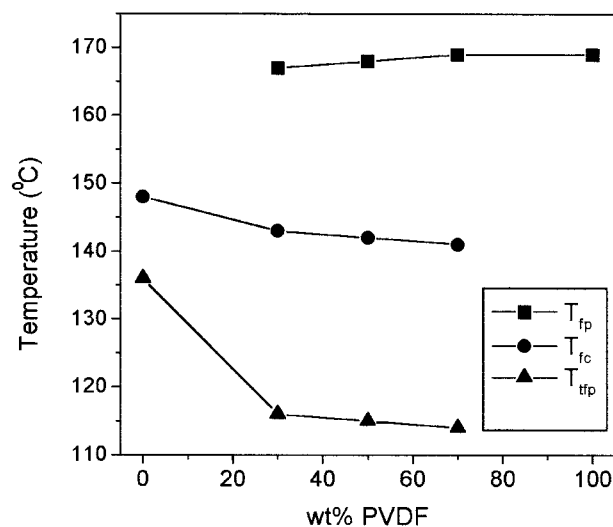


Figure 3 Variation of the thermal transition temperatures as a function of wt % PVDF.

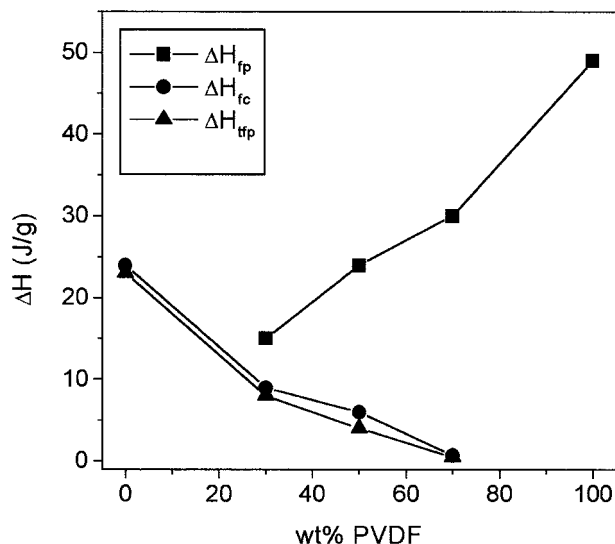


Figure 4 Variation of fusion and phase-transition enthalpies as a function of wt % PVDF.

well as of the ferro-paraelectric phase-transition enthalpy (ΔH_{tpf}) of the copolymer, as a function of wt % PVDF. The variation in ΔH_{fp} practically corresponds to the percentage reduction of PVDF in the blend, showing that PVDF crystallinity was scarcely affected by the presence of the copolymer. On the other hand, the values of ΔH_{fc} and of ΔH_{tpf} were strongly reduced with PVDF inclusion (for the 70/30 blend these values were less than 1 J/g). This means that during crystallization of the blend, when both components crystallize in the ferroelectric phase, the presence of PVDF reduces the crystallinity of the copolymer and, consequently, the ferro-paraelectric transition that it undergoes on heating. These results suggest a certain degree of miscibility between the components in solution, and that the intimate mixture between the components remains during crystallization, resulting in partial miscibility in the crystalline phase, despite the fact that no cocrystallization occurs.

Figure 5 shows the DSC curves on cooling, subsequent to the heating shown in Figure 2. In this case, the two blend components crystallize, from the melt, in the paraelectric phase. PVDF presented an exotherm, with a maximum at 145°C, corresponding to its crystallization and the 72/28 copolymer presented two exotherms, with peaks at 133 and 79°C, corresponding to the crystallization and to the para-ferroelectric transition, respectively. The blends with different compositions presented the three exotherms, once

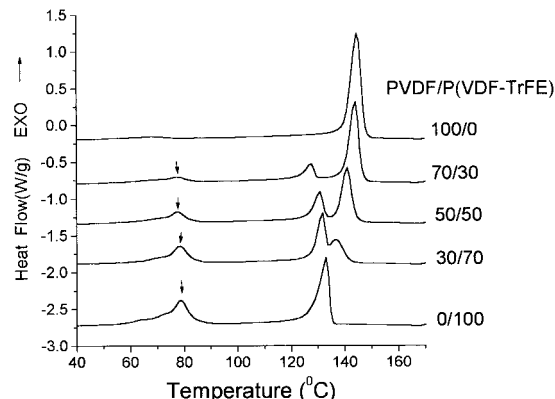


Figure 5 DSC curves, on cooling, of the blends with different wt % PVDF.

more indicating the immiscibility of the components in the crystalline phase. However, the decrease in crystallization temperatures of PVDF (T_{cp}) and of the copolymer (T_{cc}), shown in Figure 6, indicates a strong interaction between the monomers of the components in the melt, hindering both crystallization processes and reducing the temperature at which they occur. On the other hand, the para-ferroelectric transition temperature (T_{tpf}) hardly varied with wt % PVDF, suggesting that stability of the paraelectric phase of the copolymer was scarcely affected by the presence of PVDF. Variation of the crystallization enthalpy of PVDF (ΔH_{cp}), as well as of the copolymer's crystallization (ΔH_{cc}) and para-ferroelectric phase-transition enthalpies (ΔH_{tpf}) as a function of wt % PVDF, is shown in Figure 7. In this

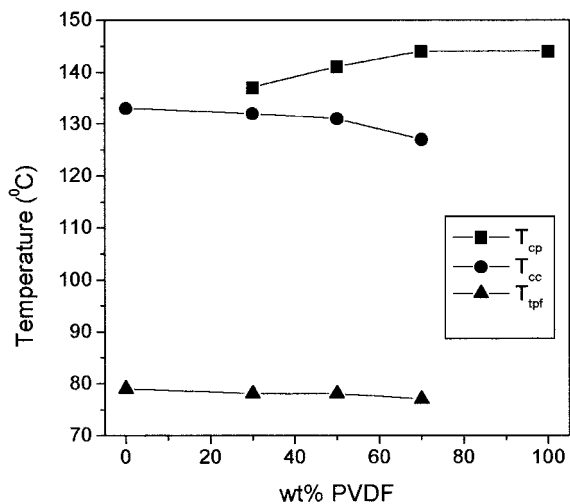


Figure 6 Variation of thermal transition temperatures as a function of wt % PVDF, on cooling.

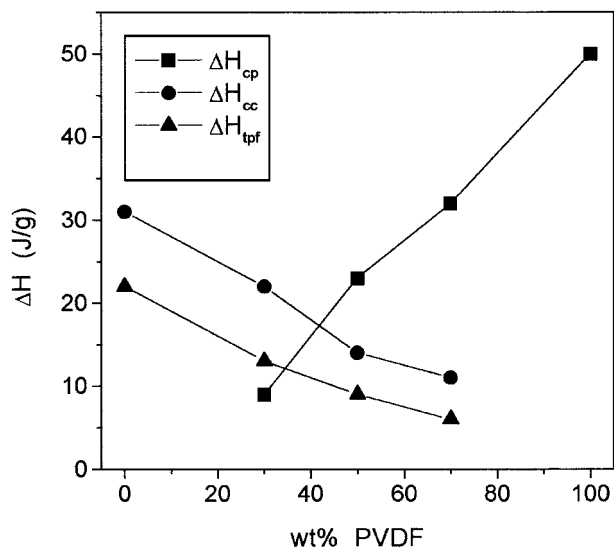


Figure 7 Variation of crystallization and phase-transition enthalpies as a function of wt % PVDF, on cooling.

case it is clear that the reduction in the enthalpies corresponds to the percentage variation of the blend components, indicating that the presence of one component does not interfere in the crystallinity of the other. Consequently, the reduction in ΔH_{tpf} also followed the percentage decrease of the copolymer. The only exception was the value of ΔH_{cp} of the 30/70 blend, which presented a small reduction. This may have happened because, in this blend, crystallization of the copolymer initiated before crystallization of PVDF had been terminated, as shown in Figure 5.

Figure 8 shows the DSC curves, in the second heating, subsequent to the cooling presented in

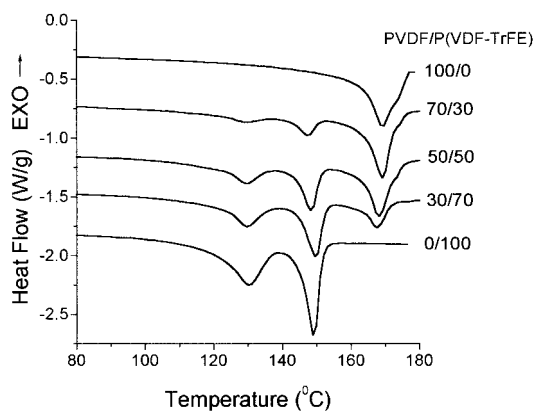


Figure 8 DSC curves, in the second heating, subsequent to the cooling shown in Figure 5.

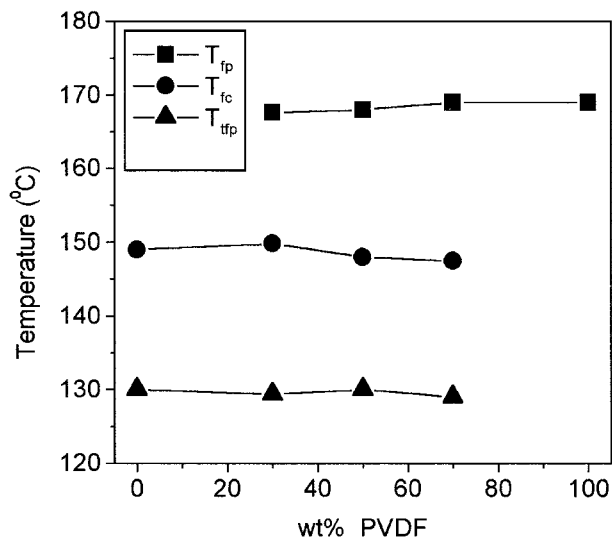


Figure 9 Variation of the thermal transition temperatures as a function of wt % PVDF for the second heating.

Figure 5. In this case, T_{fp} , T_{fc} , and T_{tfp} are essentially independent of the blend composition, as shown in Figure 9. The values of the melt enthalpies of PVDF and of the melt and ferro-paraelectric transition enthalpies of the copolymer were compatible with the percentage of each component in the blend (Fig. 10), indicating that the crystallinity of both was practically not altered in the mixture. Again, the sole exception was the value of ΔH_{fp} , a little less than that expected,

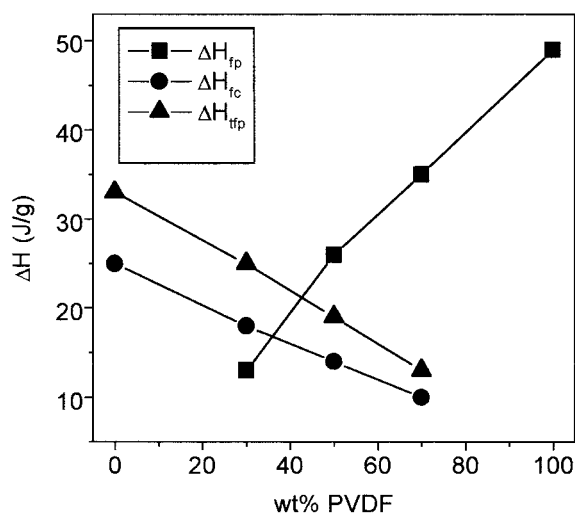


Figure 10 Variation of fusion and phase-transition enthalpies as a function of wt % PVDF for the second heating.

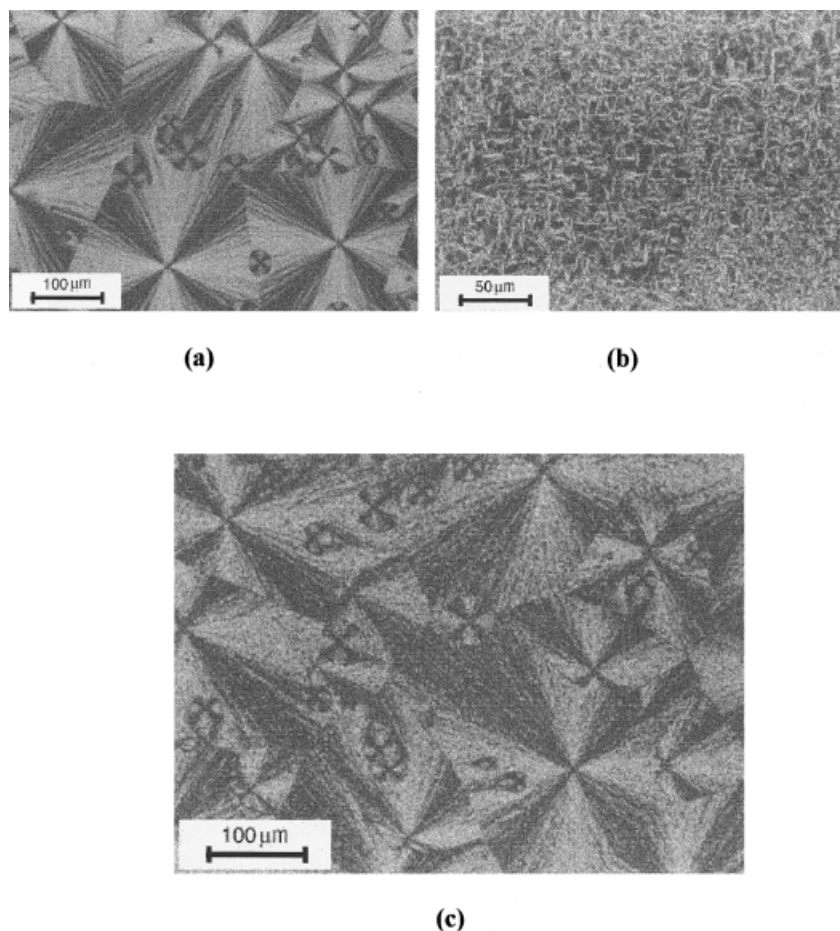


Figure 11 Morphologies presented by the samples: (a) PVDF; (b) P(VDF-TrFE); (c) 50/50 blend.

agreeing with the results obtained on cooling, where the value of ΔH_{cp} was less than expected. Therefore, during crystallization from the melt, where the two components crystallized in their paraelectric phases, the presence of one component scarcely interfered in the crystallization of the other, suggesting complete immiscibility in the crystalline phase.

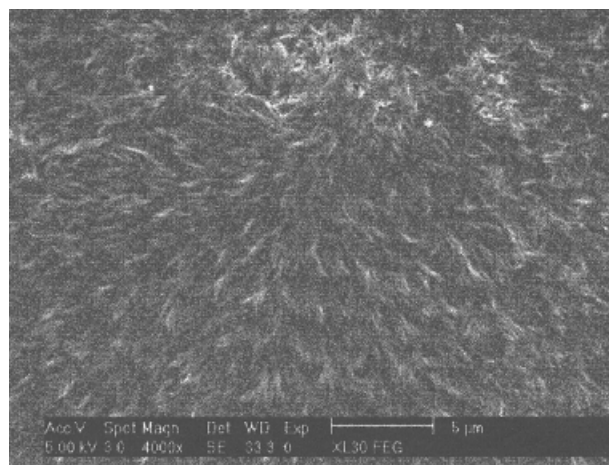
Miscibility in the crystalline phase (cocrystallization) between two semicrystalline polymers depends basically on two factors, that is, the chemical attraction between their monomers, so as to promote miscibility between these in solution or in the melt, and the similarity between their crystalline structure. In the case of PVDF and of the PVDF/P(VDF-TrFE) copolymer, containing the 72/28 copolymer, the chemical similarity between the monomers and the existence of dipolar interaction should favor miscibility between them either in solution or in the melt. Yet,

the difference between the network parameters, in both the paraelectric and ferroelectric phases, should impede cocrystallization. A strong indication of blend component miscibility in the solution was given when both components crystallized in the ferroelectric phase. The strong interaction between the monomers resulted in the lower crystallinity of the copolymer and in less perfect crystals in both components. The lower stability of the copolymer's ferroelectric phase was also evidenced by the strong reduction in the ferro-paraelectric transition temperature. The greater facility in diffusion of the polymer chains in solution and the strong interaction between the different monomers would improve dilution between the copolymer and the PVDF.

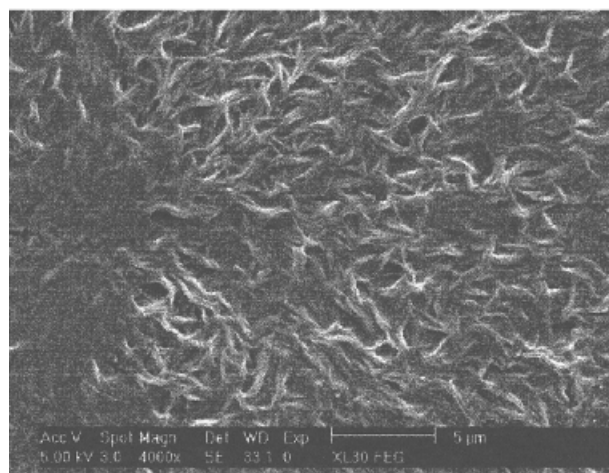
When both components crystallized in the paraelectric phase, from the melt, the interaction between the components was likely lower, practically not interfering in the crystallinity or stabil-

ity of this phase, for both PVDF and the copolymer. The lower diffusivity of the polymer chains in the melt might also have hindered miscibility during crystallization. However, even in this case, the decrease in crystallization temperatures of the two components indicated a strong interaction between these in the melt, which hindered the crystallization process. The PVDF, that had crystallized before, experienced the effect of the copolymer that acted as a diluent. On the other hand, the copolymer when crystallized underwent the restrictive effect of the already formed PVDF crystals. However, the second heating showed that in this case there was complete immiscibility in the crystalline phase.

Nevertheless, strong evidence of miscibility on a lamellar level between PVDF and the P(VDF-TrFE) copolymer in the melt was given by the morphology presented by the blends. Samples with different compositions were melted at 210°C for 10 min and quickly cooled (50°C/min) to 160°C, where they were maintained for 10 h. Next, they were quickly cooled to 145°C, kept at this temperature for 10 h, and cooled down to room temperature. This was the most favorable condition for the occurrence of immiscibility in the crystalline phase, given that the PVDF crystallized completely at 160°C, in a medium containing the molten copolymer acting as a diluent. This copolymer crystallized only at 145°C, after the second cooling. At 160°C the pure PVDF crystallized into two types of spherulites, large ringed and small nonringed, as shown by the micrograph in Figure 11(a). The ringed spherulites are predominantly formed by the nonpolar paraelectric PVDF α -phase and the nonringed spherulites predominantly by the polar γ -phase.¹⁵ These spherulites completely take up the sample after about 5 h of crystallization. The morphology presented by the pure copolymer is presented in Figure 11(b), apparently composed of axialites. The morphology presented by the 50/50 blend is shown in Figure 11(c). This blend presented large and small spherulites filling up the entire sample, similar to what occurred with pure PVDF, although with a different texture from that presented in PVDF. This irregular texture, yet homogeneous throughout the entire sample, is evidence of the presence of the copolymer molecules within the spherulites, probably in the interlamellar regions. This means that during crystallization of PVDF the copolymer molecules were not rejected and segregated in the interspherulitic regions. If this were the case, the blend would



a)



b)

Figure 12 Morphology of the region near the center of a ringed spherulite of (a) PVDF and (b) the 50/50 blend, observed through scanning electron microscopy.

present regions between the spherulites with a morphology similar to that presented by the pure copolymer [Fig. 11(b)], composed of axialites, and the spherulites would present only an irregular texture close to these regions (i.e., at their boundaries). However, this did not occur, despite the fact that the sample contained 50% copolymer. The spherulites completely filled up the sample and presented an irregular texture evenly distributed throughout the extent of the sample, evidencing nonoccurrence of phase segregation, which could be verified by optical microscopy.

Evidence of the presence of the copolymer molecules within the spherulites was given by the

comparison between the intraspherulitic regions of pure PVDF and of the blend. Figure 12(a) and (b) present the morphology of a region near the center of a ringed spherulite, for pure PVDF and for the 50/50 blend, respectively. It can be seen that the presence of the copolymer caused variations on a lamellar level in the spherulite.

These results corroborate the assumption of miscibility at the lamellar level of the components in the melt, and also show that despite the immiscibility in the crystalline phase, an intimate mixture of the components remains during crystallization. The PVDF and P(VDF-TrFE) crystals are homogeneously distributed in the sample, coexisting with an intimately mixed amorphous phase, without the formation of distinct phases that could be observed by means of optical or electron microscopy.

CONCLUSIONS

The components of the PVDF/P(VDF-TrFE) blends, containing a 72/28 copolymer, when crystallized from solution at 65°C, where both crystallized in their ferroelectric phases, proved to be partially miscible in the crystalline phase, suggesting a certain degree of miscibility in the solution. When crystallization occurred from the melt, in the paraelectric phases, the components proved to be immiscible in the crystalline phase, although interacting strongly in the melt. Such interaction allows an intimate mixture of the components in the melt, which remains at a lamellar level during crystallization, resulting in the different crystals being evenly distributed within the sample, without the presence of distinct

phases, which could be verified by optical or electron microscopy.

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