Morphology Of PVDF, P(VDF-TrFE) Copolymers, And PVDF/P(VDF-TrFE) Blends

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Abstract

The morphology of PVDF, P(VDF-TrFE) copolymers, and PVDF/P(VDF-TrFE) blends with different compositions was investigated by scanning electron microscopy (SEM). It was observed the lamellar bundle arrangements which form the two different types of spherulites present in PVDF crystallized at 160 °C. The effect of the crystallization temperature on the morphology of the copolymer with 72 mol% of VDF was also investigated. It was observed for the PVDF/P(VDF-TrFE) blends a strong influence of the copolymer on the lamellar structures which form the two different types of PVDF spherulites, suggesting the presence of the copolymer molecules in the interlamellar regions of these structures.

Keywords: PVDF, P(VDF-TrFE), Blends, Miscibility, Morphology.

Introduction

Poly(vinylidene fluoride) (PVDF) and the copolymers formed by vinylidene fluoride (VDF) and trifluoroethylene (TrFE), containing 50 to 82 mol% of VDF, present several technological applications due to their important pyro and piezoelectric properties. In addition to these properties, PVDF also presents polymorphism, occurring in at least four distinct crystalline phases, known as α, β, γ e δ [1]. The α phase, the only unpolar one, is predominant in the crystallization from the melt at temperatures below 155 °C. The β phase can be obtained by crystallization from dimethylformamide (DMF) or dimethylacetamide (DMA) solution at temperatures below 70 °C [2]. The γ phase is formed in the crystallization from the melt at high temperatures (T >155 °C) or by annealing α phase samples between 160 and 170 °C [3]. The δ phase, a polar version of the α phase, can be obtained by polarizing this phase under high electric field [4]. Because of this polymorphism, uncommon among polymeric materials, PVDF presents a varied morphology that depends strongly on the crystallization conditions. Investigations employing polarized light optical microscopy (PLOM) showed that for the crystallization from the melt at temperatures above 155 °C PVDF presents two types of spherulites [3]. One type is highly birefringent and presents concentric rings, being formed predominantly by the α phase, and the other type is less birefringent and not ringed, in which the γ phase prevails. Annealing at temperatures between 160 and 170 °C causes on the ringed spherulites a α → γ solid-state phase transformation, which rate increases with the temperature [3]. The authors have found few references on the P(VDF-TrFE) morphology [5, 6].

The aim of this work was to investigate by scanning electron microscopy (SEM) the morphology of PVDF, P(VDF-TrFE) copolymer containing 72 mol% VDF, and the PVDF/P(VDF-TrFE) blends with weight proportions of 70/30, 50/50, and 30/70.

Materials and Methods

Films with a mean thickness of 8 μm were obtained by spreading on a glass substrate a solution of PVDF (FORAFLON® F4000, Atochem Co) or of P(VDF-TrFE) (Solvay) with 72 mol% of VDF in DMF. The blends were prepared by the dissolution of PVDF and P(VDF-TrFE) in DMF with PVDF/ P(VDF-TrFE) weight proportions of 70/30, 50/50, and 30/70. The initial concentration of the solution was 20 wt % and the solvent was evaporated at 60 °C for 1 h inside a closed hood. Then the films were cooled at room temperature (25 °C) and were easily removed from the substrate by immersion on distilled water. Samples of PVDF and copolymer films were melted at 230 °C for 10 min. After that, the PVDF samples were rapidly cooled (50 °C/min) until the temperature reached 160 °C, and then the samples remained at this temperature for 10 h. The copolymer samples were rapidly cooled and kept for 10 h at three different temperatures: 130, 145, and 148 °C. The blend samples were melted at 230 °C and crystallized in two steps: rapidly cooled to 160°C, at which temperature they remained for 10 h, and then cooled to 145 °C, at which temperature they remained for 10 h. The aforementioned heat treatments were performed in a hot stage unit (THMS 600, Linkan) connected to an automatic controller of temperature and heat rate. The micrographs of the film surfaces were obtained by two scanning electron microscopes (Leica/Cambridge Stereoscan 440 and Philips XL 30). Polarized light optical microscopy (PLOM) in transmission mode was carried out using a Leica DMRXP microscope.

Results and Discussion

Figure 1 presents the SEM micrograph of the PVDF film crystallized from the solution at 60 °C. Analysis by infrared spectroscopy indicated that β phase predominates for the samples crystallized in these conditions [2]. It can be observed that the morphology is constituted by small spherulites (mean diameter of 6 µm) and the film presents high porosity.

Figure 2 displays the PLOM micrograph of the PVDF sample crystallized at 160 °C during 10 h, from the melt. Two kinds of spherulites can be observed: large and ringed, predominantly formed by the α phase, and small and not ringed, mainly formed by the γ phase [3].

The SEM micrographs of a ringed and not ringed spherulites are presented, respectively, in figures 3a and 3b. It the can be observed for the ringed spherulite that the lamellar bundles have a radial arrangement, forming concentric circles (Fig. 3a). This causes its ringed appearance when observed by PLOM. For the not ringed spherulites the lamellar bundles are also radial, but without concentric circles.

The micrographs of the copolymer samples crystallized at different temperatures are displayed in figure 4. For the crystallization at 130 °C (Fig. 4a), P(VDF-TrFE) presents a morphology constituted by a lamellar bundles network with small pores between them. A similar morphology is observed also for samples melted and rapidly cooled. The increase in the crystallization temperature thickened the bundles and enlarged the pores (Fig. 4b). Inside them new lamellar bundles network begin (Fig.4c).

Figure 5 displays micrographs of the ringed and not ringed spherulites present in the 70/30 blend crystallized in two steps. The copolymer presence caused little effect in the lamellar arrangement for the not ringed spherulite (Fig. 5b), but a strong alteration for the ringed spherulite (Fig. 5a). The lamella bundles lost their symmetrically radial arrangement, turned partially interlaced, and the concentric rings disappeared. For the 50/50 (Fig. 5b) and 30/70 blends (Fig. 5c), on the other hand, the copolymer presence caused a strong alteration in the arrangement of the lamella bundles of both spherulites, ringed and not ringed, which turned interlaced. This result indicates the presence of copolymer molecules inside the spherulites, probably in the interlamellar regions. This indicates that in the liquid state the molecules of the blend components must be intimately mixed. Even for the PVDF crystallization at 160 °C, at which temperature the copolymer is in the liquid state, its molecules are not rejected and segregated at the interspherulitic regions, but remain intimately mixed with the PVDF molecules.

Although some recent results [7] have showed that the PVDF/P(VDF-TrFE) blend components are not miscible in the crystalline phase (cocrystallization), probably due to a significant difference in the lattice parameters, the results of this work indicate that this miscibility occurs in the liquid state and, very likely, in the amorphous solid phase. The PVDF and P(VDF-TrFE) crystals are homogeneously distributed in the sample, with no distinct phase formation observed by PLOM or SEM.

Figure 1. SEM micrograph of PVDF crystallized at 60 °C from the DMF solution.

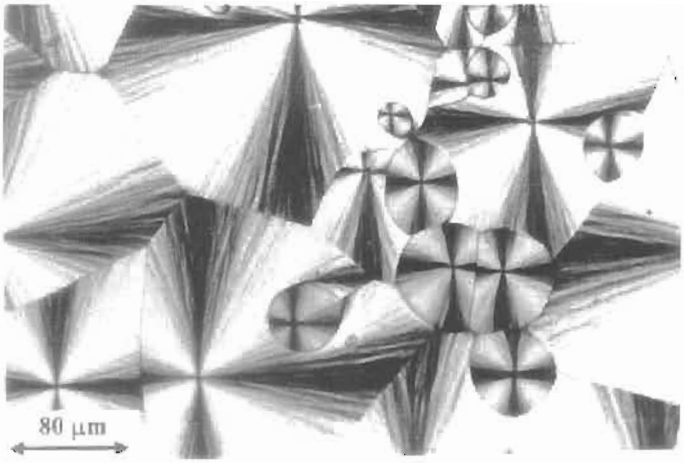
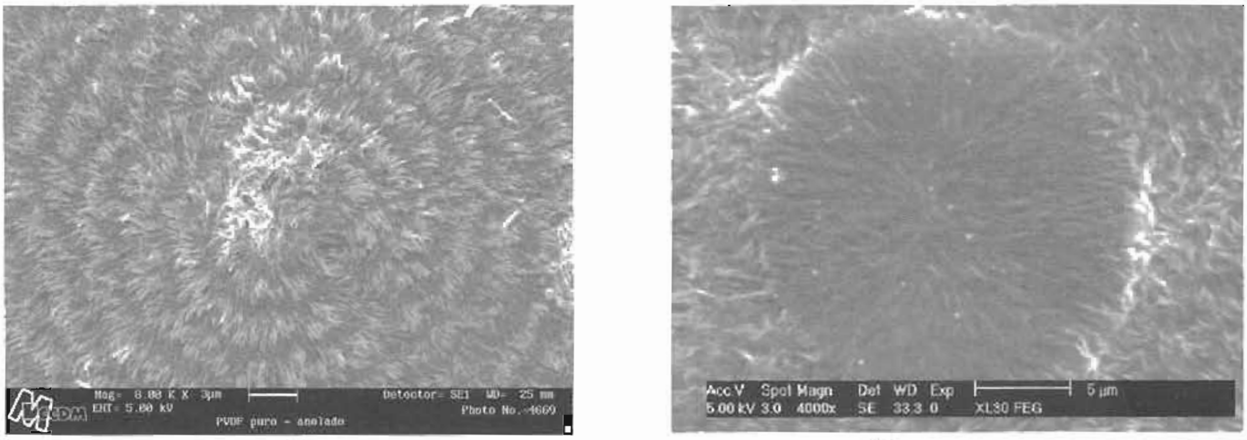
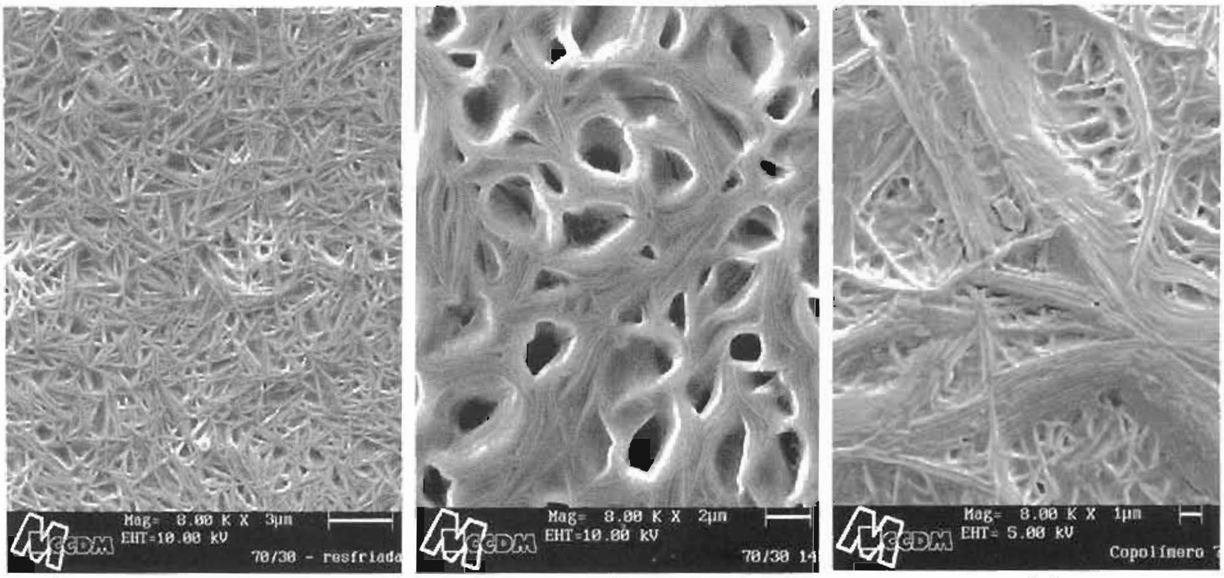


Figure 2. PLOM micrograph of PVDF crystallized at 160 °C for 10 h from the melt.



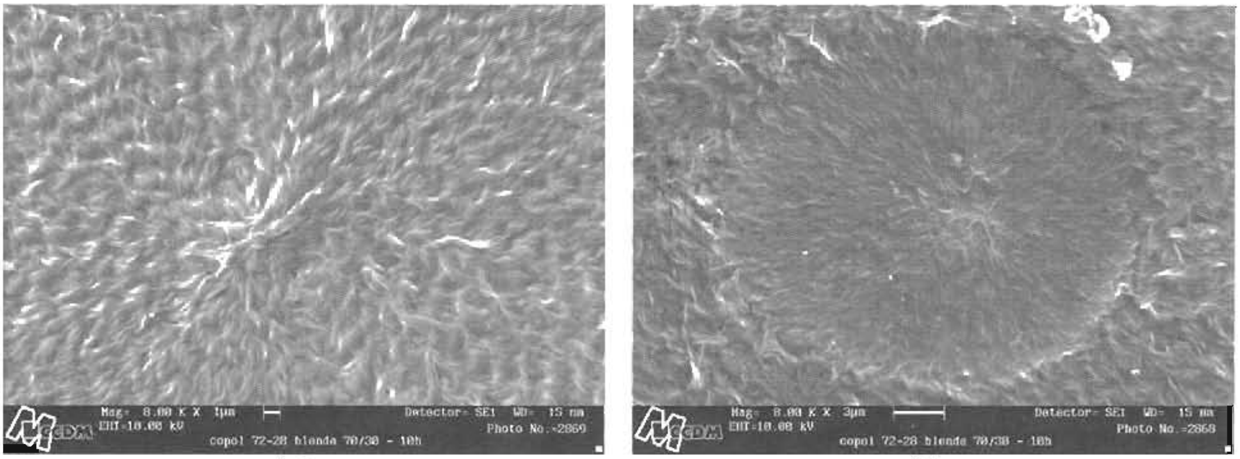
(a) (b)

Figure 3. SEM micrographs of PVDF crystallized at 160 °C for 10 h from the melt showing (a) a ringed spherulite (center region) and (b) a not ringed spherulite.



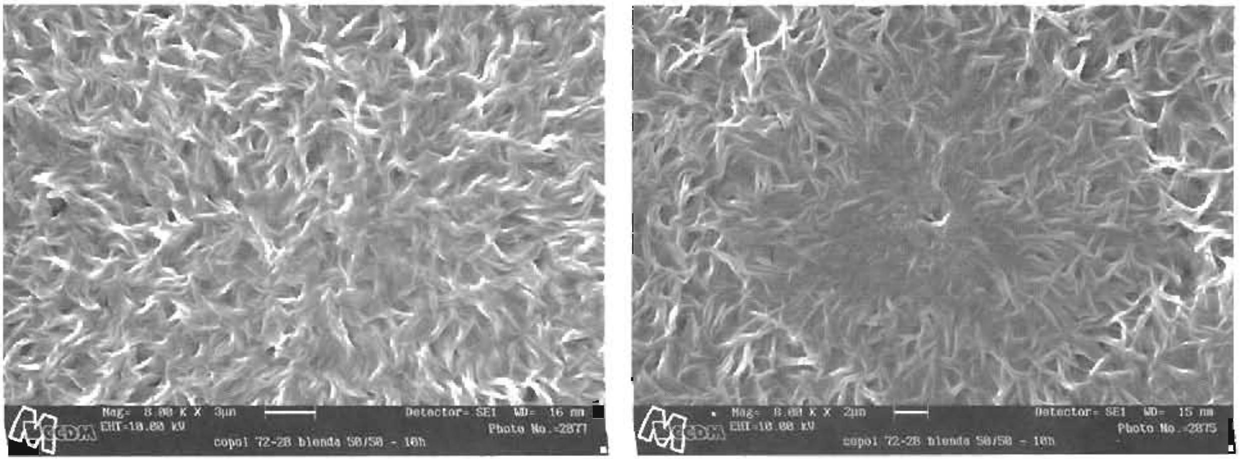
(a) (b) (c)

Figure 4: SEM micrographs of the copolymer samples crystallized form the melt at (a) 130, (b) 145, and (c) 148 °C



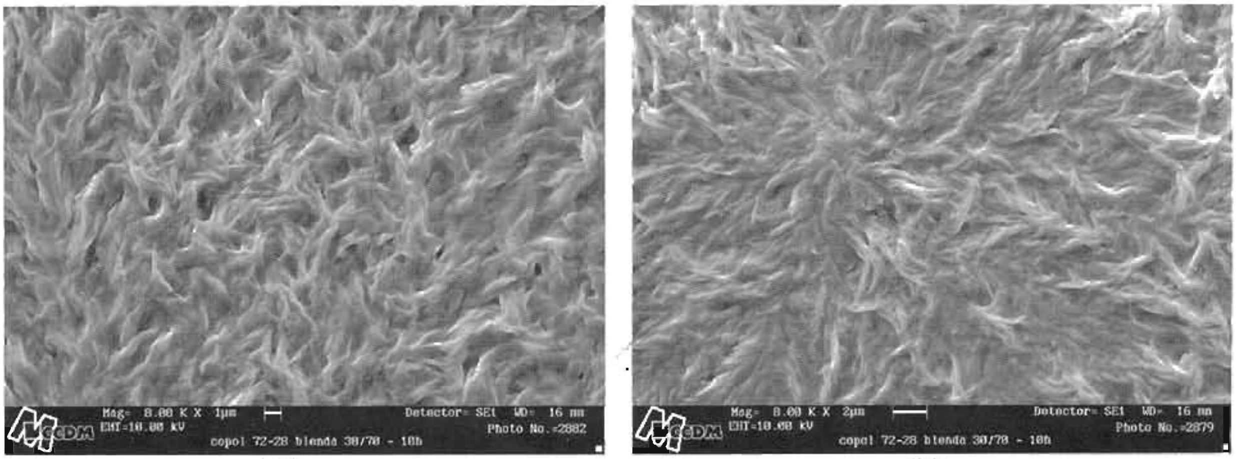
(a) (b)

Figure 5: SEM micrographs of a 70/30 blend crystallized in two steps showing (a) ringed spherulite (center region) and (b) not ringed spherulite.



(a) (b)

Figure 6. SEM micrographs of a 50/50 blend crystallized in two steps showing (a) ringed spherulite (center region) and (b) not ringed spherulite.



(a) (b)

Figure 7: SEM micrographs of a 30/70 blend crystallized in two steps showing the center region of (a) ringed spherulite and (b) not ringed spherulite.

Conclusion

PVDF crystallizes from the solution or the melt forming espherulitic structures. If the crystallization occurs above 155 °C, two kinds of spherulites are formed: ringed, with bundles of radial lamellas forming concentric circles, and not ringed, with bundles of radial lamellas. The P(VDF-TrFE) copolymer contanining 72 mol% of VDF crystallizes forming lamellar bundles network. With the increase in the crystallization temperature, the bundles thicken and more pores are created into the sample. The PVDF/P(VDF-TrFE) blends crystallized in two steps also present a morphology characterized by ringed and not ringed spherulites. Increasing the copolymer percentage leads to an interlacing of the lamella bundles which form these spherulites, evidencing the copolymer presence in the interlamellar regions. This result suggests that it occurs the miscibility among the blend components in the liquid state and, probably, in the amorphous solid state.

Acknowledgments

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