

Novel Orientation Textures of Poly(vinylidene fluoride) in the Blend with Nylon 11

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Oriented crystallization behavior of poly(vinylidene fluoride) (PVDF) in the oriented blend with nylon 11 was investigated. It was found that PVDF can crystallize into both α and β crystal forms when the stretched blends were heat-treated above the melting point of PVDF and followed by melt-crystallizing it. The *c*-axis orientation of α -PVDF for the as-drawn sample was found to change to *a*-axis orientation when isothermally crystallized at 120°C, but β -PVDF crystals keep the *c*-axis orientation under the same crystallization conditions. The mechanistic investigation ruled out the possibility of the epitaxial crystallization of PVDF on the surface of nylon 11 and it shows that the trans-crystallization of PVDF from the interface of PVDF and nylon accounts for the unique orientation textures.

Key words: polymer blend, crystallization, orientation, wide-angle X-ray diffraction

1. INTRODUCTION

Controlling the microscopic structures of polymer systems is one of the important objects for polymer scientist due to the great influence of the microscopic structures on the macroscopic properties. The oriented crystallization of semi-crystalline polymers has attracted much attention over the past decades because it may cause the unique microscopic morphology and novel orientation textures [1-4]. Recently, the studies have been extended to polymer blend systems [5,6].

In this work, we reported the oriented crystallization behaviors of poly(vinylidene fluoride) in the oriented blends with nylon 11, which is a crystalline / crystalline blend system. Although PVDF/nylon 11 is not a miscible blend system, it has been reported that there are some interactions between the two components [7,8]. When the drawn films of PVDF/Nylon 11 blend were heat-treated in the temperature range above the melting point of PVDF, some new oriented textures of PVDF were produced during melt-recrystallization in the Nylon 11 matrix. It was found that the *c*-axis orientation of α -PVDF for the as-drawn sample was changed to the *a*-axis orientation when crystallized at high temperature, whereas the *c*-axis of β -forms PVDF is always parallel to the stretching direction. The mechanism for this novel orientation textures adopted by PVDF is systematically investigated.

2. EXPERIMENTAL

PVDF and Nylon 11 samples used in this study were purchased from Scientific Polymer Products and Aldrich Chemical Company, respectively. The melting points of PVDF and nylon 11, as determined by differential scanning calorimetry (DSC), were 159°C and 193°C respectively at a heating rate of 20 °C/min. The two polymers weighted at a ratio of 50/50 were melt-blended using a single-screw extruder. The

temperatures of three zones (feed zone, extruder zone and die) for the extruder were set to 165, 185 and 210°C, respectively. The blends were then hot pressed at 215°C to a thin sheet with the thickness of 200 μ m, followed by rapid quenching into ice water. PVDF was well crystallized in the obtained blend films because of the very fast crystallization rate of PVDF, which can be confirmed by WAXD patterns of the obtained films. Oriented samples were prepared by uniaxial stretching the molded sheets to a draw ratio of 4 at 145°C and at a stretching speed of 10mm/min (hereafter designated to be **as-drawn sample**). The as-drawn samples were heat treated with fixed ends at 170°C for 5 minutes to melt the PVDF crystals, and then fast moved to a hot stage with the temperature of 120°C for isothermal crystallization (the obtained sample was hereafter designated to be **annealed sample**).

Wide-angle X-ray diffraction (WAXD) experiments were conducted using CuK α radiation (40KV, 300mA) with an X-ray diffractometer (Rigaku, Rint 2500 VH/PC) equipped with an image plate as the detector. Azimuthal profiles for WAXD patterns were obtained from the imaging plate via scans, which started from the vertical direction of the patterns. Small-angle X-ray scattering (SAXS) patterns were obtained by a fine-focused CuK α radiation (45KV, 60mA) generated by an X-ray diffractometer, Rigaku, Ultrax 4153A 172B and by an imaging plate detector. Confocal laser scanning microscope (CLSM) measurements were carried out with a laser-scanning microscope, Zeiss LSM 510. The blend was dyed with the fluorescent dye, fluorescein (Wako Pure Chemical Industries, Ltd.) prior to the observation. It was found that only nylon 11 can be stained, but PVDF cannot be stained with the fluorescent dye in the blend.

3. RESULTS and DISCUSSION

3.1 Crystal forms of PVDF in the oriented blends

It is well known that PVDF can crystallize into several kinds of different crystal forms, depending on the preparation method and crystallization conditions. α and β forms are the most common crystal forms for PVDF. Figure 1 shows the WAXD profiles of the as-drawn and annealed samples. Both the characteristic (002) reflection of the α form and the (001) reflection of β form can be observed for the two samples, which means that PVDF crystallized into a mixture of α and β forms for both samples. However, the relative intensity of the β form reflection (001) for the annealed sample is stronger than that of the as-drawn sample. Therefore, the percentage of β -PVDF in the annealed sample is higher than that in the as-drawn sample.

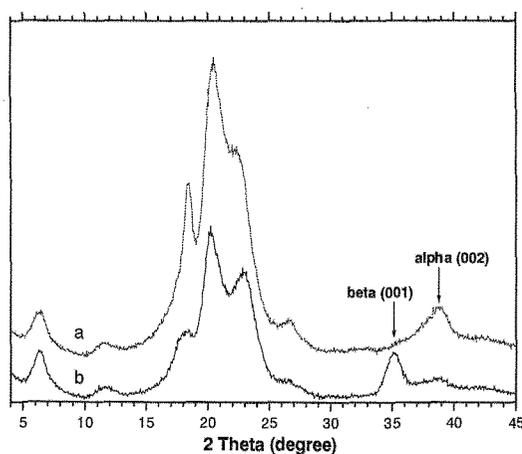


Figure 1. WAXD profiles of (a) as-drawn sample and (b) annealed sample.

3.2 Orientation behaviors of PVDF/Nylon 11 blends

Figure 2 shows the WAXD patterns of the as-drawn sample and the annealed sample. The (kh0) reflections of both nylon 11 and PVDF are observed only on the equator for the as-drawn sample, as seen in Figure 2(a), which reveals the superposition of the typical fiber textures (c-axis orientation textures) of the two polymers. However, for the samples that isothermally crystallized at 120°C, completely different orientation textures were obtained, as shown in Figure 2 (b). It was found that the reflection locations of α -PVDF crystals change from the original positions, in which the (100) reflections moves to the meridian, (110) reflection becomes to 8 arcs and locates on the quadrants, but the (020) reflection still locates on the equator. The novel reflections for the α -PVDF means that the a-axis of the α -PVDF becomes parallel to the stretching direction, indicating the molecular chains rotate 90° for this annealed sample.

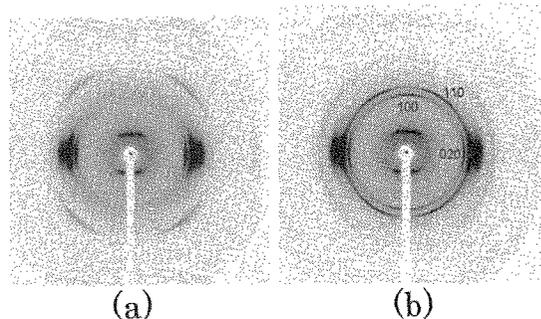


Figure 2. WAXD patterns of PVDF/Nylon 11 blends (a) as-drawn sample; (b) annealed sample

The reflections of β -PVDF at low angle ($<25^\circ$) are all overlapped with the reflections of α -PVDF and nylon 11, so it is difficult to discern the orientation textures of β -PVDF at low reflection angle scale. To clearly detect the orientation behavior of β -PVDF, we tilt the sample by 15° from the vertical direction during WAXD measurements to display the (001) reflections of β -PVDF (as shown in Figure 3). It is clear that the (001) reflections of β -PVDF is only locates on the meridian for both the as-drawn sample and annealed sample, indicating that the β -PVDF crystals is still oriented along the stretching direction for the annealed sample.

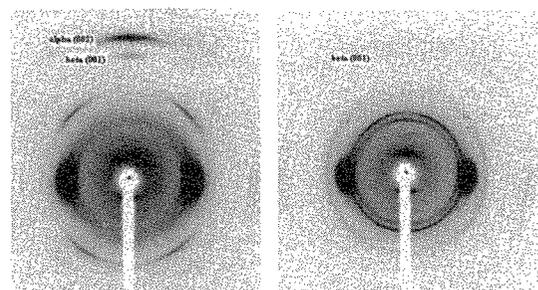


Figure 3. WAXD patterns of PVDF/Nylon 11 measured when the sample tilt 15° from the vertical direction (a) as-drawn sample; (b) annealed sample

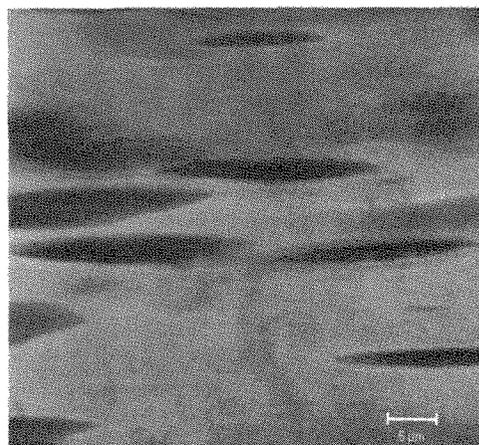


Figure 4. CLSM image of the as-drawn PVDF/nylon 11 blend

3.3 Morphologies of PVDF/Nylon 11 blends

Figure 4 displays the internal morphology of the blend observed by CLSM. It is evident from the image that the PVDF/Nylon 11 blend is not a miscible blend system. PVDF forms a kind of cylindrical domains with a diameter of about $2\text{-}5\mu\text{m}$ and a length of about $30\mu\text{m}$, and is dispersed in the matrix of nylon 11. Therefore, the nylon 11 matrix will surround the PVDF melts when the blend is heated to a temperature between melting temperatures of the two components. It is possible that the interface of nylon 11 and PVDF can act as the nucleation site during the crystallization of PVDF, which is confirmed by the crystallization kinetics of PVDF in the blend [9].

Figure 5 shows the SAXS patterns of the as-drawn sample and annealed sample measured both at room temperature and 170°C . The scattering lobes are only located in the vertical direction for the as-drawn sample, indicating that the lamellar stacks of both PVDF and nylon are oriented along the stretching direction. For the annealed sample, however, arc-like scattering is observed in the whole directions. The scattering is considered to originate only from the lamellar stacks of PVDF, because it disappears completely above its melting temperature.

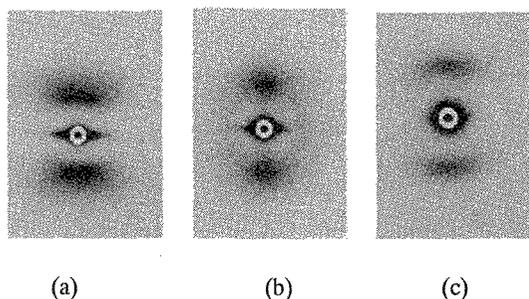


Figure 5. SAXS patterns of the (a) as-drawn sample measured at room temperature; (b) annealed sample measured at room temperature; (c) annealed sample measured at 170°C .

3.4 Mechanism of the novel orientation textures of PVDF oriented crystallized at 120°C .

It is interesting to elucidate the mechanism of the unique orientation behavior. Up to now, epitaxial crystallization [7,8,10], thermal shrinkage stress [11] and confined-growth crystallization [12] have been used to interpret some new crystalline textures found in some biconstituent fibers and PP/PE blends. The possibility of an epitaxial crystallization of PVDF on the surface of nylon 11 can be ruled out because different orientation textures were produced under different crystallization conditions. We could not find any evidence of lattice matching between the crystals of PVDF and nylon 11.

We consider that the trans-crystallization of PVDF on the surface of PVDF and nylon 11 accounts for the novel orientation textures adopted by PVDF when crystallized at high temperature. In fact, it was reported [13] that distinct trans-crystallization of PVDF can be induced by several polymeric substrates, and that the crystal b-axis aligns parallel to the radius of the

spherulites, suggesting that the crystal growth axis of PVDF is the b-axis. Based on the results of the morphology studies and the crystallization kinetics, the novel orientation textures obtained here can be explained as follows: Nucleation of PVDF crystals occurs at the interface PVDF/Nylon 11 and crystal growth proceeds perpendicular to the long axis of the cylindrical domain, in a way similar to spherulite growth at high crystallization temperature. Therefore, the crystal b-axis is highly oriented normal to the drawing direction. α -PVDF is an orthorhombic cell, and so the a-axis is forced to align to the drawing direction.

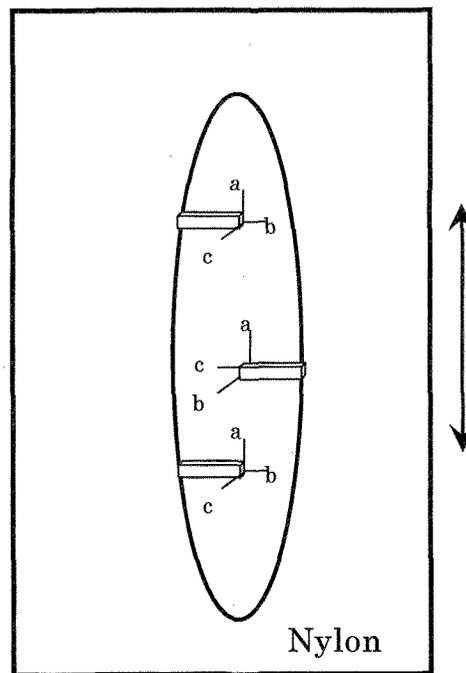


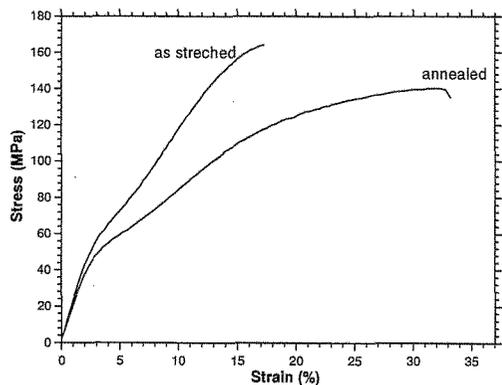
Figure 6. The schematic representations of the trans-crystallization of PVDF on the interface of PVDF/Nylon 11 (○ is the PVDF domain; \leftrightarrow is the stretching direction)

It should be mentioned that the β -forms of PVDF have an all-trans zigzag conformation and the parallel orientation of the molecular chains of β -PVDF may be stabilized by the strong interaction between the amide group of nylon 11 and CF_2 group of PVDF. Therefore, the c-axis orientation of the crystals is preserved when oriented crystallized at high temperature.

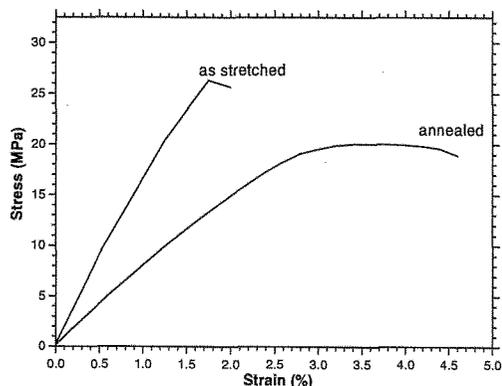
3.5 Mechanical properties of the annealed sample

The mechanical properties of the annealed samples were characterized both in the stretching direction and in the direction perpendicular to it. The results of the stress-strain curves are shown in Figure 7, the properties for the as-drawn sample is also displayed in Figure 7 for comparison. The annealed sample shows high elongation at break in both of the two directions than the as-drawn sample. It is commonly accepted that the ductility (elongation) of polymer material is mainly determined by the amorphous part in semicrystalline polymers. Not only the crystals but also the molecular chains in the

amorphous phase are oriented to the drawing direction for the as-drawn sample. The heat-treatment at 170°C makes the oriented chains in the nylon amorphous phase partially relaxed. Therefore, the annealed sample shows higher elongation at break than the as-drawn sample. The changes of the tensile strength may be attributed to the different interface for the annealed and for the as-stretched samples. It is considered the interface for the annealed sample from the solid-liquid interface during heat-treatment at 170°C is worse than the as-stretched sample, so the tensile strength of the annealed sample is lower than that of the as-stretched sample.



(a)



(b)

Figure 7. The strain-stress curves of the as-drawn sample and annealed sample in the parallel direction (a) and perpendicular direction (b).

4. CONCLUSIONS

PVDF was oriented crystallized in the matrix of the oriented nylon 11 at 120°C. The crystallization and orientation behaviors were studied. It was found that PVDF can crystallize into both α and β forms in the oriented blend with nylon 11. The crystal c-axis of β crystalline form is highly oriented to the drawing direction both for the as-drawn sample and annealed sample. On the other hand, the orientation textures of α crystalline form were found to change from c-axis orientation for the as-drawn sample to a-axis orientation when crystallized at high temperature. It is

considered that the novel orientation behavior is induced by the trans-crystallization of PVDF in the oriented nylon 11 matrix.

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