Strain Rate Mediated Microstructure Evolution for Extruded Poly(vinylidene fluoride) Polymer Films Under Uniaxial Tension

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ABSTRACT: The deformation and fracture mechanism during uniaxial tension under controlled strain rates are investigated for extruded poly(vinylidene fluoride) (PVDF) polymer films at room temperature. It was found that both the longitudinal and transversal film-samples exhibited pronounced strain rate effect, that is, the yield stress increases while the fracture strain decreases with the increasing of strain rates. For the longitudinal film samples, phase transformation from the nonpolar α-phase to the polar β-phase occurs during the uniaxial tension, and the extent of the phase transformation enhances when the strain rate decreases. For the transversal film samples, no phase transformation was detected in all tested strain rates. By combining the stress–strain behavior and the X-ray results, it can be inferred that the conformational change from α to β phase during uniaxial tension contributes to the higher fracture strain of the longitudinal films than that of the transversal films. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1786–1790, 2007

Key words: PVDF polymer film; extrusion; tensile behavior; deformation; fracture

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) and its copolymers exhibit by far the strongest piezoelectric and pyroelectric activity of all known polymers. The substantial piezoelectric effect was not found until the investigations of Kawai in 1969 on elongated and polarized PVDF films.[1] The presence of pyroelectricity was reported in 1971 by Bergman et al.[2] When compared with piezoelectric ceramics or single crystals, PVDF and its copolymers show these advantages of lower density, easier processing, and better compatibility with different forms of surfaces. Their lower mechanical and acoustic impedances also make them good candidates as sensors and transducers in ultrasonic cardiac image, blood pressure and pulse measurements, touch sensors in robotics, etc.[1–6]

PVDF polymers are a rich system for multiple phase transitions. There are at least four crystal forms, labeled as α, β, γ, and δ, which can be converted from one to the other by suitable drawing, annealing, or poling treatments.[7,8] When crystallized from the melt at normal or rapid cooling conditions, one obtains the nonpolar α-phase in which the chain adopts the $TGT\overline{G}$ conformation, and the chain packs in an antiparallel arrays such that there is no net dipole in the crystal. The α-phase has an orthorhombic unit cell with $a = 0.496$ nm, $b = 0.964$ nm, and $c = 0.462$ nm.[7] When subjected to deformation by stretching or rolling at temperatures below $\sim 100°C$, polymer chains within the α phase become extended to the all-trans (TTT) conformation and the structure is transformed into the polar β-phase. The γ-phase is obtained by melt-crystallization at high temperatures ($\sim 160°C$) or annealing above the α-phase melting point. The δ-phase, also called polar α-phase, is prepared by poling the α-phase at high electric fields.[8] In all those phases, the polar β-phase is the most desirable because it possesses piezoelectric and pyroelectric properties.

It was reported that high effective draw is a route to promote electrical response as well as stiffness in PVDF.[9] The drawing temperature has an important effect on the β-phase content and drawing at different temperatures results in different deformation mechanisms. Sajkiewicz et al.[10] reported that drawing in the range between 50 and 145°C for PVDF resulted in the transition of nonpolar α-phase into polar β-crystallites. The highest content of well oriented β-crystallites was achieved when drawing at 87°C. Matsushige et al.[11] reported that the crystal transformation from α to β phase occurred at the temperatures below 130°C, while above 140°C, on the other hand, the sample deformed uniformly without

necking and did not undergo the crystal transformation. Andre-Catagnet and Tence-Girault[12] and Castagnet et al.[13] revealed that there was no phase transition at room temperature, while nucleation and growth of microvoids as well as the splitting up and reorientation of the crystalline lamellar parallel to the tensile direction were the major micromechanisms responsible for the uniaxial tension of PVDF.

In this article, the deformation mechanism during unidirectional tension with different strain rates at room temperature is investigated for extruded PVDF film samples. To reveal the anisotropy of the extruded polymer thin films, uniaxial tensions in the directions parallel and perpendicular to the extruded direction were examined under different strain rates. X-ray diffraction experiments were carried out to reveal the microstructure evolution during the uniaxial tension. It was found that both the film samples pulled parallel to the extruded direction (termed the longitudinal film samples) and the film samples pulled perpendicular to the extruded direction (termed as the transversal film samples) exhibited pronounced strain rate effect, that is, the yield stress (σ_y) increased while the fracture strain decreased with the increasing of strain rates. For the longitudinal film samples, phase-transformation from the nonpolar α-phase to the polar β-phase occurs during the uniaxial tension. The extent of the phase transformation enhances as the strain rate decreases. For the transversal film samples, no phase transformation was detected in all tested strain rates. The deformation mechanism during the tension for both the longitudinal and transversal films will be elucidated.

EXPERIMENTAL

Melt extrusion is one of the methods commonly used to prepare poly(vinylidene fluoride) (PVDF) films.[14,15] In this study, the extruded PVDF films are provided by Beijing Institute of Plastics. Using a specialized tubular film extruder, PVDF resins were fed into the extruder and heated above its melting point, and then extruded through an annular die to obtain tubular films. The tubular films were then passed through nip rolls to be pressed into planar films and the films were drawn at a definite line speed at the same time. All the processes are conducted under controlled processing conditions. The four main processing parameters include melt extrusion temperature (die temperature), extrusion screw speed (rpm), quench height (the distance from the die exit to the air ring), and the line speed in meters per minute (mpm). Generally, the film thickness can be adjusted by the die gap, the nip gap of the squeezing rolls, and the line speed. The films were then vacuum-annealed at 135°C for 2 h to increase the crystallinity. Since the films thus obtained were subjected to unidirectional drawing during the final stage of the extrusion, the chains in the crystalline regions have a preferential orientation in the stretching direction.

Uniaxial tensile measurements were performed at room temperature in this study using a SHIMADZU tensile testing machine. PVDF films were cut into pieces of 60 mm long and 5 mm in width. To reveal the anisotropy of the extruded films, longitudinal and transversal film samples are used. Because of the viscoelasticity of the polymeric materials, the stress–strain behavior depends on the strain rate. The tensile tests were carried out at different strain rates, ranging from 3×10^{-5} to 3×10^{-3} s^{-1}, and at least 3–5 specimens were averaged to collect the tensile property of the film samples.

To reveal the microstructure change during the uniaxial tension, X-ray experiments for samples before the tensile tests, fractured both parallel and perpendicular to the extrusion direction with different strain rates, were conducted in a reflection mode by using a MX18A-HF X X-ray diffractometer with Cu Kα radiation (wavelength 0.154 nm), operated at 50 kV and 200 mA.

RESULTS AND DISCUSSIONS

The stress–strain curves for the longitudinal and transversal PVDF films were measured for many samples and the results are reproducible from different samples. Figure 1 shows the typical stress–strain curves for both the longitudinal and transversal film samples at different strain rates. It can be seen that both the longitudinal and transversal films exhibit typical ductile polymeric behavior that display a maximum in the stress, failing at higher strains. When compared with the same strain rate, the former has a higher fracture strain and the latter, a lower yield strength (σ_y). It can also be seen that the effect of the strain rate on the stress–strain behavior is pronounced. The yield stress increases while the fracture strain decreases with the increase in the strain rate. Plots of the yield strength and fracture strain versus strain rates for both the longitudinal and transversal film samples are shown in Figure 2(a,b), respectively. For all the film samples, apparent necking takes place and the distance of the necking extension increases as the strain rate decreases.

The microstructure evolution during the tensile tests for the film samples are examined by X-ray diffraction techniques. X-ray diffraction patterns for the initial film sample, the longitudinal and transversal film samples fractured at different strain rates are shown in Figure 3. It can be seen from Figure 3(a) that, for the longitudinal film samples, with the strain rate decreased, there is a tendency for conforma-
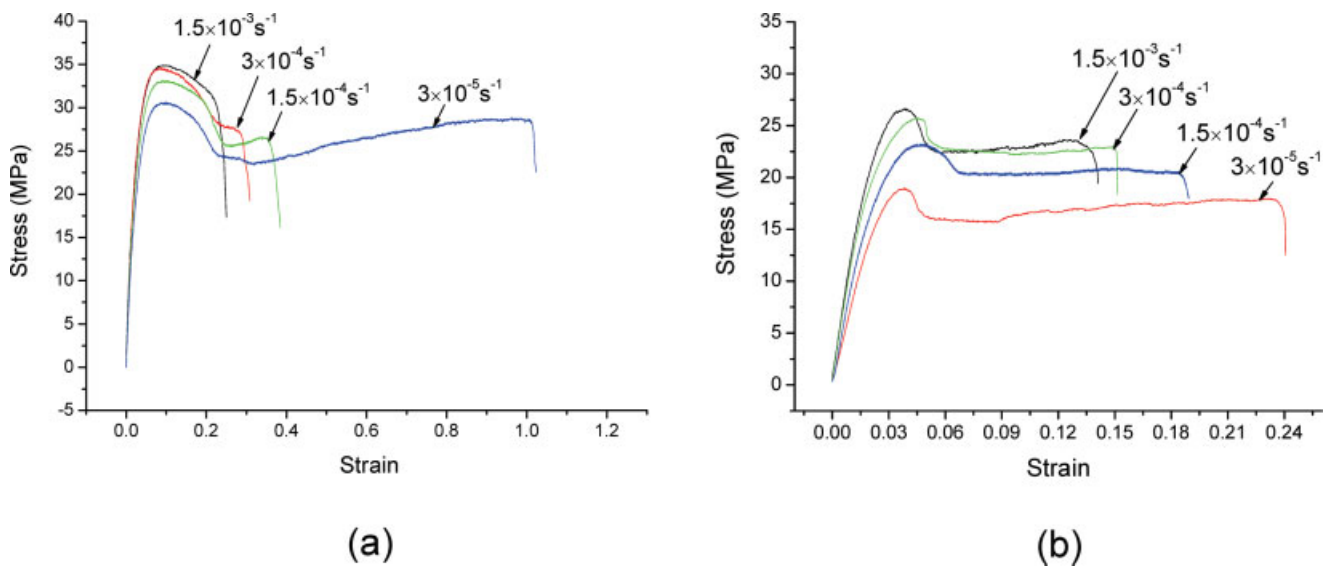
Figure 1 Stress–strain curves for (a) the longitudinal film samples and (b) the transversal film samples at different strain rates. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tional change. For the initial film sample, there are three peaks at $2\theta = 17.885°$, $18.41°$, and $20.13°$, which represent (100), (020), and (110) diffractions of the nonpolar α-phase, respectively. Although the peak intensity subsided rapidly for the film sample fractured at a strain rate of 1.5×10^{-3} s^{-1}, there was no apparent peak position change, when compared with that of the initial film sample. When the strain rate was 3×10^{-4} s^{-1}, apart from the three peaks representing the α phase, there was a small hump around $2\theta = 20.92°$, indicating that part of the α phase was transformed into the β phase. Besides, the three-peak position representing the nonpolar α-phase all shifted a little bit toward higher angle,

indicating that the interchain spacing decreased while the spacing along the polymer chain increased. When the strain rate is further decreased, at 3×10^{-4} s^{-1}, the three peaks representing the reflection of the nonpolar α-phase all disappeared, and there was only a new peak representing β (110, 200) appeared at $2\theta = 20.85$, indicating that all the α phase transformed into the β phase during the uniaxial tension.

For the transversal film samples, neither peak position changes nor new peak occurs, indicating the absence of conformational change during the uniaxial tension in all experimented strain rates, as shown in Figure 3(b).
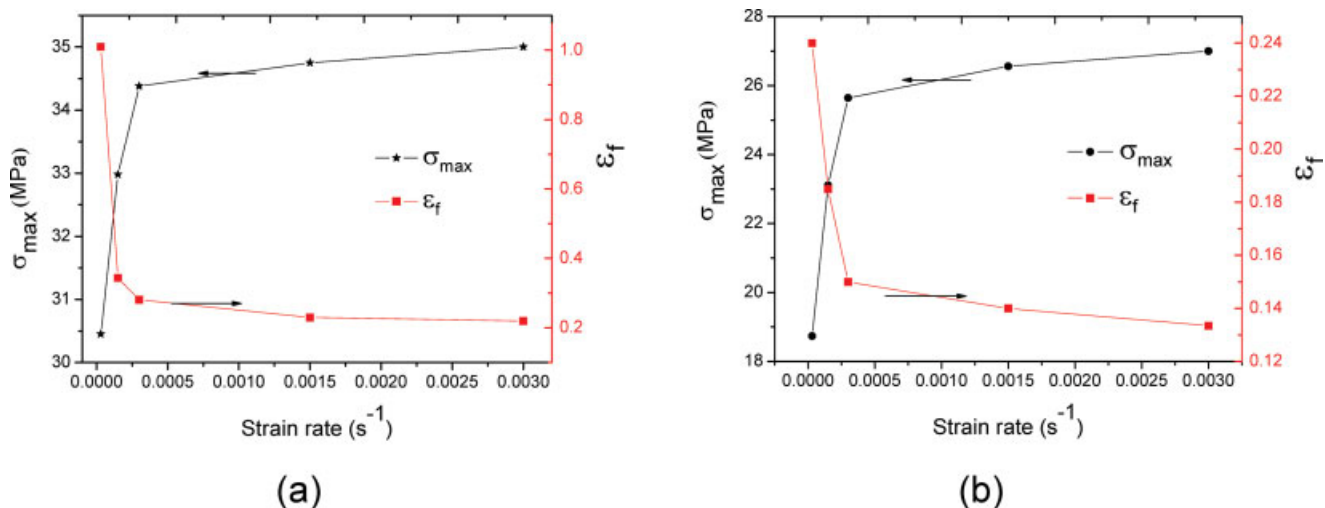

Figure 2 Plots of the yield strength (σ_y) and fracture strain (ε_f) versus strain rate for (a) longitudinal film samples and (b) transversal film samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
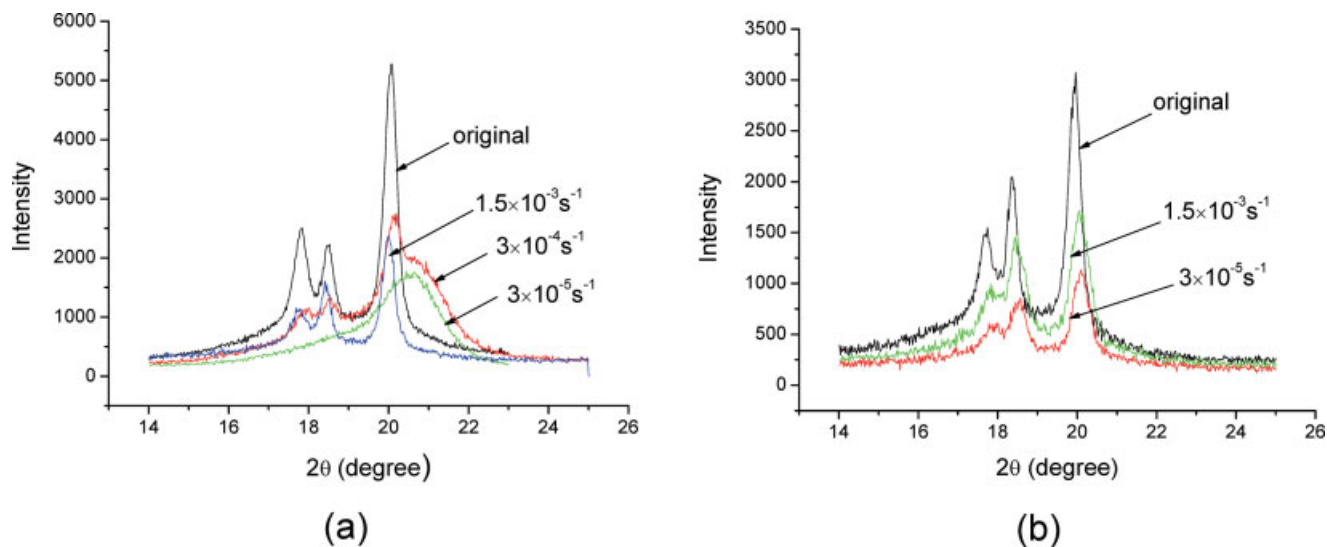
Figure 3 X-ray diffraction patterns for (a) the longitudinal sample films and (b) the transversal sample films before and after being fractured at different strain rates. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Because of the long molecular chain structure of polymeric materials, a fully crystalline state is usually hard to obtain. PVDF films show a semicrystalline structure where the nonpolar crystalline α and amorphous phases coexist at room temperature.[16,17] The crystallinity is about 50–60% depending on the amount of chain ordering defects.[18,19] Since the polymers used in our tests are prepared by extrusion of the molten polymer through fine holes and followed by unidirectional drawing, it causes a structural change from an isotropic state (molten) to a crystalline state, in which the chains show a preferential orientation in the stretching direction. Thus, the longitudinal Young's modulus improves, while the modulus in the transverse direction of the film is much lower than that in the longitudinal direction.[20] This accounts for the higher strength of the longitudinal films than transversal films at the same strain rate.

By combining the stress–strain behavior and the X-ray results, it can be inferred that the conformational change from α to β phase during unidirectional tension contributes to the higher fracture strain of the longitudinal films than that of the transversal films. During the initial stage of the uniaxial tension, the molecular chains in the amorphous region become stretched and elongated due to its higher chain mobility than that in the crystalline region. Then, the molecular chain stretching spreads into the crystalline region. Later, molecular chain slipping and disjunction occur in the crystalline region, leading to an even higher orientation degree. Necking occurs in some localized region with relatively high stress and usually exhibits a higher orien-

tation degree than that in the unnecked area. The deformation will continue to concentrate if the necking is not inhibited, and this will lead to failure. If this plastic instability (necking) is inhibited because of the local strengthening effect, necking will occur in some other regions, and the sample can suffer a larger strain before being ruptured. Schematics of the necking process for both the longitudinal and the transversal films are shown in Figures 4 and 5, respectively. The chain orientation degree is exaggerated and fibril structure is used to clarify their difference. For the longitudinal films, there are mainly
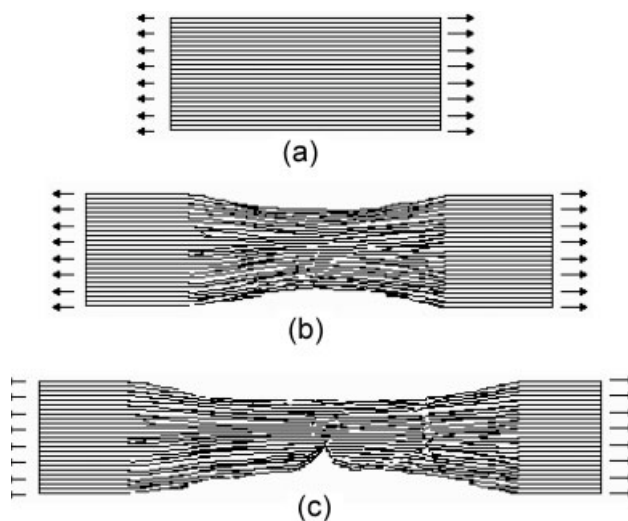

Figure 4 Schematics of the necking process for the longitudinal films: (a) initial state, (b) formation of necking and necking is inhibited, and (c) final fracture.
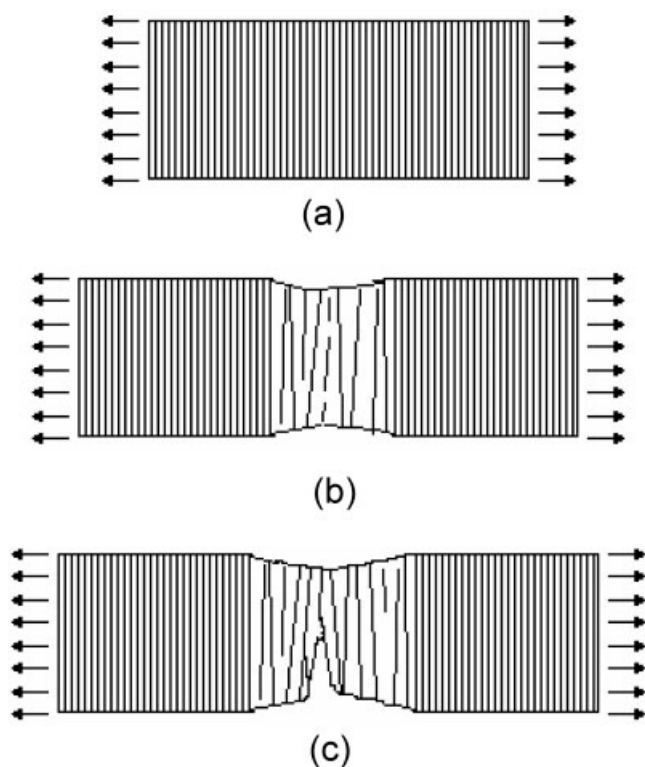
Figure 5 Schematics of the necking process for the transversal films: (a) initial state, (b) formation of necking and necking is inhibited within a relatively small region, and (c) final fracture with lower fracture strain than that of the longitudinal films.

two factors contributing to the inhibition of necking. One is the strengthening effect caused by the higher molecular orientation degree in the necking area and the other is the conformational transformation from the nonpolar α-phase to the polar β-phase. The molecular conformational change between the two-phase results in strains of more than 7% along the stretching direction.[3] The transformation from α to β phase causes the improvement of the rigidity and strength, which further leads to the inhibition of the necking.[21] For the transversal film samples, the strengthening effect is caused only by the high orientation degree in the necking area. Thus, the transversal film samples will fail in a much smaller total strain than that of the longitudinal films. For example, the total strain is 1.01 for the longitudinal film while it reduces to only 0.24 for the transversal film when both the film samples are tensioned at a strain rate of 3×10^{-5} s^{-1}. Eventually, the inter- and intra-molecular bonds break, resulting in the rupture of film samples.

CONCLUSIONS

The deformation and fracture mechanisms during uniaxial tension with different strain rates at room temperature are investigated for extruded PVDF film samples. It was found that both the longitudinal and transversal film samples exhibit pronounced strain rate effect, that is, the yield stress increases while the fracture strain decreases as the strain rate increases. For the longitudinal film samples, phase transformation from the nonpolar α-phase to the polar β-phase occurs during the uniaxial tension, and the extent of the phase transformation enhances as the strain rate decreases. For the transversal film samples, no phase transformation was detected in all tested strain rates. By combining the stress–strain behavior and the X-ray data, it can be inferred that the conformational change from α to β phase during uniaxial tension contributes to the higher fracture strain of the longitudinal films than that of the transversal films.

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