# Hard elasticity of poly(vinylidene fluoride) fibers

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Hard elastic materials are of great interest in science and technology for their unusual crystal structures and mechanical properties. The first hard elastic polymer is a polyoxymethylene fiber found in 1965 [1], which exhibits high initial elastic modulus and high elastic recoveries, e.g. elastic recoveries as high as 92% from 50% extensions. Another elastic polymer is polypropylene (PP) in filament form which appeared in the U.S. patent literature in 1966 [2]; it exhibits a tensile recovery of 82% after an elongation of 25%. Subsequently more hard elastic polymers such as poly(4-methyl-1pentene) (TPX) [3], polyethylene(PE) [4] were found. Briefly, it appears that the elasticity characteristic of the normal and highly crystalline counterpart of these fibers results from a specific molecular orientation within the material. The orientation can be easily identified by X-ray diffraction techniques. Additional work on PP hard elastic fiber showed that the fiber exhibited a porosity of a peculiar nature when it was stretched widely [5]. The mechanism of forming microvoids is due to the stacked lamellar crystal structure normal to the fiber axis within the material. When the fiber is stretched, the crystal lamellae are separated with formation of large amount of interconnected voids. That is why hard elastic polymers can be prepared into hollow fiber membranes by melt-spinning and stretching (MS-S) process. Hollow fiber membranes such as i-PP [6], PE [7] made by MS-S process have been commercialized and widely applied in water treatments. Poly(vinylidene fluoride) (PVDF) is a good material for membranes for its excellent chemical resistance. Ultrafiltration and microfiltration PVDF hollow fiber membranes made through the dry/wet spinning process are commercially available. But the hollow fiber membrane produced by MS-S process has not been reported in the literature until now. Prior to dealing with the preparation of the membrane, hard elasticity of PVDF fibers should be discussed firstly.

The structure development of PVDF in the early stages of melt spinning has been studied using *in-situ* synchrotron X-ray techniques. Shish-kebab crystals aligned along the fiber axis were detected [8–11], the defective shish-kebab structure eventually transforms into a well-defined lamellar structure [9]. Schultz and co-workers [12] recently studied the crystal development and mechanical behavior of PVDF fibers under deformation. They reported that crystallites linked by extended amorphous chains along the fiber axis coexisted with correlated microvoids. The tensile test indicated that necked and unnecked regions were developed alternately along the fiber after the yielding point at about 5–10% strain. Hard elasticity was not observed in their studies. The present work is an attempt to study the hard elasticity of PVDF fibers.

In this letter, extrusion grade PVDF was supplied by Shanghai 3F company of China. Only $\alpha$ conformation is present. The melt flow index is 5 (230 °C, 10 kg load). Its weight average molecular weight and polydispersity $M_w/M_n$ are 416, 405 and 2.8, respectively. PVDF fibers were melt-spun from a melting extruder at 260 °C. The diameter of the spinneret die was 2 mm. The melt-draw ratio, defined as the ratio of take-up speed to the extrusion rate, was 130. The extruded fiber was taken up on a homemade roller and then annealed at 140 °C for 4 hrs. Wide-angle and small-angle X-ray scattering (WAXS and SAXS) measurements were carried out at a 2D diffraction system (Bucker D8 Discover GADDS) with Cr radiation ($\lambda = 0.229$ nm). The direction of X-ray was perpendicular to the fiber axis. Mechanical properties of annealed PVDF fibers were measured by an electronic tensile tester (AG-1, Japan). Elastic recovery was determined along stretched direction of the fiber under five cycles of loading and unloading at a deformation rate of 3 mm/min at 20 °C. The fiber was drawn to 50% extension and then returned to its original gauge length for five successive times.

The results of WAXS and SAXS measurements on PVDF fibers are shown in Fig. 1. The 2D WAXS pattern (Fig. 1a) of annealed PVDF fiber exhibits three strong equatorial streaks with different $d$-spacing (0.439, 0.474 and 0.924 nm), which mainly indicate the crystalline reflections of $c$-axis orientation. The 2D SAXS pattern (Fig. 1b) of the same fibers shows that the crystals existed in the form of crystal lamellae and the lamellar planes are perpendicular to the fiber axis. The corresponding diffraction intensity curve of the fiber (Fig. 1c) indicates a primary scattering peak at $2\theta = 0.98^\circ$, which corresponds to a d-spacing of 13.4 nm.

Mechanical properties of annealed PVDF fibers under cyclic loading are shown in Fig. 2. The annealed fiber has 85% elastic recovery on the first circle, which indicates good elasticity in contrast to 64% recovery of PE hard elastic fiber at 50% room-temperature extension [4]. The initial elastic modulus is about 3.5 GPa. On the immediate and repeated cycling, the

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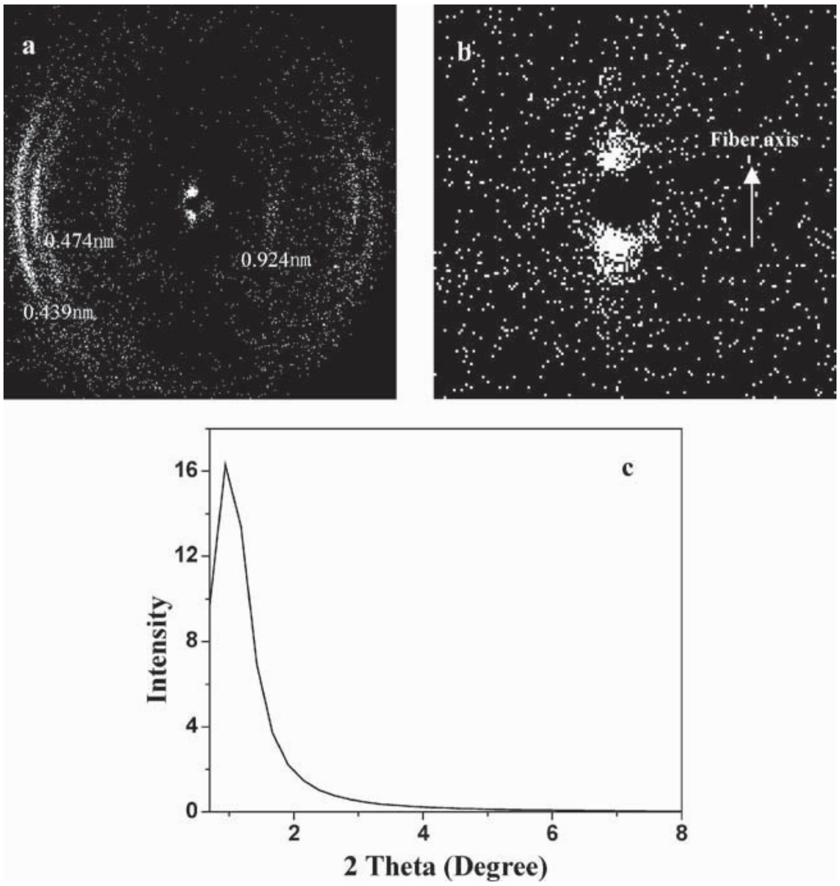

*Figure 1* WAXS and SAXS results for annealed PVDF fibers: (a) 2D WAXS pattern, (b) 2D SAXS pattern, (c) integrated intensity vs. $2\theta$.

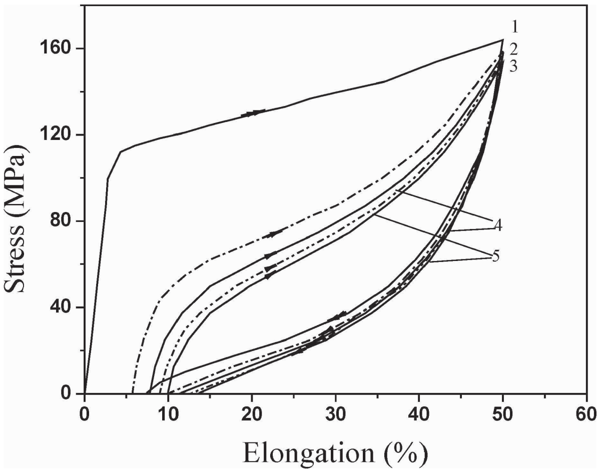

*Figure 2* Cyclic loading to 50% elongation of annealed and unannealed PVDF fibers ($R = 3$ mm/min), the numbers indicate the successive strain cycles.

"yield" point is considerably lowered and the elastic recovery decreases to about 70% after the third cycle.

The morphological and mechanical properties of the annealed PVDF fiber suggest that PVDF fiber has the characteristics of hard elasticity and the hard elasticity is related with its stacked lamellar structures. The mechanism of the hard elasticity and the in-depth work to prepare microporous membranes will be reported in the next work.

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