FLUOROPOLYMER NANOFIBERS BY ELECTROSPINNING

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ABSTRACT

The copolymer of vinylidene fluoride with 5 mol % of tetrafluoro ethylene (VDF-TFE) has the same crystal structure as pure poly(vinylidene fluoride) (PVDF) and exhibits unique electrical properties. It was used to fabricate nano fibers by the electrospinning process (ES) under different conditions. Stable ES was shown to yield nanofibers having both α- and β- crystalline phases as well as ones with only the β-phase, which is known to exhibit interesting ferroelectric and piezoelectric properties. Crystal orientation parameters and crystallte dimensions were estimated by X-ray diffraction.

Keywords: nanofibers; electrospinning, Polyvinylidene Fluoride, x-ray scattering

1 INTRODUCTION

Polyvinylidene Fluoride [PVDF] is a well-known semi-crystalline polymer, which has unique properties such as piezoelectricity, pyroelectricity and ferroelectricity [1], [2]. It has been determined that the β-form (all-trans, TTTT, chain conformations) is the crystal phase that yields the highest piezoelectric coefficients [2], [3]. In this study, electrospinnig (ES) has been used to fabricate ultra-thin nanofibers from the copolymer of vinylidene fluoride with 5 mol % of tetrafluoro ethylene (VDF-TFE). Electrospinning is a simple process that enables continuous production of fine polymer fibers, which have diameters ranging from sub-micron to less than 100 nm [4]. This copolymer was chosen because it has the same set of crystal lattices [5], [6] and about the same chemical structure as pure PVDF. Thus, its electrical properties are very similar to PVDF, but its processing to fibers is easier [6], [7]. It also exhibits similar stability to inorganic acids and bases as pure PVDF. Nanofiber mats produced by this method have extremely large surface area and flexible structure. Combining these geometrical advantages with functional material characteristics can provide a wide area of application such as sensing and actuation as well as scaffolds for active tissue engineering.

2 EXPERIMENTAL

Details of the VDF-TFE copolymer were described previously [5]. The solvents, acetone (Ac) and N,N-dimethylformamide (DMF), were purchased from Aldrich and used as received. Solutions were prepared as 10 weight % of polymer in solution. Stable electrospinning process was carried out using the solvent mixtureAc / DMF 60/40 weigth ratio, at room temperature. Air pressure of 50 mbar forced the solution out of a syringe (needle O.D.0.42 mm) at voltage of 30 kV with respect to the collector. For X-ray diffraction measurements, nanofibers were collected on a disk (diameter 19 cm) rotating at different speeds .The linear disk edge speed (V) was varied between 2.9 and 11.3 m/sec, as well as static colector (V=0)). The distance between the disk edge and the spinneret was 20 cm..

Small and wide angle x-ray scattering (SAXS and WAXS) were performed using a small angle diffractometer (Bruker AXS Nanostar, tube: KFF CU 2 K-90) with Cu K_α radiation, pinhole collimation (that results in a beam 100 micrometer in diameter in the sample) and a 10 x 10 cm^2 two-dimensional position-sensitive wire detector that is positioned 65 and 6.8 cm (for SAXS and WAXS, respectively) behind the examined sample. Uniaxially aligned nanofibers were removed from the disk edge to a metal frame of standard diffractometer sample holder.

High resolution imaging was done by scanning electron microscope (HRSEM) with a LEO 982 (Zeiss) field emission gun digital scanning electron microscope operated at acceleration voltage of 2 and 10 kV. A typical working distance was 4 mm. An in-lens detector of secondary electrons was used for image.

3 RESULTS

We have investigated the effect of polymer concentration, electric field strength, and solvent compositionon the electrospinning process. The conditions that provide a more stable fabrication process at room temperature are described above. Evenreasonable fiber formation was achieved from acetone alone.

WAXS data (Fig. 1, 2) indicate the presence of the β-phase in every fiber sample. Spinning on a static surface (V = 0) yielded non oriented fiber mats containing only β-phase crystals. Increasing the rotation speed of the collection disc beyond V $\geq$ 5.2 m / sec d resulted in appearance of additional α- phase crystals((trans - gauche, TGTG', chain conformation). However, upon further increasing of the disk rotation speed the amount of α- phase decreases (Fig. 2). In the meridional direction the ratio between the α- phase (first peak area) and the sum of α- and β-phases (second peak area) is about the same for speeds 5.2 and 11.3 m / sec, but the value of this ration in the equatorial drection is less for fibers obtained by collection speed of 11.3 m / sec. So, it points out that by varying the fabrication conditions we have the possibility to obtain highly oriented β-fibers using high speed received disk.

The WAXS patterns were used to calculate the crystal orientation parameters of different fibers. The graph along first α-(200) and second α-(110)+ β-(200) rings gives us the profiles containing information about these crystal plane orientation along drawing direction. The simple orientation parameter, δ_{hkl}, is half width of the [hkl] peak at half of its height. The orientation coefficient k_{hkl} (eq. 1) characterizes the crystal plane orientation as a proportional value (Table 1).

$$k_{hkl} = \frac{90 - \delta_{hkl}}{90} \qquad (1)$$

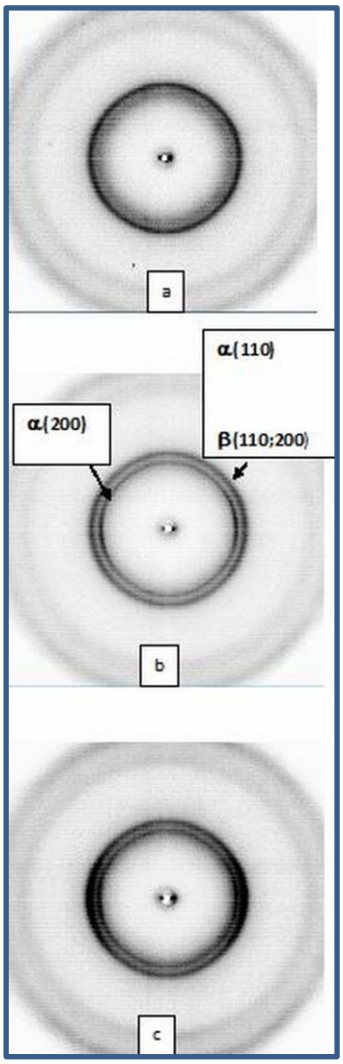

Figure 1. Wide angle X-ray patterns of VDF-TFE copolymer nanofibers fabricated at colelction speeds (m/s): 2.93 (a); 5.24 (b**)**; 11.31 (c**).**
Fiber axis vertical

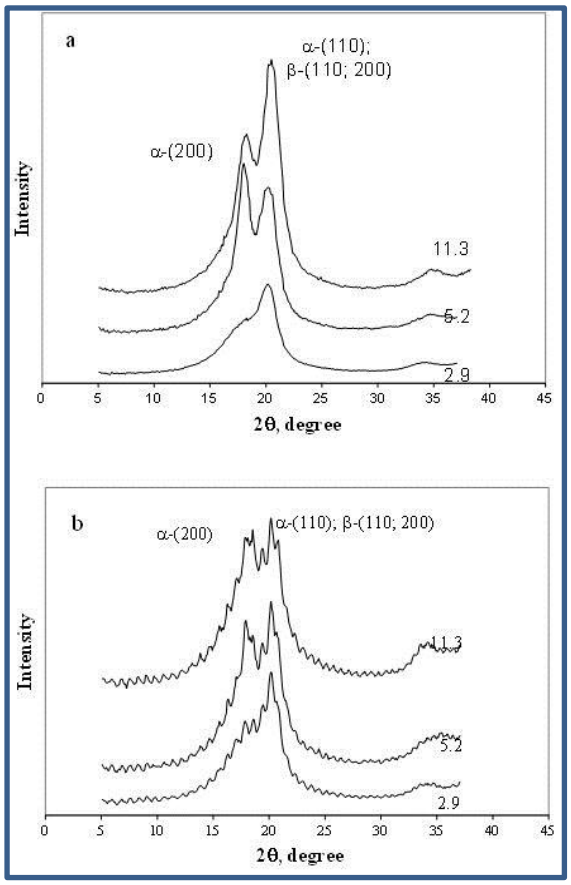

Figure 2: WAXS profile of VDF-TFE nanofibers in the equatorial (a) and meridian (b) directions. Linear speed (m/sec) of received disk is pointed near the curves.

Speed V, m/sec	Kα	Kα+β
2.9		0.61
5.2	0.73	0.64
11.3	0.70	0.70

Table 1 Orientation coefficient, k_{hkl} (eq. 1), dependence on speed of receive disk, V

Strong scattering near the primary beam of the SAXS patterns (Fig. 3) indicates a microporous structure of the fabricated nanofibers. (The contrast of each SAXS photo pattern was chosen to clarify the presence of crystalline long period.) The profiles along the meridian direction (Fig. 4) also show the presence of long period in the fabricated nanofibes due stacking of lamellar crystal periodically along the fiber axis. Table 2 contains the calculated parameters of the oriented (fibril) part of nanofibers [8], [9].

Parameters of the long periods of all investegated fibers are close to each other (Table 2) but the meridional

peak intensity (Fig 3, 4) increases with collection speed and orientation. This points to increase of the density difference between crystal and amorphous parts of long period and/or a high quantity of stacked lamellar crystals.

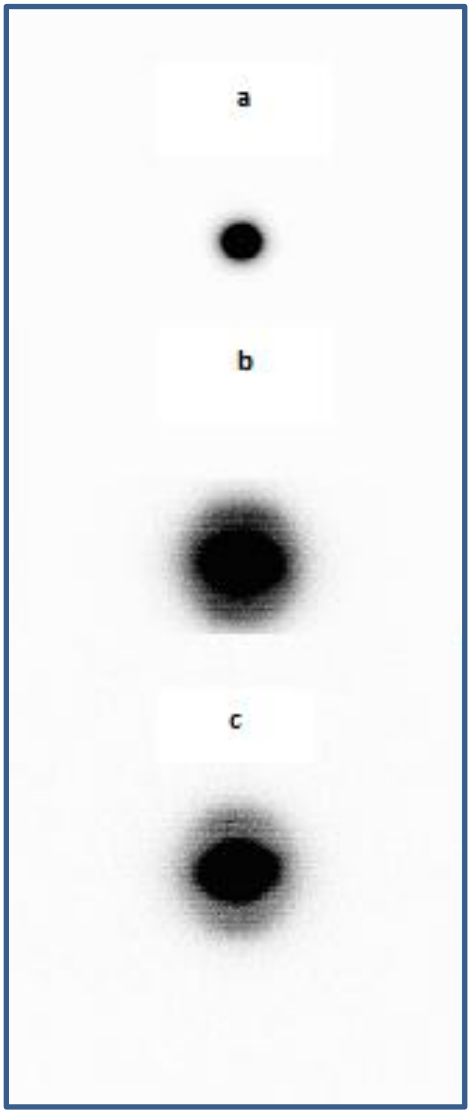

Figure 3: Small angle X-ray pattern of VDF-TFE nanofiber yarn fabricated with collection speeds of:
2.9 (a); 5.2 (b); 11.3 (c) m/sec). Fiber axis is vertical.

Electron microscope images have also shown that fiber diameters have values ≤ 1 μm at all the studied collection speeds (Fig 5).

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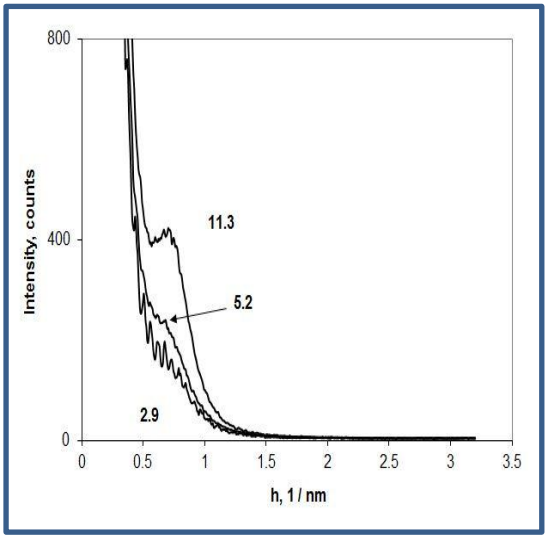

Figure 4: SAXS profile of VDF-TFE nanofiber in the meridian directions. Collection speed (m/sec) indicated near curves. $h = 4\pi \sin\theta/\lambda$, θ is half of scattering (2θ) angle.

Linear received disk speed, m / s	2.9	5.2	11.3
Measured long period, *d*, nm	8.4	8.6	8.5
Calculated long period, *C*, nm	8.8	9.1	8.9
Crystal length, nm	6.3	6.5	6.7
Length of the amorphous parts, nm	2.5	2.6	2.2
Fibril crystallinity	0.72	0.72	0.75
Long period variation, $\Delta C / C$ [9]	0.16	0.16	0.15

Table 2: Fiber crystal structure parameters.
(Accuracy of Fibril crystallinity and $\Delta C / C$ calculation is about 0.01. Accuracy of other Fibril parameters in of Table 2 is about 0.1 nm).

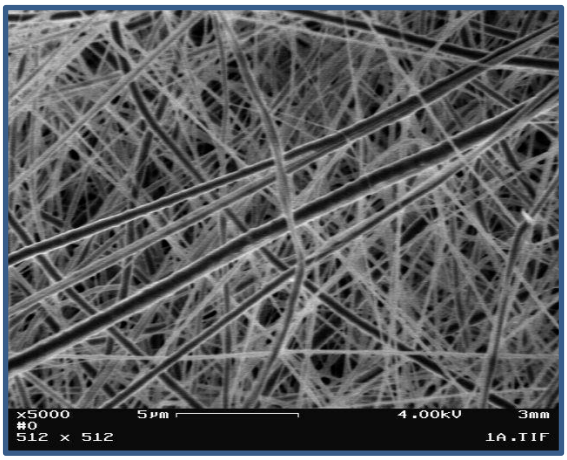

Figure 5: HRSEM micrographs of VDF-TFE nanofibers (static colector, V=0)

CONCLUSIONS

- It was shown that vinylidene fluoride copolymer with 5 mol % of tetrafluoro ethylene (VDF-TFE), which has the same crystal structure and unique electrical properties as pure PVDF can be used to fabricate nano fibers by electrospinning at different conditions.
- A stable process was described to fabricate nanofibers that contain either a mixture of the α- and β- crystalline phases or only the β-phase.
- For every collection speed studied the diamters of the fabricated fibers were smaller than 1 μm;
- The nanofibers exhibit a meridional long period due to stacking of lamellar crystals along the fiber axis. The average long period (crystal length + amorphous layer length along the fiber axis) is about 8.5 nm.
- Fibril crystallinity and orientation of β crystals increase with the collection speed.

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