

EFFECT OF GAS FLOW RATE ON CRYSTAL STRUCTURES OF ELECTROSPUN AND GAS-JET/ELECTROSPUN POLY(VINYLIDENE FLUORIDE) FIBERS*

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Abstract The effect of gas flow rate on crystal structures of electrospun and gas-jet/electrospun poly(vinylidene fluoride) (PVDF) fibers was investigated. PVDF fibers were prepared by electrospinning and gas-jet/electrospinning of its *N,N*-dimethylformamide (DMF) solutions. The morphology of the PVDF fibers was investigated by scanning electron microscopy (SEM). With an increase of the gas flow rate, the average diameters of PVDF fibers were decreased. The crystal structures and thermal properties of the PVDF fibers were investigated by attenuated Fourier transform infrared spectroscopy (AT-FTIR), wide angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC). It was found that electrospinning and gas-jet/electrospinning of PVDF from its DMF solutions promoted the formation of β phase. Moreover, gas-jet/electrospun PVDF fibers exhibited higher crystallinity and β phase content than electrospun fibers did. Similar with electrostatic force, the drawing force of gas jet may induce the conformational change to all-*trans* (TTTT) planar zigzag conformation, and then promote the formation of the β phase.

Keywords: Gas-jet/electrospinning; Poly(vinylidene fluoride) (PVDF); Polymorphism.

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) has received wide attention for 3–4 decades due to its piezoelectric, pyroelectric and ferroelectric activities^[1–4]. PVDF exhibits five different crystalline phases^[5,6]. These crystalline phases involve three different chain conformations, namely: (1) all-*trans* (TTTT) planar zigzag for β phase, (2) TGTG' for α and δ phases, and (3) T₃GT₃G' for γ and ϵ phases^[7]. Among these phases, the β form is the most important phase with outstanding piezoelectric, pyroelectric and ferroelectric properties. The β phase could be obtained by various processes such as mechanical drawing of the α phase films or fibers at temperatures between 70°C and 100°C^[5,8], poling the α phase thin films under high field^[9], milling of PVDF powders using a cryogenic mechanical ball milling^[10], crystallization from the melt under high pressure^[11] or at very high cooling rates^[12], and crystallization from a PVDF solution in *N,N*-dimethyl formamide (DMF) or *N,N*-dimethyl acetamide (DMAc) at 60°C^[13–15], or with addition of hydrated salts^[3,16].

Electrospinning is a simple and versatile method for producing fibers with diameters in the range of several micrometers to tens of nanometers^[17–19]. In the publications of PVDF electrospinning, the effects of various processing parameters on the diameter, morphology, and structure of electrospun PVDF fibers are investigated in detail^[20,21]. Electrospun PVDF fiber membranes have been prepared as a filtration membrane for liquid separation^[22] and a polymer electrolyte for lithium ion polymer battery^[23–28]. Previous studies show that electrospun PVDF fibers are semi-crystalline^[21,25], and its polymorphic behavior also is reported^[7,20,26]. Gao *et al.* reported that the electrospinning process transformed PVDF from α phase to γ phase^[26]. In contrast, the electrospinning process also induced the formation of the β phase^[7,20]. Though the formation of the crystal structure of electrospun PVDF fibers was affected by many processing parameters, Gao *et al.* and Yee *et al.* both

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indicated that the γ or β phase was formed mainly due to the tensile strain of PVDF jets in high voltage field^[7, 26].

Yao *et al.* designed a gas-jet/electrospinning apparatus combining the electrospinning with a gas-jet device^[29, 30]. It is different from the standard electrospinning apparatus in the spinneret. In the spinneret of a gas-jet/electrospinning apparatus, the inner capillary of spinning fluid is circled with the outer tube of the gas jet. Their experimental results of preparations of polysulfone^[29, 30] and poly(ether sulfone)^[31] fibers by gas-jet/electrospinning showed that the gas flow rate was an important parameter during the gas-jet/electrospinning because of the drawing action of the gas jet on the polymer fluid jets. Especially, as the gas flow rate increased from 7.5 L/min to 10.0 L/min, the average diameter of the fibers decreased remarkably from 393 nm to 208 nm. As the gas flow rate was further increased to 15.0 L/min, the average diameter of the fibers decreased slightly. So, the drawing action of the gas jet was exhibited obviously until the gas flow rate exceeded 10.0 L/min. However, there is little information about the effect of gas flow rate on the crystal structures of electrospun and gas-jet/electrospun PVDF fibers. In this study, electrospun and gas-jet/electrospun PVDF fibers were prepared by electrospinning and gas-jet/electrospinning at gas flow rates of 10.0 L/min and 15.0 L/min, respectively, and the crystalline phase variation in electrospun and gas-jet/electrospun PVDF fibers was investigated.

EXPERIMENTAL

Materials

PVDF powders (FR904) were purchased from Shanghai 3F New Materials Co. Ltd. (Shanghai, China), and the intrinsic viscosity was 1.6 dL/g. *N,N*-dimethyl formamide (DMF) was purchased from Chengdu Kelong Chemical Plant (Chengdu, China). PVDF and DMF were both employed without further purification. Nitrogen (99.9%) was supplied by Chengdu Haoru Gas Sale Co. Ltd. (Chengdu, China).

Electrospinning and Gas-Jet/Electrospinning

PVDF powders were dissolved for about 4 days at room temperature in DMF, where the concentration of PVDF, namely the polymer/solution weight ratio, was 10 wt%. The PVDF solutions were electrospun and gas-jet/electrospun using the gas-jet/electrospinning apparatus shown in Ref. [29–31]. It is different from the standard electrospinning apparatus in the spinneret. The spinneret consisted of two coaxial tubes. The inner capillary delivered the PVDF solutions, while the outer tube delivered nitrogen gas. The electrospinning and gas-jet/electrospinning process consisted of the following components. A DC high-voltage supply (ZGF-60, Chengdu Chuandian Huayun High Voltage Electrical Apparatus Co. Ltd., China) was applied to produce voltages ranging from 0 to 60 kV. The PVDF solution was placed in a 5 mL syringe. A syringe pump was used to feed the polymer solution into the inner capillary having an inner diameter of 0.24 mm. The high voltage was applied to the spinneret, through which the polymer solution passed to be spun, namely electrospinning. At the same time, nitrogen gas in the storage was delivered through a pipe to the spinneret, and a gas jet was occurred. The gas jet was ejected from the outer tube. The polymer solution was spun under the actions of high voltage and gas jet. It was the gas-jet/electrospinning. The fibers were collected on a steel wire netting (the collector) connected to ground under the spinneret. The applied voltage was fixed at 32 kV, the tip-collector distance at 20 cm and the feeding rate at 6.0 mL/h. The gas flow rate was 0 (namely electrospinning), 10.0 L/min and 15.0 L/min and was controlled by a gas flowmeter. All electrospun and gas-jet/electrospun PVDF fibers were dried for 6 h in vacuum at room temperature prior to characterization.

Cast-Coating

The 10 wt% PVDF solution was used for cast-coating. The thin film obtained was dried 6 h in vacuum at room temperature prior to characterization.

Characterization

The morphologies of the electrospun and gas-jet/electrospun PVDF fibers were observed with a JEOL JSM-5900LV SEM. Each sample was sputter-coated with gold for analysis. The average diameter of every kind

PVDF fibers was measured by SigmaScan Pro 2.0 software based on three different SEM images with a magnification rate of 5000. The fiber number of every sample was more than 300.

FTIR spectra were recorded using a Digilab FTS 3000 IR spectrometer with a horizontal attenuated total reflection (ATR) accessory. The samples were placed on the top of the ATR set and scanned from 4000 cm^{-1} to 650 cm^{-1} .

WAXD patterns were recorded with a Dandong Fangyuan DX-2500 X-ray diffractometer using $\text{Cu K}\alpha$ radiation with experiment conditions of 36 kV and 28 mA. The scan rate was $0.6\text{ (}^\circ\text{)/min}$, and the samples were scanned in the 2θ range of 10° – 50° .

DSC curves of the materials were measured with a Netzsch DSC 200 differential scanning calorimeter. The samples were heated at 10 K/min from 25°C to 200°C . All experiments were performed under a nitrogen purge.

RESULTS AND DISCUSSION

Effect of Gas Flow Rate on the Average Diameters of PVDF Fibers

Figure 1 shows the SEM images of PVDF fibers prepared by electrospinning and gas-jet/electrospinning from 10 wt% PVDF solutions in DMF with different gas flow rates. It was found experimentally that the PVDF fibers without bead were obtained by electrospinning and gas-jet/electrospinning. The diameter data of PVDF fibers are shown in Table 1. With an increase in gas flow rate from 0 to 15.0 L/min , the average fiber diameter decreased gradually from 357 nm to 309 nm. The results could be explained as follows. In the gas-jet/electrospinning, both of the high voltage and the gas jet were the drive force of gas-jet/electrospinning process. The gas jet could result in another stretching force. According to Yao *et al.*^[29, 30], gas-jet/electrospinning could be used to prepare thinner fibers than electrospinning because of the additional stretching force. Furthermore, a higher gas flow rate could induce a higher stretching force, which could make a thinner PVDF fiber. It is coincident with our previous study on gas-jet/electrospun poly(ether sulfone) fibers^[31]. Consequently, the diameter of PVDF fibers decreased gradually with an increase in gas flow rate.

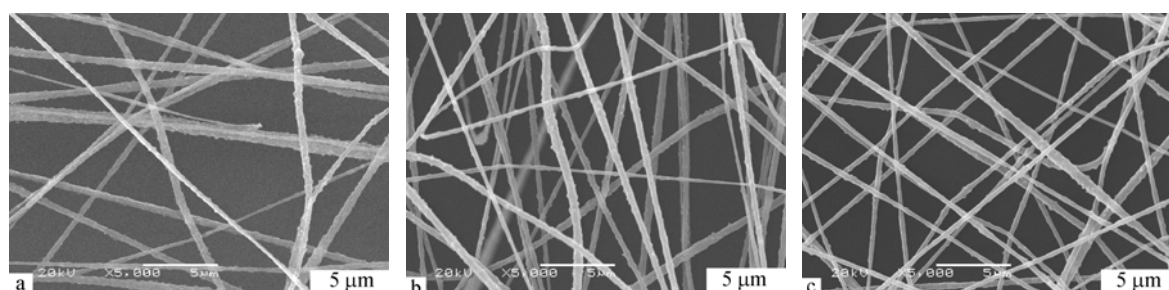


Fig. 1 SEM images of PVDF fibers prepared by electrospinning (a) and gas-jet/electrospinning at different gas flow rate of (b) 10.0 L/min and (c) 15.0 L/min

Table 1. Diameter data of electrospun and gas-jet/electrospun PVDF fibers*

Sample	Average diameter (nm)	Maximum diameter (nm)	Minimum diameter (nm)	Standard deviation
a	357	930	130	0.15
b	330	810	130	0.13
c	309	660	160	0.09

*PVDF fibers were prepared by electrospinning (a) and gas-jet/electrospinning at different gas flow rate of (b) 10.0 L/min and (c) 15.0 L/min .

Effect of Gas Flow Rate on the Crystal Structure and Crystallinity of PVDF Fibers

In order to evaluate the crystal structure of the PVDF fibers, FTIR measurements were carried out on the cast-coated PVDF film, electrospun and gas-jet/electrospun PVDF fibers. The spectral features for each phase of PVDF were reported and identified previously^[5, 16, 32, 33]. The α phase has characteristic IR bands at 530 , 765 and 795 cm^{-1} . The β and γ phases are very similar, and only a few IR bands are distinguished for them. The β phase

has two characteristic IR bands at 1431 and 1276 cm^{-1} , while the γ phase can be distinguished with its characteristic IR band at 1233 cm^{-1} . The strong peak at 840 cm^{-1} is assigned to β or γ phases. As shown in Fig. 2, the cast-coated film exhibited the characteristic IR bands of γ phase at 840 and 1233 cm^{-1} and a weak characteristic IR band of α phase at 765 cm^{-1} . IR bands at 1431 and 1276 cm^{-1} of β phase were absent. It confirms that by cast-coating PVDF crystallizes mainly in γ and α phases from its solution in DMF^[3, 7]. In contrast to the cast-coated film, electrospun and gas-jet/electrospun fibers exhibited the obvious β phase IR bands at 1431 and 1276 cm^{-1} (Fig. 2). In addition, the α phase band at 765 cm^{-1} almost disappeared, and the intensity of γ phase related band at 1233 cm^{-1} decreased. It was clear that β phase was dominant. Figure 2 also shows that the relative intensities of β phase IR bands of gas-jet/electrospun fibers were higher than those of electrospun fibers. However, the relative intensities of β phase IR bands of gas-jet/electrospun fibers changed slightly with an increase in gas flow rate from 10.0 L/min to 15.0 L/min.

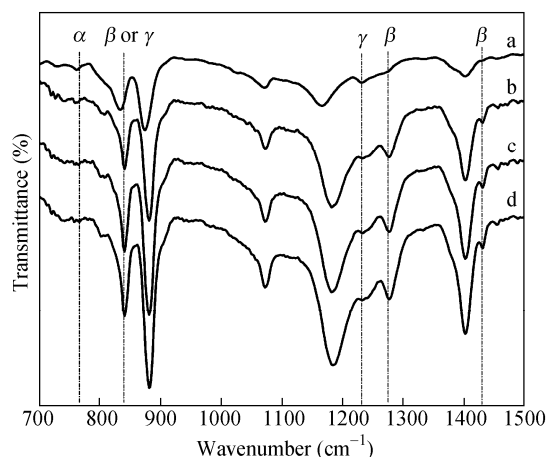


Fig. 2 FTIR spectra of PVDF cast-coated film (a), PVDF electrospun fibers (b) and PVDF gas-jet/electrospun fibers made at different gas flow rate of (c) 10.0 L/min and (d) 15.0 L/min

In addition, WAXD measurements were carried out on the PVDF cast-coated film, PVDF electrospun fibers and PVDF gas-jet/electrospun fibers made at gas flow rate of 15.0 L/min (Fig. 3). The cast-coated film showed the characteristic peak of α phase at 38.9° and the characteristic peaks of γ phase at 20.2° and 36.3° ^[26]. It indicated the co-existence of γ and α phases in cast-coated films. As shown in the curve (b) of Fig. 3, the electrospun fibers exhibited diffraction peaks at 20.5° and 36.3° . The relative intensity of the peak at 36.3° reduced and the peak at 38.9° disappeared. It indicated that the γ phase content was low and α phase vanished in PVDF electrospun fibers. On the other hand, the first peak at the curve (b) of Fig. 3 was shifted to 20.5° because of the coexistence of γ and β phase, which had the characteristic peak at 20.8° ^[10]. In contrast with the electrospun fibers, the gas-jet/electrospun fibers showed that the intensity of the peak at 36.3° further decreased and the first peak was further shifted from 20.5° to 20.7° . It indicated γ phase decreased, while β phase was increased. There was an obvious coincidence between WAXD and FTIR results.

In order to determine the degree of crystallinity and thermal properties of PVDF cast-coated film, PVDF electrospun and gas-jet/electrospun fibers, DSC measurements were carried out. DSC thermograms of PVDF cast-coated film, PVDF electrospun and gas-jet/electrospun fibers are shown in Fig. 4. Four samples showed similar endothermic peaks at about 167°C . Melting points and melting enthalpy of these samples are shown in Table 2. The degree of crystallinity (ΔX_c) of the samples was calculated from the enthalpy of the melting peak (ΔH_f), taken into consideration the enthalpy for a full crystallized PVDF ($\Delta H_{100} = 104.7 \text{ J/g}$)^[26], according to the following equation:

$$\Delta X_c = \frac{\Delta H_f}{\Delta H_{100}} \times 100\% \quad (1)$$

The order of crystallinity is as follows: PVDF cast-coated film > PVDF gas-jet/electrospun fibers > PVDF electrospun fibers. The crystallization of PVDF was weakened by electrospinning and gas-jet/electrospinning. Gas-jet/electrospun fibers showed a higher crystallinity compared with electrospun PVDF fibers. But the crystallinity of gas-jet/electrospun fibers varied slightly with an increase in gas flow rate from 10.0 L/min to 15.0 L/min.

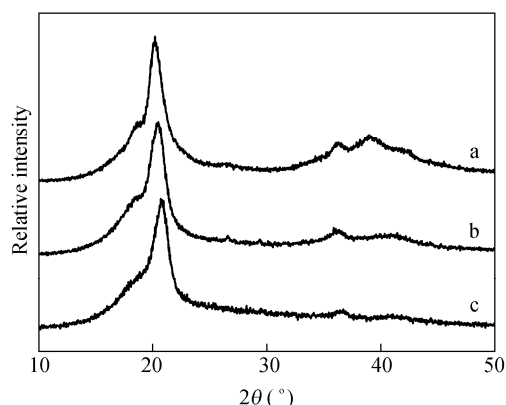


Fig. 3 WAXD patterns of PVDF cast-coated film (a), PVDF electrospun fibers (b) and PVDF gas-jet/electrospun fibers (c) made at gas flow rate of 15.0 L/min

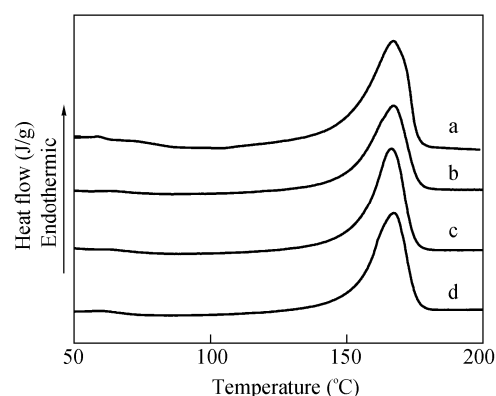


Fig. 4 DSC thermograms of PVDF cast-coated film (a), PVDF electrospun fibers (b) and PVDF gas-jet/electrospun fibers made at different gas flow rate of (c) 10.0 L/min and (d) 15.0 L/min

Table 2. DSC data of PVDF cast-coated film, electrospun and gas-jet/electrospun fibers*

Sample	T_m (°C)	ΔH_f (J/g)	ΔX_c (%)
a	167.0	75.16	71.79
b	166.9	49.05	46.85
c	166.3	54.16	51.73
d	167.0	54.27	51.83

* (a) PVDF cast-coated film; (b) PVDF electrospun fibers; PVDF gas-jet/electrospun fibers made at different gas flow rate of (c) 10.0 L/min and (d) 15.0 L/min

During the electrospinning process, the high stretching ratio of the PVDF jets may benefit the nucleation of β phase^[34]. Consequently, the stretching action of electrostatic force induced the conformational change from TGTG' and T₃GT₃G' conformations to TTTT conformation, and resulted in the transformation from α and γ phases to β phase. So electrospinning of PVDF from its *N,N*-dimethylformamide solution led to the formation of β phase. During the gas-jet/ electrospinning process, γ phase further decreased, while β phase further increased. The stretching force of gas jet may further induce the conformational change and then led to the formation of β phase, similarly with electrostatic force. Gas-jet/electrospun fibers exhibited higher β phase content than electrospun fibers did. At the same time, the gas jet resulted in a higher stretching ratio of the PVDF jet. As a result, gas-jet/electrospun fibers exhibited a higher crystallinity compared with electrospun fibers. However, crystallinity and β phase content of gas-jet/electrospun fibers varied slightly with an increase in gas flow rate from 10.0 L/min to 15.0 L/min.

CONCLUSIONS

PVDF fibers were prepared by electrospinning and gas-jet/electrospinning of PVDF from its DMF solutions. With an increase of the gas flow rate, the average diameters of PVDF fibers were decreased. FTIR and WAXD results demonstrated that the electrospinning and gas-jet/electrospinning of PVDF from its DMF solutions led to

the formation of β phase. In contrast, the γ phase and α phase were detected in the cast-coated PVDF film from the same solution. Moreover, FTIR, WAXD and DSC results indicated that the gas-jet/electrospun PVDF fibers exhibited higher crystallinity and β phase content than the electrospun fibers. It is shown that in addition to the electrostatic force, the drawing force of gas jet may induce the conformational change to all-*trans* (TTTT) planar zigzag conformation and then promote the formation of the β phase.

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