



Effect of temperature on structure, morphology and crystallinity of PVDF nanofibers via electrospinning

Fenglin Huang, Qufu Wei,* Jiaxi Wang, Yibing Cai, Yubo Huang

Key Laboratory of, Ministry of Education, Jiangnan University, Wuxi 214063, P.R. China; fax: 0086-510-85913200; e-mail: qfwei@jiangnan.edu.cn

(Received: 19 March, 2008; published: 24 November, 2008)

Abstract: Influence of temperature on morphology, structure and crystallinity of Poly (vinylidene fluoride) (PVDF) nanofibers was investigated in this study. The Wehlimy technique and viscosity testing apparatus were used to evaluate the surface tension and viscosity of electrospun solutions at various ambient temperatures. Surface morphologies and diameters of nanofibers were examined by Field-emission Scanning Electron Microscopy (FE-SEM) and atomic force microscopy (AFM). It was found that the surface morphologies were obviously affected by ambient temperature. This dependence was attributed to the change of the properties of Poly (vinylidene fluoride) solutions with temperature. The thermal properties and crystal structures of the PVDF nanofibers electrospun at different temperatures were also studied by differential scanning calorimetry (DSC), and X-ray diffraction (XRD). The results revealed that the crystallinity and thermal properties were improved by increasing the ambient temperature during electrospinning.

Introduction

Poly(vinylidene fluoride) (PVDF) has been intensively studied because of its excellent chemical and physical properties, such as piezo-, pyro- and ferroelectricity, flexibility, as well as thermostability, light weight and good processability [1]. These properties have been increasingly applied to various fields such as filtration, air cleaning, and rechargeable batteries. These applications require materials with well-defined properties and functionalities. Nanofibers based on electrospinning have attracted a great deal of attention in these applications due to its remarkable properties, such as small diameters, good pore structures as well as high surface area [2-3].

In the electrospinning of polymer solutions, a number of parameters including viscosity, elasticity, electric potential and distance between the tip and the collector are known to affect the physical properties of the nanofibers, such as fiber shape, diameter, surface morphology, and porosity [4-6]. However, another important parameter, the ambient temperature, has not been properly investigated so far. The effects of the ambient temperatures on the formation, diameter and morphology of PVDF nanofibers were investigated in this work. It is well known that crystallinity plays a vital role in mechanical properties of polymer materials, which is one of the most important factors influencing the ultimate applications of nanofibers [7]. In the electrospinning process, the sudden formation of nanofibers causes insufficient crystallization, leading to lower crystallinity of the electrospun nanofibers. In this work, the effects of the ambient temperatures on the crystallinity and thermal properties of the PVDF nanofibers were also studied.

Results and discussion

Effect on nanofiber formation

The images in Fig. 1 show the PVDF nanofibers prepared at different ambient temperatures from a definite solution. At a low temperature (5 °C), only polymer droplets are formed as shown in Fig. 1a. In electrospinning process, the coiled PVDF macromolecules in the solution are transformed by a flow of the jet into entangled fibrous networks. If the electrostatic force is not strong enough to overcome the surface tension of the solution and stabilize the jet, the beads or beaded fibers are formed [9].

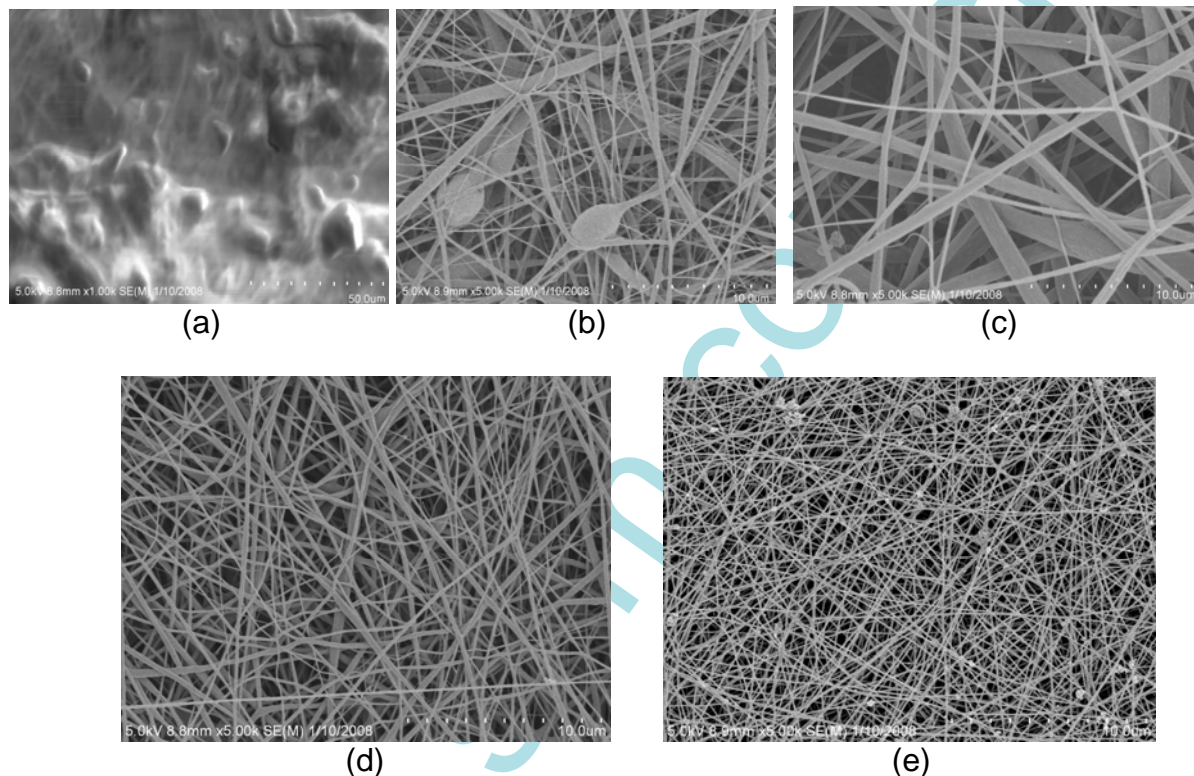


Fig.1. FE-SEM images of electrospun PVDF nanofibers prepared at ambient temperatures of (a) 5 °C, (b) 15 °C, (c) 25 °C, (d) 35 °C, (e) 45 °C.

The surface tension of the PVDF solution is about 42.75 mN/m at 5 °C as shown in Table 1. The nanofiber formation is observed at the ambient temperature near 15 °C. At this temperature, both beads and nanofibers appear, as displayed in Fig. 1b. As the temperature increases to 15 °C, the surface tension of the PVDF solution drops from 42.75 mN/m to 38.78 mN/m, which facilitates the electrostatic force to overcome the cohesive force of the solution. The minute droplets are drawn in the high electrostatic field and then deposit on the collector if the electrostatic force overcomes the cohesive force of the solution. It is observed that the number of beads in the fibrous web becomes less and less as the temperature is increased. The decrease of the surface tension contributes to the formation of nanofiber structures as the temperature is increased as illustrated in Figs. 1c and 1d. When the temperature is increased to 45 °C, some tiny beads are found again at the intersections of nanofibers, as shown in Fig. 1e. This can be attributed to the unstable jets caused by a high temperature during electrospinning.

It is also clearly observed from Fig. 2 that the average diameter of the PVDF nanofibers decreases with increasing ambient temperature. The average diameter of the PVDF nanofibers formed at 15 °C is over 850 nm. As listed in Table1, the viscosity of the solution drops to 205.8 cP at 15 °C from 241.8 cP at 5 °C. The high viscoelastic force resists rapid changes in the fiber shape resulting in the formation of nanofibers with large diameters. The viscosity of the PVDF solution is further lowered to 180.9 cP, which facilitates the formation of the nanofibers with smaller diameters, as illustrated in Fig. 2.

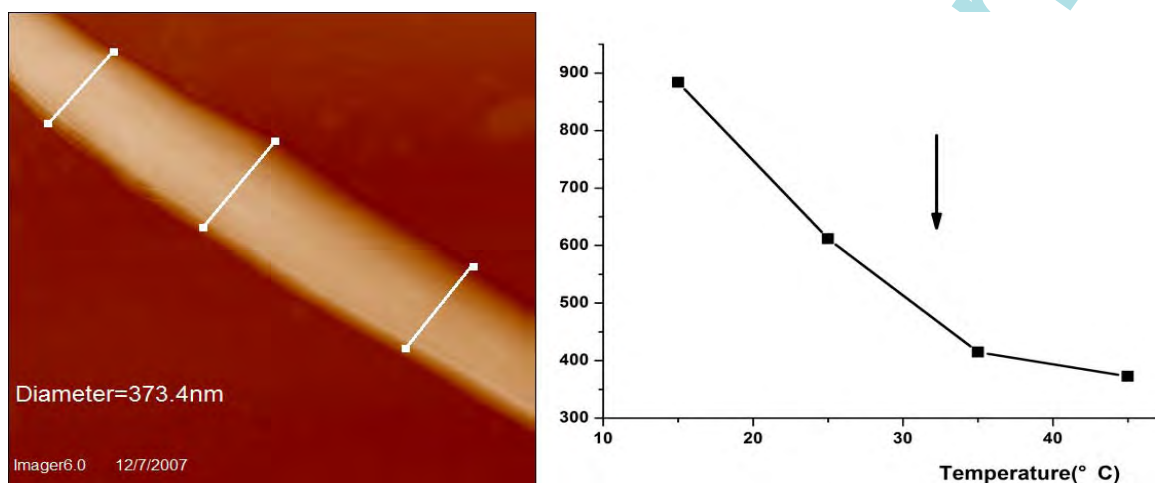


Fig. 2. AFM images of diameter testing and the distribution of electrospun nanofibers.

The average diameter of the PVDF nanofibers gradually reaches about 373.4 nm as the temperature is increased to 45 °C. The changes in surface tension and viscosity contribute to the formation of the finer nanofibers as the temperature decreases. The viscosity and surface tension of the solution drop to 112.6 cp and 27.05 mN/m respectively as the ambient temperature is increased to 45 °C, as listed in Table 1.

Tab.1. Effect of temperature on the surface tension of the solution and viscosity of electrospun solutions.

Temperature (°C)	Surface tension (mN/m)	Viscosity (cP)
5	41.23	241.8
15	38.78	205.8
25	32.26	180.9
35	29.23	150.2
45	27.05	112.6

The formation of nanofibers is mainly achieved by the stretching and acceleration of liquid jets in high electric field [4, 10]. Lower viscosity and surface tension lead to a lower resistance on the surface of ejected jet, thus the jet velocity is increased and higher elongation forces are imposed to the jet. Consequently, the diameter of PVDF nanofibers becomes gradually smaller with the increase of ambient temperature.

The SEM and AFM observations clearly reveal that the structures of the PVDF nanofibers are significantly affected by the ambient temperature. Appropriate ambient temperature is an essential condition for nanofibers formation.

Effect on morphology

The Field-emission Scanning Electron Microscopy (FE-SEM) with a higher magnification clearly reveals the surface morphology of the PVDF nanofibers electrospun at various ambient temperatures, as presented in Fig. 3.

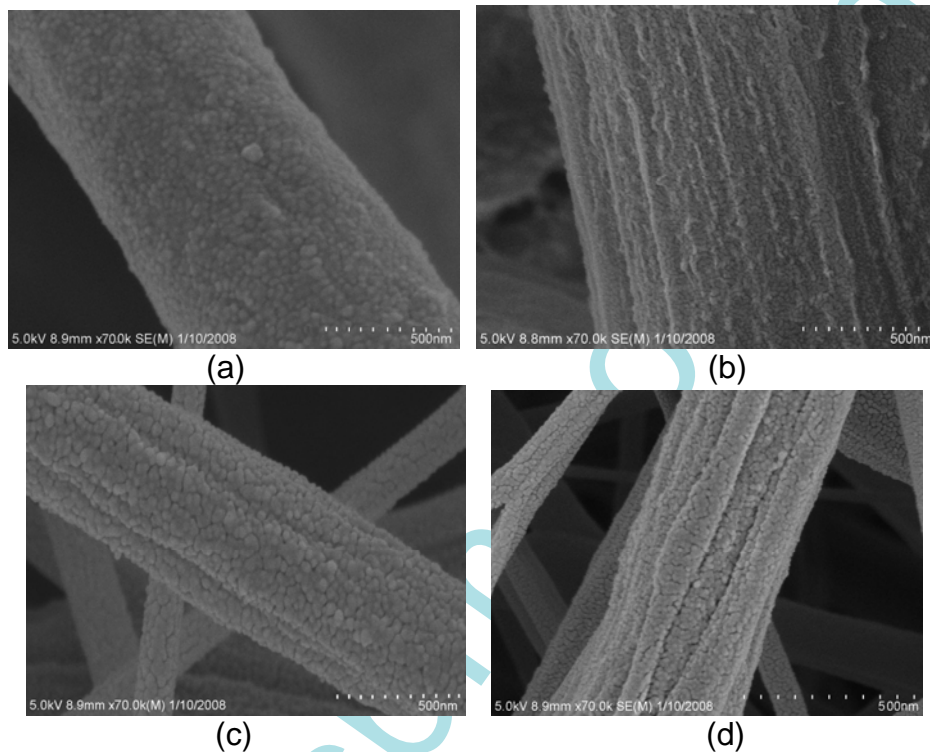


Fig. 3. Surface morphology of PVDF nanofibers electrospun with the temperature of (a) 15 °C (b) 25 °C (c) 35 °C (d) 45 °C

The nanofibers electrospun at 15 °C show a smooth surface and cylindrical shape, as presented in Fig. 3a. It should be noted that the sputtered gold particles are also observed in the SEM image. The gold particles are deposited for the SEM imaging. When the temperature rises to 25 °C, the surface of the PVDF nanofibers seems to be rougher than that of the nanofiber electrospun at 15 °C, as indicated in Fig. 3b. The fibril structures appear on the surface of the PVDF nanofibers. The fibril structures become more obvious when the temperature is increased to 35 °C, as presented in Fig. 3c. It is also observed from Fig. 3d that the grooves between the fibril structures become deeper. These observations indicate that the surface morphology of the electrospun PVDF nanofibers is significantly affected by the ambient temperature during electrospinning. This morphological evolution of the PVDF nanofibers may be attributed to the different evaporation rates of the solvents (DMF and acetone) during electrospinning. The evaporation of acetone from the fiber surface is hindered by the higher boiling point of DMF during electrospinning, which may be the reason for generating the unique surface morphology. This phenomenon becomes more obvious at a high temperature.

Crystallinity and thermal properties

The XRD patterns of the PVDF nanofibers electrospun at the ambient temperatures of 15 °C, 25 °C, 35 °C and 45 °C, are shown in Fig. 4.

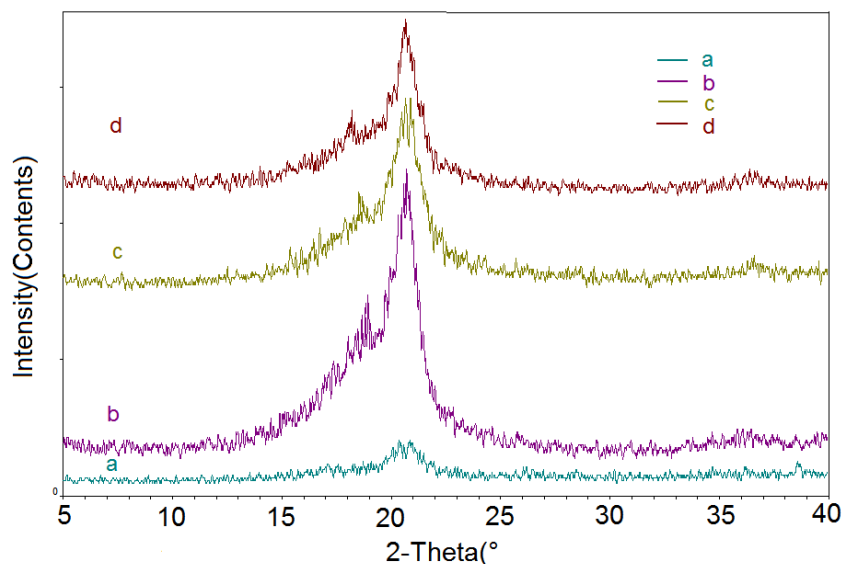


Fig. 4. XRD patterns of PVDF nanofiber nanofibers electrospun with ambient temperature of (a) 15 °C (b) 25 °C (c) 35 °C (d) 45 °C.

All the nanofibers show clear diffraction peaks at 20.0° of 2θ (β phase), and the nanofibers electrospun at 25 °C, 35 °C and 45 °C also exhibit apparent diffraction peaks at 18.4° of 2θ (α phase). The results from the XRD patterns suggest that the crystalline structure can be altered from a single structure, β , to a multiple structure, α and β through an ambient temperature changing. The result also indicates that the fraction of β phase increases to a maximal value at the temperature 25 °C, and then a slight decrease can be seen with the temperature rising. This phenomenon can be attributed to strong intermolecular interactions in the PVDF molecular chains and the sensitivity of chains movement to the ambient temperature.

The DSC analysis reveals the thermal properties of PVDF nanofibers electrospun at various ambient temperatures, as displayed in Fig. 5. It can be shown from the image that the endothermic peaks of the PVDF nanofibers prepared at different ambient temperatures are nearly the same, from 147 °C to 173 °C. However, some disparities in melting point (T_m) and melting enthalpy (ΔH_f) of these nanofibers can be seen from the DSC curves, which are listed in Table 2. The degree of crystallinity (θ) of PVDF nanofibers can be calculated by the following equation [11]:

$$\theta = \frac{\Delta H_f}{\Delta H_f^*} * 100\% \quad (1)$$

where ΔH_f and ΔH_f^* represent melting enthalpies of the present sample and of perfectly crystalline PVDF (104.7 Jg⁻¹ [12]), respectively.

The calculated values in Table 2 indicate that the crystallization of PVDF is insufficient in the nanofibers formed by electrospinning, which can be attributed to the rapid formation of stretched PVDF molecular chains under high elongational rate

during electrospinning. It is generally known that temperature is an important fact influencing the crystallization rate [13]. It is observed that the crystallinity of PVDF nanofibers reaches to a maximum of 52.9 % from an initial 38.5% when the ambient temperature rises to 25 °C from 15 °C. The increase of temperature, however, also accelerates the jet velocity and shortens the solidification time during electrospinning, which will hinder the crystallization of the nanofibers. Thus, the crystallinity of PVDF nanofibers shows a little decrease, from 52.9%, 15°C, to 44.9% and 44.8% corresponding to the ambient temperature 35 °C and 45 °C.

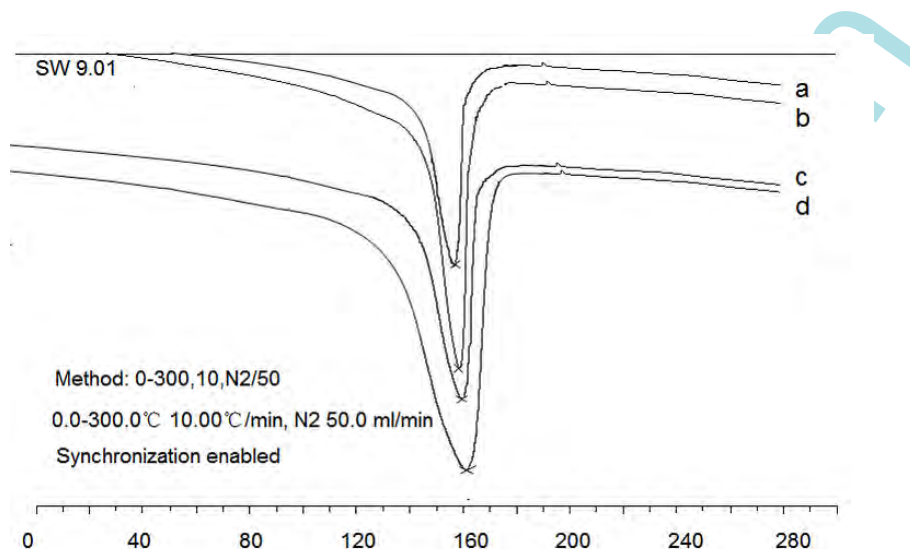


Fig. 5. DSC curves of PVDF nanofiber (a) 15 °C (b) 25 °C (c) 35 °C (d) 45 °C.

Tab. 2. Thermal properties of PVDF nanofibers prepared with various ambient temperatures.

Sample	Melting point (T_m) (°C)	Enthalpy (ΔH_f) (Jg ⁻¹)	Crystallinity (%)
15	160.11	43.2	38.5
25	160.93	55.4	52.9
35	160.62	47.1	44.9
45	160.99	47.0	44.8

Conclusions

This study has explored the effects of temperature on the formation, morphology, diameter, structure and crystallinity of PVDF nanofiber via electrospinning. The formation of the nanofibers was strongly dependent on the ambient temperature. The FE-SEM and AFM observations revealed the decrease in nanofibers diameter with rise in temperature. The experimental results also indicated that the surface morphology of the electrospun PVDF nanofibers was significantly affected by the ambient temperature during electrospinning. The analysis of XRD showed that the crystalline structure of PVDF nanofibers could be changed by the temperature alteration. It was concluded from the DSC analysis that the improvement of crystallinity of the nanofibers could be attributed to the crystallization rate and solidified time.

Experimental part

Materials

PVDF with average molecular weight (M_n) of $5.5 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$ was supplied by Shanghai 3F New Materials Co., Ltd (China). N,N- Dimethyl formamide (DMF) and acetone were purchased from Sinopharm Chemical Reagent co., Ltd (China) and used without further purification. DMF/acetone mixtures were prepared at DMF/acetone weight ratio of 20/80. PVDF was dissolved in the solvent mixtures with a PVDF concentration of 15 wt%. Mechanical stirrer was applied for obtaining a homogeneous solution.

Electrospinning

The apparatus for electrospinning included a plastic syringe, an 18 gauge stainless steel needle, a microinfusion pump (Medical Instrument Co., Zhejiang, China), a high-voltage power supply (Dongwen Co., Tianjing, China), and an aluminum foil as the collector. PVDF solution was drawn horizontally from the needle tip by the electrostatic force, which was formed between the tip and the collector by the high voltage. The ejection rate of the solution was set at 1.0 ml/h, and the distance between the tip and the collector was 15.0 cm. The electrospun nanofibers deposited on the aluminum foil collector in the form of a non-woven mat after the evaporation of the solvent. The electrospinning was performed at 5 °C, 15 °C, 25 °C and 35 °C respectively in an adjustable-temperature lab cabinet.

Surface tension and viscosity of electrospinning solutions

The surface tensions of electrospun PVDF solutions were tested at different temperatures using a CDCA-100F made by the Camtel Ltd in the UK. The surface tension was measured based on the Wilhelmy Ring technique [8].

A Brookfield DV-III Rheometer equipped with the HB 0 mobile was used to measure the viscosities of the PVDF solutions at a speed of 2.45 rev/min.

FE-SEM and AFM observations

The morphology and surface structures of the nanofibers were examined using field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800, Japan). Before SEM imaging, the samples were sputtered with thin layers of aurum.

Morphology observation was also performed employing a CSPM-4400 atomic force microscopy (AFM, China). The imaging software Imager4.6 was used to calculate the diameters of nanofibers. In this study, scanning was carried out in contact mode AFM using a silicon nitride cantilever CSC11 with a nominal force constant of $0.35 \text{ N} \cdot \text{m}^{-1}$.

The diameters of nanofibers were analyzed using the AFM imaging software Imager 6.0. The diameter is measured three times on a representative fiber, and the average diameter was auto-calculated by the software.

XRD and DSC analysis

X-ray diffraction spectra (XRD) of the PVDF nanofibers was obtained from a X-ray diffractometer in D8 ADVANCE (Bruker, Germany) equipment using nickel-filtered Cu K α radiation operated at 40 kV and 40 mA. Diffraction data were recorded using continuous scanning with a rate of 0.02 °/s.

The melting point and crystallinity of the PVDF nanofibers were characterized by a differential scanning calorimeter (DSC 822e, METTLER-TOLEDO, Switzerland). The DSC analysis was performed at the range between 0 °C and 300 °C, with a heating rate of 10.0 °C /min. All experiments were performed under a nitrogen purge.

Acknowledgements

This work was supported by the Program for New Century Excellent Talents in University (NCET-06-0485) and the Innovation Project of Jiangsu Graduate Education (No.: CX07B-152Z).

References

- [1] Khayet, M.; Feng, C. Y.; Khulbe K. C.; Matsuura, T. *Polymer* **2002**, *43*, 3879.
- [2] Wang, X.; Drew, C.; Lee, S.H.; Senecal, K.J.; Kumar, J.; Samuelson, L.A., *Nano. Lett.* **2002**, *2*, 273.
- [3] Gao, K.; Hu, X.; Dai, C.; Yi, T.F. *Mater. Sci. Eng. B.* **2006**, *131*, 100.
- [4] Reneker, D.H.; Yarin, A.L.; Fong, H. *J. Appl. Phys.* **2000**, *87*, 4531.
- [5] Yarin, A.L.; Koombhongse, S.; Reneker, D.H. *J. Appl. Phys.* **2001**, *90*, 4836.
- [6] Theron, A.; Zussman, E.; Yarin, A. L. *Nanotechnology* **2001**, *12*,384.
- [7] Zong, X. H.; Ran, S. F.; Fang, D. F.; Hsial, B. S.; Chu, B. *Polymer* **2003**, *44*, 4959.
- [8] Wilhelmy, J. *Ann. Physik.* **1863**, *119*, 177.
- [9] Huang, Z. M.; Zhang, Y. Z.; Kotaki, M. Ramakrishna, S. *Compos. Sci. Technol.* **2003**, *63*, 2223.
- [10] Qin, X.H.; Wan, Y.Q.; He, J.H.; Zhang, J.; Yu, J.Y.; Wang, S.Y. *Polymer* **2004**, *45*, 6409.
- [11] Kong, Y.; Hay, J. N. *Polymer* **2002**, *43*, 3873.
- [12] Rosemberg, Y.; Sigmann, A.; Narkis, M.; Shkolnik, S. *J. Appl. Polym. Sci.* **1991**, *43*, 535.
- [13] Kim, G. M.; Michler, G.H.; Ania, F.; Calleja, B. *Polymer* **2007**, *48*, 4814.