# Electrospun Nanofibers from Crosslinked Poly(vinyl alcohol) and Its Filtration Efficiency

**Xiao-Hong Qin, Shan-Yuan Wang**

*College of Textiles, Donghua University, Songjiang, Shanghai 201620, China*

Received 1 July 2007; accepted 29 November 2007
DOI 10.1002/app.28003
Published online 11 April 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Nanoscaled crosslinked poly(vinyl alcohol) PVA fibers were prepared by electrospinning. This study described its electrospinning process, structure, and filtration applications. The fibers were found to be efficiently crosslinked by maleic acid. Vitriolic acid was used as a catalyst activator during crosslinking. Scanning electron micrograph and differential scanning calorimetric techniques as well as infrared reflection–absorption spectroscopy (FTIR) were employed to characterize the morphology and structure of crosslinking of PVA fibers, PVA fibers as well as PVA powder. Moreover, the filtration properties of crosslinked PVA nanofibers were tested. During the experiments, crosslinked PVA nanofibers layers with different area weight were placed on the spunbond or meltblown sublayers. The result shows that the filtration efficiency increases sharply when crosslinked PVA nanofibers layers were added to the sublayers. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 951–956, 2008

**Key words:** electrospinning; nanofiber; poly(vinyl alcohol); crosslinking; maleic acid; filtration

## INTRODUCTION

Poly(vinyl alcohol) (PVA) is a water-soluble polyhydroxy polymer and the largest volume for resin produced in the world.[1] The excellent chemical resistance, physical properties, and biodegradability have led PVA to broaden its practical applications.[2] Despite the fact that PVA has good mechanical properties in the dry state, its applications were limited by its high hydrophilicity.[2–4] PVA fibers can be readily crosslinked to improve mechanical properties and antiwater solubility.[5,6]

Electrospinning is a relatively simple method to produce submicron fibers from solutions of different polymers and polymer blends. In general, fibers with diameter less than 1000 nm are called nanofibers in electrospinning. Electrospinning nanofibers are of interest in many applications.[7–12] These include filter media, composite materials, biomedical applications (tissue engineering, scaffolds, bandages, and drug release systems), protective clothing, optoelectronic devices, photonic crystals, and flexible photocells.

Filtration is necessary in many engineering fields. Fibrous materials used for filter media provide advantages of high filtration efficiency and low air resistance.[13] Filtration fineness is one of the most important concerns for the filter media performance. Since the channels and structural elements of a filter must be matched to the scale (as small as 0.3 μm) of the particles or droplets that are to be captured in the filter, one direct way of developing high efficient and effective filter media is by using nanometer sized fibers in the filter structure.[14] In general, due to the very high surface area to volume ratio and resulting high surface cohesion, tiny particles of the order of <0.5 μm can be easily trapped in the electrospun nanofibrous structured filters and hence the filtration efficiency can be improved. Moreover, the strength of nanofibers web is too low to use for filter, meltblown and spunbonded nonwoven are always as sublayers to support nanofibers web.

However, the crosslinked PVA nanofibers and its filtration are difficult to find in periodicals and monographs. The purpose of present work was to prepare the crosslinked nanoscaled PVA fibers, and investigate the structure of crosslinked PVA. Moreover, the filtration properties of electrospinning crosslinked PVA nanofibers were tested and analyzed.

## EXPERIMENTAL

### Materials

Polyvinyl alcohol (PVA, molecular weight $M = 88 \times 10^3$ g/mol) was purchased from Shanghai Chemical Fibers Institute. Maleic acid (MA) and vitriolic acid ($H_2SO_4$) were purchased from Pinjiang Chemical Company.

*Correspondence to:* X.-H. Qin (xhqin@dhu.edu.cn).
Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 10602014.

Journal of Applied Polymer Science, Vol. 109, 951–956 (2008)

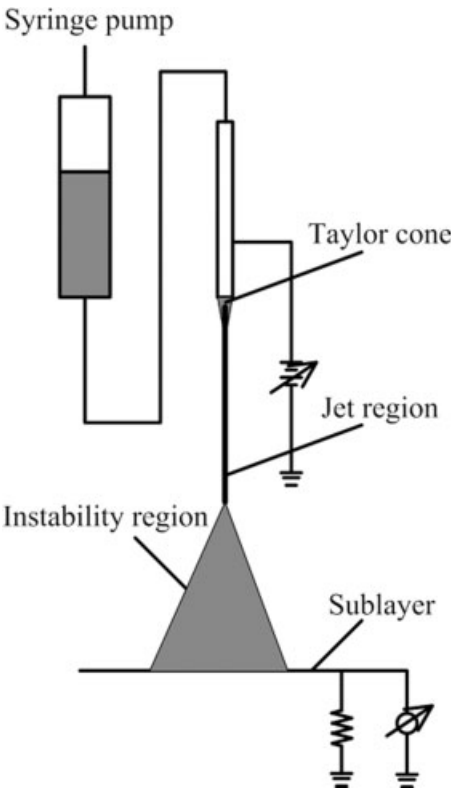



**Figure 1** Experiment set-up.

Polypropylene (PP) spunbonded sublayer and PP meltblown sublayer were purchased from Chinese nonwoven company. The square meter weight of spunbonded sublayer and meltblown sublayer is 18 g/m$^2$. In electrospinning (see Fig. 1), two kinds of sublayers were put in the collecting screen and used to collect PVA nanofibers web, respectively.

### Preparation of PVA solution and crosslinked PVA solution

PVA solution was prepared from PVA powder, distilled water at a temperature of 80°C with vigorous stirring. After 2 h, PVA solution was prepared well.

To get crosslinked PVA solution, MA and $H_2SO_4$ were added into PVA solution at a temperature of 80°C with vigorous stirring. The concentration of PVA solutions tested was 8 wt %. The content of MA added into PVA solution was 10 wt %. PH value of crosslinked PVA solution was controlled within 5 by adding $H_2SO_4$.

### Electrospinning setup

Experimental set-up device used for electrospinning process is shown in Figure 1. Variable high voltage power supply was used for the electrospinning. It was used to produce voltages ranging from 0 to 50 kV, the voltage used in the experiment was about 20 kV, and the current was adjusted to be constant. PVA solution was poured in a syringe attached with a capillary tip of 1 mm diameter, and the flow rate was uniform, 0.5 mL/h.

### Measurements

The nanofibers webs are weighed with the electron balance manufactured by Shanghai Apparatus Company.

The fiber morphology and fiber diameter of the electrospun PVA fibers were determined using scanning electron microscopy (SEM). A small section of the fiber mat was placed on the SEM sample holder and sputter-coated with gold (Denton Desk-1 Sputter Coater). An Amray 3000 SEM using an accelerating voltage of 20 kV was employed to take the SEM photographs. The results are shown in Figure 2.

The hydrolysis-resistant of PVA membranes and crosslinked PVA membranes were tested in boiling water, respectively. The results are shown in Table I. The structure of PVA fibers and crosslinked PVA fibers as well as PVA powder were characterized by

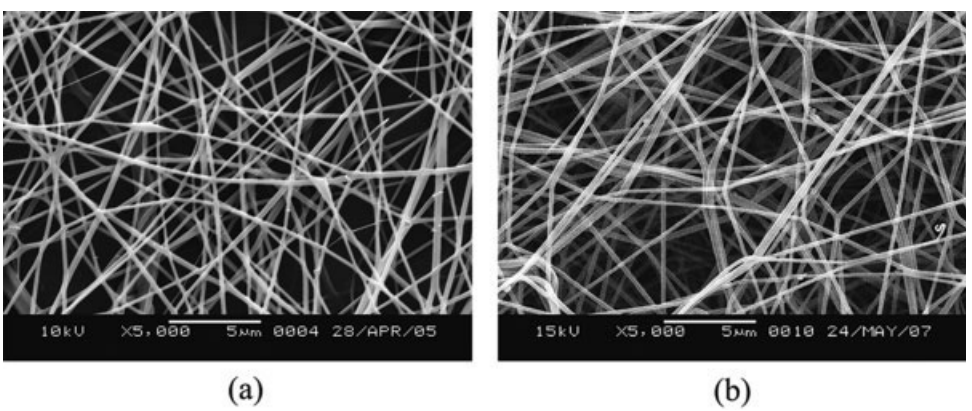



**Figure 2** Compare of conductance of solutions with different kinds of concentration and added salt. (a) 8 wt % PVA membrane (b) 8 wt % crosslinked PVA membrane.

**TABLE I**
**Test of Hydrolysis-Resistant**

| | $G_1$, dry weight before boil (g) | $G_2$, dry weight after boil (g) | $W$, rate of weight loss (%) |
|---|---|---|---|
| PVA membranes | 0.0083 | 0 | 100 |
| Crosslinked PVA membranes | 0.0183 | 0.0177 | 3.28 |

Fourier transform infrared spectrophotometry (FTIR) and differential scanning calorimetry (DSC).

NJL-3 Sodium flame method, manufactured by Qinghua University, was used to test the filtration efficiency of nanofibers webs and sublayers (Fig. 6). The method is based on the NaCl aerosol particles with the mean size 0.6 μm, which penetrate into the test samples. The penetrating velocity of NaCl particles is 5 m/min and the area of the sample is 100 $cm^2$. All the experiments were made according to the British Standard BS 4400.

## RESULTS AND DISCUSSION

### The hydrolysis-resistant of PVA membranes and crosslinked PVA membranes

PVA membranes and crosslinked PVA membranes were cooked in the boiling water for 2 h. The rate of weight loss was calculated according to formula (1). The results are shown in Table I. The rate of weight loss of crosslinked PVA membrane is 3.28% and that of PVA membrane is 100%, which implies the crosslinked PVA membrane has perfect hydrolysis-resistant.

$$W = \frac{(G_1 - G_2)}{G_2} \times 100\% \quad (1)$$

### Structure comparison

From Figures 2 and 3, the average fibers diameter of PVA membrane in Figure 2(a) is about 260 nm, the average fibers diameter of crosslinked PVA-MA membrane in Figure 2(b) is about 230 nm. It is obvious that the diameter of fibers in Figure 2(b) is a little smaller than that of fibers in Figure 2(a). Moreover, the beads phenomena is obvious in Figure 2(a), but after crosslinking, the beads disappear entirely in Figure 2(b) which implies that the crosslinking agent (MA) react in the process. From Figure 3(a,b), the diameter distribution histogram of PVA nanofibers membrane and crosslinked PVA-MA crosslinked nanofibers membrane is similar. The dispersion of Figure 3(a) is 32%, that of Figure 3(b) is 30%, which implies that the crosslinking agent (MA) has not much influence on the diameter of nanofibers.

### Infrared spectrum

Crosslinking reaction Mechanism of PVA and MA is represented in Scheme 1.

The effect of esterification of PVA crosslinked with MA has three forms: complete reaction (form two ester bonds); single esterification (one end forms ester bond and another end has no reaction); and no reaction (dissociating in the form of duality acid among the macromolecule chain).

Figure 4 shows infrared spectrum of PVA particles, PVA nanofibers, and crosslinked PVA nanofibers. The result of chemical reaction crosslinking of PVA fibers should incarnate some characteristic bands of —C=O , —C=C—, C—O—C and COOH. From Figure 4, the ester-carboxyl(—C=O) of crosslinked PVA shows a band around 1718 $cm^{-1}$, compared with that of PVA shows a band around 1734 $cm^{-1}$, the wavenumbers decreased, which explained

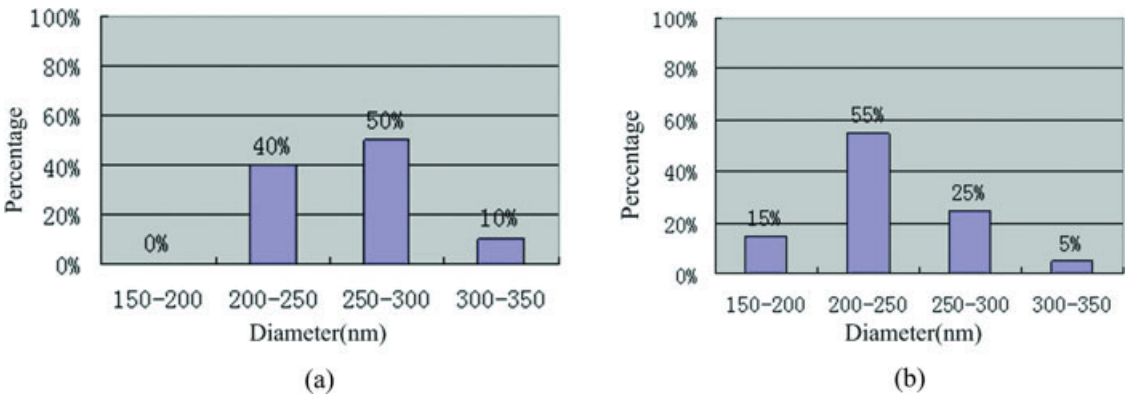
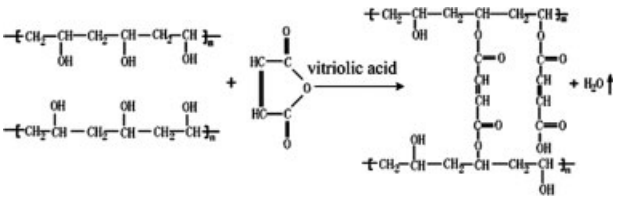



**Figure 3** Diameter distribution histogram. (a) Diameter distribution histogram of PVA nanofibers membrane. (b) Diameter distribution histogram of crosslinked PVA nanofibers membrane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]




**Scheme 1** Chemical reaction crosslinking of PVA fibers.

that —C=O is conjugated with —C=C— in crosslinking structure. Moreover, in the spectrum of crosslinked PVA, —C=C— shows a band around 1637 $cm^{-1}$. Its intensity is much more distinct because it is conjugated with —C=O. Furthermore, C—O—C shows a band around 1090 $cm^{-1}$, we found the intensity of C—O—C in crosslinked PVA fibers was much higher than that in uncrosslinked PVA fibers and PVA powder. From Scheme 1 chemical reaction crosslinking of PVA fibers, it is obvious that C—O—C is the important feature of crosslinked PVA fibers. So this also explained that chemical reaction crosslinking of PVA fibers have occurred. Finally, O—H shows a band around 1260 and 3450 $cm^{-1}$, the former apex is bend oscillation, the later is flex oscillation. We found there was apex around 1260 $cm^{-1}$ in PVA fibers and PVA powder, but was not apex around 1260 $cm^{-1}$ in crosslinked PVA fibers. This explained that O—H decreased after PVA fibers were crosslinked. But we found there was still apex around 3450 $cm^{-1}$ in crosslinked PVA fibers, which showed that some O—H still existed in the crosslinked PVA fibers. It is the reason why there is the weight loss of crosslinked PVA membrane in the test of hydrolysis-resistant in Table I.

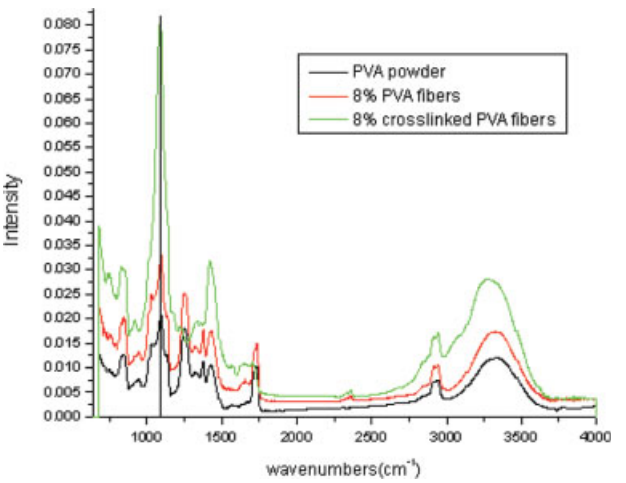



**Figure 4** Infrared spectrum of PVA powder, PVA fibers, and crosslinked PVA fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

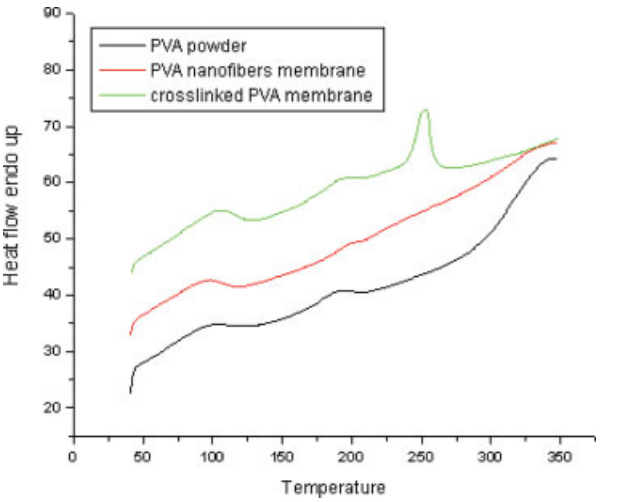



**Figure 5** DSC of PVA powder, PVA membrane, and crosslinked PVA membrane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

## Differential scanning calorimetry

DSC was a valuable technique for investigating the curing reaction of crosslinkable polymers. Figure 5 presented the DSC thermograms over the temperature range 50–350°C for PVA fibers, PVA powder, and crosslinked PVA fibers. As shown in Figure 5, clear melting endothermic point and enthalpy of fusion appeared in 252°C when PVA fibers were crosslinked because the crystal structure formed by crosslinking of PVA and MA during electrospinning.

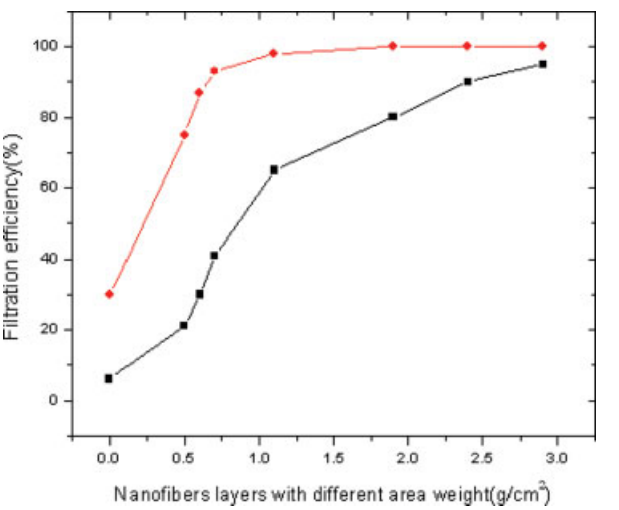



**Figure 6** Comparison of filtration efficiency. The top line shows that crosslinked nanofibers mats electrospun on the meltblown sublayer; the bottom line shows that crosslinked nanofibers mats electrospun on the spunbonded sublayer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

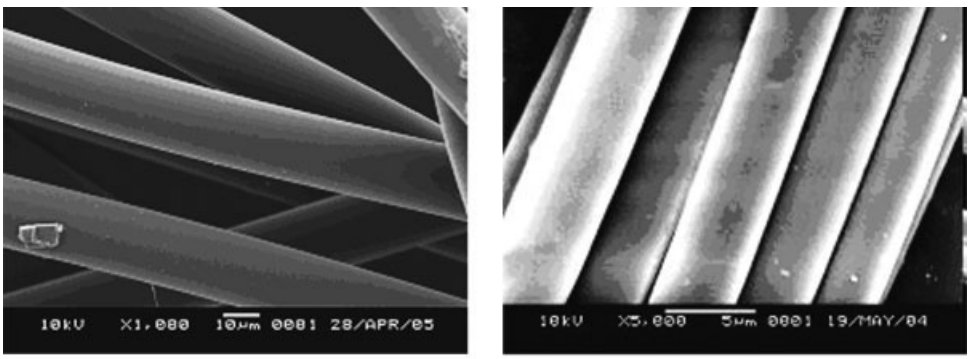



**Figure 7** The morphology of spunbonded sublayers and meltblown sublayers. The average fibers diameter of spunbonded sublayers in (a) is about 13 μm, the average fibers diameter of meltblown sublayers in (b) is about 4 μm. (a) The morphology of spunbonded sublayers. (b) The morphology of meltblown sublayers.

But no clear melting endothermic peak appears in thermogram of PVA nanofibers membrane and PVA powder, because the crystal structure destroyed when PVA powder dissolved in water. PVA fibers were in an amorphous state after electrospinning.

### Filtration efficiency of crosslinked PVA nanofibers membrane

The test of filtration efficiency of uncrosslinked PVA nanofibers membrane has been reported in our former article.[15] We report the filtration efficiency of crosslinked PVA nanofibers membrane. The result is shown in Figure 6.

The filtration efficiency of meltblown sublayers is 30%, the filtration efficiency of spunbonded sublayers is 6%. It is obvious that filtration efficiency of complex is much higher than sublayers after 0.5 g/$m^2$ crosslinked nanofibers membrane was electrospun on the sublayers. Moreover, filtration efficiency of complex is about 100% when 1.9 g/$m^2$ nanofibers web was electrospun on the meltblown sublayers. At the same condition, 2.9 g/$m^2$ crosslinked nanofibers web was needed to electrospining on the spunbonded sublayers, filtration efficiency of complex can only achieve 95%. The results prove that crosslinked nanofibers webs can improve filtration efficiency effectively. The reason is that the diameter of crosslinked nanofibers is smaller than sublayers and the pore diameter of crosslinked nanofibers webs is smaller than sublayers (see Fig. 7). Particles with small diameter are easier to be filtrated in nanfibers webs.

## CONCLUSIONS

PVA has good mechanical properties in the dry state, its applications were limited by its high hydrophilicity. PVA fibers can be readily crosslinked to improve antiwater solubility. Electrospinning nanofibers are provided with good adsorbability and excellent filtration properties due to its smaller diameter(about 200 nm in this article) and the very high surface area to volume ratio. Fiber diameter, chemical reaction crosslinking of PVA fibers, degree of crosslinking as well as filtration efficiency of crosslinked PVA membrane was measured through a series of experiments. Conclusions are drawn as following:

1. The crosslinked PVA membrane has perfect hydrolysis-resistant. Compared with PVA nanofibers membrane, the diameter and diameter distribution crosslinked PVA membrane did not change much.
2. Compared with PVA nanofibers and PVA powder, some characteristic bands of —C=O, —C=C—, C—O—C and COOH of crosslinked PVA nanofibers are distinct in the infrared spectrum. In DSC curves, the melting point and enthalpy of fusion appeared in 252°C when PVA fibers were crosslinked that of PVA fibers and PVA powders is around 350°C. We guess that the melting point moves ahead because of the crosslinking structure forming in the PVA macromolecule.
3. The fiber average diameter of nanofibers web is about 0.2 μm. The average fibers diameter of meltblown sublayers is about 4 μm. The average fibers diameter of spunbonded sublayers is about 13 μm. The filtration efficiency is higher when the diameter of fibers is smaller.
4. Filtration efficiency increase obviously after crosslinked PVA nanofibers web was electrospun on sublayers. The filtration efficiency of complex can almost achieve 100%, when

1.9 g/m$^2$ nanofibers web was electrospun on meltblown sublayer in which filtration efficiency is 30%.

## References


1. Blomstrom, T. P. Vinyl Alcohol Polymers; Pergamon: Oxford, 1991; Vol. 16, p 168.
2. Martien, F. L. Encyclopedia of Polymer Science and Engineering; Wiley: New York, 1986; Vol. 17, p 167.
3. Buchko, C. J.; Chen, L. C.; Shen, Y.; Martin, D. C. Polymer 1999, 40, 7397.
4. Deitzel, J. M.; Kleinmeyer, J. D.; Hirvonen, J. K.; Beck Tan, N. C. Polymer 2001, 42, 8163.
5. Carraher, C. L. E.; Moore, J. Modification of Polymers; Plenum: New York, 1983.
6. Maréchal, E. Chem Modification of Synthetic Polymers; Pergamon: Oxford, 1989; Vol. 6, pp 1–47.
7. Reneker, D. H.; Chun, I. Nanotechnology 1996, 7, 216.
8. Fong, H.; Reneker, D. H. Structure Formation in Polymer Fibers; Hauser: Munich, 2000; p 225.
9. Doshi, J.; Mainz, M. H.; Bhat, G. S. In Proceedings of the 10th Annual International TANDEC Nonwovens Conference, November 7–10, 2000; p 1.
10. Doshi, J. Nonwovens World 2001, 4, 64.
11. Huang, Z. M.; Zhang, Y. Z.; Kotaki, M.; Ramakrishna, S. Compos Sci Technol 2003, 63, 2223.
12. Jukub, H. In Strutex Conference, Czech, 2004.
13. Tsaia, P. P.; Schreuder-Gibson, P. Different electrostatic methods for making electret filters. J Electrostatics 2002, 54, 333.
14. Graham, K.; Ouyang, M.; Raether, T.; McDonald, B.; Knauf, P. In Fifteenth Annual Technical Conference and Expo of the American filtration and Separations society, Galveston, TX, April 9–12, 2002.
15. Qin, X.-H.; Wang, S.-Y. J Appl Polym Sci 2006, 102, 1285.