

Fabrication of Discontinuous Fibers of Poly (*N*-vinylpyrrolidone) Containing Metalloporphyrin Molecules

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ABSTRACT: This study described the preparation of discontinuous fibers of poly (*N*-vinylpyrrolidone) (PVP) containing metalloporphyrin (Manganese (III) tetrakis (1-methyl-4-pyridyl) porphyrin pentachloride) molecules using electrospinning method. SEM images showed that before adding the metalloporphyrin molecules, the electrospun nanofibers are straight and smooth, while after adding metalloporphyrin molecules into the PVP solutions, the SEM images clearly showed that there were two different

types of fibers: the thinner fibrous phase and the thicker discontinuous fibers. The chemical composition of the resulting PVP/metalloporphyrin composite fibers was characterized by Fourier-transform infrared (FTIR) and energy dispersive X-ray (EDX) analysis. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 6017–6022, 2006

Key words: electrospinning; poly (*N*-vinylpyrrolidone); metalloporphyrin molecules; discontinuous fibers

INTRODUCTION

Within the last decade, the electrospinning technique has attracted much attention because of its potential applications in the fields of catalysis, electronics, biomedicine, membrane, and filtration.¹ The electrospinning technique has been proven to be a versatile and effective method for manufacturing micro- to nanoscale fibers. So far, a lot of polymers including commercial, conducting, biological and liquid crystalline polymers have been fabricated to polymer fibers by using this electrospinning method.^{2–6} Recently, inorganic and hybrid (organic/inorganic) compounds have also been prepared by this method.^{7–11} The nonwoven mats composed of electrospun fibers are excellent candidates for applications in filtration,^{12,13} drug delivery,¹⁴ separation membranes,¹⁵ reinforcement in composite materials,¹⁶ energy aerospace and medical devices,^{17–21} as well as biomaterials for wound dressings¹⁴ and scaffolds for tissue engineering,²² because of their large surface areas and small pore sizes in comparison with commercial textiles. So far,

more than 40 different types of polymers have been fabricated for nanofibers by electrospinning.¹ Among those polymers, poly (*N*-vinylpyrrolidone) (PVP) is an important synthetic polymer with good complexation and adhesion properties, excellent physiological compatibility, low chemical toxicity, and reasonable solubility in water and most organic solvents. Using electrospinning to fabricate PVP fibers was also reported by Bognitzki et al.²³ in 2001 and they obtained polylactide (PLA)/PVP blend fibers. Composite nanofibers composed of PVP and TiO₂ (or SnO₂) were prepared by Xia and coworkers.^{24,25} However, there is no report on the fabrication of PVP nanofibers containing functional organic molecules (e.g., porphyrin) up to now.

In recent years, porphyrin molecules are becoming increasingly studied. The redox process involving the oxidation and reduction of the central metal has been elucidated and further to obtain ideally suited properties for applications in molecular photonic and electronic devices.²⁶ The multiporphyrin systems are quite promising candidates for molecular devices since the optical and redox properties of porphyrins can be finely tuned by their chemical modifications and these pigments can be arranged into various architectures either by covalent or noncovalent bonds.²⁷ Recently, external electric field effects on photoelectric properties have been examined for compounds of porphyrin molecules doped in a polymer film.²⁸ At present, it is found that adding some functional organic molecules into the polymer solutions can influence the morphology of the electrospun nanofibers.²⁹ In this article, we

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studied the effect of metalloporphyrin molecules on fibrous PVP produced by electrospinning. Thus we could obtain discontinuous fibers of PVP/metalloporphyrins composite.

EXPERIMENTAL

Materials

Poly(*N*-vinylpyrrolidone) (PVP, $M_w = 1300,000$, Aldrich Chemical Company, St. Louis, MO), metalloporphyrin (Manganese (III) tetrakis (1-methyl-4-pyridyl) porphyrin pentachloride), (J and K Chemical, Beijing, China), ethanol (Beijing Chemicals, Beijing, China; AR), dimethyl sulfoxide (DMSO) (Tianjin Chemicals, Tianjin, China; AR) were used without further purification. The PVP and metalloporphyrin chemical structure is showed in Scheme 1.

Preparation of PVP/metalloporphyrins (manganese (III) tetrakis (1-methyl-4-pyridyl) porphyrin pentachloride) composite fibers by electrospinning

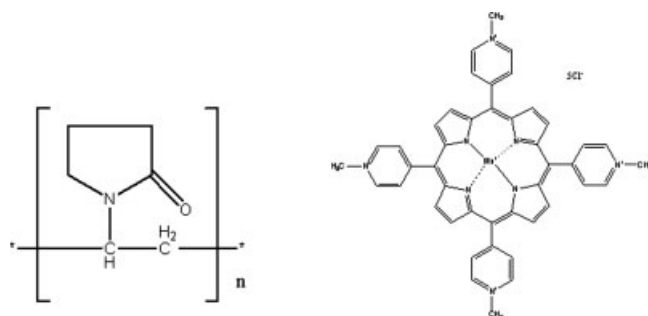
In a typical procedure to electrospin PVP/metalloporphyrins composite fibers, 0.2 g of PVP (Aldrich, $M_w = 1300,000$) was mixed with 1.8 g ethanol or DMSO/H₂O (mass ratio, 4 : 1) in a small bottle, followed by magnetic stirring for 1 h to ensure the dissolution of PVP. 0.28 mg of Manganese (III) tetrakis (1-methyl-4-pyridyl) porphyrin pentachloride was then added into the solution and stirring was continued for about one day. The mixture was then loaded into a plastic syringe equipped with a 14-cm long needle (the top diameter is about 0.5 mm) made of copper. The needle was connected to a high-voltage supply that was capable of generating direct current voltages of up to 30 kV. In our experiment, different voltage from 5 to 20 kV was applied for electrospinning. A piece of flat aluminum foil was placed 15 cm from the tip of the needle to collect the nanofibers. The electrospinning was conducted in air.

Measurements

The fiber images were taken using scanning electron microscopy. The sample electrospun on the aluminum foil was used for SEM measurements. The SEM measurements were performed on a SHIMADZU SSX-550 microscope with an acceleration voltage of 15 kV. Elemental analysis by energy dispersive X-ray (EDX) was done using the SSX-550 scanning electron microscope coupled to an X-ray detector for EDX. Fourier-transform infrared (FTIR) spectra of KBr powder-pressed pellets were recorded on a BRUKER VECTOR22 Spectrometer. Photoluminescence measurements were performed with an Eidingberg spectrofluorimeter. The mechanical properties were measured by an AG-I Universal Testing Machine (Shimadzu, Japan).

RESULTS AND DISCUSSION

It is known that the solution concentration is a key factor determining the morphology and the diameter of the electrospinning polymers, which has been discussed in our previous report.³⁰ Increasing the concentration of PVP in ethanol solution, smooth nanofibers can be changed to discontinuous-shaped fibers. In this study, 10 wt % of PVP in ethanol solvents was chosen to study the effect of adding metalloporphyrin molecules on fibrous PVP produced by electrospinning. Figure 1 shows the SEM images of 10 wt % of PVP in ethanol solvents before and after adding metalloporphyrin molecules. It was found that before adding the metalloporphyrin molecules, the electrospun fibers were straight and smooth. The fibers had a diameter about 1 μm and length about several millimeters. While after adding 0.28 mg metalloporphyrin molecules into the PVP solutions, SEM images clearly showed that there were two different types of fibers: the thinner fibrous phase and the thicker discontinuous fibers. The thin fibers have similar diameter and length with those of without adding metalloporphyrin molecules. The thicker discontinuous fibers are straight and composed of short fibers. The average diameter of the discontinuous fibers is about 10 μm . Although we did not know how the thicker discontinuous fibers formed, we think that it may be ascribed to the polarization of metalloporphyrin molecules in the PVP matrices under high voltage. In an effort to elucidate the mechanism for the discontinuous fibers formation process, SEM images of PVP/metalloporphyrin composite fibers under different voltage in the synthesis under optimal conditions are shown in Figure 2. It is found that when the voltage is low such as 5 kV, parallel discontinuous fibers can be observed. When the voltage becomes higher, we can not found the parallel discontinuous fibers any longer. When the voltage reached to 20 kV, crossed parallel discontinuous fibers are obtained. These phenomena



Scheme 1 Chemical structure of (a) PVP and (b) Manganese (III) tetrakis (1-methyl-4-pyridyl) porphyrin pentachloride.

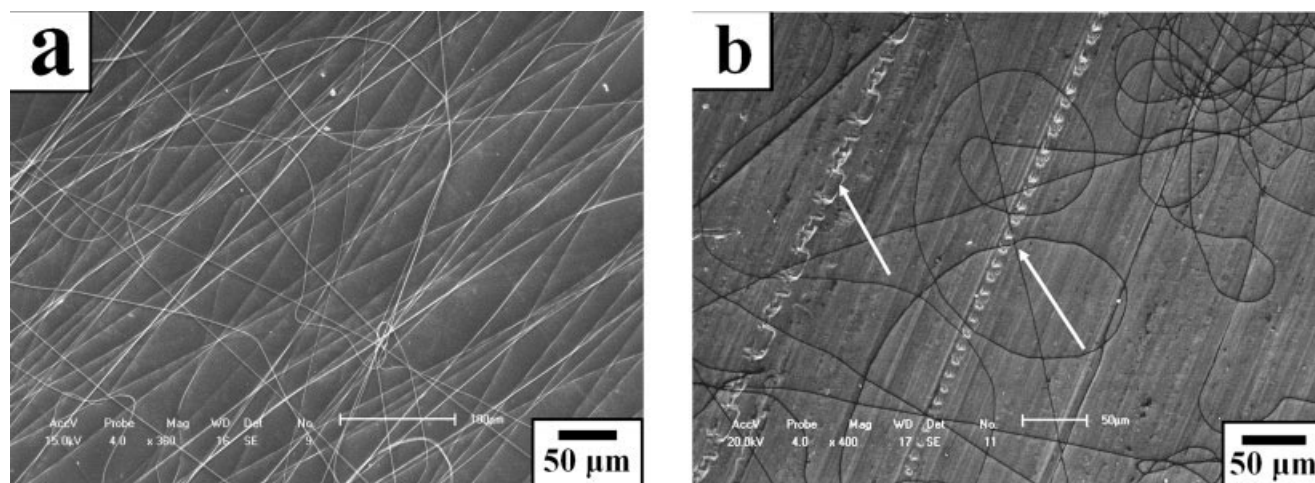


Figure 1 SEM images of PVP fibers electrospun from ethanol solution under 10 kV voltage without (1) and with (2) containing metalloporphyrin molecules.

were probably attributed to the different polarization ability of metalloporphyrin molecules in the PVP matrices under different voltage. Besides the voltage, the

effect of the solvents to the morphology of PVP/metalloporphyrin composite fibers was also studied. It is well known that the morphology and size of electro-

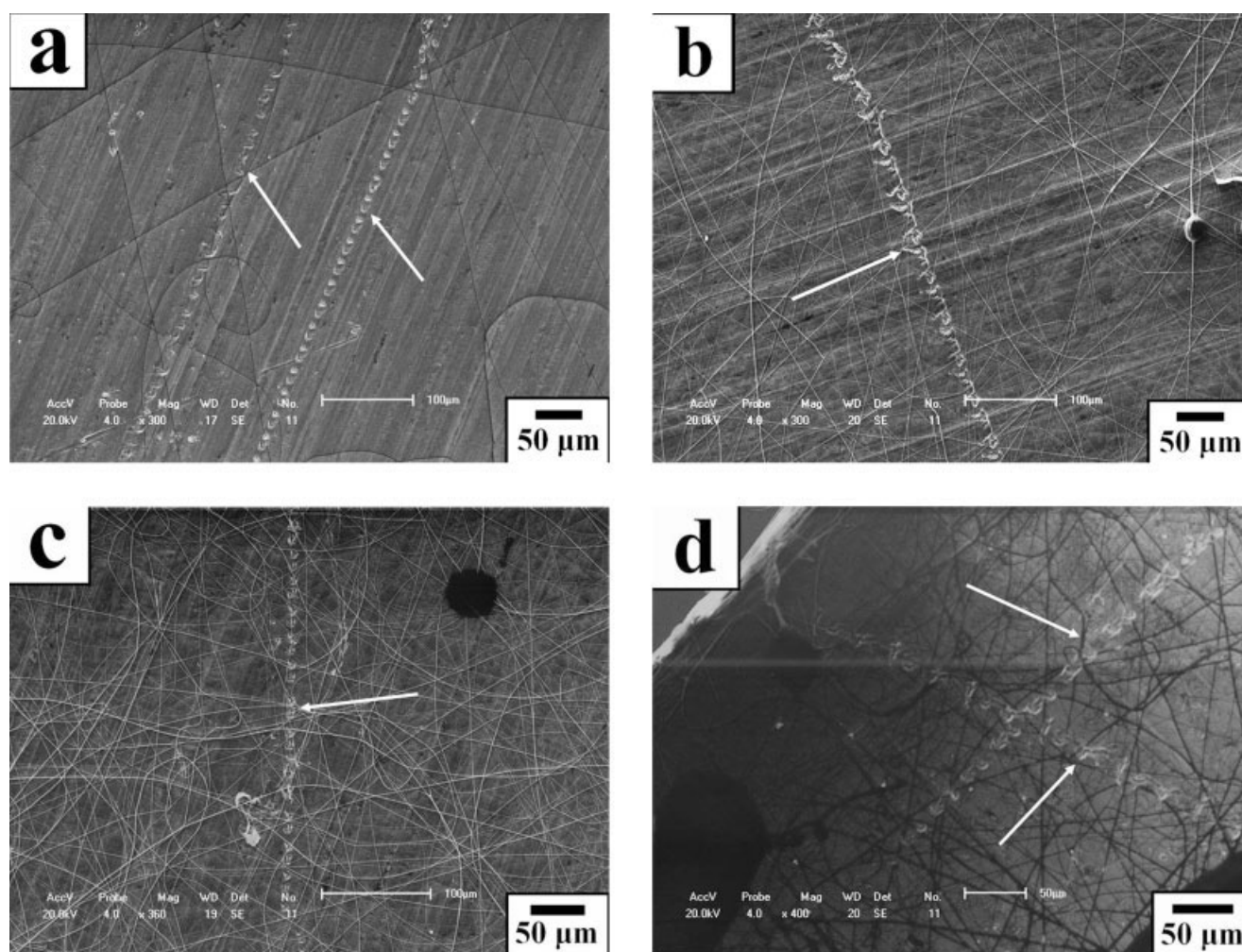


Figure 2 SEM images of PVP fibers containing metalloporphyrin molecules electrospun from ethanol solution under different voltages. (a) 5 kV; (b) 10 kV; (c) 15 kV; (d) 20 kV.

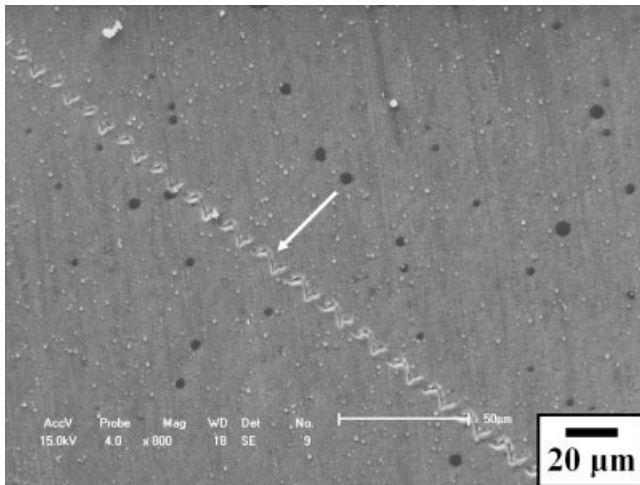


Figure 3 SEM image of PVP fibers containing metalloporphyrin molecules from DMSO/H₂O solutions under 10 kV voltage.

spun fibers strongly depend on solution properties such as viscosity and surface tension.³⁰ DMSO was a good solvent for the charged PVP because it facilitated

the dissolution of the polymer by separating the ion pairs. In addition its presence in the solution could raise the charge density and surface tension. Since the smoothed thinner fibers and discontinuous fibers were obtained from the PVP ethanol solution, we also investigated the effect of the solvent DMSO and mixed solvents DMSO/H₂O. It was found that the similar results were obtained for the two solvent systems. Figure 3 shows the SEM images of PVP/metalloporphyrin composite fibers in DMSO/H₂O solvents, it is found that the thinner fibers could not be found, while the discontinuous fibers could still be obtained. The above result shows that the solvent only affect the formation of the thinner PVP fibers, but did not affect the polarization of metalloporphyrin molecules in PVP molecules. So the discontinuous fibers are still obtained. We also studied the quantity of metalloporphyrin molecules to the morphology of electrospinning composite fibers. It was found that when the quantity of metalloporphyrin was small, no discontinuous fibers could be found. On the other hand, when adding larger quantity of metalloporphyrin to the polymer, the fibers become more

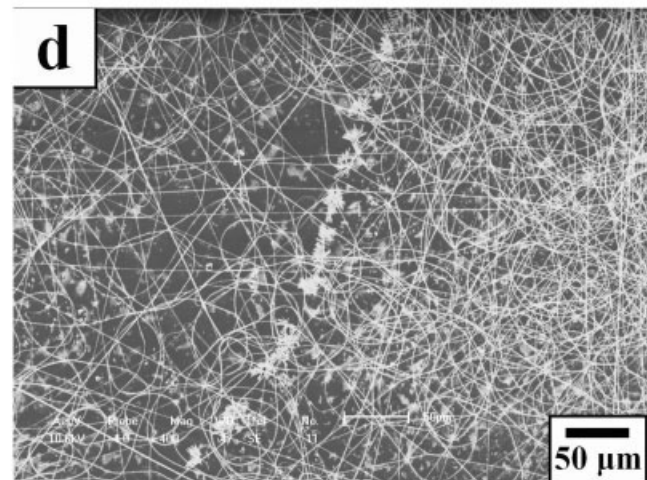
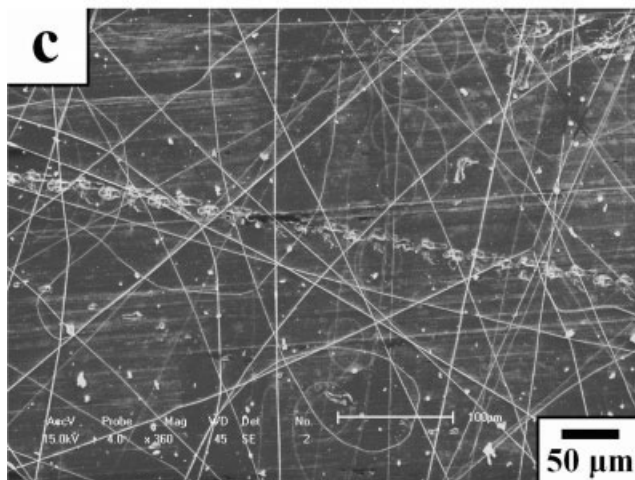
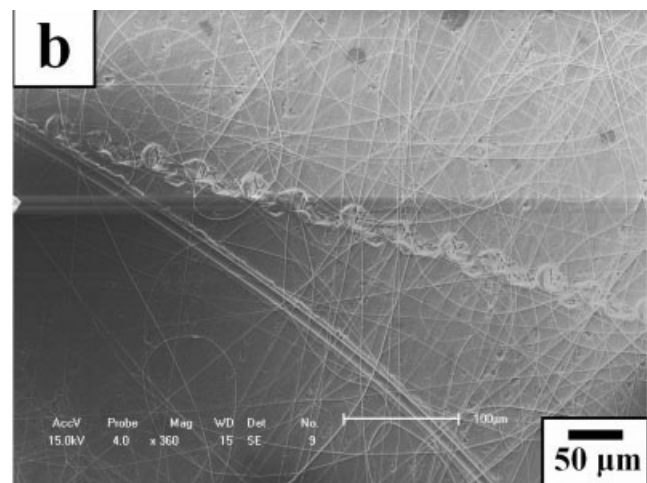
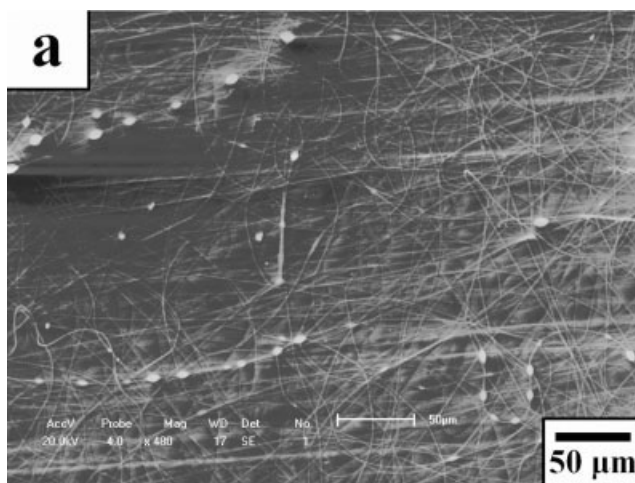


Figure 4 SEM image of PVP fibers containing different quantity of metalloporphyrin molecules from ethanol solution. (a) 0.1 mg; (b) 0.3 mg; (c) 2 mg; (d) 3 mg.

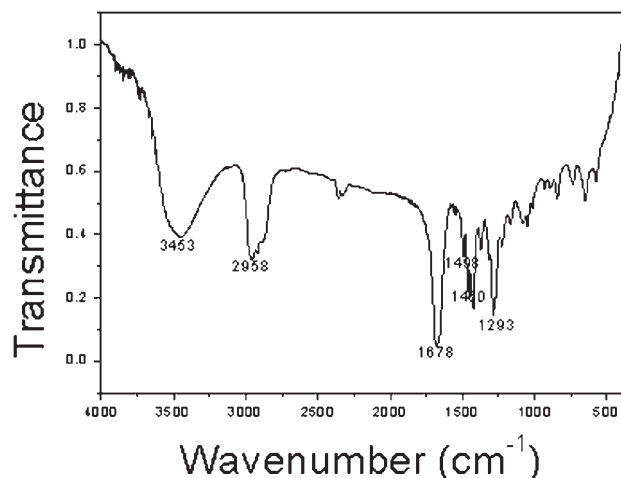


Figure 5 FTIR spectrum of PVP fibers containing metalloporphyrin molecules electrospun from ethanol solution.

discontinuous. And every part of the discontinuous fibers becomes irregularly (Fig. 4).

The chemical composition of the resulting PVP/metalloporphyrin composite fibers was characterized by FTIR and EDX spectra. The peak at 1293 cm^{-1} is the characteristic absorption of C–N stretching in *N*-vinylpyrrolidone ring. The peak at 1678 cm^{-1} can be assigned to C=O stretch vibration of PVP. The main peak at 2958 cm^{-1} corresponds to the stretching vibration of C–H in PVP. The peak at 3453 cm^{-1} can be attributed to the O–H stretching vibration combined with metalloporphyrin molecules. The peak at 1498 cm^{-1} corresponds to the C=N stretching vibration in metalloporphyrin molecules. The peak vibration absorption of C=C at 1460 cm^{-1} is also observed and these data also indicated the existence of metalloporphyrin in the composite fibers (Fig. 5). The chemical composition of the resulting composite fibers was also determined by EDX analysis (Fig. 6). The peaks of Mn, O, C, and N are found,

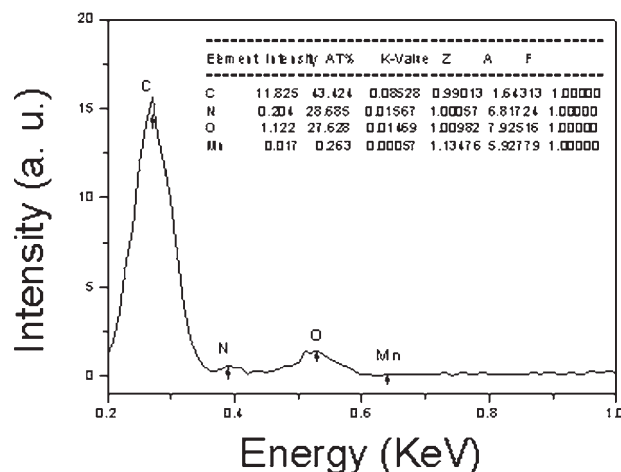


Figure 6 EDX spectrum of PVP fibers containing metalloporphyrin molecules electrospun from ethanol solution.

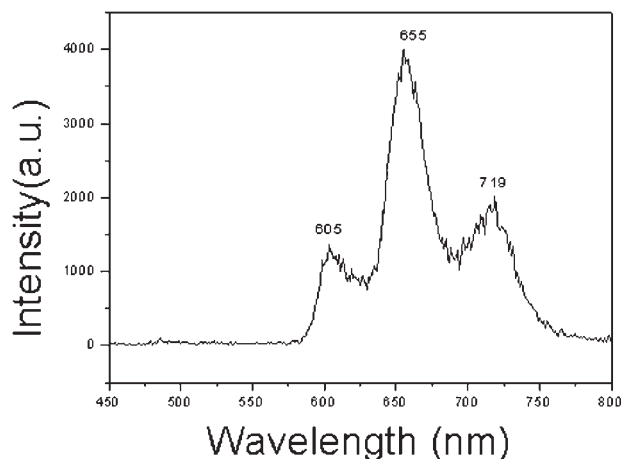


Figure 7 Room temperature photoluminescence spectra of the electrospinning PVP fibers film containing metalloporphyrin molecules.

indicating that the composite fibers are products of PVP and Manganese (III) tetrakis (1-methyl-4-pyridyl) porphyrin pentachloride molecules. Because of the low content of metalloporphyrin, the peak of Mn element is too small to be detected. However, EDX

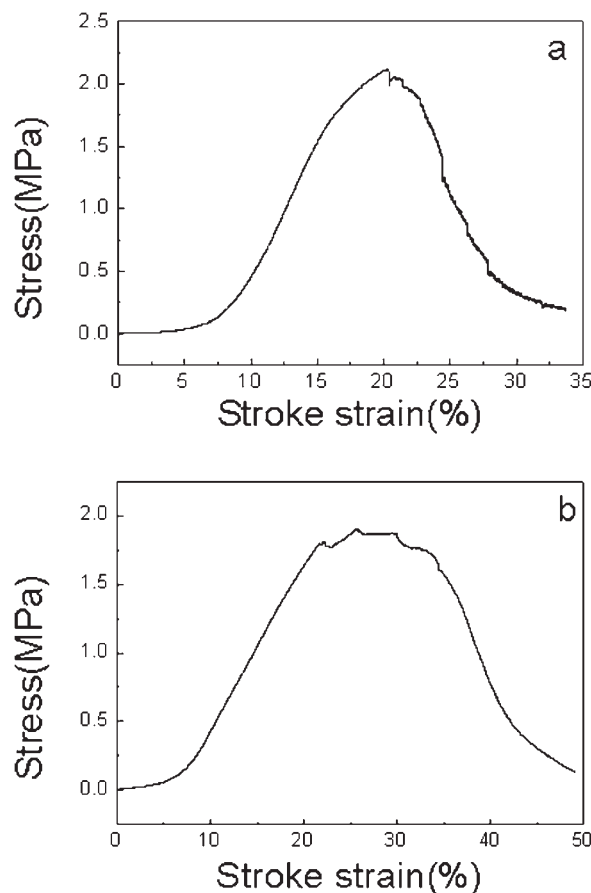


Figure 8 Tensile stress (τ) strain (ϵ) curves for (a) electrospinning PVP fibers and (b) PVP/metalloporphyrin composite fibers.

quantitative analysis revealed that the existence of Mn element in the composite fibers.

Photoluminescence spectra of PVP/metalloporphyrin composite fibers film are also shown in Figure 7. The peaks at 605, 655, and 719 nm can be assigned to Q (0–0), Q (0–1), and Q (0–2) transition of metalloporphyrin molecules, which is similar to that of metalloporphyrin molecules themselves.

Figure 8 shows the tensile strength of PVP fibers and PVP/metalloporphyrin composite fibers, which is measured by an AG-I Universal Testing Machine (Shimadzu, Japan). Compared with properties of PVP fibers, there is some change in modules and ultimate tensile strength. About pure PVP fibers, the modules of elasticity and ultimate tensile are 23.9 and 2.1 MPa, respectively. However, for PVP/metalloporphyrin composite fibers, the modules of elasticity and ultimate tensile are 12.4 and 1.9 MPa. The reason for the decrease of the mechanical properties may be due to the effect of the metalloporphyrin molecules.

CONCLUSIONS

We have described the preparation of discontinuous fibers of PVP containing metalloporphyrin molecules using electrospinning method in ethanol solution. SEM images clearly showed that there were two different types of material to be visible: the thinner fibrous phase and the thicker discontinuous fibers. When electrospun in DMSO/H₂O solutions, it was found that the thinner fibers could not be found, while the discontinuous fibers could still be obtained. The formation of the discontinuous fibers may probably be ascribed to the polarization of metalloporphyrin molecules in the PVP matrices under high voltage.

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