

# Evaluation of Swelling Capacity of Poly(vinyl alcohol) Fibrous Mats Dealt with Polyoxometalate Containing Vanadium

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**ABSTRACT:** Poly(vinyl alcohol) (PVA) fibrous mats dealt with polyoxometalate containing vanadium were prepared by electrospinning method. The fibrous mats were characterized by infrared spectra, X-ray powder diffraction patterns, and scanning electron microscopy photographs. The results showed that PVA could combine with polyoxometalate by intermolecular H-bonding. The studies of the diameter distributions indicated that the average diameter of the fibrous mats was about 260–420 nm. The effects of the polyoxometalate content, electrode potential,

temperature, and time on the swelling capacity of the fibrous mats in water were investigated. The existence of the polyoxometalate containing vanadium was advantaged for the crosslinking of PVA fibrous mats. The swelling degree of PVA fibrous mats containing polyoxometalate dealt with 383 K for 18 h approached zero in water. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1677–1682, 2007

**Key words:** fibrous mats; poly(vinyl alcohol); polyoxometalate; vanadium; swelling

## INTRODUCTION

Inorganic metal oxide cluster anions, a class of inorganic compounds, are believed to have extensive prospects of application in synthesis chemistry, analysis chemistry, biology, medicine, catalysis, and materials science.<sup>1–4</sup> Polyoxometalate-based hybrid inorganic–organic materials have received an increasing attention over the last few years as a result of their specific properties.<sup>5</sup> These new materials have the possibility of becoming very useful, having both the advantages of organic materials and of inorganic materials. Recently, there has been growing interest in a novel fiber production technology known as electrospinning.<sup>6</sup> Up to now, most of the work on electrospinning has focused either on polymer<sup>7,8</sup> or on metal ceramic fibers.<sup>9,10</sup> This technique has been recently rediscovered for applications such as high performance filters,<sup>11</sup> biomedicine,<sup>12</sup> and fiber templates for the preparation of functional nanomaterials.<sup>13</sup>

Poly(vinyl alcohol) (PVA) is a water-soluble polyhydroxy polymer. The excellent chemical resistance, physical properties, and complete biodegradability of PVA resins have led to broad practical applications.<sup>7</sup> However, the applications are limited by the high hydrophilicity of PVA. To improve the high hydrophilicity of PVA, crosslink of PVA has been studied with great interest to date. Bonspasta et al. have decreased the hydrophilicity of PVA by adding Ca<sup>2+</sup> into PVA solution.<sup>14</sup> Ding et al. have investigated the hydrophilic ability of PVA by using glycol and heat treatment.<sup>7</sup> Yamaura and coworkers have improved the hydrophilic ability of PVA by mixing maleic acid into PVA solution.<sup>15</sup> Obviously, it is significant for the applications of PVA to explore the novel functional properties, morphology, and improving the high hydrophilicity.

Encouraged by our success in improving the hydrophilic ability of PVA by using polyoxometalate (H<sub>4</sub>SiMo<sub>12</sub>O<sub>40</sub> and H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>),<sup>16,17</sup> in the present work, we prepared PVA fibrous mats dealt with polyoxometalate containing vanadium by an electrospinning technique. The fibrous mats were characterized by infrared (IR) spectra, X-ray powder diffraction (XRD), and scanning electron microscopy (SEM) photographs. Swelling property of the PVA fibrous mats was investigated.

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## EXPERIMENTAL

### Materials and equipment

$\text{H}_5\text{SiW}_{11}\text{VO}_{40}$ ,  $\text{H}_7\text{SiW}_9\text{V}_3\text{O}_{40}$ , and  $\text{H}_7\text{P}_2\text{W}_{17}\text{VO}_{62}$  (abbreviated as  $\text{SiW}_{11}\text{V}$ ,  $\text{SiW}_9\text{V}_3$ , and  $\text{P}_2\text{W}_{17}\text{V}$ , respectively) were synthesized according to the literature method,<sup>18–20</sup> respectively, recrystallized twice, and examined by IR spectra. PVA was purchased from Tianda Chemical Company (97%, average Mr 77,000–79,000). All of the other chemicals were of analytical grade. The water used in all experiments was distilled. The morphology of the composite fiber mats was measured by a scanning electron microscope FEI QUANTA200 operated at 20 kV with gold sputtered on samples. FTIR spectra were obtained by using an Alpha-Centauri 560 Fourier transforms infrared spectrophotometer (frequency range 4000–400  $\text{cm}^{-1}$ ). The X-ray diffraction study was performed on a D/Max  $\beta\text{C}$  X-ray diffractometer by using Cu  $\text{K}\alpha$  radiation source. Scans were made from 3 to 45° at the speed of 2°/min. For testing the degree of swelling of each sample, the gravimetric method was used.<sup>7</sup> The test pieces were immersed in water with the same time, wiped thoroughly, and reweighted. It was found that the equilibrium degree of swelling was attained after an immersion time of 24 h. The degree of swelling was calculated according the relation:  $m = (m_a - m_b) / m_b$ , where  $m_a$  and  $m_b$  are the weight of the PVA fibers after swelling and subsequent drying, respectively.  $m$  was the water uptake per gram of the PVA fibrous mats.

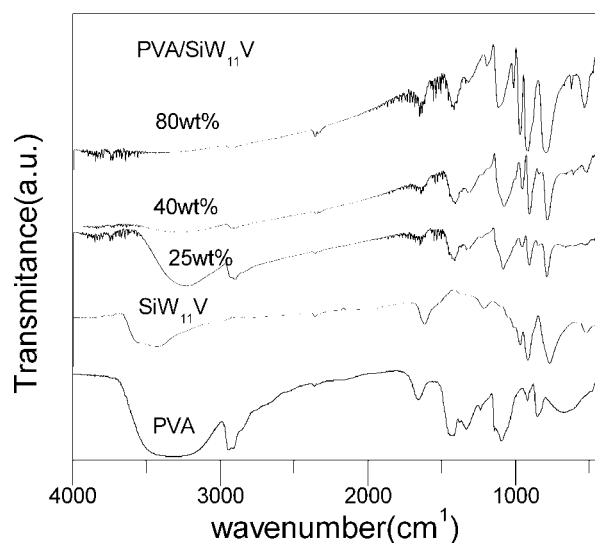
### Preparation of fibrous mats

PVA solution (10 wt %) was prepared by dissolving PVA powder in distilled water and heating at 80–90°C with vigorous stirring for 2 h. The solution was stirred for 24 h at room temperature. The polyoxometalate was added into PVA aqueous solution with stirring for 24 h at room temperature. Then, the solution was placed in a plastic syringe at a fixed distance (8 cm) from a metal cathode. A copper pin connected to a high-voltage generator was placed in the solution. The negative terminal was attached to the aluminum foil target electrode, and the solution was kept in the capillary by adjusting the angle between capillary and the aluminum foil. The voltage applied between the anode and cathode was kept about 18 kV. The fibrous mats contained 25, 40, and 80 wt % content of polyoxometalate, respectively were obtained and dried 6 h at 40°C.

## RESULT AND DISCUSSION

### IR spectra

Figure 1 showed the IR spectra of the PVA/ $\text{SiW}_{11}\text{V}$  composite fibrous mats and corresponding pure PVA and  $\text{SiW}_{11}\text{V}$ . The IR spectra of the composite



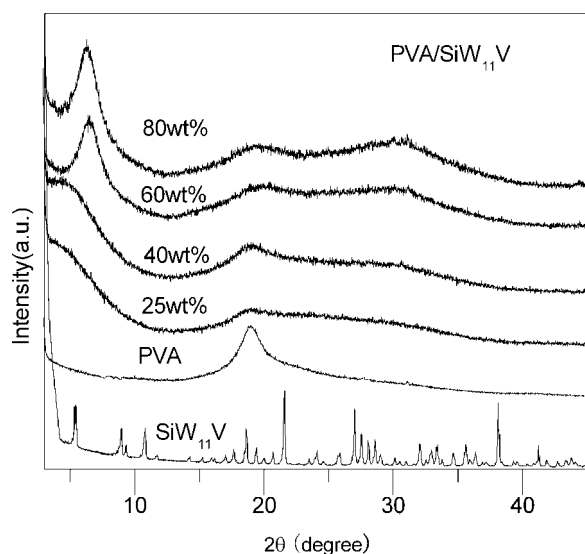
**Figure 1** FTIR spectra of the fibrous mats with different  $\text{SiW}_{11}\text{V}$  contents.

fibrous mats showed four characteristic bands of  $\text{SiW}_{11}\text{V}$  in the range of 700–1100  $\text{cm}^{-1}$ , which explained that the Keggin geometry of  $\text{SiW}_{11}\text{V}$  was still preserved inside the composite fibrous mats. The intensity of the four characteristic bands of  $\text{SiW}_{11}\text{V}$  increased with increasing  $\text{SiW}_{11}\text{V}$  content. Meanwhile, the bands in composite fibrous mats related with  $\text{SiW}_{11}\text{V}$  were all shifted by only a few wavenumber contrasted to corresponding pure  $\text{SiW}_{11}\text{V}$ , which suggested strong Coulombic interaction between  $\text{SiW}_{11}\text{V}$  and PVA matrix.<sup>19,21</sup>

In comparison with the change of characteristic bands of PVA (the bands at about 3440, 2930, 1640, 1427, 1345, and 1094  $\text{cm}^{-1}$ , corresponding to  $\nu_{\text{O-H}}$ ,  $\nu_{\text{C-H}}$ ,  $\nu_{\text{C=O}}$ ,  $\nu_{\text{C-C}}$ ,  $\nu_{\text{C-OH}}$ , respectively),<sup>22</sup> the variational characteristic bands of PVA in composite fibrous mats were  $\nu_{\text{O-H}}$ . The O–H stretching vibration at about 3400  $\text{cm}^{-1}$  widened with increasing the content of  $\text{SiW}_{11}\text{V}$ , which suggested that utilizing the intermolecular hydrogen bond between PVA and  $\text{SiW}_{11}\text{V}$  formed PVA/ $\text{SiW}_{11}\text{V}$  composite.<sup>23</sup>

### X-ray diffraction

XRD patterns of the fibrous mats, PVA, and  $\text{SiW}_{11}\text{V}$  were shown in Figure 2. Only one broad hump (ca.  $2\theta = 19.9^\circ$ ) of pure PVA was observed. The peak belongs to the semicrystallization of PVA because of the hydroxyl groups of PVA in its side-chain.<sup>23</sup> However, the peak of semicrystallization broadened and weakened for the PVA fibrous mats with increasing  $\text{SiW}_{11}\text{V}$  contents, because the hydroxyl groups (H–O–) of PVA molecules would combine with  $\text{SiW}_{11}\text{V}$  by H-bonding, proved by IR spectra, resulting in the decrease of the amounts of H–O–



**Figure 2** XRD patterns of  $\text{SiW}_{11}\text{V}$ , PVA, and PVA/ $\text{SiW}_{11}\text{V}$  fibrous mats.

for the fibrous mats.<sup>24</sup> These results illustrated that the crystal growth of PVA was extremely inhibited by  $\text{SiW}_{11}\text{V}$  in the fibrous mats and PVA became an amorphous state. A new peak gradually appeared in  $2\theta < 10^\circ$  and shifted toward high  $2\theta$  with increasing  $\text{SiW}_{11}\text{V}$  contents. As we know, polymer doped with simple inorganic acids led to a more ordered structure with relatively distinct Bragg reflections.<sup>25,26</sup> So the appearance of the new peaks suggested that the PVA molecule was in order with a short interlayer distance.<sup>27</sup> No peaks from any crystalline form of  $\text{SiW}_{11}\text{V}$  could be observed indicating that  $\text{SiW}_{11}\text{V}$  particles were homogeneously dispersed inside the PVA matrix.<sup>3,28</sup> Two broad bands centered around  $2\theta = 20^\circ$  and  $2\theta = 31^\circ$ , which were imputed to the periodicity parallel and perpendicular to the PVA chains, respectively, also appeared with increasing the content of  $\text{SiW}_{11}\text{V}$ .<sup>25</sup> This indicated that the order of the composite fiber mats increased from low content of  $\text{SiW}_{11}\text{V}$  to high content of  $\text{SiW}_{11}\text{V}$ .

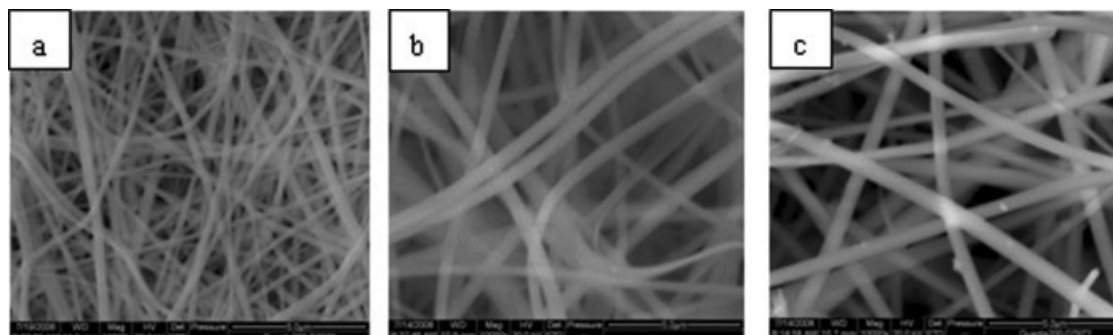
### SEM photograph

Figure 3 showed SEM photographs of PVA/ $\text{SiW}_{11}\text{V}$  fibrous mats with different  $\text{SiW}_{11}\text{V}$  content (25, 40, and 80 wt %, respectively). The morphology of the fibrous mats had a regular change with increasing  $\text{SiW}_{11}\text{V}$  content. The higher the  $\text{SiW}_{11}\text{V}$  content was, the thicker the average diameter of the fibrous mats was i.e. 261 nm for 25 wt %, 380 nm for 40 wt %, and 420 nm for 80 wt %, respectively. Usually, higher viscosity and conductivity favored the formation of fibrous mats. Table I showed the viscosity and conductivity of different PVA/ $\text{SiW}_{11}\text{V}$  solution and the average diameter of the fibrous mats. The result of the experiment showed that the average diameter of the fibrous mats increased with decreasing viscosity of the solution and increasing conductivity of the solution. We conjectured the reason why the average diameter of the fibrous mats increased with increasing  $\text{SiW}_{11}\text{V}$  content was higher ion charge because of the higher  $\text{SiW}_{11}\text{V}$  content.<sup>16</sup> When the content of  $\text{SiW}_{11}\text{V}$  increased, the conductivity of the solution increased. The increase of the conductivity of solution favored the elongation flow of the jet into oriented networks. So, the higher charge density not only favored the formation of fibrous mats, but also favored the formation of wider diameter fibers.<sup>29</sup>

### Swelling behavior

The studies on the swelling behavior of PVA in water have received increasing attention recently because of a very promising application in the preparation of biomedical materials.<sup>30</sup> PVA could become insoluble in water for sufficiently large degree of crosslinking. As we know, heat-treatment and crosslinking agent affected the degree of crosslinking for PVA. Polyoxometalate was an important crosslinking agent because of intermolecular H-bonding between polyoxometalate and PVA.

Figure 4 showed the swelling curve of water uptake of PVA/ $\text{SiW}_{11}\text{V}$  fibrous mats with different  $\text{SiW}_{11}\text{V}$  contents, heat-treatment temperature, and time. The results of the experiment showed that the



**Figure 3** SEM images of the PVA/ $\text{SiW}_{11}\text{V}$  fibrous mats. (a) 25 wt %, (b) 40 wt %, and (c) 80 wt %.

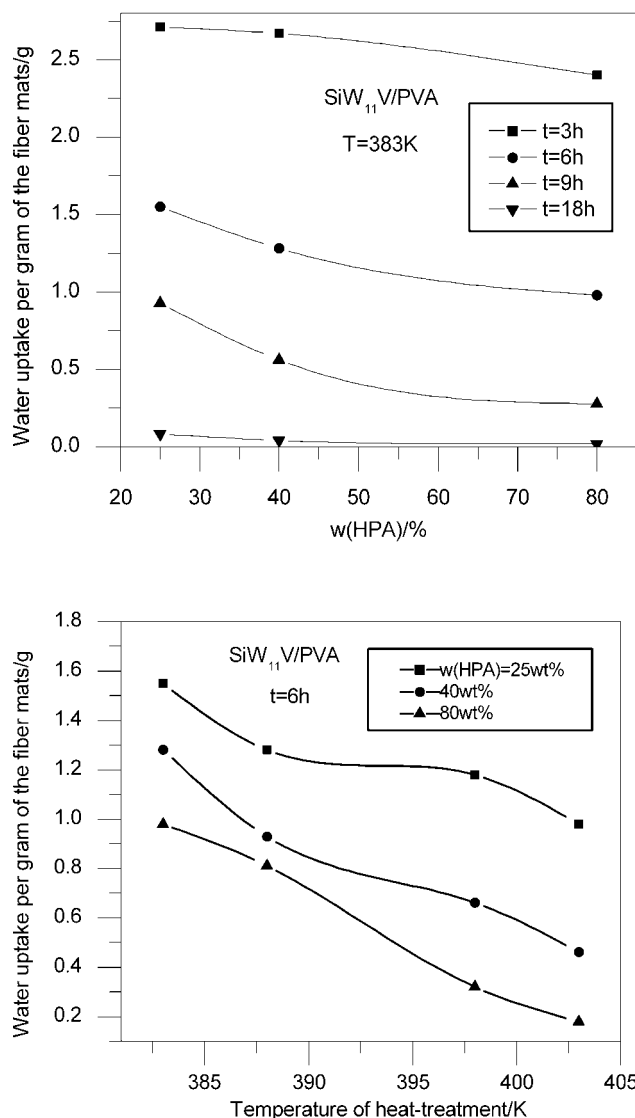
**TABLE I**  
Data of Viscosity and Conductivity of the PVA/SiW<sub>11</sub>V Solution

Content of SiW <sub>11</sub> V in PVA/SiW <sub>11</sub> V solution (wt %)	Viscosity (mPa s)	Conductivity (S m <sup>-1</sup> )	Average diameter of the fibrous mats (nm)
25	2320	1.28	261
40	2032	2.94	380
80	1290	10.6	420

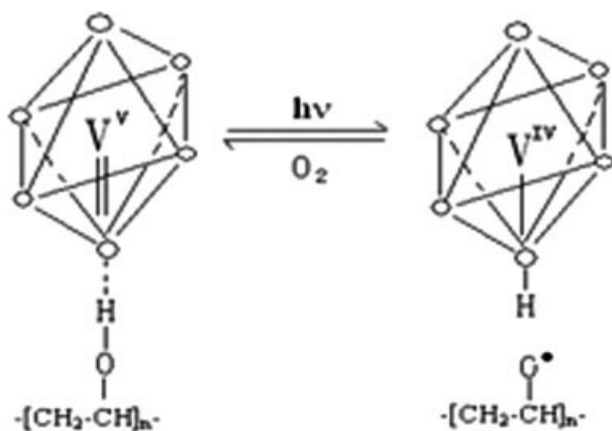
degree of swelling decreased with increasing SiW<sub>11</sub>V contents, heat-treatment temperature, and time, respectively. Here, the water uptake of pure PVA fibrous mats treated at 383 K for 6 h was also checked. The water uptake of the pure PVA fibrous mats was 34.4 g g<sup>-1</sup>. However, at the same condition, the water uptake of PVA fibrous mats contained 25 and 80 wt % SiW<sub>11</sub>V was 1.55 and 0.98 g g<sup>-1</sup>, respectively. Compared with the water uptake of the pure PVA fibrous mats, the change of the water uptake of the fibrous mats with 25 wt % SiW<sub>11</sub>V was 32.85 g g<sup>-1</sup>. Obviously, the lower contents of SiW<sub>11</sub>V and higher change of the water uptake of the PVA fibrous mats indicated that the crosslinking of the PVA fibrous mats was stronger affected by SiW<sub>11</sub>V. When the SiW<sub>11</sub>V content changed from 25 to 80 wt %, the change of the water uptake of PVA fibrous mats was only 0.57 g g<sup>-1</sup>. This result indicated that the effect on the swelling degree of PVA was weakened with increasing SiW<sub>11</sub>V content. Figure 4 also showed the swelling curve of the water uptake of PVA/SiW<sub>11</sub>V fibrous mats at different heat-treated time at the same temperature. Results showed that the water uptake of the fibrous mats decreased with prolonging heat-treated time. After the PVA fibrous mats containing SiW<sub>11</sub>V from 25 to 80 wt % were treated at 383 K from 3 to 18 h, the water uptake changed obviously. The effect of heat-treated temperature on the water uptake showed that the water uptake of the fiber mats decreased with increasing heat-treated temperature. After the PVA fibrous mats containing SiW<sub>11</sub>V from 25 to 80 wt % were treated at 383 K for 18 h, the water uptake approached zero. All this indicates that the higher the SiW<sub>11</sub>V content, the heat-treatment temperature, and heat-treated time were, the higher the crosslinking density of the PVA fibers was and the less the swelling of PVA fibrous mats was in water.

Compared with prior report about swelling of PVA fibrous mats treated with H<sub>5</sub>PW<sub>12</sub>O<sub>40</sub> and H<sub>4</sub>SiMo<sub>12</sub>O<sub>40</sub>,<sup>16,17</sup> we found that the swelling degree of the PVA fibrous mats treated with polyoxometalate containing vanadium decreased and approached zero in the same condition. To investigate the reason

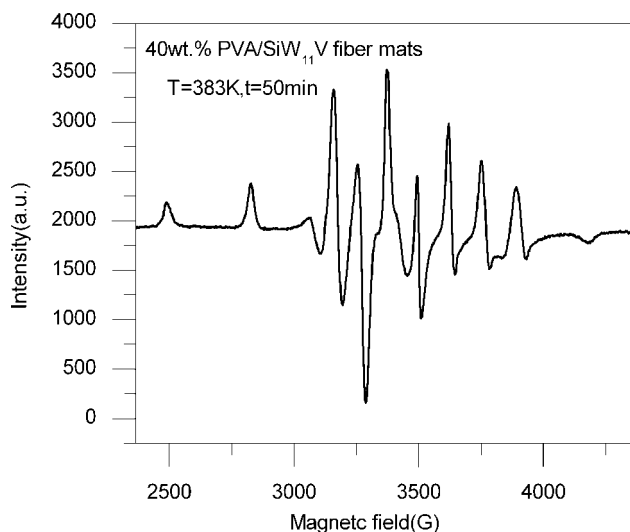
of lower swelling degree of PVA fibrous mats treated with polyoxometalate containing vanadium, the electron spin resonance (ESR) of the fibrous mats treated with 50 min at 383 K was determined and shown in Figure 5. As showed in Figure 5, the typical ESR signal of V<sup>4+</sup> was observed. This result indicated that the redox occurred in the process of heat-treatment. We deduced that the heat-treatment mechanism was similar to that reported in Refs. 17 and 29. Because there was no any ESR signal about W<sup>5+</sup>, so we thought that heat-excitation of the O=V ligand-to-metal charge transfer of VO<sub>6</sub> led to the transfer of electron of oxygen atom to the vanadium atom. Result induced that the polyoxometalate was reduced and the PVA was oxidized. The oxidation-reduction process was shown as follow:



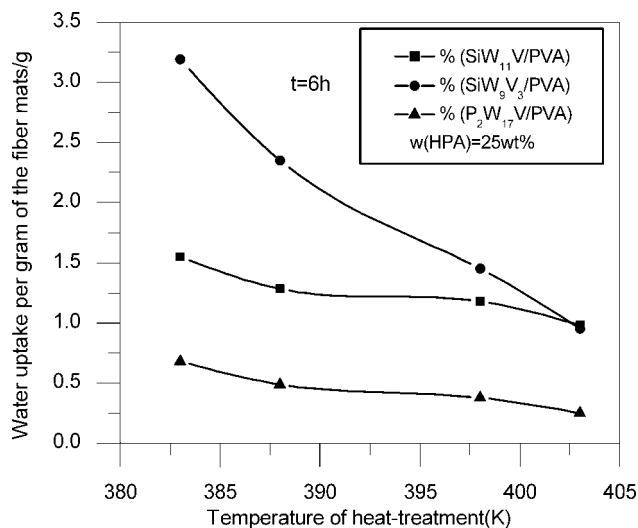
**Figure 4** Swelling curve of water uptake of the fibrous mats with different factors.



This result was easy to consider that polyoxometalate, a good oxidizing agent, was an advantage for decreasing the swelling of the PVA fibrous mats in water. To investigate the effect of oxidizing ability of polyoxometalate on the swelling of PVA fibrous mats in water, Figure 6 showed the swelling curve of the water uptake of the PVA fibrous mats contained 25 wt %  $\text{SiW}_{11}\text{V}$ ,  $\text{SiW}_9\text{V}_3$ , and  $\text{P}_2\text{W}_{17}\text{V}$ , respectively. As shown in Figure 6, the hydrophobic ability of the PVA fibrous mats containing  $\text{P}_2\text{W}_{17}\text{V}$  was higher than that containing  $\text{SiW}_9\text{V}_3$ , and  $\text{SiW}_{11}\text{V}$ . As we known, the electrode potential of the polyoxometalate was  $\text{P}_2\text{W}_{17}\text{V} > \text{SiW}_9\text{V}_3 > \text{SiW}_{11}\text{V}$ .<sup>31,32</sup> Obviously, the elements with high positive electrode potentials were good oxidizing agents when in the high oxidized form, and were easy reduced the low oxidized form. The results of the experiment, as showed in Figure 6, supported our viewpoint, i.e. the degree of swelling was affected by the sort of polyoxometalate. The stronger the oxidizing ability of polyoxometalate was, the easier the reduce reaction of



**Figure 5** ESR spectrum of PVA fibrous mats (40 wt %).



**Figure 6** Swelling curve of water uptake of the PVA fibrous mats containing different polyoxometalate.

polyoxometalate was, and the lower the hydrophilic ability of PVA containing polyoxometalate was.

## CONCLUSIONS

PVA fibrous mats treated with different content of polyoxometalate containing vanadium were successfully prepared by an electrospinning technique. XRD patterns, IR spectra, and SEM images characterized the PVA fibrous mats. The effects of polyoxometalate content, electrode potential, heat-treatment temperature, and time on hydrophobic ability of the PVA fibrous mats were investigated. Results indicated that the degree of swelling of the PVA fibrous mats decreased due to the addition of polyoxometalate. High content and electrode potential of polyoxometalate were advantaged for the crosslinking of PVA. The swelling degree of PVA fibrous mats treated with polyoxometalate containing vanadium approached zero in water. A conceivable heat-excited oxidation-reduction mechanism was suggested.

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