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Beaded Fiber Mats of PVA Containing Unsaturated Heteropoly Salt

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Abstract: Poly(vinyl alcohol) (PVA) fiber mats containing unsaturated heteropoly salt was prepared for the first time. IR, X-ray diffraction and SEM photographs characterized the beaded fiber mats. The viscoelasticity and the conductivity of the solution were the key factors that influence the formation of the beaded fiber mats.

Keywords: Fiber mats, unsaturated heteropoly salt, bead, electrospinning, SEM.

The PVA fiber mats containing heteropoly acid has been reported[1,2]. However, preparing the PVA fiber mats containing polyanion is limited because most of the polyanions can only be their salts. It is more difficult for the unsaturated polyanions. One is their bad link with PVA; another is their bad solvability in water. In the present paper, a new PVA fiber mats containing unsaturated polyanion is prepared. The factors of influence the formation of the fiber mats are investigated.

10 g of the 10 % PVA solution was added to 0.14, 0.25, 0.67 and 1.50 g of $K_8SiW_{11}O_{39}$ (SiW_{11}), respectively. The solutions were stirred vigorously for 24 h. The viscous solutions of 12, 20, 40 and 60 wt.% $K_8SiW_{11}O_{39}$ were obtained, respectively. The $K_8SiW_{11}O_{39}$/PVA fiber mats were prepared by an electrospinning method[3]. The distance from tip to collector is 10 cm. The voltage applied to the solution was 25 kV. The fiber mats were dried under vacuum for 24 h at 40 ^oC.

Figure 1 showed IR spectra of the fiber mats with different compositions. Four characteristic bands of $K_8SiW_{11}O_{39}$ appeared in 700-1100 cm^{-1}. The data of the IR spectra were showed in **Table 1**. This indicated the existence of $K_8SiW_{11}O_{39}$ in PVA matrix[4]. The O-H stretching vibration at *ca.* 3400 cm^{-1} became a broader band with an increasing $K_8SiW_{11}O_{39}$ content. It was suggested that intermolecular H-bonding between PVA and $K_8SiW_{11}O_{39}$ formed[5].

XRD spectra of the fiber mats showed the same crystal bands of the $K_8SiW_{11}O_{39}$. However, compared with the pure $K_8SiW_{11}O_{39}$, the bands of the fiber mats broadened. According to the Debye-Scherrer formula, the broadening of the crystal bands indicated that the size of the $K_8SiW_{11}O_{39}$ decreased[6].

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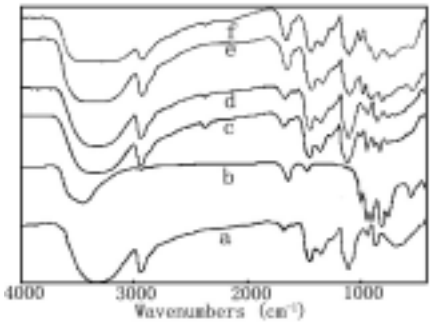
The SEM photographs of the fiber mats were shown in **Figure 2**. The results of the viscosity and conductivity of the solutions were summarized in **Table 2**. As shown in **Figure 2**, beads and beaded fiber mats are less likely to be formed with increasing $K_8SiW_{11}O_{39}$ content. Usually, higher viscosity favors formation of fiber mats without beads[7]. Comparing with the solution viscosity of the different $K_8SiW_{11}O_{39}$ contents, we found that the lower the $K_8SiW_{11}O_{39}$ content was, the higher the viscosity of the solution was, and the more the beads were. As we know, increasing the viscosity favored the formation of fiber mats without beads. Obviously, the major competition was between the viscosity and conductivity of the solution, *i.e.* the conductivity of the solution was the key parameter for forming smooth fiber mats in the electrospinning process. As shown in **Table 2**, although the viscosity of the solutions decreased, the conductivity of the solutions increased. The increase of the conductivity favored the elongational flow of the jet into oriented networks. This indicated that higher conductivity favored formation of the fiber mats without beads.

Figure 1 IR spectra of the fiber mats containing different contents of $K_8SiW_{11}O_{39}$



a: PVA; b: $K_8SiW_{11}O_{39}$; c:12 wt%; d: 20 wt%; e:40 wt%; f:60 wt%

Table 1 IR spectra data of the SiW11/PVA fiber mats (cm-1)

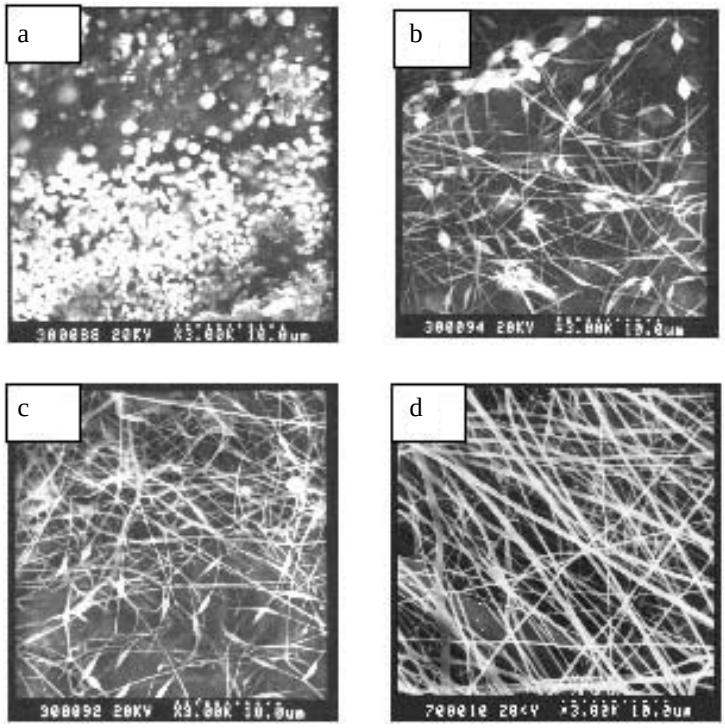
Sample	$\nu_{as}(X\text{-}O_a)$	$\nu_{as}(M\text{-}O_d)$	$\nu_{as}(M\text{-}O_b\text{-}M)$	$\nu_{as}(M\text{-}O_c\text{-}M)$
$^aSiW_{11}$	921.15	974.41	881.11	791.53
$^bSiW_{11}$	918.77	969.71	849.62	801.35
$^cSiW_{11}$	918.23	970.25	833.14	802.31
$^dSiW_{11}$	920.43	968.43	851.23	800.61
$^eSiW_{11}$	919.25	974.61	855.42	799.32

a- SiW_{11} b-12 wt.% c-20 wt.% d-40 wt.% e-60 wt.%

Table 2 Viscosity and conductivity of the solution containing different contents of $K_8SiW_{11}O_{39}$

Solution	Viscosity (cp)	Conductivity (10^{-3}S/cm)
12% SiW_{11}/PVA	2700	0.76
20% SiW_{11}/	400	1.55
40% SiW_{11}/PVA	2200	3.16
60% SiW_{11}/PVA	1800	4.32

Figure 2 SEM photographs of the fiber mats containing different contents of $K_8SiW_{11}O_{39}$



a: 12 wt%; b: 20 wt%; c:40 wt%; d:60 wt%

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References

1. J. Gong , C. L. Shao, G. C. Yang, Y. Pan, L. Y. Qu, *Inorg. Chem. Comm.*, **2003,** *6*, 916.
2. J. Gong, X. D. Li, B. Ding, D. R. Lee, H. Y. Kim, *J. Appl. Polym. Sci.*, **2003**, *89*, 1573.
3. B. Ding, H. Y. Kim, S. C. Lee, D. R. Lee, K. J. Choi, *Fiber and Polym.*, **2002,** *3*,73.
4. J. Gong , X. J. Cui, Z. W. Xie, S. G. Wang, L. Y. Qu, *Synth. Met*., **2002,** *129*, 187.
5. C. S. Ha, H. D. Park, C. W. Frank, *Chem. Mater.*, **2002,** *12*, 839.
6. T. Ito, K. Inumaru, M. Misono, *J. Phys. Chem.*, **1997**, *101*, 9958.
7. H. Fong, I. Chun, D. H. Reneker, *Polym.*, **1999**, *40*, 4585.

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