Structure and Properties of Polyvinyl Alcohol Amidoxime Chelate Fiber

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SYNOPSIS

Polyvinyl alcohol amidoxime (PVAAO) chelate fiber prepared in our laboratory is a good adsorbent. Comparing with other adsorbents, it has many advantages, such as higher hydrophilicity, better adsorbability and easier synthesis. In this work, the synthesis course, structure and properties of PVAAO fiber have been studied by the means of FT-IR, SEM, ESR, and TG. The structural changes of the fiber associated with adsorbed copper ions have also been investigated using ESR, FT-IR, and XPS. In addition, chelating mechanisms of the fiber-adsorbing copper ions have been discussed. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Chelate fibers and resins are effective adsorbents used for enriching and separating some metal ions. They are very useful because they have higher selectivity and larger adsorbing capacity than other adsorbents, and they are also easy to elute and regenerate. They have received more attention in recent years.[1-3]

Polyvinyl alcohol amidoxime (PVAAO) chelate fiber was prepared in our laboratory.[4] Its attributes include easy synthesis, high hydrophilicity, and fast adsorption rate. In addition, it can selectively adsorb metal ions, such as palladium[5] and mercury.[6] This provides an economical and effective method of separating or purifying these two ions. The chelate fiber can be used to recover metal ions and protect the environment. In order to further clarify the chelate mechanism and explore optimum adsorption conditions, we investigated the structure and properties of the fiber and structural changes related to adsorbed copper ions. All of these will be important to develop new types of chelate fibers.

EXPERIMENTAL

Synthesis

Polyvinyl alcohol (PVA) fiber was irradiated with ^{60}Co-γ rays, which were produced by a 100,000 Ci ^{60}Co-γ source, in air at room temperature, and its dosage was 20 mrad. The fiber was immersed in acrylonitrile (AN) at 80°C for 4 h to copolymerize AN, followed by amidoximation of cyano groups of grafted chains by reacting the grafted fiber with a 3% hydroxylamine aqueous solution at 80°C for 2 h. PVA, a commercial product, was cut into 5-mm lengths before the experiment. Acrylonitrile (AR) was distilled before use.

PVAAO fiber containing adsorbed copper ions was obtained by equilibrating 0.25-g PVAAO samples with excess copper ion solution at room temperature for 2.5 h, and then was filtered, rinsed, and dried.

Adsorbing Capacity

Samples of 0.25-g PVAAO were equilibrated with excess copper ion solution at room temperature for different times and then the adsorption rate was determined.

Solvent-Resisting Property

Every sample of 0.25-g PVAAO dry fiber was submerged in 50 mL solvent at room temperature for 24 h. After that, the samples were rinsed, dried and then changes of its surface and weight were investigated.

IR spectra were obtained from KBr pellets of various fibers with a 5DS Fourier transform infrared
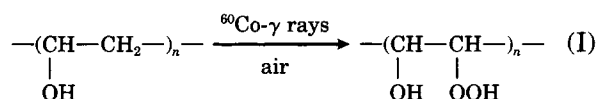
spectrometer. Electron spin resonance (ESR) spectra were obtained by a JES-FE3AX electron spin resonance spectrometer. Scanning electron micrography (SEM) photographs were taken by a JXA-840 scanning electron microscope, TGS-2 thermogravimetry gave thermal stability results and X-ray photon spectroscopy (XPS) was used.
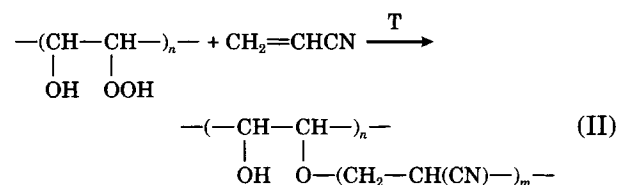
RESULTS AND DISCUSSION

Synthesis Course

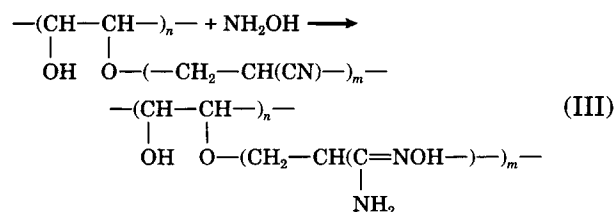According to the experimental method above we found that the synthesis course of PVAAO fiber was:

Initiation:

$$-(CH-CH_2-)_n- \xrightarrow[air]{^{60}Co-\gamma \; rays} -(CH-CH-)_n- \quad (I)$$
$$\qquad | \qquad\qquad\qquad\qquad | \quad |$$
$$\; OH \qquad\qquad\qquad\qquad OH \; OOH$$

Grafting:

$$-(CH-CH-)_n- + CH_2=CHCN \xrightarrow{T}$$
$$\quad | \quad |$$
$$\; OH \; OOH$$

$$-(-CH-CH-)_n- \qquad (II)$$
$$\qquad | \quad |$$
$$\quad OH \; O-(CH_2-CH(CN)-)_m-$$

Amidoximation:

$$-(CH-CH-)_n- + NH_2OH \longrightarrow$$
$$\quad | \quad |$$
$$\; OH \; O-(-CH_2-CH(CN)-)_m-$$

$$-(CH-CH-)_n- \qquad (III)$$
$$\qquad | \quad |$$
$$\quad OH \; O-(CH_2-CH(C=NOH-)-)_m-$$
$$\qquad\qquad\qquad\qquad | $$
$$\qquad\qquad\qquad\quad NH_2$$

This is only a general description of the reactions and in practice the procedure is quite complicated.

Structure of PVAAO Fiber

From the FT-IR spectra of the polymers (I, II, III) obtained from synthesis of PVAAO fiber, we found that the functional groups clearly changed. This is evident in Figure 1. A new peak, which is characterized as the $-C\equiv N$ stretching vibration at 2242 cm^{-1} was found in AN-grafted PVA (PVA-g-AN) fiber in Fig. 1 (b) compared with PVA fiber in Fig. 1 (a). This indicates that the AN has been grafted
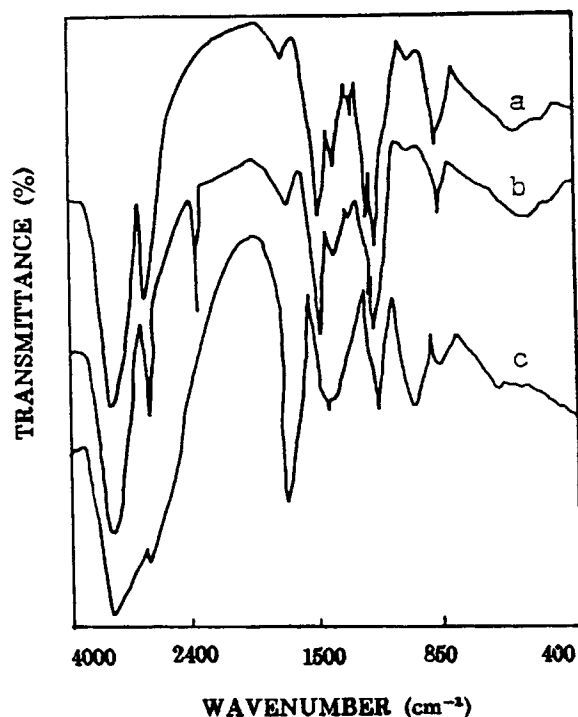

Figure 1 FT-IR spectra of the fibers, (a) PVA, (b) PVA-g-AN, and (c) PVAAO.

onto PVA fiber and the structure of the grafting product is polymeric (II). The SEM results are shown in Figure 2. From Figure 2 (b), we can see that the surface of the PVA-g-AN fiber is uneven compared with its original complex, PVA fiber in Figure 2 (a). This confirms the reaction above and shows that the PVA-g-AN fiber also has a high grafting rate since its surface obviously changed. This shows that the PVA-g-AN fiber has a high grafting rate. After amidoximation of the grafted fiber, the $-C\equiv N$ peak vanished and a new strong one, attributed to the $-C=N$ stretching vibration at 1658 cm^{-1} appeared in Figure 1 (c). This shows that the $-C\equiv N$ groups have reacted and $-C=N$ double bonds have been produced. In addition, the band in the range of 3000–3500 cm^{-1}, which is due to $-O-H$ and $-N-H$, became wider and the peaks for the $-C-N$ group at 1360–1030 cm^{-1} varied distinctly. All these are consistent with the structure distinction of the amidoxime group $-C(NH_2)=NOH$.

Change of the Structure during Adsorption of Copper(II) Ions by PVAAO Fiber

The amidoxime group can coordinate some metal ions selectively, therefore we studied the ESR results
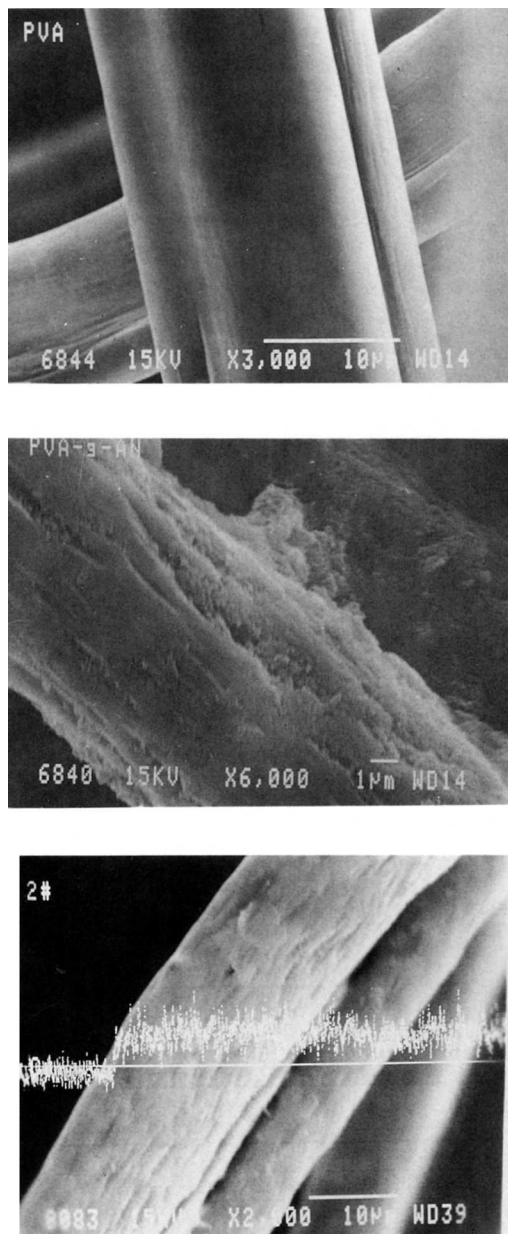
Figure 2 SEM photograph of (a) PVA, (b) PVA-*g*-AN, and (c) PVAAO-Cu.

for PVAAO fibers containing adsorbed copper(II) ions (Fig. 3) at room temperature. The signal is characteristic of the hyperfine structure of the copper(II) spectrum and has obvious anisotropy.[7-9] At the low-field end of the spectrum, hyperfine structure of the parallel side is clear. The peak is well resolved into four peaks because of hyperfine coupling. The values of the *g* factor and constants for hyperfine structure A can be measured directly. They are $g_{\parallel}$ = 2.206, $A_{\parallel}$ = 18.81 mT. At the high-field end of the spectrum, the vertical side appears

as two sharp peaks, not a clear hyperfine spectrum. The *g* factor obtained is $g_{\perp}$ = 2.042. The spectrum and parameters are characteristic of the binding copper(II) ions. This verified that copper(II) ions were bonded with amidoxime groups after PVAAO fiber-adsorbed copper(II) ions, and the adsorption is a chemical procedure. Another conclusion drawn from the SEM [Fig. 2(c)] results is that the distribution of copper(II) ions is uniform at the grafting points.

The FT-IR spectra of PVAAO with and without adsorbed copper(II) ions are shown as Figure 4. The wide peak, due to the presence of hydrogen bonds from 2500 to 3600 cm^{-1}, changed obviously in these two spectra. But a sharp peak, which is due to the — O — H stretching vibration of PVA on the main chain, at the end of this wide peak remained the same. The results indicate that the degree of hydrogen bonding decreased when the fiber adsorbed copper(II). So it can be concluded that the copper(II) ions had coordinated with the — OH and — NH$_2$ groups in the amidoxime group. Both the change of the peak at 1100 cm^{-1}, which is due to — N — H stretching vibration, and the — C — N peak at 1415 cm^{-1} becoming weaker proved that the copper(II) ions coordinate with — NH$_2$ groups. The fact that the peak — C = N stretching vibration in amidoxime group at 1658 cm^{-1} becomes weaker also indicate the coordination of copper(II) ions with — OH and — NH$_2$ groups.

The XPSs results also show that the electronic combined energy N$_{1s}$ and O$_{1s}$ have no difference between the two samples above. This further confirms the above conclusion.

Therefore, we infer that the structure of fiber coordinated with copper(II) ions is perhaps in two
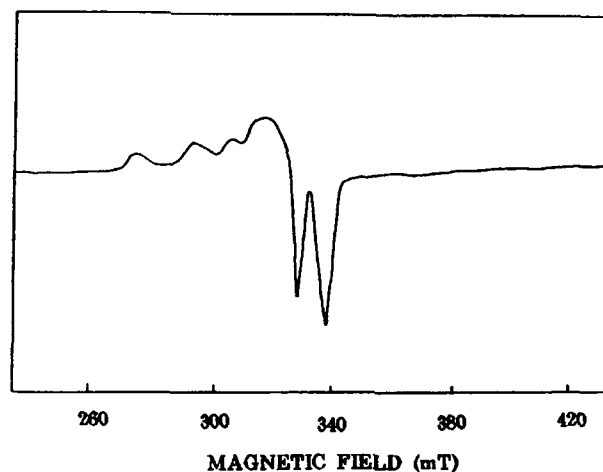

Figure 3 ESR spectroscopy of the PVAAO-Cu.

Figure 4   FT-IR spectra of (a) PVAAO fiber and (b) PVAAO-Cu.

forms. One coordination is with a functional group; the other coordination is with two functional groups. The probable mechanisms are shown below.

Coordination with a functional group:

Coordination with by two functional groups:

These results make it clear that the structure of PVAAO fiber-adsorbed copper(II) ions and the

Figure 5   Adsorption rate of the PVAAO fiber.

substituting group of the carbon in the amidoxime group will influence the adsorbability of the PVAAO fiber.

Properties of the PVAAO Fiber

Adsorption Rate

The adsorption rate of PVAAO fiber, which has higher adsorbing capacity, is shown in Figure 5. The adsorbing capacity of PVAAO fiber was saturated with copper(II) ions within 2.5 h. The fiber did have fast adsorption rate.

Figure 6   Influence of pH value on adsorbing capacity of PVAAO fiber.

Table I   Solvent-Resisting Property of PVAAO Fiber

Solvent (N)	HNO$_3$		NaOH				DMF	THF	Alcohol
	2.5	3.5	1	2.5	5	10			
$\dfrac{\Delta W}{W}$ (%)	1.39	1.98	3.39	4.86	4.16	14.16	0.63	0.58	0.00
Surface changes	N	N	N	Y	Y	Y	N	N	N
Adsorbing capacity[a] (meqCu^{2+}/g)	1.83	1.80	1.96	2.26	2.19	1.89	—	—	—

[a] The original sample is 1.85 meqCu^{2+}/g fiber.

Influence of pH Value

It was observed that the influence of pH value on the adsorbing capacity of the PVAAO fiber-adsorbed copper(II) was quite high during a given range of pH value, and the fiber had better adsorbability in the pH range of 3–5. This result is shown in Figure 6.

Solvent-Resisting Property

Table I shows that the PVAAO fiber has good solvent resistance and can be used in a wide range of pH value. The fiber treated with dilute caustic is increased in absorbing capacity. In the table, W and W' are weights of original sample and sample treated with solvent. $\Delta W = W - W'$; N indicates no change and Y expresses change.

Thermal Stability

Figure 7 indicates that the decomposition temperature of PVA, PVA-g-AN, and PVAAO fibers are all higher than 200°C in an N$_2$ atmosphere. There-fore, they all have good thermal stability. The two samples of PVAAO chelate fibers, using different grafting rates, have the best thermal stability.

CONCLUSIONS

The fiber we produced is PVAAO chelate fiber. It has fast adsorption rate, good solvent-resistance, and good thermal stability as well.

Through examination of the adsorption structure of PVAAO fiber containing adsorbed copper(II) ions, we found that the coordination of PVAAO fiber with metal ions is accomplished by $-$NH$_2$ and $-$OH groups in the amidoxime group. In addition, there are two groups (NH$_2$, $-$OH) in the amidoxime group that greatly influence adsorbability of the fiber. Therefore, adsorbability of the fiber can be improved by changing the substituent bonding with carbon on the $-$C$=$N group.
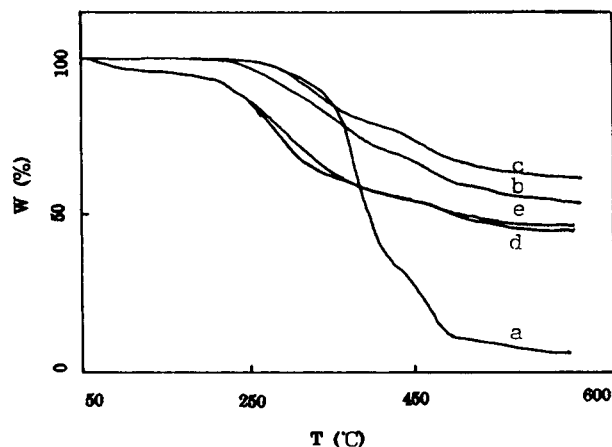

Figure 7 Thermogravimetry results of (a) PVA, (b & c) PVA-g-AN whose grafting rate is 116.8 and 179.8%, respectively, and (d & e) PVAAO obtained from (b & e) PVA-g-AN.

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