

GRAFTING OF HUMIC ACID ONTO COTTON CELLULOSE (II)*

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ABSTRACT

Cotton cellulose reacted with epichlorohydrin under the catalytic action of HClO_4 and H_2O to form 3-chloro-2-hydroxypropyl ether with a substitution degree of 0.61. The chlorine-containing product was treated with aliphatic diamines (ethylenediamine, propylenediamine, etc.) to produce nitrogen-containing cellulose which further reacted with humic acid to give black fibrous graft cellulose. This product contains 27–35% humic acid, 0.90 meq/g acidic groups, possesses 0.49 meq/g Cu^{2+} -complexing capacity and good mechanical strength, and can be used under pH12.

INTRODUCTION

In spite of the fact that humic acid (HA) has excellent ion-exchange and complexing capacity with various metal ions^[1,2], it can not be used as an ion-exchanger or a complexing agent directly due to its lack of mechanical strength and resistance against alkali. Based on a patent work^[3], we have reported a modified method for preparing HA-cellulose graft polymer through the reaction of the phenolic hydroxyl group of HA with the chemically attached epoxy group of the cellulose^[4]. The graft polymer can be used as a fibrous ion-exchanger under pH 11. The content of HA in the graft polymer is only 8% due to some side-reactions occurring simultaneously during the preparation.

In HA, the content of carboxyl group is dominant and its reactivity is also the greatest. If they can be employed in the graft reaction, a higher grafting efficiency will be expected.

It has been reported that starch^[5], crosslinked-starch^[6], and processed bead, powder, crosslinked cellulose^[7] can react with epichlorohydrin with HClO_4 and H_2O as catalysts to give 3-chloro-2-hydroxyl-propyl cellulose, which further reacts with nitrogen-containing or sulphur-containing compounds to introduce cationic, anionic or chelating groups. By referring to the principle of that method, the present work deals with the method of grafting HA onto cotton cellulose which has a much higher crystallinity but relatively weaker reactivity than other species of cellulose^[8]. The reaction mechanism as well as the structure of the products involved in the graft reaction is also discussed.

EXPERIMENTS

Materials

Absorbent cotton was used in the present work. Other reagents were all analytically pure (Beijing Chemical Reagent Works). HA was obtained by extracting the weathered coal with alkali according to the method described elsewhere^[10].

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Preparation of chlorine-containing cellulose

0.5–1.2 g cotton cellulose, 5 ml distilled water and 1.0 ml 70% HClO_4 aqueous solution were mixed in a 250 ml-flask equipped with a condenser and a thermometer. The mixture was stirred and heated for 1–6 h at 80–120°C. After cooling, cotton cellulose was washed several times with acetone and followed with distilled water. The Cl-containing cellulose thus obtained contains 4–6% of Cl. The yield was over 95%.

Preparation of nitrogen-containing cellulose

1.2 g Cl-containing cellulose was immersed in excess aliphatic diamines (e.g. ethylenediamine, propylenediamine, hexanediamine, and N-methylpropylenediamine), and allowed to react for 2 h at 80–120°C. After cooling, the product was washed with dilute NaOH solution followed with distilled water. 1.2 g nitrogen-containing cellulose was obtained which contains 2–3% nitrogen.

Preparation of HA-cellulose graft polymer

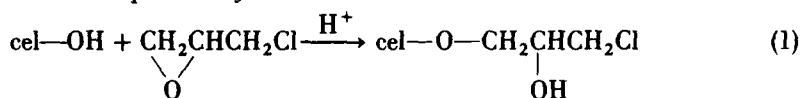
1.14 g nitrogen-containing cellulose was immersed in 50 ml 2–5% HA/DMSO solution and reacted 2 h at 100–120°C. After cooling, the graft polymer was washed with 0.01 N NaOH solution repeatedly to remove the unreacted HA until the washings remained colorless after 2 h immersion. The product was washed repeatedly with distilled water and then dried. 1.24–1.75 g black fibrous HA–cotton cellulose graft polymer was obtained which contains 8–33% HA.

Characterization of different reaction products

IR spectra of the products were measured with PE 683 IR Spectrophotometer and their nitrogen contents were determined with Carlo Erba 1102 Elemental Analyzer. Chlorine contents were measured by Hg titration. The acidic groups content and the Cu^{2+} -complexing capacity were analyzed by conventional acid-alkali and EDTA back titration method, respectively.

RESULTS AND DISCUSSION

1. The reaction of cellulose with epichlorohydrin



The above reaction was significantly catalyzed by HClO_4 and H_2O , and the chlorinity of the product increased with increase of the amount of HClO_4 and H_2O used in the reaction, as shown by the results in Table 1. HClO_4 played the main role in breaking the strong hydrogen bonds in and between the cellulose molecules and in enlarging the spacing of the crystal lattices of crystal region [8, 10, 11]. The water molecules that entered these interspaces would prevent the resumption of hydrogen bonds and thus rendered the epichlorohydrin molecules more accessible and reacted more readily with the hydroxyl groups of the cellulose [8,11] H^+ ion also catalyzed the reaction of epoxy group with hydroxyl group. The reaction order of HClO_4 and H_2O (value m and n in Table 1) was decreased with increasing temperature as shown in Table 1. This is due to the fact that HClO_4 and H_2O can also catalyze and take part in some side-reactions, such as oxidative degradation of cellulose under the catalytic action of strong acids with high oxidizability [10,11,12] acid catalyzed auto-polymerization of epichlorohydrin [6]. Increasing reaction temperature is more favorable for the progression of these side-reactions.

The chlorinity of the product increased with increase of reaction temperature, and the value of apparent activation energy calculated from the $\ln(\text{Cl}\%) - (1/T)$ plot, according to the Arrhenius'

Table 1 The effect of HClO_4 and H_2O on the reaction of cotton cellulose with epichlorohydrin^{a)}

Temperature (°C)	HClO_4 (%)	H_2O (%)	Cl (%)	S_{Cl} ^{b)}	Reaction order ^{c)} <i>m</i>	<i>n</i>
100	0		<0.3	/		
	0.24		2.92	0.14		
	0.50	4.85	4.28	0.22	0.49	
	0.70		4.57	0.24		
	1.00		6.04	0.33		
		1.10	1.38	0.07		
		2.00	3.08	0.15		
	1.05	3.00	2.85	0.14		0.92
		4.00	6.04	0.33		
	0.26		1.68	0.08		
120	0.50	2.01	1.73	0.08	0.42	
	1.10		3.02	0.15		
		1.10	2.49	0.12		
	1.10	2.20	3.02	0.15		0.28

Note: a) reaction conditions: epichlorohydrin (ml)/cotton cellulose (g) = 180, reaction time = 6h, concentrations expressed as volume %.

b) $S_{\text{Cl}} = 162 (\% \text{Cl}) / (3550 - 92.5 (\% \text{Cl}))$, when $S_{\text{Cl}} = 3.00$, all the hydroxyl groups of cellulose were converted into $\text{CH}_2\text{ClCHCH}_2\text{O}-$.

c) Value m and n were calculated from equation: $\ln(\% \text{Cl}) = m \cdot \ln(\text{HClO}_4) + n \cdot \ln(\% \text{H}_2\text{O}) + \text{constant}$, based on the data tabulated in Table 1.

Table 2 The effect of temperature on the reaction of cotton cellulose with epichlorohydrin^{a)}

Time (h)	Temperature (°C)	Cl (%)	S_{Cl}	Apparent Activation energy (kJ/mol)
6	90	3.84	0.19	
	100	6.04	0.33	54.6
	110	9.88	0.61	
4	100	3.58	0.18	
	110	5.60	0.30	53.2

Note: a) Reaction conditions: epichlorohydrin (ml)/cotton cellulose (g) = 180, $\% \text{HClO}_4 = 0.9$, $\% \text{H}_2\text{O} = 4.7$.

equation, is 54 kJ/mol, as shown in Table 2. As this reaction system is an exothermic one, proper control of reaction temperature is very essential otherwise it may lead to violent oxidative

degradation of cellulose and autopolymerization of epichlorohydrin. Under overheating condition that is temperature over 120°C, the reaction mixture would quickly turn into black and viscous state and the cotton cellulose would lose its original fibrous structure.

From Table 3, it is observable that the chlorinity of the product tends to decrease and then increase as the reaction time is prolonged. This is probably due to the fact that the chlorine-containing cellulose segments which were broken down in the oxidative degradation may dissolve in the reaction liquid and unable to be recovered. This side-reaction, however, consumes oxidant so they will not proceed further. Under appropriate reaction conditions, as shown in Table 2, the chlorinity of the cellulose may reach 9.88%, which corresponds to about 20% hydroxyl groups of the cellulose has been converted into 3-chloro-2-hydroxypropyl group. This result is quite similar to that of the reaction of processed powder, bead, and crosslinked cellulose, starch, and crosslinked starch with epichlorohydrin as reported by Rayford et al.^[5,6,7]

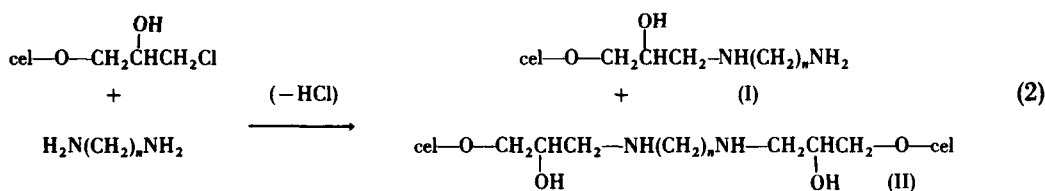
Table 3 The effect of reaction time on the reaction of cotton cellulose with epichlorohydrin^{a)}

Reaction time (h)		1.0	2.0	3.0	4.0	5.0	6.0
Cl	(%)	8.19	4.69	3.07	4.41	5.30	6.04
S _{Cl}	•	0.48	0.24	0.15	0.23	0.28	0.33

Note: a) reaction conditions: reaction temperature 100°C, the rest were the same as those in Table 2.

No obvious differences were observed between the IR spectra of chlorine-containing cellulose and that of original cellulose (Fig. 1. a and b), indicating that the glycopyranoside structure of the cellulose was basically maintained in the product. The intensity of absorption bands which characterized 3-chloro-2-hydroxypropyl group, such as 1050 cm⁻¹ (ν_{C-O}), 2840—2980 cm⁻¹ (ν_{CH_2}), 740 cm⁻¹ and 600 cm⁻¹ (ν_{C-Cl}), were slightly enhanced, due to the fact that the amount of this group grafted onto cellulose was relatively small.

2. The reaction of chlorine-containing cellulose with aliphatic diamines



Experimental results showed that any changes in diamines, ratio of reactants, reaction temperature, reaction time, and amination times used in this reaction, the nitrogen content of the products remained nearly unchanged. It was related only to the chlorinity of the chlorine-containing cellulose. As illustrated in Table 4, every chlorine atom is replaced by 1.39—1.67 nitrogen atoms, and corresponds to 39—67% of structure I and 61—33% of structure II in the reaction product. According to theoretical calculation, in structure I, each chlorine atom should convert into two nitrogen atoms, while in structure II only one nitrogen atom. By comparing the IR spectrum of nitrogen-containing cellulose (Fig. 1. c) with that of chlorine-containing cellulose, it revealed that the

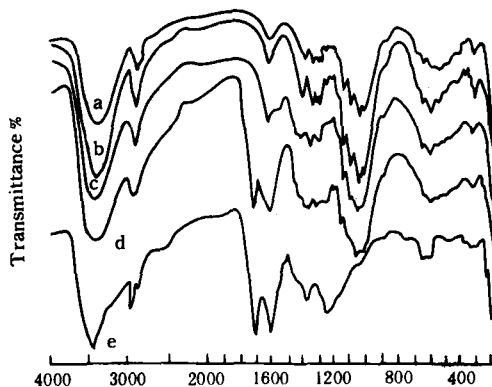
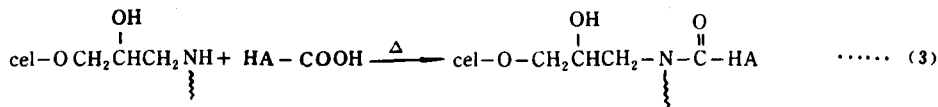


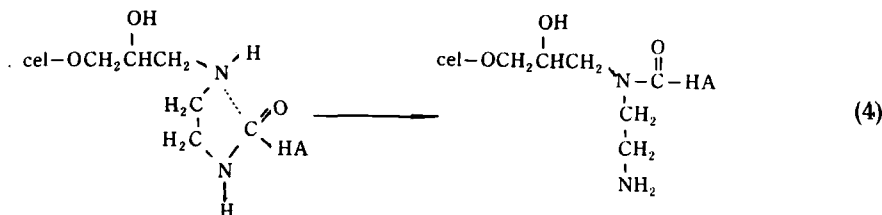
Fig.1 IR spectra a. cel-OH; b. cel-O-CH₂CHCH₂Cl; c. N-containing cellulose; d. HA-cellulose, graft polymer; e. HA

absorption bands at 740 cm⁻¹ and 600 cm⁻¹ disappeared or weakened, while a new shoulder peak appeared in 1590 cm⁻¹ (δ_{N-H}) and the absorption bands in 1050–1200 cm⁻¹ (δ_{C-N}) became broader. Doubtlessly, these changes evidenced that the chlorine atoms were substituted by nitrogen atoms.

3. The reaction of nitrogen-containing cellulose with HA



In the case of chlorine-containing cellulose or methylated HA (all the carboxyl and phenolic hydroxyl groups of the HA were blocked by using CH₂N₂), the above reaction did not occur under the same reaction conditions. Thus, the only reaction which can occur is that of carboxyl group of HA with the amino groups of nitrogen-containing cellulose, resulting in the formation of amide linkage^[13]. The carboxyl group of the HA and the secondary amino group of the cellulose are sterically hindered, and the interaction between them is likely very difficult to be realized. But the terminal primary amino group can react readily with HA. Naturally, the secondary amino group can also readily take part in the reaction through the following intramolecular amide-amino exchange reaction.



Experimental results showed that the reactivity of nitrogen-containing cellulose prepared from various amines with HA followed this order: propylenediamine, ethylenediamine, N-methylpropylenediamine, hexanediamine. This is due to the fact that propylenediamine and ethylenediamine can form stable six-member and five-member cyclic transition structures in the reaction, thus resulting in greater reactivity. The terminal N-methyl in N-methylpropylenediamine has greater steric hinderance, the reactivity of which is decreased. Hexanediamine can not form cyclic transition structure, therefore its reactivity is the lowest.

Table 4 Nitrogen content of the product from reaction (2) (ethylenediamine)

Chlorine-containing Cellulose Cl (%)	Nitrogen-containing Cellulose			Number of nitrogen atoms introduced for each chlorine atom ^{b)}
	N _{theor} ^{a)} (%)	N _{exptl} (%)	Cl (%)	
2.91	2.25	1.18	<0.3	1.67
4.48	3.43	2.81	<0.3	1.64
5.47	4.16	2.89	<0.3	1.39

Note: a) N_{theor} corresponds to the nitrogen content when each chlorine atom was substituted by two nitrogen atoms

(i.e. product I), equals to $\frac{28(\%Cl)}{35.5} \cdot \frac{1}{100 - (\%Cl) + (\%Cl) \cdot 59/35.5}$

b) Number of nitrogen atoms = $2 \cdot (\%N_{exptl.}) / (\%N_{theor.})$

4. The structure and chemical characteristics of HA-cellulose graft polymer

The IR spectrum (Fig. 1. d) of the graft polymer is basically an overlap of HA's and cellulose's. Some characteristic absorption bonds of HA (i.e. 3400, 1700, 1620, 1400, and 1250 cm⁻¹) appeared distinctly in the IR spectrum of the graft polymer. The amide linkage formed in the above reaction should exhibit its characteristic absorption bands at 1695—1610 cm⁻¹ ($\nu_{C=O}$), 3335 and 3075 cm⁻¹ (ν_{N-H}), and 1540 cm⁻¹ (δ_{N-H}), respectively. Nevertheless, these bands were covered up by the strong and broad absorption bands of HA and cellulose at the corresponding wavenumbers, and thus became undistinguishable. In the IR spectrum of the graft polymer, the absorption band of carboxyl group at 1700 cm⁻¹ ($\nu_{C=O}$) is still considerably strong, indicating that only a part of carboxyl group of HA took part in the reaction. Chemical analysis of acidic groups also indicated that about 50% of carboxyl groups of HA disappeared after the reaction. Common amido bonds are easy to be hydrolyzed under the catalysis of alkaline, but the amino bond in the graft polymer is very stable because of the protection induced by the adjacent bulky substituents, i.e. HA and cellulose rigid-chain macromolecules. No degradation of HA was found when the graft polymer was treated repeatedly with pH 12 NaOH solution at room temperature. Only 7% of the acidic groups were lost even if the graft polymer was treated with the same solution over 5 h at 96°C.

The Cu²⁺-complexing capability of the graft polymer was increased by one to three order of magnitudes in comparison with the original HA, and the concentration of Cu²⁺ ions (at pH 4) solution dropped to the utmost of 10⁻⁹M. Although about half of the carboxyl group of HA in the graft polymer was used up in the grafting reaction, 54% of the remaining half could complex with Cu²⁺ ions, as compared with the original HA in which only 28% of the carboxyl group could complex with Cu²⁺ ions. Therefore, 5% of the Cu²⁺-complexing capacity of the HA in the graft-polymer was reduced. The experimental results showed that the graft polymer possesses 0.90 meq/g acidic groups and 0.49 meq/g Cu²⁺-complexing capacity. The graft polymer also has some more kinds of complexing sites than the original HA for complexation, as shown by their Cu²⁺-complexing titration curves, which will be reported in another paper.

Keywords:

Humic acid; Cotton cellulose; Grafting; Complexation

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