

Preparation and Application of Acrylonitrile-Grafted Cyanoethyl Cellulose for the Removal of Copper (II) Ions

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ABSTRACT: Cyanoethyl cellulose (CE-Cell) with two different degrees of substitution of 0.37 and 0.60 were prepared from cotton linter. The ionic-xanthate method was used to graft the acrylonitrile onto CE-Cell to form acrylonitrile-grafted cyanoethyl cellulose (GCE-Cell). The conditions of grafting such as sodium hydroxide concentration, grafting time, monomer concentration, and temperature were optimized. The hydrolyzed CE-Cell and

GCE-Cell were applied for the adsorption of copper (II) ions from aqueous solution. IR spectroscopy was also used for further evaluation of CE-Cell and GCE-Cell. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 329–334, 2006

Key words: fibers; graft copolymers; infrared spectroscopy; ion exchangers

INTRODUCTION

Heavy metal ions dissolved in water are one of the worst pollutants of the environment as it accumulates in living tissues, causing many harmful effects. For example, cupric ion in waste waters can eliminate all fish and plants from streams for miles downstream from the source.¹ During recent years, the removal of heavy metal ions both from waste and natural waters has gained wide importance in minimizing the major causes of water pollution. Various methods such as precipitation, adsorption, extraction, and sorption or ion exchange are proposed to remove and recover heavy metal ions from industrial waters and waste waters.² Adsorption of heavy metal ions by synthetic polymers can reduce

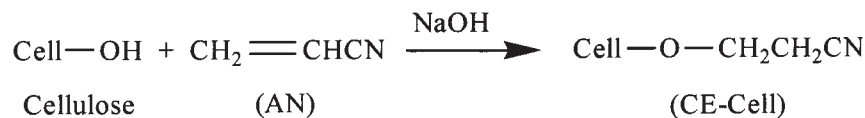
the concentration of these ions to a lower level than any other method can, but this method is not economically viable. Therefore, many methods based on inexpensive materials were studied for removing and entrapping heavy metals from contaminated water.³ Among all studied methods, cellulose ion exchange is being considered attractive because it is an effective and relatively simple method for the removal of heavy metal ions.⁴ Moreover, cellulose is cheap, renewable, biodegradable, and can provide permanent and an environmentally safe source of materials for the preparation of ion exchangers.^{5–6}

Cellulose itself has low ion-exchange or adsorption capacity as well as poor physical stability. For this reason, chemical modification, copolymerization, or crosslinking should be carried out for the cellulose to achieve efficient ion-exchange capacity.⁷ Chemical modifications give cellulose new properties such as hydrophilic or hydrophobic character, improved elasticity, water sorbency, ion-exchange capability, and thermal resistance.^{8–10} Modified cel-

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lulose products, having ion exchanging properties, have been obtained by different methods. One of them was to introduce cyanoethyl group into cellulose

lose by treatment of cellulose with acrylonitrile (AN) in the presence of sodium hydroxide.¹¹ The reaction is presented as follows:



The ionic-xanthate method of grafting can also be applied to graft vinyl monomers onto cellulosic materials.¹²⁻¹³ Grafting by this method is based on the introduction of a small number of xanthate groups into cellulose hydroxyls in the absence of any catalyst. This method was also used to graft AN onto water-soluble cellulose such as carboxymethyl cellulose.¹⁴

The aim of this work was to graft AN on cyanoethyl cellulose (CE-Cell) with two different degrees of substitution (DS) by using ionic-xanthate method to prepare acrylonitrile-grafted cyanoethyl cellulose (GCE-Cell). The reaction involves the production of cyanoethyl cellulose xanthate (CE-CellX), which was then reacted with vinyl monomer. Different grafting conditions such as reaction time, temperature, sodium hydroxide, and monomer concentration were optimized. The structure of the grafted product was investigated using IR spectroscopy. Also, adsorption behavior of hydrolyzed CE-Cell and GCE-Cell for cupric ions in aqueous solution at different pH was investigated.

EXPERIMENTAL

Materials

Purified cotton linter from Abo Zable Chemicals Company (Abo Zable, Egypt) was used for cyanoethyl cellulose (CE-Cell) preparations. Acrylonitrile (AN) (Fluka) was purified according to the method of Bamford.¹⁵ Carbon disulfide (Fluka) was of pure grade and used without further purification.

Methods

Cyanoethylation

Two samples of CE-Cell were prepared having DS of 0.37 and 0.60 according to the method described by El-Wakil.¹⁶ Nitrogen content was determined.¹⁷ The degree of substitution (DS) was calculated using the following equation:¹⁸

$$\text{DS} = \frac{11.57 \times N}{1 - (3.79 \times N)}$$

where, N is the percentage of nitrogen.

Grafting of AN onto CE-Cell

The ionic-xanthate graft polymerization was carried out using two-stage method:¹²

Stage A -Formation of cyanoethyl cellulose xanthate solution (CE-CellX): CE-CellX formed from the reaction between CE-Cell with CS_2 and NaOH (17.5% w/v) in a ratio of 1:3:6, respectively. Samples were placed in a reaction bottle of 100 mL at 30°C for 1 h; the bottle was shaken for another 1 h at room temperature.

Stage B -Polymerization stage: the CE-CellX solution formed in the first stage was polymerized homogeneously with AN in the ratio of 1:3 (CE-Cell: AN = 1:3) at 30°C for 2 h with occasional shaking. Dilute HCl, as precipitating agent, precipitates GCE-Cell, which is then filtered and washed with distilled water until neutrality, dried at 60°C for 24 h under vacuum. Grafting yield and grafting efficiency were determined by extracting the homopolymer with dimethyl formamide, which can be calculated as follows

$$\text{Grafting yield (\%)} = \frac{A - B}{B} \times 100$$

$$\text{Grafting efficiency (\%)} = \frac{A - B}{C - B} \times 100$$

where, A is the weight of product after extraction, B is the weight of dry CE-Cell, and C is the weight of product before extraction in grams.

Infrared spectra

The samples were subjected to investigation by Fourier Transform Infrared Spectrophotometer (FTIR-3000 E). All measurements were carried out using the KBr disc technique.

Hydrolysis

The aim of hydrolysis is to convert the $-\text{CN}$ groups to COOH and $-\text{COONa}$ groups depending on the hydrolysis degree and hydrolyzing agent. By this way, the functional groups removing Cu (II) or metal ions can be formed. Five grams of CE-Cell or GCE-Cell was hydrolyzed with 125 mL 1N NaOH under reflux for

1 h and it was filtered and washed with distilled water. The product was dipped in a solution of 1N HCl over night and then filtered and washed with distilled water.

Adsorption of metal ions

0.1 g hydrolyzed CE-Cell or GCE-Cell was added to 50 mL of the buffered copper acetate solution of 5 mmol Cu (II) ions. The mixture was kept for 24 h at room temperature in a 100-mL glass Stoppard Erlenmeyer flask. The suspension was filtered through G3 sintered glass funnel. Filtrate was used to determine the concentration of the remaining Cu (II) ions in a solution. The adsorbed copper amount was calculated from the difference between the initial and final concentration of Cu (II) in solution.

RESULTS AND DISCUSSION

Effect of sodium hydroxide concentration

The effect of sodium hydroxide concentration on the grafting yield and grafting efficiency of AN grafting on CE-Cell using the ionic-xanthate method is shown in Figure 1. It can be noticed from the figure that the grafting yield (%) increased significantly with increase in the concentration of NaOH from 7.5% to 27.5% and the maximum grafting yield was obtained at the highest NaOH concentration (27.5%), regardless the DS of CE-Cell. This result may be attributed to the possible increase in the number of xanthate groups at high NaOH concentration, which leads to more grafting yield.¹³ The grafting efficiency reached maximum at 12.5% NaOH concentration, then decreased again with increase in the concentration. This behavior can be explained on the basis of formation of more ho-

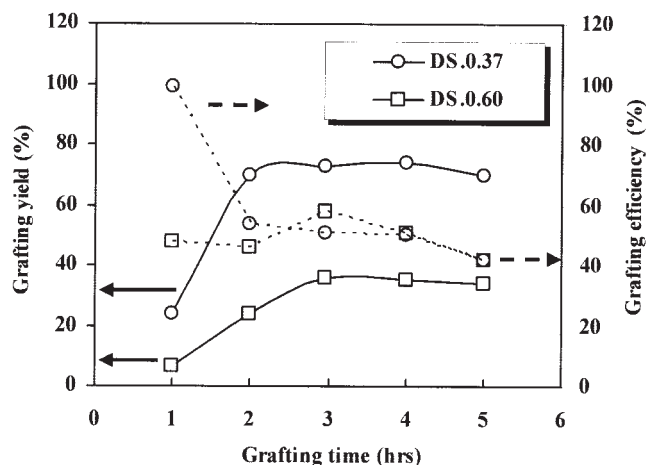


Figure 2 Effect of grafting time on both grafting yield (%) and grafting efficiency (%). Conditions: CE-Cell: monomer (AN) = 1:3 at 30°C.

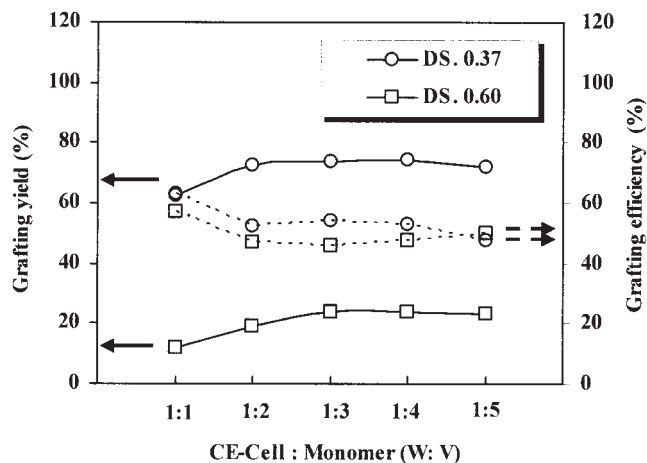


Figure 3 Effect of monomer concentration on both grafting yield (%) and grafting efficiency (%). Conditions: 30°C for 2 h.

mopolymer at higher NaOH concentration, which is dissolved by extraction with dimethyl formamide. The recommended concentration for the best grafting efficiency was found to be 12.5% NaOH.

Effect of grafting time

The duration of AN grafting on CE-Cell was varied from 1 to 5 h, and the results are shown in Figure 2. It is clear from the figure that the grafting yield % increased with increase in the reaction time and was much higher for CE-Cell with DS 0.37 than that for CE-Cell with DS 0.60. Also, the maximum grafting yield for CE-Cell with DS 0.37 was obtained after 2 h compared to 3 h for CE-Cell with DS 0.60. This result indicates that the grafting yield % is highly dependent on the DS of CE-Cell. On the other hand, it was found

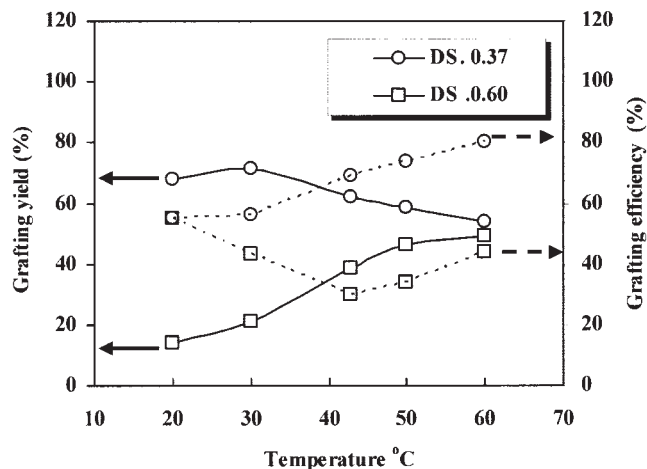


Figure 4 Effect of grafting temperature on both grafting yield (%) and grafting efficiency (%). Conditions: (G-Cell: monomer/AN) 1:3 for 2 h.

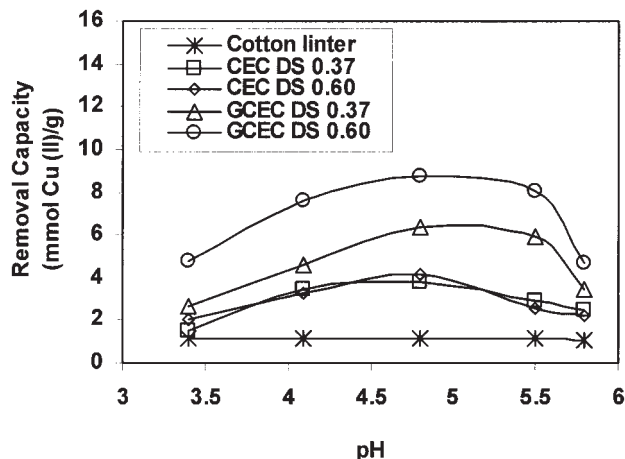


Figure 5 Effect of pH on the amount of adsorbed Cu (II) ions. Conditions: 0.1 g sample + 50 mL of 5 mmol Cu (II) solution at room temperature for 24 h.

that the grafting efficiency decreased with increase in the reaction time in spite of the increase in grafting yield %. This result may be attributed to the excess formation of homopolymer over grafting with increase in the reaction time. So on extraction, the homopolymer was eliminated, which led to decrease in the grafting efficiency. Generally, it can be concluded that the best grafting performance was obtained at 2 h for CE-Cell with DS 0.37 and 3 h for CE-Cell with DS 0.60.

Effect of monomer concentration

Figure 3 shows the effect of monomer concentration on the grafting yield and grafting efficiency for the

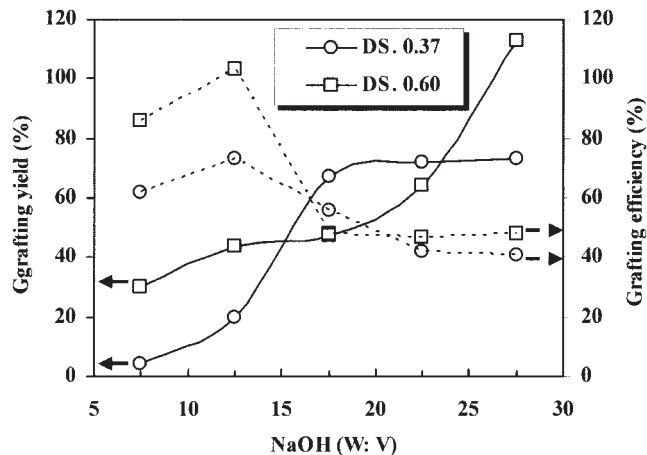


Figure 1 Effect of NaOH concentration on both grafting yield (%) and grafting efficiency (%). Conditions: 1 g CE-Cell + 3 mL CS₂ + 6 mL NaOH solution at 30°C for 2 h.

grafting reaction onto CE-Cell. It is evident from the figure that the grafting yield increased with increase in the ratio of CE-Cell to monomer concentration till 1:2 (g CE-Cell:mL AN) for CE-Cell of DS 0.37 and till 1:3 at DS 0.60 then the grafting yield was slightly changed. Regarding the grafting efficiency, it showed maximum value at CE-Cell to AN ratio of 1:1 (w:v) regardless the DS of the CE-Cell. The decrease in grafting efficiency with increase in the monomer concentration more than 1:1 can be explained by the fact that the increase in monomer concentration allows more polymerization while the active sites at the substrate are the same, and accordingly more homopolymer are formed.

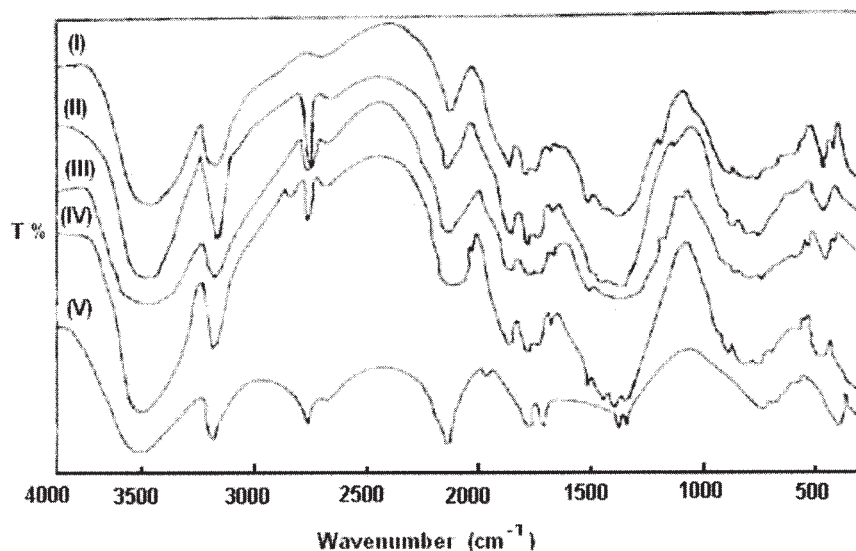


Figure 6 IR spectroscopy of untreated cotton linter (I); CE-Cell (DS 0.37), (II); CE-Cell (DS 0.60), (III) and GCE-Cell (IV) and (V) possessing grafting yield of 2.51 and 72.82, respectively.

TABLE I
IR Specification of Cotton Linter, CE-Cell and GCE-Cell

Samples	γ_{OH} (cm^{-1})	Asymmetry index	Mean hyd. Bond strength	Crystallinity index	A_{2250} (cm^{-1})	A_{1320} (cm^{-1})	A_{1050} (cm^{-1})
Cotton linter	3335	0.91	0.80	1.05		1.27	1.62
CE-Cell (DS 0.37)	3345	0.88	1.16	1.07	0.80	1.82	1.81
CE-Cell (DS 0.60)	3360	0.87	1.28	0.90	1.21	1.94	2.68
GCE-Cell (DS 0.37)	3380	0.75	1.44	1.05	0.50	0.79	1.08
GCE-Cell (DS 0.60)	3440	0.76	1.38	0.88	0.82	0.83	0.87

Effect of grafting temperature

The results of the effect of grafting temperature on the grafting efficiency are shown in Figure 4, it is clear that maximum grafting yield for CE-Cell with DS of 0.37 was obtained at 30°C and that for CE-Cell with DS of 0.60 was obtained at 60°C. On the contrary, the grafting efficiency for CE-Cell of DS 0.37 showed maximum values at 60 and 20°C for the other sample having DS of 0.60. Increasing or decreasing the grafting yields with increasing temperature can be explained according to Le Chatelier's principle.¹⁹ CE-CellX with DS of 0.6 has lower free hydroxyl group to react with AN when compared with DS of 0.37, so it may require higher temperature to react with cellulosic free hydroxyl group instead of homopolymer formation. The temperature at which the grafting yields reached maximum values is known as ceiling temperature and it is known that these temperatures are affected with the type of cellulose substrate used in grafting reaction.¹³ So, the ceiling temperature of the grafting of AN onto CE-Cell of DS 0.37 is 30°C while it is 60°C for CE-Cell of DS 0.60.

Adsorption of Cu (II) Ions

The adsorption behavior of the ion-exchanger towards metal-ion removal depends on the protonation and deprotonation properties of its acidic and basic groups, accordingly, the adsorption behavior is greatly affected by pH value.²⁰ Therefore, the adsorption dependence on the pH for the metal ions was examined in detail. Figure 5 shows the amount of adsorbed Cu (II) after 24 h contact time for untreated cellulose (cotton linter), hydrolyzed CE-Cell and GCE-Cell at different pH values ranging from 3.4 to 5.8. It is clear from the figure that untreated cellulose has no affinity for Cu (II) ions removal at all pH values studied as the amount of adsorbed copper are identical before and after a prolonged time. On the other hand, the adsorption behavior for CE-Cell and GCE-Cell show dependence on the pH values. At higher acidic conditions, i.e., low pH of about 3.4, little Cu (II) ions adsorption was occurred. This result may be related to the protonation of the carboxyl group at higher acidic conditions which in turn limits the ability of the sam-

ple to adsorb Cu (II) ions. The amount of adsorbed Cu (II) ions increased with increase in the pH of the solution and maximum adsorption was obtained at pH 4.8. This result may also be attributed to less protonation of carboxyl groups at high pH leading to more grafting of carboxyl groups. It is also clear from the figure that the amount of Cu (II) ions removed from the solution by GCE-Cell was much higher than that for CE-Cell due to the increase in the number of grafted carboxyl groups. For the same reason GCE-Cell with DS of 0.6 shows higher Cu II removal than GCE-Cell with DS of 0.37.

Infrared spectra

The infrared absorption spectra of untreated cotton linter, CE-Cell possessing DS 0.37 and 0.60, and GCE-Cell possessing grafting yields 2.51% and 72.87% are shown in Figure 6. The absorbency of different bands and IR specification of the same samples were measured (Table I)

From Figure 6, it is obvious that the OH stretching band broadening towards higher frequency occurred at 3300–3500 cm^{-1} led to a decrease in a symmetry index. The mean hydrogen bond strength measured ($A_{\text{OH}}/A_{\text{CH}} = A_{3420}/A_{1640}$)²¹ indicates lowering in the values due to the possible decrease in the number of hydroxyl groups. A new characteristic band occurs at 2250 cm^{-1} , which is assigned to the cyano group ($-\text{C} \equiv \text{N}$) was observed in the CE-Cell and GCE-Cell samples. The decrease in mean hydrogen bond strength values is also related to the replacement of the OH group by cyano group (Table I). The crystalline indices of the samples were measured using professional ratio (A_{3420}/A_{1640}).²² The increase in crystalline index of CE-Cell of high DS and GCE-Cell may be due to the dissolution of the short fibers by NaOH during the cyanoethylation and grafting processes, whereas decrease in crystalline index in case of CE-Cell (DS 0.60) and GCE-Cell possessing grafting yield of 72.87% refracts the disordering occurred in the sample due to the progressed reaction. The bands at 1320 cm^{-1} is assigned to the OH bending and stretching in COOH group²³ and the absorbency of this band is also increased by cyanoethylation and decreased by graft-

ing which may be related to the possible disruption in the crystalline state. The bands at 1050 cm^{-1} assigned to skeletal vibration involving stretching of both C—O and C—C bonds attached to the glucose ring.²⁴ The absorbency was increased by cyanoethylation and decreased by grafting process.

CONCLUSIONS

GCE-Cell was prepared from CE-Cell having two different DS of 0.37 and 0.60 by using ionic-xanthate grafting method. The conditions of grafting such as sodium hydroxide concentration, grafting time, monomer concentration, and temperature were studied. The grafting yield and grafting efficiency were determined. The optimum conditions for grafting of AN onto CE-Cell were monomer to CE-Cell ratio (1:1) and sodium hydroxide concentration 12.5% for 2 h at 30°C (DS 0.37) and 3 h at 60°C (DS 0.6). The application of hydrolyzed CE-Cell and GCE-Cell on the adsorption of Cu (II) ions from aqueous solution was also done. The results obtained showed that the adsorbed amount increased with increase in the DS of CE-Cell, and GCE-Cell gave much higher adsorption than CE-Cell. FTIR results showed that the cyanoethylation or grafting of CE-Cell is accompanied with the formation of a new band at 2250 cm^{-1} due to cyano group ($-\text{C}\equiv\text{N}$) resulting in a decreasing of asymmetry index and mean hydrogen bond strength while crystallinity index was increased.

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