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Preparation and characterization of saponified delignified cellulose polyacrylonitrile-graft copolymer

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Abstract

Acrylonitrile was graft polymerized onto delignified cellulose using ceric ammonium nitrate as initiator. Polymerization typically yield cellulose-*g*-polyacrylonitrile containing 45.05 g acrylonitrile per 100 g sample. The resulting copolymer was saponified with (0.75 M) sodium hydroxide. The treatment was carried out at 100°C for different time duration. The extent of saponification was assessed by estimating carboxyl content, nitrogen content, acrylonitrile and acrylic acid before and after saponification. The alkaline treatment results in a decrease in nitrogen content and increase in carboxyl content. Moreover, beside the conversion of cyanide groups to carboxyl groups, alkaline treatment brings about cleavage of ether linkage of the copolymer.

The potential value of the saponified modified cellulose is serve as a water absorbance was assessed through measurements of critical properties such as solubility and absorbance of water, saline water and synthetic urine. Also, the property of the prepared sample of swelling to gel was used to absorb water from ethanol–water mixture. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Delignified cellulose; Saponification; Absorbence

1. Introduction

Living plants constitute some of the most complex and formulated polymeric composites known to man. Although polymeric plant constituents have many useful properties that would be difficult to duplicate synthetically, usage of these materials could be greatly expanded if there were convenient methods for modifying some of the properties of these natural polymers for specific end-use applications. Graft polymerization is one excellent way of achieving this goal, and our previous work was on starch grafting (Bayazeed, Farag, Shaarawy & Hebeish, 1998; Khalil & Farag, 1998; Bayazeed, Farag & Hebeish, 1986) was published. Lignocellulosic materials derived from a number of different plant sources also used as substrates in these polymerization reactions (Fazilat & Rostamie, 1979; Hon 1982). Use of whole-plant materials as substrates is less common in the literature. Major contribution in this category have been in the area of wood–plastic composite (Meyer, 1981). Attempts to initiate graft polymerizations with ceric ammonium nitrate resulted in little or no grafting, presumably due to the inhibiting effect of lignin (Mansour, Nagaty, Beshay & Nisseir, 1983). To carry out this work, cellulose was delignified to avoid the hydrophobic and recalcitrant nature of lignin component towards water absorbance. Since cereal straw is an abundant source of biomass, we studied its reactivity in graft polymerization reaction using acrylonitrile as monomer and ceric ammonium nitrate as initiator.

Our previous work dealt with alkaline hydrolysis of polyacrylonitrile–starch graft copolymer and used as exchanger (Khalil, Farag & Hebeish, 1991). Graft polymerization of acrylonitrile onto ground wheat straw constituents (cellulose, hemicellulose, and lignin) was also determined by Fanta, Burr and Doane (1987). Acrylonitrile was chosen as monomer because it readily graft polymerizes onto starch and cellulose in the presence of a number of different initiating systems.

Because of the paramount importance of water as the major functional component of biological and inanimata systems on Earth, particular interest has been aroused by the development of a saponified polyacrylonitrile-grafted-delignified cellulose which exhibits high water absorbency, which is marketed particularly for personal care products, such as, disposable diapers and agricultural uses, such as seed and root coating and as addition to sandy soils to improve water retention. These properties of the absorbent are also relevant to its potential use in drying ethanol (gasohol program (Kelm, 1980)) as a functional ingredient

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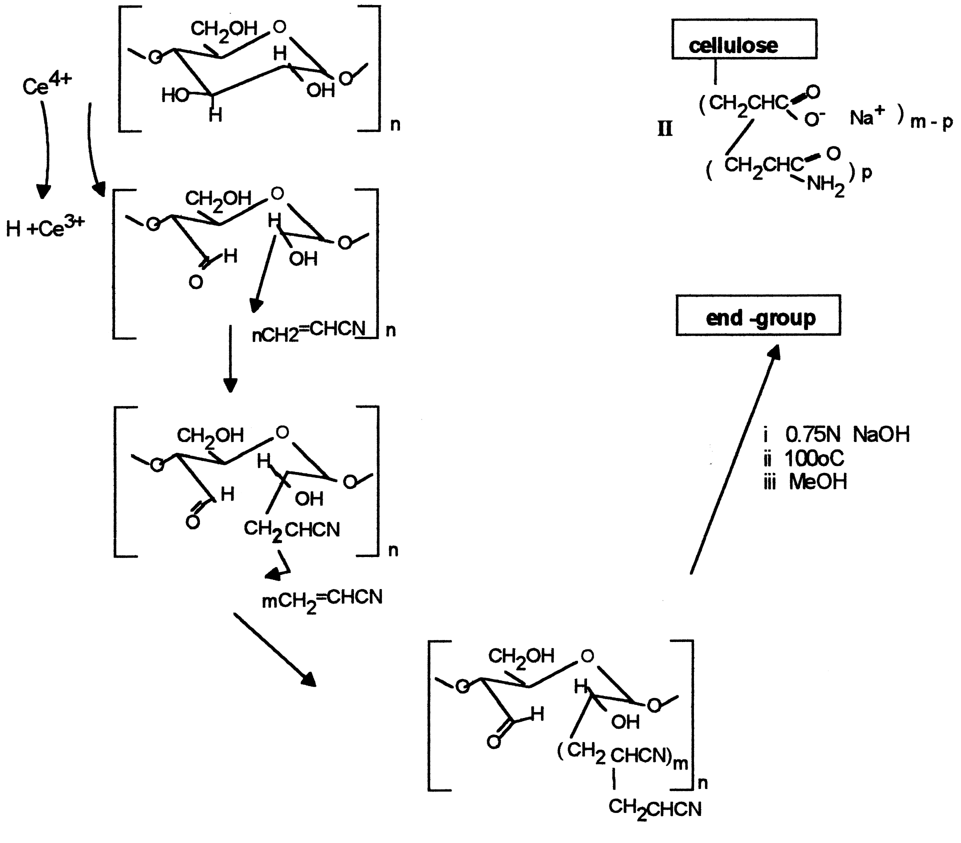

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Fig. 1.

of disposable soft goods for hygienic and medical purposes (Lindsay, 1976).

The chemical reactions, presumably, involve information about the saponified PAN copolymer are depicted in Fig. 1 in accordance with the account of Ranby and Rodehed (1981).

This work was undertaken to study the alkaline hydrolysis of polyacrylonitrile delignified cellulose graft copolymer and its properties as absorbent.

2. Experimental

2.1. Materials

Acrylonitrile, Eastman practical grade, was distilled at atmospheric pressure through a 14-in Vigreux column, and a center cut was collected and stored at 5°C. Ceric ammonium nitrate was Fisher certified ACS grade. Sodium chloride, synthetic urine (reagent grade, BDH) were used as test of solutes effect. To carry out the investigation, cellulose was extracted from certain agricultural wastes (sugar-exhausted sugar cane fibers and maize cob). In the procedure, a sample of the crude in coarse powder (400 g) was added to an acidic mixture (400 cm^3) consisting of nitric acid (3.5% w/v) and sodium nitrite (0.001% w/v) and heated at 90°C for 3 h to remove soluble nitrolignins. The residue was collected by filtration and then digested (50°C, 2 h) with 4 l alkaline mixture of sodium hydroxide and sodium sulphite, each 2% w/v. After filtration the residue was bleached successively at 50°C first with sodium hypochloride (0.3% w/v) and later with a solution of hydrogen peroxide (6% w/v). The residue was washed several times with water, dried at 50°C for 3 h, (moisture content of about 8%) and then pulverized (Okor, Iwu-Anyanwu & Khamafe, 1992).

2.2. Graft polymerization

Ceric-initiated grafting onto deliginified (Adams, 1965) cellulose, 15.0 g of acrylonitrile was added to a nitrogen-spraged suspension of 15.0 g of delignified cellulose in 300 cm^3 of water. After 5 min, a solution of 0.5 g of ceric ammonium nitrate in 5 cm^3 of 1 M nitric acid was added and the mixture was stirred for 3 h at room temperature. The yield of air-dried copolymer was 12% moisture content.

Kjeldahl nitrogen analysis, carboxyl content analysis of the resulting delignified cellulose-graft-PAN was carried out by the method reported by Kunin (1971).

Table 1
Effect of alkaline treatment on the nitrogen and carboxyl contents of delignified cellulose polyacrylonitrile-graft copolymer (experimental conditions: 10 g (dry basis) of delignified cellulose-*g*-PAN = (11.9 N%); 200 cm^3 of 0.75 M sodium hydroxide; temperature 100°C)

Saponification time (min)	Carboxyl content (mmol/100 g sample)	Nitrogen content (mmol/100 g sample)	COOHN	Acrylonitrile (g/100 g sample)	Acrylic acid (g/100 g sample)	Total polymer	Cellulose
0	2.5	850.0	0.009	45.05	0.18	45.23	54.77
15	268	536.7	0.50	28.40	19.30	47.70	52.30
30	293	478.5	0.61	25.40	21.10	46.50	53.50
45	301	343.0	0.88	18.17	21.67	39.84	60.16
60	306	257.0	1.20	17.64	22.03	35.67	64.33
90	309	228.5	1.40	12.11	22.25	34.36	65.64
120	308	214.3	1.44	11.40	22.20	33.60	66.40

2.3. Saponification of delignified cellulose-g-PAN

A mixture of 10.0 g (dry basis) of delignified cellulose-*g*-PAN and 200 cm^3 of 0.75 M sodium hydroxide in a loosely stoppered flask was heated in a 100°C oven for different period of time (15–20 min). The reaction mass was separated by stirring with methanol and air-dried. PAN contents of all fractions was calculated from Kjeldahl nitrogen and carboxyl analyses.

2.4. Solubility of saponified cellulose-g-PAN (Fanta, Burr & Doane, 1979)

To rapidly determine copolymer solubility, an accurately weighed 1 g sample was dispersed in 200–800 cm^3 water, and the dispersion was allowed to stand overnight at room temperature. The volume of water was accurately measured, and the amount used depended on the water absorbency or the degree of swelling of the copolymer. The mixture was allowed to gravity filter through fluted paper, and an accurately weighed portion of the clear filtrate was freeze-dried. Percent water-soluble was calculated from the weight of freeze-dried solid.

2.5. Measurement of water absorbency (Fanta et al., 1979)

An accurately weighed 20–100 mg sample of polymer (amount used depended on absorbency) was allowed to stand 30 min in 50 cm^3 deionized water. The swollen polymer was separated from unabsorbed water by screening through a tared 280-mesh sieve that was 4.8 cm in diameter. The polymer on the sieve was allowed to drain 20 min, and the sieve was weighed to determine the weight of water-swollen gel. Absorbency was calculated as grams of water per gram of dry copolymer, taking into account the initial moisture content of the copolymer. No correction was made for the percentage of the copolymer that was soluble in water, the absorbency values would thus be higher if based only on insoluble copolymer.

2.6. Removal of water from ethanol–water vapor

Saponified cellulose-*g*-PAN copolymer was dried in an oven (30–50 g) was packed in a jacketed (thermostat) horizontal tube, through which was then passed a stream of nitrogen gas (15 cm^3/min) that had been bubbled through an ethanol–water (4:1) mixture maintained at 60°C. Therefore, the vapor was condensed from the nitrogen stream and collected in a benzine trap until first turbidity appeared. The weight increase in the trap measured the amount of pure ethanol obtained.

2.7. Effect of solutes on swelling

The saponified cellulose-*g*-PAN were soaked in synthetic urine (composition: 0.64 g $CaCl_2$; 1.14 g $MgSO_4$, 7 l solution H_2O; 8.2 g NaCl; 20 g urea and water) until equilibrium was reached and the absorption capacity was determined by weighing the swollen gels on a 170 mesh sieve to constant weight (Castel, Ricard & Audebert, 1990). Also, immersion of saponified delignified cellulose-*g*-PAN in dilute solution of sodium chloride (0.5%)

Table 2
Essential properties of saponified delignified cellulose polyacrylonitrile-graft copolymer (experimental conditions: 20 mg sample; 50 cm^3 deionized water; time 30 min)

Sample no	Carboxyl content (mmol/100 g sample)	Nitrogen content (mmol/100 g sample)	Water solubility (%)	Absorbency (g H_2O/g sample)
1	2.5	850.0	9.0	13
2	268	536.7	18.0	350
3	293	478.5	25.0	380
4	301	343.0	26.0	398
5	306	257.0	26.5	418
6	309	228.0	26.7	423
7	308	214.3	26.7	423

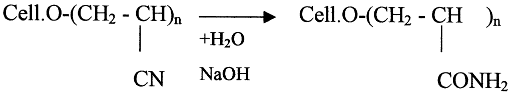
diminished the enhanced absorbency of product was determined as mentioned above.

3. Results and discussion

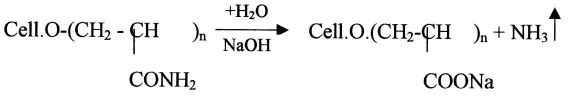
The prepared copolymer acquired 850 mmol nitrogen/100 g sample was subjected to the action of 0.175 M sodium hydroxide (liquor ratio = 1:100) for different period of times (15–120 min), at 100°C. The results (Table 1) signify that alkaline hydrolysis is accompanied by a decrement in the nitrogen content of the copolymer. It is further noted that the decrement in the nitrogen content during the first 15 min hydrolysis is relatively high, and beyond 15 min hydrolysis, the decrement in nitrogen content continues but in a regular manner.

In system containing poly acrylonitrile–cellulose graft copolymer, sodium hydroxide and water, several reactions are expected to occur. Among these reactions mentioned are made of the following:

(i) Hydrolysis of the cyanide groups to carboxyl groups as shown:

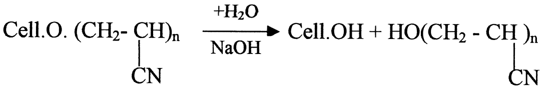


$$\mathrm{Cell.O\text{-}(CH_2\text{-}\underset{\underset{CN}{|}}{CH})_n \xrightarrow[\substack{+H_2O\\ NaOH}]{} Cell.O\text{-}(CH_2\text{-}\underset{\underset{CONH_2}{|}}{CH}\ )_n} \quad (1)$$

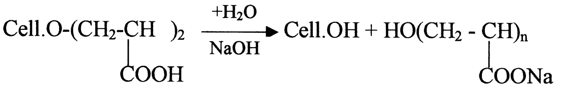


$$\mathrm{Cell.O\text{-}(CH_2\text{-}\underset{\underset{CONH_2}{|}}{CH}\ )_n \xrightarrow[NaOH]{+H_2O} Cell.O.(CH_2\text{-}\underset{\underset{COONa}{|}}{CH}\ )_n + NH_3\uparrow} \quad (2)$$

(ii) Cleavage of the ether bond linking the polyacrylonitrile graft to the cellulose backbone as shown:



$$\mathrm{Cell.O.\ (CH_2\text{-}\underset{\underset{CN}{|}}{CH})_n \xrightarrow[NaOH]{+H_2O} Cell.OH + HO(CH_2\text{-}\underset{\underset{CN}{|}}{CH}\ )_n} \quad (3)$$



$$\mathrm{Cell.O\text{-}(CH_2\text{-}\underset{\underset{COOH}{|}}{CH}\ )_2 \xrightarrow[NaOH]{+H_2O} Cell.OH + HO(CH_2\text{-}\underset{\underset{COONa}{|}}{CH})_n} \quad (4)$$

Table 1 also shows the carboxyl content of the prepared copolymer before and after alkaline hydrolysis. It is seen that the increment in the carboxyl during the first 15 min of hydrolysis is higher as compared to those formed during the next equal periods of hydrolysis.

The remarkable ability of hydrophilic saponified delignified cellulose graft copolymer to absorb aqueous fluids is shown in Table 2. The absorbents have values on the order of 350 g H_2O/g sample to 423 g H_2O/g sample (based on dry weight sample). Water solubilities of these absorbent range from about 18–26.7%. This soluble polymer does not contribute to absorbency; it can be observed that the gel obtained could swell well in deionized water.

These qualitative findings accord well with a mechanistic model of the enhanced water sorbence of acrylate-grafted polysaccharides that is essentially the same as that described (Grignon & Scallan, 1980) for the swelling of cellulose gels. Swelling is accordingly considered to be caused by an osmotic pressure differential resulting from a difference in concentration of mobile ions between the interior of the gel and the external solution. The fundamental feature within the gel, bringing about the unequal distribution, is the presence of ionizing acidic groups attached to the macromolecular network.

Table 3
Treatment of ethanol–water mixture with saponified delignified cellulose polyacrylonitrile-graft copolymer (experimental conditions: 50 cm^3 of 80% ethanol/water mixture; 5 g prepared sample; treatment, 3 h, temperature, 60°C)

Carboxyl content (mmol/100 g sample)	Sorbency (g H_2O/g sample)	Alcohol yield (%)
2.5	7	2
268	210	10
293	267	22
301	279	24
306	283	25
309	288	28
308	286	28

The applicability of the saponified cellulose graft copolymer onto ethanol–water mixture was demonstrated in Table 3, where we can observe that the prepared copolymer could swell in the ethanol water mixture, the copolymer produce 28% of absolute alcohol at temperature 60°C. This value is not more efficient, and this is due to interactions between the polar molecules of the alcohol and the ionic groups of the prepared samples (Rodehed & Ranby, 1986). Positive results were obtained in a vapor-phase system when a carrier-gas stream was used. Table 4 shows the absorbency as a function of synthetic urine and sodium chloride. Any change in the external parameter will also affect significantly the swelling of the absorbent. The decrease of the expansion of the chains is due to screening of the ionic charges bound to the chains of the prepared sample and to the decrease of the osmotic pressure difference between the prepared copolymer and the external solution when the ionic strength increases. Also because of the decreased electrostatic repulsion of the chains at higher ionic strength, and the cumulative pore volumes in each size of the swollen copolymer in aqueous sodium chloride or synthetic urine were larger than those in pure water. Small quantities of divalent or trivalent ions can decrease drastically the swelling values. Also, Ca^{2+} ions can be due to the complexing ability of carboxylate groups inducing intramolecular and intermolecular complexes formation. This behavior is in agreement with the results reported by Gugliemelli, Weavor, Russell & Rist (1969).

The swelling behavior of saponified delignified cellulose graft polyacrylonitrile absorbents is related to its structure, its chemical composition, and the nature of solvent used. The expansion of the prepared copolymer is promoted by

Table 4
Effect of salts on absorbence of saponified delignified cellulose polyacrylonitrile-graft copolymer (experimental conditions: 10 g sample; 1000 cm^3 synthetic urine; 10 g sample, 1000 cm^3 sodium chloride at room temperature, treatment time, 3 h)

Sample no.	Carboxyl content (mmol/100 g sample)	Synthetic urine (g/g)[a]	0.5% NaCl (cm^3/g)
1	2.5	11	9
2	268	72	179
3	293	77	183
4	301	78	191
5	306	80	198
6	309	85	210
7	308	85	210

[a] Synthetic urine composition: 0.64 g $CaCl_2$; 1.14 g $MgSO_4$; 7 l solution H_2; 8.2 g NaCl; 20 g urea.

the charge containing chains. However, an excess of charges results in a swelling decrease. This behavior is explained in terms of screening effect.

For a given ionic strength, the absorbency of saponified delignified cellulase-graft-polyacrylonitrile absorbent in presence of solution containing multivalent salts decreases strongly by comparison with NaCl solution.

The copolymer absorbent activity could be regenerated afresh time by drying after repeated sorption, indicating the essential reversibility of the sorption process, and also suggesting its potential suitability in a recycling batch process.

4. Conclusions

Water sorbence by saponified polyacrylonitrile-grafted delignified cellulose was studied in relation to practical end uses. Absorbence increases as carboxyl groups increase. Also, the prepared copolymer have utility in absorbence of urine and solute. In the case of ethanol–water mixutres, there are many techniques that were applied to superabsorbent, however, the prepared sample did not produce enrichment in the ethanol content (the copolymer produce 28% of absolute alcohol). The obtained copolymer is efficient substrate for water absorbence and its activity could be regenerated afresh by drying after repeated sorption.

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