

GRAFTING OF SOME MONOMERS ONTO CELLULOSE AND DETERMINATION OF METAL AND WATER UPTAKE PROPERTIES

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Some new cellulosic materials with water uptake capacity and being suitable for the sorption of metal ions were synthesized by the grafting of cellulose with monomers, such as N-(4-nitrophenyl)acrylamide (4NPA), N-cyclohexylacrylamide (NCA), 4-vinylpyridine (4VP), acrylamide (AM), methacrylamide (MAM), diacetoneacrylamide (DAAM), methylmethacrylate (MMA) and diallylamine (DA). Firstly, cellulose methacrylate (Cell.met) was prepared by esterification of the primary -OH group of cellulose with methacryloyl chloride with a 21.3% yield by mole. The monomers were grafted into cellulose methacrylate via free radical polymerization using 2,2'-azobisisobutyronitrile (AIBN) as an initiator in acetonitrile. The graft copolymers were characterized by FT-IR spectra, elemental analyses and thermal analysis. The thermal stabilities of the graft copolymers were determined by the TGA method and it was established that the thermal stability of the copolymers decreased with grafting. The water uptake capacity of 8 graft copolymers and their metal ion sorption tendency (Ni^{2+} , Co^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+} , Fe^{3+} and Cr^{3+}) were found to improve with grafting.

Keywords: cellulose, graft copolymer, metal ion and water uptake

INTRODUCTION

Unmodified cellulose has a low heavy metal adsorption capacity, as well as variable physical stability. Therefore, chemical modification of cellulose can be carried out to achieve adequate structural durability and efficient adsorption capacity for heavy metal ions. Chemical modification can be used to vary certain properties of cellulose, such as its hydrophilic or hydrophobic character, elasticity, water sorption, adsorptive or ion exchange capability, resistance to microbiological attack and thermal resistance. The β -D-glucopyranose units that make up the cellulose chain contain one primary hydroxyl group and two secondary hydroxyl groups. Functional groups may be attached to these hydroxyl groups through a variety of chemistries. The principle and main routes of direct cellulose modification in the preparation of adsorbent materials are esterification, etherification, halogenation and oxidation.¹ Recently, the attention of many research groups has been drawn to the synthesis and characterization of cellulose derivatives.² Thus, functional groups, such as

xanthogenate,³ calix(4)arene,⁴ glycidyl,⁵ ethyleneimine,⁶ succinate,⁷ 4-vinylpyridine,⁸ N-vinyl-2-pyrrolidone,⁹ vinylimidazole,¹⁰ glycidyl-methacrylate,¹¹ acrylonitrile,¹² acrylamide,¹³ methacrylamide,¹⁴ N-vinylformamide¹⁵ and even functional polymers,^{1,16} were successfully incorporated into the cellulose matrix by performing adequate functionalization.

This paper firstly reports the preparation, characterization, and sorption properties towards some selected metal ions Ni^{2+} , Co^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+} , Fe^{3+} and Cr^{3+} of cellulose-grafted 4NPA, NCA, 4VP, AM, MAM, DAAM, MMA and DA polymers.

EXPERIMENTAL

Materials

The synthesis of cellulose methacrylate (Cell.met), 4NPA and NCA monomers was carried out as reported in previous works.¹⁷⁻²⁰ $\text{Ni}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$, $\text{Cr}(\text{NO}_3)_3$ solutions and all the other solvents were of analytical grade and were used as received.

Instrumental measurements

IR spectra were recorded with a Perkin Elmer Spectrum One FT-IR spectrophotometer on solid samples as KBr pellets. Thermal analysis was performed with a Shimadzu TGA-50 thermo balance at a heating rate of 10 °C min⁻¹ under nitrogen flow of 10 ml min⁻¹. Leco CHNS-932 was used for elemental analysis. Perkin Elmer A Analyst 400 model atomic absorption spectrophotometer (AAS) was used to determine the metal ions.

Synthesis of graft copolymers

Cellulose methacrylate and its graft copolymers were prepared by a method adapted from the literature.¹⁷⁻¹⁹ 1 g Cell.met, 5 g monomer (4NPA, NCA, 4VP, AM, MAM, DAAM, MMA and DA), 50 mL acetonitrile and 0.05 g AIBN as a free radical initiator were added into a polymerization tube, and argon was passed through for 15 min; then, it was sealed. The monomer was allowed to graft onto cellulose at 70 °C for 24 h. Grafted copolymers were filtered and thoroughly washed with N,N-dimethylformamide, water, ethanol, acetonitrile, acetone, and diethyl ether to eliminate oligomers and homopolymers formed in the reaction as products. Obtained graft copolymers were dried under vacuum at 40 °C.

Metal ions sorption of graft copolymers

Standard stock solutions of 250 ppm of Ni²⁺, Co²⁺, Cu²⁺, Cd²⁺, Pb²⁺, Fe³⁺ and Cr³⁺ ions were prepared in double distilled water. 50 mg of polymer sample, 2.5 mL of stock solution, and 5 mL of KH₂PO₄/Na₂HPO₄ buffer solution (pH=6.2) were added to an Erlenmeyer flask and diluted to 25 mL with distilled water, and then sealed. The mixture was stirred constantly at room temperature for 24 h. The mixture was filtered in order to eliminate the polymer, and the solution was diluted with distilled water, and the filtrate was analyzed for the amount of metal remaining after sorption onto the polymers. The relationships used to determine the sorption behavior are as follows:^{17,21}

$$\% \text{ uptake } (P_i) = \frac{\text{Amount of metal ion in the polymer}}{\text{Amount of metal ion in the feed}} \times 100$$

$$\text{Partition coefficient } (K_d) = \frac{\text{Metal ion in the polymer}}{\text{Metal ion left in the solution}} \times \frac{\text{Volume of solution (mL)}}{\text{Weight of dry polymer (g)}}$$

$$\text{Retention capacity } (Q) = \frac{\text{Amount of metal ion in the polymer (meq)}}{\text{Weight of dry polymer (g)}}$$

Water uptake properties of pellet graft copolymers

A known amount (w_1) of each polymer was vacuum-dried, was pressed into a pellet under a pressure of 10 tons, some water was added into each

tube and they were stored at 25 °C for 24 h. Then, the pellet graft copolymers were dried slightly with filter paper and weighed (w_2). Water uptake was calculated as follows:

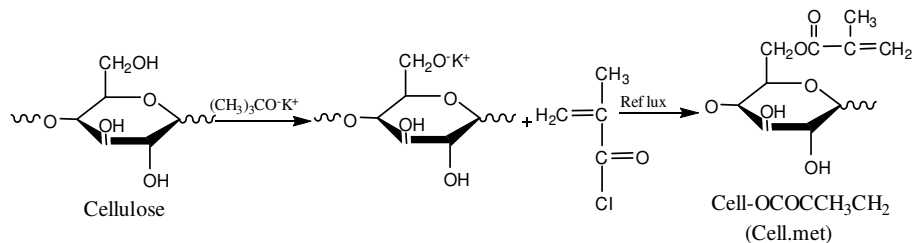
$$\text{Water uptake (\%)} = \frac{w_2 - w_1}{w_1} \times 100$$

RESULTS AND DISCUSSION

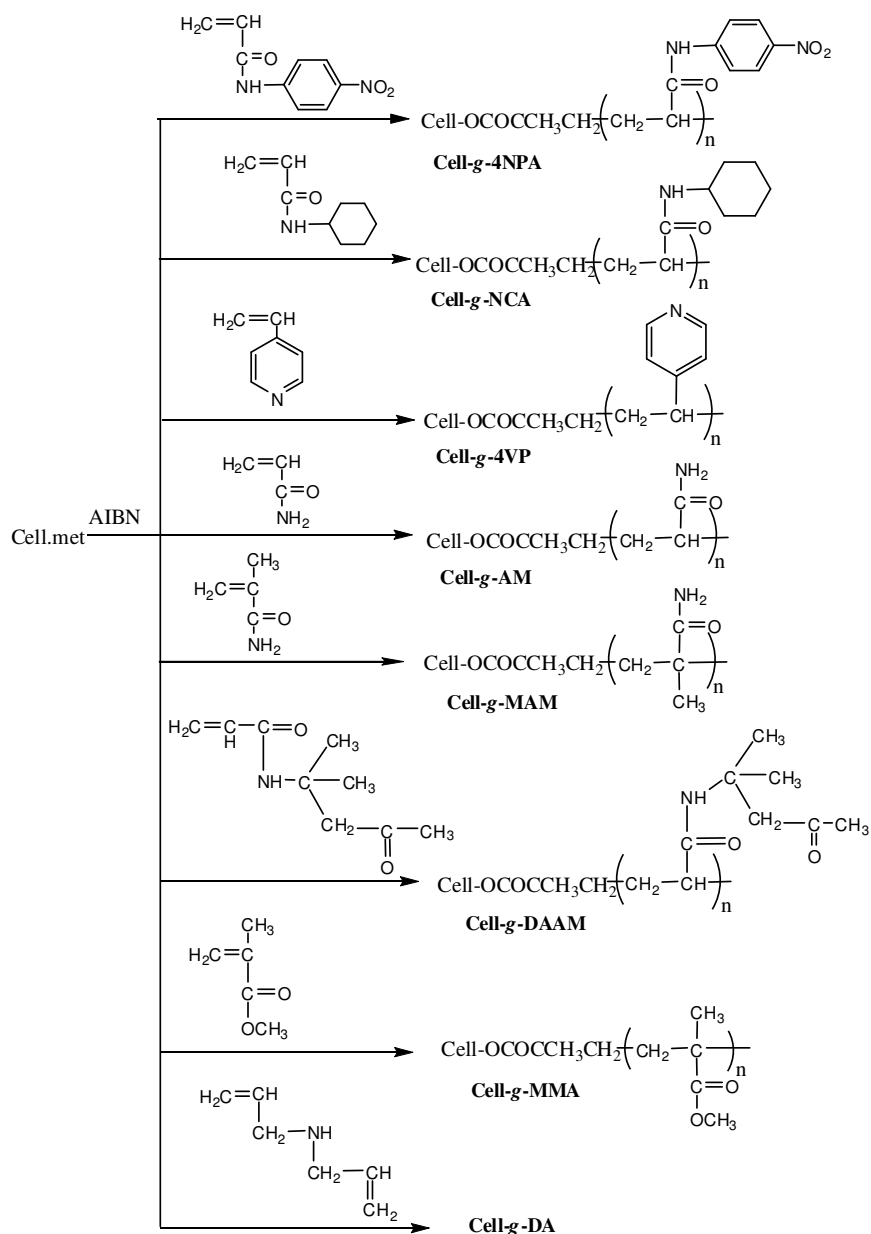
Grafting of cellulose and its characterization

The primary OH groups in cellulose were first transformed to ester groups with methacryloyl chloride and Cell.met was synthesized and grafted with 4NPA, NCA, 4VP, AM, MAM, DAAM, MMA, DA in the presence of AIBN as initiator. The synthesis of Cell.met and all grafting reactions on cellulose are indicated in Schemes 1 and 2. FT-IR spectra of cellulose, Cell.met and the graft copolymers of cellulose with 4NPA (Cell-g-4NPA), NCA (Cell-g-NCA), 4VP (Cell-g-4VP), AM (Cell-g-AM), MAM (Cell-g-MAM), DAAM (Cell-g-DAAM), MMA (Cell-g-MMA) and DA (Cell-g-DA) are shown in Figure 1. The presence of a new band at 1730 cm⁻¹ (-C=O stretching), in which there is no band for cellulose, indicates that the methacrylate group has become attached to cellulose. The C=O stretching of the amide group around 1650 cm⁻¹ in the graft copolymers Cell-g-4NPA, Cell-g-NCA, Cell-g-AM, Cell-g-MAM, Cell-g-DAAM is a characteristic band. An intensity increase for both amide stretching and ester band at 1730 cm⁻¹ is seen for Cell-g-DAAM. Also, the Cell-g-MMA ester band and the Cell-g-4VP N-H pyridine ring tension increase at 1603 cm⁻¹, while the ester band decreases.

The substitution degree (n) in the glucose units of cellulose was calculated as 21.3% by mole from the percentage of carbon as given in the literature. The levels of grafting achieved on cellulose were expressed as the weight fraction (x) of the corresponding monomers.^{17,22} The elemental analyses of all the polymers, x and n values calculated above are shown in Table 1. It can be seen that the grafting degree of these monomers on cellulose is relatively low (between 0.13-0.02 as weight fraction, x, and between 4.75-0.14 as the ratio of monomer to methacrylate groups in cellulose, n).



Scheme 1: Synthesis of cellulose methacrylate



Scheme 2: Grafting of cellulose with some monomers

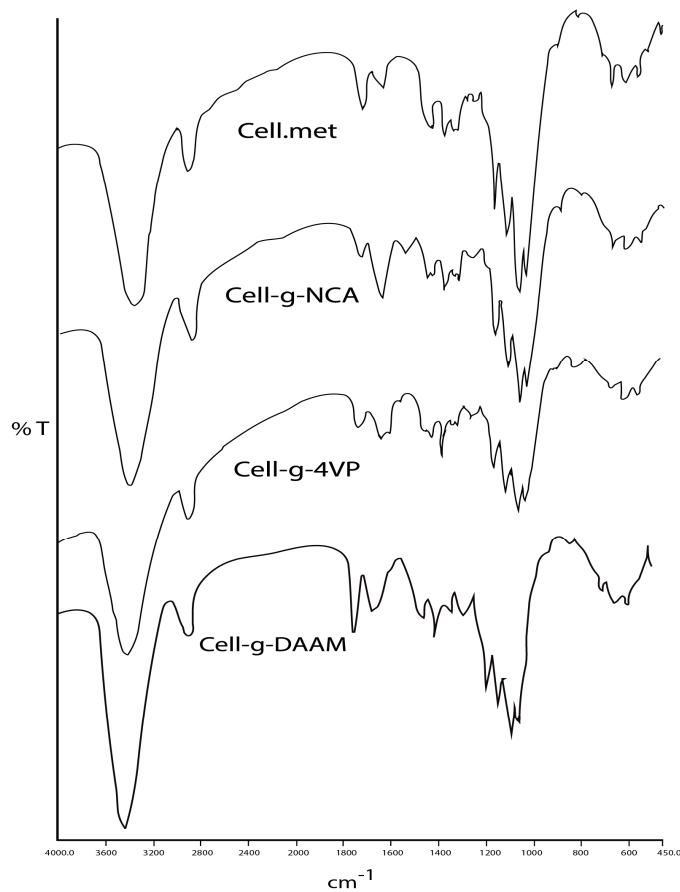


Figure 1: IR spectra of some graft copolymers

Table 1
Elemental analysis results of grafting some monomers onto cellulose

Polymer	C (%)	H (%)	N (%)	Weight fraction of monomer (x)	Ratio of segments to cellulosic units (n)
Cellulose	42.03	5.55	-	-	-
Cell.met	44.18	5.60	-	-	-
Cell-g-4NPA	45.68	6.36	1.12	0.13	0.62(0.58)*
Cell-g-NCA	45.80	6.80	0.95	0.08	0.42(0.45)*
Cell-g-4VP	44.78	5.85	2.26	0.02	0.14(0.11)*
Cell-g-AM	46.05	6.21	2.74	0.29	4.75(4.52)*
Cell-g-MAM	47.08	7.04	5.3	0.24	3.00(2.77)*
Cell-g-DAAM	46.88	6.66	0.89	0.14	0.78(0.88)*
Cell-g-MMA	46.60	6.40	-	0.15	1.49(1.63)*
Cell-g-DA	46.02	5.40	0.45	0.10	0.99(0.85)*

*Values in brackets were obtained by gravimetric analysis

Table 2
Sorption behavior of cellulose, substituted cellulose, and its graft copolymers towards metal ions

Polymer	Ni ²⁺			Co ²⁺			Cu ²⁺			Cd ²⁺			Pb ²⁺			Fe ³⁺			Cr ³⁺		
	P _u	K _d	Q	P _u	K _d	Q	P _u	K _d	Q	P _u	K _d	Q	P _u	K _d	Q	P _u	K _d	Q	P _u	K _d	Q
Cellulose	40.0	333.3	0.170	38.4	311.7	0.163	40.0	333.3	0.157	35.2	311.7	0.085	41.6	356.2	0.05	53.0	559.3	0.355	51.2	524.6	0.369
Cell.met	43.2	380.3	0.184	40.0	333.3	0.170	41.6	356.2	0.164	38.4	271.6	0.078	48.0	461.5	0.058	56.0	636.4	0.376	53.0	559.3	0.381
Cell-g-4NPA	49.6	492.1	0.211	41.6	356.2	0.176	51.2	524.6	0.202	56.0	636.4	0.125	44.8	405.8	0.054	48.0	461.5	0.322	56.0	636.4	0.404
Cell-g-NCA	44.8	405.8	0.191	43.2	380.3	0.183	57.6	679.2	0.227	30.4	218.4	0.068	40.0	333.3	0.048	64.0	888.8	0.430	52.8	559.3	0.381
Cell-g-4VP	43.2	380.3	0.184	44.8	405.8	0.190	49.6	492.1	0.195	41.6	356.2	0.093	36.8	291.1	0.044	62.4	829.8	0.419	57.6	679.2	0.415
Cell-g-AM	36.8	291.1	0.157	43.2	380.3	0.183	43.2	380.3	0.170	56.0	636.4	0.125	43.2	380.3	0.052	48.0	461.5	0.322	49.6	492.1	0.358
Cell-g-MAM	36.8	291.1	0.157	48.0	461.5	0.204	40.0	333.3	0.157	30.4	235.3	0.071	41.6	356.2	0.050	46.4	432.8	0.312	51.2	524.6	0.369
Cell-g-DAAM	40.0	333.3	0.170	41.6	356.2	0.176	46.4	432.8	0.183	43.2	380.3	0.096	57.6	679.2	0.069	54.4	596.5	0.365	52.8	559.3	0.381
Cell-g-MMA	36.8	291.1	0.157	40.0	333.3	0.170	49.6	492.1	0.195	36.8	291.1	0.082	43.2	380.3	0.052	53.0	559.3	0.355	52.8	559.3	0.381
Cell-g-DA	40.0	333.3	0.170	48.0	461.5	0.204	46.4	432.8	0.183	49.6	492.1	0.110	36.8	291.1	0.044	54.4	596.5	0.365	57.6	679.2	0.415

Table 3
Water uptake values of the polymers

Polymer	Water uptake (%)
Cellulose	188
Cell.met	211
Cell-g-4NPA	293
Cell-g-NCA	254
Cell-g-4VP	232
Cell-g-AM	365
Cell-g-MAM	350
Cell-g-DAAM	304
Cell-g-MMA	343
Cell-g-DA	275

Metal ions sorption of graft copolymers

The results of the study on Ni²⁺, Co²⁺, Cu²⁺, Cd²⁺, Pb²⁺, Fe³⁺ and Cr³⁺ sorption behaviors of the graft copolymers (Cell-g-4NPA, Cell-g-NCA, Cell-g-4VP, Cell-g-AM, Cell-g-MAM, Cell-g-DAAM, Cell-g-MMA and Cell-g-DA) are summarized in Table 2. Metal ions are partitioned between the swollen polymer and the liquid phase, and they are reflected in the high values of the partition coefficient (K_d). All sorption values of the cellulose substituted for Cell.met are higher than those of cellulose and the graft copolymers. Amide groups and electronegative atoms in the graft copolymers and methacrylate groups bonded to cellulose interact more easily with water, as compared with hydroxyl groups in cellulose, and this means that raw cellulose swells in water less than the others. Sorption values of all metals include percent uptake (U_p), partition coefficient (K_d) and retention capacity (Q), and these values are higher for the graft copolymers than for Cell.met, which indicates the presence of C=O groups on Cell.met.

Water uptake of graft copolymers

Water uptake results for cellulose, Cell.met and its synthesized graft copolymers are given in Table 3. Water can form hydrogen bonds with amide groups in the side-chain of graft copolymers with amide monomer and electronegative atoms. Thus, the solubility of the graft copolymers in water is increased. It has been reported that the water uptake capacity increased by grafting cellulose with N-vinyl-2-pyrrolidone,⁹

vinylimidazole,¹⁰ N-vinylformamide¹⁵ and 4-acryloylmorpholine, 2-methacrylamidopyridine, N-phenyl methacrylamide.¹⁷

Thermogravimetric study of graft copolymers

The thermogravimetric curves for cellulose, Cell.met and Cell-g-4NPA, Cell-g-NCA, Cell-g-4VP, Cell-g-AM, Cell-g-MAM, Cell-g-DAAM, Cell-g-MMA, Cell-g-DA graft copolymers prepared by the free radical polymerization method, obtained under heating from room temperature to 500 °C at a heating rate of 10 °C/min under nitrogen flow, are given in Figure 2. TGA results of the copolymers are summarized in Table 4. It has been noted that the thermal stability of all the grafted polymers decreased compared to the original raw cellulose. While the initial decomposition temperature (IDT) of cellulose was about 290 °C, that of Cell.met of 272 °C, those of the graft copolymers varied between 261-210 °C. While 85% of cellulose decomposed in a narrow temperature range (between 390-350 °C), the others decomposed over a wider range. The graft copolymers left a residue between 6.2-15.3%, while that of cellulose was 7% and that of Cell.met of 9.3%. Similar thermal behavior has been indicated for cellulose grafted with 4-acryloylmorpholine, 2-methacrylamidopyridine, N-phenylmethacrylamide,¹⁷ N-(4-nitrophenyl)acrylamide with methylmethacrylate by atom transfer radical polymerization^{18,19} and cellulose partially esterified with some long-chain organic acids.²³

Table 4
Thermal stabilities of cellulose, substituted cellulose, and its graft copolymers

Polymer	(%) Initial decomposition temperature (°C)	Temperature of 50% wt loss (°C)	Residue (%) at 500 °C
Cellulose	290	370	7.0
Cell.met	272	340	9.3
Cell-g-4NPA	240	332	8.2
Cell-g-NCA	225	327	9.0
Cell-g-4VP	255	335	14
Cell-g-AM	251	341	15.3
Cell-g-MAM	248	352	12.3
Cell-g-DAAM	247	334	13.0
Cell-g-MMA	261	344	6.2
Cell-g-DA	210	325	14.3

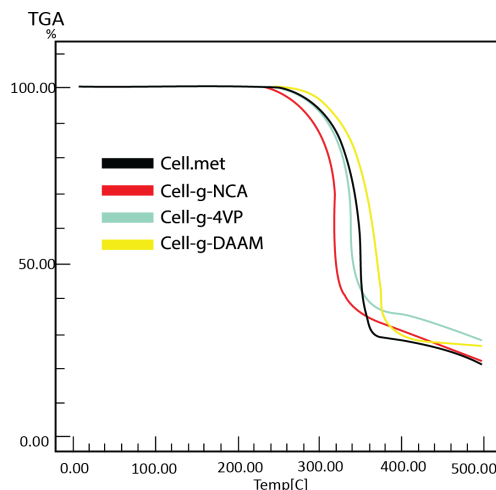


Figure 2: TGA curves of some graft copolymers

CONCLUSION

In this study, firstly cellulose methacrylate was prepared by esterification of primary -OH group with methacryloyl chloride with a 21.3% yield by mole. Monomers, such as 4NPA, NCA, 4VP, AM, MAM, DAAM, MMA and DA, were grafted onto cellulose methacrylate via free radical polymerization, using AIBN as initiator in acetonitrile. The graft copolymers were characterized by FT-IR, elemental and thermal analyses. The thermal stabilities of the graft copolymers were determined by the TGA method and were found to decrease with grafting. The water uptake capacities and the metal ion sorption tendency (Ni^{2+} , Co^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+} , Fe^{3+} and Cr^{3+}) improved with grafting. The results obtained lead to the conclusion that +3 valence metals hold onto graft copolymers better than +2 valence metals, and that Cell.met sorbs metals better than cellulose.

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