

## GRAFT COPOLYMERISATION OF ACRYLAMIDE ON CARBOXYMETHYL CELLULOSE (CMC)

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### ABSTRACT

Graft copolymers of acrylamide (AA) on unmodified holocellulose and holocellulose containing carboxy methyl moieties (of degree of substitution (DS): 0.215; 0.120 and 0.057) were prepared using  $Ce^{4+}$  initiator in aqueous medium at 29°C. The results indicate that carboxymethylation enhances the graftability of the cellulose substrate. The graft levels and molecular weights of grafted polyacrylamide chains on CMC were higher than those obtained on cellulose. Increases in graft levels of up to 70% and 50% for graft copolymer involving CMC with DS 0.215 and 0.120 respectively were observed. The grafting frequencies of polyacrylamide were less on CMC (DS 0.215) than on CMC (DS 0.120) and on cellulose.

This study provides information on the grafting characteristics of AA on CMC, a substrate of particular interest because of its wide range of applications. The influence of ceric ion concentration, degree of substitution of substrate, monomer concentration, time of reaction on the extent and rate of graft copolymerisation of AA onto modified and unmodified cellulose were examined.

**Key words:** copolymer, holocellulose, degree of substitution, carboxymethyl cellulose, acrylamide, graft.

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### INTRODUCTION

In recent years, the use of ceric ions to initiate the graft copolymerisation of vinyl monomers on cellulose materials has received much attention from the practical and fundamental points of view<sup>1-5</sup>. Grafting of polysaccharides in general, is of interest because of its potential as a technique for modifying the chemical and physical properties of these polysaccharides.

Polyacrylamides, which are especially useful as flocculants for fine solids suspended in water, thickening agents and pigment retainers, can impart these properties onto CMC through grafting, thus enlarging the already remarkable diversity of its practical and potential applications<sup>6</sup>.

Sodium carboxymethyl cellulose (or sodium cellulose glycolate) is the most widely used water-soluble cellulose derivative. Depending on its type of viscosity (grade), it is used in food and pharmaceutical industries, laundering, well drilling, paints, etc.

### EXPERIMENTAL

#### Materials

Acrylamide reagent (99.9% pure for electrophoresis, Bio Rad Laboratories), chloroacetic acid (from BDH Ltd) and all other regular laboratory reagents were used without further purification. *Triplochiton scleroxylon* (Obeche) wood meal was obtained from a commercial saw mill in Benin City (Nigeria). It was air-dried and sieved between a 425- $\mu$ m mesh and 355- $\mu$ m mesh screen. The portion of the meal retained on the 355- $\mu$ m mesh was used for the preparation of holocellulosic material.

### Preparation of holocellulose

The sulphite pulping method<sup>7</sup> was used to prepare the holocellulose from the tropical soft wood. A 25.0-g sample of air-dried wood meal was Soxhlet-extracted with 99.7-100% ethanol (v/v) for 6 hours to remove waxes and resinous materials. The resin-free wood meal was then treated with 10% sodium sulphite for eight hours with continuous heating and stirring. The holocellulose obtained was thoroughly washed with water and air dried.

Chlorine gas, generated by the reaction of concentrated hydrochloric acid (60 mL) with potassium permanganate (20 g), was bubbled into 180 mL of cold 2-M sodium hydroxide solution. The resulting sodium hypochlorite solution was mixed with 90 mL of 0.5 M nitric acid solution. The holocellulose meal was then steeped in this hypochlorite solution and heated to boil for 15 minutes. The resultant bleached holocellulose was then filtered off, washed with de-ionised water and air-dried.

### Carboxymethylation of holocellulose

2.00 g of cellulose were added to 39.3 mL isopropanol and 38.5 mL benzene in a mixer. Stirring was commenced and 10.1 mL of aqueous x (= 30, 45, and 60%) sodium hydroxide (w/v) were added in one minute and the mixture was shaken at 30°C for y minutes. z mmol of sodium monochloroacetic acid were added and the reaction mixture was kept at a temperature of 65°C for 70 minutes while shaking<sup>8</sup>. Excess sodium hydroxide was neutralised by drops of acetic acid and the product pressed to remove the solution and then washed with isopropanol and dried.

To determine the degree of substitution<sup>9</sup>, 0.5 g of dried sodium CMC was ashed gently between 450 and 550°C for 24 hours, and then dissolved in 100 mL of distilled water. 20 mL of this solution were titrated with 0.1 N sulphuric acid, using methyl red as indicator. After the first end point, the solution was boiled and titrated to a sharp end point. The carboxymethyl content was calculated as the degree of substitution:

$$DS = \frac{0.162B}{1 - 0.08B} \quad (1)$$

where B is given by the expression  $B = \frac{0.1 b}{G}$ ; b is the volume (in mL) of 0.1 N sulphuric acid and G is the mass of pure sodium CMC in grams.

### Graft copolymerisation

The polymerisation procedure was based on the method described by Lepoutre and Hui<sup>10</sup> using variable amounts of ceric ion and monomer and a constant amount of the cellulosic material (1.0 g) dispersed in 100 mL of deionised water. Polymerisation was stopped after 1 hour by adding 2 mL of quinol solution (5% w/v in acetone) to the reaction mixture which was filtered and the residue air-dried and weighed. The ungrafted poly AA was extracted by stirring the residue in 500 mL of deionised water overnight at room temperature. The grafted cellulosic substrate was then air-dried and reweighed. The percentage graft level,  $P_g$  and the percent efficiency grafting,  $P_e$  were calculated as follows:

$$P_g = \frac{\text{mass of grafted polymer (m}_g\text{)}}{\text{mass of modified pulp (m}_s\text{)}} \times 100 \quad (2)$$

$$P_e = \frac{\text{mass of grafted polymer (m}_g\text{)}}{\text{mass of homopolymer (m}_h\text{)} + \text{mass of grafted polymer (m}_g\text{)}} \times 100 \quad (3)$$

The average molecular weights of isolated PAA grafts were determined from viscosity measurements in water at 25°C using the relationship<sup>11</sup>:

$$\log \eta = \log 6.31 \times 10^{-5} + 0.80 \log M_v \quad (4)$$

where  $\eta$  is the viscosity and  $M_v$  is the viscosity-average molecular weight.

After determination of molecular weights, the frequency of grafting,  $F_g$  defined as the number of moles of grafted AA per  $10^4$  AGU (anhydrous glucose units) was calculated as follows<sup>12</sup>:

$$F_g = \frac{m_g \times M_{AGU}}{M_v} \times 10^4 = n_g \times M_{AGU} \times 10^4 \quad (5)$$

and the rate of graft copolymerisation,  $R_g$  calculated by the relationship:

$$R_g = \frac{m_g}{M_v \times \text{reaction time (t)} \times \text{reaction volume (V)}} \times 1000 \quad (6)$$

## RESULTS AND DISCUSSION

The results in Table 1 show that the degree of substitution increases as the concentration of sodium hydroxide increases. This is probably due to greater swelling and hence easy penetration of carboxymethyl groups in the cellulose structure.

The dependence of grafting parameters of AA on ceric ion concentration is shown in Figure 1. The level of incorporation of polyacrylamide graft copolymer on the holocellulose increased by up to 70% and 50% following the modification of the cellulose substrate (DS: 0.215 and 0.120 respectively). These results agree generally with those reported by Kantouch *et al.*<sup>13</sup> who grafted the same monomer on native cotton, alkali-treated cotton and partially carboxymethylated cotton. Okiemien and Eboaye<sup>5</sup> reported that during polymerisation, ceric ions are consumed by the initiation process and by adsorption onto the cellulose material; the unreacted or adsorbed ceric ions present in the continuous aqueous phase initiate homopolymerisation by charge transfer to monomer<sup>14,15</sup>. Thus, the graft level and the efficiency of grafting depend on the relative amounts of ceric ions present. The slight decrease in percent grafting at higher initiator concentration could be due to the fact that at higher ceric ion concentration, an increase is expected in the reaction steps involving ceric ion, leading to an increase in active sites. In fact, this results in termination (combination or disproportionation) prior to monomer addition. Another contributing factor is the increase in homopolymer formation which competes with the grafting reaction for available monomer thus giving the slight decrease observed at high ceric ion concentration.

Figure 2 shows the variation of the extent of graft polymer formation on the substrates with monomer concentrations. This suggests that acrylamide was more reactive towards carboxymethylated cellulose than cellulose. This is expected, since the former has a greater accessibility than the latter. During swelling of CMC in the reaction medium, there is a break down of many hydrogen bonds in the amorphous region of the cellulose and the chain molecules are then able to move apart. Hence, there will be a tendency for the reacting molecules of monomer and initiator to approach the crystalline regions better than when the reaction is performed on unmodified cellulose.

With a further increase in the concentration of acrylamide, grafting was found to decrease. This is explained by the fact that at higher monomer concentration, the ceric ion preferably enters into complex formation with the monomer, leading to a higher homopolymer formation than grafting, thus decreasing the grafting efficiency. The decrease beyond 43.8 M may also be related to the higher viscosity of the reaction medium, thus limiting monomer diffusion<sup>16</sup>.

The influence of initiation time on the grafting characteristics of acrylamide on cellulose and sodium carboxymethylcellulose using 4.36 mmol of  $Ce^{4+}$  salt, 30 mmol of monomer at a constant polymerisation time of 60 minutes at 29°C is shown in figure 3 below. The result showed an increase in level of grafting with initiation time. The initial increase in graft level may result from an increase in the number of active sites formed on the polymeric substrate. The levelling off around the initial time of 30 minutes may be explained in terms of a limited number of active groups in the polymeric substrate with which the ceric ions would react (formation of a ceric ion complex)<sup>17</sup> and a reduction of the ease of reaction of ceric ions with active groups within the polymeric substrate. It can also be attributed to a decrease in monomer concentration (rapid exhaustion) as well as to the retardation of diffusion due to the formation of polymer at the substrate surface.

Table 1 presents the influence polymerisation time of graft level of acrylamide on unmodified and partially carboxymethylated cellulose using 4.36 mmol of  $Ce^{4+}$  salt, 30 mmol of monomer at a constant initiation time of 30 minutes at 29°C. The  $P_g$  increased with reaction time; the substrate with high DS had

the higher graft level but  $P_g$  were almost unchanged. This can be explained by the fact that the longer the reaction time, the greater the number of sites on the CMC activated by ceric ions, followed by greater grafting. This can also result from the difference in intrinsic characteristics: with the increase in the DS, the swellability of the CMC is enhanced, the effect of increasing polymerisation time will accentuate the swelling properties, improve the solubility of acrylamide, accelerate its diffusion from the polymerisation medium into the modified materials thus enhancing the propagation of graft.

The molecular weight data of PAA graft on unmodified and carboxymethylated holocellulose and of associated homopolymer using 30 mmol of monomer are shown in table 2. It is observed that the molecular weight of grafted PAA decreased with increase in ceric ion concentration, which indicates a contribution of the excess ceric ion in the termination step. The molecular weight of homopolymer associated with grafting on CMC D.S: 0.120 was slightly higher than that on CMC D.S: 0.215. This suggests that the amount of monomer present in the continuous phase is higher in the former than in the latter polymerisation mixture.

It can be seen that the lower number of grafted PAA per gram of substrate lead to a lower frequency of grafting. The number of grafted polymer molecules per  $10^4$  AGU varied from two to eleven. Although the values of graft level and molecular weight of grafted polymer were higher for CMC (DS: 0.215), the levels of incorporation of PAA copolymer grafts into the substrate was higher for CMC (DS: 0.120) and unmodified cellulose than CMC (DS: 0.215). This discrepancy can be explained by the suggestion that initiation of graft polymerisation by ceric ion occurs by hydrogen abstraction from the carbon atom carrying hydroxyl groups. The relatively high frequency of grafting of (DS:0.120) may result from the fact that this substrate possesses the double advantage of having a moderate number of  $-\text{CH}_2\text{COOH}$  groups which helps in opening its structure compared to that of unmodified cellulose and has a sufficient number of hydroxyl sites where initiation can take place compared to the highly substituted CMC.

The values of  $R_g$  were generally low and its variation at higher concentration of ceric ion confirms the participation of  $\text{Ce}^{4+}$  in the termination of growing grafted chains, resulting in a decrease in the rate of graft copolymerisation.

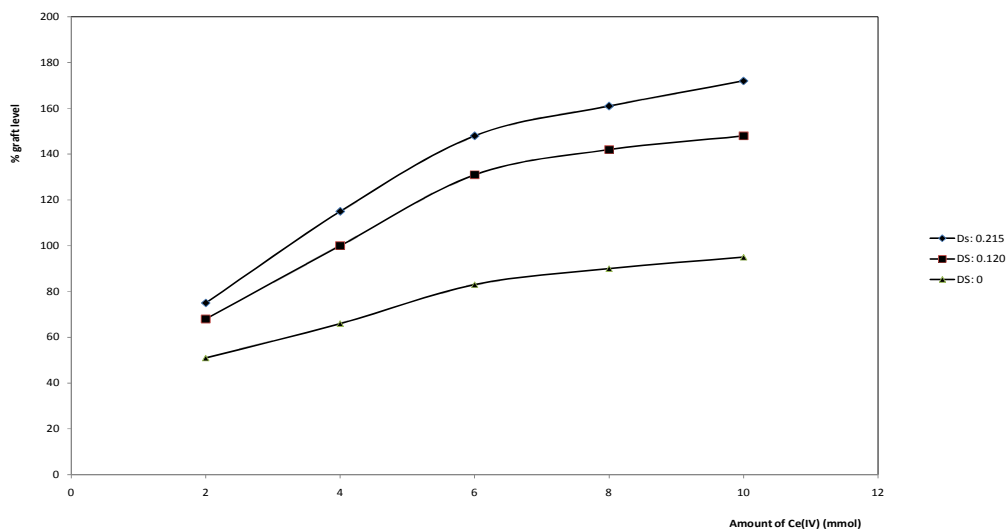


Fig.-1: Effect of  $\text{Ce}^{4+}$  concentration on the graft level of AA on unmodified and CMC using 30 mmol monomer, 1 g substrate at  $29^\circ\text{C}$  for 1 hr

Table-1: Variation of the DS of sodium carboxymethyl cellulose with NaOH concentration after soaking for 2 hours

Sodium monochloroacetic acid z (mmol)	Sodium hydroxide x% (w/v)	Reaction time y (hrs)	DS
8.5	60	2	0.215
5.3	45	2	0.120
2.1	30	2	0.057

Table-2: Grafting characteristics of acrylamide on holocellulose with ceric ion concentration, using 30 mmol of monomer

DS of CMC	Amount of Ce <sup>4+</sup> (mmol)	M <sub>v</sub> . (10 <sup>-5</sup> g)	M <sub>v</sub> of homopolymer (10 <sup>-5</sup> g)	N <sup>o</sup> of grafted PAA chains (10 <sup>3</sup> n <sub>g</sub> /100 g substrate)	F <sub>g</sub>	R <sub>g</sub> (10 <sup>7</sup> mol L <sup>-1</sup> min <sup>-1</sup> )
0.215	2	7.01	2.3	0.106	1.65	1.7
	4	5.9	2.8	0.196	3.05	3.25
	6	5.06	3.5	0.292	4.56	4.8
	8	4.1	4.2	0.393	6.13	6.5
	10	3.6	4.9	0.478	7.45	7.9
0.120	2	5.6	2.5	0.122	1.9	2.03
	4	4.1	3.5	0.245	3.82	3.3
	6	3.02	4.2	0.432	6.74	7.2
	8	2.8	4.5	0.507	7.90	8.4
	10	2.1	5.1	0.707	11.03	11.7
0.00	2	4.3	2.9	0.118	1.85	1.9
	4	3.2	3.5	0.206	3.21	3.4
	6	2.6	4.2	0.320	4.98	5.3
	8	2.1	4.9	0.430	6.68	7.1
	10	1.9	5.2	0.500	7.8	8.3

Table-3: Influence of polymerisation time on graft levels on unmodified and partially CMC

DS of CMC	Polymerisation time (mins)	m <sub>g</sub> (g)	m <sub>h</sub> (g)	P <sub>e</sub> (%)	P <sub>g</sub> (g)
0.215	10	1.19	0.033	97.2	119
	30	1.27	0.043	96.3	127
	60	1.36	0.044	96.8	136
	80	1.35	0.052	96.4	135
	100	1.34	0.061	96	134
0.120	10	0.86	0.047	94.7	86
	30	0.90	0.050	94.6	90
	60	1.01	0.059	94.4	100
	80	1.03	0.073	93.3	103
	100	1.05	0.047	95.6	105
0.00	10	0.20	0.01	95.0	20.5
	30	0.30	0.03	90.0	30
	60	0.41	0.09	82.0	41
	80	0.44	0.12	78.0	44
	100	0.45	0.14	76.0	45

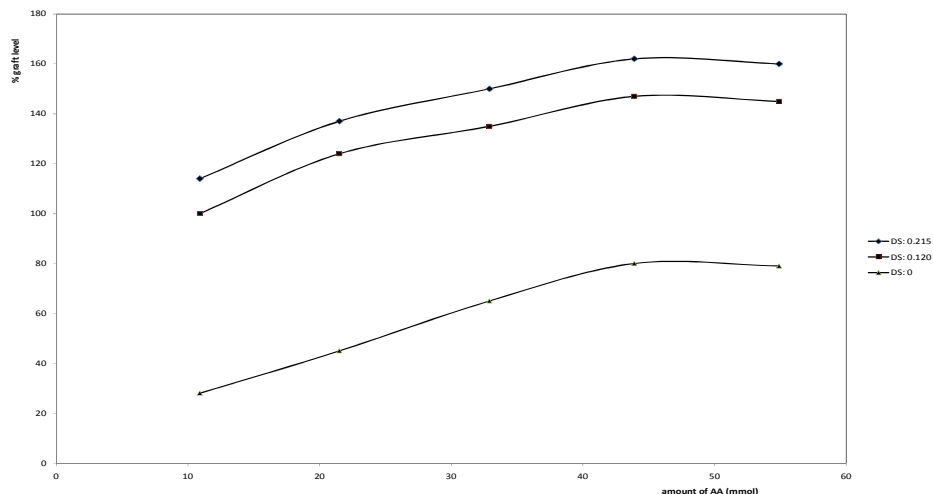


Fig.-2: Effect of monomer concentration on graft level of AA on unmodified and modified holocellulose using 6 mmol of  $Ce^{4+}$  at 29°C for 1 hour

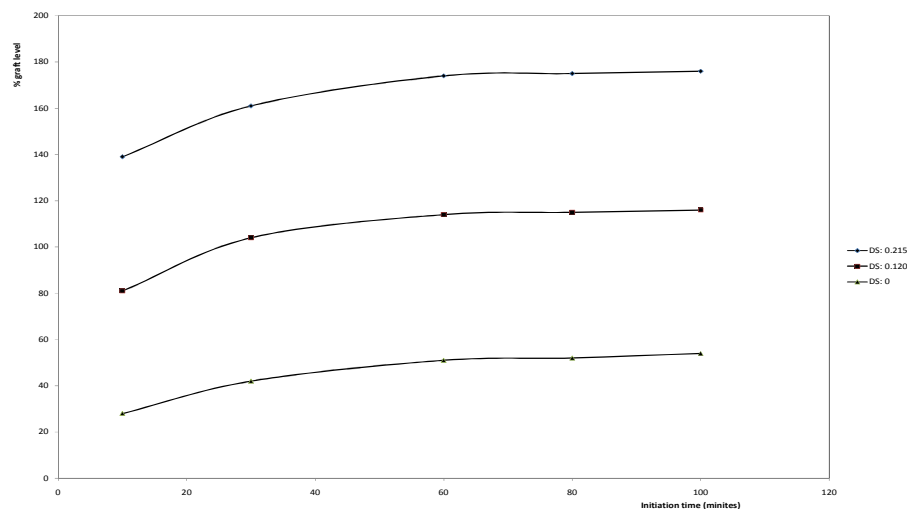


Fig.-3: Effect of initiation time on graft level of AA on unmodified and modified holocellulose using 4.36 mmol of  $Ce^{4+}$ , 30 mmol of monomer at 29°C for 1 hour

### CONCLUSION

The results from this study are consistent with the view that graft copolymerisation onto cellulose is sensitive to the degree of swelling i.e. accessibility of the substrate.

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