

Preparation, Characterization, and Properties of Cellulose–Polyacrylamide Graft Copolymers

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ABSTRACT: Graft copolymers of acrylamide on cellulose materials (α -cellulose 55.8%, DP 287.3) obtained from *Terminalia superba* wood meal and its carboxymethylated derivative (DS 0.438) were prepared using a ceric ion initiator and batch polymerization and modified batch polymerization processes. The extent of graft polymer formation was measured in graft level, grafting efficiency, molecular weight of grafted polymer chains, frequency of grafting as a function of the polymerization medium, and initiator and monomer concentrations. It was found that the modified batch polymerization process yielded greater graft polymer formation and that graft copolymerization in aqueous alcohol medium

resulted in enhanced levels of grafting and formation of many short grafted polymer chains. Viscosity measurements in aqueous solutions of carboxymethyl cellulose-g-polyacrylamide copolymer samples showed that interpositioning of polyacrylamide chains markedly increased the specific viscosity and resistance to biodegradation of the graft copolymers. The flocculation characteristics of the graft copolymers were determined with kaolin suspension. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 913–923, 2003

Key words: graft copolymerization; acrylamide; carboxymethyl cellulose

INTRODUCTION

The use of ceric ions to initiate graft copolymerization of vinyl monomers on synthetic and natural polymers has been reported by many researchers.^{1–10} Graft copolymer formation is often considered to result from propagation by radicals formed on the backbone polymer by interaction with ceric ions. Consequently, the loci of initiation of polymer formation on the cellulosic backbone polymer are radicals formed by the oxidative reactions of ceric ions with cellulosic chain ends containing hemiacetal linkages,¹¹ glycol linkages leading to C–C bond cleavage (between C₂ and C₃),¹² and/or carboxyl groups in the cellulosic backbone polymer.¹³ Graylord and coworkers^{14–16} proposed a mechanism by which it was believed that the formation of graft polymer was a result of a donor–acceptor type of interaction between the cellulose–water–monomer–ceric ion complex and uncomplexed monomer. However, the low efficiency and frequency of grafting associated with ceric-ion-initiated graft copolymerization were inconsistent with the idea of graft polymer formation resulting mainly from propagation of radicals formed on the cellulosic backbone polymer. For instance, enhanced grafting (increased graft level, efficiency of grafting, and frequency of grafting) has been reported for grafting in the presence of alco-

hols^{17,20} and thiols^{19,20} suggesting that propagation by radicals formed on the backbone polymer may not be the only route to graft polymer formation. In addition, it was found^{21,22} that in comparable reaction conditions, the frequency of grafting vinyl monomers was not on the same order of magnitude but depended on monomer type. It is now generally well accepted that graft polymer formation results via the propagation of radicals formed on the backbone polymer and/or by a combination of homopolymer chains with radical sites on the backbone polymer. Despite the gap in detailed knowledge of the mechanism of graft copolymer formation, grafting as a technique for modifying natural and synthetic polymers is preferred to physical blending because the grafted polymer chains are covalently linked and interpositioned on the backbone polymer. Hence, the chemical, physical, and mechanical properties of graft copolymer correlate closely with the size and distribution pattern of the grafts on the backbone polymer. Thus, an important aspect of graft copolymerization studies is achieving optimization of the molecular weight and frequency of interpositioning of the polymer grafts on the backbone polymer. The physical state of the polymerization medium is an important factor affecting the extent of graft polymer formation. Graft polymerization in an aqueous medium is essentially a heterogeneous system in which accessibility of the backbone polymer to the reactants may depend on its physical state. In addition, the reactants will be partitioned between the backbone, or polymer-rich, phase and the continuous, or aqueous, phase, and the transfer of reactants across the phase

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TABLE I
Characteristics of CMC-g-Polyacrylamide Copolymer Samples Used in Flocculation Studies

Sample identity	Graft level (P_g %)	Molecular weight of grafted polyacrylamide ($M_v \times 10^{-5}$)	Frequency of grafting $F_g(N_g/100 \mu\text{g}) \times 10^4$
A	338.22	1.51	24.44
B	370.75	1.46	25.36
C	389.40	1.20	35.45
D	351.05	1.01	41.63
E ^a		Commercial-grade flocculant	

^a Sample was supplied by Petroleum Training Institute, Warri.

boundaries could be diffusion controlled. In this report the influence of process variables on the grafting characteristics of acrylamide on cellulosic materials obtained from *Terminalia superba* (white afara) and some rheological properties and flocculation characteristics of the cellulose-polyacrylamide graft copolymers are examined.

EXPERIMENTAL

Materials

Acrylamide and ceric ammonium nitrate (both from BDH Ltd.) were used with further purification. Holo-cellulosic materials were obtained by the chlorite pulping method,²³ using wood meal from *Terminalia superba* (white afara) with particle size corresponding to the ASTM mesh No. 5. The α -cellulose content and degree of polymerization of the cellulosic material were determined to be 55.8% and 287.3%, respectively. Carboxymethylation of the cellulosic material was carried out by the standard solvent method,²⁴ using monochloroacetic acid-sodium hydroxide in an alcohol mixture. The degree of substitution of the etherified cellulosic material was determined²⁵ to be 0.438.

Grafting procedure

Graft copolymerization of acrylamide on cellulosic materials (unmodified cellulosic material and the carboxymethylated derivative) was carried out at 29°C using a batch process and a modified batch process. The batch polymerization was based on the method described by Lepoutre and Hui.²⁶ A known amount of the cellulosic material (1 g) was dispersed in 200 mL of deionized water containing the ceric ion initiator. The initiator was allowed to interact with the backbone polymer for 30 min, and then the monomer was added to the mixture. Polymerization was allowed to proceed for 120 min, and the reaction was stopped by the addition of 1 mL of 2% quinol solution to the reaction mixture. In the modified batch polymerization process, the same amounts of ceric ion and of the monomer as in the batch process were used, except that one-half of the initiator was initially mixed with 1 g of cellulosic material dispersed in 200 mL of deionized

water. After allowing the initiator to interact with the cellulosic material for 30 min, one-half of the monomer was added to the mixture. The reaction was allowed to proceed for 60 min, and the remaining one-half of both the initiator and the monomer were added to the reaction mixture. The reaction was allowed to proceed for another 60 min and was stopped by the addition of quinol solution to the reaction mixture. The mixture was poured into a large excess of ethanol and filtered, and the residue was air-dried and weighed. Graft copolymerization studies were carried out in aqueous alcohol (methanol, ethanol, and propanol) mixtures using various ceric ion and acrylamide concentrations. The ungrafted polyacrylamide was extracted with morpholine. The cellulose-polyacrylamide graft copolymer was then air-dried and weighed. The percent graft level, P_g , is reported as the weight of the grafted polymer divided by the weight of the cellulosic material used, multiplied by 100. The percent efficiency, P_e , is reported as the weight of the polymer divided by the weight of total polymer formed, divided by 100.

Isolation and molecular-weight determination of grafted polymer chains

The grafted polymer chains were isolated from the backbone polymer by a treatment with a glacial acetic acid/perchloric acid mixture.²⁷ The mixture was filtered, and the resulting filtrate was poured into a large excess of methanol. The polyacrylamide recovered was purified by dissolution in warm water and precipitation in methanol. The molecular weight of the isolated polymer was determined by viscosity measurements in an aqueous 1M NaNO₃ solution using the relationship²⁸

$$[\eta] = 3.73 \times 10^{-4} \bar{M}_v^{0.66} \quad (1)$$

The number of grafted polymer chains, N_g , given as the ratio of the weight of the grafted polymer to the average molecular weight of the grafted polymer chains, is reported as the frequency of grafting, F_g .

TABLE II
Graft Copolymerization of Acrylamide (1.406 mmol L⁻¹) on Cellulosic Materials Using Ceric Ion (7.50 mmol L⁻¹) and Batch Polymerization Process in Aqueous Alcohol Mixtures at 29°C

Polymerization medium (% alcohol)	Graft level P_g (%)			Grafting efficiency P_e (%)		
	MeOH	EtOH	PrOH	MeOH	EtOH	PrOH
0.0		33.35			25.01	
5.0	46.73	63.10	42.95	25.87	32.44	24.72
10.0	48.76	64.85	47.31	28.64	33.15	31.00
20.0	51.92	68.19	46.26	33.42	36.45	29.38
30.0	44.13	62.08	41.78	24.03	24.09	23.60
40.0	42.80	61.60	39.11	24.00	24.14	22.43
50.0	42.04	61.40	38.67	23.25	24.77	21.86
100.0	37.91	47.68	34.67	21.59	16.33	11.68

MeOH = methanol; EtOH = ethanol; PrOH = *n*-propanol.

Viscosity measurements

The viscosity of the aqueous solutions of CMC and CMC-*g*-polyacrylamide copolymer was measured using a Bariod Hank Crank-type rotary viscometer²⁵ at a shear rate of 200 s⁻¹. Viscosity measurements were made on an aqueous solution of CMC and CMC-*g*-polyacrylamide copolymer sample at 25°C and 50°C in the presence of various amounts (0.2M, 0.4M, 0.6M, and 0.8M) of Na⁺ and Al³⁺ ions after various periods of time (up to 35 days).

Flocculation tests

The characteristics of the CMC-*g*-polyacrylamide graft copolymer sample used in this study are given in Table I. Graft copolymer samples A, B, C, and D were prepared by using ceric ion concentrations of 5.0, 7.5, 12.25, and 17.25 mmol, respectively, with a constant acrylamide concentration (40 mmol) and modified batch polymerization done at 29°C. Flocculation tests were carried out on kaolin suspension (0.15% w/v) using the standard jar-test procedure.²⁹ The flocculants were dispersed in water by adding 0.2 g to 150 mL of distilled water. The mixture was heated in

boiling water for 30 min, cooled to room temperature, and diluted to 1 L with distilled water. Portions of the kaolin suspension of about 400 mL were placed in 1-L beakers and dosed with various amounts of the flocculant; the suspensions were stirred at 75 rpm for 2 min and then at 20–25 rpm for 5 min. The suspensions were allowed to settle for 10 min, and the turbidity of the aliquots of the supernatants was measured using a digital nephelo turbidity meter.

RESULTS AND DISCUSSIONS

Grafting on cellulosic materials

Effects of medium of polymerization on grafting characteristics

Graft copolymerization studies were carried out in an aqueous medium in the presence of various amounts of methanol, ethanol, and propanol. The variation in graft levels and the efficiency of grafting with the alcohol content of the polymerization medium are given in Tables II and III for the batch and modified batch polymerization processes, respectively. The results in Table II show that the amount of polyacrylamide added to the

TABLE III
Graft Copolymerization of Acrylamide (1.406 mmol L⁻¹) on Cellulosic Materials Using Ceric Ion (7.50 mmol L⁻¹) and Modified Batch Polymerization Processes in Aqueous Alcohol Mixtures at 29°C

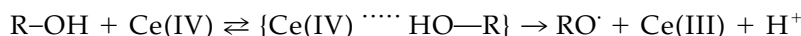
Polymerization medium (% alcohol)	Graft level P_g (%)			Grafting efficiency P_e (%)		
	MeOH	EtOH	PrOH	MeOH	EtOH	PrOH
0.0		51.57			60.08	
5.0	100.60	103.11	98.16	46.60	50.74	41.64
10.0	100.60	113.75	99.84	45.36	53.75	41.77
20.0	73.80	121.85	85.52	37.75	54.79	32.08
30.0	72.12	106.72	78.91	30.56	46.22	26.47
40.0	77.50	100.46	78.89	28.10	36.10	27.13
50.0	70.55	99.39	76.35	26.85	35.15	21.00
100.0	40.60	95.04	50.74	18.21	33.17	13.00

MeOH = methanol; EtOH = ethanol; PrOH = *n*-propanol.

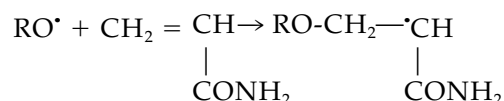
backbone polymer was higher in the aqueous alcohol mixtures than in the single solvents. Enhanced grafting

in aqueous alcohol mixtures has been explained in terms of the following reaction sequence.^{17,18,30,31}

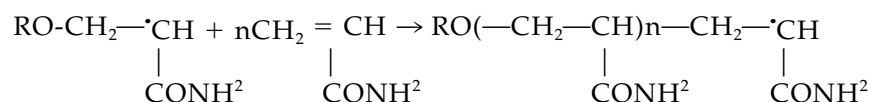
a. Interaction of ceric ion with alcohol



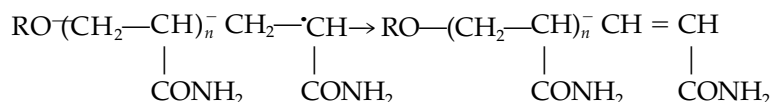
b. Initiation by alcohol radical



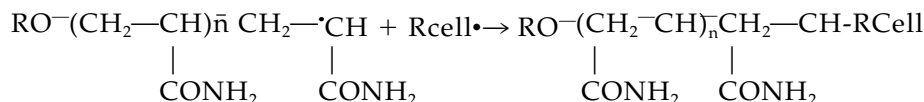
c. Propagation (homopolymer formation)



d. Disproportionation of homopolymer



e. Formation of graft polymer chain



ROH = alcohol, Rcell = backbone polymer

The observed enhanced grafting in the presence of reductant alcohol molecules is indicative of the involvement of homopolymer chains in graft polymer formation.^{17,30} Graft polymerization of acrylamide onto cellulosic materials in an aqueous medium is inherently a heterogeneous process. Phase separation occurs, resulting in the formation of discrete cellulosic-rich and polymer-rich phases and a continuous phase. In pure alcohol (100% alcohol), in which polyacrylamide has a lower solubility than in water, occlusion of the growing polymer radical in the polymer-rich phase leads to reductions in the rate and extent of graft polymer formation. The results in Table II show that the values of the measured grafting parameters were lowest in *n*-propanol and highest in ethanol.

Table III gives the grafting characteristics of acrylamide on cellulosic materials in an aqueous medium and in the presence of various amounts of methanol, ethanol, and *n*-propanol using the modified batch polymerization process. The results shown in Table III indicate that the amount of polyacrylamide added on

to the backbone polymer and the efficiency of the grafting associated with the modified batch polymerization process were higher (by as much as twofold) than with the batch process. A similar trend was observed for the graft copolymerization of methyl acrylate on starch using the batch and modified batch polymerization processes.²⁰ The low efficiency and frequency of grafting associated with ceric ion-initiated graft copolymerization is often considered to result from consumption of ceric ions in reactions other than formation of reactive sites on the backbone polymer.³² The wastage reactions of ceric ions include homopolymer formation. In addition to the difficulties often presented in separation of the homopolymer and the consequent implications on the accurate characterization of the graft copolymer, such reactions reduce the frequency of grafting. In our previous studies we used an initiation method in which unreacted/unadsorbed ceric ions were removed from the polymerization system prior to the addition of monomer in order to study the graft copolymerization of vinyl mono-

TABLE IV
Molecular Weight and Frequency of Grafting of Acrylamide (40 mmol L⁻¹) on Cellulosic Materials Using Ion (7.5 mmol L⁻¹) and Batch and Modified Batch Polymerization Processes at 29°C

Polymerization medium	Average molecular weight $10^{-5} M_v$		Frequency of grafting (Ng/100 g cellulosic) $\times 10^4$	
	Batch	Modified batch	Batch	Modified batch
100% water	1.08	2.86	1.06	2.31
100% methanol*	1.05	1.66	3.61	5.27
100% ethanol*	1.47	2.15	2.36	3.24
100% propanol*	1.40	2.09	1.99	2.52
20% methanol	1.60	3.58	3.31	5.81
10% ethanol	1.87	—	3.42	—
20% ethanol	—	3.85	—	7.21
10% propanol	1.54	3.33	2.51	3.02

* Purity of alcohol not ascertained.

mers onto polysaccharides.³²⁻³⁴ The results from these studies showed a marked increase in the molecular weight of grafted polymer chains, but the frequency of grafting was less markedly enhanced. Removal of unadsorbed/unreacted ceric ions was thought to preclude or reduce the extent of homopolymer formation. Graft copolymerization in aqueous alcohol mixtures was associated with a higher extent of graft copolymer formation than were single solvents. The results from this study indicate that relatively higher values of graft levels are obtained at an alcohol content of about 10%–20% of the medium of polymerization.

Effect of medium of polymerization on molecular weight of grafted polymer chains and frequency of grafting acrylamide on cellulosic materials

Table IV gives the variation in molecular weight of the grafted chains and the frequency of grafting with the amount of alcohol in the medium of polymerization. The results show that the molecular weight of the grafted polymer chains were about the same order of magnitude but somewhat higher in aqueous alcohol mixtures than in the single solvents alone. The values of frequency of grafting showed the same trend for molecular weight in their dependence on the medium of polymerization. It can be seen that the modified batch polymerization process had a higher extent of graft copolymerization than did the batch process. Although the modified batch process led to enhanced frequency of grafting, it should be noted that less than 0.5% of the anhydroglucose units of the backbone polymer were involved in graft polymer formation. The apparent low reactivity of the backbone polymer has been attributed to the two-phase nature of the polymerization system and the state of aggregation of the backbone polymer,^{35,36} considered the determinant of the availability of the anhydroglucose units for grafting. It has been suggested that efforts aimed at improving the frequency of grafting on cellulosic materials and the extent of modification of the backbone

polymer must consider methods of enhancing the accessibility of the backbone polymer to reactant molecules and the number of reaction sites in the polymerization medium and of extending the duration of homogeneity during the reaction process.³⁷

Grafting onto carboxymethyl cellulose

Grafting acrylamide onto carboxymethyl cellulose was carried out using various ceric ion and acrylamide concentrations and the modified batch polymerization process.

Figure 1 shows the variation in graft level and efficiency of grafting with ceric ion concentration using 40 mmol at acrylamide and the modified batch polymerization process at 29°C. The results show an initial increase in graft level with an increase in the initiator concentration. The highest graft level (403.80%) and grafting efficiency (64.88%) were obtained at a ceric ion concentration of 10 mmol⁻¹, and this corresponds with the lowest level of homopolymer formation (35.12%). A decrease in the level of grafting was observed with a further increase in the ceric ion concentration, which is consistent with the results of previous studies, both in our laboratories^{18-22,32,33} and elsewhere.³⁸⁻⁴¹ When it was thought that propagation by radicals formed on the backbone polymer was the main route to graft polymer formation, the ceric ion concentration at which maximum graft levels is attained was considered to correspond to the reductive equivalent of the backbone polymer.²⁰ However, results from this study and from other reports^{39,41} suggest that only a small proportion of ceric ions is consumed in the oxidative interactions with the backbone polymer. Thus, the ceric ion concentration at which maximum graft level is attained overestimates the reductive equivalent of the backbone polymer. The decrease in the graft-level values at relatively high ceric ion concentrations has been explained by the formation of a complex ion with the backbone polymer,^{42,43}

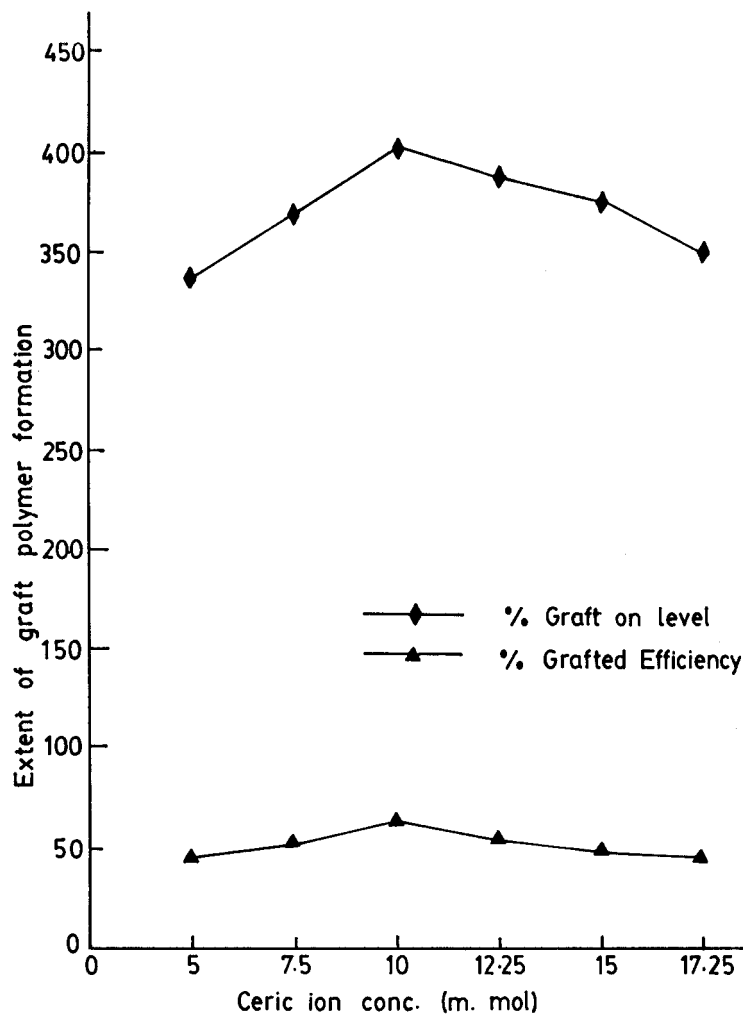


Figure 1 Effect of ceric ion concentration on the % graft level and grafting efficiency of acrylamide on carboxymethyl cellulose.

which reduces both the number of grafting sites on the backbone polymer and the amount of ceric ions available to initiate graft polymer formation.

Figure 2 shows that an increase in monomer concentration using a constant initiator concentration of 10.0 mmol resulted in an initial increase in the graft level, with further increases in monomer concentration leading to reduced levels of grafting. It can be seen that the efficiency of grafting is generally lower than 50%, indicating that less than one-half of the total polymer formed was grafted on the backbone polymer. The monomer concentration at which the maximum graft level was attained was found to be 60 mmol. Thus, it would appear that under the conditions of the present study the optimum grafting of acrylamide onto carboxymethyl cellulose may be obtained using 10.0 mmol⁻¹ of ceric ions, and 60.0 mmol⁻¹ of acrylamide. The decrease in graft-level values at relatively high monomer concentrations can be explained using the mechanism proposed by Gaylord and coworkers,¹⁴⁻¹⁶ which suggests that the extent of

graft copolymer formation depends on the amount of the monomer involved in the polymeric substrate-water-monomer-ceric ion complex. In a polymerization system containing fixed amounts of water, backbone polymer, and ceric ions, the maximum amount of acrylamide monomer that can be complexed will be fixed. An increase in monomer concentration beyond the maximum value would not be expected to lead to an increase in graft level. The factors that affect graftability of monomers include polarity (electronic charge, *e*-value), solubility in the polymerization medium, and monomer size.^{44,45}

The effect of ceric ion concentration on the molecular weight of grafted polyacrylamide chains and the frequency of interpositioning of the polymer grafts on carboxymethyl cellulose is shown in Table V. The results show that the average molecular weight of the grafted polyacrylamide chains decreased with an increase in ceric ion concentration corresponding to reductions of about 26.34% in molecular weight of the grafted chains as ceric ion concentration was increased

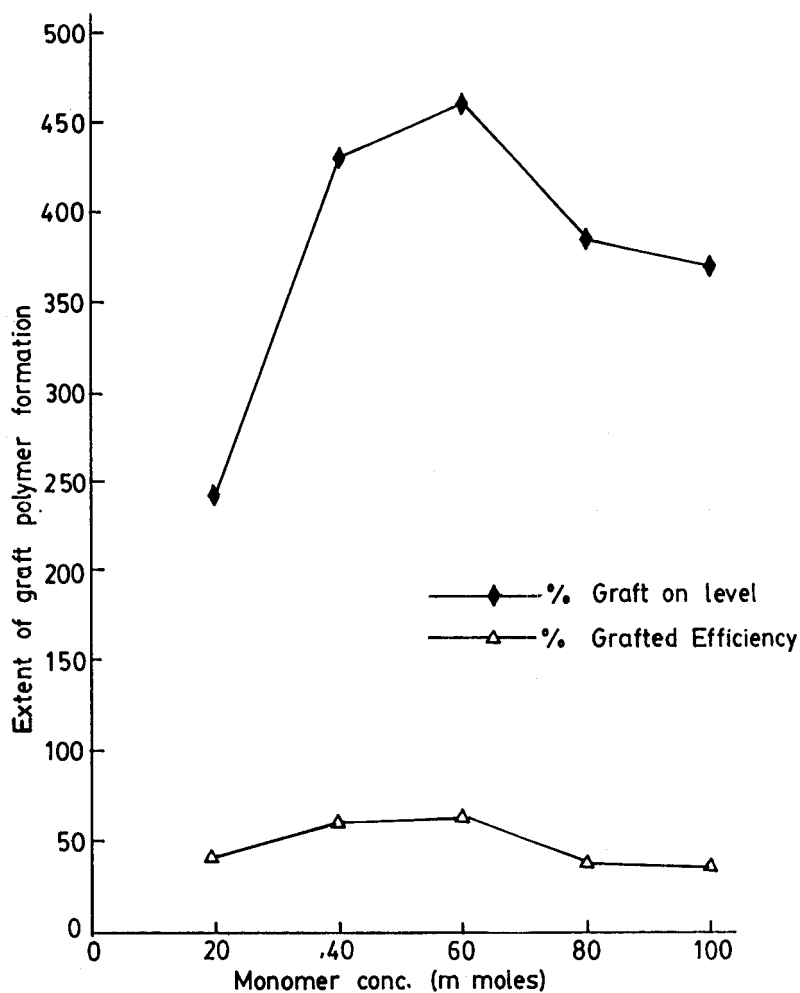


Figure 2 Effect of monomer concentration on the % graft level and grafting efficiency of acrylamide on carboxymethyl cellulose.

from 5.0 to 17.25 mmol^{-1} . The dependence of the molecular weight of grafted polymer chains on ceric ion concentration is thought to indicate that termination of graft copolymerization may be by way of interaction of the growing graft polymer chain with ceric ions. In fact, a similar mechanism of termination was proposed for grafting acrylamide on dextrin butyl

acrylate on gelatin³⁹ and ethyl acrylate on starch.³⁶ However, the amounts of initiator used in this study were small compared with the monomer concentration. It is unlikely that the marked reductions in the molecular weight of the grafted polymer chains would be a result of this type of interaction. At high ceric ion concentrations, a large number of homopolymer

TABLE V
Variation of Molecular Weight of Grafted Chains and Frequency of Grafting Acrylamide on Carboxymethyl Cellulose (Monomer Concentration 40.0 mmol L^{-1} , Temperature 29°C)

Ceric ion concentration (mmol L^{-1})	Molecular weight of grafted chains ($10^{-5} M_w$)	Frequency of grafting (104 Ng/100 g CMC)
5.00	1.51	24.44
7.50	1.46	25.36
10.00	1.22	33.15
12.25	1.20	35.45
15.00	1.12	38.61
17.25	1.11	41.63

TABLE VI
Variation of Molecular Weight of Grafted Chains and Frequency of Grafting Acrylamide on Carboxymethyl Cellulosic (Initiator Concentration 10.0 mmol L^{-1} , Temperature 29°C)

Monomer concentration (mmol L^{-1})	Molecular weight of grafted chains ($10^{-5} M_w$)	Frequency of grafting (104 Ng/100 g CMC)
20.0	1.21	20.00
40.0	1.26	34.35
60.0	1.38	33.35
80.0	1.60	24.16
100.0	1.93	19.26

TABLE VII
Absolute Viscosity at 200 s^{-1} Shear Rate of Aqueous
Solutions of CMC and CMC-g-Polyacrylamide
Copolymer Samples

Polymer sample/concentration	Viscosity of aqueous solution (103 Pas)	
	Temperature of measurement ($^{\circ}\text{C}$)	
	29	50
Ungrafted CMC		
0.25 wt %	36.8	20.5
1.00 wt %	74.6	52.3
CMC-g-polyacrylamide copolymer*		
0.25 wt %	61.5	53.4
1.00 wt %	154.4	125.0

* CMC-g-polyacrylamide copolymer; $P_g = 527.21$; $\bar{M}_v = 1.49 \times 10^5$; $F_g = 35.37 \text{ N}_g/100 \text{ g}$.

chains with small degrees of polymerization would be initiated in the continuous phase. Combination of these polymer chains with radical centers on the backbone polymer would account for the observed dependence on ceric ion initiation of the molecular weight of the grafted polymer chains. The frequency of grafting of acrylamide on carboxymethyl cellulose (Table V) is relatively high, corresponding to at least 250 anhydroglucose units separating two grafted polyacrylamide chains. It has been shown from ^{13}C -NMR studies that the distribution of carboxymethyl moieties on cellulose follows the order $\text{C}_2 > \text{C}_6 > \text{C}_3$.⁴⁶ Therefore, it is thought that carboxymethylation of cellulose might reduce the sites available for interaction with ceric ions and should be accompanied with low values of frequency of grafting. However, the extent of graft copolymer formation on carboxymethyl cellulose is higher than on unmodified cellulose.^{21,22,47,48} It is pertinent to note that graft copolymerization on carboxy-

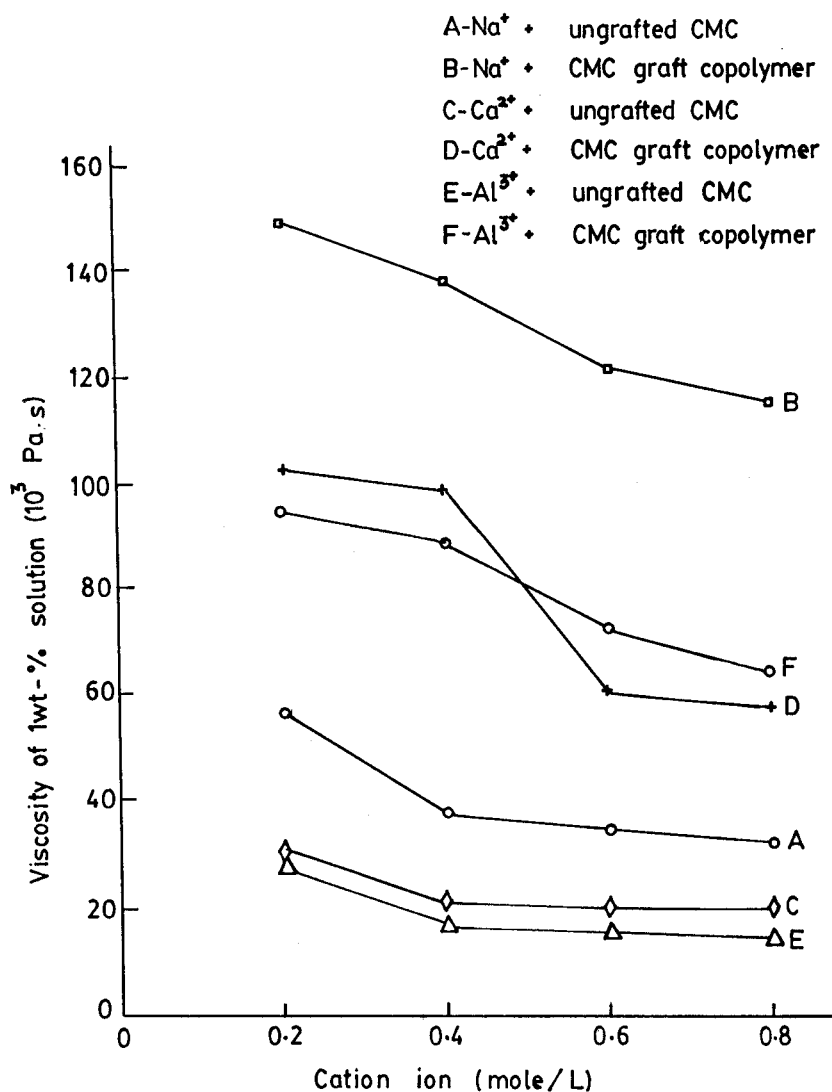


Figure 3 Effect of cations on the specific viscosity of CMC and CMC polyacrylamide graft copolymer samples at 29°C .

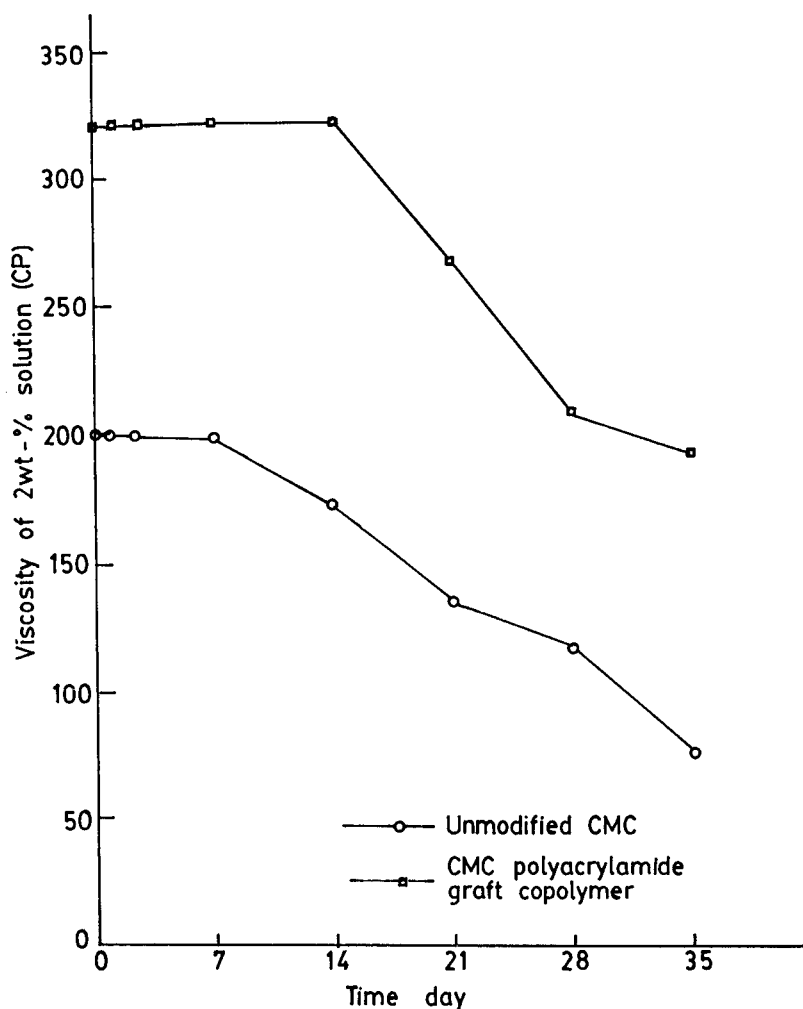


Figure 4 Changes in the viscosity of solutions of ungrafted CMC-polyacrylamide graft copolymer at 50°C as a function of time.

methyl cellulose is initially a homogenous process, whereas grafting onto unmodified cellulose is a heterogeneous process throughout the reaction period. The difference in the physical state of the reaction mixture and the ionization state of the carboxymethyl moieties may be responsible for the observed high frequency of grafting of polyacrylamide onto carboxymethyl cellulose.

Table VI gives the molecular weight of the grafted polymer chains and frequency of grafting of polyacrylamide onto carboxymethyl cellulose as a function of monomer concentration. It can be seen that the molecular weight of the grafted polymer chains increased from 1.21 to 1.93×10^5 as the monomer concentration was increased fivefold from 20.0 to 100.0 mmol^{-1} . The variation in frequency of grafting with monomer concentration is relatively high (a change of about 57%) and is about the same order of magnitude as the variation of molecular weight of grafted polymer with monomer concentration. The variation (dependence) of frequency of grafting is considered in-

dicative of the involvement of homopolymer chains in graft polymer formation.

These results suggest that changes in process variables, namely, the medium of polymerization and polymerization process, led to significant improvements in the extent of graft polymer formation on cellulosic materials. This represents important modifications of existing procedures for the preparation of modified polysaccharides via grafting with vinyl polymers. Graft copolymers of polysaccharides and synthetic polymers are of interest because of their potential as improved viscosifiers in enhanced petroleum oil recovery applications, in the development of biodegradable polymers, and in other areas.

Viscosity measurements

The absolute viscosity of aqueous solutions (0.25 and 1.0 wt %) of ungrafted CMC and CMC-*g*-polyacrylamide copolymer samples (P_g 527.21 \bar{M}_v 1.49×10^5 , F_g 35.37 $N_g/100$ g) measured at 29°C and 50°C with a

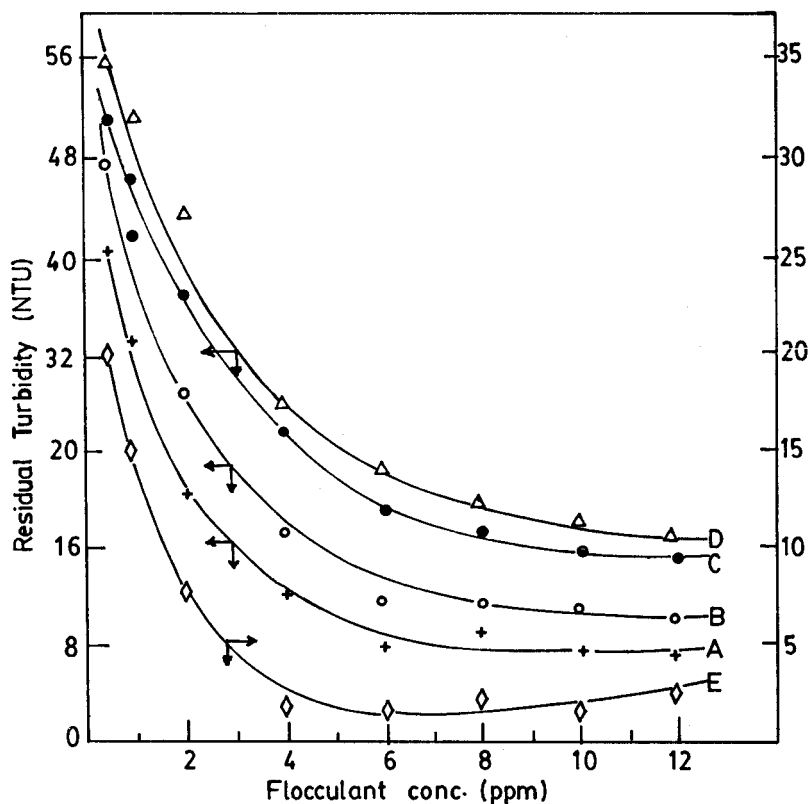


Figure 5 Flocculation of kaolin suspension (0.15% w/v); comparison of carboxymethyl cellulose polyacrylamide graft copolymer samples and commercial polyacrylamide flocculant.

constant shear rate of 200 s^{-1} are given in Table VII. The results show that the absolute viscosity of the graft copolymer samples was about 50% higher than the value for the ungrafted CMC. The reductions in absolute values of the polymer solutions associated with an increase (nearly twofold) in temperature were 30% and 10% for the ungrafted CMC and CMC-g-polyacrylamide copolymer samples, respectively. The relatively small variation in the viscosity of the CMC-g-polyacrylamide copolymer sample with a change in temperature is a desirable property of materials for use in enhanced oil recovery operations. The effect of mono-, di-, and trivalent cations on the absolute viscosity of aqueous solutions of CMC and CMC-g-polyacrylamide copolymer samples are shown in Figure 3. Reductions in viscosity of the polymer solutions in the presence of the cations were generally higher for ungrafted CMC than for the CMC-g-polyacrylamide copolymer sample. Within the range of cation concentrations used in this study, reductions in viscosity were 43.16%, 73.19%, and 81.23% for Na^+ , Ca^{2+} , and Al^{3+} ions, respectively, for solutions of CMC, whereas the corresponding values for the CMC-g-polyacrylamide copolymer sample were 23.10%, 63.66%, and 58.54% in the presence of Na^+ , Ca^{2+} , and Al^{3+} ions, respectively. Changes in the viscosity of the polymer solutions as a function of time are shown in Figure 4. The viscosity of the polymer solutions was measured

frequently over a period of time to monitor biodegradation.⁴⁹ The results (Fig. 4) show that the incorporation of the polyacrylamide graft on the CMC backbone polymer markedly reduced the susceptibility of the material to biodegradation.

Flocculation characteristics

Figure 5 shows the flocculation of the aqueous suspension of kaolin with CMC-g-polyacrylamide copolymer samples and, for comparison, with a commercial flocculant. All four CMC-g-polyacrylamide copolymer samples showed flocculation activity. However, effectiveness as a flocculant depended on the length (molecular weight) rather than on the number (frequency of grafting) of the polyacrylamide chains. The presence of a small number of long chains of polymer grafts was associated with a larger increase in hydrodynamic volume of the graft copolymer than a large number of short polymer chains.^{50,51} Long graft polymer chains are considered to have better approachability to the colloidal particles and thus to be a more effective flocculant.⁵²

CONCLUSION

Graft copolymers of cellulosic materials and polyacrylamide were prepared using ceric ions at 29°C in

aqueous and alcohol media using batch and modified batch polymerization procedures. The results show that manipulation of the process variables can lead to the production of copolymers within a desired range of number and size of polymer grafts. Graft copolymers of CMC and polyacrylamide were shown to have good flocculation properties even at low flocculant dosage, enhanced viscosity stability in the presence of added cations, and reduced susceptibility to biodegradation. A potential application of CMC-g-polyacrylamide copolymer as an alternative flocculant in the treatment of wastewaters and in enhanced oil recovery and oil-well flooding processes is indicated. The large quantities of wood residues that are presently unutilized or underutilized can be used as starting materials for the production of these useful and versatile polymer materials.

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