

# Graft Copolymerization of 2-Acrylamido-2-methyl-1-propanesulfonic acid onto Carboxymethylcellulose (Sodium Salt) by $\text{H}_2\text{O}_2/\text{Fe}^{+2}$ Redox Pair

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**ABSTRACT:** The effect of the reaction conditions on the grafting parameters during grafting of 2-acrylamido-2-methyl-1-propanesulfonic acid onto sodium carboxymethylcellulose using  $\text{H}_2\text{O}_2/\text{Fe}^{+2}$  redox pair are studied at 30°C. The grafting ratio, add on, and conversion initially increase with the  $\text{H}_2\text{O}_2$  concentration in the range of  $(10.0\text{--}15.0) \times 10^{-2} \text{ mol dm}^{-3}$ . Thereafter, these parameters decrease with the  $\text{H}_2\text{O}_2$  concentration. The grafting ratio, add on, and conversion increase when increasing the ferrous ion concentration from  $(0.5 \text{ to } 4.0) \times 10^{-2} \text{ mol dm}^{-3}$  and decrease with a further increase in the concentration. It is observed that the grafting ratio and add on increase with the monomer concentration, whereas the conversion decrease. The hydrogen ions seem to be facilitating the grafting reaction up to a

certain concentration and after this concentration seem to be retarding the process. The grafting ratio, add on, and conversion decrease with the sodium carboxymethylcellulose concentration. When increasing the time period from 60 to 90 min, the grafting parameters increase but decrease thereafter. Similarly, when increasing the temperature from 25 to 30°C, the grafting parameters increase and decrease thereafter. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4819–4825, 2006

**Key words:** graft copolymerization; sodium carboxymethylcellulose; 2-acrylamido-2-methyl-1-propanesulfonic acid;  $\text{H}_2\text{O}_2/\text{Fe}^{+2}$  redox pair

## INTRODUCTION

Sodium carboxymethylcellulose (NaCMC) is water-soluble cellulose ether. It is one of the widely used gums. The basic properties that enhance its commercial value are its ability to thicken water, suspend solids in aqueous media, stabilize emulsions, and absorb moisture from films. These properties have been utilized in its various applications since 1941.<sup>1–4</sup> In recent years it has been used in the pharmaceutical industry for preparation of antiadhesives in surgical lesions.<sup>5</sup> It is also being utilized in producing packing materials with controllable decomposition, ensuring environmental cleanness.<sup>6</sup> Graft copolymer with acrylamide is used as a flooding material in enhanced crude oil recovery in the petroleum industry.<sup>7</sup> Therefore, an attempt has been made to graft poly(2-acrylamido-2-methyl-1-propanesulfonic acid) onto it. 2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS) is characterized by its hydrophilicity and ionic character. It has been used to prepare high swelling capacity polymer hydrogels<sup>8</sup> and its copolymers with some

vinyl monomers such as acrylamide, methyl methacrylate, and dimethylaminoethyl acrylate have been reported.<sup>9,10</sup> The redox initiation technique is applied for grafting, and the Fenton reagent  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  system is chosen for this purpose. Graft copolymerization of methyl methacrylate onto oil palm fiber from empty fruit bunches using this redox system is reported by Ibrahim et al.<sup>11</sup> This article studies the influence of reaction parameters to ascertain optimum conditions. The graft copolymer is characterized by IR spectroscopy and thermal analysis of it is also done.

## EXPERIMENTAL

### Materials

AMPS (Sigma) was used as received. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) was diluted to the desired concentration and its strength was found titrimetrically. CMC (sodium salt, BDH) and ferrous sulfate (E. Merck) were used as received. A desired concentration of sulfuric acid ( $\text{H}_2\text{SO}_4$ , E. Merck) was used for hydrogen ions.

### Graft copolymerization procedure

The NaCMC solution was prepared for each experiment by adding a desired amount to 50 mL of triple distilled water in a reactor. The reaction was carried

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TABLE I  
Effect of Hydrogen Peroxide

Sample no.	[H <sub>2</sub> O <sub>2</sub> ] × 10 <sup>2</sup> mol dm <sup>-3</sup>	G (%)	A (%)	C (%)
1	10.0	79.8	44.3	9.6
2	15.0	108.0	51.1	13.0
3	20.0	52.0	34.2	6.3
4	25.0	50.2	33.4	6.0

[Fe<sup>2+</sup>] = 1.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>; [AMPS] = 4.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>; [H<sup>+</sup>] = 10.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>; [NaCMC] = 1.0 g dm<sup>-3</sup>; time = 120 min; temp. = 30°C.

out under a nitrogen atmosphere at constant temperature. A calculated amount of AMPS, ferrous sulfate, and sulfuric acid solutions were added. The stream of nitrogen gas was allowed to pass through the solution into the reactor and H<sub>2</sub>O<sub>2</sub> solution for 0.5 h. The reaction was initiated by the addition of H<sub>2</sub>O<sub>2</sub>. After a desired interval of time, the reaction was stopped by letting air into the reactor. The grafted sample was precipitated by pouring the reaction mixture into a water-methanol mixture. The precipitate was separated, dried, and weighed. There was no formation of homopolymer under these reaction conditions.

## RESULTS AND DISCUSSION

The graft copolymer was characterized according to Fanta's definitions<sup>12</sup>:

$$\text{grafting ratio (\%)} = \frac{\text{grafted polymer}}{\text{weight of substrate}} \times 100$$

$$\text{add-on (\%)} = \frac{\text{synthetic polymer}}{\text{graft copolymer}} \times 100$$

$$\text{conversion (\%)} = \frac{\text{polymer formed}}{\text{monomer charged}} \times 100$$

TABLE II  
Effect of Ferrous Ion

Sample no.	[Fe <sup>2+</sup> ] × 10 <sup>2</sup> mol dm <sup>-3</sup>	G (%)	A (%)	C (%)
1	0.5	32.0	24.2	3.5
2	1.0	52.0	34.2	6.3
3	2.0	99.3	49.9	12.0
4	4.0	170.0	62.9	20.5
5	6.0	72.5	42.0	8.8

[H<sub>2</sub>O<sub>2</sub>] = 20.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>; [AMPS] = 4.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>; [H<sup>+</sup>] = 10.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>; [NaCMC] = 1.0 g dm<sup>-3</sup>; time = 120 min; temp. = 30°C.

TABLE III  
Effect of AMPS

Sample no.	[AMPS] × 10 <sup>2</sup> mol dm <sup>-3</sup>	G (%)	A (%)	C (%)
1	2.0	32.7	24.7	7.9
2	4.0	52.0	34.2	6.3
3	6.0	55.2	35.6	4.4
4	8.0	60.6	37.8	3.6

[Fe<sup>2+</sup>] = 1.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>; [H<sub>2</sub>O<sub>2</sub>] = 20.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>; [H<sup>+</sup>] = 10.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>; [NaCMC] = 1.0 g dm<sup>-3</sup>; time = 120 min; temp. = 30°C.

### Effect of hydrogen peroxide concentration

The grafting reactions were conducted by varying the concentration of H<sub>2</sub>O<sub>2</sub> from (10.0 to 25.0) × 10<sup>-2</sup> mol dm<sup>-3</sup> (Table I). The grafting ratio, add on, and conversion increased with the H<sub>2</sub>O<sub>2</sub> concentration from (10.0 to 15.0) × 10<sup>-2</sup> mol dm<sup>-3</sup>. A decrease in the values of these parameters was observed with further increases in the H<sub>2</sub>O<sub>2</sub> concentration. The decrease in grafting parameters is due to termination between growing chains and oligomeric vinyl radicals because of excess free radicals.

### Effect of ferrous ion concentration

The effect of the ferrous ion was studied by varying the concentration of ferrous sulfate from (0.5 to 6.0) × 10<sup>-2</sup> mol dm<sup>-3</sup>. The grafting ratio, add on, and conversion increased on increasing the concentration from (0.5 to 4.0) × 10<sup>-2</sup> mol dm<sup>-3</sup> and decreased with further increases in concentration (Table II). The increase in grafting parameters with the increase in the Fe(II) concentration up to the cited range is attributed to the increase in concentration of free radicals produced by the H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> redox pair, resulting in the production of NaCMC radicals at a faster rate. The

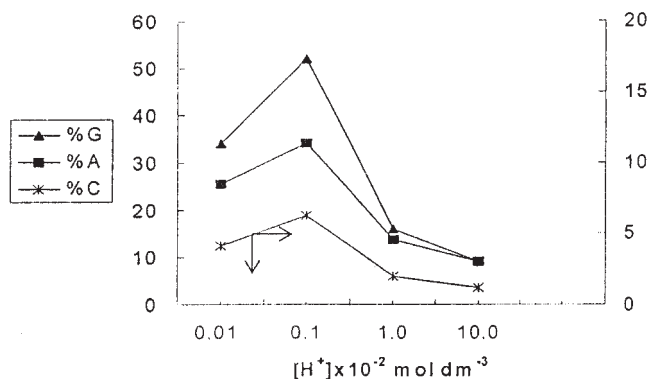
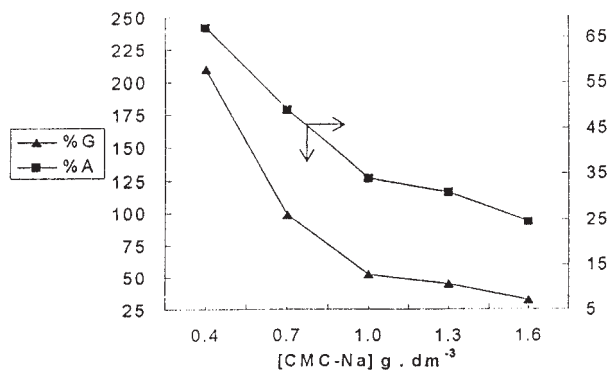
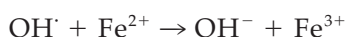


Figure 1 The effects of hydrogen ions: [Fe<sup>2+</sup>] = 10 × 10<sup>-2</sup> mol dm<sup>-3</sup>; [AMPS] = 4.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>; [H<sub>2</sub>O<sub>2</sub>] = 20 × 10<sup>-2</sup> mol dm<sup>-3</sup>; [NaCMC] = 1.0 g dm<sup>-3</sup>; time = 120 min; temperature = 30°C.



**Figure 2** The effects of NaCMC:  $[\text{Fe}^{2+}] = 10 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[\text{AMPS}] = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[\text{H}^+] = 10.0 \times 10^{-4} \text{ mol dm}^{-3}$ ;  $[\text{H}_2\text{O}_2] = 20 \times 10^{-2} \text{ mol dm}^{-3}$ ; time = 120 min; temperature = 30°C.

decrease in grafting parameters beyond  $4.0 \times 10^{-2} \text{ mol dm}^{-3}$  is attributable to a detrimental factor arising from the consumption of OH· free radicals:

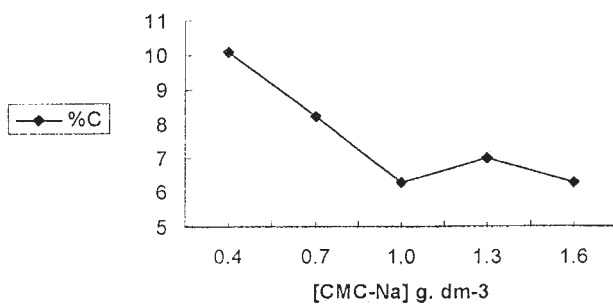


#### Effect of AMPS concentration

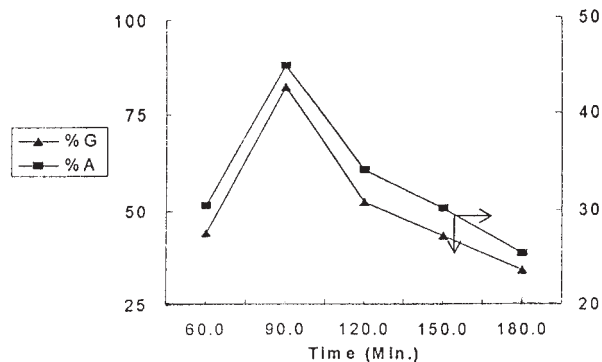
Table III shows that the grafting ratio and add on increased with increases in the AMPS concentration, which decreased the conversion. The increase in the grafting ratio may be attributed to the easy accumulation of monomer in close proximity to the polymer backbone. The monomer molecules that are in the immediate vicinity of the reaction sites become acceptors of NaCMC radicals, resulting in chain initiation. Thereafter, they become free-radical donors to the neighboring molecules, leading to lowering of termination.

#### Effect of hydrogen ion concentration

The effect of the hydrogen ion concentration was studied by varying the concentration of hydrogen ions from  $(0.01 \text{ to } 10.0) \times 10^{-2} \text{ mol dm}^{-3}$ . As their concentration was increased from  $(0.01 \text{ to } 0.1) \times 10^{-2} \text{ mol}$



**Figure 3** IR spectra of NaCMC.



**Figure 4** The effects of the time period:  $[\text{Fe}^{2+}] = 10 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[\text{AMPS}] = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[\text{H}^+] = 10.0 \times 10^{-4} \text{ mol dm}^{-3}$ ;  $[\text{H}_2\text{O}_2] = 20 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[\text{NaCMC}] = 1.0 \text{ g dm}^{-3}$ ; temperature = 30°C.

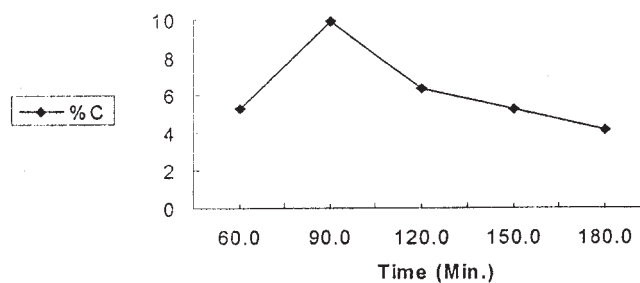
$\text{dm}^{-3}$ , the grafting ratio, add on, and conversion increased but then decreased with further increases in their concentration (Fig. 1). This could be interpreted in terms of an accelerated oxidation/reduction at higher hydrogen ion concentration.

#### Effect of NaCMC concentration

We observed that the grafting ratio, add on, and conversion decreased when increasing the NaCMC concentration (Figs. 2, 3). The decrease in grafting ratio is attributed to the fact that, with the increase in NaCMC concentration, its utilization ratio becomes smaller, because not enough AMPS reacted with NaCMC.<sup>14</sup> In addition, the increased viscosity hinders the movement of free radicals, as is evident from the decrease in total conversion of the monomer.

#### Effect of time period

The grafting ratio, conversion, and add were increased as the time period was increased from 60 to 90 min. However, on further increasing the time period, these parameter showed a decreasing trend (Figs. 4, 5). This could be due to degeneration of growing grafted chains with increases in the time period.



**Figure 5** The effects of time period.

TABLE IV  
Effect of Temperature

Sample no.	Temp. (°C)	G (%)	A (%)	C (%)
1	25	57.6	36.5	6.9
2	30	61.7	38.1	7.4
3	35	52.0	34.2	6.3
4	40	49.0	32.8	5.9
5	6.0	72.5	42.0	8.8

$[\text{Fe}^{2+}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[\text{H}_2\text{O}_2] = 20.0 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[\text{H}^+] = 10.0 \times 10^{-4} \text{ mol dm}^{-3}$ ;  $[\text{NaCMC}] = 1.0 \text{ g dm}^{-3}$ ;  $[\text{AMPS}] = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$ ; time = 120 min.

### Effect of temperature

The increase in grafting ratio, add on, and conversion was observed as the temperature was increased from 25 to 30°C. However, with further increases in temperature, a decrease was observed in these parameters (Table IV). The increase in grafting parameters may be ascribed to the increased rate of diffusion of monomer onto the backbone and the increased rate of production of primary free radicals. The decrease in these parameters may be attributed to the premature termination of growing grafted chains by an excess of free radicals.

### Evidence of grafting

When comparing the IR spectra of NaCMC and NaCMC-g-AMPS, we observed additional peaks in the spectra of NaCMC-g-AMPS (Figs. 6, 7). The bands at 1641 and 1620  $\text{cm}^{-1}$  are due to C=O stretching

vibrations (amide group) and N—H bending vibrations. The C—N stretching band of the amide group appeared at 1451.1  $\text{cm}^{-1}$ . A broad medium band in the 825.1–720.2  $\text{cm}^{-1}$  region is due to out of plane N—H wagging. These bands and peaks confirm the grafting of AMPS onto NaCMC.

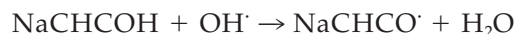
### Mechanism of grafting copolymerization

A hydroxyl radical ( $\text{OH}\cdot$ ) is generated by the reaction of Fe(II) and  $\text{H}_2\text{O}_2$ .<sup>14</sup>

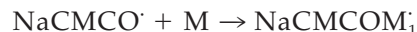


The hydroxyl radical abstracts the hydrogen atom from the NaCMC molecule, producing an NaCMC free radical ( $\text{NaCMCO}\cdot$ ). The monomer molecules, which are in close vicinity to the reaction sites, become acceptors of NaCMC radicals, resulting in chain initiation. Thereafter, they become free radical donors to neighboring molecules. In this way, grafted chains grow. These grafted chains terminate by coupling to yield the graft copolymer.

The reaction mechanism can be represented by the following steps:



Initiation:



Propagation:

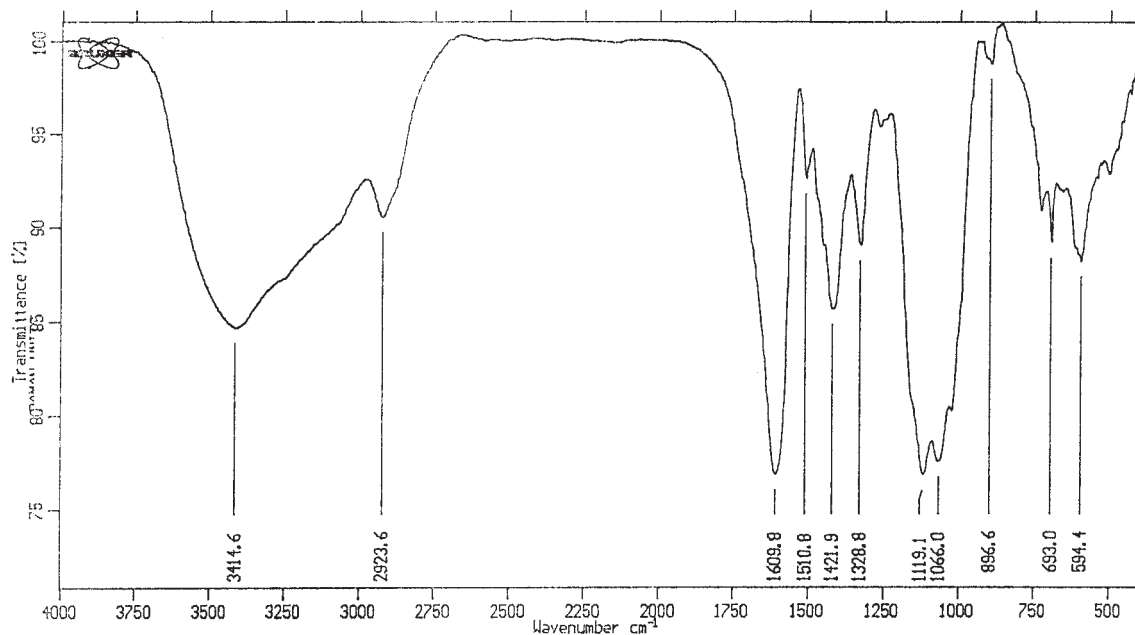


Figure 6 IR spectra of NaCMC.

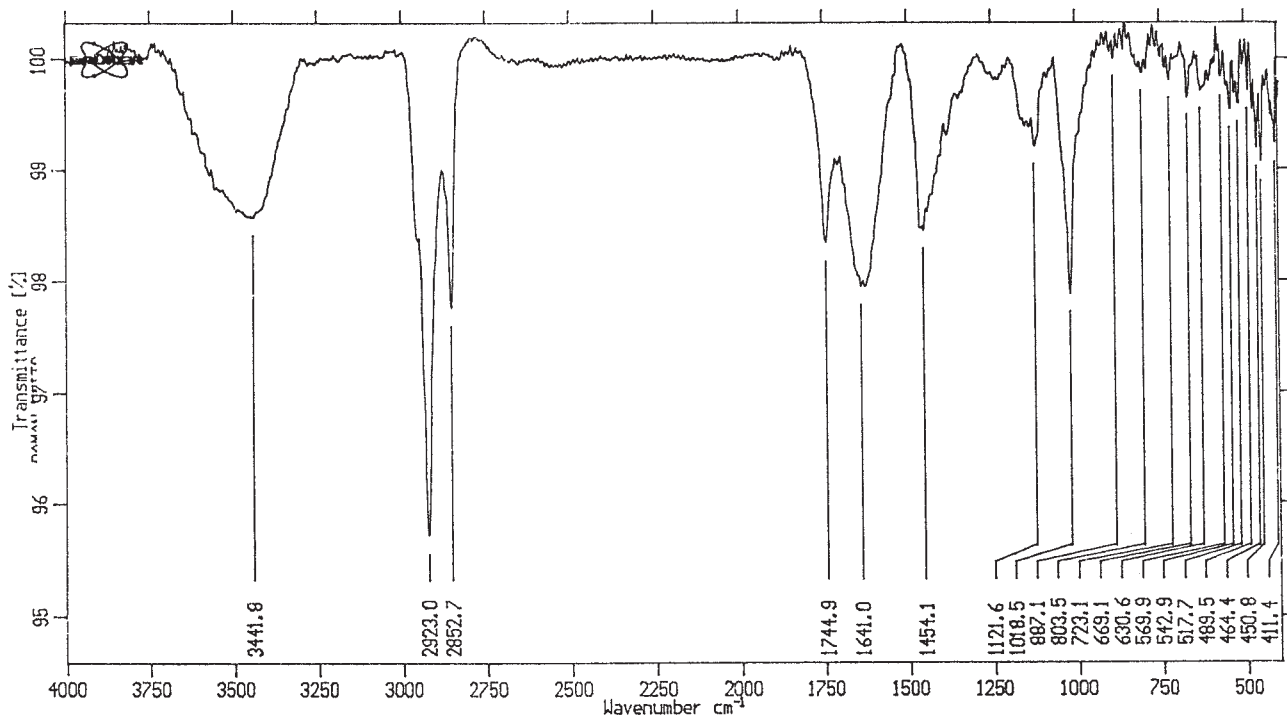
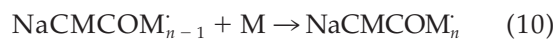


Figure 7 IR spectra of NaCMC-g-AMPS.



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Termination:

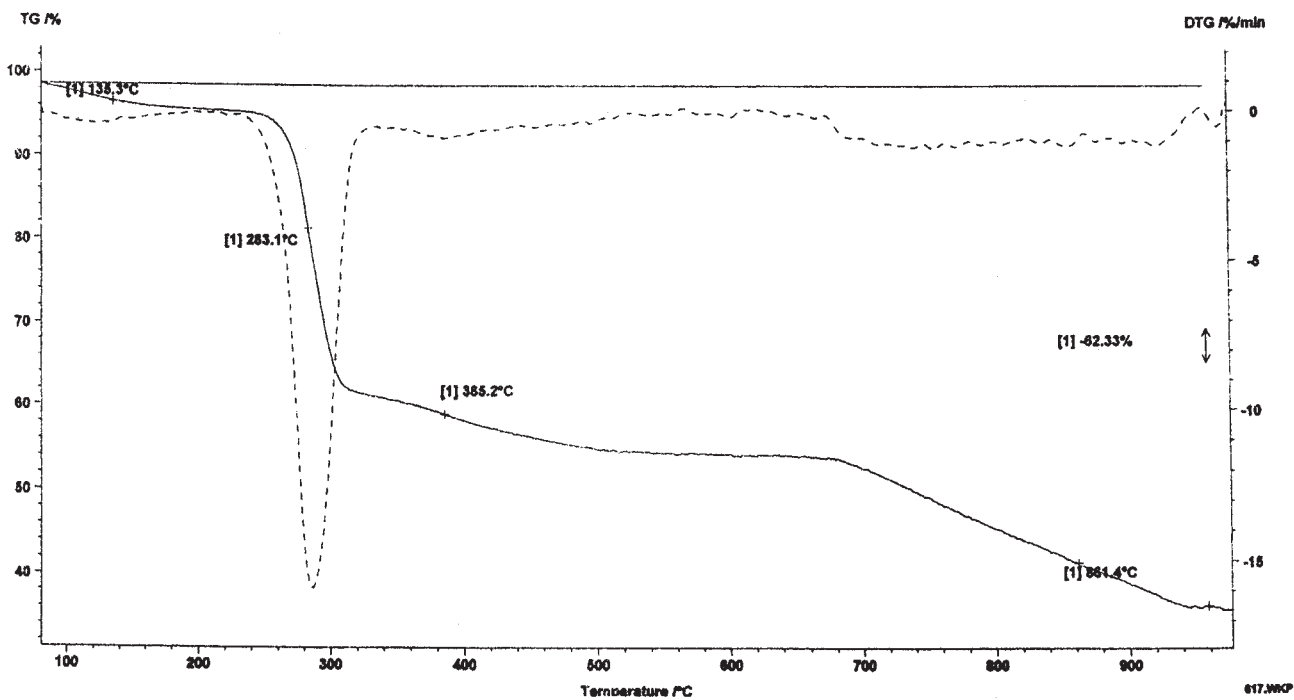


Figure 8 Thermogravimetric trace of NaCMC.

TABLE V  
Weight Loss at Different Temperatures

Temp. (°C)	Weight loss (%)	
	Sodium carboxymethyl cellulose	Sodium carboxymethyl cellulose-g-AMPS
100	1.2	1.5
200	2.9	7.1
300	29.4	25.0
400	38.8	43.5
500	42.9	52.8
600	43.0	60.0
700	44.7	65.0
800	52.3	71.4



### Thermogravimetric analysis of NaCMC and NaCMC-g-AMPS

#### NaCMC

The degradation of NaCMC started at about 135.3°C and occurred in two stages from 135.3 to 283.1°C and from 283.1 to 385.2°C. About 40% weight loss occurred between 200 and 400°C. The rate of weight loss increased on increasing the temperature to 285°C, but then it decreased. The polymer decomposition temperature (PDT), final DT (FDT), maximum temperature ( $T_{\max}$ ), and integral procedural DT (IPDT) were found to be 135.2, 385.2, 283.1, and 294.5°C, respec-

tively. Table V reveals that the weight loss in the temperature range from 400 to 700°C is almost constant. The char yield of 38% was obtained at 924°C (Fig. 8).

#### NaCMC-g-AMPS

The NaCMC-g-AMPS graft copolymer was obtained by grafting AMPS onto NaCMC using the  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  redox pair. The graft copolymer began to degrade at about 180°C. However, the weight loss up to 114.8°C may be attributed to the absorbed water. The degradation appears to be a two-stage process from 254.6 to 328°C and from 328 to 427°C (Fig. 9). The  $T_{\max}$ , PDT, and FDT were found to be 254.6, 208, and 427°C, respectively. About 50% weight loss occurred between 176 and 500°C and 26% char yield was obtained at 860°C. The IPDT was found to be 344.4°C.

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### References

- (a) Toulmin, Jr., H. A. U.S. Pat. 2,731,349 (1956); (b) Toulmin, Jr., H. A. Chem Abstr 1956, 50, 12348.
- (a) Peake, P. Q. U.S. Pat. 2,764,843 (1941); (b) Peake, P. Q. Chem Abstr 1957, 51, 2224.
- (a) Stahly, G. L.; Carlson, W. W. U.S. Pat. 2,229,941 (1941); (b) Stahly, G. L.; Carlson, W. W. Chem Abstr 1941, 35, 3012.
- Zhang, L. M.; Tan, Y. B. J Appl Polym Sci 2000, 77, 195.
- (a) Kim, D. S.; Kim, D. H.; Lee, J. K. (to Amitie Co. Ltd.). Eur. Pat. Appl. EP 1,323,423 (CL A61215128), 2003; (b) Kim, D. S.;

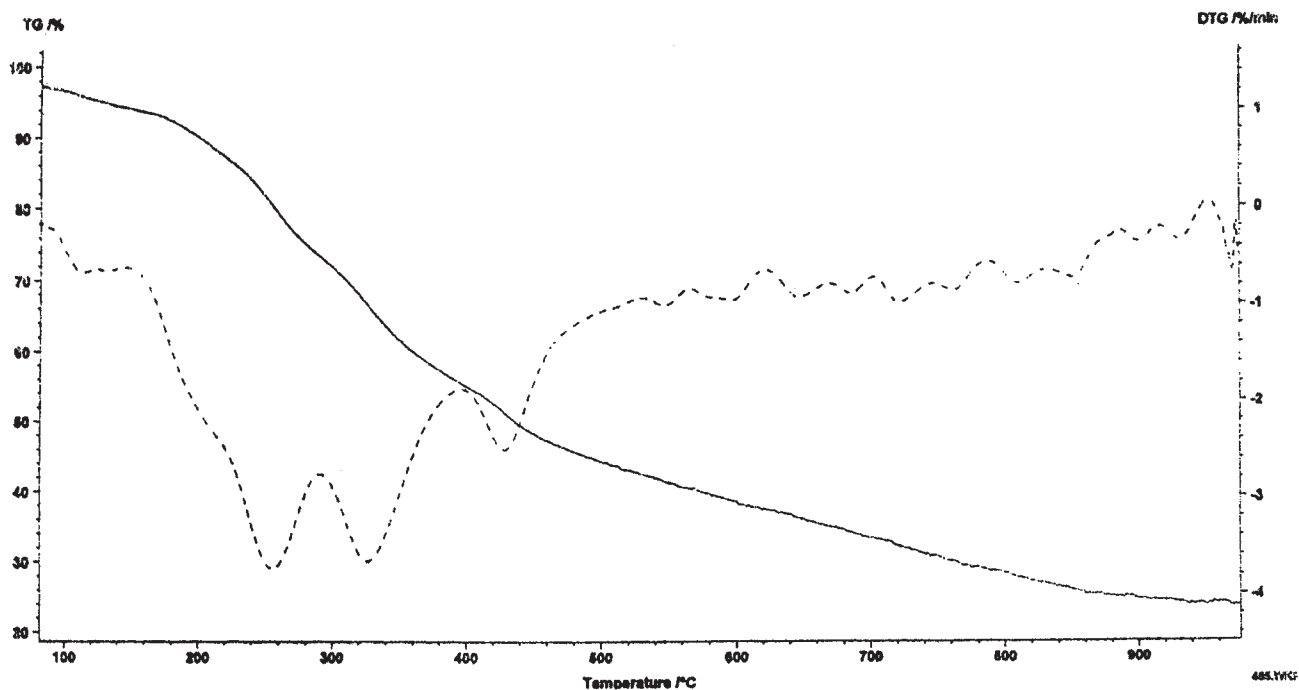


Figure 9 Thermogravimetric trace of NaCMC-g-AMPS.

- Kim, D. H.; Lee, J. K. (to Amite Co. Ltd.). Kor. Pat. Appl. 65,986, 2003.
6. (a) Georgiev, I. V.; Angelov, K. I. Bulg. Pat. PCT Int. Appl. WO 0351,989 (Cl. COSL. 29/04), 2003; (b) Georgiev, I. V.; Angelov, K. I. Bulg. Pat. Appl. 106,225, 2001.
7. Idehen, K. L. Pakistan J Sci Ind Res 2002, 45, 363.
8. Kulicke, W. M.; Nottlemann, H.; Aggour, Y. A.; Elsabee, M. Z. Mater Sci Eng 1989, 61, 393.
9. Aggour, Y. A. Polym Degrad Stabil 1994, 45, 71.
10. Aggour, Y. A. Polym Degrad Stabil 1994, 45, 273.
11. Ibrahim, N. A.; Yunus, W. M. Z. W.; Abu-Ilaiwi, F. A.; Ab Rahman, M. Z.; Bin Ahmad, M.; Dahlan, K. Z. M. J Appl Polym Sci 2003, 89, 2233.
12. Fanta, G. F. In Block and Graft Copolymerization; Ceresa, R. J., Ed.; Wiley-Interscience: New York, 1973; p 1.
13. Tan, Y.; Zhang, L.; Zhuomie, L. J Appl Polym Sci 1998, 69, 879.
14. (a) Jefcoate, C. R. E.; Lindray-Smith, J. R.; Norman, R. O. C. J Chem Soc B Phys Org 1969, 1013; (b) Andrew Brook, M.; Castle, L.; Lindray-Smith, J. R.; Higgins, R.; Morris, K. P.; J Chem Soc Perkin Trans 1982, 2, 687.