

# NOTE

## Cellulosic Absorbents for Water Synthesized by Grafting of Hydrophilic Vinyl Monomers on Carboxymethyl Cellulose

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### INTRODUCTION

In a previous article,<sup>1</sup> photografting was applied to functionalize cellulose and its derivatives; that is, highly water-absorbing cellulosic materials were synthesized by photografting of acrylic acid (AA) on fibrous carboxymethyl cellulose [CMC; degree of substitution (DS) = 0.1–0.4] in the presence of *N,N'*-methylenebisacrylamide (MBAAm) as a crosslinker. This article deals with the effect of grafting initiation system on water-absorbing characteristics of AA- and methacrylic acid (MAA)-grafted CMC samples.

Various grafting techniques can be utilized for synthesizing cellulosic absorbents for water. Williams and Stannett<sup>2</sup> synthesized highly water-absorptive cellulose by postdecrystallization of AA-grafted cellulose, which was prepared by preirradiation method. Vitta et al.<sup>3</sup> studied the water and saline retention values of AA- and MAA-grafted celluloses prepared by ceric salt-initiation method and obtained the water absorbency, up to 40 g/g, after suitable posttreatment. Sakata et al.<sup>4–6</sup> reported that the partially hydrolyzed graft copolymers of crosslinked polyacrylamide on cellulose and its derivatives synthesized by using ceric salt-initiation method can absorb more water than other absorbents from starchy and synthetic polymers do. Lepoutre et al.<sup>7</sup> studied cellulosic absorbent for water prepared by grafting of acrylonitrile on cellulose, followed by posthydrolysis, and reported that water absorbency of the absorbent is independent of the grafting initiation systems, such as ceric salt, cellulose xanthate–hydrogen peroxide, and ferrous ion–hydrogen peroxide.

In this study, ceric salt- and  $\gamma$ -ray-initiated graftings were used in comparison with photografting because both are a typical initiation system for chemically initiated and radiation-initiated graftings on cellulosic materials, respectively. Thus, water-absorbing function of AA- and MAA-grafted CMC samples prepared by photo-, ceric salt-, and radiation-initiated systems was compared to understand the characteristics of photografting for the functionalization of cellulose and its derivatives.

### EXPERIMENTAL

#### Materials

Dissolving pulp from softwoods was used as a cellulose sample. Fibrous CMC (DS = 0.1–0.2) was prepared by reaction of the cellulose sample with chloroacetic acid according to the ordinary method.<sup>8</sup> MBAAm and ceric ammonium nitrate ( $\text{Ce}^{4+}$ ) were all of reagent grade and used without further purification. AA, MAA, and methyl methacrylate (MMA) were purified by distillation under reduced pressure.

#### Grafting

Photografting (photo system) was carried out in a Pyrex<sup>TM</sup> glass tube containing 0.40 g CMC peroxide and 40 mL water, in which 0.015M monomer and a known quantity of MBAAm were dissolved, at 30°C under nitrogen atmosphere. The CMC peroxides with peroxide type<sup>1</sup> was prepared by treating the CMC sample (0.50 g) with 10 mL aqueous hydrogen peroxide (30%) in the presence of 2 mL concentrated sulfuric acid at

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25°C for 3 h. Irradiation with a high-pressure mercury lamp (400 W) was carried out at 30°C using a Riko rotary photochemical reactor (RH400-10W), around which the Pyrex<sup>TM</sup> glass tube were rotated.

With Ce<sup>4+</sup>-initiated grafting (Ce<sup>4+</sup>-system), 0.40 g CMC and 30 mL water, in which 0.015M monomer and a known quantity of MBAAm were dissolved, were placed in a Pyrex<sup>TM</sup> glass tube. A solution containing 10 mM Ce<sup>4+</sup> in 10 mL of 0.1M nitric acid was then injected. The grafting was performed at 50°C in nitrogen atmosphere.

Radiation-initiated grafting (radiation system) was carried out by mutual irradiation method. Pyrex<sup>TM</sup> glass tube containing 0.40 g CMC and 40 mL water, in which 0.015M monomer and a known quantity of MBAAm were dissolved, was irradiated under nitrogen atmosphere with  $\gamma$ -ray from Co 60 at 25°C. Dose rate was 10 kGy/h.

The polymerized samples were extracted for three days with hot water (ratio of liquor to solids was 200 : 1) to remove homopolymers. The water was exchanged four to five times in the first day of the extraction and then twice a day. The MBAAm content was determined by nitrogen analysis and represented as percentage of nitrogen. The percentage of grafting was taken as the percentage of weight increase of the original sample. The grafted CMC samples thus prepared by photo, Ce<sup>4+</sup>, and radiation systems were denoted as photo, Ce<sup>4+</sup>, and radiation samples, respectively.

#### Reaction of CMC with MBAAm

Reaction of CMC with MBAAm was carried out in the same system without monomer as the grafting system described in the above section. The MBAAm content of the treated sample was determined by nitrogen analysis.

#### Measurement of Water Absorbency

AA- and MAA-grafted CMC samples were treated with aqueous solution of 0.5M sodium hydroxide at 25°C for 2 h to yield their sodium salt. The grafted sample ( $W_o$ , g), which was put into a tea bag of nonwoven fabric, was immersed in deionized water at 25°C for 24 h. The treated tea bag was allowed to hang on a holder for 20 min to separate the swollen sample ( $W_s$ , g) from the unabsorbed water. Water absorbency was defined as follows:

$$\text{Water absorbency (g/g)} = \frac{W_s - W_o}{W_o}$$

#### Average Molecular Weight of Grafted Chains

MMA-grafted CMC samples were prepared according to the same methods described in the above section.

The resultant grafted samples were treated with 72% sulfuric acid<sup>9</sup> to isolate poly(MMA) as the grafted chains. The average molecular weight of grafted chains was determined from the viscosity of benzene solution at 25°C using the following equation<sup>10</sup>:

$$[\eta](\text{dL/g}) = 8.69 \times 10^{-5} \cdot \bar{M}n$$

The molar number of grafted chains per 100 g of CMC calculated from the percent grafting and the average molecular weight of grafted chains was indicated as the number of grafted chains.

## RESULTS AND DISCUSSION

### Grafting Behavior

Table I shows the grafting of AA and MAA on CMC in three initiation systems. In the case of photografting on CMC, into which peroxide groups with peracid type are introduced, the percent graftings higher than 100% were recorded for the both monomers at a relatively short irradiation time. On the other hand, the graft efficiencies of MAA, which were taken as the weight percent of grafted polymer relative to total conversion of monomer in a system, were less than 40%. The percent grafting of MAA in Ce<sup>4+</sup> system was higher than that of AA, and the graft efficiencies of MAA were less than 10%. With the radiation system, a maximum percentage of grafting was afforded for MAA at a certain total dose, though the percentage of grafting of MAA was considerably higher than that of AA. It is inferred that radiation energy works to degrade MAA-grafted chains being formed in the grafting system as well as to introduce the grafted chains; as a result, the percentage of grafting decreases beyond a certain total dose. The graft efficiencies of MAA were less than 10%, showing a preferential formation of homopolymers.

Thus, the percentage of grafting higher than 100% was recorded for AA and MAA in the photo system using CMC peroxides among the three initiation systems, though grafting conditions were different from each system. In the Ce<sup>4+</sup> and radiation systems, on the other hand, the percentage of grafting of AA was especially low (~ 20%). It is supposed that radiation energy and Ce<sup>4+</sup> work directly to polymerize AA and MAA monomers to yield the homopolymers preferentially, resulting in a suppressed formation of grafted polymer. It is conceivable accordingly that the photo system using CMC peroxides is useful for preparation of AA- and MAA-grafted CMC samples.

### Water Absorbing Characteristics

Figure 1 shows the water absorbency of AA- and MAA-grafted CMC samples prepared by photo, Ce<sup>4+</sup>, and

**Table I** Grafting of AA and MAA on CMC

Initiation System	Temperature (°C)	Time (min)	Grafting (%)	
			AA	MAA
Photo system <sup>a</sup>	30	2	31.4	46.8 (12.7) <sup>b</sup>
	30	3	70.5	81.6 (18.1)
	30	6	100.3	155.1 (32.9)
	30	10	125.8	180.1 (35.5)
Ce <sup>4+</sup> system <sup>c</sup>	50	30	3.3	34.2 (9.7)
	50	60	7.8	55.7 (7.5)
	50	120	10.0	56.3 (4.9)
	50	240	15.1	55.8 (3.1)
Radiation system <sup>d</sup>	25	30	3.2	68.2 (9.2)
	25	60	5.1	80.7 (8.0)
	25	120	12.0	59.3 (5.3)
	25	180	20.3	55.1 (5.1)

DS of CMC = 0.17; [MBAAm] = 0.1 wt %.

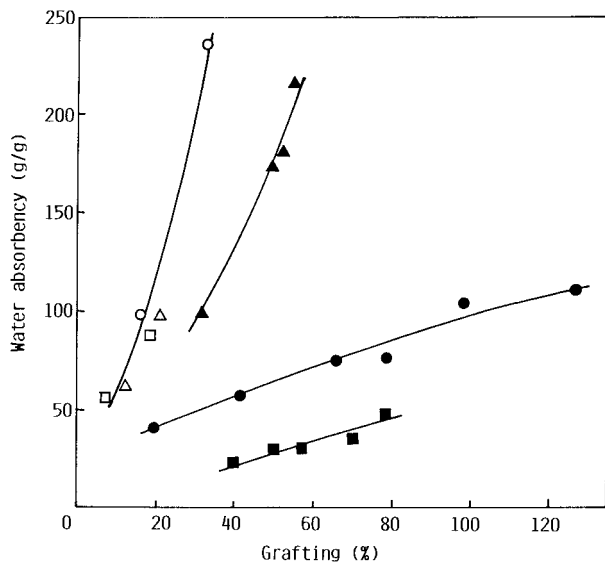
<sup>a</sup> Amount of peroxide = 16.8 mequiv/100 g CMC.

<sup>b</sup> Values in parenthesis are graft efficiencies of MAA, which were taken as the weight percent of the grafted polymer relative to total conversion of monomer in a system.

<sup>c</sup> [Ce<sup>4+</sup>] = 10 mmol/L.

<sup>d</sup> Dose rate = 10 kGy/h.

radiation systems. The AA-grafted sample exhibited a higher ability to absorb water than the MAA-grafted sample in relatively low range of percentage of graftings though there was no large difference in the ability



**Figure 1** Water absorbency of AA- and MAA-grafted CMC samples. AA-grafted sample: (○) photo sample; (△) Ce<sup>4+</sup> sample; (□) radiation sample; N% = 0.8–0.9. MAA-grafted sample: (●) photo sample; (▲) Ce<sup>4+</sup> sample; (■) radiation sample; N% = 0.3–0.4; DS of CMC = 0.17.

among the three samples. On the other hand, the water absorbency of MAA-grafted sample could be examined in the wide range of percentage of graftings compared to the AA-grafted sample, and the results are also included in the figure. The water absorbency increased with an increase in the percentage of grafting, and the extent of the magnitude was largest for the Ce<sup>4+</sup> sample among the three samples. The water absorbency decreased in the order of Ce<sup>4+</sup> > photo > radiation samples when compared at a nearly equal percentage of grafting. It was thus found that the ability of MAA-grafted sample prepared in the photo system to absorb water lies between those prepared in the Ce<sup>4+</sup> and radiation systems.

It seems that the difference in water absorbency among the MAA-grafted samples prepared in the three initiation systems may originate from the structure of the grafted samples. It is not simple to compare the structure of the grafted samples because of different grafting conditions according to each initiation system. However, the average molecular weight of grafted chains and location of crosslink points were studied to obtain the information on the structure of grafted samples.

First, the average molecular weight and number of grafted chains were examined to characterize the grafted samples. Unfortunately, the isolation method of MAA-grafted chains from cellulose substrate was not available in literature; so MMA-grafted CMC samples were prepared in photo, Ce<sup>4+</sup>, and radiation systems because the grafted chains could be isolated easily by

**Table II Average Molecular Weight of MMA-Grafted Chains**

Initiation System	Grafting (%)	$\bar{M}_n \times 10^{-4}$	Number of Grafted Chains (mmol/100 g CMC)
Photo system	33.7	5.71	0.59
	62.1	8.83	0.70
	101.4	11.4	0.89
Ce <sup>4+</sup> system	35.0	10.1	0.35
	50.5	14.0	0.36
	62.2	18.4	0.34
Radiation system	42.4	18.8	0.23
	60.8	27.4	0.22
	75.3	28.0	0.27

Average molecular weight of poly(MMA) was determined from the viscosity of benzene solution at 30°C.

using 72% sulfuric acid.<sup>9</sup> Table II presents the average molecular weight and number of MMA-grafted chains, though these are indirect data on the structure of MAA-grafted samples. The grafted CMC samples prepared in the photo system using CMC peroxides were characterized by a lower average molecular weight and higher number of grafted chains compared to those prepared in the Ce<sup>4+</sup> and radiation systems. Castel et al.<sup>11</sup> studied the relationship between water absorbency and the average molecular weight of grafted chains in acrylonitrile-grafted starch and observed that the absorbency increases by increasing the average molecular weight of grafted chains up to  $5 \times 10^5$ . In this study, the radiation sample exhibited the lowest absorbency among the three samples, though its average molecular weight of grafted chains may be predicted to be higher than those of the Ce<sup>4+</sup> and photo samples. With the radiation system, it is plausible that CMC substrate is also susceptible to radiation-induced degradation, resulting in a decrease in the molecular weight of the substrate. This

may be a negative effect for the water absorbing function of the grafted samples. Yoshinobu et al.<sup>12</sup> synthesized the partially hydrolyzed graft copolymers of cross-linked polyacrylamide on hydroxyethyl cellulose by using ceric salt-initiated grafting and found that their water absorbency decreases with a decrease in the molecular chain length of the trunk polymer. In any case, the difference in water absorbency, which was observed in this study, could not be explained simply by the average molecular weight of grafted chains.

Second, in order to examine the location of crosslink points in grafted samples, reaction of CMC with MBAAm was carried out, and MBAAm content was determined. As seen in Table III, the MBAAm content was in the following order: photo > Ce<sup>4+</sup> > radiation systems. In the present study, MAA-grafted CMC samples were prepared by grafting in the presence of MBAAm crosslinker. It is conceivable accordingly that crosslink points locate at both the CMC substrate and MAA-grafted chains. In a previous article<sup>1</sup> on the water

**Table III Reaction of CMC with MBAAm**

Reaction System	Temperature (°C)	Time (min)	MBAAm Content (mmol/100 g CMC)	MAA-grafted CMC <sup>a</sup>		
				Grafting (%)	MBAAm Content (mmol/100 g copolymer)	Water Absorbency (g/g)
Photo system	30	3	40.4	80.6	10.4	78.3
	30	10	45.9	180.1	11.8	163.1
Ce <sup>4+</sup> system	50	30	28.6	33.1	10.7	82.7
	50	60	27.9	55.7	14.3	215.0
Radiation system	25	30	2.9	68.2	10.7	39.5
	25	60	2.7	80.7	14.3	48.8

<sup>a</sup> MAA-grafted CMC samples were prepared under the same conditions in the presence of monomer as those of the reaction system. Photo system: DS of CMC = 0.17; [MBAAm] = 0.1 wt %. Ce<sup>4+</sup> system: [peroxide] = 17.5 mequiv/100 g CMC. Radiation system: [Ce<sup>4+</sup>] = 10 mM. Dose rate = 10 kGy/h.

absorbency of AA-grafted CMC samples, it was observed that the absorbency reduced greatly when the sample was prepared by photografting on crosslinked CMC in the absence of MBAAm, where crosslink points locate only at the CMC substrate. This suggests that crosslink points are necessary to locate properly at both the CMC substrate and the grafted chains in order to generate a highly water absorbing function. Table III also includes the MBAAm content of MAA-grafted samples, which were prepared by grafting using the same conditions described in the table. Based on the comparison between the two values, it is supposed that crosslink points in the photo sample tend to localize at the CMC substrate, while they are likely to localize at MAA-grafted chains in the radiation sample compared to the  $Ce^{4+}$  sample. The localization of crosslink points at the CMC substrate or the MAA-grafted chains may be one of the reasons why the photo and radiation samples exhibit a lower water absorbency than the  $Ce^{4+}$  sample.

Based on the above investigations, it is concluded that photografting using CMC peroxides is useful for preparation of AA- and MAA-grafted CMC samples compared to  $Ce^{4+}$ - and radiation-initiated graftings, and water absorbency of the resultant MAA-grafted samples depends on the grafting conditions of each initiation system. Further studies on the structure of grafted samples are necessary to prove the absorbency depending on the initiation systems.

## REFERENCES

1. S. Kuwabara and H. Kubota, *J. Appl. Polym. Sci.*, **60**, 1965 (1996).
2. J. L. Williams and V. T. Stannett, *J. Appl. Polym. Sci.*, **23**, 1265 (1979).
3. S. B. Vitta, E. P. Stahel, and V. T. Stannett, *J. Appl. Polym. Sci.*, **32**, 5799 (1986).
4. N. Miyata and I. Sakata, *Sen-i Gakkaishi*, **47**, 95 (1991).
5. M. Yoshinobu, M. Morita, and I. Sakata, *J. Appl. Polym. Sci.*, **45**, 805 (1992).
6. M. Yoshinobu, M. Morita, M. Higuchi, and I. Sakata, *Sen-i Gakkaish*, **49**, 225 (1993).
7. P. Lepoutre, S. H. Hui, and A. A. Robertson, *J. Appl. Polym. Sci.*, **17**, 3143 (1973).
8. R. L. Whistler, *Methods in Carbohydrate Chemistry III, Cellulose*, Academic Press, New York, 1963, p. 322.
9. F. Ide, *Kogyo Kagaku Zasshi*, **64**, 1183 (1961).
10. T. G. Fox, J. B. Kinsinger, H. F. Mason, and E. M. Schuele, *Polymer*, **3**, 71 (1962).
11. D. Castel, A. Ricard, and R. Andebert, *J. Appl. Polym. Sci.*, **39**, 11 (1990).
12. M. Yoshinobu, M. Morita, M. Higuchi, and I. Sakata, *Sen-i Gakkaishi*, **50**, 263 (1994).