

## NOTE

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**Development of high-retention water absorbent from cellulosic materials: water absorbent from bleached kraft pulp**

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**Abstract** This paper describes the synthesis of high-retention water absorbents from kraft pulp and examination of their properties. A bleached kraft pulp from mixed hardwoods (LBKP) was carboxymethylated, then crosslinked with polyethylene glycol diglycidyl ethers (PEGDGE) with different degrees of polymerization under different conditions. A crosslinking agent with longer chain length might be advantageous for preparing a water absorbent with high water retention, and water retention could be improved at lower molar ratio of the crosslinking agent to the glucose unit. Isolation of carboxymethylated LBKP before crosslinking was advantageous for higher water absorbence. A water absorbent with a water retention value of as high as 500 times its weight was obtained.

**Key words** Cellulose · Carboxymethyl cellulose · Super water absorbent · Crosslinking · Water retention value

**Introduction**

Super water-absorbent polymers, which can absorb water several hundred times their own weight in a few minutes, were first developed by a group at the Northern Regional Research Laboratory, US Department of Agriculture during the early 1970s.<sup>1</sup> They have received considerable attention and are now widely used as sanitary materials, agricultural and gardening agents, industrial dehydration agents, sensors, and drying preventives. Nukushina<sup>2</sup> investigated the nature of water absorbents prepared from natural

and synthetic polymers. His results and others' recently reported<sup>3–5</sup> indicate that the water absorbence of cellulosic water absorbents prepared from carboxymethylcellulose (CMC) and other cellulosic materials was much lower than those prepared from starch and synthetic polymers except for some grafted celluloses. Cellulosic water absorbents are widely accepted around the world, probably because of their economical advantages and environmental amiability. A variety of absorbents are currently produced, such as diapers, sanitary napkins, tampons, and nursing pads, in which wood pulp is used as the cellulosic component.

For the methods used to prepare water absorbents from cellulosic materials, the introduction of hydrophilic groups (i.e., carboxymethyl<sup>4,6</sup> and sulfate<sup>7</sup>) and their crosslinking are the main reactions. It is important to note that cellulosic water absorbents are also prepared by grafting acrylonitrile<sup>5,8</sup> and acrylic acid (AA)<sup>9,10</sup> onto cellulosic materials followed by hydrolysis in the former case. Recently, Miyata and Sakata<sup>3</sup> and Yoshinobu et al.<sup>11,12</sup> prepared water absorbents by grafting acrylamide onto hydroxyethyl cellulose and cellulose followed by hydrolysis. Kuwahara and Kubota<sup>13</sup> prepared a cellulosic absorbent for water by photografting AA onto fibrous CMC at 30°C in the presence or absence of *N,N'*-methylenebisacrylamide as a crosslinking agent. They found that the water absorbence increased with the increasing degree of grafting of AA and degree of substitution (DS) of the carboxymethyl group, and that it was considerably lower when the absorbents were prepared in the absence of a crosslinking agent.

There are great demands for water absorbents with improved absorbence (super water absorbents) as sanitary materials and as agricultural and gardening agents. Super water absorbents from biodegradable natural polymers are especially wanted. In this study we tried to develop super water absorbents from a commercial bleached hardwood kraft pulp (LBKP). LBKP was carboxymethylated (CM-LBKP) and then crosslinked with polyethylene glycol diglycidyl ether (PEGDGE) that had different chain lengths under various conditions. The effect of the chain length of the crosslinking agents on the water absorbence of crosslinked CM-LBKP was examined.

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## Experimental

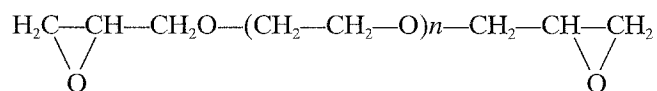
### Materials

The cellulosic raw material used was LBKP. The pulp was washed thoroughly three times with 100 times each of deionized water and then washed two times with acetone and dried in the air. Crosslinking agents used in this study (PEGDGE) were obtained from Nagase Chemicals. They were different in their degree of polymerization ( $n = 2, 4, 9$ ). Ethylene glycol diglycidyl ether denoted "PEGDGE,  $n = 1$ " was purchased from Wako Pure Chemical. Other chemicals used in this study were guaranteed-grade reagents and were purchased from Wako.

### Preparation of water absorbents

#### Method A

The LBKP was carboxymethylated using a standard solvent method.<sup>14,15</sup> Air-dried LBKP (15g oven-dried weight, which corresponds to 92.6mmol anhydroglucose unit) was mixed with 400ml of 2-propanol with vigorous stirring in a cylindrical glass reactor equipped with a rigid stirrer; 40ml of 30% (w/w) aqueous sodium hydroxide was added dropwise for 30min at room temperature. After stirring for another hour, 18g (190mmol) of monochloroacetic acid was added for a period of 30min. The reaction mixture was then stirred for another 3h at 55°C. After carboxymethylation, various amounts of the crosslinking agent – PEGDGE with different chain lengths denoted by  $n$  ( $n = 1, 2, 4, 9$ ) – was added to the reaction mixture



and stirred for different periods at a given temperature. The glucose unit in pulp/PEGDGE molar ratio changed from 1.0:0.5 to 1:1. The treated LBKP was filtered, suspended in 1l of 80% (w/w) aqueous methanol, and the suspension neutralized with acetic acid. After filtration, the product was washed three times with the 80% aqueous methanol, twice with absolute methanol, and once with diethyl ether; it was then dried in air.

#### Method B

The LBKP (15g oven-dried weight) was carboxymethylated as in method A, then filtered and suspended in 1l of 80% (w/w) aqueous methanol; the suspension was then neutralized with acetic acid. After filtration, the product was washed three times with the 80% aqueous methanol, twice with absolute methanol, and once with diethyl ether; it was then dried in air. The CM-LBKP thus prepared was mixed with 400ml of 2-propanol with vigorous stirring in a cylindrical glass reactor equipped with a rigid stirrer while 40ml aqueous sodium hydroxide with different concentrations (NaOH/cellulose weight ratio 0.01–0.27) was added

dropwise for 30min at room temperature. After stirring for another 15min, PEGDGE,  $n = 1$  was added (glucose unit in pulp/crosslinking agent molar ratio 1:1) to the reaction mixture and stirred for various periods at 65°C. Finally, the reaction product was isolated as mentioned for method A.

### Degree of substitution of the carboxymethyl group

The DS of the carboxymethyl group was measured by <sup>1</sup>H-nuclear magnetic resonance (NMR) spectroscopy developed by Floyd and Klosiewicz<sup>16</sup> and Bach Tuyet et al.<sup>17,18</sup> using a Bruker AC300 spectrometer.

### Water retention value

The water retention value (WRV) was measured by a centrifugation technique<sup>10,19</sup> in which a sample of about 0.045g oven-dried weight was equilibrated with 20ml deionized water for at least 24h before being subjected to centrifugation. Each sample was placed in a centrifuge tube and centrifuged at 900g for 30min. The centrifuge tube was equipped with a sintered glass filter (G3) to allow excess water to drain away from the sample. During centrifugation, the tube was sealed with aluminum foil to prevent evaporation of water. The weight of a sample equilibrated with water (WET) was recorded, and the oven-dried weight (DRY) of the sample was then determined after drying in an oven at 105°C. The WRV value was calculated as follows:

$$\text{WRV (g/g)} = (\text{WET} - \text{DRY})/(\text{DRY})$$

which is the amount of absorbed water (g)/oven dry weight of the sample (g).

### Water solubility

A weighed sample of known water content up to 0.1g was placed in a 50-ml beaker, and 30ml deionized water was added. After 24h at room temperature, the water-insoluble fraction was separated by a 1G4 sintered glass filter of known weight. Water solubility was calculated as follows:

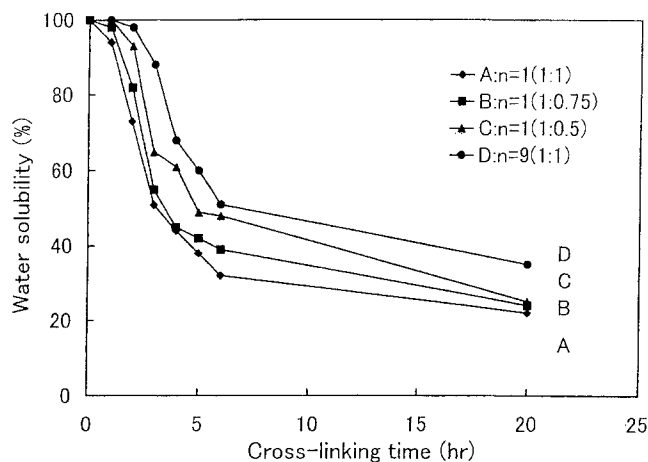
$$\text{Water solubility (\%)} = [A \times (1 - C) - B] \times 100/[A \times (1 - C)]$$

where  $A$  is the initial weight of a sample (g);  $B$  is the oven-dried weight of a sample after immersion in water and filtration (g); and  $C$  is the amount of water (g) in 1g of the sample.

## Results and discussion

### Effect of crosslinking reaction condition on water solubility of CM-LBKP

The DS of the carboxymethyl group in CM-LBKP before crosslinking, determined by <sup>1</sup>H-NMR, was in the range of

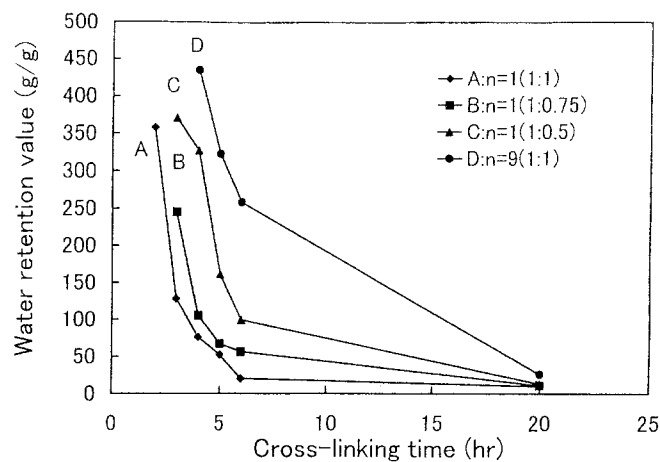


**Fig. 1.** Changes in water solubility with an increase in the crosslinking reaction time. (1:1), (1.00:0.75), (1.0:0.5), glucose unit/polyethylene glycol diglycidyl ether (PEGDGE) molar ratio;  $n$ , degree of polymerization of the ethylene glycol unit in PEGDGE

1.5–1.6. CM-LBKP was then crosslinked under various conditions. Figure 1 shows the effect of the duration of the crosslinking reaction on the water solubility of crosslinked CM-LBKP (method A). Curves A, B, and C indicate the changes in CM-LBKP crosslinked with different amounts of PEGDGE,  $n = 1$  at 55°C. (Molar ratios of the glucose unit to the crosslinking agent were as follows: A 1:1; B 1.00:0.75; C 1.0:0.5.) Curve D shows the case of CM-LBKP crosslinked with PEGDGE ( $n = 9$ ) at 65°C. (Molar ratio of the glucose unit to the crosslinking agent was 1:1.)

As CMC (DS > 0.4) is generally known to be water-soluble,<sup>20</sup> the CM-LBKP prepared in this experiment was water-soluble before crosslinking. Figure 1 indicates that the water solubility decreased rapidly at the beginning and then slowly with the crosslinking reaction time in every case; and more than 65%–75% of CM-LBKP became water-insoluble after 20h of the crosslinking reaction. In other words, it might be difficult to make it fully water-insoluble even after a prolonged period for the crosslinking reaction. This is probably due to the heterogeneous nature of CM-LBKP. It is difficult to discuss the efficiencies of two crosslinking agents ( $n = 1$  and  $n = 9$ ) based only on the behaviors shown in Fig. 1, as the reaction temperatures for the two agents were not the same and the degrees of crosslinking were not determined. It is interesting to note that even at the higher crosslinking reaction temperature, the yield of the water-insoluble fraction in the case of  $n = 9$  was obviously lower (in other words, higher water solubility) for the same crosslinking reaction time. This may be due to the lower reactivity of PEGDGE,  $n = 9$  because of its larger molecular size compared with PEGDGE,  $n = 1$ . This point is discussed in more detail after determining the degree of crosslinking.

The CM-LBKP was crosslinked with PEGDGE,  $n = 1$  (the glucose unit/crosslinking agent molar ratio was 1:1) at various temperatures from 25°C to 75°C for 4h. When CM-LBKP was crosslinked at 25°C or 35°C, the products were still almost completely water-soluble; when the tempera-



**Fig. 2.** Changes in water retention values with an increase in the crosslinking reaction time

ture was raised over 45°C the water solubility decreased gradually with the increasing reaction temperature. About 55% of CM-LBKP became water-insoluble by crosslinking at 55°C under the reaction conditions used here.

#### Effect of crosslinking on water retention value of CM-LBKP

The water-insoluble fraction prepared by crosslinking CM-LBKP was characterized in terms of its water retention value to evaluate its use as a water absorbent. As shown in Fig. 2, with an increase in the crosslinking reaction time the water retention value of the water-insoluble fraction decreased. This reaction is reasonably explained by the decreased space between cellulose chains with the increased density of crosslinkage, which permits permeation of water. Condition A for 2h and condition C for 3h produced almost the same water retention value, 350 (g/g); and the yields of the water-insoluble fraction were not much different (i.e., 27% and 35%, respectively), as simply calculated from Fig. 1. These results may indicate that water solubility (i.e., yield of the water-insoluble fraction) is a direct indication of the water retention value if the same crosslinking agent is used. This point is discussed in more detail and represented in Fig. 3 later. Incidentally, Fig. 2 indicates the possibility of a higher water retention value at even shorter crosslinking reaction times (e.g., 1h for condition A and 2h for conditions B and C). However, it was difficult to obtain reliable water retention values because most of the sample could not be retained on the G3 filter used to determine the water retention value for such a short crosslinking reaction time. Further modification of the method for determining the water retention value may be needed by using a G4 filter and a higher  $g$ -value during centrifugation.

The water retention value decreased with the increase in crosslinking temperature, which indicates that a lower reaction temperature is preferable when preparing a water absorbent, provided the water-insoluble fraction is obtainable at an acceptable yield. From these standpoints, the

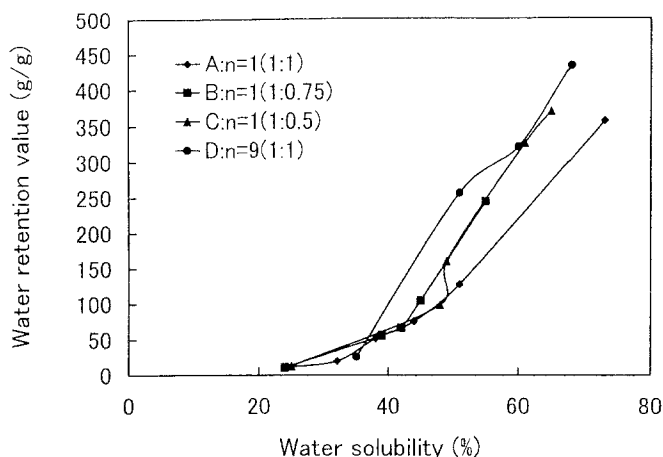


Fig. 3. Relation between water solubility and the water retention value

crosslinking reaction temperature for PEGDGE,  $n = 1$  was determined to be  $55^{\circ}\text{C}$ , as shown in Figs. 1 and 2.

As shown in Fig. 3, the dependence of the water retention value on water solubility increased with an increase in the glucose unit/crosslinking agent molar ratio in the case of  $n = 1$ . A higher water retention value for the water absorbent can be obtained at a lower agent/glucose unit ratio. This may indicate a more homogeneous reaction with a lower amount of crosslinking agent.

In terms of the effect of the chain length of the crosslinking agent on the water retention value, Figs. 2 and 3 show higher values with condition D, in which PEGDGE,  $n = 9$  was used as the crosslinking agent. A water retention value of about  $450\text{ (g/g)}$  was attained only by condition D compared to about  $350\text{ (g/g)}$  by conditions A and C at the similar level of water solubility. The longer chain length of the crosslinking agent may give higher flexibility and a larger space in the crosslinked cellulose in which to keep water.

To discuss the effect of the chain length of the crosslinking agent on the water retention value, the crosslinking agents PEGDGE,  $n = 1, 2, 4, 9$  were tried at  $65^{\circ}\text{C}$  at a molecular ratio of  $1:1$ . The water solubility (i.e., yield of the water-insoluble fraction) changed with the  $n$  value (i.e., from  $n = 1$  to  $n = 9$ ), as shown in Fig. 4. It is striking to see the major increase in water retention value with the increase from  $n = 1$  to  $n = 9$ , as shown in Fig. 5. It is also interesting to compare the water retention value in the case of  $n = 2$  at 2 h and  $n = 4$  at 4 h, where the water solubility was at similar levels (40%–45%) but the water retention values were about 100 and 300 (g/g), respectively. These data strongly indicate the advantage of using a crosslinking agent with a longer chain length for a higher water retention value of the reaction product. This phenomenon may be explained by Fig. 6. Cellulose chains crosslinked with an agent of longer chain length may have higher flexibility and a larger space in which to keep water at the same crosslinking density. Although this mechanism must be confirmed after determining the crosslinking degree, it is informative to note that the water retention value

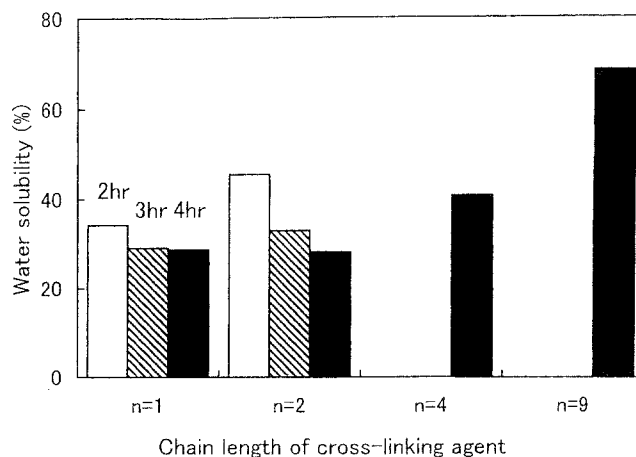


Fig. 4. Effect of the chain length of the crosslinking agent on water solubility at different crosslinking reaction times. Temperature  $65^{\circ}\text{C}$

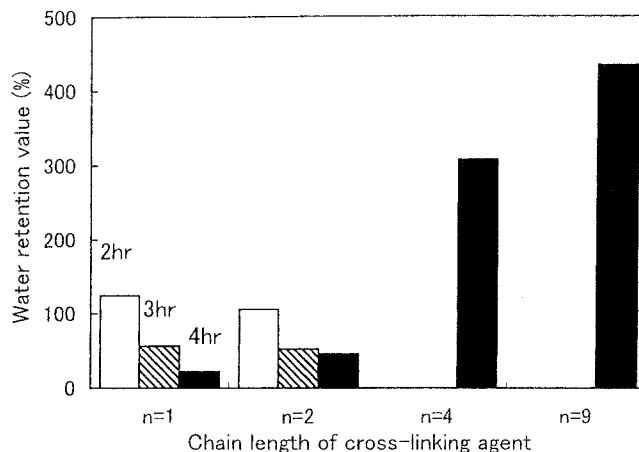


Fig. 5. Effect of the chain length of the crosslinking agent on the water retention value at different crosslinking reaction times. Temperature  $65^{\circ}\text{C}$

in relation to the amount of network space was discussed in detail by Yoshinobu et al.<sup>11</sup> for crosslinked polyacrylamide-grafted cellulose using the solute exclusion technique. Their results indicated that the absorbents were highly porous, and a major part of the absorbed water existed in pores larger than  $560\text{ \AA}$ . These results may be useful for understanding our results.

#### Effect of preparation procedure on nature of crosslinked CM-LBKP

The crosslinking reaction of cellulose with PEGDGE can be catalyzed by both alkali and acid. In the case of the acid-catalyzed reaction, the acid-catalyzed opening of the epoxy ring in PEGDGE to form a crosslinkage between cellulose molecules should be the main reaction, but acid-catalyzed polymerization of the agent itself and hydrolytic cleavage of the cellulose chain may not be avoidable. Therefore, a crosslinking reaction catalyzed by alkali was used in this study. In this case the crosslinking reaction may be sensitive

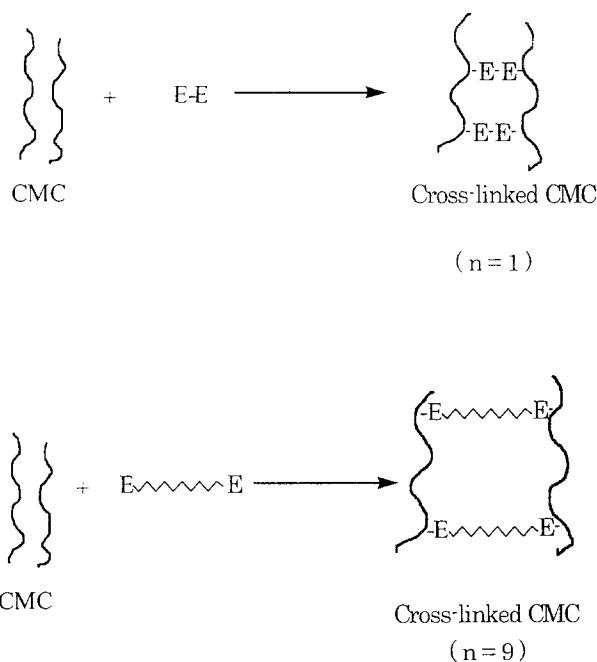


Fig. 6. Model of carboxymethylcellulose (CMC) crosslinked with PEGDGE. E, bonding site of crosslinking agent;  $n$ , see Fig. 1

to the concentration of alkali. To determine the effect of the alkali concentration, crosslinked CM-LBKPs were prepared by method B and were characterized in terms of the water solubility of the products and the water retention value of the water-insoluble fraction. As already mentioned, with method B the CM-LBKP isolated after the carboxymethylation stage was applied to the crosslinking with PEGDGE and various amounts of alkali. That is different from method A, in which the crosslinking agent was added directly to the reaction mixture at the carboxymethylation stage. Therefore, the actual concentration of alkali at the crosslinking stage was known in the case of method B.

Table 1 shows the effect of the amount of alkali added to the crosslinking reaction on the water solubility of crosslinked CM-LBKP. It was found that when the NaOH/cellulose weight ratio was 0.01 the crosslinked sample was still 100% water-soluble even after 6h. It means that the crosslinking reaction may not be enabled at this mild alkali condition. When the weight ratio was in the range of 0.027–0.108, water solubility decreased with the increase in amount of alkali and with the crosslinking time. When the weight ratio increased to 0.189, the water solubility of the crosslinked sample increased again; and when the weight ratio was 0.27, CM-LBKP was completely water-soluble even after a crosslinking reaction time of 6h. Although this phenomenon is not completely understandable, it must indicate consumption of the epoxy group without formation of crosslinkage because of too high alkalinity. From the results obtained here, an NaOH/cellulose ratio of 0.027–0.108 is the range for the purpose of this study.

The water retention value (Table 2) showed a basically similar tendency. Here it is interesting to note that the water

Table 1. Water solubility of crosslinked CM-LBKP

NaOH/cellulose weight ratio	Water solubility (%)				
	2h	3h	4h	5h	6h
0.010	100	100	100	100	100
0.027	64.3	56.3	41.0	35.1	33.8
0.054	61.6	52.9	38.4	31.9	26.9
0.108	60.0	51.6	43.7	38.4	35.7
0.189	67.8	66.3	57.5	–	–
0.270	100	100	100	100	100

CM-LBKP, carboxymethylated bleached kraft pulp from mixed hardwoods; PEGDGE, polyethylene glycol diglycidyl ether  
Crosslinking conditions: cellulose concentration is 3.4%, and temperature is 65°C. The crosslinking agent is PEGDGE,  $n = 1$

Table 2. Water retention values of crosslinked CM-LBKP

NaOH/cellulose weight ratio	Water retention (g/g)				
	2h	3h	4h	5h	6h
0.010	–	–	–	–	–
0.027	500	240	87	61	54
0.054	431	132	62	44	36
0.108	473	138	82	65	43
0.189	345	281	312	–	–
0.270	–	–	–	–	–

Crosslinking conditions: see Table 1. Crosslinking agent is PEGDGE,  $n = 1$

retention value after 2h of the crosslinking reaction at an NaOH/cellulose ratio of 0.027 was as high as 500 (g/g), and the yield of the water-insoluble fraction was not as low, 36%. The water retention value obtained here by method B was high compared with that obtained with method A, shown in Fig. 2. This indicates that some by-products of the carboxymethylation stage had a disturbing effect on the following crosslinking reaction in method A.

Because the reported values of water retention of crosslinked CMC are generally lower than 200 (g/g), the water retention values for crosslinked CM-LBKP with PEGDGE,  $n = 1$  prepared in this study were extraordinary high. Even higher values are expected with a crosslinking agent of higher chain length, which will be reported in a later paper.

To increase the yield of the water-insoluble fraction with high water retention, the water-soluble fraction is treated again with a crosslinking agent. The nature of the newly formed water-insoluble fraction is then evaluated for its water absorbance.

## Conclusions

1. A water-absorbent agent with a high water retention-value can be prepared by crosslinking a carboxymethylated bleached kraft pulp (CM-LBKP) with polyethylene glycol diglycidyl ethers of various chain lengths.

2. A crosslinking agent with long chain length may be advantageous for preparation of a water-absorbent with a high water retention value.
3. The water retention value of a water absorbent can be improved by a lower crosslinking agent/glucose unit molar ratio.
4. The crosslinking reaction of CM-LBKP can be catalyzed by NaOH, and the optimum NaOH/original cellulose weight ratio is be 0.027–0.108.
5. Water absorbency was increased when the CM-LBKP was isolated before the crosslinking reaction, and a water retention value of a crosslinked CM-LBKP can be reached up to 500 (g/g), which is much higher than the values reported for carboxymethylcellulosic water absorbents.

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