低質セルロース資源からの高性能吸水剤の開発(3)

—吸水性の改善—

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Development of Super Water-absorbent from Cellulosic Materials (3)

—Improvement of Water Absorbency—

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Water absorbents were prepared from bleached hardwood kraft pulp by carboxymethylation (CM-LBKP) and cross-linking with polyethylene glycol diglycidyl ether having different chain length by two stages method. Water retention value reached up to as high as 670 g/g for deionized water, and 64 g/g for 0.9% saline solution (physiological saline). Higher D.S. of carboxymethyl group of LBKP was advantageous for a higher water retention value, when $D.S. \leq 1.42$. Water retention value of cross-linked CM-LBKP decreased with the increase of the amount of bound cross-linking agent.

Keywords : cellulose, carboxymethyl cellulose, super water-absorbent, cross-linking, water retention value

分類: Y₄ セルロース化学, W₀ その他

1. Introduction

In our previous papers^{1,2)}, it was described that water absorbents with high water retention value were prepared by cross-linking of carboxymethylated bleached kraft pulp (CM-LBKP) with polyethylene glycol diglycidyl ethers (PEGDGE) of different chain length by one stage method and two stages method. Water retention value of a cross-linked CM-LBKP reached up to 500 (g/g), which was extremely higher than the values reported for cellulosic water absorbents.

In this study, the effects of chain length of cross-linking agents and structure of water absorbent on water absorbency of water absorbents prepared by two stages method were further discussed. Preparation procedures for water absorbents were improved to attain a higher water absorbency and a higher

yield of products. Water absorbency in physiological saline solution was also discussed in comparison with that in deionized water.

2. Experimental

2.1 Materials

A commercial bleached hardwood kraft pulp was used as the cellulosic raw material. Pulp was thoroughly washed three times with 100 times each of deionized water, then washed two times with acetone and dried in the air.

Cross-linking agents, PEGDGE, $n=2, 4, 9$, used in this study were kindly given by Nagase Chemicals Ltd. Ethylene glycol diglycidyl ether denoted as PEGDGE, $n=1$ was purchased from Wako Pure Chemical Industries Ltd. NaCl and HCl for atomic absorption analysis were of grade for the determination of metal element, and other chemicals used in this study were

of guaranteed grade reagents and purchased from Wako Pure Chemical Industries Ltd.

2.2 Instruments

In this research, besides common instruments, following instruments were also used : Bruker AC 300 NMR spectrometer and Shimadzu AA 680 Atomic Absorption/Flame Emission Spectrophotometer.

2.3 Methods

2.3.1 Preparation of cross-linked carboxymethylated LBKP

Water absorbents were prepared by two stages method as described in Scheme 1.

LBKP was carboxymethylated by standard solvent procedure^{3,4)}. After carboxymethylation, the product was washed three times with 80% aqueous methanol, twice with absolute methanol, one time with diethyl ether and then dried in the air. Then CM-LBKP was cross-linked with polyethylene glycol diglycidyl ether having various chain lengths to prepare water insoluble CM-LBKP.

2.3.2 Determination of water solubility

Water solubility was measured by a method described in the previous paper¹⁾. A weighed sample of known water content up to 0.1 g was placed in a 50

ml beaker and 30 ml of deionized water was added. After 24 hr at room temperature, the water insoluble fraction was separated by a 1 G 4 sintered glass filter of known weight. Water solubility was calculated from the weight of water insoluble fraction

2.3.3 Determination of water retention value

Water retention value was measured by a centrifugal technique^{1,5,6)} at 900 G (G is centrifugal force) for 30 min.

2.3.4 Determination of D.S. of carboxymethylated LBKP

D.S. of carboxymethyl group was measured by atomic absorption spectrometry⁷⁾. Accurately weighed CM-LBKP or cross-linked CM-LBKP of less than 1 mg and 20 ml of 1 M HCl were taken in a glass tube with a plastic cap and were shaken vigorously for a few minutes. In this case, Na^+ concentration was adjusted to be lower than 10 ppm. After placing for 24 hours in the static state, Na^+ concentration was determined by atomic absorption spectrophotometer using a calibration curve prepared by NaCl in 1 M HCl solution. D.S. was calculated by formulae (1), (2) and (3).

Determination of the weight fraction of Na^+ (C_{Na}) in a sodium CM-LBKP from the calibration curve is as

Scheme 1. Preparation procedure of cross-linked carboxymethylated kraft pulp (CM-LBKP)

follows :

$$C_{Na} = \frac{\text{Amount of Na + from calibration curve (mg)}}{\text{Weight of Na-CM-LBKP (mg)}} \quad \dots\dots(1)$$

From this value, D.S. of carboxymethyl group can be expressed as the following relation with C_{Na} ,

$$C_{Na} = \frac{23 \text{ D.S.}}{162 - \text{D.S.} + 58 \text{ D.S.} + 23 \text{ D.S.}} \quad \dots\dots(2)$$

where,

23 : atomic weight of Na

162 : molecular weight of anhydroglucopyranosyl unit (AGU)

58 : molecular weight of carboxymethyl group ($-\text{CH}_2\text{COO}^-$)

Therefore,

$$\text{D.S.} = \frac{162 C_{Na}}{23 - 80 C_{Na}} \quad \dots\dots(3)$$

These equations are based on the assumption that all sugar units in LBKP are anhydroglucopyranosyl units. Although a considerable amount of pentosan and other hexose units has been known to be contained in LBKP, the effect of the above assumption to the calculated values were found to be quite small.

2.3.5 Determination of number of bound cross-linking agent per anhydroglucopyranosyl unit

Number of bound cross-linking agent per sugar unit (M.R.) was calculated from the following equations.

$$C'_{Na} = \frac{23 \text{ D.S.}}{162 - \text{D.S.} + 58 \text{ D.S.} + 23 \text{ D.S.} + \text{M.S.} \times M_w} \quad \dots\dots(4)$$

where C'_{Na} is the weight fraction of Na^+ in a cross-linked CM-LBKP.

So,

$$\text{M.R.} = (23 \text{ D.S.} / C_{Na} - 80 \text{ D.S.} - 162) / M_w \quad \dots\dots(5)$$

M_w : Molecular weight of cross-linking agent

3. Results and discussion

3.1 Effect of D.S. of carboxymethyl group on nature of cross-linked CM-LBKP

CM-LBKPs of different D.S. were prepared by changing the amount of monochloroacetic acid at the carboxymethylation step, and the other conditions were the same as mentioned in the previous paper²⁾. D.S. values of CM-LBKP were 0, 0.47, 0.82, 1.06, 1.42, 2.62 respectively which were determined by atomic

absorption spectrometry. CM-LBKPs were cross-linked with PEGDGE of $n=1$, at 65°C for various periods and the weight ratio of NaOH to LBKP in CM-LBKP was kept at 0.108. Relation between water solubility and cross-linking reaction time for different CM-LBKPs with different D.S. is shown in Fig. 1. Water solubility decreased with the increase of reaction time. This should be due to the increased cross-linkage between cellulose chains with the cross-linking time. Water solubility is higher for a sample with higher D.S. of CM-group at any cross-linking time.

Fig. 2 shows the effect of D.S. of carboxymethyl group on water retention values. Water retention value decreased with the extension of cross-linking reaction. It was also found that water retention value increased with the increase of D.S. of CM group when D.S. was less than 1.42, at which, the highest water retention value was obtained. This figure also shows a quite different behavior of the case of D.S. = 2.62. This is probably due to the quite severe chain degradation by the repeated alkalization-etherification at the carboxymethylation step⁸⁾.

According to the above two figures, increase of D.S. of carboxymethyl group would be advantageous for the higher water retention value, if that is in the range of D.S. ≤ 1.42 . Cross-linking reaction time was better to be shorter than 2 hr to obtain a product of higher water absorbency and of not too high water solubility.

3.2 Effect of chain length of cross-linking agent on nature of cross-linked CM-LBKP

Purified CM-LBKP was cross-linked with PEGDGE, $n=1, 2, 3, 4$ separately under 65°C at the molar ratio of 1 : 1 of PEGDGE to sugar unit in CM-LBKP. The effects of chain length of cross-linking agents on the relation between water retention value and water insolubility are shown in Fig. 3. Water retention value increased with the decrease of water insolubility for every cross-linking agent, and water retention value reached as high as 640 g/g and 671 g/g for $n=4$ and $n=9$ respectively at water insolubility of 35%. In the case of $n=1$ and 2, the highest water retention value was about 500 g/g which was obtained at around 40% water insolubility. This value was much lower than those in the case of $n=4$ and $n=9$, strongly indicating an advantage of a cross-linking agent with a longer

Fig. 1. Effect of D.S. of carboxymethyl group on water solubility
 Cross-linking conditions : Weight ratio of NaOH to LBKP : 0.108
 Temperature : 65°C
 Cross-linking agent : PEGDGE, n = 1, (1 : 1)

Fig. 2. Effect of D.S. of carboxymethyl group on water retention value
 Cross-linking conditions : Weight ratio of NaOH to CM-LBKP : 0.108
 Temperature : 65°C
 Cross-linking agent : PEGDGE, n = 1

Fig. 3. Effect of chain length on water retention value and water insolubility
 Cross-linking conditions : Temperature : 65°C
 Molar ratio of AGU to PEGDGE : 1 : 1
 Cross-linking agent : PEGDGE, $n = 1, 2, 4, 9$

chain length for water absorbent with a higher water retention value.

3.3 Effect of amount of bound cross-linking agent on water absorbency

As mentioned before, it is difficult to determine separately the amount of the grafted and the cross-linked polyethylene glycol diglycidyl ether on CM-LBKP²⁾. So the water absorbency of a sample was discussed in relation with M.R. (molar ratio of bound cross-linking agent per sugar unit in original LBKP) in this paper.

The relationships between water retention value and the amount of cross-linking agent bound to CM-LBKP and M.R. are shown in Fig. 4 and 5. The values of bound PEGDGE and M.R. were different for different cross-linking agents. In the case of $n = 1$ and $n = 2$, M.R. was in the range of 0.06 to 0.31, on the other

Fig. 4. Relationship between water retention value and amount of cross-linking agent bound to CM-LBKP
 D.S. of CM-LBKP : 1.42
 % : Weight percent of PEGDGE to CM-LBKP

Fig. 5. Relationship between water retention value and M.R.

D.S. of CM-LBKP : 1.42

% : Weight percent of PEGDGE to CM-LBKP

hand, in the case of $n=4$ and $n=9$, it was in the range of 0.03 to 0.08. Very low M.R. values in the latter cases indicate the lower reactivity of cross-linking agent with longer chain length.

It is known that cross-linked network structure plays an important role for water absorbency, but a too high density of cross-linking restrains water absorbency of polymer. As shown in these Figures, water retention value decreased with the increase of the amount of cross-linking agent bound to CM-LBKP for every cross-linking agent. It is very important to note that water retention values depend significantly on cross-linking reaction conditions even at the same amount of bound agents to CM-LBKP. In the case of $n=2$, two different water retention values, 298 (g/g) and 148 (g/g) were found at M.R. = 0.19. In the case of $n=9$, two different water retention values of 671 and 443 (g/g), were found at M.R.

= 0.04. These are probably due to the different contributions of grafting reaction and cross-linking reaction even at same M.R. level. For these two points, CM-LBKP was cross-linked with PEGDGE of $n=9$ at 65°C at the same molar ratio of 1 : 1 of cross-linking agent to sugar unit in original LBKP, but the amount of isopropanol and cross-linking time were different. For the result of 671 (g/g), the ratio of original pulp to isopropanol (w/v) was 1 : 40, and cross-linking time was 16 hours. Another result was obtained at the ratio of original pulp to isopropanol (w/v) of 1 : 27, and cross-linking time of 3.5 hours. It was suggested that an increased amount of isopropanol suppressed the reaction of cross-linking agent, and resulted in more loose cross-linked network. This should be the reason of a higher water retention value under the former condition.

M.R. values of cross-linked CM-LBKPs of 0.03 to

0.31 shown in Fig.5 means that only 3 to 31% of cross-linking agent added was retained by CM-LBKP. Major part of cross-linking agent (69% to 97%) did not react with CM-LBKP and was wasted. Therefore, to improve the reaction efficiency of cross-linking agent to CM-LBKP should be one of the important research targets in future.

3.4 Water absorbency in saline solution

Since high water absorbents are a kind of polyelectrolytes, salt concentration in solution has an important effect on water absorbency. Water absorbency generally decreases remarkably in salt solution⁹⁾. In fact, high water absorbents are used to absorb solutions containing inorganic salts such as urine, blood and agricultural fertilizer water. Therefore, the development of high water absorbents for electrolyte solution is more important than that for deionized water.

Table 1 shows water absorbency in 0.9% saline solution (physiological saline solution) of water absorbents prepared from CM-LBKP cross-linked with PEGDGE of $n=1, 2, 4, 9$ under different cross-linking conditions. It was found that water retention values were remarkably low in saline solution, and were about 10% of those in deionized water. This may be explained by two mechanisms. One explanation will be electronic double layer mechanism. There are quite a lot of carboxymethyl groups in the products, but are already neutralized. In this case, thickness of

electronic double layer may have already shrunk and may not further shrink even in the presence of saline solution. In other words, effect of the thickness of electronic double layer may not be large on the water retention value. Another explanation will be ion osmotic pressure mechanism¹⁰⁾. Cross-linked CM-LBKP is polyelectrolyte, and when it contacts with water, it dissociates into polymer anion ($-\text{CH}_2\text{COO}^-$) and low molecular cation (Na^+). It gives difference in ion concentration between inside and outside of polymer and produces osmotic pressure to penetrate water into the polymer. If ion concentration of outside of polymer increases, osmotic pressure will decrease and then the amount of water penetrating into polymer will decrease. This may be the reason why water retention value of cross-linked CM-LBKP is smaller in saline solution than that in deionized water.

It is very important to note that water retention value in saline solution of water absorbents prepared from cross-linked LBKP can reach as high as 64 (g/g), which is more than double of the corresponding commercial synthetic products.

4. Conclusion

1) Water absorbency was improved when CM-LBKP was isolated before cross-linking reaction, and water retention value of a cross-linked CM-LBKP was reached up to 671 (g/g) for deionized water, 64

Table 1 Water retention values of various cross-linked CM-LBKPs

Cross-linking agent of PEGDGE		Water retention values (g/g) ^{a)}				
n=1	b	437	138	82	65	43
	c	51	26	19	17	17
n=2	b	460	298	148	102	73
	c	55	46	28	21	18
n=4	b	641	562	342		
	c	55	59	45		
n=9	b	671	443	300	190	
	c	64	55	38	28	

a) : Samples of various cross-linked CM-LBKPs have different water retention values in deionized water as same as in Fig. 3

b) : Water retention value in deionized water

c) : Water retention value in 0.9% saline solution

g/g for 0.9% saline solution, which are extremely higher than the values of commercial products.

2) Increase of D.S. of carboxymethyl group on LBKP is advantageous to get higher water retention value when $D.S. \leq 1.42$.

3) Water retention value of cross-linked CM-LBKP decreased with increase of the number of bound cross-linking agent.

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