

# Preparation of Superabsorbent Polymers from Kenaf

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## INTRODUCTION

Superabsorbent polymers are lightly crosslinked, water-insoluble, hydrophilic polymers capable of absorbing and holding large amounts of water or saline solution, even under pressure. There has been considerable interest in waterswellable polymers since the first superabsorbent polymers were reported by the U.S. Department of Agriculture (USDA). Because of the unique characteristics, these materials have been used in a wide range of applications such as disposal diapers, sanitary napkins, additives for soil in agriculture and horticulture, medicine for drug delivery systems, gel actuators, water-blocking tapes, absorbent pads, etc. Most commercially available superabsorbent polymers are crosslinked sodium polyacrylates with extremely high molecular weights, and they have no biodegradability. Their use may result in environmental pollution because their major applications are in disposable goods. Therefore, biodegradable superabsorbent polymers as a substitute for conventional synthetic polymers have been actively studied. Cellulose is cheap, renewable, biodegradable, and is the most abundant organic raw material in the world. In recent years, the research on cellulose-based superabsorbent polymers, produced by graft copolymerization of various vinyl monomers onto cellulose such as cotton, wheat straw, and jute fiber, has become a very important field.

In this study, the bleached kraft pulp extracted from kenaf core, bast, and whole stalk was used to prepare a series of biodegradable superabsorbent polymers by graft copolymerization with AA, and AM using NMBA as crosslinking agent

and SBS/APS as the redox initiator. The characteristics of the copolymers derived from different kenaf cellulose were examined by means of FTIR, SEM, and TGA, the effects of pH values and salt solutions on the swelling behaviors, and the water retention of swollen gel at high temperatures.

## EXPERIMENTAL

### Materials

Kenaf plant was cultivated with Tainung2 cultivar for 152 days in Korea in 2006. AA(Junsei Co., LTD) was freshly distilled under vacuum before use. AM, SBS, CaCl<sub>2</sub>, and NaOH were from Yakuri Pure Chemicals Co., LTD. NMBA was obtained from Lancaster, and was used directly as received. APS and NaClO<sub>2</sub> were purchased from Kanto Chemical Co., INC. Ethanol and NaOCl (DAEJUNG), NaCl (SHINYO), FeCl<sub>3</sub> (HAYASHI), HCl (ORIENTAL), and Na<sub>2</sub>S (SIGMA) and other chemicals were of analytical grade.

### Pulping

The kenaf core, bast, and whole stalk were cooked by kraft pulping process to prepare pulp in a 3-L-capacity electrically circulation digester, respectively. The pulping conditions were as described under the following: Total chemical and sulfidity as Na<sub>2</sub>O was 18% and 20%, liquor to fiber ratio was 10:1. The cooking cycle employed at time from room temperature to 160°C was 1h, and time for cooking at 160°C was 40min.

### Bleaching

Bleaching of the core, bast, and whole stalk pulp was done by the D1E1D2E2D3 process. The conditions of the five stages were described in Table 1.

Table 1 Bleaching conditions of kraft pulp

Stage	ClO <sub>2</sub> (%)	NaOH(%)	Temperature °C	Time(min.)	Consistency(%)
D <sub>1</sub>	3		60	60	10
E <sub>1</sub>		2	70	30	10
D <sub>2</sub>	2		70	60	10
E <sub>2</sub>		2	70	60	10
D <sub>3</sub>	1		70	60	10

#### Preparation of SAPs

A 500 ml, three-necked flask equipped with a reflux condenser, a thermometer, and a nitrogen line was used as reaction vessel. Partly neutralized AA solution was prepared by gently dropping AA in sodium hydroxide solution under cold water bath in the flask. The molar ratio of sodium hydroxide to AA was 4:5 to approach 80% neutralization degree. A weighed quantity of AM, NMBA, and bleached pulp (core, bast, or whole stalk) were added into the reaction vessel in turn. Then the reaction medium was deoxygenated by nitrogen with magnetic stirring for 30 min. A given quantity of SBS and APS was added and, after 60min at 60°C, the resulting product was cut into small pieces and washed 2-3 times by ethanol (95%). The product was then dried in a vacuum oven at 60°C for 24h. The dried product was milled and sieved through a 40-mesh sieve. A white powdered superabsorbent polymer was obtained. The feed compositions of samples are listed in Table 2.

Table 2 Compositions of SAPs derived from kenaf cellulose, AA, and AM

Sample Codes	Cellulose	AA(g)	AM(g)	H <sub>2</sub> O(g)	Q(g/g)
C1	Kenaf core, 1.58g	18	12	100	440
C2	Kenaf core, 3.34g	18	12	100	351
B1	Kenaf bast, 1.58g	18	12	100	687
B2	Kenaf bast, 3.34g	18	12	100	635
W1	Whole stalk, 1.58g	18	12	100	459
W2	Whole stalk, 3.34g	18	12	100	366

The weight of NMBA is 0.06g, SBS 0.14g, APS 0.31g.

## Characterization

### Infrared Spectra

IR spectra of kenaf cellulose (core and bast) and the superabsorbent samples were recorded on a Bio-Rad Excalibur FT-IR Model FTS 3000 MX.

### Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of the samples was carried out using a thermal analyzer. The samples were heated to temperature of 800°C at a rate of 2 0°C/min starting from 50°C under nitrogen atmosphere.

### Absorbency in Deionized Water

The dried sample (0.1 g) was immersed in the excess of deionized water for at least 10h to reach the swelling equilibrium at room temperature. The swollen gel was filtered on sieve to remove residual water for 5min, then it was weighed and equilibrium absorbency,  $Q_{eq}$ , was calculated by the following equation:

$$Q_{eq} \text{ (g/g)} = \frac{\text{swollen gel (g)} - \text{dried sample (g)}}{\text{dried sample (g)}}$$

### Absorbency in Saline Solutions

The dried sample (0.5 g) was immersed in an excess of saline solutions with different concentrations (NaCl (eq), CaCl<sub>2</sub> (eq), FeCl<sub>3</sub> (eq)), retained there for at least 10h and then filtered and weighed. The water absorbency in the above saline solutions was obtained.

### Absorbency in Solutions of Various pH Values

The method was the same as the water absorbency in saline solutions. The pH values of the external solution were adjusted by adding HCl or NaOH in water.

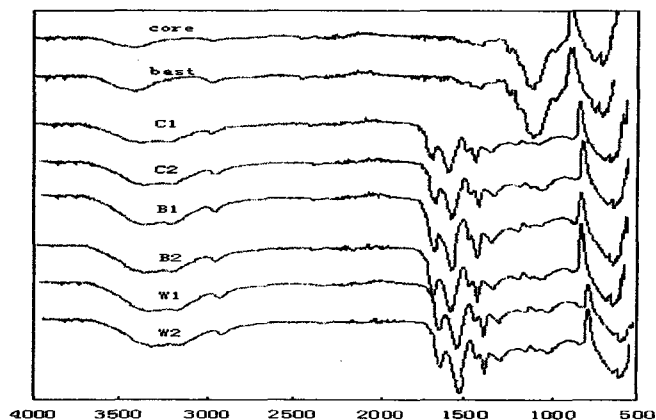
### Water Retention

Saturated swollen gel (18g) was placed in an oven at 100°C under forcing convection. The gel was weighed at each time interval and the weight loss of water was calculated.

## RESULT AND DISCUSSION

Superabsorbent polymers derived from kenaf were characterized by the following methods.

### IR Analysis



Wavenumber ( $\text{cm}^{-1}$ )

Figure 1 IR spectra of bleached pulp of kenaf core, bast, and SAP samples.

IR spectroscopy is a valuable tool of identifying graft copolymerization reaction, which is used to establish the evidence of grafting, and to determine the functional group of the grafted samples.

Grafting acrylic acid and acrylamide onto bleached kenaf pulp was established by IR spectroscopy shown in Figure 1. In the case of bleached kenaf core and bast pulp, there was a broad absorption at  $3300\text{-}3400\text{cm}^{-1}$  due to hydrogen-bonded O - H vibration and  $2933\text{cm}^{-1}$  for C - H stretching vibration. The peak at  $1035\text{cm}^{-1}$  was attributed to the C - O - C stretching vibration of the cellulose macromolecules. As compared to kenaf pulp, in the case of SAP samples (C1, C2, B1, B2, W1, W2), the absorption band at  $3200\text{-}3500\text{ cm}^{-1}$  was attributed to N - H stretching of the AM unit, which overlapped the O - H stretching band of the cellulose portion of the copolymer. The peak at  $1660\text{cm}^{-1}$  was due to  $>\text{C}=\text{O}$  stretching vibration in amide moiety of the AM unit. The peaks at  $1560\text{ cm}^{-1}$  and  $1406\text{ cm}^{-1}$  were attributed to

the carbonyl stretching of the carboxylic acid and acrylate groups, respectively. In addition to the above peaks, weak and broad peaks at  $1070\text{cm}^{-1}$ , corresponding to C - O - C stretching vibration of 5% or 10% cellulose content in SAP samples, were also observed. From the above IR data, it was observed that the monomeric units were incorporated into the copolymer chain.

### Thermal Analysis

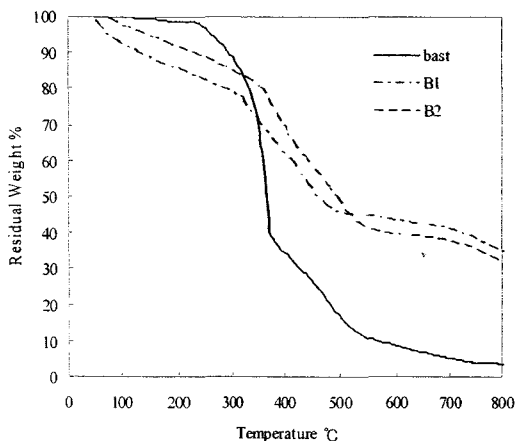


Figure 2 TGA thermograms of bast, B1 and B2.

The thermal behavior of kenaf bast pulp, and SAP samples (B1 and B2) were studied as representative examples by comparing their primary thermograms (TGA curves) as shown in Figure 2. The temperature of decomposition (TD) and residual mass were influenced by composition of the samples. From the curves, the temperature of decomposition (TD) was found to be  $244^{\circ}\text{C}$  for bast pulp,  $324^{\circ}\text{C}$  for B1, and  $355^{\circ}\text{C}$  for B2. Residual mass for bast pulp, B1 and B2 was found to be 3%, 35%, and 32%, respectively. Obviously, the TD values and residual mass increased significantly in the case of SAPs (B1 and B2) derived from bast pulp, indicating higher thermal stability of the graft copolymers over the base fiber. Therefore, the SAPs derived from kenaf cellulose were moderately thermally stable.

Effect of salt solution on water absorbency

Table 3 Effect of concentration of NaCl solution on swelling capacity of the SAPs

SAPs	NaCl, wt %						
	0	0.05	0.1	0.3	0.6	0.9	1.5
C1	440	94	61	48	43	33	27
C2	351	75	45	39	31	31	21
B1	687	127	81	78	56	51	39
B2	635	83	56	53	44	37	29
W1	459	98	71	61	46	41	31
W2	366	72	46	45	31	33	23

Table 4 Effect of concentration of CaCl<sub>2</sub> solution on swelling capacity of the SAPs

SAPs	CaCl <sub>2</sub> , wt %						
	0	0.05	0.1	0.3	0.6	0.9	1.5
C1	440	82	57	17	6	5	4
C2	351	64	42	19	5	5	4
B1	687	102	62	18	5	5	3
B2	635	81	58	20	5	5	6
W1	459	95	63	18	6	5	5
W2	366	70	48	17	5	5	3

The water absorbencies for SAPs derived from kenaf, as a function of different salt concentration for NaCl(aq), CaCl<sub>2</sub>(aq), and FeCl<sub>3</sub>(aq), were shown respectively in Tables 3 - 5. According to swelling capacity of SAPs in deionized water as shown in Table 3, the absorbency sequence of samples was found to be B1>W1>C1 and B2>W2>C2. In other words, on the condition of same cellulose content, the absorbency of SAPs derived from kenaf were in the sequence of bast>whole>core. This result was in agreement with the average length sequence of kenaf cellulose, bast>whole>core. Maybe longer cellulose can form better network for water absorbing. In the case of same cellulose, the absorbency of SAP decreased on

increasing of the cellulose content. This was due to the lower hydrophilic nature of cellulose macromolecule than graft polymer chain.

Table 3 also showed the effect of the various concentrations of NaCl solution on swelling

Table 5 Effect of concentration of FeCl<sub>3</sub> solution on swelling capacity of the SAPs

SAPs	FeCl <sub>3</sub> , wt %						
	0	0.05	0.1	0.3	0.6	0.9	1.5
C1	440	64	34	6	4	3	2
C2	351	51	15	6	6	4	3
B1	687	99	38	9	5	4	3
B2	635	61	11	7	5	4	3
W1	459	82	21	7	5	3	2
W2	366	56	10	12	6	3	3

capacity of the SAPs synthesized in this work. The data indicated that changing the NaCl

concentration higher than 0.3% had no significant influence on absorbency of the hydrogels. The effects of CaCl<sub>2</sub> and FeCl<sub>3</sub> on the absorbency were similar to NaCl, which was shown in Table 4 and 5. This could be attributed to the cations in the salt solution such as Na<sup>+</sup>, Ca<sup>2+</sup>, and Fe<sup>3+</sup>. The cation would neutralize the carboxylate group. The difference in ionic osmotic pressure, between the gel and the external solution, reduced with increasing ionic concentration of the salt solutions. Thus, the water absorbency decreased when the ionic strength in the external solution increased. From data of these three tables, decreased swelling capacity was also observed with an increase in the charge of the cation (Na<sup>+</sup> > Ca<sup>2+</sup> > Fe<sup>3+</sup>). This could be attributed to the higher complexing ability arising from the coordination of the multivalent cations with carboxylate groups of grafted copolymers.

Effect pH on water absorbency

The swelling behavior of SAPs derived from kenaf was investigated in pH values



solutions ranged from 1 to 13 (Fig. 3). The absorbencies decreased in acidic pHs. The remarkable decrease in swelling was due to the interaction of H<sup>+</sup> ions with carboxylate groups. A decreased repulsion of anionic groups lead to a decreased swelling capacity. At higher pHs (5-9), some of carboxylate groups were ionized and the electrostatic repulsion between COO<sup>-</sup> groups caused an enhancement of the swelling capacity. The decreased absorbency at higher basic pHs (pHs > 9) was related to "screening effect" of excess cations in the external solutions.

The water retention properties of saturated swollen hydrogels were determined in an oven at 100°C under forcing convection. The results were given in Figure 4. As shown in Figure 4, the water loss of the samples increased continuously with prolonged heating time, and all the SAPs could retain more than 50% absorbed water after 30min. Then the rate of water losses reduced, which was due to the membrane formed on the surface of the swollen hydrogels as the samples were dried. Additionally, water was bound to copolymer chains via hydrogen bonds formed between SAPs and water molecules, leading to a decrease in the drying rate. This remarkable high water absorption and retention capacity of the grafted copolymers opened the door to their use as commercial superabsorbents in diapers and sanitary napkins.

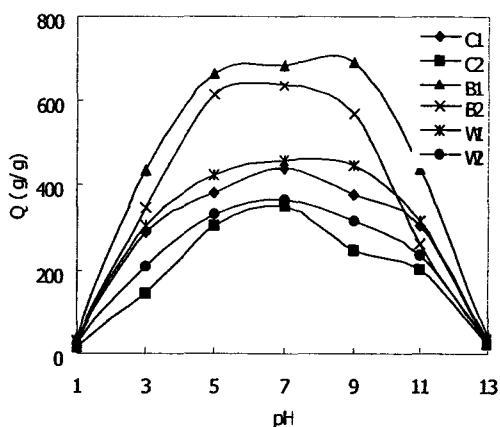


Figure 3 Effect of pH values on swelling capacity of SAPs derived from kenaf

### Water retention at high temperature

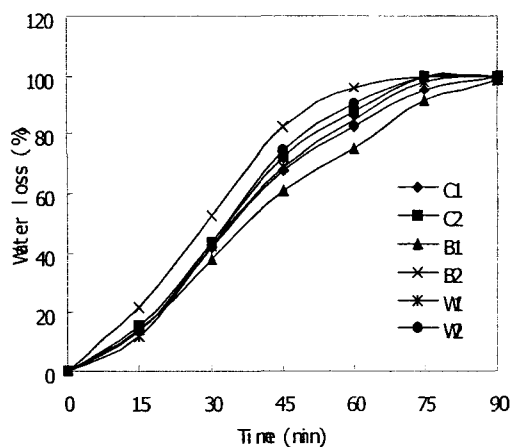


Figure 4 Thermal effects on water retention of SAPs derived from kenaf at 100°C

## CONCLUSION

A series of new cellulose-based superabsorbent polymers were prepared by the grafting polymerization of AA and AM onto bleached kenaf pulp, bast, core, and whole stalk, respectively. The SAPs were characterized by FTIR and TGA. FTIR studies suggested that AA and AM monomers were graft-copolymerized onto macromolecular chains of kenaf cellulose. TGA data revealed that the SAPs derived from kenaf were moderately thermally stable. The swelling behavior of the grafted copolymers is related to the chemical composition and the nature of the external solution. The water absorbency decreased with an increase of the cellulose ratio in the copolymer. Also, the superabsorbent swelling capacity exhibited high sensitivity to the pH and ionic concentration of solutions. In addition, the SAPs derived from kenaf had good water retention at high temperature.

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