

## Superabsorbent Polymer Prepared Using Carboxymethyl Cellulose Derived from *Ceiba pentandra* (L.) Gaertn. (Kapok) Cotton

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**ABSTRACT:** Superabsorbent polymers (SAPs) were synthesized by grafting acrylic acid and butyl acrylate onto carboxymethyl cellulose (CMC) modified from *Ceiba pentandra* (L.) Gaertn. (kapok) cotton, with *N,N'*-methylenebisacrylamide as a crosslinker and ammonium persulphate as initiator. The effect of distilled water, saline solution, and applied pressure on superabsorbent was investigated. The product exhibited the maximum water absorbency of 554 g/g in distilled water and 96 g/g in saline solution. The SAP achieved the highest water absorbency under load of 83 g/g under applied pressure of 7.6 g/cm<sup>2</sup>. The kapok cotton modified cellulose-based SAP exhibited stronger gel strength than the SAP based on commercial CMC. This is probably due to the higher grafting efficiency (78.3%) of the former. The SAP was characterized by FTIR analysis, thermogravimetric analysis, and scanning electron microscopy. Thermogravimetric analysis results showed that the SAP, with AA and BA grafted onto CMC, had better thermal stability than CMC alone. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40808.

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### INTRODUCTION

Most of the current SAPs available commercially are synthetic polymers based on acrylic acid or acrylamide, which are expensive, poorly degradable and harmful to the environment.<sup>1</sup> In view of the gradual depletion of petroleum resources and rising issues of global environmental pollution, material biodegradability has been the focus of current researches conducted and it was the main concern of this study.

Although there are numerous literatures regarding graft copolymerization of vinyl monomers onto polysaccharides, synthesis of SAP derived from modified kapok cotton has not been reported so far.

Among the polysaccharides, cellulose is a prime candidate as it is the most abundant natural polymer with excellent biodegradability and biocompatibility. The various sources of native cellulose are cotton, flax, hemp, jute, ramie and wood.<sup>2</sup> However, this high molecular weight polysaccharide is generally insoluble in water and organic solvents due to its strong intramolecular and intermolecular hydrogen bonding.<sup>3</sup>

Cellulose can be converted to carboxymethyl cellulose (CMC), ethyl cellulose, hydroxymethyl cellulose, methyl cellulose and cellulose nitrate via chemical modifications.<sup>4</sup> Among these derivatives, CMC was chosen for this study due to its

water-soluble properties derived from the carboxylic groups in the molecules.

In this study, cotton linters taken from *Ceiba pentandra* (L.) Gaertn. (or commonly known as kapok among Malaysians) were modified into CMC via etherification. Kapok was originated in tropical America but has spread to West Africa, Polynesia, Indonesia and Southeast Asia over the years.<sup>5</sup> Kapok cotton was chosen due to its availability in Malaysia and its high cellulose content. Kapok cotton linters comprise of 64% cellulose, 13% lignin, and 23% pentosan.<sup>6</sup> The degree of substitution and intrinsic viscosity of the CMC obtained were compared with those of commercial CMC.

The CMC modified from kapok cotton (KCMC) was used in the synthesis of SAP. The CMC-based hybrid SAP was prepared via free radical polymerization, by grafting vinyl monomers namely acrylic acid and butyl acrylate, onto CMC backbone, with *N,N'*-methylenebisacrylamide as a crosslinker and ammonium persulphate as thermal initiator. Water absorbency of SAP in distilled water, saline solution and under applied pressure (AUL) was investigated. Other characterizations include FTIR analysis, TGA and SEM. SAP based on commercial CMC was also synthesized as a comparison to KCMC-based SAP. Grafting efficiency of the SAPs was determined and compared.

## EXPERIMENTAL

### Materials

Acrylic acid (AA) and butyl acrylate (BA) from Sigma Aldrich Chemicals, USA, were used as monomers. *N,N'*-methylenebisacrylamide (MBA, Sigma Aldrich Chemicals, USA) was utilized as crosslinker. Ammonium persulfate (APS, R & M Chemicals, UK) was used as thermal initiator. Sodium carboxymethyl cellulose (CMC) was purchased commercially from R & M Chemicals, UK, while ethanol and sodium chloride were purchased from J. Kollin, UK.

In the etherification of kapok cotton linters, hydrogen peroxide was used as bleaching agent while acetic acid was employed as neutralizing agent. Sodium carbonate was used to fix the pH of the medium. Sodium silicate was used as a stabilizer. Sodium hydroxide was employed in the scouring and basification process. All these chemicals as well as isopropanol and acetone were purchased from R & M Chemicals, UK. Monochloroacetic acid (MCA) was purchased from Merck, Germany.

### Preparation of Carboxymethyl Cellulose from Kapok Cotton Linters (KCMC)<sup>7</sup>

About 100 g of kapok cotton linters were freed from hulls and other foreign matters and boiled in distilled water for 30 min. The linters were then filtered, submerged into 400 mL of 1% sodium hydroxide solution and boiled for 2 h. The linters were filtered and again boiled in distilled water for 30 min. After that, the linters were washed with 0.5% acetic acid solution followed by distilled water until neutral. The linters were then air dried. The dried linters were bleached at 30°C with 0.8% of hydrogen peroxide solution containing 1% each (based on weight of linters) of sodium carbonate and sodium silicate for 30 min. The linters were thoroughly washed with water and air dried after that.

About 4 g of the bleached linters were immersed in 100 mL of aqueous alcoholic 18% NaOH solution ((H<sub>2</sub>O : isopropanol = 1:4) and the mixture was stirred at 30°C for 2 h. To carry out carboxymethylation, the temperature of the mixture was raised to 50°C and 0.034 moles of MCA solution was added drop-wise into it. The mixture was refluxed for 6 h. After cooling to room temperature, the content was filtered under suction. The mass on the filter was washed thoroughly with 80% ethanol, which contained 1–2 drops of acetic acid, and dried under suction. The crude KCMC was dissolved in distilled water and the unreacted linters were removed. The crude KCMC was precipitated with excess acetone, which was dried at 60°C to a constant weight.

### Degree of Substitution

The degree of substitution of CMC sample was determined according to ASTM D1439-2003.<sup>8</sup>

### Synthesis of CMC-Based Hybrid SAP

CMC (3.0 g) was gelatinized in 100 mL of distilled water with sufficient stirring at 60°C. A total amount of 21.6 g of AA and BA in the molar ratio of 98.6 : 1.4 was added into the CMC solution with continuous stirring. Prior to that, AA was partially neutralized with 50 mL of 6 mol/L of sodium hydroxide. After that, 0.4 mol % of MBA, based on total monomer, was

dissolved in 25 mL of distilled water and added into the solution, followed by 0.3 mol % of APS based on total monomer (dissolved in 25 mL of distilled water). The mixture was maintained at 60°C with continuous stirring for 90 min. The gel solution was poured into an excess amount of ethanol and the precipitate obtained was filtered to remove excess water. The precipitate was dried at 60°C to a constant weight. The dried product was kept in a desiccator for future use. All the CMC-based SAPs used in this study were synthesized under similar processing conditions.

### Determination of Intrinsic Viscosity

CMC and CMC-based SAP were dissolved in 0.05M NaCl. The solvent flow time and solution flow time were determined using an Ubbelohde viscometer (size OB) suspended in a water bath at 30°C. An average of three readings was taken for each concentration. A plot of the reduced viscosity,  $\eta_{red}$  against the concentration,  $c$  of the polymer, gives the intrinsic viscosity,  $[\eta]$  at the  $y$ -intercept of the plot.

### Grafting Efficiency

After a dry SAP sample had been stirred in 300 mL of distilled water at room temperature for 24 h, the mixture was centrifuged to separate the undissolved graft copolymer. The procedure was repeated to ensure complete removal of the water-soluble component. The remaining SAP obtained after water extraction was dehydrated with methanol and dried overnight in an oven at 60°C. The dried SAP was weighed to determine the amount of the water-soluble component, which consists of free PAA and ungrafted CMC.<sup>9</sup> The dried SAP was extracted subsequently with acetone for 24 h by Soxhlet extraction to remove free PBA.<sup>10</sup> After that, the residue was dried in an oven at 60°C to a constant weight. The extraction procedure was repeated twice for each sample. The grafting efficiency of SAP was calculated using eq. (1).

$$\text{Grafting efficiency (\%)} = \left[ \frac{W'_1 - W'_0}{W'_2} \right] \times 100 \quad (1)$$

where  $W'_1$ ,  $W'_0$ , and  $W'_2$  denote, respectively, the final weight of the product after water and acetone extractions, the original weight of CMC used, and the original weight of monomers used.

### Swelling Measurement

About 0.10 g of dry SAP was immersed in distilled water or saline solution for 48 h. At fixed interval, the swollen SAP gel was filtered using a wire mesh (300 #), drained for 10 min and weighed ( $W_1$ ). The SAP gel was dried in an oven at 60°C to a constant weight ( $W_2$ ). The swelling capacity or water absorbency ( $Q$ ) of SAP was calculated using eq. (2).

$$Q \text{ (g/g)} = \frac{(W_1 - W_2)}{W_2} \quad (2)$$

where water absorbency of SAP is equilibrium water absorption defined as grams of water absorbed per gram of polymer sample.

### Absorbency under Load (AUL)

With a screen fabric made of nylon placing on top, a macroporous support was placed in a Petri dish. A fixed amount of

dried SAP sample was distributed evenly on the screen fabric. A cylindrical solid load (varied in weight) which could slip freely in a cylinder with an external diameter of 30 mm was used to apply the pressure (between 7.6 and 30.3 g/cm<sup>2</sup>) on the sample. Then, the dish was filled with 0.9 wt % of NaCl solution until the liquid level was equal to the height of the porous support. The SAP sample was allowed to soak in the solution at room temperature for a defined duration (1–24 h). The entire setup was covered to prevent evaporation of water.<sup>11</sup> At certain time intervals, the swollen particles were weighed and AUL was calculated using eq. (3).

$$\text{AUL} = \frac{(W_1'' - W_0'')}{W_0''} \quad (3)$$

where  $W_0''$  and  $W_1''$  are the weight of dry and swollen SAP respectively.

#### FTIR Analysis

FTIR spectra were obtained in the 4000–400 cm<sup>-1</sup> region using KBr pellets (Perkin Elmer FTIR Spectrum RX1).

#### Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed using TGA/SDTA 851 (Mettler Toledo) with a nitrogen gas flow of 20 mL/min. A sample (1–5 mg) was heated in a standard 150  $\mu$ L alumina pan holder at a constant heating rate of 10°C/min in the temperature range of 25–800°C.

#### Surface Morphology

The micrographs of SAP samples were taken using JSM-6701F Scanning Electron Microscope (JEOL). A sample was mounted on a copper holder and sputter-coated with platinum before SEM observation.

## RESULTS AND DISCUSSION

### Preparation of Carboxymethyl Cellulose from Kapok Cotton Linters (KCMC)

Compared to other bleaching agents, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was opted in this study because it works best on cotton and cellulose fiber.<sup>12</sup> In addition, peroxide bleaching causes less cellulose chain oxidation, resulting in an increase of shelf life and brightness stability.<sup>13</sup>

In fiber bleaching, the pH of the medium was best regulated at pH 10. This is because at pH higher than 10.8, the decomposition of peroxy carbonate ion is too rapid, resulting in the formation of O<sub>2</sub> that has no bleaching property. Sodium silicate was added as a buffering agent in order to minimize peroxide decomposition and the degradation of cotton linters.<sup>14</sup>

Under optimized conditions, the KCMC produced has a DS of 0.75, whereas the commercial CMC used in this study has a DS of 0.97 (Table I).

### Synthesis of CMC-Based Hybrid SAP

To initiate the grafting process, the persulfate initiator was first decomposed under the heating temperature of 60°C to generate sulfate anion radicals. The radicals then extract hydrogen from the hydroxyl groups of CMC to form alkoxy radicals on the substrate. The monomers molecules, which are in close vicinity with the radical sites, accept CMC radicals resulting in chain

**Table I.** Degree of Substitution of KCMC and Commercial CMC, and Grafting Efficiency of KCMC-Based SAP and Commercial CMC-Based SAP

Sample	Degree of substitution (DS)	Grafting efficiency (%)
KCMC	0.75 ± 0.01	–
Commercial CMC	0.97 ± 0.03	–
KCMC-based SAP	–	78.3 ± 1.55
Commercial CMC-based SAP	–	50.9 ± 0.34

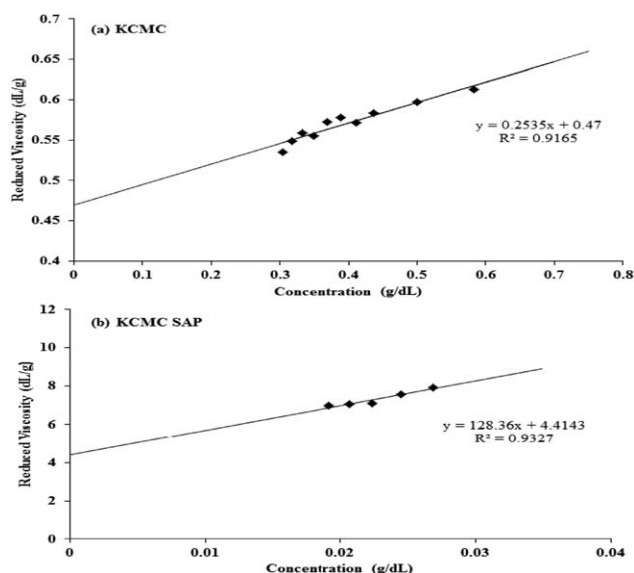
initiation reaction. As a result, the monomer molecules become free radical donor to the neighboring molecules in support of the grafted chains to grow.<sup>15</sup> In order to minimize free radical degradation of the polysaccharide by persulfate initiator, APS was added after the addition of the monomers, AA and BA.<sup>16</sup>

During chain propagation, the end vinyl groups of the cross-linker, MBA react synchronously with different polymer chains to form three-dimensional network. The crosslinking reaction takes place through any site in the growing polymer chains by opening the double bonds of the two vinyl groups of MBA.<sup>9</sup>

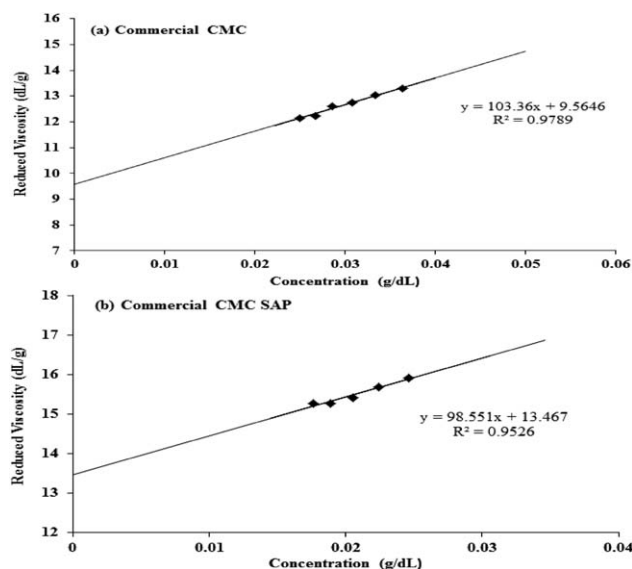
Although the presence of CMC increases the biodegradability of SAP, excessive amount of CMC would result in high viscosity of the medium, which in turn will limit the diffusion of monomers to the active sites on CMC to enable efficient network formation in SAP. Besides, a high CMC concentration could result in more CMC macro radicals, which could interact with one another to terminate the reaction.<sup>17</sup>

### Determination of Intrinsic Viscosity

The intrinsic viscosities of KCMC and KCMC-based SAP were 0.47 and 4.41 g/dL respectively [Figure 1(a,b)]. The increase in the intrinsic viscosity of the SAP produced indicates that



**Figure 1.** Reduced viscosities of (a) KCMC (b) KCMC-based SAP against concentration of sample.



**Figure 2.** Reduced viscosities of (a) commercial CMC (b) commercial CMC-based SAP against concentration of sample.

grafting of monomers onto KCMC had been successful. However, the viscosity method is generally not suitable to branched molecules as it only applied to linear and slightly branched molecules.<sup>18</sup> Therefore, this method can only serve as an indication of an increase in molecular weight of the SAP produced.

Comparatively, the intrinsic viscosities of commercial CMC and the CMC-based SAP were 9.56 and 13.46 g/dL respectively [Figure 2(a,b)].

The low intrinsic viscosity of KCMC was probably due to breaking down (depolymerization) of the cellulose backbone by NaOH during pre-treatment and the etherification process. Other researchers encountered similar problems with different polysaccharides.<sup>19,20</sup>

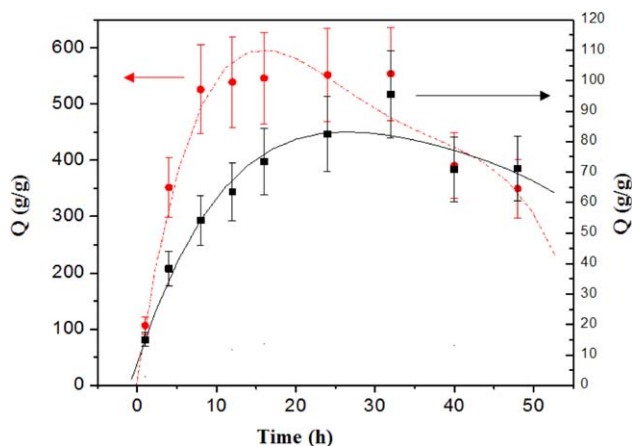
### Grafting Efficiency

The KCMC-based SAP has the grafting efficiency of 78.3% (Table I), which was higher than the 50.9% of the commercial CMC-based SAP. This is probably due to the much lower molecular weight of KCMC compared to commercial CMC. The processing of KCMC-based SAP in a reaction medium of lower viscosity facilitates the movement of free radicals in it. This increases the initiation efficiency, thus leading to an improvement in grafting efficiency.

### Swelling in Distilled Water and Saline Solution

Figure 3 displays the  $Q$  of KCMC-based SAP, which was grafted with AA to BA in the molar ratio of 98.9:1.1, in distilled water and in 0.9 wt % of NaCl solution over 48 h. The highest  $Q$  was 554 g/g in distilled water and 96 g/g in saline solution, which was reached at about 15 h and 30 h of immersion respectively.

The results show that there was deswelling of the SAP after it had reached its maximum  $Q$  values. The  $Q$  of the SAP in distilled water dropped gradually to 350 g/g (37%), while the same in saline solution dropped steadily to 71 g/g (26%) after 48 h of immersion. Upon prolonged soaking, the polymer network



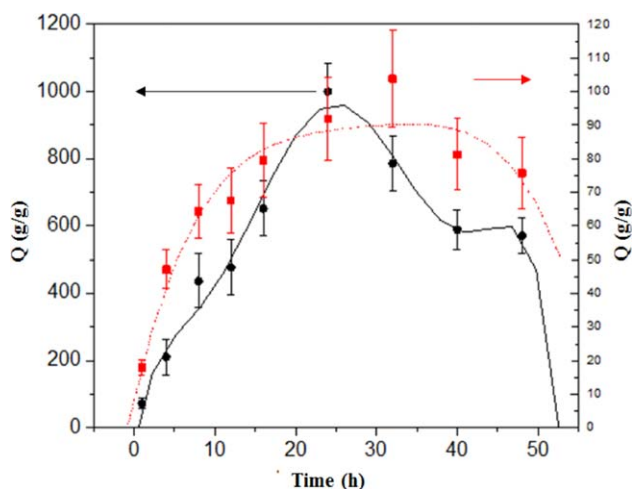
**Figure 3.** Effect of water absorbency of KCMC-based SAP in (●): distilled water (■): 0.9 wt % of NaCl against time of swelling. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

could not hold up the water molecules and allowed water to seep out from the network gradually.

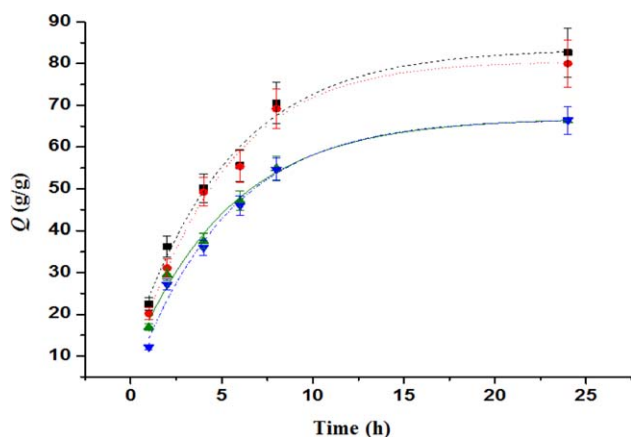
During the swelling process, water is absorbed to overcome the osmotic pressure inside the SAP. The lower water absorbency of SAP in saline solution is attributed to the charge screening effect of the sodium cation, causing a nonperfect anion–anion electrostatic repulsion that leads to the decrease in the difference of osmotic pressure between the gel and the solvent phase.<sup>21,22</sup>

Figure 4 shows the  $Q$  values of commercial CMC-based SAP namely CMC-g-P(AA-co-BA) immersed in distilled water and saline solution over 48 h. The highest  $Q$  of the SAP obtained was 1000 g/g in distilled water and 104 g/g in saline solution. The maximum  $Q$  values of the SAP in distilled water and saline solution were reached after about 24 h and 32 h, respectively.

Compared to the commercial CMC-based SAP, the  $Q$  values of KCMC-based SAP were obviously lower in distilled water but



**Figure 4.** Effect of water absorbency of commercial CMC-based SAP in (●): distilled water (■): 0.9 wt % of NaCl against time of swelling. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

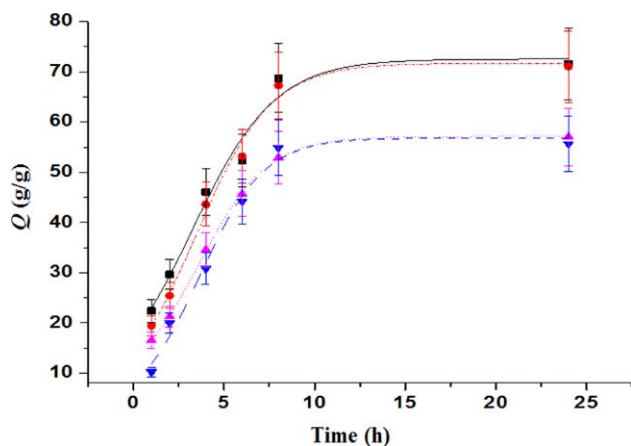


**Figure 5.** Absorbency under load of KCMC-based SAP sample against time (Symbols: (■) 7.6 g/cm<sup>2</sup>, (●) 15.1 g/cm<sup>2</sup>, (▲) 23.0 g/cm<sup>2</sup> and (▼) 30.3 g/cm<sup>2</sup>). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

the difference was less in saline solution. This could be due to the lower DS value and molecular weight of KCMC. Lower DS value indicates that lesser carboxymethyl groups are present in KCMC. Hence, the hydrophilicity of the KCMC-based SAP is lower, compared to its commercial CMC counterpart. Besides, the molecular weights of KCMC as well as the SAP produced are lower. As a result, the polymer network was not able to hold as much water as the commercial CMC-based SAP.

#### Absorbency Under Load (AUL)

AUL is a useful test to investigate the swollen gel strength for the application of SAP.<sup>23</sup> In AUL test, the swelling capacity of SAP was measured by soaking it in 0.9 wt % of NaCl solution against a certain applied pressure. Figures 5 and 6 show the AUL values of KCMC-based SAP and commercial CMC-based SAP respectively. In this study, the AUL values of both SAPs attained under different applied pressure increased until they reached a maximum and maintained there upon prolonged soaking. As shown in Figure 5, the peak AUL values of



**Figure 6.** Absorbency under load of commercial CMC-based SAP sample against time (Symbols: (■) 7.6 g/cm<sup>2</sup>, (●) 15.1 g/cm<sup>2</sup>, (▲) 23.0 g/cm<sup>2</sup> and (▼) 30.3 g/cm<sup>2</sup>). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table II.** Rate of Solvent Uptake of KCMC-Based SAP Under Load Against Time of Saline Immersion

Time (h)	Rate of solvent uptake ( $\times 10^{-2}$ g/min)					
	1	2	4	6	8	24
7.6	6.7	5.4	3.8	2.8	2.6	1.0
15.1	6.0	4.7	3.7	2.8	2.6	1.0
23.0	5.1	4.4	2.8	2.4	2.1	0.8
30.3	3.6	4.1	2.7	2.3	2.0	0.8

KCMC-based SAP decreased from 83 to 66 g/g as applied pressure increased from 7.6 to 30.3 g/cm<sup>2</sup> and these values were reached in shorter time with increasing applied pressure. While commercial CMC-based SAP recorded the highest AUL value of 72 g/g and decreased to 55 g/g as applied pressure increased from 7.6 g/cm<sup>2</sup> to 30.3 g/cm<sup>2</sup> (Figure 6).

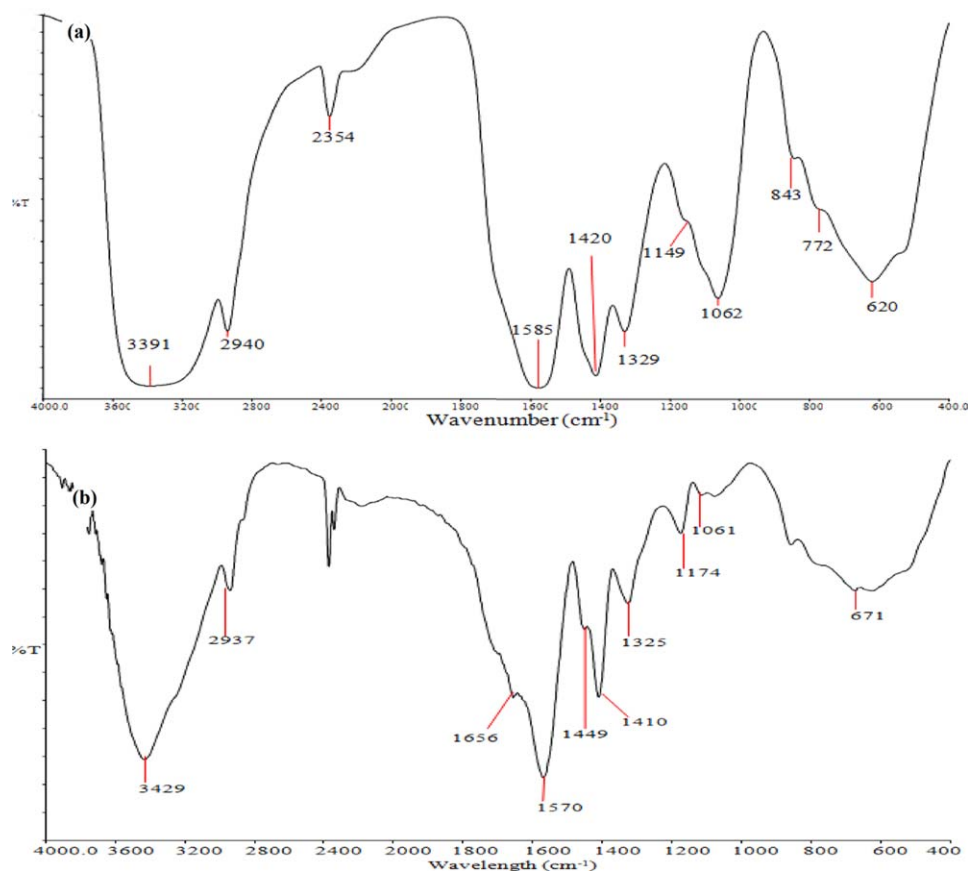
In comparison with the AUL values of commercial CMC-based SAP, the values of KCMC-based SAP were generally higher. This indicates that the gel strength of the later was stronger than the former. With better grafting efficiency of 78.3%, KCMC-based SAP with higher amount of P(AA-co-BA) copolymers grafted onto the KCMC chains would form a stronger polymer network, thus resulting in better gel strength.

Other than studying the AUL values of the CMC-based SAPs, the rates of solvent uptake measured as gram of solvent per minute were determined (Tables II and III). In the initial hour of immersion, water diffused rapidly into SAP due to the huge difference in osmotic pressure between the gel and solvent phase. The huge pressure difference generates a strong driving force for the solvent to diffuse into gel phase. However, the rates of solvent uptake for all applied pressure slowed down upon reaching the sixth hour of saline immersion. This occurred owing to the decreasing pressure difference between the gel and solvent phase as the SAP swells up to accommodate the incoming saline solution.

The rates of solvent uptake for both SAPs decreased as the applied pressure increased at all stages of saline immersion. For example, the rate of solvent uptake of KCMC-based SAP in the first hour of saline immersion under applied pressure of 7.6 g/cm<sup>2</sup> was  $6.7 \times 10^{-2}$  g/min. It decreased steadily as applied pressure increased and dropped to  $3.6 \times 10^{-2}$  g/min under applied pressure of 30.3 g/cm<sup>2</sup> (Table II). Similarly, the rate of

**Table III.** Rate of Solvent Uptake of Commercial CMC-Based SAP Under Load Against Time of Saline Immersion

Time (h)	Rate of solvent uptake ( $\times 10^{-2}$ g/min)					
	1	2	4	6	8	24
7.6	6.3	4.2	3.3	2.5	2.4	0.8
15.1	5.1	3.4	2.9	2.4	2.2	0.8
23.0	4.4	2.8	2.3	2.0	1.8	0.6
30.3	2.5	2.5	1.9	1.8	1.7	0.6



**Figure 7.** FTIR spectra of (a) KCMC (b) KCMC-based SAP. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

solvent uptake of commercial CMC-based SAP in the first hour of saline immersion under applied pressure of  $7.6 \text{ g/cm}^2$  was  $6.3 \times 10^{-2} \text{ g/min}$ . It dropped to  $2.5 \times 10^{-2} \text{ g/min}$  under applied pressure of  $30.3 \text{ g/cm}^2$  (Table III).

#### FTIR Analysis

The FTIR spectra of KCMC and, KCMC-*g*-P(AA-*co*-BA) are shown in Figure 7(a,b), respectively.

In Figure 7(a), the broad band stretch around  $3391 \text{ cm}^{-1}$  is attributed to hydrogen bonded OH stretching frequency. The broad peak could be explained by the presence of intramolecular and intermolecular hydrogen bonds as well as the absorbed water.<sup>24</sup> The peak at  $2940 \text{ cm}^{-1}$  is due to C—H stretching vibration.<sup>25</sup> The absorption peaks found at 1585, 1420, and  $1329 \text{ cm}^{-1}$  are assigned as asymmetric stretching of COO-groups, CH<sub>2</sub> scissoring, and OH bending respectively. The characteristic peaks at  $1585 \text{ cm}^{-1}$  and  $1420 \text{ cm}^{-1}$  indicated the presence of carboxymethyl substituent.<sup>26</sup> Whereas, the absorption peak at  $1060 \text{ cm}^{-1}$  signified the carbonyl stretch C—O—C of ether bond of 1,4- $\beta$ -D-glucosidic linkage.<sup>27</sup>

Compared with Figure 7(a), Figure 7(b) has weaker absorption peaks for O—H bending ( $1325 \text{ cm}^{-1}$ ) and C—O—C bond ( $1061 \text{ cm}^{-1}$ ). This could be due to the lesser amount of CMC (one seventh) used in the grafting of the hybrid SAP. Besides, the appearance of new peaks around  $1656 \text{ cm}^{-1}$  as well as peaks at

$1449 \text{ cm}^{-1}$  and  $1410 \text{ cm}^{-1}$  are attributed to the C=O stretching and symmetric stretching of COO<sup>-</sup> group respectively. These new peaks indicate the presence of P(AA-*co*-BA) in the sample.

There was also slight shifting of the representative peaks of carboxymethyl group at  $1570 \text{ cm}^{-1}$ ,  $1325 \text{ cm}^{-1}$ , and  $1061 \text{ cm}^{-1}$  in the spectrum of KCMC-based SAP compared to the peaks of CMC alone, which are at  $1585 \text{ cm}^{-1}$ ,  $1329 \text{ cm}^{-1}$ , and  $1062 \text{ cm}^{-1}$  respectively [Figure 7(a)]. This indicates less interaction of the carboxymethyl groups of CMC in KCMC-based SAP, which is likely due to the presence of P(AA-*co*-BA) in the sample.

#### Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was conducted to characterize the thermal properties of KCMC and KCMC-*g*-P(AA-*co*-BA).

The thermogram of KCMC in Figure 8(a) basically shows three stages of degradation. The first stage of degradation is attributed to traces of moisture found in the sample. It was followed by a gradual second stage of degradation occurred at inflection temperature of  $170^\circ\text{C}$  and then a more drastic degradation stage occurred at inflection temperature of  $290^\circ\text{C}$ . The second degradation step with a residue mass of 80.2% represents the volatilization of unknown volatile matter with lower molecular weight.<sup>24,28</sup> While the third degradation step with a gradual mass loss of 31.4% could be due to dehydration of saccharide

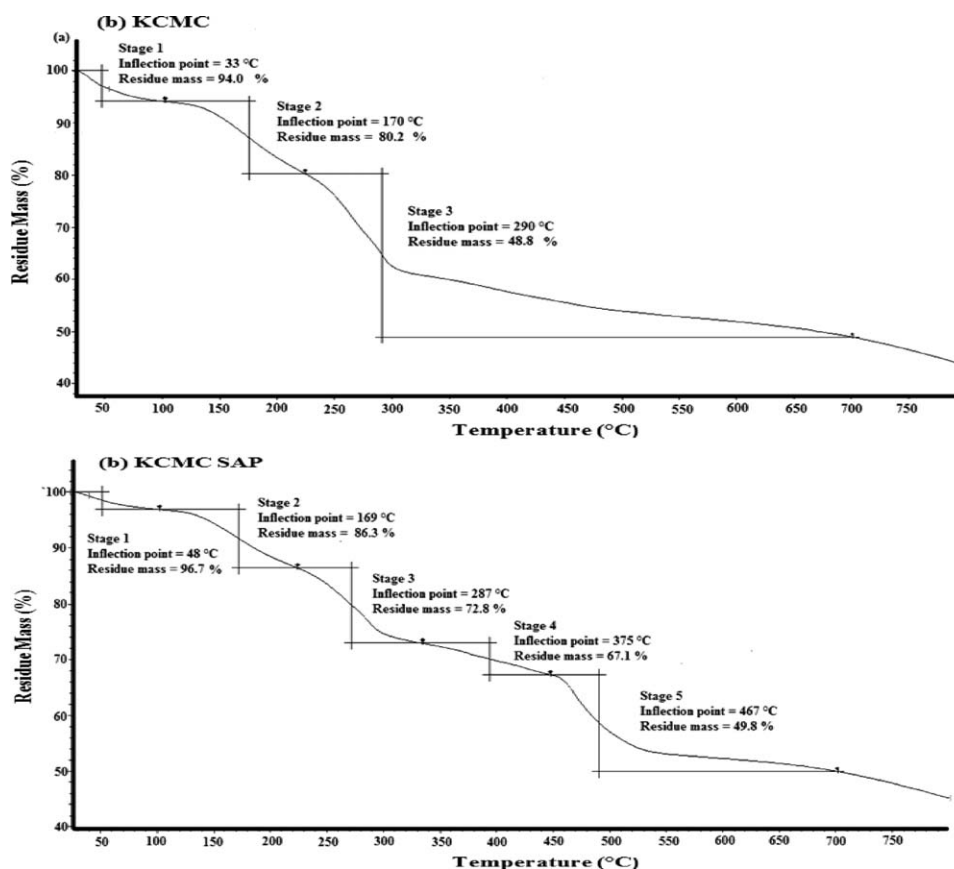


Figure 8. TGA thermograms of (a) KCMC (b) KCMC-based SAP.

rings and the breaking of C—O—C bonds.<sup>29</sup> Further heating to 700°C resulted in carbonization and ash formation.

In the case of KCMC-*g*-P(AA-*co*-BA), the thermogram in Figure 8(b) shows five stages of degradation. The initial stage occurred at the inflection point of 48°C indicates the loss of moisture in the sample. Degradation occurred in the second and third degradation stages at the inflection points of 169°C and 287°C respectively are likely contributed by KCMC as explained earlier.

On the other hand, the fourth stage that occurred at inflection point of 375°C is attributed to decarboxylation of PAA<sup>30</sup> while

the fifth stage that occurred at inflection point of 467°C with a residue mass of 49.8% is probably caused by further degradation of the polymer chain and matrices.<sup>9</sup>

Higher residue mass of KCMC-*g*-P(AA-*co*-BA) after the third degradation stage could be a result of the KCMC-graft-copolymer forming a crosslinked network. When heated, the crosslinked network will form an insulative carbonaceous char barrier on the surface to inhibit degradation.<sup>31</sup> From the TGA results we conclude that the SAP, with P(AA-*co*-BA) grafted onto CMC, had better thermal stability than CMC alone.

### Surface Morphology

SEM image of the hybrid SAP sample (Figure 9) show that its surface was uneven and porous. The appearance of pores on SAP surface could be due to evaporation of ethanol during the drying process.<sup>1</sup> The porous structure increases the surface area and aids diffusion of solvent into the gel.

### CONCLUSIONS

In this study, superabsorbent polymers were synthesized by grafting partially neutralized acrylic acid and butyl acrylate onto carboxymethyl cellulose modified from cellulose obtained from Kapok cotton, with *N,N'*-methylenebisacrylamide as a cross-linker and ammonium persulfate as initiator. The effect of distilled water and saline solution on the water absorbency of the SAP was evaluated. The highest water absorbency achieved was 554 g/g in distilled water and 96 g/g in saline solution.

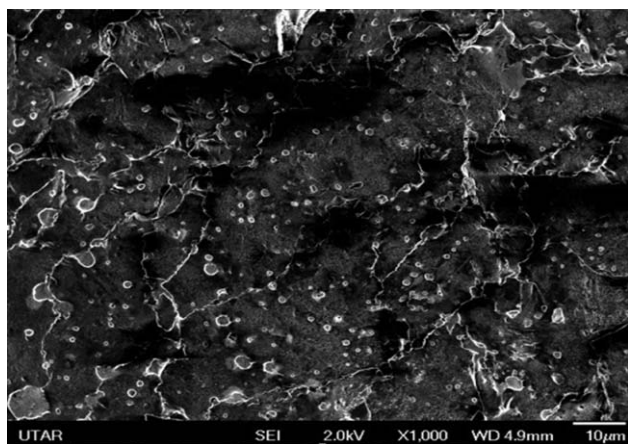


Figure 9. SEM image of KCMC-based SAP at ×1000 of magnification.

Although KCMC-based SAP had lower water absorbency values in distilled water than commercial CMC-based SAP, which was probably related to the much lower intrinsic viscosity of the former, it showed stronger gel strength while subjected to increasing applied pressure (7.6–30.3 g/cm<sup>2</sup>) in saline solution. The former was found to have higher in grafting efficiency (78.3%) than the latter (50.9%). FTIR peaks of KCMC and KCMC-based SAP were compared. TGA results concluded that the SAP, with P(AA-co-BA) grafted onto CMC, had better thermal stability than CMC alone. SEM image showed that the surface of the hybrid SAP was uneven and porous.

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