Alkaline Hydrolysis of Methyl Acrylate Grafted Cellulose Fibers

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ABSTRACT: In this work, methyl acrylate grafted cellulose fibers were hydrolyzed in an aqueous NaOH solution to obtain a superabsorbent hydrogel. The effect of process variables, such as the hydrolysis reaction time, temperature, and NaOH concentration, during alkaline hydrolysis were carefully determined and optimized. The degree of hydrolysis was estimated on the basis of the determination of the carboxylate group contents. The material loss during hydrolysis followed a first-order reaction mechanism. The differences in the behavior of the grafted fibers during hydrolysis could be explained by their structural differences. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3885–3890, 2008

Key words: degradation; graft copolymers; hydrogels; infrared spectroscopy; swelling

INTRODUCTION

In the first article of this series,[1] we found that pulp fibers, grafted under low and medium consistency conditions, had different water retention values (WRVs), despite having the same grafting yield. WRV was higher for fibers grafted under the medium consistency condition.

In the literature, many efforts to improve the water absorbency of grafted and then hydrolyzed cellulose fibers have been reported. Richards and White[2] hydrolyzed methyl acrylate grafted cellulose fibers in a cold 2.5N NaOH solution. Later, Vitta et al.[3] hydrolyzed acrylic acid grafted fibers in a hot 3% NaOH solution. Zaharan et al.[4] tried to improve the absorbency of acrylic acid grafted cellulose fibers by decrystallization in a 70% $ZnCl_2$ solution followed by alkaline hydrolysis to achieve a high water absorbency.

In this work, we studied the details of the hydrolysis reaction of grafted cellulose fibers. The effects of process variables during alkaline hydrolysis, such as the hydrolysis reaction time, temperature, and NaOH concentration, were carefully analyzed and optimized.

EXPERIMENTAL

Materials

In this study, bleached softwood sulfite pulp, methyl acrylate, and ceric ammonium nitrate (CAN) as the initiator were used as described in the previous article.[1] Distilled and deionized water was used in all the experiments.

Graft copolymerization

Methyl acrylate was graft-copolymerized onto softwood sulfite pulp fibers at a 10% fiber concentration (FC) in a plastic bag with CAN as the free-radical initiator. Details of the process have been given elsewhere.[1]

Alkaline hydrolysis

Grafted pulp fibers were hydrolyzed in an aqueous NaOH solution under reflux for various times and temperatures, and the reaction mixture was stirred with a magnetic stirrer. After completion of the hydrolysis, the reaction mixture was filtered and then washed with water thoroughly.

Water absorbency

The water absorbency of the hydrolyzed grafted fibers was determined with the centrifugal technique (at 900g for 30 min):[3]

$$\text{WRV (g/g)} = \frac{(W_2 - W_1)}{W_1}$$

where W_2 and W_1 are the weights of the wet sample (after 900g for 30 min) and oven-dried sample, respectively.

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Saline retention value (SRV)

The hydrolyzed grafted fibers were washed and filtered to remove excess water. The fibers were then soaked in acetone twice for 1 h each time and dried *in vacuo*. After that, the dried fibers were soaked in a 0.9% (w/w) NaCl solution for 16 h and then filtered and centrifuged (at 900g for 30 min), and the weight of the wet sample was denoted S_2. Lastly, the fibers were oven-dried at 105°C overnight to measure the SRV, and the weight of the oven-dried sample was denoted S_1:

$$\text{SRV (g/g)} = \frac{(S_2 - S_1)}{S_1}$$

Yield

The yield during the alkaline hydrolysis was determined on the basis of the dry weight of the material before and after hydrolysis:

$$\text{Yield (\%)} = \frac{B}{A} \times 100$$

where A and B are the dry weights of the grafted fibers before and after hydrolysis, respectively.

Carboxylate group determination

It is imperative to know the degree of hydrolysis of the hydrolyzed grafted fibers as it directly affects the water absorbency. The degree of hydrolysis was determined from the carboxylate content. The conductometric titration method was chosen for the carboxylate group determination.[5] A VWR digital conductivity meter was used for titration. The grafted cellulose fibers after hydrolysis were washed thoroughly in water and then filtered to remove excess water. After that, the sample was soaked thrice in a 0.1M hydrochloric acid solution for 15 min each time and stirred slowly with a magnetic stirrer. Subsequently, the fibers were washed thoroughly with water to remove any acid. The washed fibers were dispersed in 250 mL of a 0.001M NaCl solution. Before titration was started, 10 mL of a 0.1M HCl solution was added. The titration was carried out by the addition of 0.1M NaOH from a pipette. A plot of the conductance versus the NaOH titrant consumption was obtained, and the carboxylic group content corresponded to the titrant consumption for the constant conductance region of the titration curve.[5] After completion of the titration, fibers were washed in water and oven-dried at 105°C.

Attenuated total reflectance (ATR)–infrared (IR) analysis

ATR spectra were recorded under the ambient conditions for hydrolyzed grafted fibers and residue recovered from the hydrolysis filtrate. The samples were ground and then screened to get a finer powder that was used for ATR. A Thermo Spectra Tech Ge horizontal ATR cell was used.

X-ray diffraction analysis

X-ray diffraction analysis was carried out for the hydrolyzed grafted fibers. After hydrolysis, the samples were washed in water thoroughly, and then the swollen fibers were soaked in acetone twice for 1 h each time and dried *in vacuo* at 60°C overnight. The subsequent procedures were the same as those described earlier.[1]

RESULTS AND DISCUSSION

Yield loss during alkaline hydrolysis

The loss of material during alkaline hydrolysis was not only due to the hydrolysis of methyl esters but also due to the loss of grafted fibers. This was confirmed by the appearance of suspended polymers upon the addition of methanol to the filtrate from the hydrolysis reaction.[6] The IR spectrum for the suspended polymers is shown in Figure 1(b). Included in Figure 1(a) is also the spectrum of hydrolyzed grafted fibers.

The hydrolyzed grafted fiber [Fig. 1(a)] showed one broad absorption band in the 3100–3500-cm^{-1} region and a strong peak at 1026 cm^{-1} that confirmed the presence of cellulose.[7,8] The presence of carboxylate groups was confirmed by the asymmetrical stretching band near 1550 cm^{-1} and another symmetrical band at 1400 cm^{-1}.[9,10] On the other hand, the residue recovered from the alkaline hydrolysis filtrate solution by precipitation with methanol [Fig. 1(b)] showed the strong absorption bands at 1560 and 1400 cm^{-1}. The weak bands at 3100–3500 and 1026 cm^{-1} confirmed the presence of cellulose in the residue.
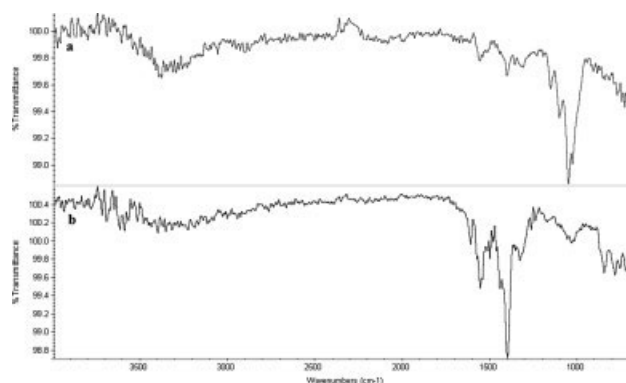

Figure 1 IR spectra of (a) hydrolyzed grafted fibers and (b) residue recovered from the hydrolysis filtrate.
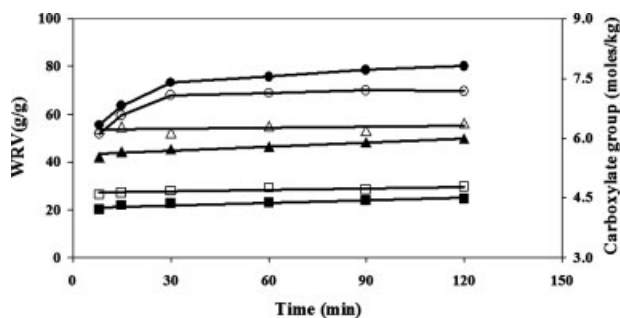
Figure 2 Effect of the hydrolysis time on WRV and the carboxylate group content [NaOH concentration = 3.0% (w/w), temperature = 105°C, and FC = 1.0% (w/v)]. The filled symbols are for WRV, and the open symbols are for the carboxylate group content: (■) 1 : 1, (▲) 2 : 1, and (●) 3 : 1 M/pulp.

On the basis of these results, it can be concluded that both cellulose and grafted polymer are lost during the hydrolysis reaction.

Effect of the hydrolysis time

The swelling capacity and degree of hydrolysis of the methyl acrylate grafted fibers were studied as a function of the hydrolysis time. In Figure 2, the results are shown for samples obtained at monomer/pulp (M/pulp) ratios of 1 : 1, 2 : 1, and 3 : 1 with grafting yields of 80, 166, and 250%, respectively. For samples obtained at M/pulp ratios of 1 : 1 and 2 : 1, the results were similar: complete hydrolysis was achieved within 8 min, as evidenced by the constant carboxylate group content. A slight increase in WRV with time was caused by the decrystallization of wood fibers due to aqueous alkali at a high temperature. In the case of the sample obtained from an M/pulp ratio of 3 : 1, both the WRV and carboxylate group content increased rapidly up to 30 min. A small increase in WRV after 30 min was again due
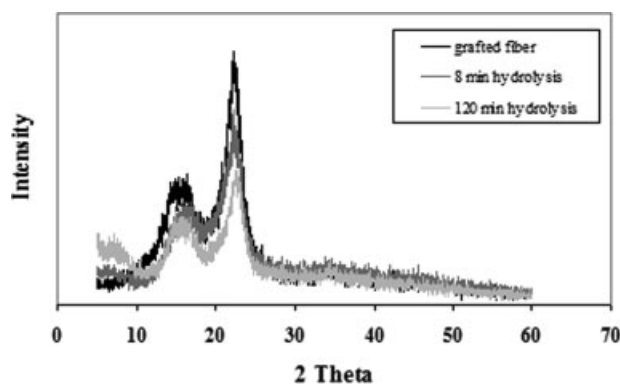
to the decrystallization as the carboxylate group content was constant. To confirm the cellulose decrystallization, we carried out X-ray diffraction analysis of grafted fibers from an M/pulp ratio of 1 : 1, which were alkali-hydrolyzed for 8 and 120 min. The results are shown in Figure 3, supporting the conclusion that decrystallization of the grafted fibers takes place during alkaline hydrolysis, as evidenced by the short and wide peaks of the hydrolyzed fibers.

Therefore, fibers with different grafting yields behave differently during alkaline hydrolysis, and samples with a lower grafting yield can be hydrolyzed in a shorter time, whereas those with a higher grafting yield require a longer time.

The yield loss (expressed on a logarithmic scale) during hydrolysis is shown in Figure 4. For each sample, there was a rapid yield loss at the beginning, and thereafter the yield loss was much less pronounced. On a logarithmic scale, the yield loss consists of two straight lines of different slopes for each sample, and each may be regarded as approximately first-order:

$$L = C_1 e^{-K_1 \cdot t} \text{ for } t \leq 15 \text{ min} \tag{1}$$

$$L = C_2 e^{-K_2 \cdot t} \text{ for } t \geq 15 \text{ min} \tag{2}$$

where L is the amount of grafted fiber left (%), K_1 and K_2 are first-order rate constants (min^{-1}), C_1 and C_2 are coefficients, and t is the time (min).

With respect to the effect of the M/pulp weight ratio on K_1, K_2, C_1, and C_2 values, we obtained correlations based on the results in Figure 4 as follows:

$$K_1 = 0.0011x + 0.002 \tag{3}$$

$$K_2 = 0.0001x + 0.0001 \tag{4}$$

$$C_1 = -0.0088x + 4.6036 \tag{5}$$

$$C_2 = -0.0644x + 4.4688 \tag{6}$$

where x is the M/pulp ratio.

Figure 3 Effect of the hydrolysis time on the crystallinity of cellulose for an M/pulp ratio of 1 : 1 [hydrolysis conditions: NaOH concentration = 3.0% (w/w), temperature = 105°C, and FC = 1.0% (w/v)].
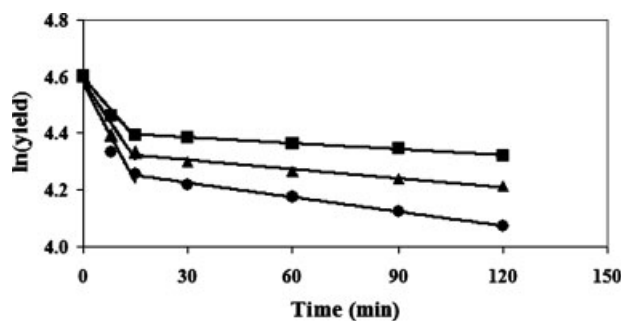

Figure 4 Yield loss (expressed on a logarithmic scale) versus the hydrolysis time (the hydrolysis conditions are the same as those in Fig. 2): (■) 1 : 1, (▲) 2 : 1, and (●) 3 : 1 M/pulp.
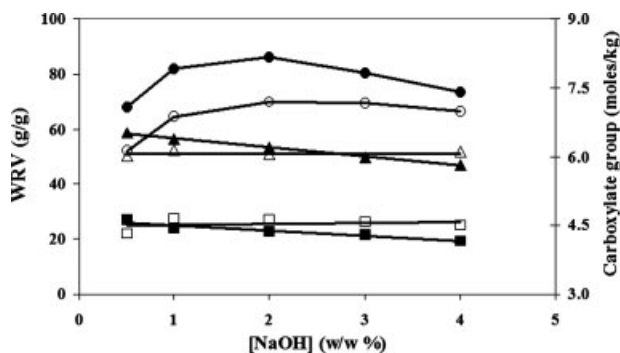
Figure 5 Effect of the NaOH concentration on WRV and the carboxylate group content [hydrolysis time = 120 min, temperature = 105°C, and FC = 1.0% (w/v)]. The filled symbols are for WRV, and the open symbols are for the carboxylate group content: (■) 1 : 1, (▲) 2 : 1, and (●) 3 : 1 M/pulp.

By substituting K_1, K_2, C_1, and C_2 from eqs. (3)–(6) into eqs. (1) and (2), we obtained the following:

$$L = (-0.0088x + 4.6036)e^{-(0.0011x+0.002)\cdot t} \text{ for } t \leq 15 \text{ min}$$
(7)

$$L = (-0.0644x + 4.4688)e^{-(0.0001x+0.0001)\cdot t}$$
$$\text{for } t \geq 15 \text{ min} \quad (8)$$

Effect of the NaOH concentration

The results are shown in Figure 5. For samples obtained at M/pulp ratios of 1 : 1 and 2 : 1, complete hydrolysis was achieved at 0.5% NaOH concentration, as evidenced by the constant carboxylate group contents upon a further increase in the NaOH concentration. The maximum WRV was obtained at a 0.5% concentration; thereafter, WRV decreased. The decreased WRV (at a constant carboxylate group content) with increasing NaOH concentration can be attributed to the increased yield loss, as shown in Figure 6. However, for samples obtained at an M/pulp ratio of 3 : 1, WRV first increased with the NaOH concentration and then decreased upon further increase in the NaOH concentration. The initial increase (up to a 2% NaOH concentration) in WRV was in agreement with the increased carboxylate group content; at higher than a 2% NaOH concentration, the carboxylate group content remained almost constant, whereas WRV decreased. This again was due to the increased yield loss.

One can conclude that for samples obtained from M/pulp ratios of 1 : 1 and 2 : 1, alkaline hydrolysis occurred readily (at a very low NaOH concentration), whereas for the sample from an M/pulp ratio of 3 : 1, a much higher concentration, around 2%, was needed to reach complete hydrolysis. Such a difference may be caused by the structural difference

of the grafted polymers. As we have shown earlier,[1] at a lower M/pulp ratio, the grafted polymer chains are shorter, and their structure is less compact, whereas at a higher M/pulp ratio, the grafted polymer chains are longer, and their structure is much more compact. Consequently, grafted polymer chains with higher molecular weights need a higher NaOH concentration to reach a well swollen state and thus complete hydrolysis.

The yield loss as a function of the NaOH concentration is shown in Figure 6. The majority loss of the material took place at a 0.5% NaOH concentration, and after that, the yield loss for the three samples could be regarded as a first-order; the correlation is as follows:

$$L = (-0.0863x + 4.5085)e^{-(0.0035x+0.0032)\cdot c} \text{ for } c \geq 0.5\%$$
(9)

where c is the NaOH concentration (w/w %).

Effect of the hydrolysis temperature

Figure 7 shows the effect of the hydrolysis temperature on the WRV and carboxylate group content. For samples obtained at an M/pulp ratio of 1 : 1, WRV increased up to 90°C and then decreased. However, the carboxylate group content was almost constant in the temperature range studied. The decreased WRV above 90°C was due to the increased yield loss, as shown in Figure 8. The samples from M/pulp ratios of 2 : 1 and 3 : 1 followed the same trend as that from an M/pulp ratio of 1 : 1. The carboxylate group content increased up to 70°C, and this led to a corresponding increase in WRV; a constant carboxylate group content and slight increase in WRV from 70 to 90°C may be due to the greater swelling of the polymer chains at a higher temperature. Upon further increase in the temperature, the decreased WRV again was due to the increased material loss.
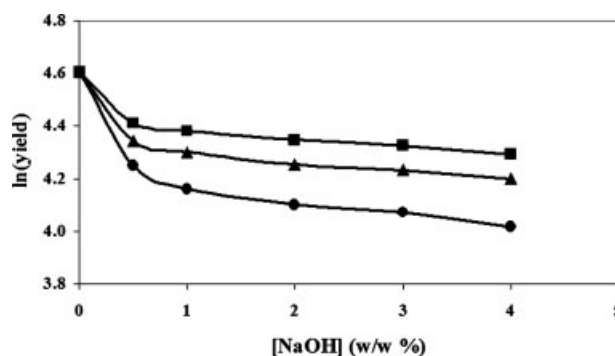

Figure 6 Yield loss (expressed on a logarithmic scale) versus the NaOH concentration (the hydrolysis conditions are the same as those in Fig. 5): (■) 1 : 1, (▲) 2 : 1, and (●) 3 : 1 M/pulp.
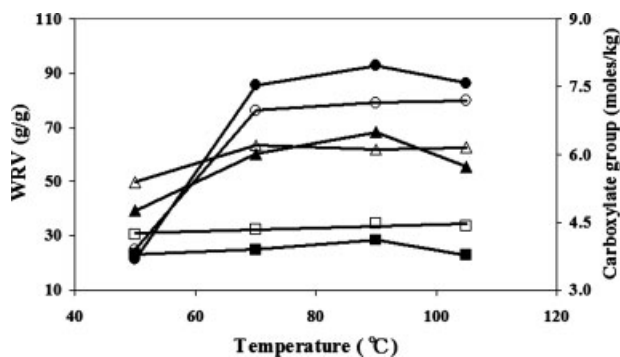
Figure 7 Effect of the hydrolysis temperature on WRV and the carboxylate group content [hydrolysis time = 2.0 h, NaOH concentration = 2.0% (w/w), and FC = 1.0% (w/v)]. The filled symbols are for WRV, and the open symbols are for the carboxylate group content: (■) 1 : 1, (▲) 2 : 1, and (●) 3 : 1 M/pulp.

It was also noted that at 50°C, the carboxylate group content for the samples obtained at an M/pulp ratio of 3 : 1 was lower than that at an M/pulp ratio of 2 : 1. Such a difference can be explained by the structural differences of the grafted polymers. At a lower grafting yield (M/pulp ratio = 2 : 1), the polymer chains are shorter, providing less resistance for the diffusion of NaOH. However, at a higher grafting yield, much longer polymer chains and much more compact structures are formed, providing more resistance for the diffusion of NaOH.

Therefore, it can be concluded that samples with less grafted polymers can be hydrolyzed almost completely at a low temperature (50–60°C), but for a higher grafted sample, a higher temperature is required to complete the hydrolysis.

The yield loss as a function of the hydrolysis temperature is shown in Figure 8. All samples obtained from M/pulp ratios of 1 : 1 to 3 : 1 followed a first-order reaction mechanism in the temperature range studied. However, for the sample with an M/pulp ratio of 3 : 1, the yield loss line has a different slope for a low temperature range (50–70°C), which again
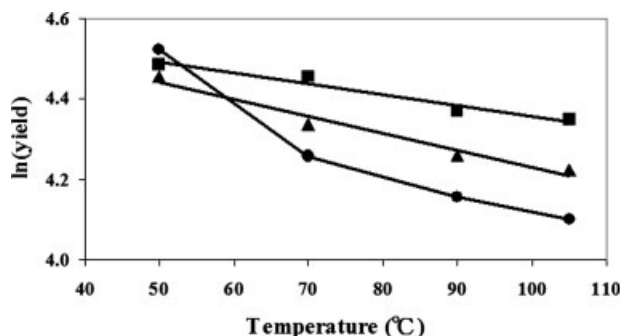

Figure 8 Yield loss (expressed on a logarithmic scale) versus the hydrolysis temperature (the hydrolysis conditions are the same as those in Fig. 7): (■) 1 : 1, (▲) 2 : 1, and (●) 3 : 1 M/pulp.

TABLE I
Absorbency in Water (Q_1) and 0.9% Saline Solutions (Q_2)

M/pulp	Grafting yield (%)	Q_1	Q_2	Q_2/Q_1 (%)
1 : 1	80	30.76	11.42	37.13
2 : 1	166	70.10	19.67	28.05
3 : 1	217	92.68	22.93	24.74

Hydrolysis condition NaOH concentration = 2.0% (w/w); temperature = 90°C; time = 2.0 h.

is an indicator of the structural difference of the grafted polymer at a higher M/pulp ratio.

Effect of the salt concentration

For many applications, the results of absorbency in a physiological solution, usually simulated in a 0.9% aqueous NaCl solution, are of practical importance. The absorbency in water (Q_1) and 0.9% saline solutions (Q_2) is listed in Table I. As expected, Q_2 was smaller than Q_1 for the same grafted sample. Table I shows that both Q_1 and Q_2 increased with increasing M/pulp ratio. However, the Q_2/Q_1 ratio decreased with increasing M/Pulp ratio. These results can be explained by the decreased osmotic pressure of the grafted fibers in the saline solution, which then led to a lower SRV than WRV.

CONCLUSIONS

Various process variables during alkaline hydrolysis were found to be important for achieving complete hydrolysis with maximum water absorbency, and they can be summarized as follows:

1. A hydrolysis time of 30 min is enough for complete hydrolysis of the sample, regardless of the grafting yield.
2. The NaOH concentration is a critical parameter for the alkaline hydrolysis. For samples obtained from M/pulp ratios of 1 : 1 and 2 : 1, a 0.5% NaOH solution is sufficient for complete hydrolysis. For samples obtained from an M/pulp ratio of 3 : 1, a 2% NaOH solution is required to reach complete hydrolysis.
3. The hydrolysis temperature is more critical in affecting the hydrolysis of grafted samples obtained from an M/pulp ratio of 3 : 1 than the hydrolysis of others from lower M/pulp ratios. This is likely due to the structural differences of the grafted polymer.

The experimental results show that fibers with different grafting yields behave differently during an alkaline hydrolysis reaction. A significant yield loss has been observed, and in most cases, the yield loss follows first-order kinetics.

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