

Creation of Reactive Centers on Cotton. II

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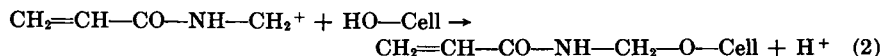
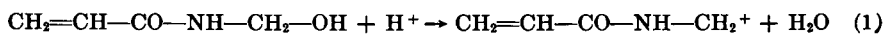
Synopsis

Acrylamidomethylated cellulose (AMC) was prepared by reacting cellulose with N-methylolacrylamide or its ethers in acidic medium under a variety of conditions. The extent of the reaction, expressed as mmole double bonds per 1 g cellulose, increased by increasing the concentration of N-methylolacrylamide or its ethers. However, the pad-dry-cure technique produced AMC with greater amounts of double bonds than the pad-batch technique. Also, the reactivity of the etherifying agents follow the order N-methylolacrylamide > N-methoxymethylacrylamide > N-methoxymethylmethacrylamide. Furthermore, the behavior of AMC in neutral, alkaline, and acidic media was studied. No change in the amount of the pendent double bonds of AMC occurred in neutral medium regardless of the conditions employed. On the contrary, disappearance of the double bonds took place in alkaline medium. The extent of disappearance depends on the kind of alkali used as well as on the conditions implemented. It was disclosed that consumption of the pendent double bonds of AMC occurred mainly via addition of the cellulose hydroxyls to yield a crosslinked cellulose. Treatment with hydrochloric acid, on the other hand, resulted in partial splitting of the acrylamidomethyl groups as well as addition of the acid on the pendent double bonds of AMC.

INTRODUCTION

In part I of this series, hexahydro-1,3,5-triacryloyl-s-triazine was used to effect formation of reactive centers on cotton in alkaline medium. Such reactive cotton could be dyed with colorants containing active hydrogen, and the dyeings obtained proved to withstand extraction with 50% aqueous pyridine or dimethylformamide.¹

N-Methylolacrylamide (MAM) with two different functional groups has been used as such² or after grafting³ as crosslinking agent for cellulose. In this case, cellulose was first reacted with N-methylolacrylamide under acid conditions where acrylamidomethylated cellulose is formed:



Preparation of acrylamidomethylated cellulose via reaction of N-methylolacrylamide with cellulose has been reported.⁴ In a separate alkali-catalyzed step, suitable active hydrogen compounds, such as thio-phenols, were reacted with the pendent double bonds of acrylamidomethyl cellulose to render the fabric hydrophobic. Treatment of the acrylamido-

methylated cellulose in the absence of other reagents under alkaline conditions caused addition of the cellulose hydroxyls to the pendent double bonds thereby forming crosslinks of the following nature:



The general kinetics of grafting of vinyl monomers onto acrylamino-methylated cellulose under the catalytic influence of ceric ions have recently been studied.⁵

In this laboratory, there is a research program to investigate the following points: (1) most suitable conditions for preparation of acrylamido-methylated cellulose; (2) behavior of this modified cellulose toward different reagents; and (3) possibility of combining more than one reagent in one step to obtain different useful effects. This work partially fulfills the first two objectives. Acrylamidomethyl cellulose is referred to as AMC.

EXPERIMENTAL

Materials

Cotton Fabric. Mill-scoured, bleached, and mercerized cotton fabric (Poplin, Kafr-El Dawar, Alexandria) was treated with a solution containing 10 g/l. sodium carbonate and 5 g/l. soap at the boil for 4 hr. It was then thoroughly washed and dried at ambient temperature.

Reagents. N-Methylolacrylamide, N-methoxymethylacrylamide, and N-methoxymethylmethacrylamide were kindly supplied by Badische Anilin- & Soda Fabrik AG, Ludwigshafen am Rhein, West Germany. These reagents were used without further purification.

Catalysts. Ammonium chloride, magnesium chloride, and concentrated hydrochloric acid were of analytical grade.

Preparation of Acrylamidomethyl Cellulose

Pad-Dry-Cure Method. The cotton fabric was impregnated in an aqueous solution containing specific concentration of N-methylolacrylamide or its ether in presence of NH_4Cl (1%, w/w) as catalyst. The fabric was squeezed between two rubber rollers to give a wet pick up of ca. 90%. After being dried at 70°C, the fabric was cured at 150°C for 4 mins. The fabric was washed with water, followed by treatment in aqueous solution of 2% sodium nitrite (a polymerization inhibitor) at 80°C. Finally it was washed in cold water and dried at ambient temperature.

Pad-Batch Method. This method consists of padding the fabric in an aqueous solution of 75% magnesium chloride (w/w) containing the requisite amount of N-methoxymethylacrylamide together with concentrated hydrochloric acid (0.8%, w/w) to a pickup of ca. 90%. The reaction was allowed to proceed by storing the padded fabric overnight at room temperature. The treated fabric was then washed with water, neutralized with an aqueous solution of sodium carbonate (1%), washed thoroughly with water, and dried as usual.

Water Treatment

AMC sample (0.5 g) was placed in an Erlenmayer conical flask. To this, distilled water (20 ml) was added. The flask was then kept in a thermostat at a temperature high enough to make the content of the flask boil, for periods varying from 5 to 60 min.

Alkali Treatment

The action of sodium hydroxide on AMC was carried out under a variety of conditions. The general procedure adopted was as follows: AMC sample (0.5 g) was transferred to a stoppered Erlenmayer conical flask. A known concentration of aqueous sodium hydroxide solution (20 ml) was added and the reaction was allowed to proceed at a specific temperature for various intervals of time. Details of this is given in the discussion.

Treatment of AMC with ammonium hydroxide was performed at room temperature as follows: The AMC sample (0.5 g) was impregnated in ammonium hydroxide solution (20 ml) of known concentration for different lengths of time with continuous shaking. The concentrations used ranged from 0.27*N* to 14.2*N* while the reaction time was varied from 5 to 60 min.

Acid Treatment

AMC sample was treated with hydrochloric acid of known concentration at various conditions (see discussion). The experimental technique adopted was as follows: AMC sample (0.5 g) was impregnated in hydrochloric acid solution (20 ml) at a specific temperature for different periods of time. The treated sample was then washed with distilled water and air dried.

Determination of Double Bond

Reagent. The double bonds of acrylamide or its derivatives were determined as follows⁶: The acrylamide derivative (1–2 moles) in an amount of distilled water (10 ml) was treated with an aqueous solution of mercaptoethanol (3%, 10 ml) and sodium hydroxide solution (2*N*, 2 ml) and left for 15 min at room temperature in a closed vessel. The mixture was acidified with hydrochloric acid (1*N*, 5 ml), and after the addition of starch, it was titrated against a 0.1*N* iodine solution until disappearance of the blue color.

Fabric. The amount of double bonds on AMC was estimated according to the following procedure⁶: A finely divided sample of AMC (1–2 g) in distilled water (40 ml) was treated with an aqueous solution of mercaptoethanol (6%, 10 ml) and sodium hydroxide solution (2*N*, 5 ml) for 1 hr at 20°–25°C and under continuous shaking in a closed vessel. After acidification with hydrochloric acid (2*N*, 6 ml), titration was carried out against 0.1*N* iodine solution. A blank experiment was carried out using the same amount of fabric.

RESULTS AND DISCUSSION

Preparation of AMC

AMC is prepared by using N-methylolacrylamide or its ethers under the catalytic influence of ammonium chloride. In this case, the pad-dry-cure technique is employed. Attempts were also made to make use of the pad-batch technique for the preparation of AMC. This particular technique consists of padding the fabric in a solution containing N-methylolacrylamide or its ether, a cellulose swelling agent (75% magnesium chloride w/w), and hydrochloric acid as catalyst. The treated fabric is stored for 24 hr.

Figure 1 shows the effect of N-methylolacrylamide concentration on the extent of the reaction when the pad-cure technique and the pad-batch technique were employed. The extent of the reaction is expressed as mmole double bond per 1 g cellulose.

It is apparent that increasing the concentration of N-methylolacrylamide causes a substantial increase in the extent of the reaction. This is observed in both techniques. However, for a given concentration, the extent of reaction is considerably higher in case of the pad-cure method as compared with the pad-batch technique. The higher reactivity of N-methylolacrylamide at the elevated temperature of curing may account for this. It is rather possible that some of the pendent double bonds add hydrochloric acid during the batching stage and hence decreasing the amount of double

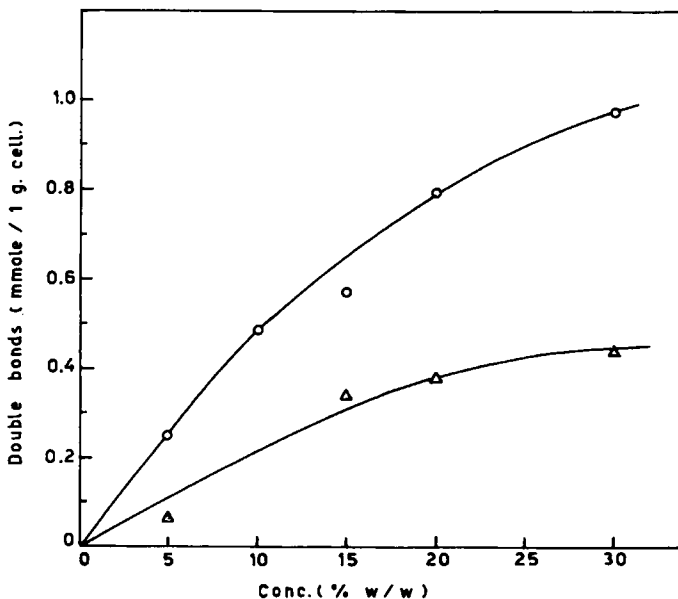


Fig. 1. Effect of N-methylolacrylamide concentration on the extent of reaction using the pad-cure method and pad-batch method: (○) pad-dry-cure method; (△) pad-wet-batch method.

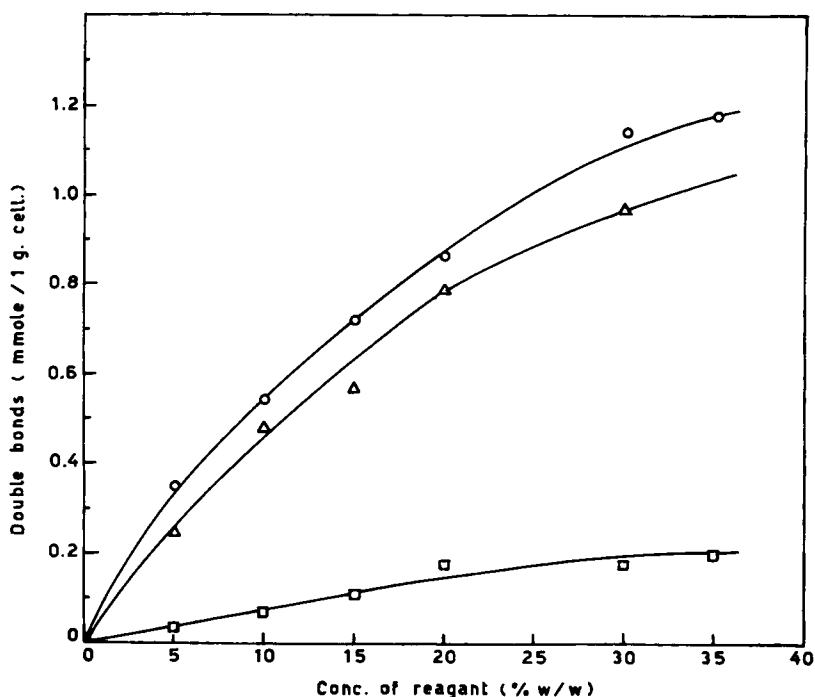


Fig. 2. Comparison between reactivity of N-methylolacrylamide and its two ether derivatives at different concentrations using the pad-dry-cure method: (○) N-methylolacrylamide; (△) N-methoxymethylacrylamide; (◻) N-methoxymethylmethacrylamide.

bonds already introduced. This certainly results in a decrease in the extent of reaction.

Figure 2 shows the reaction of N-methylolacrylamide, N-methoxymethylacrylamide, and N-methoxymethylmethacrylamide with cellulose at various concentrations using the pad-cure technique. Here, too, with the three reagents studied, the extent of reaction increases as the concentration of the reagent increases. But N-methylolacrylamide shows higher reactivity than N-methoxymethylacrylamide, and the latter shows much greater reactivity than N-methoxymethylmethacrylamide.

It appears that cleavage of the carbon-oxygen bond in case of N-methylolacrylamide to yield a carbonium ion which reacts with cellulose occurs more easily than cleavage of the same bond in case of N-methoxymethylacrylamide. This and the fact that the latter is more volatile than N-methylolacrylamide would account for the relatively lower reactivity of N-methoxymethylacrylamide.

On the other hand, the greatly inferior reactivity of N-methoxymethylmethacrylamide could be attributed to the presence of the methyl group at the α -carbon atom. This seems to cause two effects: (a) increasing the molecular weight of the reagent thereby decreasing its diffusion into the cellulose molecules for a reaction to occur, and (b) partially inhibiting the

cleavage of the carbon-oxygen bond of N-methoxymethylmethacrylamide, thus lowering its reactivity.

Based on the above findings, the AMC to be studied was prepared by reacting N-methylolacrylamide with cellulose using the pad-cure technique.

Chemical Behavior of AMC

Behavior in Neutral Medium

To start with, the effect of treatment of AMC having 0.9 mmole double bonds per 1 g cellulose with distilled water at the boil for various intervals of time was performed. It was observed that no change in the amount of the pendent double bonds of AMC occurred regardless of the duration of treatment. This indicates that under neutral conditions the vinyl groups are quite stable. It is not susceptible to the addition of neither water hydroxyl nor cellulose hydroxyl.

Behavior in Alkaline Medium

In order to understand the behavior of AMC in alkaline medium, the latter was treated with sodium hydroxide under a variety of conditions. Variables studied include alkali concentration as well as reaction time and temperature.

Alkali Concentration. The effect of sodium hydroxide concentration on the amount of double bonds of AMC is shown in Figure 3. Increasing the alkali concentration up to 0.5*N* is accompanied by a significant reduction

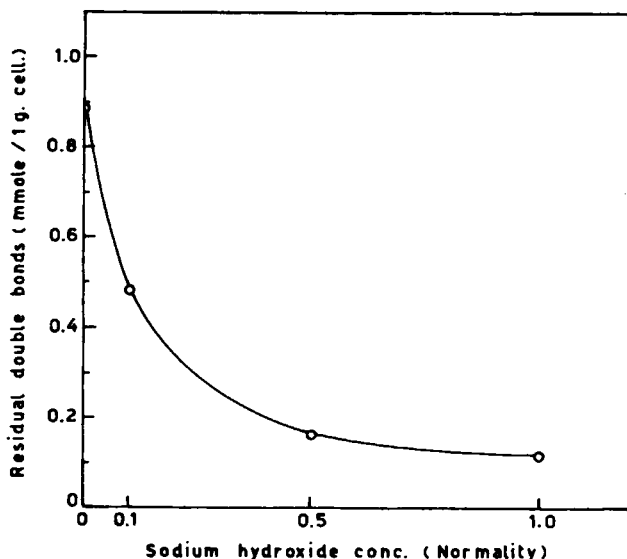


Fig. 3. Concentration of sodium hydroxide vs. residual double bonds of AMC. Reaction time of alkali treatment, 30 min; material:liquor ratio, 1:40; temperature, 70°C.

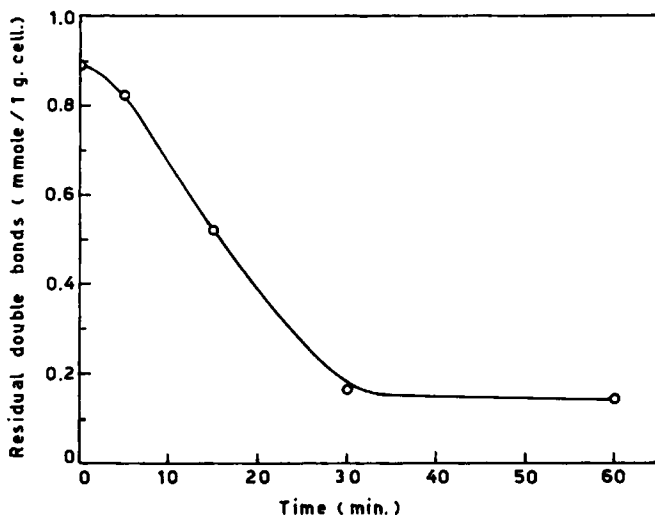


Fig. 4. Residual double bonds of AMC as a function of reaction time. Sodium hydroxide concentration, 0.5*N*; material:liquor ratio, 1:40; temperature, 70°C.

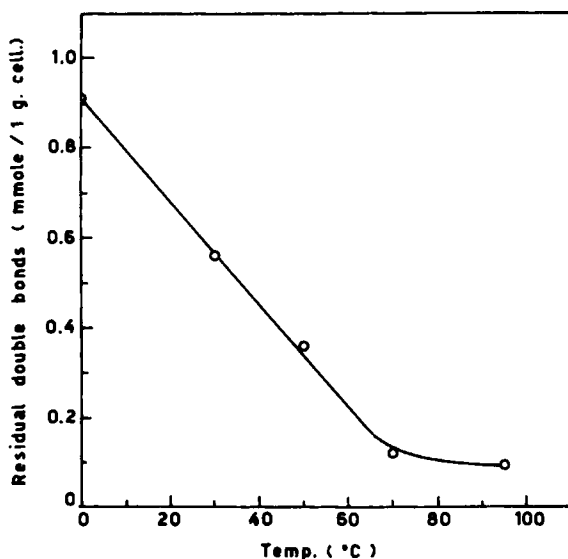


Fig. 5. Effect of reaction temperature on the consumption of double bonds of AMC. Sodium hydroxide concentration, 1*N*; material:liquor ratio, 1:40; reaction time, 30 min.

time between AMC and the alkali solution brings about a rapid fall in the amount of double bonds of AMC. This is observed up to a contact time of 30 min. Beyond this, no further reduction in the amount of double bond occurred. Here, again, about 15% of the double bonds remain intact.

The rapid fall in the amount of double bonds of AMC by reaction time is unequivocally due to the fact that at longer contact duration, there will be

a better chance for cellulose to swell and to ionize, thus facilitating the reaction to take place.

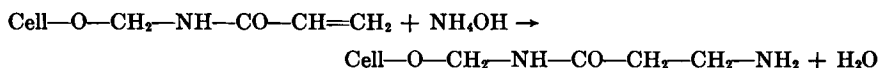
Temperature of the Reaction. In order to examine the effect of temperature on the reactivity of AMC, the latter was treated in 1*N* sodium hydroxide at 30°, 50°, 70°, and 95°C for 30 min. Results of this investigation are illustrated in Figure 5. It is clear that the amount of double bonds of AMC decreases significantly as the temperature was raised from 30° to 70°C. No further drop in the amount of double bonds was observed at higher temperature, i.e., 95°C. Here, also, it is interesting to note that no full consumption of the double bonds was attained.

The fast rate of disappearance of double bonds at higher temperatures could be anticipated in view of the greater swellability of cellulose and ionizability of its hydroxyls. A temperature of 70°C or more seems to constitute an optimum at which a reaction can proceed best.

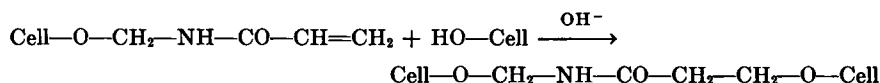
Treatment with Ammonium Hydroxide

Figure 6 shows the residual double bonds of AMC as a function of reaction time when AMC was treated with different concentrations of ammonium hydroxide. It is clear that the extent of disappearance of double bonds of AMC increases by increasing the reaction time, the disappearance being more significant at higher concentration of ammonium hydroxide. However, no full consumption of the double bonds was attained in any of the three concentrations studied. For instance, a disappearance of about 60% of the double bonds of AMC was achieved when the latter was treated with 0.78*N* ammonium hydroxide at room temperature for 60 min. A similar treatment but with higher concentrations of ammonium hydroxide resulted in an enhancement of the double bond consumption; full consumption was observed at a concentration of ca. 14*N*. This may be realized from Figure 7.

The disappearance of double bonds could be ascribed to the following reasons: (1) addition of ammonia to the double bonds of AMC:



(2) addition of adjacent cellulose hydroxyls to the double bonds of AMC, i.e., crosslinking, under the catalytic influence of the alkaline medium of ammonium hydroxide:



(3) addition of the elements of water to the double bonds of AMC in the presence of ammonium hydroxide:

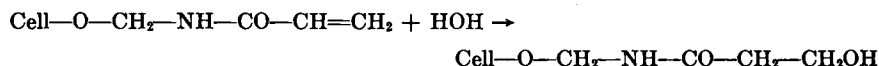


TABLE I
Variation in Crease Recovery of AMC with Different Treatments

Treatment	Crease recovery	
	Dry	Wet
Untreated cellulose	105	165
AMC	169	229
AMC + NH ₄ OH (14.2 <i>N</i> , 1 hr)	268	292
AMC + NH ₄ OH (14.2 <i>N</i> , 1 hr) + NH ₄ Cl (1%), baking at 150°C for 4 min	260	284

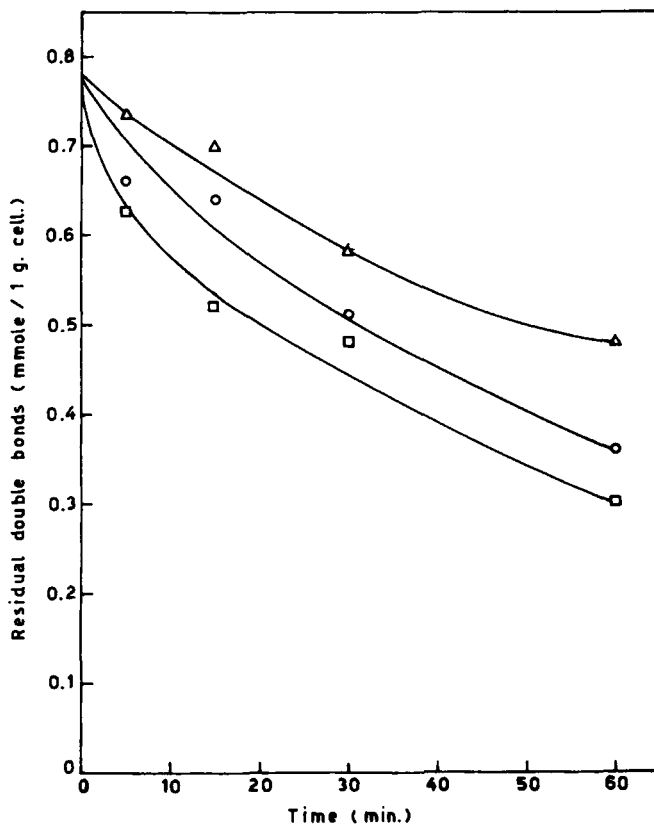


Fig. 6. Residual double bonds of AMC vs. reaction time of ammonium hydroxide treatment. Material:liquor ratio, 1:40; temperature, 25°C; (Δ) 0.27*N* ammonium hydroxide; (\odot) 0.51*N*, ammonium hydroxide; (\square) 0.78*N* ammonium hydroxide.

The first reason can be ruled out, since no increment in the nitrogen content was detected after treating AMC with ammonium hydroxide. The validity of the second reason is apparent from the significant increase in wrinkle recovery of AMC after being treated with ammonium hydroxide (cf. Table I).

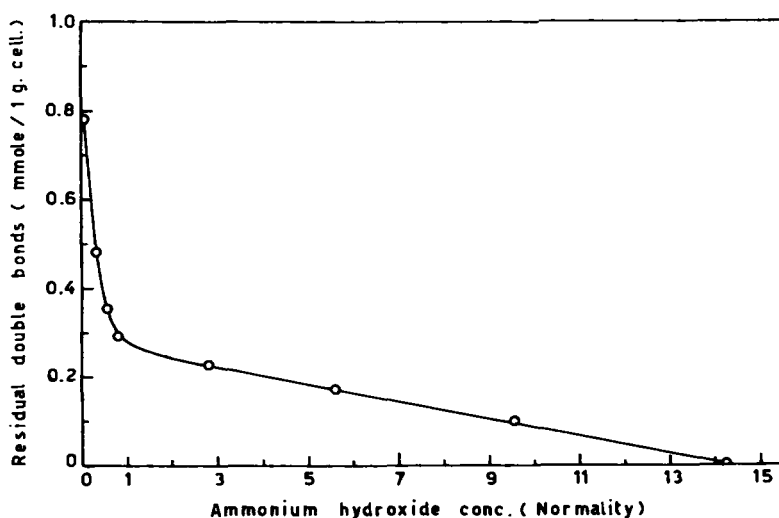


Fig. 7. Effect of ammonium hydroxide concentration on the disappearance of double bonds of AMC. Material:liquor ratio, 1:40; temperature, 25°C; reaction time, 60 min.

To check the validity of the third possibility, AMC was treated with 14.2*N* ammonium hydroxide at room temperature for 1 hr. After being thoroughly washed and dried, the sample was impregnated in 1% ammonium chloride solution, squeezed to ca. 90% pickup, dried at room temperature, and then cured at 150°C for 4 min. Such treatment, it was thought, would cause an improvement in wrinkle recovery, particularly in the dry state perhaps due to the presence of $-\text{CH}_2\text{OH}$ groups. The results in Table I do not agree with the expectation. On the contrary, a decrease in the wrinkle recovery was observed, probably owing to breaking of some of the preformed crosslinks under the acidic conditions during the curing stage.

Behavior in Acidic Medium

As already pointed out, *N*-methylol resin compounds react with cellulose to give crosslinks and/or resinification products in cellulose. Removal of the "resin" from cellulosic fabrics depends mainly on the hydrolysis of the $\text{N-CH}_2\text{-O-Cell}$ bonds. For this to occur, several conditions of acid hydrolysis have been published.^{7,8} Data are presented here on the effect of acid treatment on AMC under various conditions to establish the tolerance of the pendent acrylamidomethyl groups to acid hydrolysis. Furthermore, addition of the acid to the double bonds of the pendent groups is also elucidated.

Since the main aim of the study is to outline the activity of cellulose due to the presence of the double bonds, attention has been paid to determine them after acid treatment. However, the possibility of addition of the acid to the double bonds have been checked as follows: AMC having

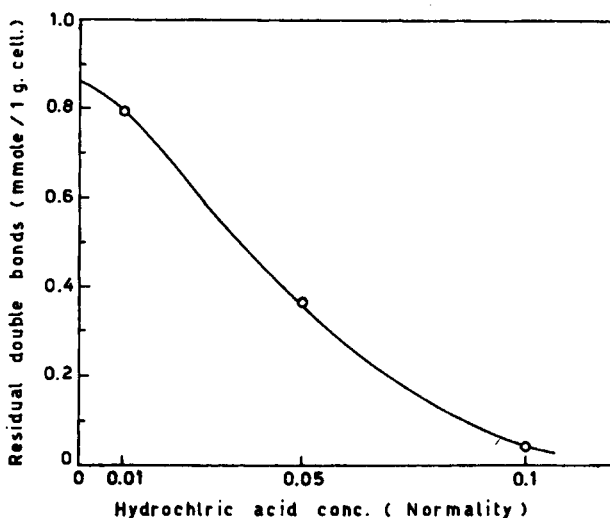


Fig. 8. Influence of concentration of hydrochloric acid on the disappearance of double bonds of AMC. Material: liquor ratio, 1:40; temperature, 70°C; reaction time, 30 min.

10.80 mmoles double bonds per 1 g cellulose was treated with 0.05*N* hydrochloric acid at 70°C for 30 min. The residual acrylamidomethyl groups were determined either via the double bond estimation using the mercaptoethanol iodine procedure or via nitrogen analysis using the Kjeldahl method. Both methods have been reported to give identical results.²

It was observed that measuring the acrylamidomethyl groups of AMC after acid treatment by determining double bonds resulted in disappearance of 98.8% of the original groups, whereas measuring the same groups by estimation of nitrogen content revealed only a disappearance of 33.3% of the original groups. This discrepancy indicates that during acid treatment of AMC, some of the double bonds of acrylamidomethyl groups disappeared due to acid hydrolysis and some of them disappeared due to addition of the acid to the double bonds of these groups. Hence, the word "disappearance" of double bonds which will be used below corresponds to partial splitting of the groups by acid hydrolysis as well as to addition of the acid to the double bonds.

Concentration of the Acid. The effect of acid concentration on the pendent acrylamidomethyl groups of AMC may be realized from Figure 8. The acid treatment was carried out at 70°C for 30 min using a liquor ratio of 40. Obviously, 0.01*N* hydrochloric acid leaves the amount of the pendent groups practically unaltered, whereas using a concentration of 0.05*N* of the same acid resulted in partial disappearance of the pendent groups. On the other hand, a concentration of 0.1*N* hydrochloric acid caused a disappearance of about 95% of the pendent groups. Reason for this is that at higher concentration of the acid, the possibility of addition of the latter to the double bonds would be enhanced. Further, the activation energy is enough to cause rupture of the N—CH₂—O—Cell bond.

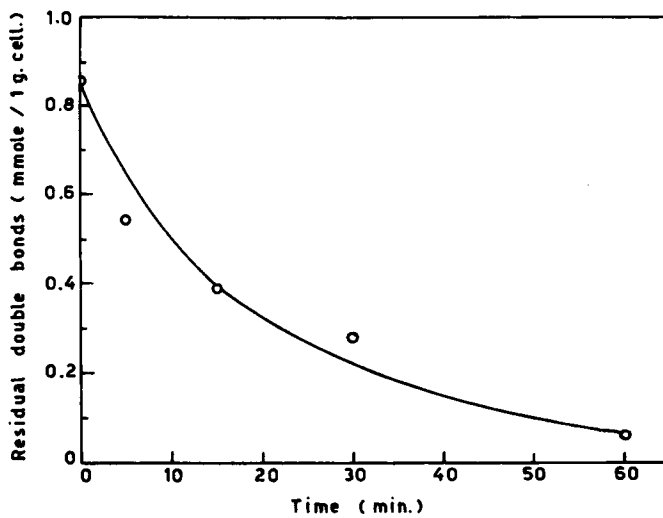


Fig. 9. Reaction time of hydrochloric acid treatment as a function of residual double bonds of AMC. Hydrochloric acid concentration, 0.05*N*; material:liquor ratio, 1:40; temperature, 70°C.

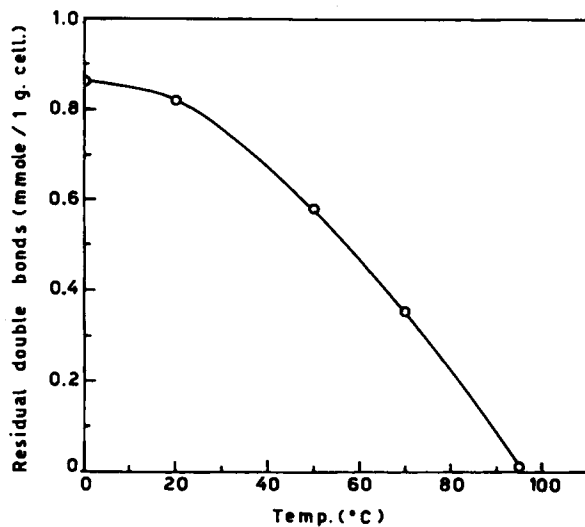


Fig. 10. Effect of temperature of hydrochloric acid treatment on the disappearance of double bonds of AMC. Hydrochloric acid concentration, 0.05*N*; material:liquor ratio, 1:40; reaction time, 30 min.

Duration of Acid Treatment. In order to investigate the effect of time of acid treatment on the pendent groups of AMC, the latter was treated with 0.05*N* hydrochloric acid at a temperature of 70°C and a liquor ratio of 40 for various intervals of time. Results of this investigation are shown in Figure 9.

It is apparent that prolonging the time of acid treatment is accompanied by a significant increase in the disappearance of the double bonds. This is expected, since enough time of contact between AMC and the acid will allow the reaction to proceed both through addition of the acid to the double bonds and splitting off of the pendent groups. It is also likely that the pendent groups to which hydrochloric acid was added splits off at longer time of contact.

Temperature of Acid Treatment. Figure 10 shows the effect of temperature of acid treatment on the acrylamidomethyl groups of AMC. The treatment was performed in 0.05*N* hydrochloric acid for 30 min using a liquor ratio of 40. As can be seen, the effect of raising the temperature is to bring about a significant influence on the disappearance of the pendent groups of AMC. A temperature of 30°C has practically no effect on the pendent groups. Treatment at 50°C causes a considerable scission and/or addition of hydrochloric acid to the double bonds of the pendent groups. Complete disappearance of these double bonds occurred at a temperature of 95°C under the conditions studied.

By increasing the temperature of acid treatment, the activation energy of the system increases. As a result, the chance of rupturing of the N—CH₂—O—Cell bond as well as addition of hydrochloric acid to the CH₂=CH bond will be greater. The possibility of splitting off of the pendent groups to which hydrochloric acid was added would also be there, thereby decreasing the amount of the pendent groups.

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