Synthesis and Applications of Reactive Carbohydrates. IV. Reactive Finishes Based on CMC and Oxidized CMC Copolymers

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Synopsis

Carboxymethyl cellulose (CMC) and persulfate-oxidized CMC samples were assessed for acidic and reducing properties before and after graft copolymerization with acrylamide using $K_2S_2O_8$ as initiator. The acidic properties were expressed as milliequivalents of carboxyl groups/100 g CMC while the copper number was taken as a measure for the reducing properties. Results obtained signify that increasing the duration of persulfate oxidation from 15 to 60 min causes a significant enhancement in the carboxyl content of CMC particularly during the first 50 min of oxidation. The same holds true for the copper number, but no further significant enhancement could be observed after 30 min. The copolymerization reaction decreases substantially the acidic and reducing groups of the CMC substrates examined. The results showed also that oxidation of CMC increases its susceptibility toward grafting: The higher the extent of oxidation, the higher the extent of grafting. Methylolation of the polyacrylamide–CMC graft copolymers results in reactive finishes. The latter were applied either alone or together with etherified methylolated melamine to cotton fabric samples according to the conventional pad–dry–cure method. The treated samples withstand severe washing, suggesting the occurrence of chemical bonding between the methylolated CMC products and cotton.

INTRODUCTION

The instability of prices and dwindling supplies of petroleum have evoked considerable interest for utilization of natural polymeric products such as cellulose and starch as raw materials in the chemical industry. By way of example, mention is made of the utilization of carboxymethyl cellulose (CMC) in the textile chemical technology. CMC is used in printing pastes,[1-5] sizes,[6,7] and finishes.[8,9]

In the previous parts[10-12] of this series, we have reported on the synthesis and properties of different hydrolyzed starches and carboxymethyl starches as well as carboxymethyl celluloses. Included also in these reports were studies of graft copolymerization of these substrates with acrylamide and methylolation of the copolymers so formed as a means for producing reactive finishes having different characteristics.

In this work, oxidation of CMC with potassium persulfate is conducted with a view of studying the effect of oxidation on the acidic and reducing properties of CMC as well as the susceptibility of the latter toward graft copolymerization with acrylamide. The onset of grafting on the reducing and acidic properties of CMC is also reported. Furthermore, methylolation of the

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copolymerized products and their application to cotton fabric are investigated.

EXPERIMENTAL

Materials

Carboxymethyl cellulose (CMC) having 258 meq COOH/100 g cellulose was of technical grade. Potassium persulfate ($K_2S_2O_8$), acrylamide (Aam), formaldehyde (37%), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) and ammonium chloride (NH_4Cl) were of laboratory grade. Etherified methylolated melamine (EMM) was of technical grade.

Oxidation Procedure

Samples of CMC were steeped in aqueous solution of potassium persulfate (60 mmol/L) at 80°C for different periods of time (15–60 min), keeping a material-to-liquor ratio of 1 : 10. After the desired oxidation time, ethyl alcohol was added to the reaction mixture and agitated. The reaction product was then filtered, washed with 80% aqueous ethyl alcohol, and dried in the air at room temperature.

Copolymerization Procedure

Unless otherwise stated, the graft copolymerization was carried out as follows. The CMC sample was introduced in a solution consisting of potassium persulfate (60 mmol/L) and acrylamide (40% based on the weight of the sample) at 50°C, keeping a material-to-liquor ratio of 1:20. The reaction was allowed to proceed for 30 min. At the end, ethyl alcohol was added to the reaction mixture and agitated. The product was then filtered, washed with 80% aqueous ethyl alcohol to remove homopolymer, and air-dried at room temperature.

Methylolation Procedure

The grafted sample (ca. 20 g) was dissolved in 220 mL of water at 60°C for 15 min in a stoppered conical flask. After complete dissolution, it was cooled down to room temperature, and 30 mL of 37% formaldehyde were added. The pH was adjusted to 9 by a dilute solution of sodium carbonate. The methylolation reaction was conducted at room temperature for 12 h. Precipitation of the methylolated product in ethyl alcohol followed by drying resulted in a product which is difficult to dissolve in water most probably due to partial conversion to crosslinked product. Hence, it was applied to the cotton fabric from its solution which contained 5% of reactive solid.

Application of the Methylolated Products

Unless otherwise stated, sample of bleached plain weave (23 ends × 23 picks) was impregnated in a solution containing the methylolated product (50 g/L) and magnesium chloride hexahydrate (10 g/L) for 5 min at room temperature followed by squeezing to a wet pick up of ca. 90%, drying at 70°C

for 5 min and then curing at 160°C for 3 min. After curing, the sample was rinsed in running tap water for 5 min, squeezed, and finally air-dried.

Analysis

The carboxyl content was determined by the alkalimetry method,[13] and the copper number by the micro Braidly method as modified by Heyes.[14] The graft yield was expressed as percent nitrogen (N%) and the latter was determined by the Cole and Parks modification of Semimicro Kjeldehl method.[15] Total formaldehyde was determined according to a method described elsewhere.[16, 17]

RESULTS AND DISCUSSION

In order to achieve the objective cited above for this work, oxidation of CMC with potassium persulfate was carried out at 80°C for different periods of time ranging from 15 to 60 min. The acidic and reducing properties of the oxidized CMC samples along with those of the original CMC sample were monitored before and after graft copolymerization with acrylamide, using also potassium persulfate but in this case as initiator for the copolymerization reaction. The onset of oxidation of CMC on its susceptibility towards the copolymerization reaction was clarified, and methylolation of the CMC copolymers and their application to cotton fabric were performed. Results obtained along with their appropriate discussion are given below.

Acidic Properties

Figure 1 shows the effect of the duration of persulfate oxidation on the acidic properties of CMC, expressed as meq carboxyl group/100 g CMC. It is seen that the carboxyl content of CMC increases significantly by increasing the duration of oxidation from 15 to 60 min. Nevertheless, significant enhancement in the carboxyl content is only observed during the first 30 min oxidation. That is, the oxidation reaction is characterized by an initial fast rate followed by a slower rate. At any event, enhancement in the carboxyl content of CMC is a direct consequence of the oxidative attack of the decomposition products of the persulfate[18, 19] on the aldehydic and hydroxyl groups of CMC. On the other hand, slowing down of the rate of oxidation during the later stages of the reaction is due to depletion in persulfate concentration along with structural changes occurring in CMC as the oxidation reaction proceeds. Oxidized CMC formed during the initial stages of the reaction seems to be less susceptible towards further oxidation.

Figure 1 shows also that graft copolymerization of the original CMC and oxidized CMC samples with acrylamide causes significant decrement in their carboxyl content, in contrast with previous report dealing with similar studies on acid-hydrolyzed CMC samples.[10] It is certain, however, that the carboxyl content of the oxidized CMC samples is still much higher than that of the original CMC sample.

The decrement in the carboxyl content of the CMC samples after copolymerization suggests formation of highly soluble short chains CMC copolymers which are difficult to recover the courses of precipitation and filtration.
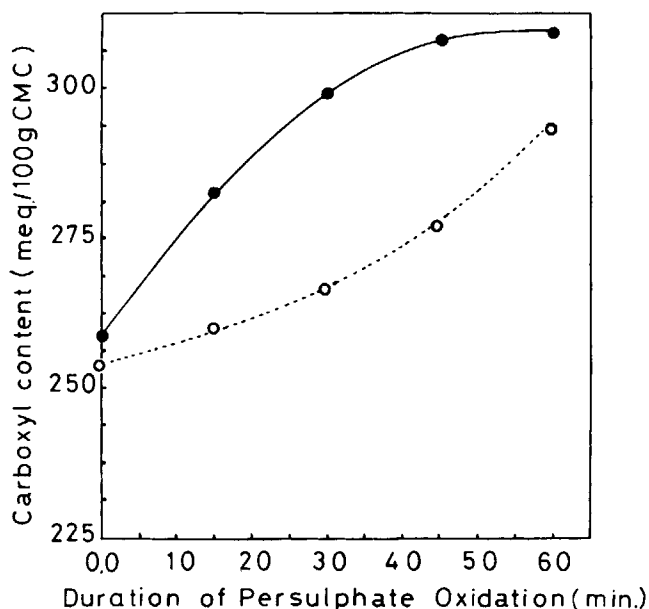
Fig. 1.   Effect of duration of persulfate oxidation on carboxyl content of CMC before and after grafting: (-●-) before grafting; (··· O ···) after grafting. Oxidation conditions [$K_2S_2O_8$], 66 mmol/L; temp, 80°C; material to liquor ratio, 1/10. Grafting conditions: [Aam], 40% based on weight of sample; [$K_2S_2O_8$], 60 mmol/L; temp, 50°C; time, 30 min; material to liquor ratio, 1 : 10.

It is also likely that some of the acidic groups (carboxylmethyl and/or carboxyl groups) of the CMC samples form strong salt linkages with the amide groups of the graft, thereby making them unavailable for determination. As a result, the carboxyl content apparently decreases.

Reducing Properties

Figure 2 shows the effect of duration of persulfate oxidation on the reducing properties of CMC, expressed as copper number. As is evident, the copper number increases significantly by increasing the duration of oxidation up to 30 min. Beyond this, the enhancement in copper number proceeds through a much slower rate. This is rather the trend observed with the acidic properties and could be explained on a similar basis. It is understandable that creation of reducing aldehydic groups in the molecular structure of CMC is unequivocally due to the oxidation of the CMC hydroxyls under the oxidative action of the decomposition products of the persulfate. The results indicate that this copolymerization decreases the copper number of the oxidized samples while leaving the copper number of the original CMC sample intact, but with the certainty that the copper number value of the latter is still much smaller than those of the former. The oxidized CMC samples, by virtue of their high reducing properties, seem to form an effective redox system for initiation of graft copolymerization in addition to oxidation of the aldehydic groups to carboxylic groups. Stated in other words, the decrement in the copper number of the oxidized CMC samples after copolymerization could be ascribed to
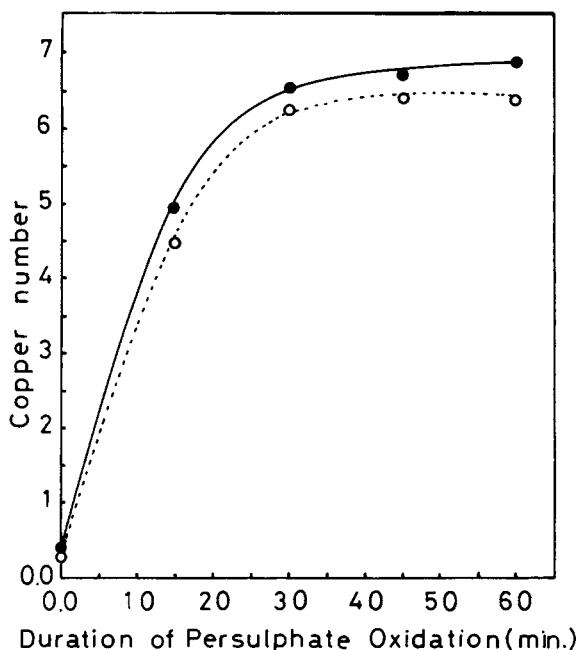
Fig. 2. Effect of duration of persulfate oxidation on the copper number of CMC before and after grafting: (–●–) before grafting; (· · · O · · ·) after grafting. Oxidation conditions: [$K_2S_2O_8$], 60 mmol/L; temp, 80°C; material to liquor ratio, 1 : 10. Grafting conditions: [Aam], 40% based on weight of sample; [$K_1S_2O_8$], 60 mmol/L; temp, 50°C; time, 30 min; material to liquor ratio, 1 : 10.

partial conversion of the aldehydic groups to carboxylic groups under the oxidative action of the initiator (i.e., $K_2S_2O_8$) during grafting, in accordance with previous reports.[10–12]

It is as well to note that the response of the oxidized CMC samples to oxidation—under the very mild conditions of the graft copolymerization—is due to abundance of aldehydic groups within their molecules. This is not the case with the original CMC sample with which the hydroxyl groups are abundant. It is well known that the hydroxyl groups are less susceptible to oxidation than the aldehydic groups. This would account for the finding that CMC did not respond to oxidation by the initiator during the graft copolymerization reaction.

Graft Copolymerization with Acrylamide

Figure 3 shows the rates of graft copolymerization of acrylamide onto the original CMC sample and the 60 min-oxidized CMC sample using $K_2S_2O_8$ as initiator. It is observed that, with both substrates, the grafting reaction proceeds initially very fast and then slows down in time. This could be associated with the decrement in monomer and initiator concentration, shortage of available grafting sites (CMC hydroxyls), structural changes in the substrate, and the magnitude of grafting vis-à-vis homopolymerization as the polymerization reaction proceeds. However, leveling off of grafting occurs after 60 min in the case of the oxidized CMC sample while grafting continues to proceed for up to 120 min in the case of the original CMC sample.
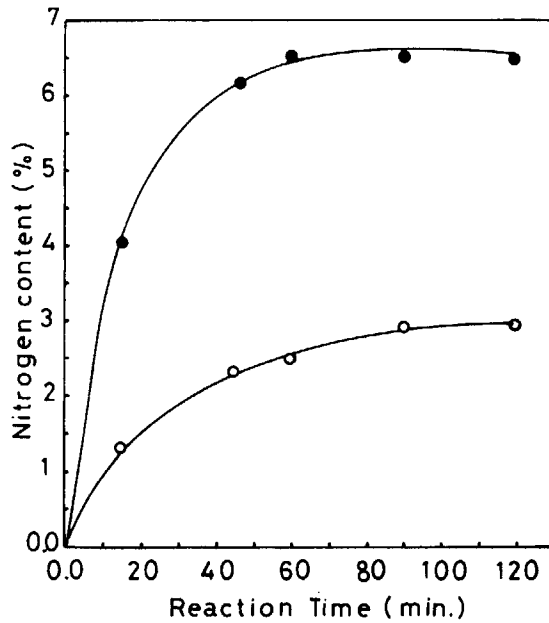
Fig. 3. Rates of graft copolymerization of acrylamide onto original CMC and 60 min-oxidized CMC samples: (O) original CMC; (●) 60 min-oxidized CMC. Oxidation conditions: [$K_2S_2O_8$], 60 mmol/L; temp, 80°C; time, 60 min; material to liquor ratio, 1 : 10. Grafting conditions: [Aam], 40% based on weight of sample; [$K_2S_2O_8$], 60 mmol/L; temp, 50°C; material to liquor ratio, 1 : 10.
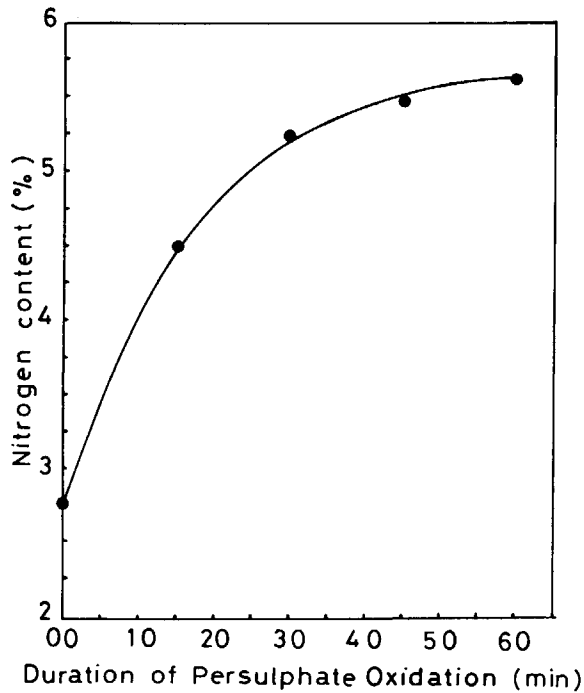

Fig. 4. Susceptibility of CMC and different oxidized CMC samples towards graft copolymerization with acrylamide. Oxidation conditions: [$K_2S_2O_8$], 60 mol/L; temp, 80°C; material to liquor ratio, 1 : 10. Grafting conditions: [Aam], 40% based on weight of sample; [$K_2S_2O_8$]. 60 mmol/L; temp, 50°C; time, 30 min; material to liquor ratio, 1 : 10.

TABLE I
Analysis of Fabric Samples Treated with Reactive CMC Products

Methylolated product derived from the copolymer of	add-on (%)		Retained add-on (%)	Total HCHO (%)		Retained total HCHO (%)	N%		Retained N(%)
	a	b		a	b		a	b	
Original CMC	1.93	1.39	72.02	0.801	0.576	71.91	0.181	0.132	72.92
15 min-oxidized CMC	2.30	1.84	80.80	0.850	0.680	80.00	0.318	0.254	79.87
30 min-oxidized CMC	2.35	2.21	94.04	0.882	0.828	93.87	0.400	0.374	93.5
45 min-oxidized CMC	2.40	2.25	93.75	0.881	0.824	93.53	0.410	0.384	93.65
60 min-oxidized CMC	2.40	2.25	93.75	0.883	0.830	93.99	0.412	0.388	94.17

[Methylolated copolymers], 50 g/L; [MgCl$_2$ · 6H$_2$O], 10 g/L, curing temp, 160°C; curing time 3 min.
[a] The treated fabric was rinsed in running tap water.
[b] The treated fabric was rinsed in running tap water, soaped with solution containing 2 g/L detergent at 60°C for 15 min and then washed thoroughly with tap water.

Furthermore, the extent and rate of grafting of the oxidized CMC sample are much higher than those of the original CMC sample.

The above findings imply that oxidation of CMC with persulfate prior to grafting enhances significantly the susceptibility of CMC towards grafting. The highly reducing characteristic of the oxidized CMC enables the latter to act efficiently as a reductant capable of forming strong redox system with the initiator (i.e., $K_2S_2O_8$), thereby leading to higher grafting.

Figure 4 shows the graft yield, expressed as %N, obtained with the original CMC sample and different oxidized CMC samples versus duration of oxidation. Obviously, the susceptibility of CMC towards grafting increases significantly by increasing the duration of oxidation, a point which confirms the foregoing findings. Similar observations were also reported when CMC, starch or carboxymethyl starch (CMS) was subjected to acid treatment.[10-12]

Reactive Finishes

Reactive finishes based on CMC were prepared by converting the $CONH_2$ groups of the poly(Aam)–CMC and poly(Aam)–oxidized CMC graft copolymers to methylol groups. The methylolated products either alone or together
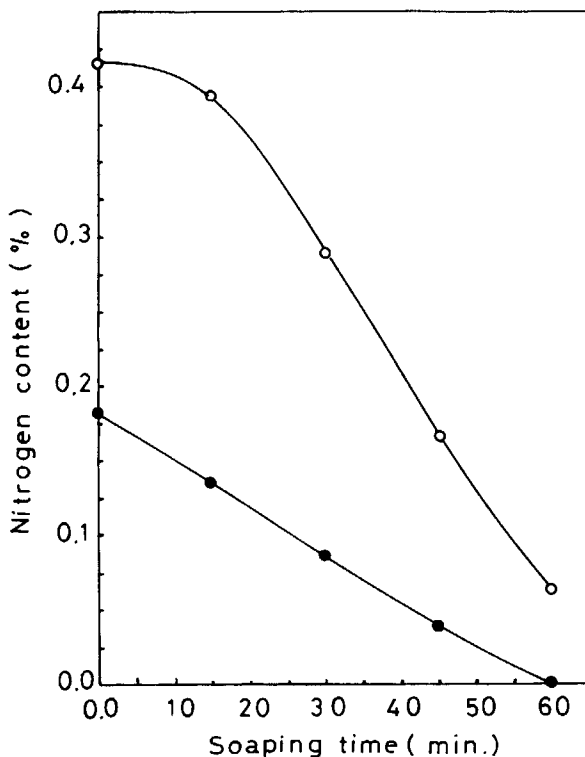

Fig. 5.   Effect of duration of soaping on nitrogen content of fabric treated with methylolated poly(Aam)–CMC copolymers: (●) original CMC; (○) 60 min-oxidized CMC. Treatment conditions: [methylolated copolymer], 50 g/L; [$MgCl_2 \cdot 6H_2O$], 10 g/L; pH, 7; curing temp, 160°C; curing time 3 min. Soaping conditions: [detergent], 2 g/L; temp, 60°C.

with etherified methylolated melamine (EMM) were applied to samples of
bleached plain weave cotton fabric according to the conventional pad–dry–cure
method. Preparation of the methylolated copolymers and their application are
given in detail in the experimental section. The cotton samples were then
monitored for add-on, total formaldehyde, and nitrogen content. The results
obtained are set out in Table I.

It is seen (Table I) that the add-on, nitrogen content, and total formalde-
hyde of fabric samples treated with the methylolated products of the oxidized
CMC are higher than their corresponding products derived from the original
CMC. Meanwhile there is no significant difference in the values of these
properties among samples treated with the oxidized CMC, with the exception
of that treated with 15 min oxidized CMC which acquires lower values. This
trend persists even after soaping the treated fabric samples in a solution
containing 2 g/L detergent at 60°C for 15 min followed by a thorough
washing with tap water.

However, a close examination of the results of Table I would indicate that
the fabric sample treated with the methylolated product of original CMC
retains about 72% of this finish after soaping and washing. This is against an
average of 94% for the methylolated products of oxidized CMC irrespective of
the duration oxidation. The higher percentage of retained finish observed with
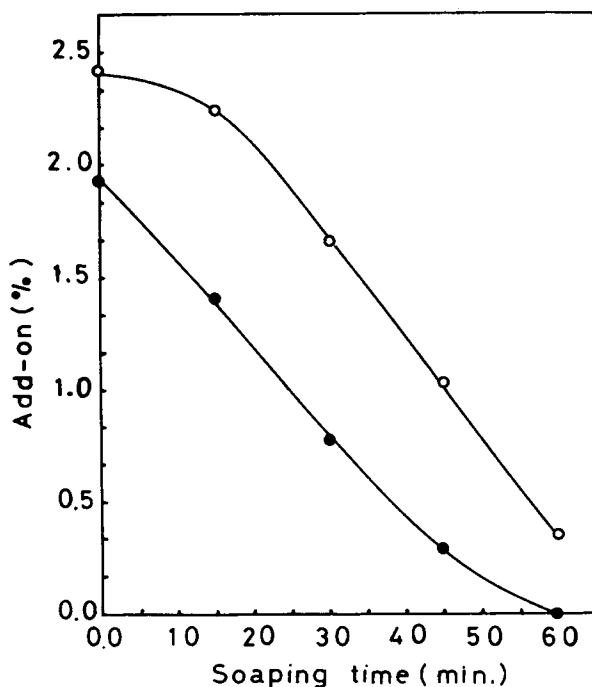the methylolated products of oxidized CMC as compared with their mate

Fig. 6. Effect of duration of soaping on percent add-on of fabric treated with methylolated
poly(Aam)–CMC copolymers: (●) original CMC; (○) 60 min-oxidized CMC. Treatment condi-
tions: [methylolated copolymer], 50 g/L; [$MgCl_2 \cdot 6H_2O$], 10 g/L; ph, 7; curing temp, 160°C;
curing time, 3 min. Soaping conditions: [detergent], 2 g/L; temp, 60°C.

derived from the original CMC reflects differences in ability to diffuse in, adsorb on, and interact with the cotton cellulose.

Figures 5 and 6 show the ability of fabric samples treated with the methylolated products of the original CMC and the 60 min-oxidized CMC to withstand soaping for different periods of time. Obviously, the amount of the finish, expressed as add-on and %N, decreases sharply as the duration of soaping increases, but with the certainty that the retained finish is higher with fabric sample treated with the methylolated product of oxidized CMC than the sample treated with the methylolated product of original CMC. Absence of chemical reaction of the methylolated CMC products and cotton cellulose (fabric) under the application conditions used seems to be responsible for the sharp decrement in the amount of the finish by washing for increasing periods of time.
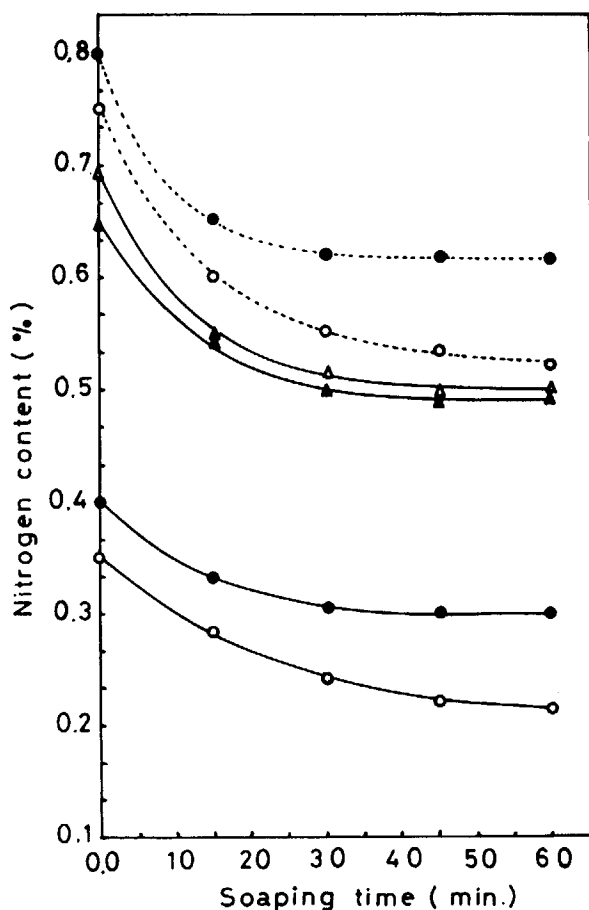

Fig. 7.   Effect of duration of soaping on nitrogen content of fabric treated with reactive CMC finishes in the presence and absence of EMM: (-○-), 50 g/L methylolated product of original CMC; (---○---), 25 g/L methylolated product of original CMC + 25 g/L EMM; (-●-), 50 g/L methylolated product of 60 min-oxidized CMC; (---●---), 25 g/L methylolated product of 60 min-oxidized CMC + 25 g/L EMM; (△) 25 g/L original CMC + 25 g/L EMM; (▲) 25 g/L EMM; treatment conditions: [NH$_4$Cl], 10 g/L; pH, 3; curing conditions, 140°C; time 5 min.
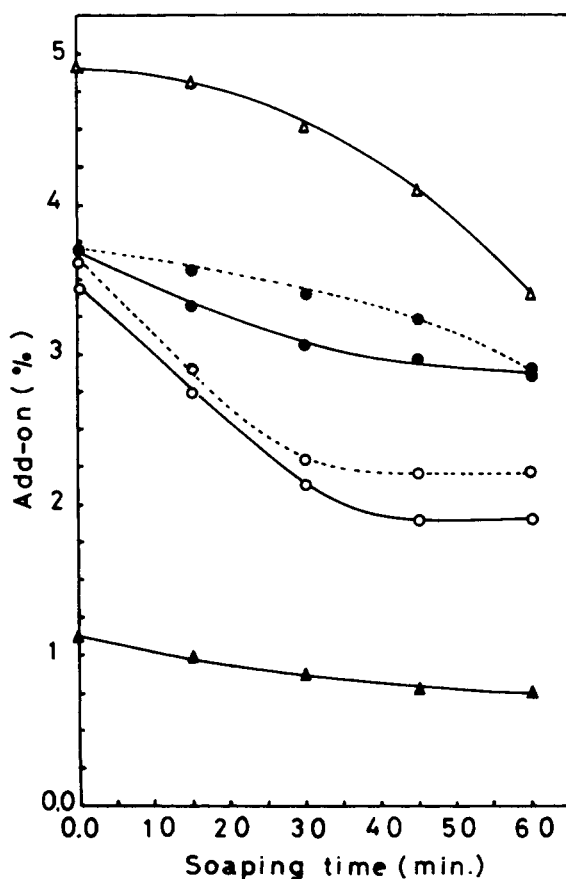
Fig. 8.   Effect of duration of soaping on add-on percentage of fabric treated with reactive CMC finishes in presence and absence of EMM: (- O -) 50 g/L methylolated product of original CMC; (--- O ---) 25 g/L methylolated product of original CMC + 25 g/L EMM; (-●-) 50 g/L methylolated product of 60 min-oxidized CMC; (---●---) 25 g/L methylolated product of 60 min-oxidized CMC + 25 g/L EMM; (△) 25 g/L original CMC + 25 g/L EMM; (▲) 25 g/L EMM. Treatment conditions: [NH₄Cl], 10 g/L; pH, 3; curing conditions, 140°C; time, 5 min.

To ensure chemical attachment of the methylolated CMC copolymers to the cotton fabric, the latter was treated with the former either alone or together with EMM using NH_4Cl as a catalyst instead of $MgCl_2 \cdot 6H_2O$. The treated fabric samples were then subjected to soaping for different duration followed by rinsing thoroughly with water and drying. Results of analysis of the treated fabric before and after washing are given in Figures 7 and 8.

It is clear (Figs. 7 and 8) that the amount of the finish decreases substantially only during the first 30 min of washing and then remains almost constant, particularly with the fabric sample treated with the methylolated product of the oxidized CMC. This is observed in the presence and absence of EMM, suggesting the occurrence of chemical bonds between the methylolated CMC copolymers and the cotton cellulose of the fabric. Needless to say, the initial substantial decrease in the amount of the finish is unequivocally due to removal of unreacted and surface adhered chemicals.
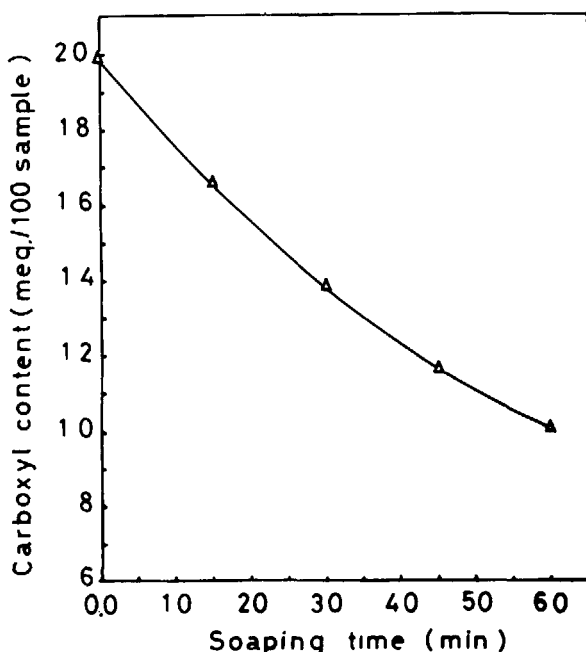
Fig. 9. Effect of duration of soaping on carboxyl content of fabric treated with original CMC in presence of EMM: (△) 25 g/L original CMC + 25 g/L EMM. Treatment conditions: [NH$_4$Cl], 10 g/L; pH, 3; curing temp, 140°C; curing time 5 min.

Figure 9 shows the effect of duration of soaping on the amount of finish on the cotton fabric when the latter was treated with original CMC in the presence of EMM using NH$_4$Cl as a catalyst. The amount of CMC finish is expressed as meq carboxyl group/100 g sample. As is evident, the amount of the finish decreases progressively by prolonging duration of soaping within the range examined. Due to the absence of the reactive methylol group in the CMC used, attachment of the latter to the cotton fabric will occur via physical forces. Chemical bonding between cotton and CMC is only possible in the case under investigation through EMM bridging. This possibility is rather questionable and, indeed, the continuous fall in the amount of the CMC finish observed in Figure 9 substantiates the chemical bonding suggested above for the methylolated product of CMC finish.

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