Novel Application of Partial Carboxymethylation in the Wet Processing of Linen Fabric

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ABSTRACT: Scoured linen fabrics were treated with NaOH at different concentrations (1–7*N*). Unscoured (gray) linen fabrics were modified via partial carboxymethylation under different conditions, including monochloroacetic acid concentration (1–4*N*), sodium hydroxide concentration (0.5–3.5*N*), reaction time (30–180 min), and reaction temperature (30–90°C). Alkali treated and partially carboxymethylated linen fabrics were bleached using H_2O_2 (20 g/L), sodium silicate (3 g/L), and nonionic wetting agent (1 g/L) at pH 10 for 150 min at 95°C. The unbleached and bleached linen fabrics (alkali treated and partially carboxymethylated) were assessed for technical properties, namely, whiteness index (W.I.), loss in fabric weight, copper number, carboxyl content, and H_2O_2 decomposition percent. A comparison was made between the properties of the two substrates. It indicates that the properties of partially carboxymethylated linen fabric were comparable, if not superior, to alkali treated linen fabric. Hence it is advantageous to introduce partial carboxymethylation in the wet processing of linen fabrics since scouring and alkali treatment can be omitted. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 996–1001, 2007

Key words: carboxymethylation; linen; wet processing; alkali treatment; bleaching

INTRODUCTION

A perusal at the literature reveals that flax cellulose has been chemically modified via partial carboxymethylation under conditions that have been used generally for cotton cellulose[1–3]. Chloroacetic acid reacts with the hydroxyl groups in flax-cellulose in presence of caustic soda to yield the partially carboxymethylated flax. Bleached flax fibers were used as starting material for carboxymethylation.

In this work a novel application of partial carboxymethylation of linen fabrics in the wet processing is introduced with the primary objective of improving fabric properties without increasing the number of the conventional operations in wet processing. It seems logical to perform the partial carboxymethylation on gray linen fabric. In general the wet processing prior to dyeing or final finishing of linen fabrics involves scouring, bleaching, and sometimes alkali treatment. Knowing the function of each operation, one would suggest that scouring and alkali treatment can be omitted by introducing partial carboxymethylation in the wet processing of gray linen fabric. The work is further extended to build up more basic information about the partial carboxymethylation of gray linen fabric and the behavior of the alkali treated and the partially carboxymethylated fabrics towards bleaching

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EXPERIMENTAL

Materials

Flax fabric

Locally available gray linen fabric (480 g/m^2; weaving density 14 × 14 threads/cm) was used as the starting substrate. Microscopical examination showed that the fabric consists of 100% flax fibers. Chemical analysis carried out as per a reported method[4] confirmed the absence of other fibers.

Chemicals

Sodium carbonate, sodium hydroxide, sodium sulfite, sodium sulfide, potassium permanganate, hydrogen peroxide, sodium silicate, hydrochloric acid and monochloroacetic acid were of laboratory grade chemicals.

Procedures

Scouring

Gray linen fabric was scoured in a solution containing 16 g/L sodium hydroxide, 2 g/L sodium sulfide, 2 g/L sodium sulfite, and 1 g/L nonionic wetting agent (Egyptol®) at 95°C for 30 min using a material to liquor ratio of 1 : 10^3.

TABLE I
Dependence of the Bleaching Effect of H_2O_2 on NaOH Concentration Used for Alkali Treatment of Scoured Flax

	Alkali treated linen fabric before bleaching				Alkali treated linen fabric after bleaching				
[NaOH] (N)	W.I. (%)	loss in fabric weight (%)	COOH content (meq./100 g S)	Cu number	loss in fabric weight (%)	COOH content (meq./100 g S)	Cu number	H_2O_2 decomposition (%)	W.I. (%)
1	12	3.1	23.0	0.51	4.0	19.0	0.63	55.0	55.0
3	17	5.1	26.0	0.6	6.2	28.8	0.51	64.0	64.0
5	20	7.3	34.0	0.7	8.6	30.5	0.66	65.0	66.0
7	24	8.4	38.0	0.9	9.6	33.0	0.61	66.0	67.0

Material to liquor ratio = 20.

Alkali treatment

Gray linen fabrics were scoured as described earlier, then subjected to alkali treatment using sodium hydroxide solution of different concentrations (1–7*N*) for 15 min at room temperature using a material to liquor ratio of 1 : 20. The fabrics were then washed, acidified, washed again, and dried. The so obtained alkali treated samples will serve as a control for the partially carboxymethylated flax.

Partial carboxymethylation

Samples of the gray linen fabric were impregnated in aqueous sodium hydroxide solution of various concentrations (0.5–3.5*N*) for 15 min at room temperature using a material to liquor ratio 1 : 20 followed by squeezing to a wet pick-up of ~60% and finally left in air for 15 min. The alkali treated samples were steeped in aqueous monochloroacetic acid (in the sodium form using sodium carbonate[5,6]) solutions of different concentrations (1–4*N*) for 15 min at room temperature followed by squeezing to ~ 100% wet pick-up. The samples were then packed in polyethylene bags and subjected to different temperatures (30–90°C) for different periods of time (0.5–3.0 h). At this end the samples were washed several times by tap-water, acidified with aqueous hydrochloric acid (3%), washed thoroughly with distilled water till pH 7.0, and finally dried at ambient conditions[3].

Bleaching

Scoured, alkali treated and partially carboxymethylated linen samples were bleached in a solution containing H_2O_2 (5–20 g/L), sodium silicate (3 g/L), and nonionic wetting agent (1 g/L) at different temperatures (75–95°C) and pH values (4–10) for different periods of time (30–150 min) using a material to liquor ratio 1 : 20. The pH was adjusted using orthophosphoric acid after all bleaching ingredients were added. After bleaching, the fabrics were thoroughly washed with water then dried at ambient conditions.

Testing and analysis

- The copper number was determined according to a method described elsewhere.[7]
- The carboxyl content (expressed as meq./100 g fabric) was determined as per a reported method.[8]
- H_2O_2 decomposition percent was determined at different durations according to a reported method.[9]
- The degree of whiteness expressed as whiteness index (W.I.) was measured using a Hunterlab Reflectometer (Model D-25). The whiteness index was calculated in terms of CIEY (Green) and Z (Blue) reflectance components using the equation.[10]

$$\text{W.I.} = 4Z/1.18 - 3Y$$

where Y and Z are the reading of the device.

RESULTS AND DISCUSSION

Alkali treatment of linen fabrics

Gray linen fabrics were scoured as described in the experimental section, then subjected to alkali treatment using sodium hydroxide solution of various strengths for 15 min at room temperature. After being washed and dried, the fabrics were bleached as described in the experimental section. The alkali treated fabrics before and after bleaching were analyzed for copper number, loss in fabric weight, carboxyl content and, whiteness index. The analysis includes also H_2O_2 decomposition. These analyses will be taken all-together as a measure of the bleaching effect as shown in Table I.

It is seen from Table I that the extent of H_2O_2 decomposition, expressed as percent decomposed H_2O_2, increases as the sodium hydroxide concentration increases from 1 to 3*N*, then remains almost constant. This implies that the linen material undergoes structural changes under the influence of alkali

TABLE II
Dependence of the Bleaching Effect of H_2O_2 on NaOH Concentration Used for Partial Carboxymethylation of Linen Fabric

	PCM linen fabric before bleaching			PCM linen fabric after bleaching				
[NaOH] (*N*)	loss in fabric weight (%)	COOH content (meq./100 g S)	Cu number	loss in fabric weight (%)	COOH content (meq./100 g S)	Cu number	H_2O_2 decomposition (%)	W.I. (%)
0.5	3.1	51.0	1.43	4.3	38.0	3.1	64.5	56.0
1.0	4.7	64.0	1.15	5.9	54.0	3.4	66.0	56.0
1.75	5.5	83.0	1.0	6.3	71.0	3.9	66.0	58.0
2.5	6.8	90.0	0.9	7.93	82.0	4.2	66.0	62.0
3.0	7.0	97.0	0.8	8.1	84.0	4.4	67.0	63.0
3.75	7.4	103.0	0.75	8.3	84.0	4.3	68.0	64.0

Material to liquor ratio = 1 : 20. PCM: Partially carboxymethylated.

and these changes are sodium hydroxide dependent up to a concentration of 3*N*. Further structural changes in the linen material, if any, occurring at sodium hydroxide concentrations higher than 3*N* cause no practical changes in the extent of H_2O_2 decomposition. Considering the dependence of the bleaching effect on the sodium hydroxide concentration used for alkali treatment of the scoured linen, results of Table I signify that the carboxyl content increases considerably by increasing the alkali concentration within the range studied. This is observed before and after bleaching. Nevertheless bleaching is accompanied by decrement in the carboxyl content.

Enhancement in the carboxyl content by increasing the alkali concentration suggests that the linen cellulose undergoes oxidation under the influence of atmospheric and/or occluded oxygen in the presence of alkali. On the other hand, decrement in the carboxyl content after bleaching seems to be a manifestation of the removal of noncellulosics containing carboxyl groups particularly the pectins.

With respect to oxidative action on copper number, the results (Table I) indicate that it exhibits higher values at higher alkali concentrations before bleaching. Bleaching lowers these values of copper number and lessens the difference among them. Removal of noncellulosic with reducing properties may account for this. However conversion of the aldehydic groups to carboxylic groups under the influence of H_2O_2 cannot be ruled out.

Data on loss in fabric weight (Table I) make it evident that the scoured linen fabric losses much of its weight after alkali treatment. This loss is higher with higher concentration. The situation is more aggravated after bleaching. This is rather a direct consequence of the combined effect of alkali treatment and H_2O_2 bleaching on the noncellulosics of the linen fabric. Degradation of these noncellulosics during the alkali and bleaching treatment followed by their removal during washing are responsible for the loss in weight of the fabric which in so doing it becomes more susceptible to bleaching as evidenced by the data of the whiteness index.

Partial carboxymethylation of linen fabrics

Gray linen fabrics were partially carboxymethylated by first padding the fabrics with aqueous sodium hydroxide solution of different concentrations (0.5–3.5*N*) to a wet pick-up of $\sim$ 60%. The fabrics were then left to stand in air for 15 min These alkali treated linen fabrics were impregnated in 2*N* aqueous monochloroacetic acid (in the sodium form) solution for 15 min followed by squeezing to 100% wet pick-up. The so treated linen fabrics were subjected to heat treatment at 70°C while they were in a closed atmosphere (polyethylene bag) for 60 min. After washing and drying, the resultant partially carboxymethylated linen fabrics were given H_2O_2 bleaching treatment (20 g/L H_2O_2, 3 g/L sodium silicate and 1 g/L nonionic wetting agent at pH 10, for 150 min at 95°C using a material to liquor ratio of 1 : 20). Fabric samples before and after bleaching were monitored for copper number, carboxyl content, loss in fabric weight, and extent of H_2O_2 decomposition. Whiteness index was also monitored for the bleached samples. All these parameters will be taken as a measure for the bleaching affect as already indicated.

Given below are the dependence of the bleaching effect on factors controlling the partial carboxymethylation of linen fabric.

Sodium hydroxide concentration

Table II shows the dependence of the bleaching effect on sodium hydroxide concentration used in the partial carboxymethylation of linen fabric. It is clear that the extent of H_2O_2 decomposition slightly increases by increasing sodium hydroxide concentration from 0.5 to 1*N*. Above this value the extent of H_2O_2 decomposition remains almost constant. This

TABLE III
Dependence of the Bleaching Effect of H_2O_2 on the Concentration of Monochloroacetic Acid Salt Used for the Preparation of Partially Carboxymethylated Linen Fabrics

Sodium chloroacetate concentration (*N*)	PCM linen fabric before bleaching			PCM linen fabric after bleaching				
	loss in fabric weight (%)	COOH content (meq./100 g S)	Cu number	loss in fabric weight (%)	COOH content (meq./100 g S)	Cu number	H_2O_2 decomposition (%)	W.I. (%)
1.0	4.9	52.0	1.22	6.9	43.0	0.7	67.0	62.0
2.0	6.0	93.0	1.03	7.95	82.0	1.2	66.5	62.0
3.0	6.9	126.0	0.93	10.3	110.0	2.3	70.0	63.0
4.0	7.8	171.0	0.73	12.0	155.0	2.9	71.0	63.0

Material to liquor ratio = 1 : 20. PCM: Partially carboxymethylated.

is rather the trend observed with the alkali treatment given earlier and, hence could be explained on similar lines.

Table II shows the dependence of the bleaching effect on the concentration of sodium hydroxide used in the partial carboxymethylation of linen fabrics. The results signify the following points: (i) The extent of partial carboxymethylation increases by increasing sodium hydroxide concentration up to 10% then remains constant thereafter. This means that, activation of the cellulosic material of the linen fabric as well as catalysis of the partial carboxymethylation reaction occur at sodium hydroxide of 10% concentration. In the meantime, it is likely that greater hydrolysis of the reactive sodium chloroacetate to the inactive sodium glycolate takes place at alkali concentration higher than 10%, thereby diminishing any further enhancement in the partial carboxymethylation. (ii) The extent of partial carboxymethylation, expressed as meq. COOH/100 g fabric, decreases after bleaching irrespective of the sodium hydroxide concentration. This suggests that decarboxymethylation or decarboxylation occurs under the oxidation effect of H_2O_2 thereby lowering the carboxyl content. (iii) The copper number increases after bleaching most probably due to the conversion of some hydroxyl groups of the cellulosic material of the linen fabric to aldehydic groups under the action of H_2O_2 decomposition products. It is also believed that during measurements of copper number, partially carboxymethylated linen fabric is in a slightly swollen state, which allows easier oxidation under the action of the highly alkaline solution used for determination of copper number. (iv) Loss in fabric weight increases after bleaching. This is due to the action of H_2O_2 decomposition products on the noncellulosic materials. The latter are converted to water soluble degraded products, which are removed during washing. (v) W.I. of the bleached linen fabrics increases by increasing sodium hydroxide concentration from 1 to 2.5*N*; no further significant improvement in W.I. is observed at 3*N* sodium hydroxide.

Monochloroacetic acid salt concentration

Table III shows the effect of monochloroacetic acid salt concentration used in the partial carboxymethylation of gray linen fabric on the bleaching effect. Here the gray linen fabrics after being treated with 2.5*N* sodium hydroxide were treated with different concentrations of monochloroacetic acid salt solutions (1–4*N*) and the carboxymethylation reaction was effected at 70°C for 60 min while the fabric samples were placed in polyethylene bags. Fabrics were then bleached by using 20 g/L H_2O_2, 3 g/L sodium silicate, and 1 g/L nonionic wetting agent at 95°C for 150 min.

Results of Table III reveal that decomposition of H_2O_2 marginally increases by increasing monochloroacetic acid salt concentration used for the chemical modification of the linen fabric. In the meantime increasing the acid salt concentration is accompanied by significant enhancement in the carboxyl content as a result of introduction of more and more carboxymethyl groups. It is understandable that the hydroxyl groups of the cellulosic material of linen are immobile and their reaction with sodium chloroacetate will rely on the availability of the molecules of the latter in the vicinity of the cellulose. Needless to say that higher concentrations of sodium chloroacetate provide larger amounts of molecules of the latter in the proximity of cellulose, thereby increasing the magnitude of the carboxymethylation reaction and in turn the carboxyl content. Nevertheless for a given sodium chloroacetate concentration (i.e., acid salt solution), the carboxyl content is higher before rather than after bleaching, suggesting that the latter causes decarboxymethylation or decarboxylation. On the contrary the copper number increases significantly after bleaching and the increase is more significant with linen sample which were modified using higher concentrations of the acid salt solution. Opening up of the linen structure accompanied by high swellability seem to account for this. It is logical that the linen fabric will be in a state that provides (a) larger surface area for H_2O_2 attack and

TABLE IV
Dependence of the Bleaching Effect of H_2O_2 on the Temperature Under which the Partially Carboxymethylated Linen Fabrics Were Prepared

	PCM linen fabric before bleaching			PCM linen fabric after bleaching				
Temperature (°C)	loss in fabric weight (%)	COOH content (meq./100 g S)	Cu number	loss in fabric weight (%)	COOH content (meq./100 g S)	Cu number	H_2O_2 decomposition (%)	W.I. (%)
30	4.2	27.0	1.1	4.2	23.6	1.4	49.5	51.0
40	4.7	43.0	0.9	4.5	29.3	1.0	55.0	53.0
50	5.1	51.6	0.61	7.0	39.9	0.69	67.0	62.0
60	8.6	47.0	0.9	10.3	37.4	0.8	90.0	67.0

Material to liquor ratio = 1 : 20. PCM: Partially carboxymethylated.

(b) guarantee higher diffusion of the bleaching agent and its decomposition inside the linen structure. Once this is the case, one would expect more exposure of the cellulose hydroxyls as well as the noncellulosics to the action of the oxidizing species of the bleaching agent. Indeed, decrement in copper number with the magnitude of carboxymethylation through increasing concentrations of acid salt solutions reflects the ease of removal of noncellulosics having reducing power from the modified linen fabrics which are characterized by open structure and high swelling properties.

It is also seen from Table III that loss in fabric weight increases as the concentration of monochloroacetic acid salt solution increases, and the situation is more pronounced after bleaching. This implies that the concentration of the acid salt solution not only enhance the magnitude of carboxymethylation but also help removing the noncellulosics. It is further supposed that the noncellulosic materials become more amenable for degradation after carboxymethylation using higher concentrations of the acid salt solution as evidenced by the significant enhancement in loss in fabric weight after bleaching. It is further seen (Table III) that W.I. exhibits values that are very comparable irrespective of the concentration of the acid salt solution. This indicates that the removal of the natural coloring matters during bleaching is independent of the magnitude of carboxymethylation when the latter is governed by the contribution of the acid salt solution.

Temperature of partial carboxymethylation

Table IV shows the dependence of the bleaching effect on the temperature of partial carboxymethylation of gray linen fabrics. As previously described the fabrics were treated subsequently with sodium hydroxide (2.5*N*) and the sodium salt of monochloroacetic acid (1*N*). the reaction was allowed to proceed for 60 min at different temperatures (30, 50, 70, and 90°C). The resultant partially carboxy-methylated linen samples were bleached using H_2O_2 (20 g/L), sodium silicate (3 g/L), and nonionic wetting agent (1 g/L) at 95 °C for 150 min using a material to liquor ratio 1:20. The bleaching effect, is expressed as carboxyl content, copper number, loss in fabric weight, and W.I. Decomposition of H_2O_2 is also shown in Table IV.

It is clear from Table IV that the extent of the H_2O_2 decomposition increases considerably as the carboxymethylation temperature raises. This means that the partially carboxymethylated linen fabric catalyzes the decomposition and the magnitude of catalysis relies on the structural changes underwent by the partially carboxymethylated linen during the bleaching treatment. Partially carboxymethylated linen fabrics prepared at higher temperatures seem to be more susceptible to dissolution and/or decarboxymethylation or decarboxylation and the ultimate effect of this is faster catalysis of H_2O_2 decomposition. Indeed, the significant decrement in carboxyl content of the modified linen fabrics after bleaching is in conformation with this. It is likely that the carboxymethylation temperature not only determine the extent of carboxymethylation but also the location and distribution of the carboxymethyl groups on the cellulose molecules as well as the magnitude of oxidation of linen occurring simultaneously with carboxymethylation under the influence of alkali in presence of atmospheric and/or occluded oxygen.

Table IV also shows that the effect of raising the carboxymethylation temperature is to bring about modified linen samples with increased copper number and loss in fabric weight. It is certain, however, that bleaching changes this trend for the copper number, after bleaching the copper number decreases as the carboxymethylation temperature increases; a point which can be associated with easier removal of noncellulosics with high reducing power from partially carboxymethylated linen prepared at higher temperatures. On the other hand, the W.I. exhibits values that increase by raising the temperature of the modified linen preparation. Higher carboxyme-

TABLE V
Dependence of the Bleaching Effect of H_2O_2 on the Time Allowed for the Reaction to Occur during the Preparation of Partially Carboxymethylated Linen Fabrics

	PCM linen fabric before bleaching			PCM linen fabric after bleaching				
Reaction time (hr)	loss in fabric weight (%)	COOH content (meq/100 g S)	Cu number	loss in fabric weight (%)	COOH content (meq./100 g S)	Cu number	H_2O_2 decomposition (%)	W.I. (%)
0.5	5.4	66.0	0.55	6.3	33.0	0.6	53.0	59.0
1.0	6.0	79.0	0.61	7.1	40.0	0.7	66.0	68.0
2.0	7.5	83.0	0.92	7.3	52.0	1.1	67.0	68.0
3.0	7.1	89.0	1.3	7.5	62.7	1.5	70.0	69.0

Material to liquor ratio = 1 : 20. PCM: Partially carboxymethylated.

thylation temperatures seem to produce modified linen the coloring matters of which are easier to destroy during bleaching.

Duration of partial carboxymethylation

Table V shows the dependence of the bleaching effect, expressed as W.I., carboxyl content, copper number, loss in fabric weight and H_2O_2 decomposition on the durations that were allowed for the partial carboxymethylation to occur. Partial carboxymethylation of linen fabrics was performed at 70°C for different periods of time using sodium hydroxide (2.5*N*) and sodium monochloroacetate (1*N*).

The so obtained modified samples were then subjected to bleaching using H_2O_2 (20 g/L), sodium silicate (3 g/L), and nonionic wetting agent (1 g/L) at 95°C for 150 min.

It is evident from Table V that the H_2O_2 decomposition increases by prolonging the time of partial carboxymethylation, indicating that the structural changes conferred on the linen fabric by partial carboxymethylation exert a considerable effect on H_2O_2 decomposition. Similarly the partial carboxymethylation time acts in favor of modified substrates in a way that (a) they exhibit higher loss in fabric weight, (b) they acquire higher copper number, and (c) they reveal significant enhancement in carboxyl content before and after bleaching. However, while bleaching decreases the carboxyl content, it increases the copper number and loss in fabric weight. Decrement in carboxyl content could be ascribed to partial dissolution of degraded modified linen that carries some of the carboxymethyl groups. In combination with this is the possibility of decarboxy-methylation and dacraboxylation as indicated already.

With respect to the W.I., results of Table V make it evident that prolonging the duration of the carboxymethylation more than half an hour exert no significant effect on the W.I. That is, the latter increases remarkably only when the duration increases from 0.5 to 1.0 h then remains almost constant thereafter.

CONCLUSIONS

Traditionally, the wet processing prior to dyeing or final finishing of linen fabrics involves scouring, bleaching, and sometimes alkali treatment. In this study, scouring and alkali treatment can be omitted by introducing partial carboxymethyl group in the wet processing of gray linen fabric. The treated samples (alkali treated and partially carboxymethylated linen fabrics) were monitored for loss in fabric weight, copper number, carboxyl content, H_2O_2 decomposition percent, and whiteness index. Results of these studies showed that the behavior of partially carboxymethylated sample is better than alkali treated sample towards bleaching.

References

1. Gokal, N.; Skelly, K. J. J Soc Dyers Colorists 1959, 75, 486.
2. Hebeish, A.; Abou-Zeid, Y. N.; Wally, A.; Higazy, A. Cell Chem Technol 1988, 22, 591.
3. Higazy, A.; Hashem, M.; Abou-Zeid, Y. N.; Hebeish, A. J Soc Dyers Colorists 1996, 112, 329.
4. American Association of Textile Chemist and Colorists (AATCC), Technical Manual, AATCC: USA, 1977, p 53.
5. Daul, C. G.; Reihardt, M. R.; Reid, D. J. Tex Res J 1952, 22, 787.
6. Daul, C. G.; Reihardt, M. R.; Reid, D. J. Tex Res J 1954, 24, 738.
7. Heyes, H, T. J Soc Chem Ind 1928, 47, T 90.
8. Pacsu, E.; Hiller, A. L. Tex Res J 1946, 16, 390.
9. Vogel, A. I. A Textbook of Quantitative Inorganic Analysis, 4th ed.; Longman: London, 1978, 369 pp.
10. ASTM Method E55–97.