Oxidative Susceptibility of Partially Carboxymethylated Cotton to Gamma Radiation

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Synopsis

Partially carboxymethylated cotton with a DS of about 0.05–0.15 retains its original fibrous nature and exhibits a number of potentially valuable properties, such as a crisp hand with a slightly starched feel, increased moisture regain, water absorbancy, water permeability, changed dyeing characteristics, increased resistance to soiling from aqueous dispersions, and greater ease of soil removal.[5–8] Furthermore, detailed studies have been reported on the behavior of partially carboxymethylated cotton toward oxidation and hydrolysis,[9] vinyl graft polymerization,[10] transfer printing,[11,12] cross-linking,[13] and thermal treatments.[14]

INTRODUCTION

Preparation and properties of partially carboxymethylated cotton have been the subject of several publications.[1–4] Partially carboxymethylated cotton may be simply prepared by padding the cotton cellulose with monochloroacetic acid or its sodium salt, followed by padding it with sodium hydroxide. The overall reaction may be written as

$$\text{Cell-OH} + \text{ClCH}_2\text{COOH} + 2\text{NaOH} \rightarrow \text{Cell-OCH}_2\text{COONa} + \text{NaCl} + 2\text{H}_2\text{O}$$

Partially carboxymethylated cotton with a DS of about 0.05–0.15 retains its original fibrous nature and exhibits a number of potentially valuable properties, such as a crisp hand with a slightly starched feel, increased moisture regain, water absorbancy, water permeability, changed dyeing characteristics, increased resistance to soiling from aqueous dispersions, and greater ease of soil removal.[5–8] Furthermore, detailed studies have been reported on the behavior of partially carboxymethylated cotton toward oxidation and hydrolysis,[9] vinyl graft polymerization,[10] transfer printing,[11,12] cross-linking,[13] and thermal treatments.[14]

The present work aims at studying the effect of changes in the physical as well as chemical structure of cotton brought about by partial carboxymethylation on the oxidative susceptibility of cotton toward gamma radiation.

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EXPERIMENTAL

Cotton Fabric

Mill-desized, scoured, bleached, and mercerized plain weave (31 picks and 36 ends/cm), supplied by El-Nasr Spinning, Weaving and Knitting Co., was used.

Partially Carboxymethylated Cotton

Partially carboxymethylated cotton was prepared according to a procedure reported elsewhere[3] using 10 *N* NaOH and sodium chloracetate. Partially carboxymethylated cotton of various degrees of substitution were obtained by using different concentrations of sodium chloroacetate ranging from 1 to 4 *N*. The samples were then washed, neutralized, washed again till free from any traces of chemicals, and dried at room temperature.

Alkali-Treated Cotton

A control sample, namely, sodium hydroxide-treated cotton, was prepared using NaOH (10 *N*) and following the procedure mentioned above except that treatment with sodium salt of monochloroacetic acid was omitted.

Radiation Treatment

Irradiation to the required radiation doses has been carried out in the cobalt-60 gamma source (8000 Ci) of the Middle Eastern Regional Radioisotope Centre (dose rate ranged between 38 and 37 rad/s.

Analysis

The copper number was determined using the procedure of Heyes.[15] The carboxyl content was estimated according to a reported method.[16] The degree of polymerization was determined using the cuprammonium hydroxide method.[17] Breaking strength and elongation at break were measured by the strip method[18] using an Instron type of machine.

RESULTS AND DISCUSSION

In order to study the effect of introduction of carboxymethyl groups in the molecular structure of cotton cellulose on oxidative susceptibility of the latter toward gamma radiation, unmodified cotton (substrate I), alkali-treated cotton (substrate II), and partially carboxymethylated cottons having 23.863, 38.617, and 46.834 milliequivalent -COOH groups per 100 g cellulose as substrates III, IV, and V, respectively, were exposed to varying radiation doses. The irradiated substrates were then analyzed for copper number, carboxyl content, and degree of polymerization, as well as tensile strength and elongation at break.

Copper Number

Figure 1 shows the copper number of substrates I through V before and after exposure to gamma radiation at different doses. It is observed that, before irradiation, the copper number values amount to 0.022, 0.076, 0.079, 0.08, and 0.09 for substrates I, II, III, IV, and V, respectively. The higher copper number exhibited by the partially carboxymethylated cottons (substrates III through V) and alkali-treated cotton (substrate II) suggests that cotton cellulose undergoes oxidation under the influence of the alkali in the presence of atmospheric and/or occluded oxygen. That is, creation of aldehydic groups via oxidation of some of the cellulose hydroxyls and/or glucosidic band scission is responsible for the higher copper number of substrates II through V compared with the unmodified cotton (substrate I).

After irradiation, it is seen (Fig. 1) that the copper number increases significantly by increasing the radiation dose from 3.199 to 31.114 Mrad. This is observed regardless of the substrate used. Nevertheless, for a given radiation dose, the unmodified cotton (substrate I) acquired a lower copper number compared with alkali-treated cotton (substrate II). Meanwhile, the latter shows a much lower copper number than partially carboxymethylated cottons (substrates III through V). This signifies that (1) the alkali-treated cotton undergoes more radiation degradation than the unmodified and (2) the introduction of carboxymethyl groups in the molecular structure of cellulose makes cotton more susceptible to degradation by gamma radiation.

A close examination of the results of copper number obtained with partially carboxymethylated cottons having different amounts of carboxyme-

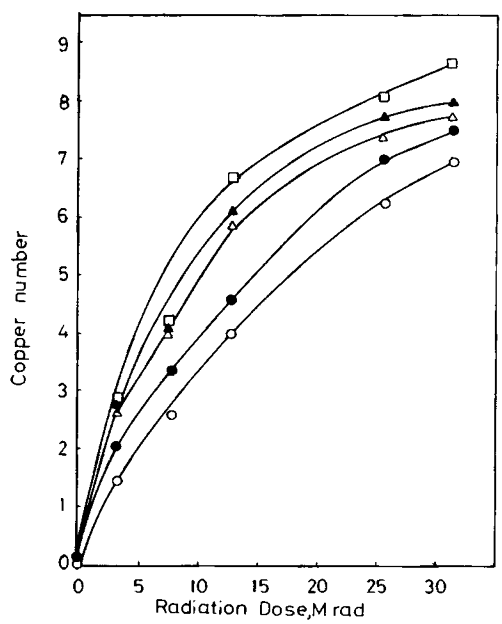

Fig. 1. Effect of gamma radiation on the copper number; (○) unmodified cotton; (●) alkali-treated cotton; partially carboxymethylated cottons (milliequivalent -COOH per 100 g cellulose): (△) 23.863; (▲) 38.617; (□) 46.834.

thyl groups would indicate that the higher the carboxymethyl content, the higher the copper number. This state of affairs is almost valid irrespective of the radiation dose employed within the range studied.

It is logical that introduction of hydrophilic carboxymethyl groups in the molecular structure of cotton cellulose under the conditions used causes opening of the cellulose structure as well as decreasing its molecular arrangements, thereby allowing accommodation of more oxygen and water. The effect of both oxygen and water in accelerating radiation degradation of cotton is well established.[19] Hence, the higher copper number of partially carboxymethylated cottons (substrates III, IV, and V) than unmodified and alkali-treated cottons (substrates I and II) could be interpreted in terms of the presence of higher amounts of oxygen and water in substrates III through V.

Carboxyl Content

Figure 2 shows the carboxyl contents of the five substrates in question before and after irradiation. It is observed that, before irradiation, the carboxyl contents of partially carboxymethylated cottons (substrates III through V) are significantly higher than those of unmodified and alkali-treated cottons (substrates I and II). This is of course due to the presence of carboxymethyl groups. Alkali treatment causes a marginal increase in the carboxyl content of cotton since the carboxyl content of alkali-treated cotton is very low.

Subjecting the unmodified cotton (substrate I) and alkali-treated cotton (substrate II) to gamma radiation is accompanied by an enhancement in the carboxy contents. This enhancement is higher the higher the radiation

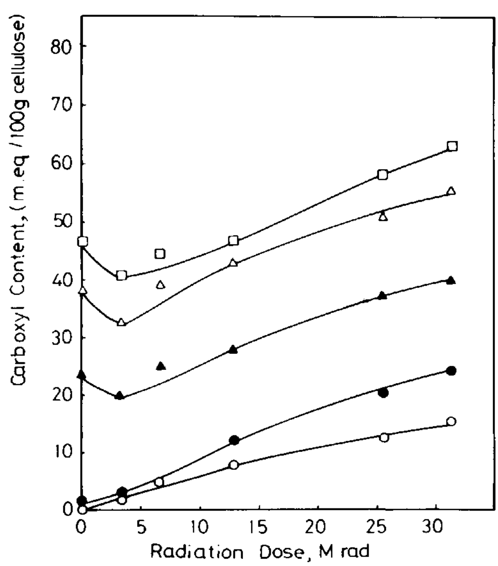

Fig. 2. Effect of gamma radiation on the carboxyl content; (○) unmodified cotton; (●) alkali-treated cotton; partially carboxymethylated cottons (milliequivalent -COOH per 100 g cellulose): (▲) 23.863; (△) 38.617; (□) 46.834.

dose. Nevertheless, for a given radiation dose, alkali-treated cotton acquires higher carboxyl content than the unmodified cotton by virtue of the increased accessibility of the former. On the other hand, the carboxyl contents of partially carboxymethylated cottons (substrates III through V) decreases upon irradiation at low doses but increases at higher radiation dose. The decrement in carboxyl contents of substrates III through V upon irradiation at lower doses is indicative of decarboxylation of some of the carboxymethyl groups, whereas the increment in the carboxyl contents at higher doses is a direct consequence of oxidation of aldehydic and/or hydroxyl groups of the cellulose to carboxylic groups.

It should be emphasized, however, that, despite the expected higher decarboxylation at higher radiation doses, the partially carboxymethylated cottons (substrates III through V) seem to undergo higher radiation degradation than the unmodified cotton (substrate I). This is evidenced when the original carboxyl content of each substrate is subtracted from the corresponding value after irradiation at higher dose (i.e., 31.194 Mrad).

Degree of Polymerization (DP)

When cellulosic materials are irradiated in the solid state by high-energy radiation, energy transfer effects lead to localization of the energy within the molecule. These energy transfer effects are generally considered to be dependent on the mechanism of energy loss by the incident radiation to the chemical molecule and initial random nonlocalized deposition (and subsequent dissipation) of the energy within the molecule and the rapid localization of the energy within the molecule. The localization of the energy in the molecule results in physical and chemical changes depending on nature of the matter irradiated, such as degradation, activation of long-lived excited sites, degradation of the molecule, or depolymerization.[20,21]

Figure 3 shows the DP of unmodified cotton (substrate I), alkali-treated cotton (substrate II), and partially carboxymethylated cottons having 23.863, 38.617, and 46.834 milliequivalent -COOH groups per 100 g cellulose (substrates III, IV, and V) before and after exposure to gamma radiation. It is clear that, before irradiation, the unmodified cotton acquires the highest DP and the partially carboxymethylated cottons the lowest. The DP of alkali-treated cotton is between these values. Furthermore, the DP is lower the higher the carboxymethyl content of the modified cotton. This indicates that cotton cellulose undergoes depolymerization via glucosidic bond scission under the influence of alkali in the presence of atmospheric and occluded oxygen. It further indicates partial carboxymethylation during alkali treatment enhances depolymerization, in accordance with previous reports.[14]

Figure 3 shows that exposing the five substrates under investigation to gamma radiation brings about a significant decrease in the DP, particularly upon using a radiation dose of 3.199 Mrad. Increasing the radiation dose to 31.194 Mrad is also accompanied by a decrement in the DP but to a much lower extent. However, the magnitude of depolymerization is higher with alkali-treated cotton than the unmodified cotton. This situation becomes more aggravated with partially carboxymethylated cottons. The DP of sub-

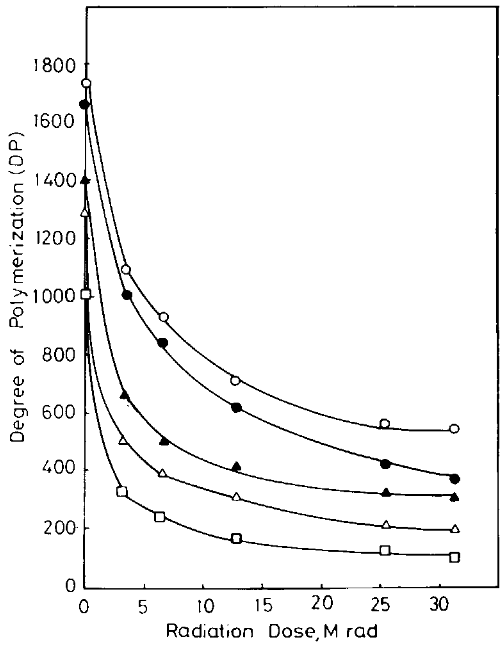

Fig. 3. Effect of gamma radiation on the degree of polymerization; (○) unmodified cotton; (●) alkali-treated cotton; partially carboxymethylated cottons (milliequivalent -COOH per 100 g cellulose): (▲) 23.863; (△) 38.617; (□) 46.834.

strate V, with the highest carboxymethyl content, decreases 10 times upon irradiation at a dose of 31.194 Mrad. This is against about 3 times in the case of the unmodified cotton.

The enhanced oxidative susceptibility of alkali-treated cotton toward gamma irradiation could be associated with the increased accessibility conferred on cotton by alkali treatment. Increased accessibility seems to help establish a favorable medium for energy localization. This same reason, together with the presence of higher amounts of oxygen and water in partially carboxymethylated cottons, due to factors cited above, would account for the much greater susceptibility of the partially carboxymethylated toward gamma radiation.

Tensile Strength

Table I shows the effect of gamma radiation at different doses on the tensile strength of the five substrates under investigation. It is observed that, before irradiation, the tensile strength of alkali-treated cotton (substrate II) is lower than that of untreated cotton (substrate I). The same situation is encountered with partially carboxymethylated cottons (substrates III, IV, and V). This is expected, since the alkali treatment as well as the partial carboxymethylation treatments were carried out without tension and therefore substrates II through V would acquire a lower degree of crystallinity and orientation than substrate I. In addition, the DP values of substrates II through V are lower than that of substrate I, as previously indicated.

TABLE I
Effect of Gamma Radiation on the Tensile Strength of Untreated Cotton (Substrate I), Alkali-Treated Cotton (Substrate II), and Partially Carboxymethylated Cottons (Substrates III–V) at Different Doses[a]

Radiation dose (M rad)	Tensile strength (kg)									
	Substrate I		Substrate II		Substrate III		Substrate IV		Substrate V	
	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft
00.00	55.80	48.50	53.96	46.35	48.65	39.40	45.00	34.73	41.87	38.10
3.199	43.33	36.92	52.83	34.00	38.67	34.33	37.50	30.83	41.83	27.50
6.399	39.10	33.13	46.80	30.00	35.87	25.50	32.93	23.80	34.03	25.17
12.797	29.83	23.66	29.90	23.83	24.85	16.18	21.90	22.70	22.37	11.53
25.595	21.98	16.65	12.83	9.97	14.73	7.55	11.70	7.92	10.67	6.17
31.194	20.50	13.17	10.33	6.67	12.50	6.42	10.50	6.17	8.50	5.57

[a] Substrate III, 23.863 milliequivalent -COOH/100 g cellulose; substrate IV, 38.617 milliequivalent -COOH/100 g cellulose; and substrate V, 46.834 milliequivalent -COOH/100 g cellulose.

TABLE II

Effect of Gamma Radiation on the Elongation at Break of Untreated Cotton (Substrate I), Alkali-Treated Cotton (Substrate II), and Partially Carboxymethylated Cottons (Substrates III-V) at Different Doses.[a]

Radiation dose (M rad)	Elongation at break (%)									
	Substrate I		Substrate II		Substrate III		Substrate IV		Substrate V	
	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft
00.00	10.70	20.80	23.33	40.83	24.83	43.21	25.33	44.83	26.83	47.25
3.199	9.17	20.83	22.52	40.63	21.84	41.17	22.67	41.50	24.33	42.83
6.399	9.83	20.03	22.37	39.05	22.83	40.30	22.67	40.50	24.50	41.66
12.797	8.83	19.81	20.11	37.33	21.33	38.37	22.33	39.85	23.58	40.72
25.194	7.50	16.33	19.33	33.66	20.66	34.72	21.33	35.83	21.96	35.93
31.194	7.17	14.17	18.18	28.83	18.66	29.33	20.50	29.50	20.67	30.66

[a] Substrate III, 23.863 millequivalent -COOH/100 g cellulose; substrate IV, 38.617 milliequivalent -COOH/100 g cellulose; and substrate V, 46.834 milliequivalent -COOH/100 g cellulose.

Irradiation of the five substrates by gamma rays causes significant losses in tensile strength; the loss in the latter is higher the higher the radiation dose. However, for a given radiation dose, the losses in tensile strength are higher with substrates II through V than substrate I. Furthermore, the losses for substrates III, IV, and V tend to be higher than substrate II. An indication of this is that alkali-treated cotton and the partially carboxymethylated cottons undergo greater deterioration than the unmodified cotton upon irradiation. Moreover, alkali-treated cotton is less susceptible to radiation deterioration compared with partially carboxymethylated cotton.

Elongation at Break

Table II shows the elongation at break of the five substrates under investigation before and after irradiation. It is seen that, before irradiation, the elongation at break of alkali-treated cotton (substrate II) and partially carboxymethylated cottons (substrates III, IV, and V) is significantly higher than that of the unmodified cotton (substrate I). It is also seen that the elongation at break of substrates III, IV, and V tends to be higher than that of substrate II. The general indication of this is that alkali treatment or the partial carboxymethylation treatments cause significant enhancement in the elongation at break of the cotton fabric, perhaps through decreased crystallinity and orientation. Also, these treatments bring about significant reduction in the DP along with certain enhancement in copper number and carboxyl content, as indicated above. Such structural changes in the cotton structure would certainly be reflected on the elongation at break since they reduce the primary and secondary forces holding the cellulose structure.

Subjecting the five substrates in question to gamma radiation is accompanied by substantial reduction in the elongation at break regardless of the substrate used. However, alkali-treated cotton and partially carboxymethylated cottons still acquire much higher elongation at break compared with the unmodified cotton. The reduction in elongation at break after irradiation suggests that the latter conferred on cotton a certain rigidity as a consequence of the structural changes in the cotton brought about by irradiation.

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