

Behavior of Chemically Modified Cottons towards Thermal Treatment. II. Cyanoethylated Cotton

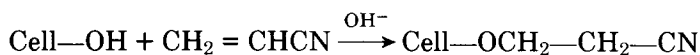
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Synopsis

Mill-scoured and bleached cotton fabric, alkali-treated cotton, and cyanoethylated cottons having 0.1%, 0.47%, 0.89%, and 1.25% nitrogen were subjected to thermal treatments. The latter were carried out at different temperatures for different durations of time. Chemical degradation of the substrates brought about by thermal treatments was assessed by copper number, carboxylic groups, nitrogen content, and degree of polymerization whereas deterioration was measured by tensile strength and elongation at break. It was found that: (a) alkali-treated cotton undergoes higher degradation than cyanoethylated cottons; (b) cyanoethylated cottons are more susceptible to degradation than the original (mill-scoured and bleached) cotton; (c) the magnitude of deterioration of the substrate is determined by the previous chemical treatments; and (d) with cyanoethylated cotton, the higher the cyanoethyl content (expressed as % nitrogen) the greater the DP and tensile strength.

INTRODUCTION

Modification of cellulose by cyanoethylation has attracted much attention, and cyanoethylated cottons are now commercially available. In this procedure, the cellulose is first impregnated with dilute sodium hydroxide and then treated with acrylonitrile at ca. 55°C, followed by rinsing with dilute acetic acid and washing with water. With care, high values of degree of substitution, DS, may be achieved.¹ The reaction between the cellulose hydroxyls and acrylonitrile is



This treatment improved resistance to rot, heat, and damage by acids and abrasion.^{2,3} Cyanoethylated cottons are more receptive than cotton to some dyes in all classes of dyestuffs and require more work than untreated cotton for rupture under tension. Furthermore, the dielectric constant of cyanoethylated cellulose is increased proportionally to the extent of reaction. The cyanoethylated cotton can be hydrolyzed to carboxyethyl cellulose.

The present work is undertaken with a view of studying the behavior of cyanoethylated cotton toward thermal treatments. For this purpose, the latter is performed at different temperatures for different durations. Certain properties of the cyanoethylated cotton samples before and after thermal treatment are compared with alkali-treated cotton and untreated cotton to clarify the

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changes in the chemical and physical structure of cotton cellulose on the behavior of the latter towards thermal treatments.

EXPERIMENTAL

Cotton Fabric

Mill-scoured and bleached plain weave (23 picks and 23 ends/cm) cotton fabric was used throughout this investigation.

Reagents

Acrylonitrile was freshly distilled before used. Sodium hydroxide of pure grade chemicals was used.

Sodium-Hydroxide-Treated Cotton

Sodium-hydroxide-treated cotton was prepared by impregnating the fabric in an aqueous solution of sodium hydroxide (5%, w/v) for 15 min followed by squeezing to ca. 100% wet pickup, and then storing in a polyethylene cover at ambient conditions for 4 h. At the end of this procedure, the fabric was thoroughly washed, neutralized with HCl (1%), washed again, and finally dried at room temperature.

Cyanoethylated Cotton

Cyanoethylated cotton (CEC) was prepared according to a method described elsewhere⁴ by impregnating the fabric in an aqueous solution of sodium hydroxide (5%, w/v) for 15 min followed by squeezing to ca. 100% wet pickup. After being batched for 10 min the alkali-treated fabric was treated with acrylonitrile and stored in a polyethylene cover. The fabric was then washed and dried as above. Cyanoethylated cotton of various degrees of substitutions were obtained by using different reaction time.

Thermal Treatment

Samples of this fabric were thermally treated for various periods (15 min–24 h) over a temperature range 160–200°C. Thermal treatment was carried out through convective heating on a laboratory-scale tenter frame using an oven with circulating air.

Analysis

Breaking strength and elongation at break were measured by the strip method.⁵

The copper number was determined using the procedure of Heyes.⁶

The carboxyl content was estimated according to a reported method.⁷

The nitrogen content was estimated according to the Kjeldahl method.

The degree of polymerization was determined using the cuprammonium hydroxide method.⁸

RESULTS AND DISCUSSION

Since the primary objective of this work is to study the behavior of cyanoethylated cotton towards thermal treatment, cotton cellulose in the fabric form was reacted with acrylonitrile in presence of sodium hydroxide in a way that cellulose bearing different amounts of cyanoethyl groups could be obtained. In addition, cotton fabric was treated with sodium hydroxide under similar conditions but in absence of acrylonitrile. Both the original cotton and alkali-treated cotton serve as control for cyanoethylated cottons. For convenience the untreated cotton fabric will be referred to as substrate I, alkali-treated cotton as substrate II, and cyanoethylated cottons having 0.1%, 0.47%, 0.89%, and 1.25% nitrogen as substrates III, IV, V, and VI, respectively.

Due to the significant role played by water molecules in the vicinity of the cellulose during thermal degradation,⁹ it was logical to determine the moisture regain of the said substrates.

Table I shows the moisture regain of untreated cotton, alkali treated cotton and cyanoethylated cottons. It is seen that alkali treatment of cotton fabric, with 5% (w/v) sodium hydroxide, causes a slight increase in its moisture regain. Cyanoethylated cottons (substrates III–VI) show lower moisture regain than that of untreated cotton (substrate I). The moisture regain depends upon the cyanoethyl content. For instance, increasing the nitrogen content of cyanoethylated cottons from 0.1% to 0.89% brings about a decrease in the moisture regain whereas further increase in the nitrogen content up to 1.25% causes enhancement in the moisture regain. The decrease in moisture at relatively low extent of cyanoethylation could be associated with the hydrophobic nature of the cyanoethyl groups. On the other hand, the enhancement in moisture regain at relatively higher extent of cyanoethylation could be interpreted in terms of opening up the cellulose structure together with relatively high amounts of carboxyethyl groups.

After being conditioned, the six substrates were heated at 160°C, 180°C, and 200°C for different lengths of time. The substrates before and after these heat treatments were analyzed for copper number, carboxyl content, nitrogen content, and degree of polymerization as well as tensile strength and elongation at break.

Copper Number

Figure 1 shows that alkali treatment or cyanoethylation of cotton cellulose causes a slight increase in the copper number of cotton. This is most probably

TABLE I
Moisture Regain of Cotton before and after Being Cyanoethylated

Substrate	Moisture regain (%)
Untreated cotton fabric substrate I	5.67
Alkali-treated cotton fabric substrate II	5.92
Substrate III	5.35
Substrate IV	4.95
Substrate V	4.97
Substrate VI	5.26

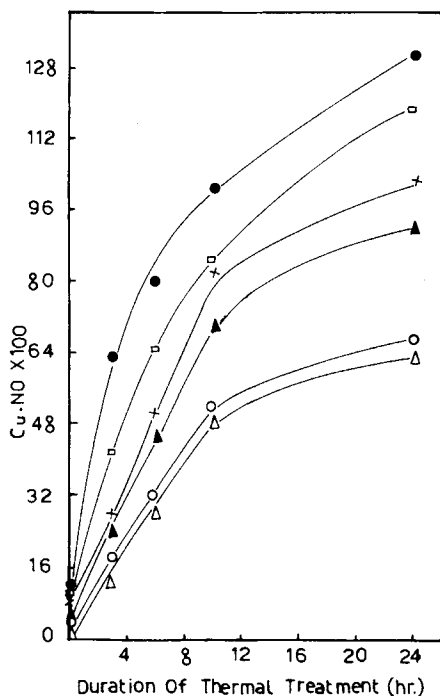


Fig. 1. Effect of duration of thermal treatment at 160°C on the copper number. (Δ) Untreated cotton; (●) alkali-treated cotton; cyanoethylated cottons (nitrogen %): (○) 0.105; (▲) 0.47; (×) 0.89; (□) 1.25.

due to oxidation of some of the cellulose hydroxyls to aldehydic groups under the influence of alkali in the presence of atmospheric and/or occluded oxygen. Subjecting the cotton cellulose alkali-treated cotton and cyanoethylated cottons to heat treatment at 160°C for up to 24 h results in a considerable enhancement in the copper number. The latter increases by increasing duration of heat treatment irrespective of the substrate used. However, for a given heat duration, the copper number of the untreated cotton (substrate I) is much lower than those of alkali-treated cotton (substrate II) and cyanoethylated cottons (substrates III–VI). Based on the data of copper number shown in Figure 1 the susceptibility of the substrates in question to heat degradation follows the order:

substrate II > substrate VI > substrate V > substrate IV >

substrate III > substrate I

The above order indicates that alkali-treated cotton (substrate II) undergoes more degradation than untreated cotton (substrate I), in accordance with previous work.¹⁰ It further indicates that introduction of cyanoethyl groups in the molecular structure of cotton cellulose decreases the magnitude of such degradation since the copper number of cyanoethylated cottons is lower than that of alkali-treated cotton. Moreover, the higher the cyanoethyl content the higher the copper number. It is understandable that the increase in the copper number is due to the occurrence of oxidation of the cellulose hydroxyls and the hydrolysis of the glucosidic bond of the cellulose chains during thermal treatments.⁹ In

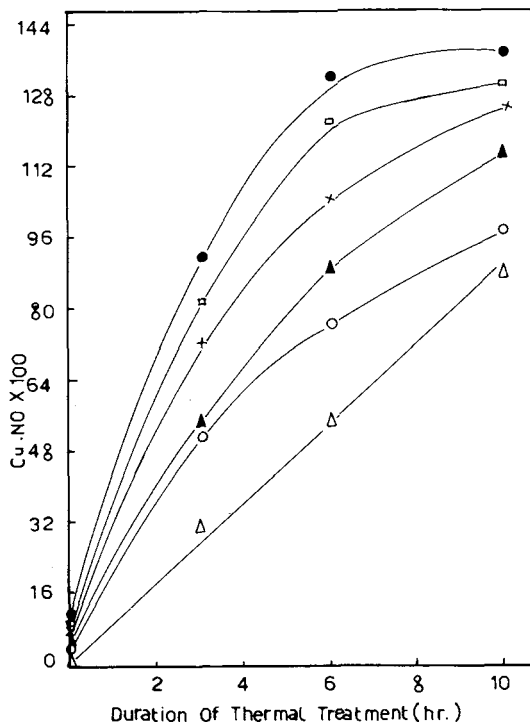


Fig. 2. Effect of duration of thermal treatment at 180°C on the copper number. (Δ) Untreated cotton; (\bullet) alkali-treated cotton; cyanoethylated cottons (nitrogen %): (\circ) 0.105; (\blacktriangle) 0.47; (\times) 0.89; (\square) 1.25.

comparison with alkali-treated cotton, the presence of cyanoethyl groups along the cellulose chains seems to impede oxidation of the hydroxyl groups or prevent chain scission or both. In combination with this is the hydrophobic nature of cyanoethyl groups as well as the blocking of some of the cellulose hydroxyls, leading to lower availability of water molecules in the substrate (cf. Table I). It is logical that the relatively lower moisture of the cyanoethylated cottons as compared with alkali-treated cotton would decrease hydrolysis of the cellulose chains as well as oxidation of cellulose hydroxyls. It may be argued that untreated cotton (substrate I) shows lower susceptibility towards thermal degradation than cyanoethylated cottons (substrates III–VI) despite the higher moisture of substrate I. Nevertheless, differences in accessibility between cyanoethylated cotton and untreated cotton together with mode of interaction of water with the cellulose molecules during the thermal treatment may account for this argument.

Figure 2 shows the effect of heating at 180°C for up to 10 h on the copper number of untreated cotton (substrate I), alkali-treated cotton (substrate II), and cyanoethylated cottons (substrates III–VI). Similar results are shown in Figure 3, but when heating was carried out at 200°C for up to 3 h. It is seen that: (a) the copper number increases by increasing the duration of heat treatment; (b) the copper number of cyanoethylated cottons are lower than that of the alkali-treated; (c) the copper number of cyanoethylated cottons and alkali-treated cotton is much higher than that of untreated cotton; and (d) the copper number

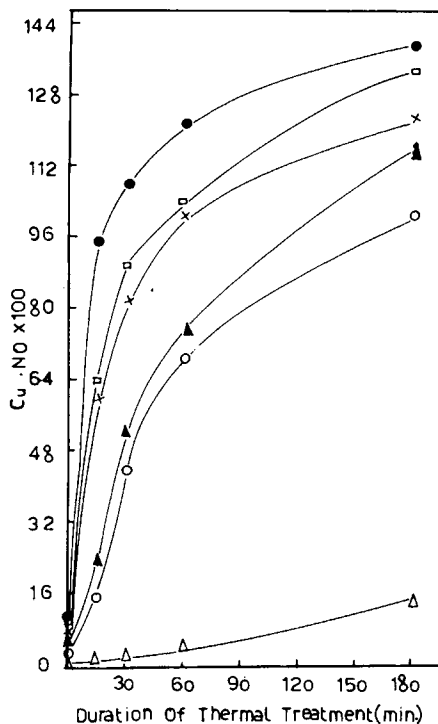


Fig. 3. Effect of duration of thermal treatment at 200°C on the copper number. (Δ) Untreated cotton; (●) alkali-treated cotton; cyanoethylated cottons (nitrogen %): (○) 0.105; (▲) 0.47; (×) 0.89; (□) 1.25.

of cyanoethylated cotton having greater cyanoethyl content is higher than its mate with lower cyanoethyl content. This is rather the trend observed when heating was performed at 160°C and could be explained on similar lines.

A comparison between Figures 1, 2, and 3 would imply that for a given duration of heat treatment the copper number of the untreated cotton (substrate I) follows the order:

$$180^{\circ}\text{C} > 200^{\circ}\text{C} = 160^{\circ}\text{C}$$

On the other hand, with alkali-treated cotton (substrate II) and cyanoethylated cottons (substrates III–VI) the copper number follows the order

$$200^{\circ}\text{C} > 180^{\circ}\text{C} > 160^{\circ}\text{C}.$$

If one assumes that the lower copper number of untreated cotton at 200°C than at 180°C is due to easier oxidation of the aldehydic groups to carboxyl groups, then the order obtained with alkali-treated cotton and cyanoethylated cotton reflects the difference in microstructural features between these substrates and untreated cotton.

Carboxyl Content

When cotton is subjected to alkali treatment or to cyanoethylation, there is an increase in the carboxyl content (Fig. 4). This is rather in accordance with previous reports.¹⁰

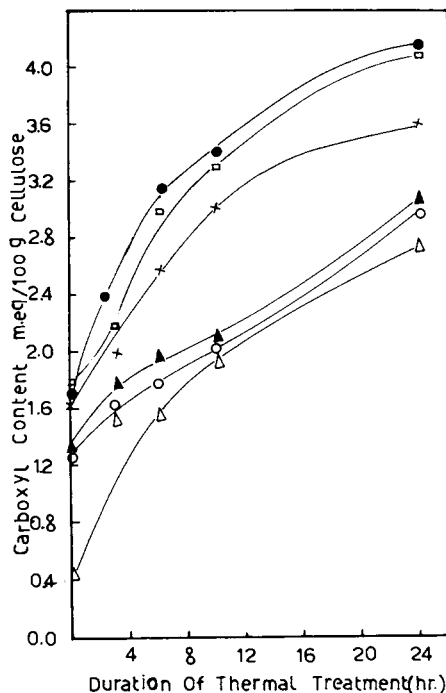


Fig. 4. Effect of duration of thermal treatment at 160°C on the carboxyl content. (Δ) Untreated cotton; (\bullet) alkali-treated cotton; cyanoethylated cottons (nitrogen %): (\circ) 0.105; (\blacktriangle) 0.47; (\times) 0.89; (\square) 1.25.

Figure 4 shows the effect of heat treatment at 160°C for different periods of time (3–24 h) on the carboxyl content of untreated, alkali-treated, and cyanoethylated cottons. It is seen that the carboxyl content increases by increasing the duration of thermal treatment irrespective of the substrate used. However, alkali-treated cotton shows the highest carboxyl content whereas untreated cotton shows the least. Cyanoethylated cottons, on the other hand, stand in midway position. The carboxyl content of the thermally treated substrate follows the order

$$\text{substrates II} \geq \text{VI} > \text{V} > \text{IV} > \text{III} > \text{I}$$

This is rather the order brought out when degradation was assessed by copper number measurement. Hence, the explanations given there would be applied here.

Figure 5 shows the effect of heat treatment at 180°C for up to 10 h on the carboxyl content of the six substrates in question. As is evident, the carboxyl content increases by increasing the duration of heat treatment regardless of the substrate used, similar to heating at 160°C. Unlike heating at 160°C, the carboxyl content of cyanoethylated cotton having 1.25% nitrogen is close to that of alkali-treated cotton after thermal treatment at 180°C. When heat treatment was performed at 200°C (Fig. 6), this cyanoethylated cotton acquires higher carboxyl content than the alkali-treated cotton. Moreover, cyanoethylated cottons having 0.89% N show roughly equal carboxyl content. This suggests that the severity of heat treatments, i.e., raising the temperature, lessens differences in degradation between cyanoethylated cottons, in particular those having higher

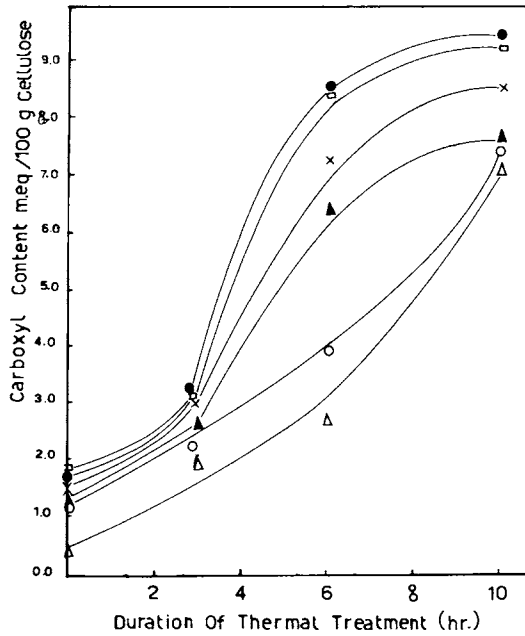


Fig. 5. Effect of duration of thermal treatment at 180°C on the carboxyl content. (Δ) Untreated cotton; (\bullet) alkali-treated cotton; cyanoethylated cottons (nitrogen %): (\circ) 0.105; (\blacktriangle) 0.47; (\times) 0.89; (\square) 1.25.

cyanoethyl content, and alkali-treated cotton. However, this statement should be taken with caution since the carboxyl content of cyanoethylated cotton may

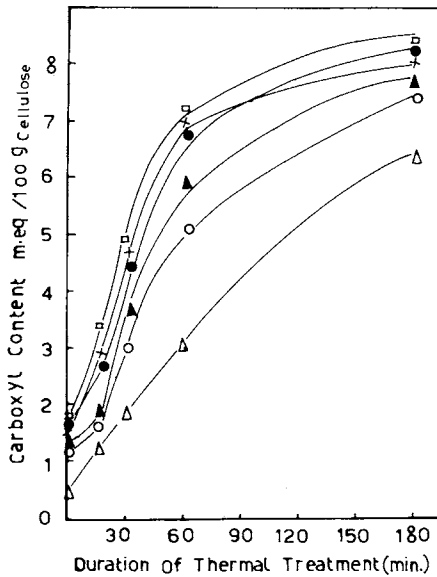


Fig. 6. Effect of duration of thermal treatment at 200°C on the carboxyl content. (Δ) Untreated cotton; (\bullet) alkali-treated cotton; cyanoethylated cottons (nitrogen %): (\circ) 0.105; (\blacktriangle) 0.47; (\times) 0.89; (\square) 1.25.

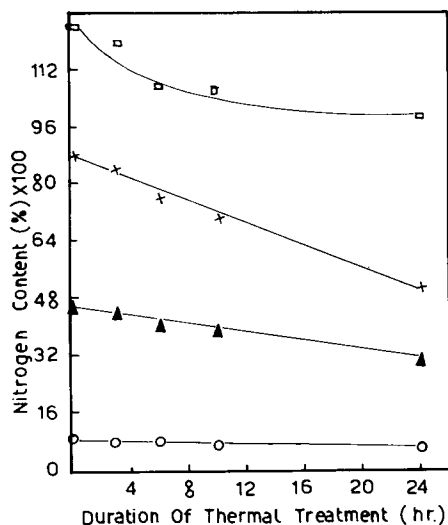


Fig. 7. Effect of duration of thermal treatment at 160°C on the nitrogen content of cyanoethylated cottons. Nitrogen %: (○) 0.105; (▲) 0.47; (×) 0.89; (□) 1.25.

be brought about by hydrolysis of cyanoethyl groups rather than oxidation an hydrolytic scission of cellulose.

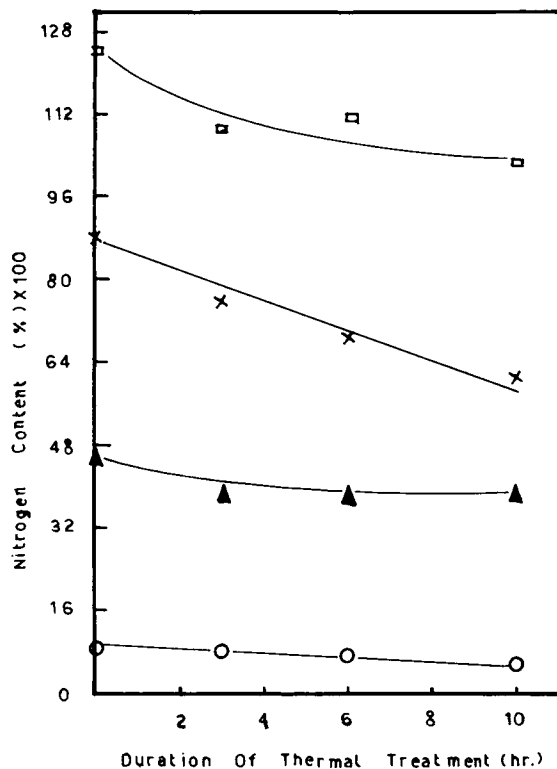


Fig. 8. Effect of duration of thermal treatment at 180°C on the nitrogen content of cyanoethylated cottons. Nitrogen %: (○) 0.105; (▲) 0.47; (×) 0.89; (□) 1.25.

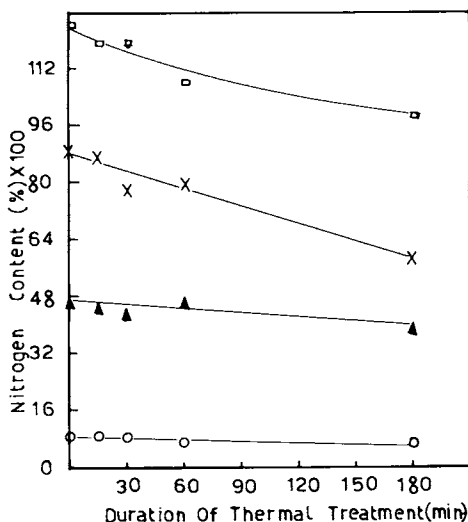


Fig. 9. Effect of duration of thermal treatment at 200°C on the nitrogen content of cyanoethylated cottons. Nitrogen %: (O) 0.105; (▲) 0.47; (X) 0.89; (□) 1.25.

A comparison between Figures 4, 5, and 6 would imply that for a given duration of heat treatment the carboxyl content of the six substrates in question follows the order

$$200^{\circ}\text{C} > 180^{\circ}\text{C} > 160^{\circ}\text{C}$$

Nitrogen Content

Figure 7 shows the effect of heat treatment at 160°C for different periods of time (3–24 h) on the nitrogen content of cyanoethylated cottons (substrates III–VI). Obviously, subjecting cyanoethylated cottons having nitrogen content of 0.1% and 0.47% (substrates III and IV) to thermal treatments brings about a marginal decrease in the nitrogen content. On the other hand, when cyanoethylated cottons having 0.89% and 1.25% (substrates V and VI) were subjected to heating at 160°C, there is a significant decrease in the nitrogen content. The same situation is encountered when thermal treatments were carried out at 180°C and 200°C as shown in Figures 8 and 9. The decrease in nitrogen content is indicative of partial hydrolysis of the cyanoethyl groups. Hydrolysis seems to be favored by abundance of cyanoethyl groups as well as by raising the temperature of thermal treatment.

Degree of Polymerization (DP)

Figures 10, 11, and 12 show the effect of thermal treatment at 160°C, 180°C, and 200°C, respectively, on the DP of untreated cotton (substrate I), alkali-treated (substrate II), and cyanoethylated cottons (substrates III–VI). It is seen that before thermal treatments, the untreated cotton shows the highest DP whereas alkali-treated cotton shows the lowest. DP's of cyanoethylated cottons

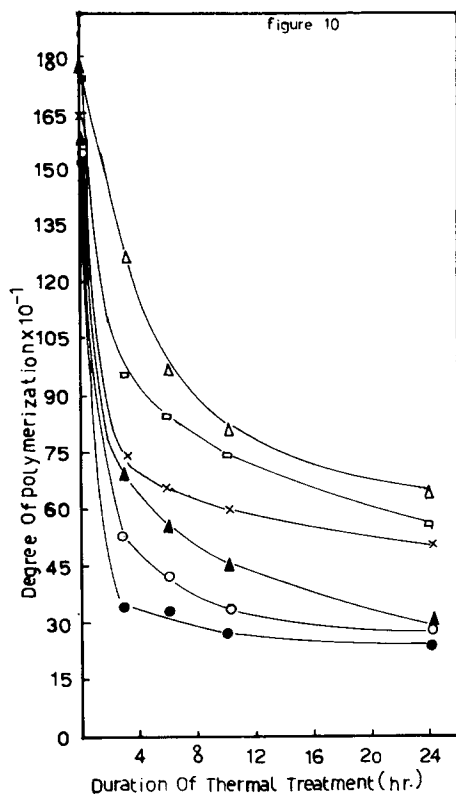


Fig. 10. Variation of the degree of polymerization with the duration of thermal treatment at 160°C. (Δ) Untreated cotton; (\bullet) alkali-treated cotton; cyanoethylated cottons (nitrogen %): (\circ) 0.105; (\blacktriangle) 0.47; (\times) 0.89; (\square) 1.25.

lie in between. The DP follows the order:

substrate I > substrate VI > substrate V > substrate IV >

substrate III > substrate II

Indications of this are that (a) certain depolymerization occurs during alkali treatment and (b) occurrence of cyanoethylation during the alkali treatment decreases the extent of depolymerization. That is, oxidation degradation of the cellulose chain molecules during alkali treatment in the presence of atmospheric and/or occluded, oxygen is impeded by the presence of acrylonitrile which react concurrently with oxidation to yield cyanoethylated cotton.

Subjecting the six substrates in question to thermal treatments brings about a remarkable decrease in the DP in the initial stages of the treatment. Thereafter, the decrease in the DP continues, but to a much lower extent. At any event, however, the above order still persists after thermal treatments.

Based on the foregoing, it is probably correct to say that alkali-treated cotton and cyanoethylated cottons are more susceptible to thermal treatments than the untreated cotton. The results of DP of alkali-treated cotton in comparison with those of untreated cotton are in full agreement with previous reports.¹⁰ The lower susceptibility of cyanoethylated cottons towards thermal degradation as

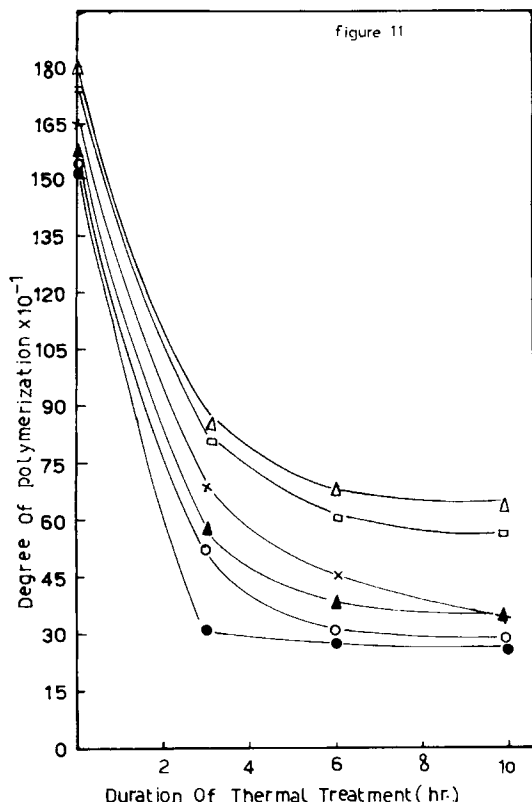


Fig. 11. Variation of the degree of polymerization with the duration of thermal treatment at 180°C. (Δ) Untreated cotton; (●) alkali-treated cotton; cyanoethylated cottons (nitrogen %): (○) 0.105; (▲) 0.47; (×) 0.89; (□) 1.25.

compared with alkali-treated cotton suggests that the presence of cyanoethyl groups in the molecular structure of cotton cellulose protects the latter from thermal depolymerization and the magnitude of this protection is higher the greater the cyanoethyl content.

A comparison between Figures 10, 11, and 12 would reveal that, for a given duration of thermal treatment, the DP follows the order:

$$160^{\circ}\text{C} > 180^{\circ}\text{C} > 200^{\circ}\text{C}$$

An indication of this is that the higher the temperature, the higher the magnitude of depolymerization, in accordance with the results of the copper number and carboxyl content given above.

Tensile Strength

Table II shows the tensile strength of untreated cotton, alkali-treated cotton, and cyanoethylated cottons before and after thermal treatments: the untreated cotton shows the highest tensile strength whereas the alkali-treated cotton the lowest. The tensile strength of cyanoethylated cottons lies in between. The

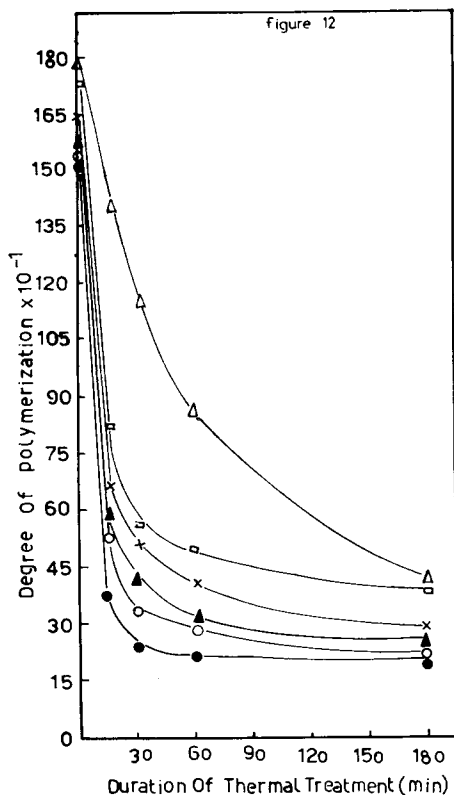


Fig. 12. Variation of the degree of polymerization with the duration of thermal treatment at 200°C. (Δ) Untreated cotton; (\bullet) alkali-treated cotton; cyanoethylated cottons (nitrogen %): (\circ) 0.105; (\blacktriangle) 0.47; (\times) 0.89; (\square) 1.25.

tensile strength follows the order:

substrate I > substrate VI > substrate V > substrate IV >

substrate III > substrate II

This is rather in accordance with the results of DP, discussed above. It is understandable that the tensile strength depends largely on the DP: the higher the latter, the greater the tensile strength.

When the substrates in question were subjected to heat treatments at 160°C, 180°C, and 200°C, the tensile strength, both in the warp and weft directions, decreases. The decrease in the tensile depends upon: (a) the nature of the substrate (the above order found before thermal treatment still persists), (b) the temperature of heating (the higher the temperature the lower the retained strength), and (c) duration of heating (the tensile strength decreases as the duration of heating increases).

Elongation at Break

Table III shows that treatment of cotton fabric with sodium hydroxide under

TABLE II
 Effect of Thermal Treatments at Different Conditions on Tensile Strength of Cotton (Substrate I) Alkali-Treated Cotton (Substrate II) Cyanoethylated Cotton
 (Substrate III-VI)

Time	Temp (°C)	Tensile strength (kg)											
		Substrate I		Substrate II		Substrate III		Substrate IV		Substrate V		Substrate VI	
		Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft
3 h	160	56	32	15	5.3	24	9	28.5	13	28.5	27.5	54	30
6 h	160	53	31	10	5	17	6.5	21.5	12	24	25.5	48	28.5
10 h	160	47	27	9.5	4	13.5	5.5	19.5	10	22.5	22.5	42	25.5
24 h	160	25.5	21	9	3.5	12.5	5.5	16.5	9.5	20	16.5	24	20
3 h	180	49	25	7.5	4.5	21	11	22.5	12	27	19.5	48	21
6 h	180	40	18.7	5.5	4.2	11.5	6	13.5	7.5	21	14	39	15
10 h	180	25.5	11	4.5	3.3	7.5	4.5	7.5	5	19	10	27	10
15 min	200	58	30	7.5	5	13	8	18	10.5	39	25.5	51	28.5
30 min	200	54	26	5	3.5	12	7	17	8	34.5	19	45	22
1 h	200	47	19	4.5	3	10.5	6.5	15	7.5	25	14	39	17
3 h	200	14	9.5	4.5	3	9	4.5	10.5	6	12	8	12.0	9.0
0	—	62	33.5	49	25	15	27	54	29	57	30.5	61	32

TABLE III
 Effect of Thermal Treatments at Different Conditions on Elongation at Break of Cotton (Substrate I) Alkali-Treated Cotton (Substrate II) Cyanoethylated Cotton (Substrate III-VI)

Time	Temp (°C)	Elongation at break (%)											
		Substrate I		Substrate II		Substrate III		Substrate IV		Substrate V		Substrate VI	
		Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft
3 h	160	8	15	7.5	8	10.5	9	9	9	11	11	12.5	12
6 h	160	8	14	6.5	5	9.5	5.5	8	6	10	9	11.5	11
10 h	160	7	13	5.5	4.5	8.5	5	7.5	5.5	9.5	8	11	10
24 h	160	6	8	5.5	4.5	8.0	5	7	5.5	9	7	11	7.5
3 h	180	7	14	6.5	6.5	8	7.5	8.5	8.5	10	11	11.5	12
6 h	180	6	13	5	6	8	7	6.5	8	9.5	10	10.5	11
10 h	180	5	12	4.5	6	7	6.5	6	7.5	9	9.5	10	10.5
15 min	200	8	15	7	7	9.5	7.5	9	9	10.5	12.5	11	14
30 min	200	7	13	6.5	6	9	6.5	8	8	9.5	11	10.5	12
1 h	200	6	13	5	4.5	8	5	7	7	8.5	9	9.5	10.5
3 h	200	3.5	6.5	3	2	6	2.5	5	3	7	4	9	5
0	—	9	16	8.5	12	11.5	13	10	13.5	12	14	13	15

the conditions used enhances significantly the elongation at break of the warp directions. The same holds true for cyanoethylated cottons, but the enhancement was lower than that of alkali-treated cotton. The elongation at break in the warp direction follows the order

substrate VI > substrate V > substrate III > substrate IV >
substrate I \geq substrate II

The reverse was observed with elongation at break of the weft direction. It was found that cyanoethylation of cotton fabric decreases significantly the elongation at break of the weft direction. The same holds true for alkali-treated cotton but to a greater extent. The elongation at break in weft direction follows the order

substrate I > substrate VI > substrate V > substrate IV >
substrate III > substrate II

Elongation at break of all the said substrates decreases by thermal treatment. This decrease is governed by the temperature and duration of heat treatment as well as by the nature of the substrate (Table III). Increasing the temperature and/or the duration of thermal treatment is accompanied by a decrease in the elongation at break regardless of the substrate used. However, the elongation at break of the said substrates follows the order given above for these substrates before thermal treatments.

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