

Effect of Degradative Treatments on Cotton Graft Copolymers. Part IV. Hydrolytic Susceptibility of Poly(acrylonitrile)-Cotton Graft Copolymers

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Synopsis

Acrylonitrile (AN) was graft polymerized to different levels onto cotton fabric using ferrous cellulose thiocarbonate-hydrogen peroxide redox system. The hydrolytic susceptibility toward 0.5 N HCl at 40°, 60°, and 80°C for 15–90 minutes of copolymers having 12, 15, and 22.5% graft was studied and compared with those of ungrafted and initiator-treated cottons. Hydrolytic susceptibility was assessed by monitoring carboxylic groups, copper number, nitrogen content (in the case of the copolymers) and tensile strength of the five substrates. Results obtained concluded that poly(AN)-cotton graft copolymers were more susceptible to acid degradation than the ungrafted and initiator-treated cottons when the acid treatment was performed under mild conditions. On the other hand, they were less susceptible when the acid treatment was carried out under relatively severe conditions.

INTRODUCTION

Synthesis, characterization, and properties of cellulose and modified cellulose graft copolymers have been extensively studied and the subject has been reviewed.^{1–3} The behavior of some of these graft copolymers toward dyeing, oxidation, thermal treatment, hydrolysis, and photodegradation have also been reported.^{4–15}

This work aims at clarifying the effect of structural changes in cotton cellulose brought about by copolymerization with poly(acrylonitrile) on the hydrolytic susceptibility of cotton. To achieve the goal, ungrafted cotton, initiator-treated cotton, and poly(acrylonitrile)-cotton graft copolymers having different graft yields were subjected to hydrochloric acid treatments under different conditions. This was followed by measurement of the extent of degradation of the copolymers in comparison with those of ungrafted and initiator-treated cottons.

EXPERIMENTAL

Cotton Fabric

Mill scoured and bleached plain weave (23 picks and 23 ends/cm) cotton fabric was used. This fabric, will be referred to as substrate I.

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INITIATOR-TREATED FABRIC

Cotton fabric was treated with the initiator under conditions identical with those used for grafting except that acrylonitrile (AN) was omitted. Initiator-treated fabric will be referred to as substrate II.

POLY(AN)-COTTON GRAFT COPOLYMERS

Poly(AN)-cotton graft copolymer was prepared according to a method described elsewhere¹⁶ using ferrous cellulose thiocarbonate-hydrogen peroxide redox system.

Fabric Thiocarbonation. The cotton fabric samples were placed in the cups of thermostatic Atlas Launder-Ometer containing freshly prepared solution consisting of sodium hydroxide (1%), carbon disulfide (2%, v/v) at 20–25°C, using a material to liquor ratio 1:30. After 45 minutes, the solution was drained and the samples were thoroughly washed with distilled water until an equilibrium (pH 7) in the washing liquor was reached. The fabric in this form will be referred to as sodium-cellulose thiocarbonate.

Metallization of Sodium-Cellulose Thiocarbonate. Metallization of sodium-cellulose thiocarbonate was carried out as follows: The sodium-cellulose thiocarbonate was immersed in the cups of thermostatic Atlas Launder-Ometer containing ferrous ammonium sulfate solution (1 mmol/L) at 25°C for 20 minutes, using a material to liquor ratio 1:30. Unreacted ferrous ions were washed out with distilled water and squeezed between two filter papers before introducing to the polymerization solution.

Polymerization Procedure. Graft polymerization reaction was carried out as follows: The cotton fabric (ferrous-cellulose-thiocarbonate) was introduced in a cup of thermostatic Launder-Ometer containing a solution consisting of vinyl monomer and hydrogen peroxide. Material to liquor ratio 1:40 was used. The pH of the reaction medium was adjusted before starting the polymerization. At the end of the desired reaction time, the same was removed, thoroughly washed, boiled with dilute oxalic acid solution and dried to constant weight. Proper solvent extraction was used for water-insoluble homopolymers.

The percentage graft yield was calculated as follows:

$$\% \text{ Graft yield} = \frac{\text{dry wt of graft sample} - \text{dry wt of original sample}}{\text{dry wt of original sample}} \times 100$$

Three poly(AN)-cotton graft copolymers having 12%, 15%, and 22.5% graft could be achieved by making use of AN concentration during grafting. These three copolymers will be referred to as substrate III with 12% graft, substrate IV with 15% graft, and substrate V with 22.5% graft.

HYDROCHLORIC ACID TREATMENTS

Heterogeneous acid hydrolysis of the ungrafted cotton, initiator-treated cotton, and poly(AN)-cotton graft copolymers was carried out by steeping the samples into 0.5 N hydrochloric acid at different temperatures (40°, 60°, 80°, and 100°).

and 80°C) for periods of time ranging from 15 to 90 minutes keeping material to liquor ratio of 1:30. After acid hydrolysis, the samples were washed repeatedly with distilled water until free from acid and air dried at room temperature.

TESTING AND ANALYSIS

Copper Number. The copper number was determined according to the micro Braid method as modified by Heyes.¹⁷

Carboxyl Content. The carboxyl content was determined by the alkalimetry method.¹⁸

Nitrogen Content. Determination of nitrogen content was carried out according to the Kjeldahl method.

Tensile Strength. The tensile strength of the fabric before and after acid treatment was measured according to the ASTM strip test.¹⁹

RESULTS AND DISCUSSION

Ungrafted cotton (substrate I), initiator-treated cotton (substrate II), and poly(AN)-cotton graft copolymers (substrates III, IV, and V) were subjected to treatments with hydrochloric acid (0.5 N) at different temperatures (40–80°C) for varying lengths of time (15–90 min). The hydrolytic susceptibility of these five substrates was assessed through monitoring carboxyl content, copper number, nitrogen content (in case of substrates III, IV, and V), and tensile strength. This was done to clarify the effect of structural changes in cotton brought about by copolymerization with poly(AN) on the susceptibility of cotton toward acid hydrolysis.

CARBOXYL CONTENT

Figures 1–3 show the effect of hydrochloric acid treatment (0.5 N) for different periods of time (15–90 min) at 40°, 60°, and 80°C, respectively, on the carboxyl content of the five substrates in question. The first observation indicates that the original carboxyl contents of these substrates are not the same. They follow the order:

Substrate V > substrate IV \approx substrate III > substrate II > substrate I

The slightly higher carboxyl content of initiator-treated cotton (substrate II) compared with ungrafted cotton (substrate I) could be associated with oxidation of cellulose hydroxyls and/or aldehydic groups to carboxylic groups under the influence of initiator. On the other hand, the higher carboxyl contents of the poly(AN)-cotton graft copolymers (substrates III–V) suggest that the —CN group in the acrylonitrile moiety of the graft undergoes partial oxidation to the carboxyl group.

Figures 1–3 show also that acid hydrolysis is accompanied by enhancement in the carboxyl contents of the five substrates under investigation, being dependent upon the nature of the substrate as well as duration and temperature of the treatment. The carboxyl contents of the copolymers (sub-

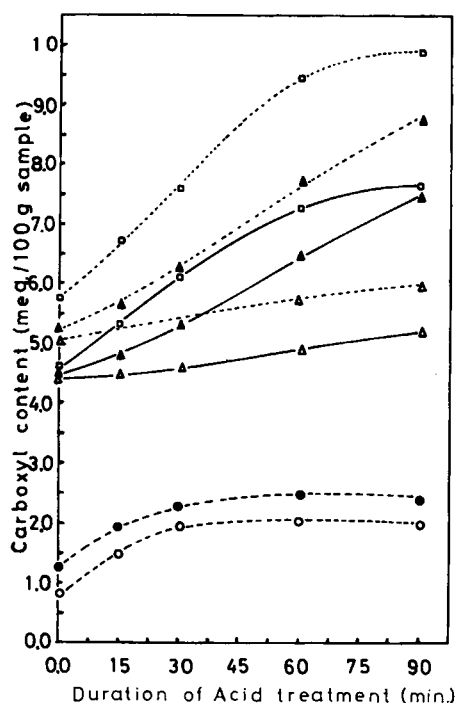


Fig. 1. Carboxyl contents of substrates I-V as a function of duration of acid treatment at 40°C. (----), Carboxyl content based on weight of cellulose; (—), carboxyl content based on weight of copolymer; (○), ungrafted cotton; (●), initiator-treated cotton; poly(AN) graft %: (△), 12; (▲), 15; (□), 22.5; HCl, 0.5 N.

strates III-V) increase by increasing the duration of the acid treatment within the range studied (15–90 min) irrespective of the temperature. This state of affairs becomes more significant when the carboxyl content of the copolymers was calculated only on the cellulose content of the copolymer (dotted lines in Figs. 1–3). On the other hand, the carboxyl content of ungrafted and initiator-treated cottons (substrates I and II) increase with increasing duration of the treatment up to 30 min then almost level off.

Since there is no reason to believe that hydrolysis creates carboxyl content in the cellulose molecules,²⁰ the enhancement in carboxyl contents of substrates I and II, though not so striking, suggests that some of the aldehydic groups formed via cellulose chain scission during acid hydrolysis were oxidized to carboxylic groups by atmospheric and occluded oxygen during the time given for drying and conditioning. On the other hand, the substantial enhancement in carboxyl contents of the copolymers (substrates III–V) suggests that the graft undergoes partial hydrolysis and, as a result, some of the —CN groups are converted to carboxylic groups. This is of course beside the conversion of some of the aldehydic groups to carboxylic groups as in case of substrates I and II.

The effect of temperature of acid treatment on the carboxyl content is rather interesting (Figs. 1–3). Raising the temperature from 40° up to 80°C has practically no effect on the carboxyl content of substrates I and II re-

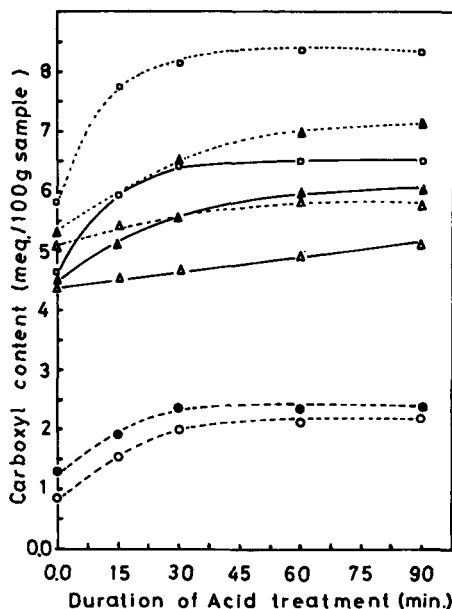


Fig. 2. Carboxyl contents of substrates I-V as a function of duration of acid treatment at 60°C. (----), Carboxyl content based on weight of cellulose; (—), carboxyl content based on weight of copolymer; (○), ungrafted cotton; (●), initiator-treated cotton; poly(AN) graft %: (Δ), 12; (▲), 15; (□), 22.5; HCl, 0.5 N.

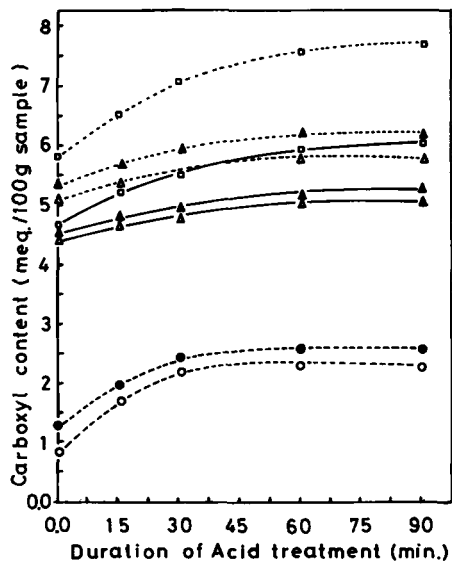


Fig. 3. Carboxyl contents of substrates I-V as a function of duration of acid treatment at 80°C. (----), Carboxyl content based on weight of cellulose; (—), carboxyl content based on weight of copolymer; (○), ungrafted cotton; (●), initiator-treated cotton; poly(AN) graft %: (Δ), 12; (▲), 15; (□), 22.5; HCl, 0.5 N.

gardless of the duration of acid treatment. With the copolymers (substrates III–V), on the other hand, the carboxyl content decreases by increasing the temperature, indicating that temperature acts in favor of decarboxylation of the carboxylic groups formed via partial hydrolysis of the poly(AN) graft, though the carboxyl content is higher at 60°C than at 40°C during the initial stages of the reaction.

COPPER NUMBER

Figures 4–6 show the effect of hydrochloric acid treatment (0.5 N) for different periods of time (15–90 min) at 40°, 60°, and 80°C, respectively, on the copper number of substrates I–V. It is seen that the copper number of the said substrates before the treatment varies considerably. It follows the order:

Substrate V > substrate IV > substrate III > substrate II > substrate I

The higher copper number of substrate II (initiator-treated cotton) compared with substrate I (ungrafted cotton) could be interpreted in terms of oxidation

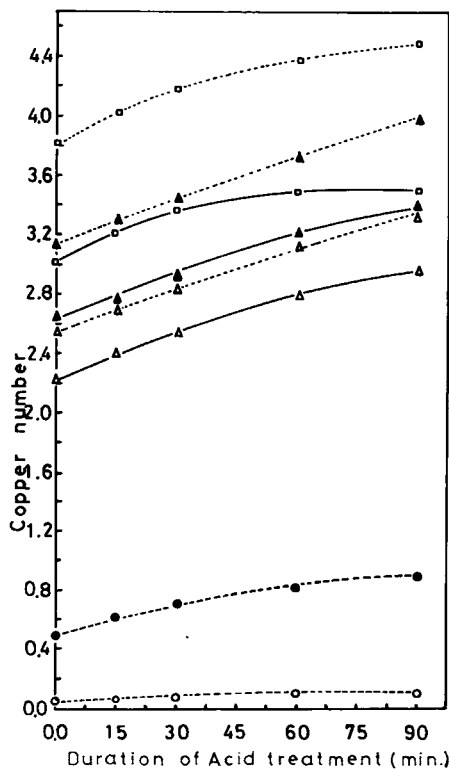


Fig. 4. Copper number of substrates I–V versus duration of acid treatment at 40°C. (---), Copper number based on weight of cellulose; (—), copper number based on weight of copolymer; (○), ungrafted cotton; (●), initiator-treated cotton; poly(AN) graft %: (△), 12; (▲), 15; (□), 22.5; HCl, 0.5 N.

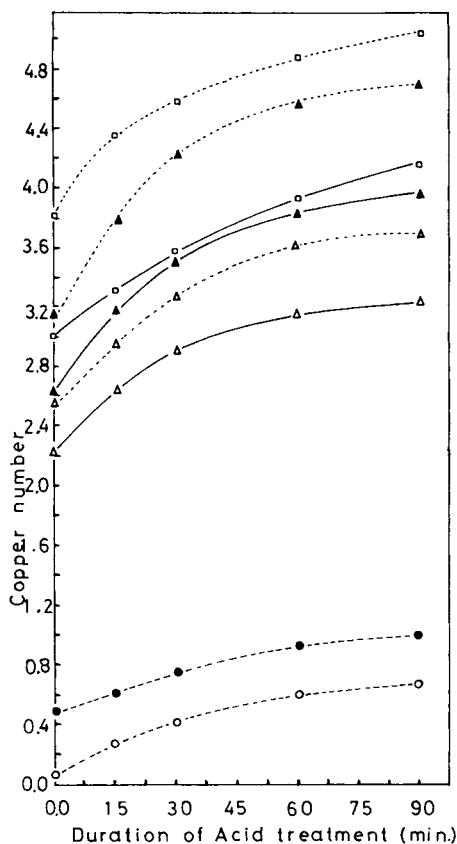


Fig. 5. Copper number of substrates I-V versus duration of acid treatment at 60°C. (----), Copper number based on weight of cellulose; (—), copper number based on weight of copolymer; (○), ungrafted cotton; (●), initiator-treated cotton; poly(AN) graft %: (△), 12; (▲), 15; (□), 22.5; HCl, 0.5 N.

of the cellulose hydroxyls to aldehydic groups under the influence of the initiator. On the other hand, the copper number of poly(AN)-cotton graft copolymers could be essentially associated with the reducing property of the —CN groups of the graft as well as its hydrolyzed form (—CONH₂ group) which may be formed during the course of copper number measurement.

Figures 4–6 show also that acid hydrolysis is accompanied by enhancement in the copper number of the five substrates under investigation, being dependent on the nature of the substrate as well as duration and temperature of the treatment. Increasing the duration and/or temperature of the acid treatment causes a substantial increment in copper number irrespective of the substrate used. This is unequivocally due to liberation of more and more end-reducing groups via cleavage of glucosidic bonds in the cellulose chain molecules.²¹ Nevertheless, the copolymers (substrates III, IV, and V) appear to acquire a higher copper number than the ungrafted and initiator-treated cottons (substrates I and II), particularly when the copper number was calculated on the cellulose content of the copolymers (dotted lines in

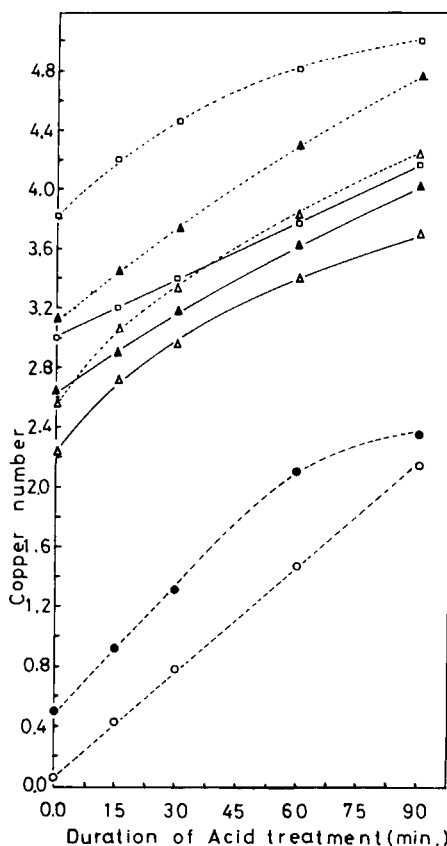


Fig. 6. Copper number of substrates I-V versus duration of acid treatment at 80°C. (----), Copper number based on weight of cellulose; (—), copper number based on weight of copolymer; (○), ungrafted cotton; (●), initiator-treated cotton; poly(AN) graft %: (△), 12; (▲), 15; (□), 22.5; HCl, 0.5 N.

Figs. 4–6). Indeed, subtracting the original copper number of each substrate from the corresponding value after acid hydrolysis confirms this provided that the acid treatment is carried out at 40° or 60°C for the duration range of the present investigation. The opposite holds true when the acid treatment was carried out at 80°C. The copper number values of the copolymers after subtracting the original value from the corresponding value after acid hydrolysis at 80°C are lower than those of the ungrafted and initiator-treated cottons. Furthermore, these values are lower the higher the % graft.

The above finding concludes that the copolymers in question are more susceptible than the ungrafted and initiator-treated cottons to acid hydrolysis when the latter was performed under relatively mild conditions. On the other hand, they are less susceptible to acid degradation under relatively severe conditions. It may be argued that the copper number cannot be taken as a measure for degradation by virtue of the reducing properties of the graft, but for comparison it seems logical particularly when subtracting the original values from their corresponding values after acid hydrolysis.

NITROGEN CONTENT

Figure 7 shows the effect of hydrochloric acid treatment (0.5 N) for different periods of time (15–90 min) at 40°, 60°, and 80°C on the nitrogen content of poly(AN)-cotton graft copolymers (substrates III, IV, and V). It is observed that the nitrogen content of the copolymers decreases after acid treatment. The decrement in nitrogen content is higher the higher the % graft. Conditions of the acid treatment also affect the magnitude of the nitrogen content. The decrement in nitrogen content increases by increasing duration and/or temperature of the acid treatment though raising the temperature from 60° to 80°C causes further slight decrement in nitrogen content.

The loss in the nitrogen content of the copolymers after acid hydrolysis suggests that some of the —CN groups of the graft are hydrolyzed to carboxylic groups. Calculation of the amount of carboxylic groups equivalent to the loss in nitrogen was made and the results are given in Table I. Obviously, the determined carboxyl content is lower than the calculated amount. This indicates that the loss in nitrogen content is due to disappearance of the —CN groups via conversion to carboxylic groups followed by decarboxylation. Indeed this would substantiate the higher carboxyl content of the copolymers, already discussed, as compared with the ungrafted and initiator-treated cottons (substrates I and II).

TENSILE STRENGTH

Table II shows the warp tensile strength of substrates I–V before and after acid treatment. It is seen that subjecting ungrafted cotton (substrate I) to either initiator treatment or graft copolymerization is accompanied by a decrement in the tensile strength. Nevertheless, the decrement in tensile strength brought about by grafting is slightly higher than that caused by

TABLE I
Calculated Amount of Carboxylic Groups Equivalent to the Loss in Nitrogen

Temperature °C	Time, min	mEq carbonate/100 g sample		
		12	Add on % 15	22.5
40	15	3.57	3.57	3.57
	30	9.3	10.7	3.57
	60	10.7	14.3	17.85
	90	10.7	23.57	21.42
60	15	3.57	10.71	10.71
	30	9.3	14.28	14.28
	60	10.7	32.14	17.85
	90	17.85	50.0	48.5
80	15	3.57	10.7	10.7
	30	10.7	14.28	17.85
	60	14.3	35.7	17.85
	90	17.85	53.57	53.7

TABLE II
 Effect of Hydrochloric Acid (0.5 N) Treatment at Different Conditions on Warp Tensile Strength and Warp Retained Tensile Strength of Ungrafted Cotton (Substrate I) Initiator-Treated Cotton (Substrate II) and Poly(AN)-Cotton Graft Copolymers (Substrates III-V)

Temperature (°C)	Time (min)	Substrate I			Substrate II			Substrate III			Substrate IV			Substrate V		
		TS	RT	TS	RT	TS	RT	TS	RT	TS	RT	TS	RT	TS	RT	
40	15	64.0	91.4	53.5	90.6	74.5	83.3	52.5	92.1	44.0	78.5					
	30	59.0	84.3	49.0	83.05	46.0	80.7	50.0	87.7	42.0	74.9					
	60	52.0	74.3	40.0	67.7	43.5	76.3	47.5	83.3	40.5	72.3					
60	90	48.0	68.5	30.0	50.8	41.5	72.8	45.0	78.9	40.0	71.4					
	15	50.0	71.4	40.0	67.8	33.5	58.7	32.5	57.01	30.5	54.4					
	30	44.5	63.5	34.0	57.6	29.5	51.7	27.5	48.2	25.0	44.6					
80	60	40.0	57.1	27.5	46.6	26.5	46.5	25.0	34.8	22.5	40.17					
	90	35.5	50.7	22.5	38.1	25.5	44.7	24.0	24.1	24.0	42.8					
	15	32.0	45.7	30.0	50.8	31.0	54.3	31.0	54.4	31.0	55.0					
Before treatment	30	24.0	34.28	21.0	35.6	22.5	39.4	22.0	38.59	25.0	44.6					
	60	12.5	17.8	11.0	18.64	17.5	30.7	17.0	29.8	19.5	34.8					
	90	10.5	14.99	10.0	16.9	12.5	21.9	11.5	20.17	14.5	25.9					
		70.0	—	59.0	—	57.5	—	57.0	—	56.0	—					

Where TS: Tensile strength (kg); RT: Retained tensile strength (%).

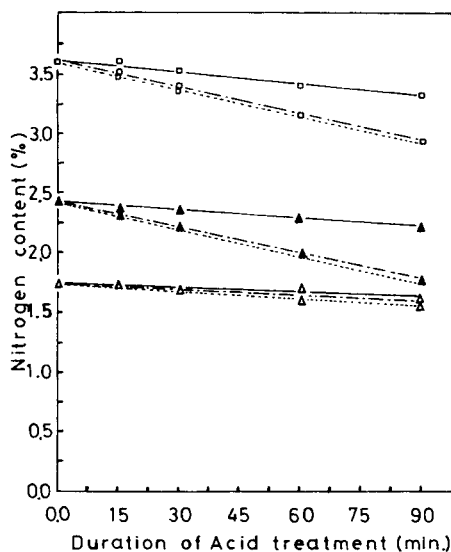


Fig. 7. Effect of duration of acid treatment on nitrogen contents of poly(AN)-cotton graft copolymers. HCl, 0.5 N; (—), 40°C; (-.-.-), 60°C; (....), 80°C; poly(AN) graft %: (Δ), 12; (\blacktriangle), (\square), 22.5.

initiator treatment. As previously reported,²² the strength loss with initiator-treated cotton (substrate II) would be attributed to degradation of cotton under the influence of the initiator. On the other hand, strength losses found with the copolymers (substrates III, IV, and V) are perhaps due to disruption of the cellulose structure by the graft. Presence of the latter in the structure of cotton cellulose acts as spikes along the molecular chain to prevent the molecules from associating and thereby loosening the structure of cotton.

Hydrochloric acid treatment causes a decrement in the tensile strength of the five substrates in question, but this decrement is determined by the nature of the substrate as well as temperature and duration of the treatment. Increasing the duration and/or temperature of treatment are accompanied by a progressive decrement in tensile strength irrespective of the substrate used. Nevertheless, the ungrafted cotton retains the highest tensile strength at relatively mild conditions (40° and 60°C) whereas poly(AN)-cotton graft copolymers retains the lowest strength. A different situation is encountered at relatively severe conditions (i.e., 80°C), the untreated cotton suffered more degradation than any other sample. In short, the loss of tensile strength of grafted copolymers varied with temperature and degree of grafting.

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