

# Effect of Degradative Treatments on Cotton Graft Copolymers. Part V. Behavior of Poly(Acrylamide)-Cotton Graft Copolymers Toward Acid Treatments

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## Synopsis

Polyacrylamide (Aam)-cotton graft copolymers having 9, 14.5, and 20% graft were synthesized using ferrous cellulose thiocarbonate-hydrogen peroxide redox system. These copolymers as well as ungrafted and initiator-treated cottons were subjected to acid treatments (0.5 N HCl) at 40°, 60°, and 80°C for 15-90 minutes. Hydrolytic susceptibility of the five substrates was assessed by monitoring carboxylic groups, copper number, nitrogen content (in case of the copolymers), and tensile strength. Results obtained concluded that the copolymers exhibit higher resistance to acid hydrolysis than the ungrafted and initiator-treated cottons. This was explained in terms of involvement of the  $-\text{CONH}_2$  groups of the graft in an interaction with HCl.

## INTRODUCTION

In their monograph on the chemistry and technology of cellulosic copolymers, Hebeish and Guthrie<sup>1</sup> have emphasized the scientific and technological interest in the chemical modification of cellulose. Basically, research and developmental work was directed toward innovation of products with useful new and interesting properties via etherification, esterification, and/or grafting of cellulosic materials. Hydrolysis and photodegradation of some cellulose graft copolymers as well as the behavior of these copolymers towards persulfate oxidation and thermal treatments have also been reported.<sup>2-9</sup> In addition, previous studies have also dealt with the behavior of poly(methacrylic acid), poly(acrylamide), and poly(acrylonitrile)-cotton graft copolymers toward hypochlorite treatments as well as the behavior of the latter copolymers toward hydrochloric acid treatments.<sup>10-13</sup>

In the present work, acid hydrolysis of polyacrylamide (Aam) cotton graft copolymers is investigated with a view to clarify the effect of changes in the chemical and physical structure of cotton cellulose brought about by grafting on the behavior of cotton toward acid hydrolysis.

## 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.

### Initiator-Treated Fabric

The cotton fabric was treated with the initiator under conditions identical with those used for grafting except that acrylamide was omitted. Initiator-treated fabric will be referred to as Substrate II.

### Poly(Aam) Cotton Graft Copolymers

Synthesis of poly(Aam)-cotton graft copolymers was carried out according to conditions detailed elsewhere<sup>14</sup> using ferrous cellulose thiocarbonate-hydrogen peroxide redox system. Three poly(Aam) cotton graft copolymers having 9, 14.5, and 20% grafts were obtained by making use of acrylamide concentration during grafting. These three copolymers will be referred to as Substrate III with 9% graft, Substrate IV with 14.5% graft, and Substrate V with 20% graft.

### Hydrochloric Acid Treatment

Heterogenous acid hydrolysis of the ungrafted cotton, initiator-treated cotton and poly(Aam)-cotton graft copolymers was carried out by steeping the samples in 0.5 N hydrochloric acid at 40°, 60°, and 80°C for different periods of time (15–90 minutes), keeping material to liquor ratio of 1:30. After acid treatment, the samples were washed repeatedly with distilled water until free from acid and dried in the air at room temperature.

### Testing and Analysis

The carboxyl content was determined by the alkalimetry method.<sup>15</sup>

The copper number was determined according to the micro Braidly method as modified by Heyes.<sup>16</sup>

Nitrogen content was determined according to the Kjeldahl method.

The tensile strength of the fabric samples were measured according to the ASTM strip test.<sup>17</sup>

## RESULTS AND DISCUSSION

Five substrates, namely, ungrafted cotton, initiator-treated cotton, and poly(Aam)-cotton graft copolymers having different graft yields were subjected to 0.5 N HCl at 40°, 60°, and 80°C for different periods of time (15–90 min). The substrates before and after those acid treatments were examined for carboxyl content, copper number, nitrogen content (in case of the copolymers), and tensile strength in order to clarify the effect of structural changes in cotton caused by grafting on the hydrolytic susceptibility of cotton.

### Carboxyl Content

Figures 1-3 show variations of the carboxyl contents of the five substrates with duration of the acid treatment at 40°, 60°, and 80°C. It is observed that before acid treatments the carboxyl contents show values of 0.87, 1.32, 4.51, 5.73, 7.36 mEq/100 g sample for Substrates I-V, respectively. While oxidation of some cellulose hydroxyls and/or aldehyde groups under the influence of initiator to carboxylic groups accounts for the difference in the

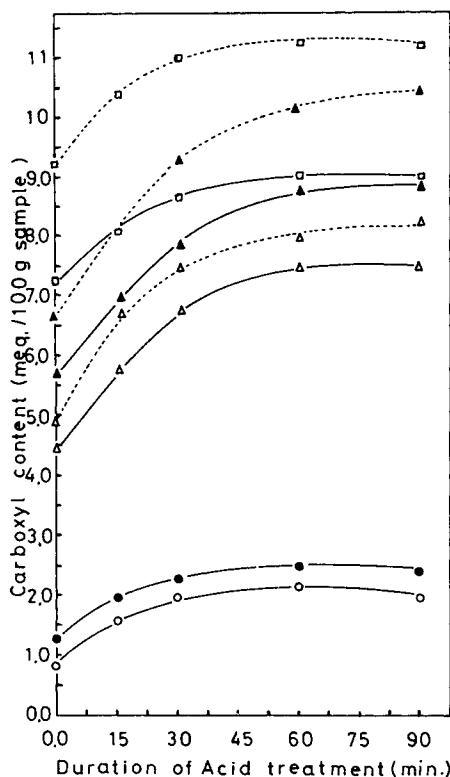


Fig. 1. Carboxyl contents of Substrates I-V as a function of duration of acid treatment at 40°C; (---), carboxyl content based on weight of cellulose; (—), carboxyl content based on weight of copolymer; (○), ungrafted cotton; (●), initiator-treated cotton; poly(Aam), graft %; (△), 9; (▲), 14.5; (□), 20; HCl, 0.5 N.

carboxyl contents between initiator-treated cotton (Substrate II) and ungrafted cotton (Substrate I), partial conversion of  $-\text{CONH}_2$  groups to carboxylic groups seems to be the essential reason for the higher carboxyl contents of the poly(Aam)-cotton graft copolymers (Substrates III-V). It is likely that the  $-\text{CONH}_2$  group in the acrylamide moiety of the graft undergoes partial oxidation to carboxyl group.

After acid treatment, the carboxyl content shows an increment, the magnitude of which is dependent upon nature of the substrate as well as duration and temperature of the treatment (Figs. 1-3). As is evident, the carboxyl contents of the copolymers (Substrates III-V) increase by increasing the acid treatment duration from 15-90 min irrespective of the temperature used. A more clarified picture of this is shown in the same figures by dotted lines representing the carboxyl contents calculated only on the cellulose content of the copolymer. On the other hand, the carboxyl contents of ungrafted and initiator-treated cottons (Substrates I and II) increase by increasing duration of the treatment up to 30 minutes then almost level off. At any event, however, the copolymers (Substrates III-V) exhibit much higher carboxyl contents than ungrafted and initiator-treated cottons (Substrates I-II) after acid treatment.

Since there is no reason to believe that acid hydrolysis creates carboxyl groups in the molecular structure of cotton cellulose,<sup>18</sup> current data suggest

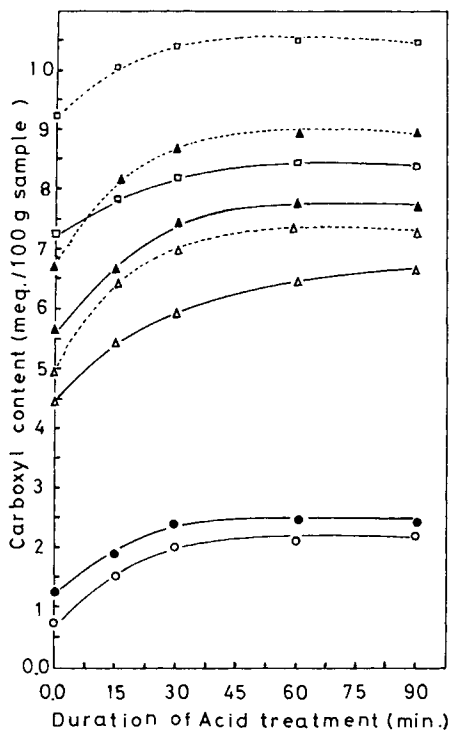
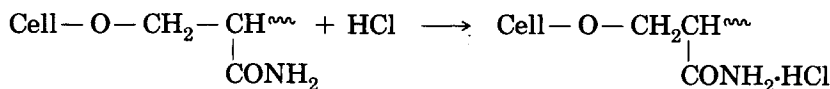


Fig. 2. Carboxyl contents of Substrates I-V as a function of duration of acid treatment at 60°C; (---), carboxyl content based on weight of cellulose; (—), carboxyl content based on weight of copolymers; (○), ungrafted cotton; (●), initiator-treated cotton; poly(Aam), graft %: (△), 9; (▲), 14.5; (□), 20; HCl, 0.5 N.

that some of the aldehydic groups formed via cellulose chain scission during acid hydrolysis are oxidized to carboxylic groups by atmospheric and occluded oxygen during the time given for drying and conditioning. Besides, the graft seems to undergo partial hydrolysis and, as a result, some of the  $-\text{CONH}_2$  groups are converted to carboxylic groups.

It is rather logical that the  $-\text{CONH}_2$  groups, by virtue of their basicity, are getting involved with HCl in an interaction as shown below.<sup>19</sup>



Once this is the case, the copolymers would acquire acidic properties which inevitably contribute to the value of the carboxyl content during carboxylic determination by the alkalimetry method used. That is why the copolymers acquire much higher carboxyl contents than the ungrafted and initiator-treated cottons. Indeed, copolymerized sample (20% graft) treated with HCl at 80°C and 60°C for 30 min showed a chlorine content of 7.53 and 5.76 mEq/100 g cellulose, respectively.

Figures 1-3 depict that the carboxyl contents of Substrates I and II after acid treatment at 40°, 60°, and 80°C are comparable, indicating that raising the temperature has practically no effect on the carboxyl contents of un-

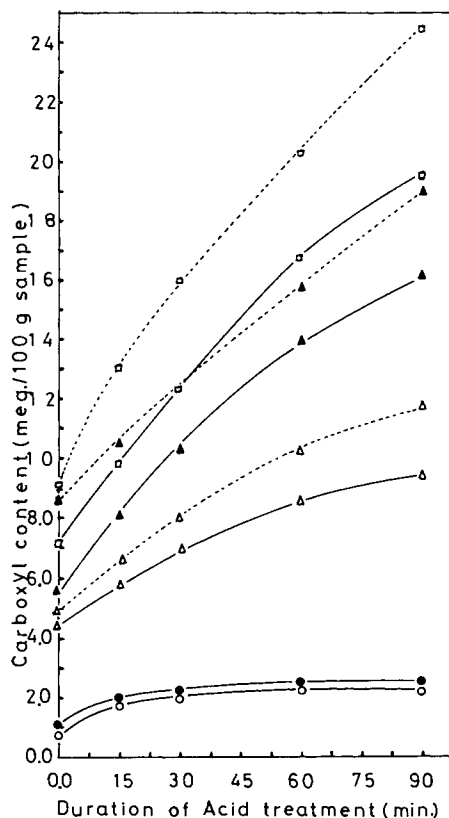


Fig. 3. Carboxyl contents of Substrates I-V as a function of duration of acid treatment at 80°C; (---), carboxyl content based on weight of cellulose; (—), carboxyl content based on weight of copolymer; (○), ungrafted cotton; (●), initiator-treated cotton; poly(Aam) graft %: (△), 9; (▲) 14.5; (□), 20; HCl, 0.5 N.

grafted and initiator-treated cottons. A similar situation is encountered with the copolymers but the carboxyl contents of the latter are significantly higher at 80°C than at 40°C and 60°C. It is logical that interaction of the  $-\text{CONH}_2$  group in the graft with HCl proceeds faster at 80°C and, therefore, the observed higher carboxyl contents. However, contribution of the carboxyl groups brought about by partial hydrolysis of the  $-\text{CONH}_2$  in the graft at such a high temperature cannot be ruled out.

### Copper Number

Figures 4, 5, and 6 show the effect of acid treatment on the copper number of the five substrates in question at 40°, 60°, and 80°C, respectively. It is observed that before acid treatments the copper number of the poly(Aam)-cotton graft copolymers are significantly higher than those of ungrafted and initiator-treated cottons. Meanwhile, it is certain that the higher the % graft, the higher the copper number. Also, the initiator-treated cotton acquires higher copper number than the ungrafted cotton.

The higher copper number of initiator-treated cotton than the ungrafted cotton could be interpreted in terms of oxidation of the cellulose hydroxyls

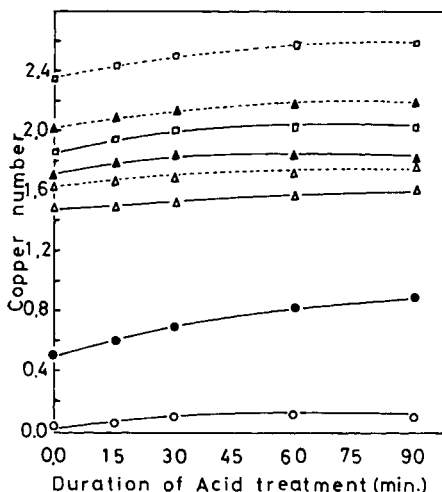


Fig. 4. Copper number of Substrates I-V versus duration of acid treatment at 40°C; (...), copper number based on weight of cellulose; (—), copper number based on weight of copolymer; (○), ungrafted cotton; (●), initiator-treated cotton; poly(Aam) %: (△), 9; (▲), 14.5; (□), 20; HCl, 0.5 N.

to aldehydic groups under the influence of initiator. On the other hand, the significantly higher copper number of poly(Aam)-cotton graft copolymers (Substrates III-V) suggests that conversion of some of the cellulose hydroxyls to aldehyde groups by the initiator during synthesis of copolymers takes place.

Figures 4-6 reveal that acid treatment is accompanied by enhancement in the copper number of the five substrates. This enhancement is much favored by increasing the duration and/or temperature of the treatment,

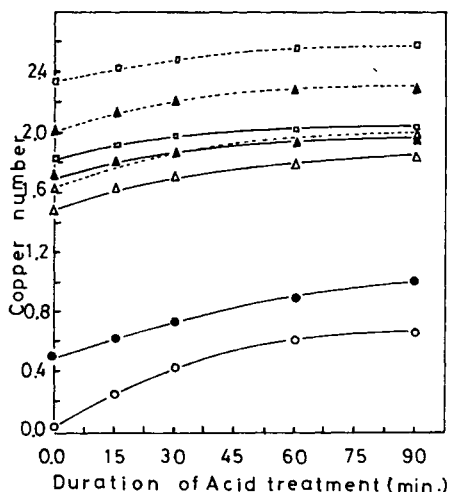


Fig. 5. Copper number of Substrates I-V versus duration of acid treatment at 60°C; (...), copper number based on weight of cellulose; (—), copper number based on weight of copolymer; (○), ungrafted cotton; (●), initiator treated cotton; poly(Aam) graft %: (△), 9; (▲), 14.5; (□), 20; HCl 0.5 N.

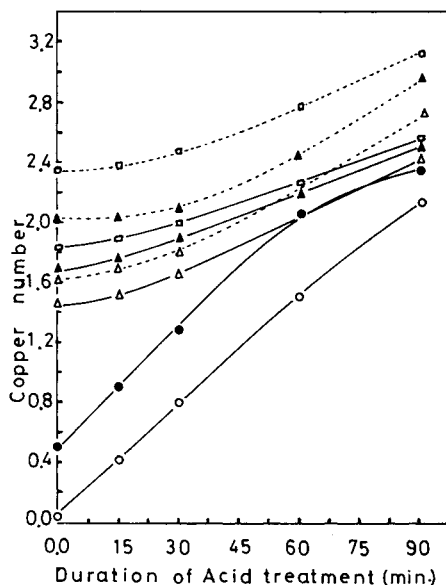


Fig. 6. Copper number of Substrates I-V versus duration of acid treatment at 80°C; (---), copper number based on weight of cellulose; (—), copper number based on weight of copolymer; (○), ungrafted cotton; (●), initiator-treated cotton; poly(Aam) graft %: (△), 9; (▲), 14.5; (□), 20; HCl, 0.5 N.

particularly when the ungrafted and initiator-treated cottons were used. It should also be emphasized that though the poly(Aam)-cotton graft copolymers still exhibit much higher copper number after acid hydrolysis than the ungrafted and initiator-treated cottons, yet the enhancement in copper number found with the latter substrates exceeds that of the copolymers. If the copper number is taken as a measure for cotton cellulose degradation, this finding would indicate that the poly(Aam)-cotton graft copolymers acquire improved resistance to acid hydrolysis. Presumably, attachment of HCl to the  $-\text{CONH}_2$  of the graft would not only reduce concentration of the acid in the hydrolyzing medium but also impede glucosidic bond scission.

### Nitrogen Content

Figure 7 shows the nitrogen content of poly(Aam)-cotton graft copolymers having 9, 14.5, and 20% graft as a function of duration of acid treatment at 40°, 60°, and 80°C. Obviously, the nitrogen content decreases as duration of the treatment increases. Raising the temperature from 40° to 60°C is also accompanied by decrement in nitrogen content. Increasing the temperature to 80°C causes further decrement in nitrogen content but to lesser extent. In addition, the decrement in nitrogen content is lower the higher the % graft.

It is interesting to note that copolymers with 9, 14.5, and 20% graft lose 25.32, 9.1, and 5.2% of their nitrogen content when hydrolysis was performed at 40°C for 90 minutes. This is against losses in nitrogen of 33.5, 14.25, and 22.75% at 80°C. These losses suggest that some of the  $-\text{CONH}_2$  groups of the graft are hydrolyzed to carboxylic groups which would, in

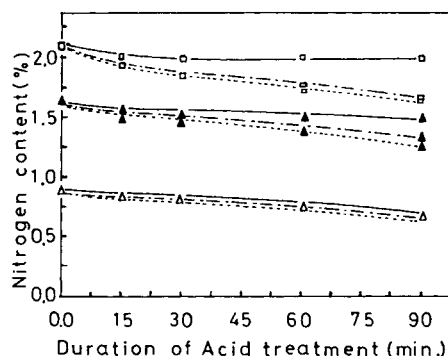


Fig. 7. Effect of duration of acid treatment on nitrogen contents of poly(Aam)-cotton graft copolymers; HCl, 0.5 N; (—), 40°C, (---), 60°C; (···), 80°C; poly(Aam) graft %: ( $\Delta$ ), 9; ( $\blacktriangle$ ), 14.5; ( $\square$ ), 20.

part, account for the higher carboxyl content of the copolymers particularly at 80°C as discussed before.

### Tensile Strength

Table I shows the warp tensile strength of cotton before and after the latter was graft copolymerized with poly(Aam). Warp tensile strength of initiator-treated cotton is also shown in the table. The first look at the original substrates indicate that grafting as well as initiator treatment decrease the tensile strength of the cotton fabric. Nevertheless, the decrement in tensile strength caused by grafting is higher than that caused by initiator treatment. While the decrement in tensile strength in case of the copolymers could be associated with the presence of the graft in an

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

Temperature °C	Time minutes	Tensile strength (Kg)				
		Substrate I	Substrate II	Substrate III	Substrate IV	Substrate V
40	15	64.0	53.5	47.5	46.0	41.5
	30	59.0	49.0	45.0	42.5	40.0
	60	52.0	40.0	40.0	39.0	36.0
	90	48.0	30.0	37.0	37.0	33.0
	Before treatment		70.0	59.0	58.0	57.0
60	15	50.0	40.0	38.0	36.5	35.0
	30	44.5	34.0	32.0	31.0	30.0
	60	40.0	27.5	29.0	27.5	26.0
	90	35.5	22.5	27.5	24.0	25.0
	80	15	32.0	30.0	32.5	29.5
30		24.0	21.0	22.5	20.0	19.0
60		12.5	11.0	16.5	15.0	13.5
90		10.5	10.0	12.5	10.0	10.0
Before treatment			70.0	59.0	58.0	57.0



disoriented amorphous state together with molecular disruption of cotton, this decrement is unequivocally due to oxidative degradation by the initiator in case of initiator-treated cotton.

When ungrafted cotton initiator-treated cottons and poly(Aam)-cotton graft copolymers were subjected to acid treatments at 40°, 60°, and 80°C, the warp tensile strength decreases. The decrease in tensile strength is higher the higher the temperature or the longer the duration of acid treatment. This is observed regardless of the substrate used. However, the copolymers are more resistant to acid hydrolysis than the ungrafted and initiator-treated cottons. This is evidenced if one considers percent strength losses calculated by dividing the difference in tensile strength of a given substrate before and after hydrolysis by the original strength of this substrate.

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