

# Graft Polymerization of Different Monomers onto Carbamated Starches Derived from Native and Hydrolyzed Starches

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**ABSTRACT:** Rice starch was hydrolyzed with hydrochloric acid so that starches would be obtained with different molecular sizes. The derived hydrolyzed starches were carbamated at various reaction times and were grafted with different monomers with a potassium permanganate/citric acid system as an initiator. The newly tailored starch-derived products were evaluated as sizing agents. The extent of carbamation increased with increasing hydrolysis and increasing reaction time. The graft yields of different monomers on carbamated starches and carbamated hydrolyzed starches increased with increasing carbamation and increas-

ing hydrolysis in the following order: acrylamide > acrylonitrile > acrylic acid. Cotton fabrics sized with grafted carbamated hydrolyzed starches acquired higher mechanical properties (tensile strength, elongation at break, and abrasion resistance) than hydrolyzed starches, carbamated starches, and carbamated hydrolyzed starches. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 959–965, 2003

**Key words:** carbamation; hydrolysis; grafting; mechanical properties

## INTRODUCTION

Starch is probably the most abundant and low-cost natural polymer commercially available. Considerable research and technical work have been reported so far, and the chemical modification of starch or modified starch via vinyl graft copolymerization constitutes the most important field for improving the properties of starch, enlarging the range of its utilization.<sup>1–6</sup> Starch graft copolymers can be achieved primarily by free-radical initiation processes.<sup>1,3,5,7</sup> Emphasis has been placed on high-energy ionization<sup>2,5,6,8</sup> and ceric ion<sup>5,9</sup> and redox systems.<sup>4,10,11</sup>

This work was undertaken for the purpose of tailoring a polymeric material based on rice starch. The latter was first subjected to acid hydrolysis to control the molecular size of starch. Starches with different molecular sizes were then carbamated and grafted with three different monomers: acrylamide (Aam), acrylonitrile (AN), and acrylic acid (AA). In this way, the carbamate groups and the chain molecules of synthetic vinyl polymers modified the molecular structure of starch through control over its molecular size and the substitution of some of the starch hydroxyls.

Finally, the newly tailored polymeric starch products were used for the sizing of cotton textiles.

## EXPERIMENTAL

### Materials

Misr Company (Alexandria, Egypt) kindly supplied rice starch for starch and yeast. AN and AA stabilized with 0.01% hydroquinone were freshly distilled at 75°C and 100 mmHg. They were stored at –10°C until they were used. Aam, urea, sodium hydroxide, hydrochloric acid, citric acid, dimethylformamide (DMF), magnesium sulfate, potassium permanganate, and ethanol were pure-grade chemicals.

### Preparation of the hydrolyzed starch

Three levels of hydrolyzed starches—H<sub>1</sub>, H<sub>2</sub>, and H<sub>3</sub>—having different degrees of hydrolysis (copper number) were prepared at different concentrations (0.25N, 0.5N, and 1N) of hydrochloric acid at 60°C for 0.5, 1.0, and 2 h with a material to a liquor ratio of 1:5. After the desired reaction time, the reaction was precipitated in 500 mL of ethyl alcohol and neutralized with a dilute sodium carbonate solution; the mixture was then washed and dried in an electric oven at 60°C for 3 h. The main characteristics of the starch and hydrolyzed starches are given in Table I.

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**TABLE I**  
Main Characteristics of the Starch  
and Hydrolyzed Starches

Substrate	Starches	
	Copper number	Apparent viscosity (mpa s)
I	0.002 ± 0.01	230
II	0.060 ± 0.02	195
III	1.410 ± 0.01	130
IV	1.820 ± 0.01	95

Substrate I = native rice starch; substrates II–IV = hydrolyzed rice starches. ± Values are the standard deviations of copper number samples measured three times. Details of the conditions used are given in the Experimental section.

### Synthesis of the starch carbamate

Soluble starch carbamate was prepared according to a reported method<sup>12</sup> as follows. Starch or hydrolyzed starches (10 g) were mixed well with 30% urea (based on the weight of starch) and magnesium sulfate (0.2 g) with an electric mixer. The mixture was transferred to a petri dish, covered, and heated at 160°C for different times (5–30 min). At the end of the reaction time, the thermally treated mixture was washed several times with an ethanol/water mixture (70:30) and finally with pure ethanol and was dried.

### Graft polymerization procedure

The graft polymerization reaction was carried out as follows. An aqueous solution of  $\text{KmnO}_4$  of a known concentration (0.1N) was placed in a glass-stoppered flask. The latter was kept in a thermostatic water bath for 15 min at 50°C. The starch or modified starch (10 g) was introduced into the flask, and the monomer (50% based on the weight of starch) was immediately added and was followed by 20 mequiv/L citric acid. The total volume was then adjusted to give a total volume of 100 mL. Nitrogen gas was purged into the reaction mixture to prevent the presence of oxygen, and the flask contents were stoppered and shaken immediately and occasionally during the course of the reaction. Grafting was carried out for 1 h. At the end of the reaction, the flask contents were poured over 500 mL of ethyl alcohol. A precipitate was formed that consisted of the starch graft copolymer and the homopolymer. The latter was removed in the case of poly(Aam) and poly(AA) by several washes with 400 mL of a water/ethanol mixture (30:70) for 15 min each at room temperature, filtered, and finally dried in an electric oven at 60°C for 2 h. It was found experimentally that washing five times with a mixture of water/ethanol (30:70 v/v) was quite enough for complete homopolymer removal in physical starch/poly(Aam) and starch/poly(AA) mixtures by the tracing of the nitrogen and carboxyl contents of these mixtures after

each wash. However, poly(AN) was removed by Soxhlet extraction with DMF for 24 h.

### Analysis

The copper number was estimated by a micro-Briady method modified by Heyes.<sup>13</sup> The nitrogen content was estimated by the Kjeldahal method,<sup>14</sup> and the carboxyl content was traced according to a reported method.<sup>15</sup> The apparent viscosity was measured with a coaxial rotary viscometer (Haake RV20, Germany) at a rate of shear of  $516 \text{ cm}^{-1}$  at 90°C.

### Sizing of the cotton fabrics

Cotton fabrics (kindly supplied by Misr Co., El-Mehala El-Kobra, Egypt, for spinning and weaving) were padded through two dips and two nips in the cooked modified starch (10%) at 90°C to a wet pickup of approximately 80% and were dried in an electric oven at 100°C for 3 min. The sized cotton fabrics were finally kept under ambient conditions for at least 48 h before they were used.

### Tensile strength and elongation at break

These were measured according to ASTM procedure D 2256-66T.

### Abrasion resistance

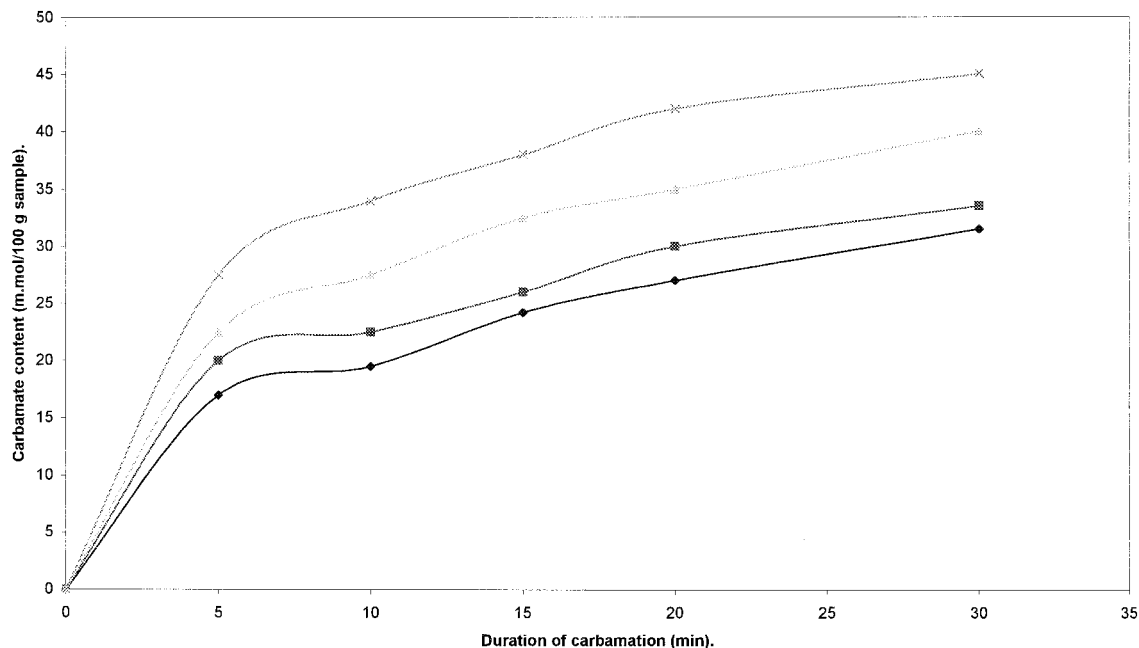
This was determined with a K-Zweigle abrader (Germany).

## RESULTS AND DISCUSSION

It is well known that the molecular structure of a polymer determines its properties and utilization. Also, the molecular structure is governed by the molecular size of the polymer backbone and the substituents present on it. Therefore, starch was hydrolyzed to obtain starches with different molecular sizes, and then some of the starch hydroxyls were substituted by carbamate groups along with poly(Aam), poly(AN), or poly(AA) chain molecules with a potassium permanganate/citric acid redox system as an initiator.

### Carbamation of starch and hydrolyzed starches

Soluble starch carbamates derived from native and hydrolyzed starches were effected through a reaction with urea in the presence of a solid catalyst. Therefore, we are dealing with a system containing starch, urea, and a catalyst. In such a system, the following main reaction is expected to occur:



**Figure 1** Effect of the duration of carbamation on the extent of carbamation (mmol of carbamate group/100 g of sample): (◆) carbamated starch, (■) carbamated H<sub>1</sub> starch, (▲) carbamated H<sub>2</sub> starch, and (×) carbamated H<sub>3</sub> starch.

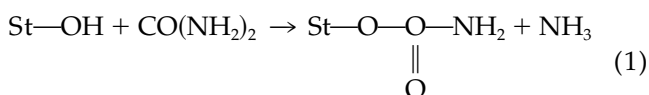


Figure 1 shows the extent of carbamation (mmol of carbamate group/100 g of sample). The data signify that the extent of carbamation of rice starch increased as the time of the carbamation reaction increased. The same held true for hydrolyzed starches. It can also be seen Figure 1 that the extent of carbamation for the hydrolyzed starches was higher than that of native starch. The higher the extent was of hydrolysis, the higher the extent was of carbamation. This can be explained by the acid hydrolysis of rice starch, which increased the susceptibility of the starch toward carbamation. Acid hydrolysis decreased the molecular size of starch, thereby increasing the surface area of starch without adversely affecting the starch hydroxyls, which would certainly lead to an increasing carbamation reaction.

#### Combined effect of the hydrolysis and carbamation of rice starch on grafting

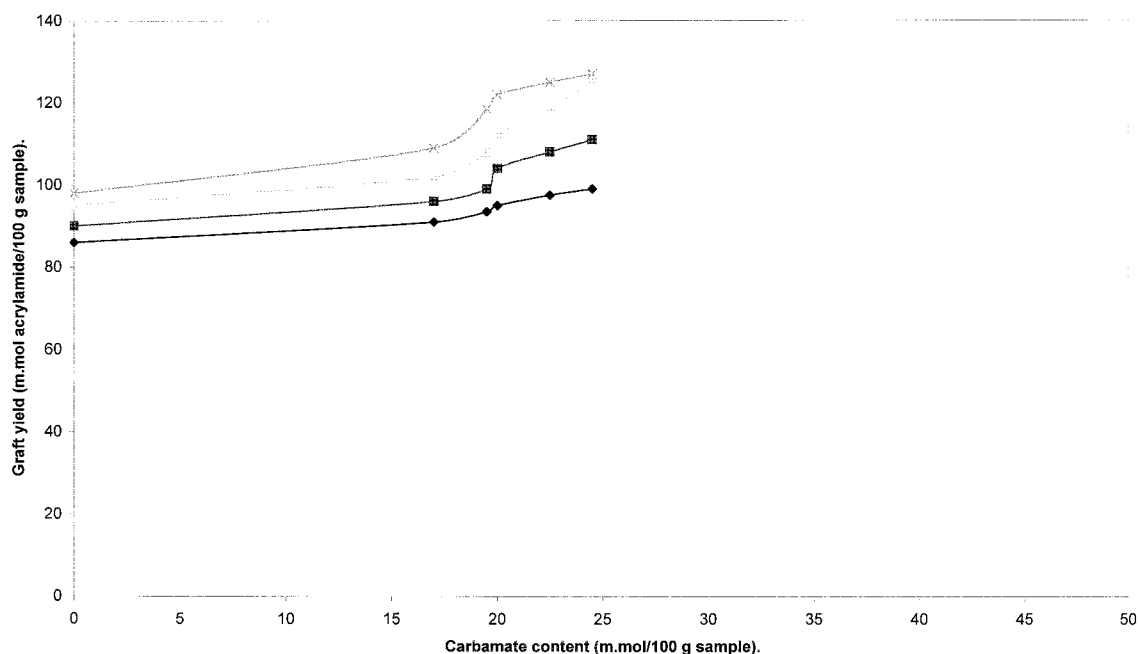
Figures 2–4 show the effects of structural changes in the molecules of rice starch produced by changes in the extent of carbamation (mmol/100 g of sample) on the graft yield (mmol of monomer/100 g of sample) with Aam, AN, and AA as the monomers and a potassium permanganate/citric acid redox system as the initiator.

The results (Figs. 2–4) signify the following main findings:

1. The graft yield obtained with hydrolyzed starches was higher than that of the native starch: the greater the hydrolysis was, the greater the graft yield was.
2. The carbamated starches derived from hydrolyzed starches exhibited much higher graft yields than the native and hydrolyzed starches, and this indicated that the combined effect of hydrolysis and carbamation increased grafting.
3. The graft yield increased with increasing carbamate contents of starch and hydrolyzed starches within the range studied.
4. The graft yields of the three monomers grafted onto carbamated starches were as follows: Aam > AN > AA.

The enhancement of the graftability of starch by acid hydrolysis could be explained in terms of a larger surface area as shown before in carbamation. That is, the graft yields were as follows: grafted carbamated H<sub>3</sub> starch > grafted carbamated H<sub>2</sub> starch > grafted carbamated H<sub>1</sub> starch > grafted carbamated starch.

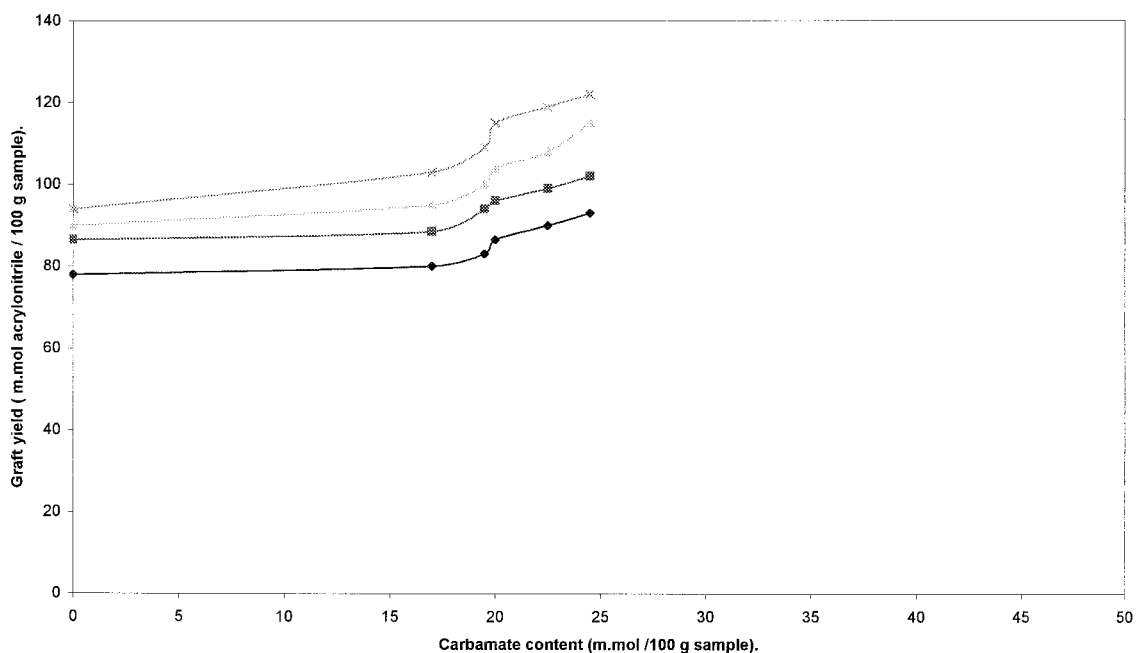
As previously stated, when native and hydrolyzed starches were carbamated before grafting, the susceptibility of the latter polymeric starch-derived products toward grafting with the vinyl monomers increased considerably. This reflected the role of carbamate groups, which afforded additional sites for grafting



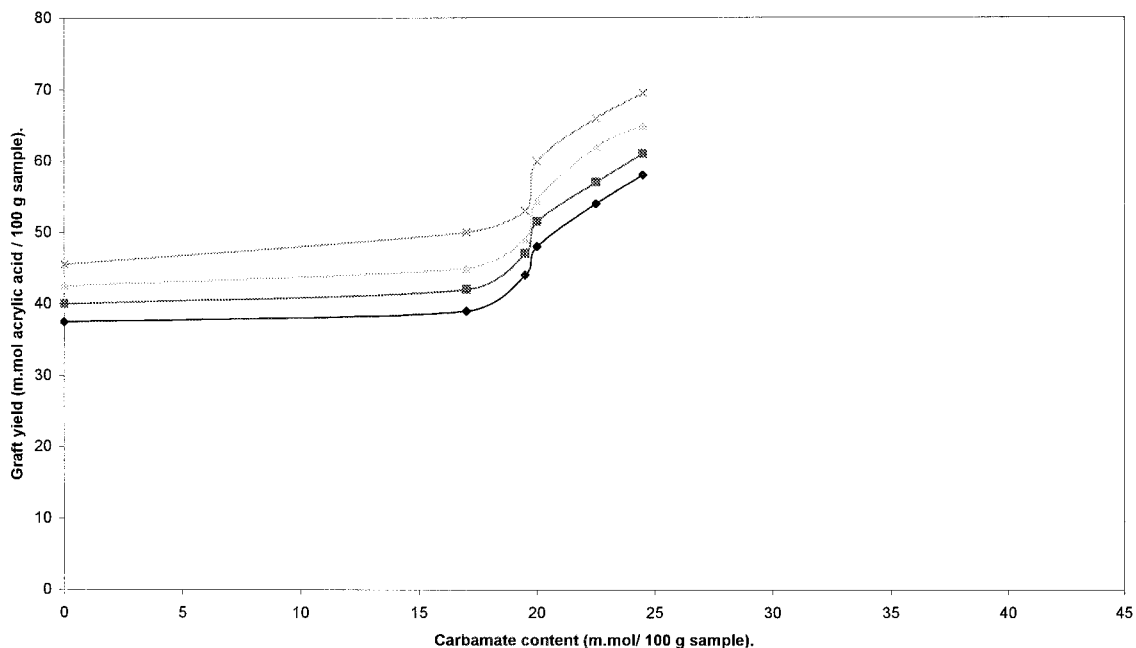
**Figure 2** Graft yield (mmol of Aam/100 g of sample) of poly(Aam) starch graft copolymer and poly(Aam)-carbamated starch graft copolymer derived from native and hydrolyzed starches versus the carbamate content (mmol/100 g of sample): (◆) carbamated starch, (■) carbamated H<sub>1</sub> starch, (▲) carbamated H<sub>2</sub> starch, and (×) carbamated H<sub>3</sub> starch.

via the abstraction of the labile hydrogen protons from imide groups of carbamated starch, and the free radical was very likely formed at the nitrogen atom of the imide group; in addition, the presence of carbamate groups and starch chains opened up the structure of

starch, and this facilitated the diffusion of the monomers, which led to increased grafting. The proposed interaction scheme of the vinyl monomer with the carbamated starch products in the presence of an initiator may be presented as follows:

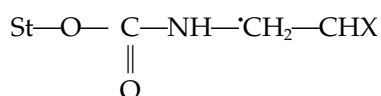
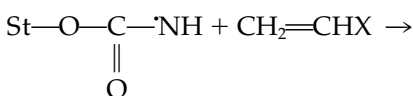
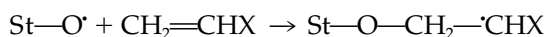
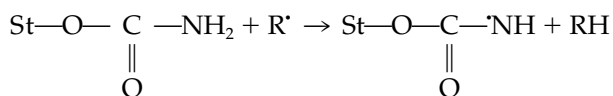
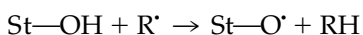


**Figure 3** Graft yield (mmol of AN/100 g of sample) of poly(AN) starch graft copolymer and poly(AN)-carbamated starch graft copolymer derived from native and hydrolyzed starches versus the carbamate content (mmol/100 g of sample): (◆) carbamated starch, (■) carbamated H<sub>1</sub> starch, (▲) carbamated H<sub>2</sub> starch, and (×) carbamated H<sub>3</sub> starch.

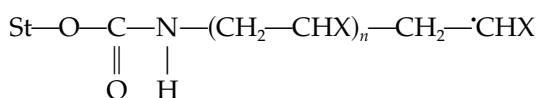
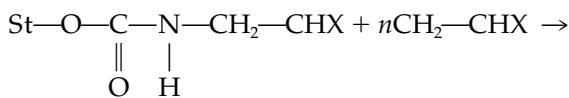
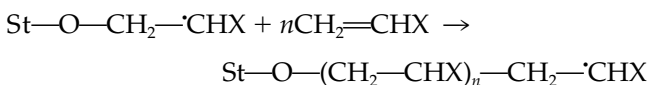


**Figure 4** Graft yield (mmol of AA/100 g of sample) of poly(AA) starch graft copolymer and poly(AA)-carbamated starch graft copolymer derived from native and hydrolyzed starches versus the carbamate content (mmol/100 g of sample): (◆) carbamated starch, (■) carbamated H<sub>1</sub> starch, (▲) carbamated H<sub>2</sub> starch, and (×) carbamated H<sub>3</sub> starch.

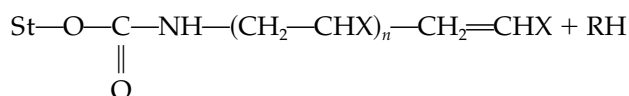
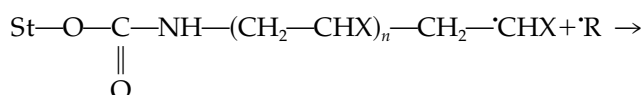
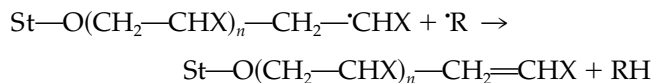
### 1. Initiation of grafting:



### 2. Propagation of grafting:



### 3. Termination of grafting:



where St—O—CO—NH<sub>2</sub> is the carbamated starch and R is the free radical formed from the redox system.

This postulation fully agrees with a previous report<sup>16</sup> that dealt with grafting onto carbamated cellulose. However, the order of graftability of the three monomers in question could be associated with the differences of these monomers with respect to (1) the polarizability of the vinyl double bond, (2) the solubility of the monomers, (3) the affinity of each monomer to starch and its ability to diffuse into the starch molecules, and (4) the ability of each monomer to homopolymerize.

### Applications for the sizing of cotton textiles

The work presented in this section was aimed at applying the newly tailored polymeric starch-derived

**TABLE II**  
**Tensile Strength, Elongation at Break, Abrasion Resistance, and Standard Deviations**  
**of Cotton Fabrics Sized with Different Modified Starches**

Modified starch	Physicochemical characteristic of starch and modified starches			Mechanical properties of sized fabrics (and their standard deviations)		
	Copper number	Nitrogen content	Carboxyl content	Tensile strength (kg)	Elongation at break (%)	Abrasion resistance (cycle)
Unsize fabric	—	—	—	21 ± 0.11	8.6 ± 0.20	880 ± 3.51
Native rice starch	0.002	—	3.5	22.5 ± 0.09	9.0 ± 0.11	900 ± 3.53
H <sub>1</sub> starch	0.060	—	—	23.5 ± 0.05	9.2 ± 0.23	940 ± 2.12
H <sub>2</sub> starch	1.410	—	—	23.0 ± 0.05	9.2 ± 0.19	920 ± 0.74
H <sub>3</sub> starch	1.820	—	—	21.5 ± 0.05	8.4 ± 0.25	896 ± 0.84
C.N.St	—	24.3	—	23.5 ± 0.04	9.2 ± 0.31	930 ± 2.35
C.H <sub>1</sub> -St	—	28.6	—	25.0 ± 0.09	9.4 ± 0.14	969 ± 1.82
C.H <sub>2</sub> -St	—	23.9	—	24.0 ± 0.09	9.4 ± 0.15	948 ± 2.79
C.H <sub>3</sub> -St	—	37.9	—	23.0 ± 0.17	9.2 ± 0.32	910 ± 2.17
P.A.G.N.St	—	—	34.1	24.5 ± 0.13	9.4 ± 0.20	946 ± 2.05
P.A.G.H <sub>1</sub> -St	—	—	38.9	26.5 ± 0.13	9.6 ± 0.11	981 ± 2.55
P.A.G.H <sub>2</sub> -St	—	—	41.2	25.5 ± 0.16	9.5 ± 0.13	956 ± 1.22
P.A.G.H <sub>3</sub> -St	—	—	44.8	23.5 ± 0.20	9.3 ± 0.11	921 ± 2.50
P.A.G.C.N.St	—	24.3	46.1	25.0 ± 0.24	9.5 ± 0.11	954 ± 2.28
P.A.G.C.H <sub>1</sub> -St	—	28.6	55.0	27.5 ± 0.19	9.7 ± 0.14	993 ± 2.12
P.A.G.C.H <sub>2</sub> -St	—	32.9	62.5	27.0 ± 0.20	9.7 ± 0.14	971 ± 2.17
P.A.G.C.H <sub>3</sub> -St	—	42.9	72.5	24.0 ± 0.09	9.5 ± 0.20	933 ± 1.11

C.N.St, C.H<sub>1</sub>-St, C.H<sub>2</sub>-St, and C.H<sub>3</sub>-St are carbamated native starch, carbamated H<sub>1</sub>-, carbamated H<sub>2</sub>-, and carbamated H<sub>3</sub>-starches, respectively. P.A.G.N.St, P.A.G.H<sub>1</sub>-St, P.A.G.H<sub>2</sub>-St, P.A.G.H<sub>3</sub>-St are poly(AA)-grafted native starch and hydrolyzed starches to different extents. P.A.G.C.N.St, P.A.G.C.H<sub>1</sub>-St, P.A.G.C.H<sub>2</sub>-St, and P.A.G.C.H<sub>3</sub>-St are poly(AA)-grafted carbamated native starch and carbamated hydrolyzed starches to different extents. ± Values are the standard deviations of the previous samples, which were measured five times each.

products to the sizing of cotton textiles. This was done to determine the suitability of the latter polymeric materials as sizing agents of cotton textiles.

Table II shows the major mechanical properties (tensile strength, elongation at break, and abrasion resistance) of cotton fabrics sized with native rice starch, hydrolyzed starches, carbamated starches, and poly(AA) starch graft copolymers derived from native and hydrolyzed starches to different levels (H<sub>1</sub>, H<sub>2</sub>, and H<sub>3</sub>) before and after carbamation. Also, the physicochemical characteristics of these starch products. such as the copper number, nitrogen content, and carboxyl content) are given in Table II.

#### Tensile strength

1. The tensile strengths of cotton fabrics sized with native starch and hydrolyzed starches were 22.5, 23.5, 23.0, and 21.5 kg for native starch, H<sub>1</sub> starch, H<sub>2</sub> starch, and H<sub>3</sub> starch, respectively. This was against a tensile strength of 21.0 kg for unsize fabric. The order was as follows: H<sub>1</sub> starch > H<sub>2</sub> starch > native starch > H<sub>3</sub> starch.
2. The tensile strengths of cotton fabrics sized with carbamated starches were 23.5, 25.0, 24.0, and 23.0 kg for carbamated starch products derived from native starch, H<sub>1</sub> starch, H<sub>2</sub> starch, and H<sub>3</sub> starch, respectively. The order was as follows: carbamated

H<sub>1</sub> starch > carbamated H<sub>2</sub> starch > carbamated native starch > carbamated H<sub>3</sub> starch.

3. The tensile strengths of cotton fabrics sized with poly(AA) starch graft copolymers were 24.5, 26.5, 25.5, and 23.5 kg for grafted native starch, grafted H<sub>1</sub> starch, grafted H<sub>2</sub> starch, and grafted H<sub>3</sub> starch, respectively. The order was as follows: grafted H<sub>1</sub> starch > grafted H<sub>2</sub> starch > grafted native starch > grafted H<sub>3</sub> starch.
4. The tensile strengths of cotton fabrics sized with poly(AA)-grafted carbamated starches were 25.0, 27.5, 27.0, and 24.0 kg for grafted carbamated starch, grafted carbamated H<sub>1</sub> starch, grafted carbamated H<sub>2</sub> starch, and grafted carbamated H<sub>3</sub> starch, respectively.
5. Finally, the increase in the tensile strengths of the sized cotton fabrics followed this general order: grafted carbamated starches > grafted starches > carbamated starches > hydrolyzed starches > native starches.

Therefore, the graft polymerization of AA onto modified starches greatly improved the sizing efficiency, regardless of the starch backbone.

#### Elongation at break

Table II reveals that the cotton fabrics sized with the modified starches under investigation exhibited

higher elongations at break than the original unsized fabrics. It followed this order: grafted carbamated starches > grafted starches > carbamated starches > hydrolyzed starches > native starches.

#### Abrasion resistance

The results of Table II reveal that (1) the abrasion resistance of all the sized fabrics was higher than that of the unsized fabrics; (2) the abrasion resistances of the fabrics sized with native starch and hydrolyzed starches ( $H_1$ ,  $H_2$ , and  $H_3$ ) were 900, 940, 920, and 960 cycles against 880 cycles for unsized fabrics; (3) the abrasion resistances of the carbamated starches were 936, 969, 948, and 910 cycles for carbamated starch, carbamated  $H_1$ , carbamated  $H_2$ , and carbamated  $H_3$  starch, respectively, against 880 cycles for unsized fabrics; (4) the abrasion resistances of the fabrics sized with poly(AA)-grafted starches were 946, 981, 959, and 921 cycles for grafted native starch, grafted  $H_1$ , grafted  $H_2$ , and grafted  $H_3$  starch, respectively (grafted  $H_1$  starch > grafted  $H_2$  starch > grafted starch > grafted  $H_3$  starch); and (5) the abrasion resistances of the fabrics sized with poly(AA)-grafted carbamated starches were 954, 993, 971, and 933 cycles for grafted carbamated starch, grafted carbamated  $H_1$ , grafted carbamated  $H_2$ , and grafted carbamated  $H_3$  starch, respectively, against 880 cycles for unsized fabrics.

Finally, there was a direct relationship between the tensile strength and the abrasion resistance, as shown in Table II.

## CONCLUSIONS

Of all the hydrolyzed starches used,  $H_1$  starch was a suitable sizing agent. All the carbamated starches under investigation were suitable as sizing agents, except for those based on  $H_3$  starch, and all the grafted starches served as superior sizing agents.

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