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Evaluation of nitrogen containing starch and hydrolyzed starch derivatives as a size base materials for cotton yarns

Kh.M. Mostafa

Textile Department, National Institute for Standards, El-Haram, El-Giza, Egypt

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Abstract

The changes in the molecular structure of native maize starch and hydrolyzed starches derived thereof brought about by introducing nitrogen containing group via cyanoethylation, carbamoylethylation, as well as carbamation were studied. The effect of these changes on the technical properties of cotton yarns sized with the latter chemically modified starches was investigated. It was found that (a) the nitrogen content of the latter derived modified starch products increases by increasing the extent of hydrolysis; (b) the apparent viscosity of these pastes prepared from those products depends on the degree of hydrolysis prior to chemical modification. On the other hand, cotton yarns sized with these starch derivatives were evaluated as sizing agent via measuring tensile strength, elongation at break and abrasion resistance. It was also found that the highest values of the latter aforementioned properties were obtained with cotton yarns sized with carbamoylethylated starch derived from native and hydrolyzed starches. © 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Cotton yarns; Hydrolyzed starches; Abrasion resistance

1. Introduction

Starches are widely used in different chemical industries. Among these in the textile industry, where large quantities of starches are used in textile warp sizing, printing and finishing (Hwang & Meng, 1996; Mostafa, 1995, 1996; Hebeish, Addel-Thalauth, Ibrahim, & El-Zairy, 1986). It is well known that, the properties of original native starches do not often cope with the properties required for a particular end used. Many starches fail to acquire stable viscosity, when their pastes are subjected to high shearing action and heated for prolonged periods. Beside some other shortcomings with respect to gelling, thickening, binding adhesive, as well as film-forming functionality. So, chemical modification via derivatization of starch is usually conducted to overcome the latter shortcoming via oxidation (Hebeish, El-Sisi, Abdel-Hafiz, Abdel-Rahman, & El-Rafie, 1992; Kerr, 1968; Peters, 1963), hydrolysis (Barth, 1969; Mostafa, 1995), esterification (Waly, Abdel-Mohdy, Higazy, & Hebeish, 1994; Whistler, 1945), etherification (Bayazeed, Farag, Sharqawy, & Hebeish, 1998; Hebeish & Khalil, 1988; Khalil, Bayazeed, Farag, & Hebeish, 1987; Khalil, Farag, Mostafa, & Hebeish, 1994; Khalil, Hasham, & Hebeish, 1990), as well as grafting (Athawale & Vidyagauri, 1998; Khalil, Mostafa, & Hebeish, 1990, 1993; Maher, 1979; Mostafa, 1997; Mostafa & El-Sanabary, 1997; Trimnell, Fanta, & Salch, 1996).

The present work is undertaken with a view of studying the effect of introducing different functional nitrogen containing groups (hydrophobic and hydrophilic) in the molecules of starch and hydrolyzed starches on the technical properties of starch and cotton yarns sized with such starches, as well as the structural changes of starch molecule. The introducing groups include carbamoylethyl ($-CH_2-CH_2-CONH_2$), cyanoethyl ($-CH_2-CH_2-CN$) and carbamate ($CO-NH_2$). For simplicity, the variation of nitrogen contents in the nitrogen containing starches is taken as a measure of chemical changes in the structure of starch molecules, while the changes in apparent viscosity is taken as a measure of physical changes in the starch molecules. On the other hand, the variation in mechanical properties (tensile strength, elongation at break, and abrasion resistance) of cotton yarns sized with the latter aforementioned starches is taken as a measure of the effect of chemical modifications of starch on the mechanical properties of cotton yarns sized with the latter aforementioned starches. On the other words, the variation in nitrogen content and apparent viscosity of these modified starches against the technical properties of cotton yarns sized with these starches are taken as a measure for structural changes (physical and

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Table 1
Tensile strength, elongation at break and abrasion resistance, as well as their standard deviations of cotton yarns sized with carbamoylethylated samples derived from native and hydrolyzed starches

Substrate	Nitrogen (%) of carbamoylethylated starch before and after hydrolysis	Tensile strength (*g*)	Elongation at break (%)	Abrasion resistance (cycles)
Crab-ES-I	1.10 ± 0.006	222 ± 2.52	3.6 ± 2.25	546 ± 3.21
Crab-ES-II	1.83 ± 0.015	247 ± 2.11	3.8 ± 3.00	574 ± 3.51
Crab-ES-III	2.29 ± 0.020	253 ± 1.95	4.0 ± 3.15	588 ± 2.95
Crab-ES-IV	2.46 ± 0.016	212 ± 1.83	3.4 ± 2.95	534 ± 2.81

Crab-ES-I, carbamoylethylated starch derived from unhydrolyzed maize starch; Crab-ES-II, carbamoylethylated starch derived from hydrolyzed starch using 0.25N HCl; Crab-ES-III, carbamoylethylated starch derived from hydrolyzed starch using 0.50N HCl; crab-ES-IV, carbamoylethylated starch derived from hydrolyzed starch using 1.00N HCl.

chemical) occurring during the chemical modification of starch.

2. Experimental

2.1. Materials

The Egyptian Starch and Glucose Manufacturing Company, Cairo supplied maize starch. Moisture content of maize starch amounted to 11.20% and its nitrogen content amounted to 0.05%. Hydrochloric acid, acrylonitrile, acrylamide, urea, and sodium hydroxide were of laboratory grade chemicals.

2.2. Methods

2.2.1. Hydrolysis

Maize starch was hydrolyzed using 0.25, 0.5, and 1.0N HCl for 15, 30 and 60 min at 50 °C in a thermostatic water bath using a material to liquor ratio 1:5. After the desired reaction time, the contents were neutralized using sodium carbonate to pH 7 and poured over 500 ml ethyl alcohol to precipitate the hydrolyzed starch. The latter was filtered and dried in an electric oven at 60 °C for 2 h.

2.2.2. Chemical modification of starch and hydrolyzed starches

2.2.2.1. Carbamoylethylation of starch and hydrolyzed starches. Maize starch before and after hydrolysis (10 g) was mixed well with (5 g) acrylamide in a 250 ml stoppered bottle. The freshly prepared catalyst NaOH (5 ml) of concentration 0.25N and 20 ml cyclohexane were added to complete the total volume to 25 ml. The reaction mixture was stirred very well and allowed to proceed at 40 °C for 1 h in a thermostatic water bath. After the desired reaction time, the mixture was poured over 500 ml of ethanol for precipitation, then washed several times with ethanol/water mixture (80:20) for 10 min for each wash on magnetic stirrer at room temperature. It was found experimentally that 3–5 times washing with the latter mixture is quite enough to remove all the contaminants (unreacted substances). This was evidenced by measuring the nitrogen% after washing for each sample till constant nitrogen% (three times measurement for each sample, as well as their standard deviations were obtained). Finally, washed with pure ethanol and air-dried.

2.2.2.2. Cyanoethylation of starch and hydrolyzed starches. Maize starch before and after hydrolysis (10 g) was slurred well with (5 ml) acrylonitrile in a 250 ml stoppered bottle. The freshly prepared catalyst NaOH (20 ml) of concentration 0.25N was added to complete the total volume to 25 ml. The reaction mixture was stirred very well and allowed to proceed at 40 °C for 1 h in a thermostatic water bath. After the desired reaction time, the mixture was poured over 500 ml of ethanol for precipitation, then washed several times with ethanol/water mixture (80:20) for 10 min for each wash on magnetic stirrer at room temperature. It was found experimentally that 3–5 times washing with the latter mixture is quite enough to remove the contaminants (unreacted substances). This was evidenced by measuring the nitrogen% after washing for each sample till constant nitrogen% (three times measurement for each sample, as well as their standard deviations were obtained). Finally, washed with pure ethanol and air-dried.

2.2.2.3. Carbamation of starch and hydrolyzed starches. Maize starch before and after hydrolysis (10 g) was mixed well with (5 g urea) and 0.2 g-cupper chloride catalyst using electric mixer. The mixture was transferred to a petri dish and covered, then heated for 30 min at 160 °C. After the desired reaction time, the thermally treated mixture was poured over 500 ml of ethanol for precipitation, then washed several times with ethanol/water mixture (80:20) for 10 min for each wash on magnetic stirrer at room temperature. It was found experimentally that 3–5 times washing with the latter mixture is quite enough to remove the contaminants (unreacted substances). This was evidenced by measuring the nitrogen% after washing for each sample till constant nitrogen% (three times measurement for each sample, as well as their standard deviations were obtained). Finally, washed with pure ethanol and air-dried.

Table 2
Tensile strength, elongation at break and abrasion resistance, as well as their standard deviations of cotton yarns sized with cyanoethylated samples derived from native and hydrolyzed starches

Substrate	Nitrogen (%) of cyanoethylated starch before and after hydrolysis	Tensile strength (*g*)	Elongation at break (%)	Abrasion resistance (cycles)
CES-I	1.01 ± 0.008	216 ± 2.62	3.2 ± 3.25	538 ± 3.27
CES-II	1.72 ± 0.019	240 ± 2.59	3.4 ± 3.54	564 ± 3.28
CES-III	2.17 ± 0.023	245 ± 2.85	3.6 ± 3.89	579 ± 3.56
CES-IV	2.32 ± 0.018	210 ± 1.99	3.0 ± 3.76	525 ± 2.98

CES-I, cyanoethylated starch derived from unhydrolyzed maize starch; CES-II, cyanoethylated starch derived from hydrolyzed starch using 0.25N HCl; CES-III, cyanoethylated starch derived from hydrolyzed starch using 0.50N HCl; CES-IV, cyanoethylated starch derived from hydrolyzed starch using 1.00N HCl.

2.2.3. Evidence of chemical modification

This was done via measuring the nitrogen% of nitrogen containing starches in questions by Kjeldahal method (well known method three times for each samples), as well as the standard deviation for each sample as shown in Tables 1–3. On the other word, both the nitrogen% and the standard deviation for each sample were taken as an evidence of chemical modification of starch.

2.2.4. Sizing of cotton yarns

Cotton yarns (kindly supplied by Misr Company for Spinning and Weaving, El-Mehala, El-Kobra) were padded through two dips and two nips in the cooked modified starch (10%) at 90 °C to a wet pick-up of ca. 80% and dried in an electric oven at 100 °C for 3 min. The sized yarns were finally kept at ambient conditions for at least 48 h before used.

2.3. Analysis

2.3.1. Copper number

It was determined by a micro Briady method as modified by Heyes (Hofreiter, 1977).

2.3.2. Nitrogen content

It was estimated by Kjeldahal method (Vogel, 1975).

2.3.3. Apparent viscosity

It was measured by using co-axial rotary viscometer (Haake RV20), with the rate of shear 516 cm^{-1} at 90 °C.

2.4. Testing

2.4.1. Tensile strength (*g*) and elongation at break (%)

These were determined according to ASTM procedure D-2296-66T.

2.4.2. Abrasion resistance

This was determined using the K-Zweigle abrader. Both tensile strength, elongation at break and abrasion resistance were measured five times for each sample.

3. Results and discussion

Maize starch was hydrolyzed with 0.25, 0.5 and 1.0N HCl for 15, 30 and 60 min at 50 °C, in a 100 ml stoppered flask using a material to liquor ratio of 1:5. The original starch (substrate I) along with the three hydrolyzed starches namely substrates (II, III and IV) were modified via carbamoylethylation, cyanoethylation, and carbamation. After being purified, the products obtained were monitored for nitrogen% and rheological properties (apparent viscosity), as well as measuring the mechanical properties of cotton yarns sized with the latter starch derivatives. More detailed about the results obtained with appropriate discussion are given latter.

3.1. Nitrogen percent

It is seen (Figs. 1 and 2) that, the nitrogen% of nitrogen containing starch in two questions namely

Table 3
Tensile strength, elongation at break and abrasion resistance, as well as their standard deviations of cotton yarns sized with carbamated samples derived from native and hydrolyzed starches

Substrate	Nitrogen (%) of carbamated starch before and after hydrolysis	Tensile strength (*g*)	Elongation at break (%)	Abrasion resistance (cycles)
CS-I	0.95 ± 0.015	210 ± 2.88	3.4 ± 3.21	527 ± 4.00
CS-II	1.63 ± 0.021	232 ± 2.62	3.6 ± 3.58	560 ± 3.58
CS-III	2.08 ± 0.025	235 ± 2.14	3.8 ± 3.91	569 ± 3.92
ES-IV	2.22 ± 0.024	207 ± 3.00	3.2 ± 4.00	518 ± 2.99

CS-I, carbamated starch derived from unhydrolyzed maize starch; CS-II, carbamated starch derived from hydrolyzed starch using 0.25N HCl; CS-III, carbamated starch derived from hydrolyzed starch using 0.50N HCl; CS-IV, carbamated starch derived from hydrolyzed starch using 1.00N HCl.

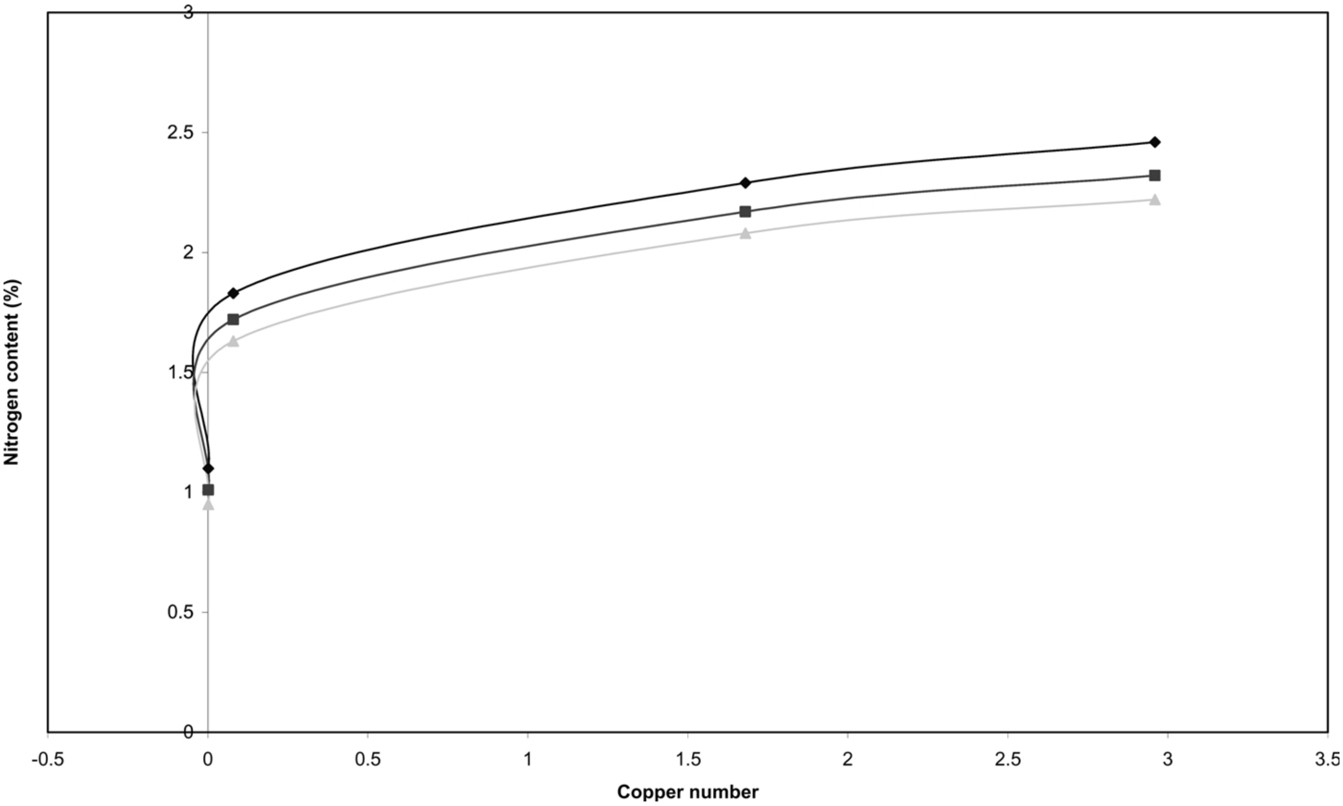

Fig. 1. Effect of the extent of hydrolysis (expressed as copper number) on the nitrogen percent of carbamoylethylated, cyanoethylated, and carbamated starch samples derived from native and hydrolyzed starches. [-•-], carbamoylethylated starch, [-■-], cyanoethylated starch, [-▲-], carbamated starch.

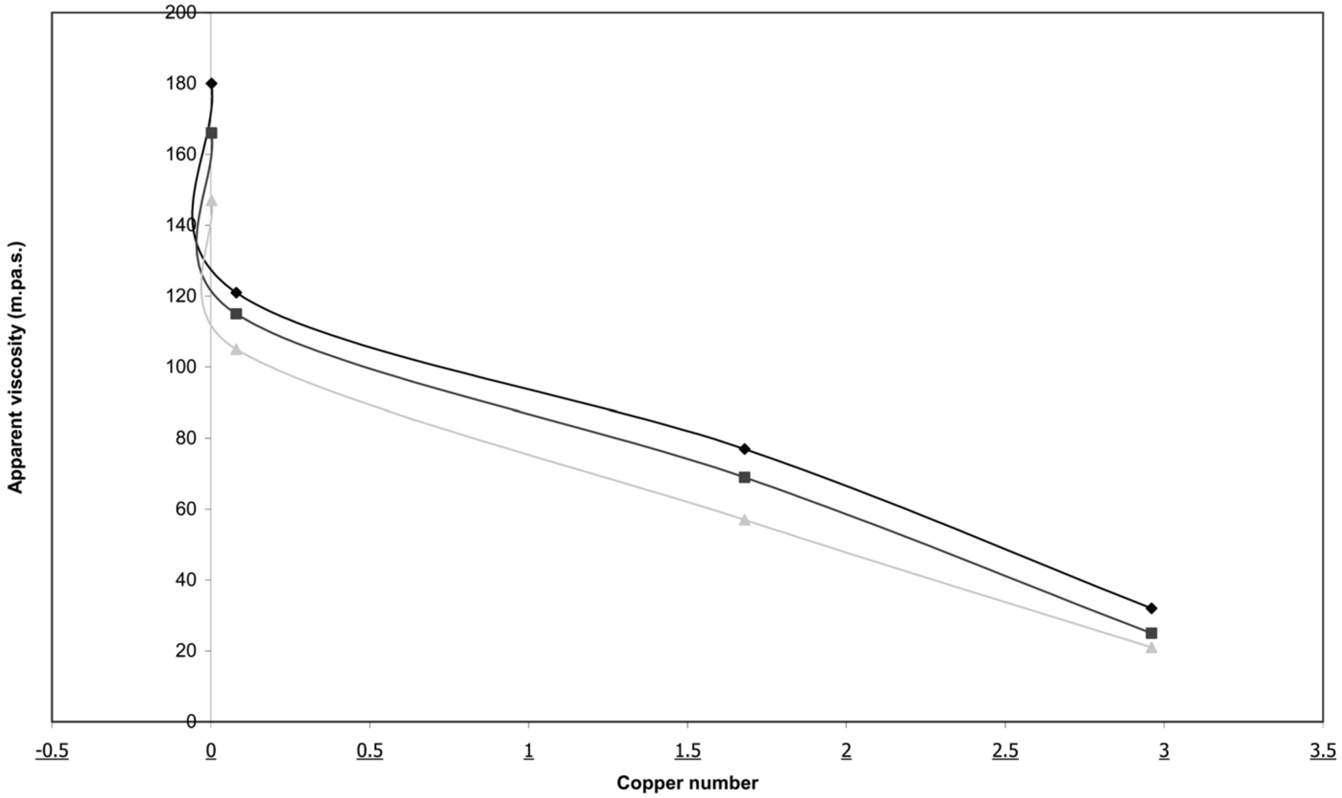

Fig. 2. Effect of the extent of hydrolysis (expressed as copper number) on the apparent viscosity (m.pa.s.) of carbamoylethylated, cyanoethylated, and carbamated starch samples derived from native and hydrolyzed starches. [-•-], carbamoylethylated starch, [-■-], cyanoethylated starch, [-▲-], carbamated starch.

(carbamoylethylated, cyanoethylated and carbamated starches) increases by increasing the extent of hydrolysis (expressed as copper number). It is further noted that, the nitrogen% of carbamoylethylated starch derived from native and hydrolyzed starches is higher than that cyanoethylated and carbamated starch samples derived from native and hydrolyzed starches. This can be explained in the manner of, acid hydrolysis of starch increases the susceptibility of starch towards derivatization (i.e. chemical modification). Acid hydrolysis decreases the molecular size of starch thereby increasing the surface area of starch without adversely affecting the available number of starch hydroxyls that would certainly leads to increases nitrogen%. While on the other hand, the higher values of nitrogen% of carbamoylethylated starches than that of cyanoethylated and carbamated starches may be duo to the difference between the substituents groups, i.e. ($-CH_2-CH_2-CONH_2$), ($-CH_2-CH_2-CN$) and ($-CO-NH_2$) in their molecular weight, solubility, hydrophilicity, as well as method of preparation. Finally, with respect to degree of hydrolysis, the nitrogen% of the three substrates in question follows the order: substrate IV > substrate III > substrate II > substrate I.

3.2. Apparent viscosity

Figs. 1 and 2 show that the apparent viscosity of carbamoylethylated, cyanoethylated, and carbamated starches decreases by hydrolysis of starch prior to chemical modification. This is observed regardless of the nature of modification. It is also further noted that, the apparent viscosity of carbamoylethylated samples prepared from native and hydrolyzed starches is higher than that of cyanoethylated and carbamated samples derived from native and hydrolyzed starches. The variation of the apparent viscosity by varying the extent of hydrolysis and subsistent groups can be explained as mention earlier in nitrogen%. It is also well known that, the chemical modification of starch induces both changes in its chemical structure as evidenced by (nitrogen%) i.e. the newly introduced substituent group and another changes in its physical structure as evidenced by changing in apparent viscosity. Finally, with respect to the nature of modification in case of the latter modified starches in question the apparent viscosity follows the order: carbamoylethylated starches > cyanoethylated starches > carbamated starches. While with respect to the degree of hydrolysis, the following order was observed: substrate IV > substrate III > substrate II > substrate I.

3.3. Mechanical properties of cotton yarns sized with nitrogen containing starch derivatives

To examine the suitability of the aforementioned chemically modified starch derivatives in sizing, cotton yarns were sized by these derivatives. After sizing, the yarns were dried on an electric oven at 110 °C for 4 min and the latter yarns were examined for tensile strength (*g*), elongation at break (%), and abrasion resistance (cycles) to see their suitability as sizing agent. The results obtained are given latter.

3.3.1. Tensile strength

The tensile strength (Tables 1–3) of sized cotton yarns seems to depend on the nature of substituent groups in the modified starch, as well as the degree of hydrolysis (expressed as copper number), i.e. combined effect of hydrolysis and chemical modification. It is seen also (Tables 1–3) that the tensile strength of cotton yarns sized with carbamoylethylated starch and hydrolyzed starches to different extent amounts to 222, 247, 253, and 212 g for carbamoylethylated starch (Crab-ES-I) and carbamoylethylated hydrolyzed starches to different extent (Crab-ES-II, Crab-ES-III, and Crab-ES-IV, respectively), while the tensile strength of cotton yarns sized with cyanoethylated starch and cyanoethylated hydrolyzed starches to different extent amounts to 216, 240, 245, and 210 g for cyanoethylated starch (CES-I) and cyanoethylated hydrolyzed starches to different extent (CES-II, CES-III, and CES-IV, respectively). On the other hand, the tensile strength of cotton yarns sized with carbamated starch and hydrolyzed starches to different extent amounts to 210, 232, 235 and 207 g for carbamated starch (CS-I) and carbamated hydrolyzed starches to different extent (CS-II, CS-III, and CS-IV, respectively). It is further noted that, cotton yarns sized the latter aforementioned modified starches exhibit tensile strength the values of which lead to the following order: carbamoylethylated starch > cyanoethylated starch > carbamated starch. This is observed regardless of the degree of hydrolysis. While the following order was observed, when the degree of hydrolysis was taken into account irrespective of the nature of modification: substrate III > substrate II > substrate I > substrate IV.

3.3.2. Elongation at break

Tables 1–3 show the elongation at break (%) of cotton yarns sized with the aforementioned modified starches in question. Evidently, the latter aforementioned starches bring about sized cotton yarns whose elongation at break lead to the following order: carbamoylethylated starch > carbamated starch > cyanoethylated starch. This is observed irrespective of the degree of hydrolysis. While on taking the degree of hydrolysis into account, the following order was observed: substrate III > substrate II > substrate I > substrate IV.

3.3.3. Abrasion resistance

Tables 1–3 show the abrasion resistance (cycles) of cotton yarns sized with the said modified starch derivatives. It is seen also (Tables 1–3) that the abrasion resistance of cotton yarns sized with carbamoylethylated starch and hydrolyzed starches to different extent amounts to 546, 574, 588 and 534 cycles for carbamoylethylated starch (Crab-ES-I) and carbamoylethylated hydrolyzed starches to different extent (Crab-ES II, Crab-ES-III, and Crab-ES-IV, respectively), while the abrasion resistance of cotton yarns sized with cyanoethylated starch and cyanoethylated hydrolyzed starches to different extent amounts to 538, 564, 579, and 525 cycles for cyanoethylated starch (CES-I) and cyanoethylated hydrolyzed starches to different extent (CES-II, CES-III, and CES-IV, respectively). On the other hand, the abrasion resistance of cotton yarns sized with carbamated starch and hydrolyzed starches to different extent amounts to 527, 560, 569, and 518 g for carbamated starch (CS-I) and carbamated hydrolyzed starches to different extent (CS-II, CS-III, and CS-IV, respectively). A comparison among the modified starches prepared from maize starch and hydrolyzed starches derived thereof would reveal that the highest value of abrasion resistance is obtained with yarns sized using carbamoylethylated samples derived from substrate III, while the lowest value of abrasion resistance is obtained with yarns sized using carbamated starch derived from substrate IV. This is in accordance with the data of tensile strength, which reflects the strong relationship between tensile strength and abrasion resistance.

References

Athawale, V. D., & Vidyagauri, V. (1998). *Starch/Starke*, *50*, 426–431.

Barth, H. (1969). *Bayer Farben Review*, *15*, 64.

Bayazeed, A., Farag, S., Sharqawy, S., & Hebeish, A. (1998). *Starch/Starke*, *50*, 89–93.

Hebeish A., Addel-Thalauth, I., Ibrahim, M.A. & El-Zairy, M.R. (1986). *American Dyestuff Reportee, 75,* 22.

Hebeish, A., El-Sisi, F., Abdel-Hafiz, S. A., Abdel-Rahman, A. A., & El-Rafie, M. (1992). *Starch/Starke*, *44*, 388.

Hebeish, A., & Khalil, M. I. (1988). *Starch/Starke*, *40*, 104.

Hofreiter, B. T. (1977). *Journal of Applied Polymer Science*, *21*, 761.

Hwang, S. K., & Meng, S. Y. (1996). *Journal of Applied Polymer Science*, *59*, 1559–1562.

Kerr, R. W. (1968). *Chemistry and industry of starch* (2nd ed). New York: Academic press, pp. 14–17.

Khalil, M. I., Bayazeed, A., Farag, S., & Hebeish, A. (1987). *Starch/Starke*, *39*, 311.

Khalil, M. I., Farag, S., Mostafa, Kh. M., & Hebeish, A. (1994). *Starch/Starke*, *64*, 312–316.

Khalil, M. I., Hasham, A., & Hebeish, A. (1990). *Starch/Starke*, *42*, 60.

Khalil, M. I., Mostafa, Kh. M., & Hebeish, A. (1990). *Starch/Starke*, *42*, 107–111.

Khalil, M. I., Mostafa, Kh. M., & Hebeish, A. (1993). *Die Angewanotte Makromolekulare Chemie*, *213*, 14.

Maher, G. G. (1979). *Journal of Applied Polymer Science*, *24*, 9.

Mostafa, Kh. M. (1995). *Journal of Applied Polymer Science*, *56*, 263–269.

Mostafa, Kh. M. (1995). *Polymer Degradation and Stability*, *50*, 189–194.

Mostafa, Kh. M. (1996). *American Dyestuff Reporter*, *85*, 85–91. September.

Mostafa, Kh. M. (1997). *Polymer Degradation and Stability*, *55*(2), 125–130.

Mostafa, Kh. M., & El-Sanabary, A. A. (1997). *Polymer Degradation and Stability*, *55*, 181–184.

Peters, R. H. (1963) (*Vol. I*). *Textile chemistry*, Amsterdam: Elsevier.

Trimnell, D., Fanta, G. F., & Salch, J. H. (1996). *Journal of Applied Polymer Science*, *60*, 285–292.

Vogel, A. I. (1975). *Elementary practical organic chemistry. Part 3. Quantitative organic analysis* (2nd ed) (p. 652) London: Longman Group Ltd.

Waly, A., Abdel-Mohdy, F. A., Higazy, A., & Hebeish, A. (1994). *Starch/Starke*, *48*, 59.

Whistler, R. L. (1945). *Advanced Carbohydrate Chemistry*, *1*, 275.