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Utilization of newly tailored modified starch products in easy-care finishing

Kh.M. Mostafa*, M.S. Morsy

Textile Department, National Institute for Standards, El-Haram, El-Giza, P.O. Box 136 Giza, Code No (12211), Egypt

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Abstract

To impart easy care properties to cotton fabrics along with decreasing the great loss in strength properties during finishing processes. Attempts have been made to add what we called tailored modified starch products in easy care finishing formulation. So, carboxymethylated starches (CMS) and poly (acrylic acid)-grafted starch copolymers (PAGS) prepared from three levels of hydrolyzed starches (H_1-, H_2-, and H_3- starch) having different degree of hydrolysis and three levels of oxidized starches (O_1-, O_2-, and O_3- starch) having different degree of oxidation were synthesized. Hydrolyzed starch (H3) was taken as a blank substrate. The impact of the latter tailored starches on fabric performance when used in the cross linking formulation (containing finishing agent and catalyst) at a concentration range 5–50 g/l was studied. The results obtained reflects the following findings: (a) the nitrogen content, crease recovery angles and tensile strength of cotton fabric finished in the presence of these modified starches increases by increasing the extent of either hydrolysis or oxidation of the parent starch, (b) increasing the concentration of the modified starches from 5 to 50 g/l in the finishing bath is accompanied by an increment in the nitrogen content and tensile strength while the crease recovery angles decrease, (c) the increase in the nitrogen content and tensile strength of the finished fabrics follow the order: carboxymethylated starches > poly (AA)-grafted starches > hydrolyzed starches and (d) the fabric samples treated in the presence of aforementioned modified starches derived from hydrolyzed starches acquire higher nitrogen content, crease recovery angles and tensile strength values than those derived from oxidized starches within the range studied.

Keywords: Modified starches; Reactant resin; Wrinkle recovery angle; Tensile strength

1. Introduction

Duo to the most serious problem occurring in durable-press finishing of cotton fabric using conventional *N*-methylol finishing agents is the great loss in its strength properties of the finished fabric. A significant research work has been directed towards modifying hydrophilic characteristics of easy-care cotton fabrics by adding polyacrylate to the cross-linking formulation (Cirino & Rowland, 1974, 1976; Rowland & Cirino, 1975; Rowland, Wade, & Cirino, 1977). Recently, condensed efforts have been made to add what we called tailored chemically modified starch products to the cross-linking formulation in order to minimize the expected great loss in the tensile strength of the finished fabrics (Ibrahim, Abo-Shosha, Elnagdy, & Gaffer, 2002; Mostafa, 1996; Mostafa & El-Sanabary, 1996; Mostafa, El-Sanabary, & Youssef, 1997).

This work is undertaken with a view of studying the technical feasibility of the newly tailored synthesized starch products in easy-care finishing. The newly synthesized starch products include: (a) hydrolyzed starches, (b) carboxymethylated starches and (c) poly (AA)-starch graft copolymers based on hydrolyzed and oxidized starches. The latter aforementioned starch products were used in the cross-linking formulation (containing the finishing agent + catalyst) at concentration range from 5 to 50 g/l. Treatment of the cotton fabric using this cross-linking formulation in presence and absence of the modified starch products was performed and the finished fabric so obtained was monitored for nitrogen content, crease recovery angles and tensile strength. This was done to find out the impact of the said modified starches on the performance of the finished fabric.

* Corresponding author. Address: Institute for Research and Consultations, King Abdel Aziz University, P.O. Box: 80271 Jeddah 21589, Saudi Arabia. Fax: +966-2-6951283.

E-mail address: kh_mostafa@hotmail.com (Kh.M. Mostafa).

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2. Experimental

2.1. Fabric

Mile scoured and bleached plane weave (23 pick × 23 ends/cm) cotton fabric (poplin, Kafer El-Dawar, Alexandria) was used throughout this investigation.

2.2. Chemicals

Dimethyloldihydroxyethyylene urea (DMDHEU) was obtained at 45% active ingredient (Arkofix NG) from Hoechst; non-ionic wetting agent was of technical grade chemicals and $MgCl_2 \cdot 6H_2O$ was of reagent grade.

2.3. Preparation of hydrolyzed and oxidized starches

Three levels of hydrolyzed starches namely H_1-, H_2- and H_3-starch having different degree of hydrolysis (expressed as copper number) have been prepared using hydrochloric acid concentration (0.25, 0.5 and 1N) for 15, 30 and 60 min at 50 °C in a thermostatic water bath using a material to liquor ratio of 1:5 (Mostafa, 2003). Also, three levels oxidized starches namely O_1-, O_2-; and O_3-starch having different degree of oxidation (expressed as oxygen consumption) have been prepared using potassium persulphate concentration (0.25, 0.5 and 1N) for 15, 30 and 60 min at 60 °C in a thermostatic water bath using a material to liquor ratio of 1:5 (Mostafa, 1992). The main characteristics of starch and degraded starches as well as the standard deviation of both copper number and oxygen consumption are given in Table 1.

2.4. Preparation of chemically modified starches

Chemically modified starches namely carboxymethylated starches and poly (AA)-grafted starches based on hydrolyzed and oxidized starches have been prepared according to a reported methods (Hebeish, Khalil, & Hasham, 1988; Mostafa, 1995). The main characteristics of these modified starches as well as the standard deviation of carboxyl content for the latter two substrate are given in Table 2.

2.5. Finishing method

The cross linking treatment was carried out as follows.

Cotton fabric samples were padded through two dips and two nips in a solution containing 100 g/l active ingredient DMDHEU + 15 g/l $MgCl_2 \cdot 6H_2O$ + 2 g/l wetting agent +X g/l modified starches to a wet pickup of ca 85%. The fabric samples were dried for 3 min at 100 °C and cured for 3 min at 160 °C. The samples were then washed at 60 °C in a small washing machine (calor 2000, France), using a solution containing 2 g/l detergent. Three washing cycles, 5 min each, were given followed by water rinse in the same washing machine. Finally, the fabrics were dried, conditioned and examined for different properties.

2.6. Analysis

Copper number was estimated by micro Briady method as modified by Heyes (Hofreiter, 1977), Oxygen consumption was determined according to a reported method (Vogel, 1961), Nitrogen content (%) was determined according to the micro-Kjeldhal method (Vogel, 1975) and Carboxyl content was determined according to a reported method (Daul, Reinhardt, & Reid, 1953).

2.7. Apparent viscosity

The apparent viscosity of cooked samples (10%) was measured by using co-axial rotary viscometer (Haake RV_{20}) with the rate of shear 516 cm^{-1}at 90 °C.

2.8. Testing

2.8.1. Tensile strength (TS)

This was determined by the strip method according to ASTM procedure D-2256-66T.

2.8.2. Dry wrinkle recovery angle (DWRA)

It was measured using the iron recovery apparatus type F. F-07 (Metrimpex).

Table 1
The main characteristics of starch and degraded starches

Substrate	Hydrolyzed starches		Substrate	Oxidized starches	
	Copper number	Apparent viscosity (centipoises)		Oxygen consumption (g oxygen/100 g sample)	Apparent viscosity (centipoises)
Maize starch	0.002 ± 0.005	280	Maize starch	0.00 ± 0.004	280
H_1-starch	0.08 ± 0.004	180	O_1-starch	0.07 ± 0.006	200
H_2-starch	1.68 ± 0.006	110	O_2-starch	1.10 ± 0.008	140
H_3-starch	2.90 ± 0.008	55	O_3-starch	1.42 ± 0.010	55

± , The standard deviation of copper number and oxygen consumption data, which are taken as an average of three readings of each one.

Table 2
The main characteristics of modified starch products derived from hydrolyzed and oxidized starches

Modified starches	Carboxymethylated starches (mmol carboxymethyl group/100 g sample)	Poly (acrylic acid)-grafted starches (mmol acrylic acid/100 g sample)
H_1-starch	160 ± 0.84	94 ± 0.20
H_2-starch	185 ± 0.92	103 ± 0.18
H_3-starch	210 ± 0.10	116 ± 0.12
O_1-starch	141 ± 0.15	82 ± 0.86
O_2-starch	130 ± 0.19	71 ± 0.55
O_3-starch	125 ± 0.20	62 ± 0.95

±, The standard deviation of carboxyl content data for the latter two substrate, which are taken as an average of two readings of each one.

3. Results and discussion

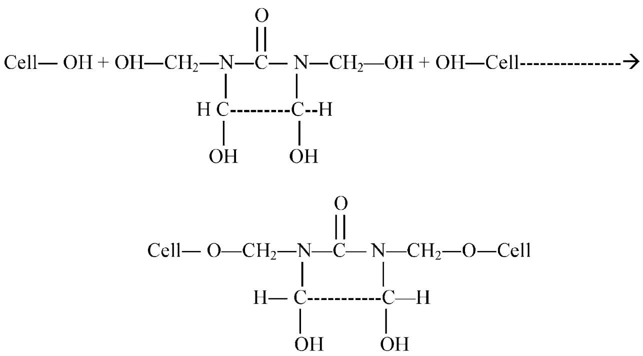
It is well established that finishing of cotton fabrics with reactant resins is accompanied by an increase in dry wrinkle recovery angle and decrease in tensile strength of the finished cotton fabrics. A decrease in the tensile strength of up to 25% is acceptable. While on the other hand, the enhancement in the wrinkle recovery angle of the finished fabrics is duo to crosslinking reaction between cellulose molecules.

When cotton fabric is treated with a reactant resin in presence of modified starch products, the following three major reactions are expected to occur.

Reaction 1: crosslinking between cellulose molecules with the resin thereby bridging two adjacent cellulose chains (cell–resin–cell).

Cellulose + Resin + Cellulose → Cellulose–Resin–Cellulose

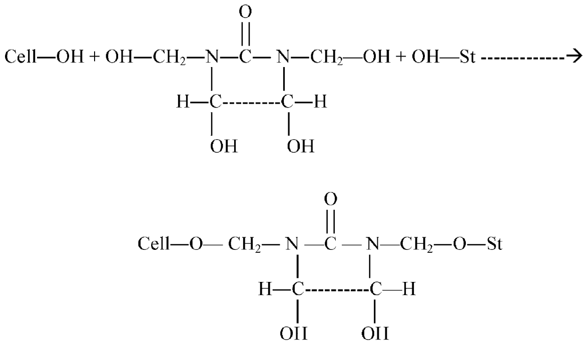
Cell–O–H + Resin + OH–Cell → Cell–Resin–Cell.



Reaction 2: crosslinking between cellulose molecules and starch molecules with the resin molecule as a bridge between cellulose molecules and starch molecules (cell–resin–starch).

Cellulose + Resin + Starch → Cellulose–Resin–Starch

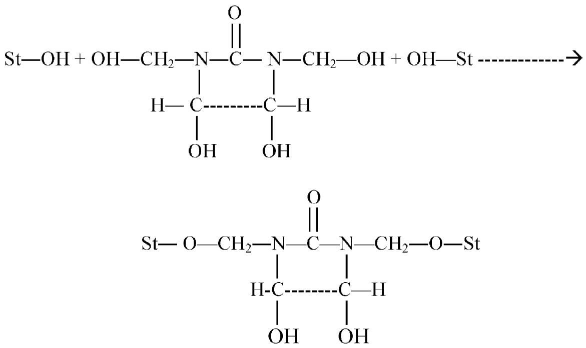
Cell–OH + Resin + OH–St → Cell–Resin–St



Reaction 3: crosslinking between starch molecules with the resin bridging two starch molecules (starch–resin–starch).

Starch + Resin + Starch → Starch + resin + Starch

St–OH + Resin + OH–St → St–Resin–St



Reaction I lead certainly to an enhancement in the dry wrinkle recovery angle and decrement in tensile strength of the finished fabric. Reaction II may also lead to an improvement in the tensile strength of the finished fabrics. On the other hand, reaction III would not exert much effect on the wrinkle recovery and tensile strength. By taking the above in mind, results of the nitrogen content, wrinkle recovery angle and tensile strength of cotton fabric treated with the reactant resin in presence of the newly tailored synthesized starch products under investigation are discussed.

3.1. Nitrogen content (%)

Figs. 1 and 2 show the nitrogen content (%) of cotton fabrics treated with DMDHEU in presence and absence of hydrolyzed starch (H_3), carboxymethylated starches and poly (acrylic acid)-starch graft copolymers based on hydrolyzed and oxidized starches. It is seen from the above figures that cotton fabric samples treated in presence of the modified starches acquire lower nitrogen content than that treated in their absence. This is observed irrespective of the nature of the modified starch used. However, cotton fabric samples treated in presence of hydrolyzed starch acquire relatively lower nitrogen content than those of all

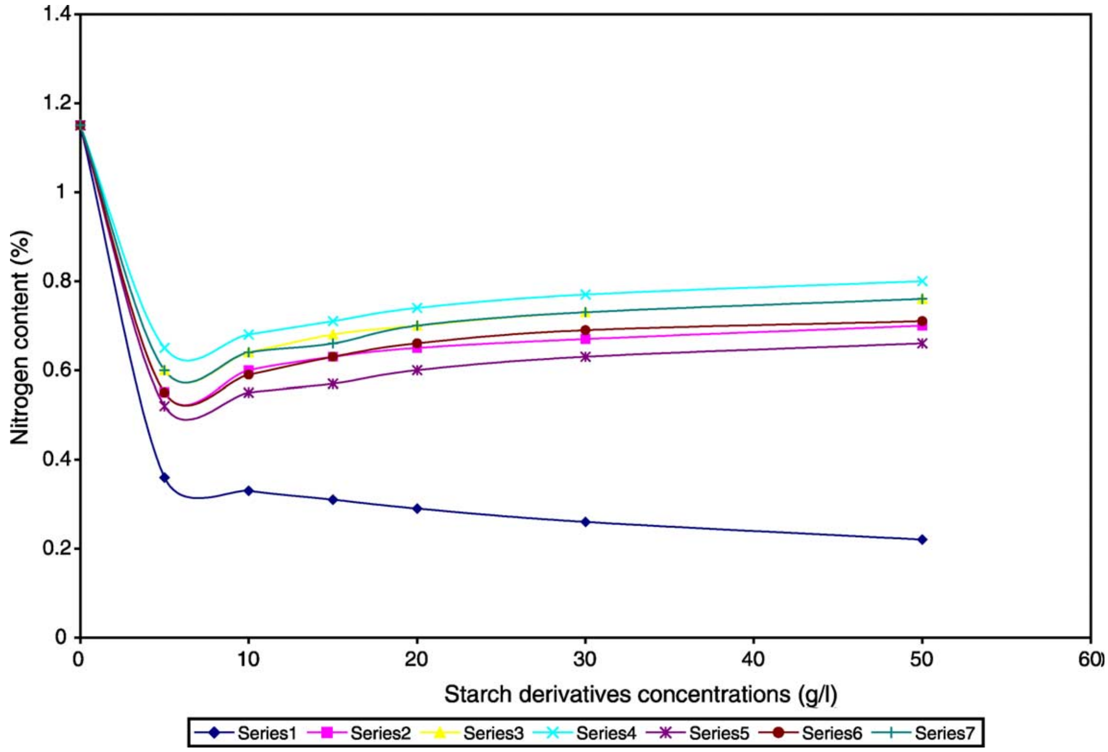


Fig. 1. Nitrogen content of cotton fabric samples treated with DMDHEU in presence of hydrolyzed starch (H_3-) and carboxymethylated starches prepared from hydrolyzed and oxidized starches. Series 1: for H_3-starch; Series 2: for carboxymethylated H_1-starch; Series 3: for carboxymethylated H_2-starch; Series 4: for carboxymethylated H_3-starch; Series 5: for carboxymethylated O_1-starch; Series 6: for carboxymethylated O_2-starch; Series 7: for carboxymethylated O_3-starch.

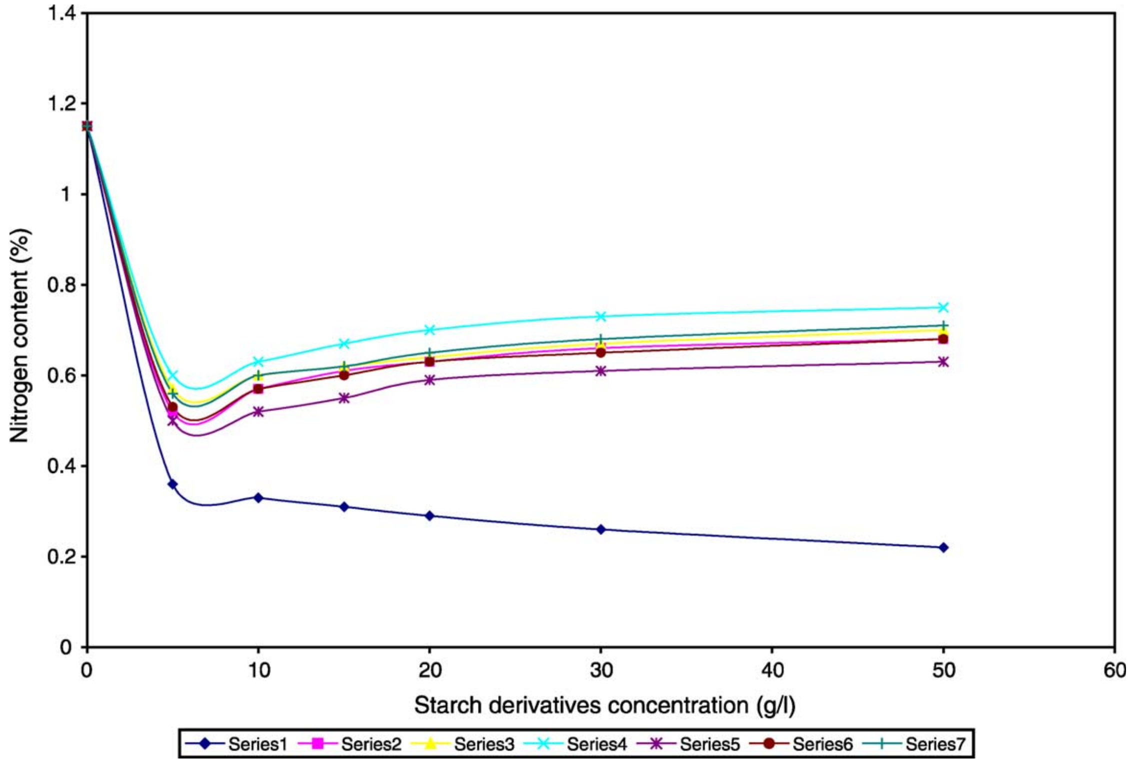


Fig. 2. Nitrogen content of cotton fabric samples treated with DMDHEU in presence of hydrolyzed starch (H_3-) and poly (acrylic acid)-grafted starches prepared from hydrolyzed and oxidized starches. Series 1: for H_3-starch; Series 2: for Poly (Acrylic acid)-grafted H_1-starch; Series 3: for Poly (Acrylic acid)-grafted H_2-starch; Series 4: for Poly (Acrylic acid)-grafted H_3-starch; Series 5: for Poly (Acrylic acid)-grafted O_1-starch; Series 6: for Poly (Acrylic acid)-grafted O_2-starch; Series 7: for Poly (Acrylic acid)-grafted O_3-starch.

other modified starches in question. It is logically to say that, the highly reactive hydrolyzed starch (H_3) as shown in (Table 1) reacts much more easily with DMDHEU than cotton cellulose. As a result reaction 3 prevails over reaction 1 and 2. Once this is the case, the nitrogen content of the treated fabric will be much lower in presence than in absence of the hydrolyzed starch. The latter consumes most of DMDHEU via reaction 3 and the resultants products are removed from the treated fabric during washing. This seems to be true because, increasing the concentration of the H_3-starch to 50 g/l decreases the nitrogen content of the treated fabrics.

Results of reactant resin DMDHEU treatment in presence of carboxymethylated starches derived from hydrolyzed and oxidized starches lead to the following observations

1. The nitrogen content of cotton fabrics treated with DMDHEU in presence of carboxymethylated modified starches are higher than those treated in presence of hydrolyzed starch (H_3) irrespective of the parent substrate of carboxymethylated starch. This shows that the carboxymethylated hydrolyzed starches in this case is less reactive than both hydrolyzed starch and cellulose which can be attributed to the difference in the number of available hydroxyl groups in each substrate and its molecular size. Nevertheless, fabric samples treated in presence of carboxymethylated starches derived from hydrolyzed starches acquire higher nitrogen contents than those derived from oxidized starches.
2. The nitrogen content of the treated cotton fabrics increases by increasing the extent of either hydrolysis or oxidation of the parent starch. This may be explained in term of (a) the differences in the number of available and accessible hydroxyl groups, duo to the differences in the degree of substitution (b) molecular size and (c) the degree of oxidation expressed as oxygen consumption in case of oxidized starch samples as shown in Tables 1 and 2. It is believed that reaction 1 and 2 appear as the major while reaction 3 minor.
3. Increasing the concentration of carboxymethylated starches in the finishing bath is accompanied by an increment in the nitrogen content of the treated cotton fabrics; implying that the magnitudes of reaction 1 and reaction 2 increases by increasing the carboxymethylated starch concentration in the finishing bath. This is rather in contrast with the results obtained when the treatment was carried out in presence of hydrolyzed starches and signifying the role played by the carboxymethyl groups.

While on the other hand, cotton fabrics treated with DMDHEU in presence of poly (acrylic acid)-starch graft copolymers the backbone of which are based on hydrolyzed and oxidized starches, exhibit the same trend as in case of carboxymethylated starches but with lesser extent. This could be explained in terms of amount, accessibility and availability of the hydroxyl and carboxyl groups in the copolymer molecules as well as the mode of chemical modification.

3.2. Dry wrinkle recovery angles

Figs. 3 and 4 show the dry wrinkle recovery angles of cotton fabrics treated with DMDHEU in presence and absence of either hydrolyzed starch (H_3-starch), carboxymethylated starches and poly (acrylic acid)-starch graft copolymers the backbone of which were hydrolyzed and oxidized starches. It is seen that fabric samples treated with DMDHEU in absence of the modified starch products acquire a dry wrinkle angle of 280°. This is against a dry wrinkle recovery angle of 135° for untreated cotton fabric. It is also seen that the values of the dry wrinkle recovery angle of cotton fabrics treated with DMDHEU in presence of any of the modified starch products under investigation are lower than those treated in absence of these products. Moreover, the values of the dry wrinkle recovery angle of fabrics treated in presence of the said modified starch products decrease by increasing concentration of the modified starch products in the finishing bath.

Figs. 3 and 4 show also that, the values of dry wrinkle recovery angle of cotton fabrics treated with DMDHEU in presence of hydrolyzed starch are lower than those treated with DMDHEU in presence of carboxymethylated starches and poly (AA)-grafted starches products. This suggest that the crosslinking reaction occurring between two adjacent cellulose chains with DMDHEU acting as a bridge (reaction 1) is adversely affected by the presence of any of the modified starch products used as has been pointed out above with respect to the results of the nitrogen content. On the other hand, duo to further modification of the hydrolyzed starches via carboxymethylation results in modified starch products that seem to accentuate reaction 1 and 2, since the dry wrinkle recovery angle increases by increasing the extent of hydrolysis. It is logical that the introduction of the carboxymethyl group in the starch molecules decreases its reactivity leading to a decrease in the extent of the reaction 3 thereby increasing the extent of reactions 1 and 2. It should be emphasized, however, that while the nitrogen content for samples treated with DMDHEU in presence of these carboxymethylated starches increase by increasing concentration of the latter, the dry wrinkle recovery angle decreases. This suggests that reaction 2 (involving cellulose molecules and the starch molecules linked together via DMDHEU molecules) increases on the expense of reaction1 (involving bridging two adjacent cellulose chains through DMDHEU molecules) that is essentially responsible for the improvement in the dry wrinkle recovery angles. A close examination of Figs. 3 and 4 would indicate that the values of dry wrinkle recovery angles of the fabric samples treated with DMDHEU in presence of carboxymethylated starches (5 g/l each) derived from H_1-, H_2-, H_3-starches and O_1-, O_2- and O_3-starches are

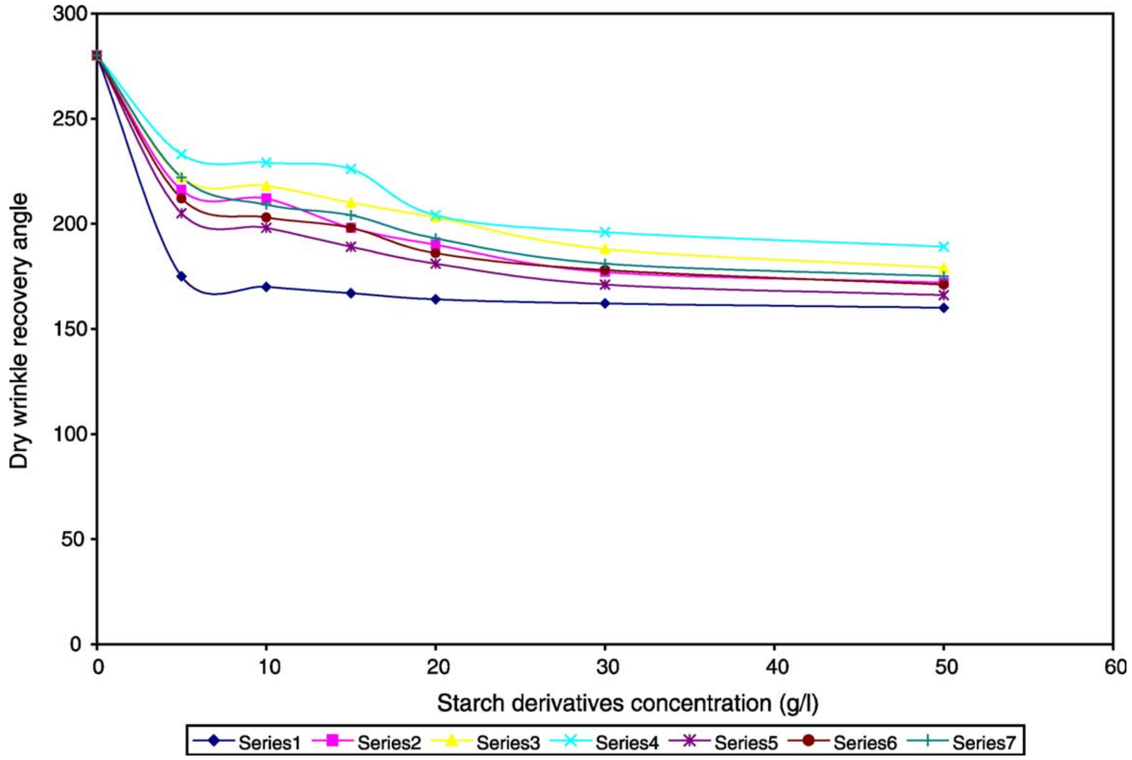


Fig. 3. Dry wrinkle recovery angle of cotton fabric samples treated with DMDHEU in presence of hydrolyzed starch (H_3-) and carboxymethylated starches prepared from hydrolyzed and oxidized starches. Series 1: for H_3-starch; Series 2: for carboxymethylated H_1-starch; Series 3: for carboxymethylated H_2-starch; Series 4: for carboxymethylated H_3-starch; Series 5: for carboxymethylated O_1-starch; Series 6: for carboxymethylated O_2-starch; Series 7: for carboxymethylated O_3-starch.

higher than that sample treated in presence of H_3-starch; a point which indicate that carboxymethylated starches derived from hydrolyzed starches can be used as additives in easy care finishing without causing adverse effect on the wrinkle recovery angle of the easy care finished cotton fabric.

Increasing the concentration of the carboxymethylated starch products in the finishing bath from 5 to 50 g/l is accompanied by a decrement in the dry wrinkle recovery angles of cotton fabrics finished with the latter modified starches. While, the value of wrinkle recovery angles of carboxymethylated starch derived from the highly hydrolyzed starch (i.e. H_3-starch) appears as the most appropriate modified starch products for utilization along with DMDHEU in easy care cotton finishing.

Figs. 3 and 4 show also that when cotton fabric samples were treated with DMDHEU in presence of poly (AA)-starch graft copolymers, the finished samples exhibit dry wrinkle recovery angles the values of which are lower as compared with those observed when the carboxymethylated starch products were used. However, the results follow the same trend with respect to concentration of the modified starch products in the finishing bath and the type and extent of degradation (extent of hydrolysis or oxidation) conferred on starch prior to further modification.

It is seen from Figs. 1–4 that the fabric samples treated with DMDHEU in presence of carboxymethylated starch products possess higher wrinkle recovery angle and nitrogen content than those similarly treated but in presence of poly (AA)-starch graft copolymers. This can be explained in terms of (a) location of the additional groups (i.e. COOH group in the substituent), (b) the magnitude of these groups and (c) physical changes accompanying these chemical changes in the starch molecules. Such effects would, in turn, determine the nature of the modified starch product and the behavior of the latter towards DMDHEU and cellulose during the finishing treatment.

Needless to say that decreasing the molecular size of starch via hydrolytic or oxidative degradation contributes in the nature of the modified starch products, which playa the key role in determining the performance of cotton fabric after finishing in Presence of the latter aforementioned tailored products. So, the fabric performance would rely on the molecular size as well as the mode and extent of modification as indicated before.

3.3. Tensile strength

Figs. 5 and 6 show the tensile strength of cotton fabric samples treated with DNDHEU in presence and absence of hydrolyzed starch, carboxymethylated starches and poly (acrylic acid)-starch graft copolymers, the backbone of which were hydrolyzed and oxidized starches. It is seen that the tensile strength of the samples treated in absence of

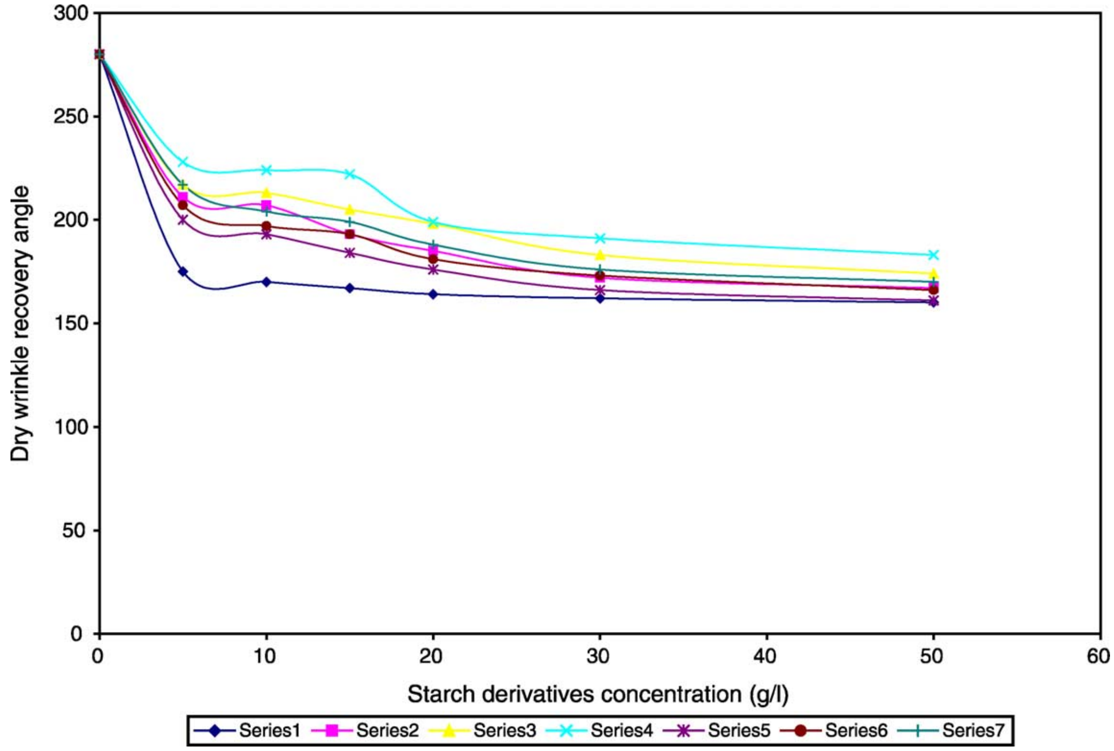


Fig. 4. Dry wrinkle recovery angle of cotton fabric samples treated with DMDHEU in presence of hydrolyzed starch (H_3-) and poly (acrylic acid)-grafted starches prepared from hydrolyzed and oxidized starches. Series 1: for H_3-starch; Series 2: for Poly (Acrylic acid)-grafted H_1-starch; Series 3: for Poly (Acrylic acid)-grafted H_2-starch; Series 4: for Poly (Acrylic acid)-grafted H_3-starch; Series 5: for Poly (Acrylic acid)-grafted O_1-starch; Series 6: for Poly (Acrylic acid)-grafted O_2-starch; Series 7: for Poly (Acrylic acid)-grafted O_3-starch.

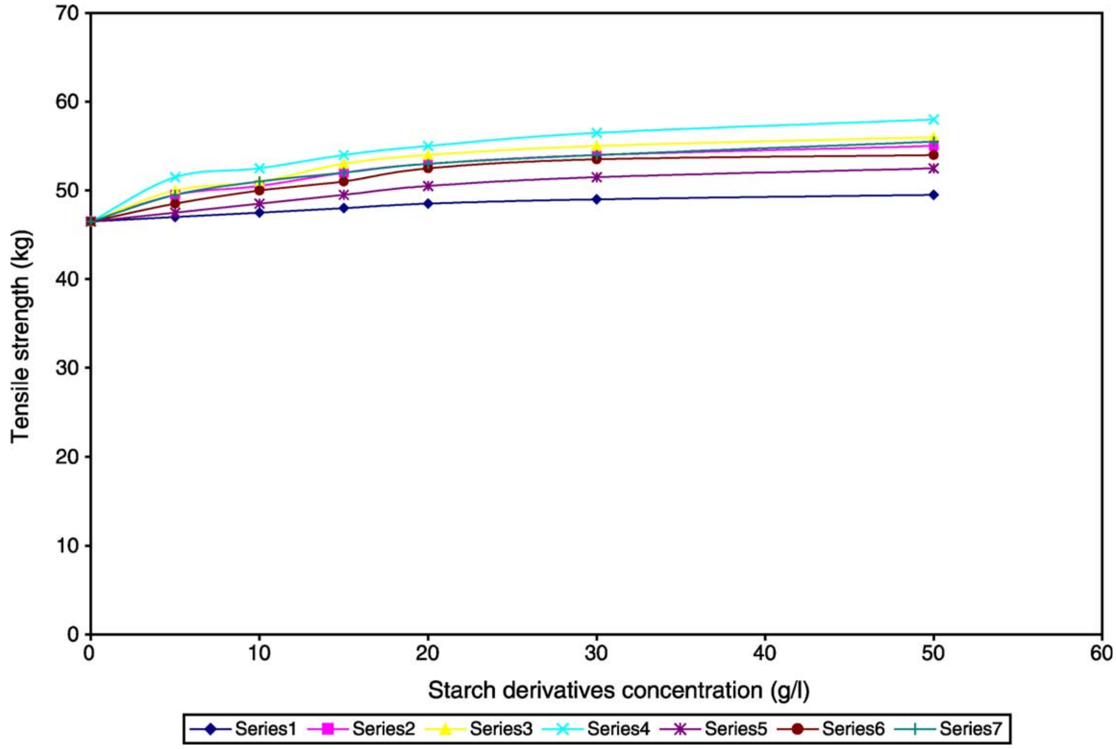


Fig. 5. Tensile strength of cotton fabric samples treated with DMDHEU in presence of hydrolyzed starch (H_3-) and carboxymethylated starches prepared from hydrolyzed and oxidized starches. Series 1: for H_3-starch; Series 1: for H_3-starch; Series 2: for carboxymethylated H_1-starch; Series 3: for carboxymethylated H_2-starch; Series 4: for carboxymethylated H_3-starch; Series 5: for carboxymethylated O_1-starch; Series 6: for carboxymethylated O_2-starch; Series 7: for carboxymethylated O_3-starch.

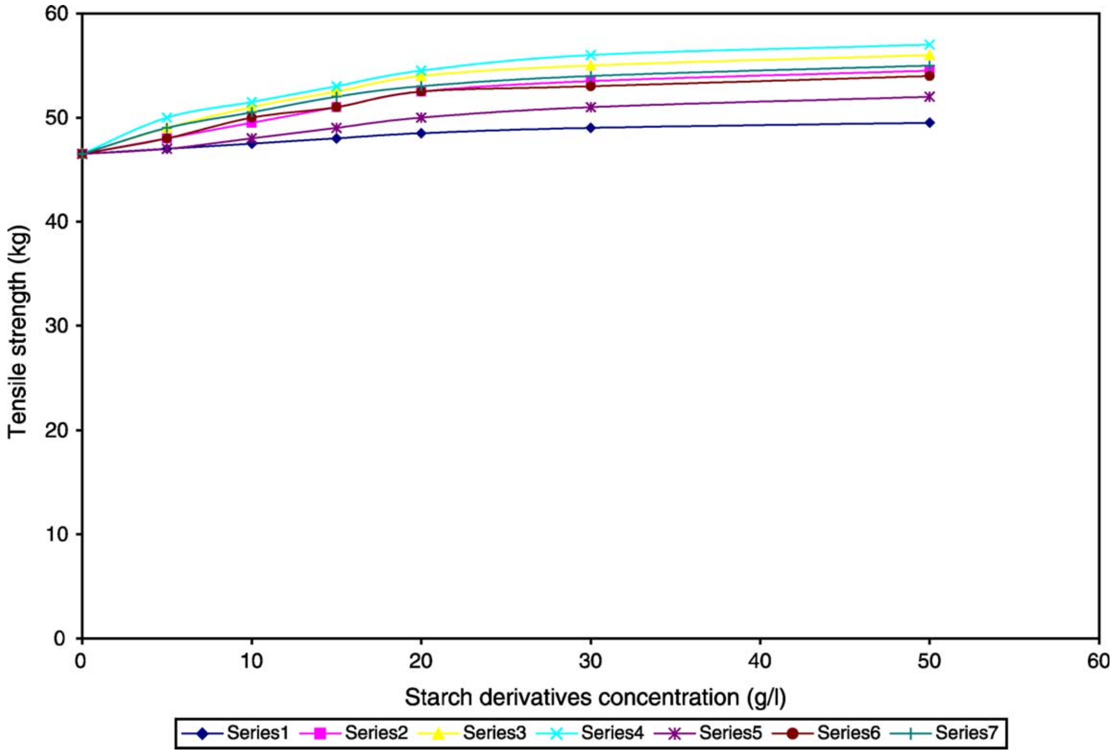


Fig. 6. Tensile strength of cotton fabric samples treated with DMDHEU in presence of hydrolyzed starch (H_3-) and poly (acrylic acid)-grafted starches prepared from hydrolyzed and oxidized starches. Series 1: for H_3-starch; Series 2: for Poly (Acrylic acid)-grafted H_1-starch; Series 3: for Poly (Acrylic acid)-grafted H_2-starch; Series 4: for Poly (Acrylic acid)-grafted H_3-starch; Series 5: for Poly (Acrylic acid)-grafted O_1-starch; Series 6: for Poly (Acrylic acid)-grafted O_2-starch; Series 7: for Poly (Acrylic acid)-grafted O_3-starch.

the modified starch products is much lower than that treated in their presence. Presence of the latter in the finishing formulation decreases substantially the loss in tensile strength of the treated fabric. Moreover, the tensile strength of the treated fabric increases by increasing the concentration of the modified starch products in the finishing bath. The tensile strength of the treated fabric reaches values that are comparable with that of untreated fabric (64 kg).

The results (Figs. 5 and 6) show the following observations.

(a) The tensile strength of fabric treated with DMDHEU in presence of any of the modified starch in question acquire higher values than those treated in presence of hydrolyzed starch;
(b) Fabric samples treated with DMDHEU in presence of modified starches based on hydrolyzed starches acquire higher tensile strength values than those based on oxidized starches;
(c) Fabric samples having the same wrinkle recovery angle as a result of treatment with DMDHEU in presence of those modified starch products exhibit tensile strength the value of which increases by increasing the extent of hydrolysis or oxidation of starch prior to further modification.

The increment in tensile strength of fabric samples treated with DMDHEU in presence of the latter said modified starch products is most probably duo to the enhancement in the reaction 2 which involves attachment of the modified starch molecule to the cellulose molecules via DMDHEU molecule.

4. Conclusions

The enhancement in the tensile strength values of cotton fabric samples finished in presence of newly tailored modified starch products in question than that finished in their absence reflects clearly the main role of starch based additives during finishing process.

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