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Cationized Starch Derived From Pre-Oxidized Starch For Textile Sizing and Printing

Maize starch was subjected first to oxidation using H_2O_2 in presence and absence of ferrous sulfate as catalyst and then to cationization using 3-chloro-2-hydroxypropyl trimethyl ammonium chloride. A thorough investigation of the chemical and rheological characteristics of the oxidized starch and oxidized-cationized starch samples was made. It was found that these modified starches display characteristics, which qualify them to function as excellent sizing agent and to less extent as thickeners for printing polyester fabric with disperse dyes. The differences among the oxidized samples prepared in acidic and alkaline media in presence and absence of ferrous sulfate with respect to carboxyl and carbonyl group content were explained on the basis of the different mechanisms involved in the oxidation reaction of starch. The amenability of the different oxidized starch samples to cationization and variation in the apparent viscosity after cationization of the oxidized starches were also reported.

Keywords: Cationization; Cotton; Printing; Sizing; Textile

1 Introduction

Over the last two decades research and technical work related to starch have been devoted to its chemical modifications. This was done with view to change the physical and chemical structure of starch thereby improving the properties of the latter. Emphasis was placed on oxidation [1–4], hydrolysis [2–4], esterification [5–7], and etherification [8–14]. Cationization is regarded as one of the most important chemical modifications of starch. Cationic starch provides many benefits such as improvement of mechanical strength of paper, better retention of fines and fillers, faster drainage and reduction of waste pollution [15–17]. A number of aqueous, dry and solvent processes have been developed for cationization of starch [18–20].

The viscosity of cationic non-oxidized starch is much higher than that required for textile sizing or printing (about 280 mPas). This indeed stimulated the present work which was undertaken to study the combined effect of oxidation and cationization on the performance properties of starch.

To the authors' knowledge no work has yet been published on the chemical modification of starch under the combined effect of oxidation and cationization, in particular, the use of such modified starch in textile sizing

and printing. The present work was undertaken to fill this gap. Hence, research was designed to study the sizing and desizing properties of cationized starch derived from pre-oxidized maize starch. Sizing and desizing processes were carried out using light cotton fabric (gauze). Sized fabrics were monitored for tensile strength, elongation at break and solubility in hot water (desizability). The work was further extended to study the rheological and printing properties of the oxidized-cationized maize starch.

2 Materials and Methods

2.1 Materials

Maize starch was kindly supplied by Cairo Company for Starch and Glucose, Cairo, Egypt. Chemical analysis showed that this starch has a moisture content of 11.2% and a nitrogen content of 0.06%. 3-Chloro-2-hydroxypropyl trimethyl ammonium chloride (Quat[®]-188, 65%) from Dow Chemical Company, Cary, NC, USA, and hydrogen peroxide (35%), were of technical grade. Ethyl alcohol, acetone, ferrous sulfate, sodium hydroxide, and acetic acid were of laboratory grade. Kelco print from ICI India Limited, Maharashtra, India, a new generation thickener based on sodium alginate, was used to disperse dye printing. Polyester fabric 100% (150 g/m²) was kindly supplied by Egyptian Developing Company, Cairo, Egypt. The disperse dye used was Palanil Brilliant Violet 4 R EL from ICI.

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2.2 Oxidation of starch

Oxidation of maize starch was carried out using hydrogen peroxide at pH 11 or 4. The experimental technique adopted was as follows: A material to liquor ratio 1:5 was employed. 100 g (0.617 mol anhydroglucose units, AGU) of maize starch was slurried in an aqueous solution using a mechanical stirrer at room temperature. Hydrogen peroxide (2.9 mL, 35%, 0.03 mol) was added with continuous stirring followed by the addition of 0.01 g anhydrous ferrous sulfate (FeSO_4) (oxidation catalyst), and the pH of the liquor was adjusted either at 11 using 1% aqueous NaOH or at 4.5 using 1% aqueous acetic acid. The temperature was then raised to 50 °C and the oxidation was allowed to proceed at this temperature for 2 h. Afterwards, the pH of the liquor was adjusted to 7 and the solution was filtered off, washed several times with 90% aqueous ethanol until free from salts, and dried at ambient conditions. Hence, four different samples of oxidized starch were obtained, varying according to the level of oxidation obtained with and without catalyst at pH 4 and at pH 11.

2.3 Cationization of starch

Cationization of the so obtained oxidized maize starch samples was carried out as described by *Kweon et al.* [21]: The reaction mixture contained 50 g starch (dry basis, 0.308 mol AGU), 1.8 g (0.042 mol) NaOH pellets pre-dissolved in 80 mL distilled water, and 26.5 mL Quat-188 (65%, 0.092 mol), were added into a conical flask, which was then placed in a shaking water bath. The reaction temperature was raised to 40 °C and the reaction proceeded for 24 h. At the end of the reaction the pH of reaction medium was adjusted to 7 using 1% HCl, and the content of the flask was filtered off using center glass funnel G_1 . Cationized starch was then washed several times using 90% aqueous ethanol. The so obtained oxidized, cationized starch was then dried at ambient condition. Finally, the dried samples were subjected to analysis for nitrogen content.

2.4 Sizing process

Oxidized cationized starch was slurried in water to a concentration of 10% solid content and the sample was mechanically stirred in a thermostated water-bath. The temperature was then raised from 25 °C to 95 °C in 30 min, keeping the rate of stirring constant at 150 rpm. After heating, strips (50 × 300 mm) of light cotton fabric were impregnated with the cooked starch samples at 40 °C, and then squeezed between two heavy rolls to a wet pick-up of approx. 100%. At this point the fabric strips were dried at 120 °C for 5 min. The samples were finally condi-

tioned at 25 °C and 65 % relative humidity for at least 48 h before testing. The percent size removal was calculated after washing the samples with hot water at 95 °C for 5 min as follows:

$$\text{Size removal (\%)} = \frac{W_1 - W_2}{W_1 - W_0} \times 100$$

Where: W_0 = Weight of sample before sizing
 W_1 = Weight of sized sample before washing
 W_2 = Weight of sized sample after washing

2.5 Stock thickening

Stock thickening paste was prepared using the following recipe

Thickening agent	X g
Water	Y g
	<hr/> 1000 g

Where the thickening agent (X) is either sodium alginate (40 g) or oxidized starch (50 g) or oxidized-cationized starch (50 g).

2.6 Printing pastes

The printing paste was prepared using the following recipe

Stock thickening	900 g
Demaroch A-110	20 g
Citric acid	2 g
Palanil Brilliant Violet 4REL	40 g
Water	X g
	<hr/> 1000 g

2.7 Printing technique

The pastes were applied to polyester fabric using the flat screen technique. Fixation of the printed goods was conducted by steaming at 100–105 °C for 30 min.

2.8 Washing and reduction clear treatments for the printed samples

After printing, the printed goods were thoroughly washed with cold water, followed by washing with hot water at 50–60 °C. Subsequently, the printed samples were treated with a solution containing 4 g/L sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$), 2g/L NaOH (44.5%), and 1 g/L detergent at 60 °C for 15 min. After reduction, the printed goods was washed with hot water at 50–60 °C, then with cold water and finally air dried.

2.9 Testing and analysis

The nitrogen content of oxidized and oxidized-cationized starch was determined according to the Kjeldahl method [22]. Based on the increase in nitrogen content after cationization, the DS values were calculated by the following equation:

$$DS = 162 \times N\% / 1400 - 117 \times N\%$$

Where: N% is the percentage of nitrogen added via cationization

Tensile strength and elongation at break of sized samples was measured according to the corresponding ASTM method [23]. The carboxyl content of the oxidized samples was determined according to a method described elsewhere [24]. The determination depends on formation of the protonated form of the carboxyl groups in starch molecules by soaking the samples in a mixture of HCl/ethanol/water (1/80/20, w/w) for 24 h, then they were filtered off and washed several times with ethanol/water (80/20, w/w) until free from HCl, then dried at 40 °C. An exact weight of the dried protonated form of oxidized starch was then soaked in an excess of aqueous NaOH (0.01 mol) for another 12 h. The excess unreacted NaOH was back titrated with 0.01 mol HCl using phenolphthalein as indicator. The carbonyl content was determined according to the hydroxylamine hydrochloride method [25]. The method depends on the oximation of the carbonyl groups with hydroxylamine hydrochloride in the presence of triethanolamine. The latter neutralizes the liberated hydrochloric acid to shift the equilibrium towards quantitative formation of the oxime. Excess triethanolamine was determined by titration with standard hydrochloric acid using bromophenol blue as indicator. Fastness to washing, rubbing and perspiration was measured according to standard methods [26].

3 Results and Discussion

3.1 Characterization of oxidized starches before and after cationization

Samples of maize starch were first subjected to oxidation with aqueous H₂O₂ (1%, w/w) at pH 4 or pH 11 in presence and absence of ferrous sulfate (catalyst for oxidation). The oxidized starch samples so obtained were cationized using Quat-188, hence oxidized-cationized starch samples could be obtained. All these starch samples were analyzed for carboxyl content, carbonyl content and nitrogen content. The results obtained are presented in Tab. 1.

As can be seen, the modified starch samples I-IV contain substantial amounts of carboxyl and carbonyl groups irrespective of the modification conditions used. Modification of these four starch samples is a direct consequence of the oxidation conditions used. Sample II, which was oxidized at pH 4 in presence of FeSO₄ as a catalyst displays the highest carboxyl content, followed by sample I, which was oxidized under the condition of sample II but in absence of FeSO₄. This signifies the role of the latter in enhancing the oxidation of starch via a free-radical mechanism as will be discussed later. The higher carboxyl content of sample IV compared to sample III is also due to the presence of FeSO₄ catalyst which was added during oxidation of sample IV. Differences between samples I and II on the one hand and samples III and IV on the other hand are due to difference in the pH of the oxidation medium.

Results (Tab. 1) of the carbonyl contents of samples I-IV imply that sample II with the highest carboxyl content exhibits the lowest value of carbonyl groups and, vice versa, sample III with the lowest value of carboxyl groups had the highest content of carbonyl groups. This suggests that starch samples containing relatively high amount of carbonyl groups undergo further oxidation, wherein the carbonyl groups are converted to carboxyl groups; that is, the value of carboxyl groups represents those formed through oxidation of the hydroxyl groups of starch by the oxidizing species of H₂O₂ plus those formed through oxidation of the carbonyl groups originally present in the molecular structure of starch.

Tab. 1 shows the nitrogen content of oxidized-cationized starches (samples V-VIII), which have been derived from the oxidized starch samples (I-IV) through cationization using Quat-188. Obviously, starch modified via oxidation in acid medium (pH 4) with and without catalyst (samples I and II) is less susceptible to cationization than that oxidized in alkaline medium (pH 11) with and without catalyst (samples III and IV). The proneness of the oxidized samples to cationization follows the order: sample IV > sample III > sample II > sample I to yield oxidized-cationized starch with the following order with respect to DS: sample VIII (from IV) > VII (from III) > VI (from II) > V (from I).

In conclusion, oxidation of maize starch with H₂O₂ yields oxidized starches with substantial amount of carboxyl and carbonyl groups depending upon the presence and absence of FeSO₄ catalyst and pH of the oxidation medium. The susceptibility of the so obtained oxidized starches towards cationization differs significantly. Samples oxidized at pH 11 in presence of FeSO₄ or even in absence of the latter are by far more susceptible to cationization than those oxidized at pH 4 in presence and absence of FeSO₄ catalyst. During the chemical mod-

Tab. 1. Carboxyl, carbonyl and nitrogen content of the modified starch samples.

Modified starch	Modification conditions	Carboxyl content [meq/100 g]	Carbonyl content [meq/100 g]	N Content [%]	N Added ^(a) [%]	DS
Oxidized						
Sample I	oxidation with 1% H ₂ O ₂ at pH 4 without catalyst	9.70	0.77	0.04	0.00	–
Sample II	oxidation with 1% H ₂ O ₂ at pH 4 with catalyst	11.20	0.63	0.04	0.00	–
Sample III	oxidation with 1% H ₂ O ₂ at pH 11 without catalyst	7.40	0.98	0.04	0.00	–
Sample IV	oxidation with 1% H ₂ O ₂ at pH 11 with catalyst	8.60	0.93	0.04	0.00	–
Oxidized and cationized						
Sample V	cationization of sample I	n.d. ^(b)	n.d.	0.47	0.43	0.052
Sample VI	cationization of sample II	n.d.	n.d.	0.58	0.54	0.065
Sample VII	cationization of sample III	n.d.	n.d.	0.65	0.61	0.074
Sample VIII	cationization of sample IV	n.d.	n.d.	0.71	0.67	0.082

^(a) Added nitrogen [%] = Total nitrogen content [%] after cationization – Residual nitrogen content [%] before cationization.

^(b) n.d. = not determined

Detailed procedures for oxidation and cationization are described in the experimental section.

Tab. 2. Apparent viscosity (mPas) of starch sample modified via oxidation or under the combined actions of oxidation and cationization at different rates of shear.

Shear rate [s ⁻¹]	Oxidized starch				Oxidized-cationized starch			
	pH 4 without	pH 4 with	pH 11 without	pH 11 with	pH 4 without	pH 4 with	pH 11 without	pH 11 with
65.1	28.00	20.00	24.50	12.0	7.14	3.93	12.10	10.00
74.4	26.00	19.80	23.00	11.20	6.25	3.75	11.30	9.38
83.7	25.50	19.60	22.00	10.00	6.11	3.64	10.60	8.89
93.0	25.00	19.00	21.00	9.90	6.50	3.57	10.00	8.50
102.0	24.00	18.80	20.40	9.69	6.36	3.50	9.95	8.18
112.0	23.50	18.50	20.20	8.93	6.25	3.46	9.58	7.92
121.0	23.00	17.90	19.60	8.70	6.15	3.35	9.23	7.69
130.0	20.00	16.40	19.20	8.60	5.36	3.33	8.93	7.58
140.0	19.60	15.60	18.90	8.50	5.33	3.31	8.67	7.55

The viscosity of the samples was measured at the same concentration 2.5% (w/v).

Without = oxidation was carried out in absence FeSO₄.

With = oxidation was carried out in presence of FeSO₄.

ification by oxidation, especially at alkaline pH, starch seems to undergo physical changes, which cause its activation and make it more amenable to cationization (changes under alkaline conditions are well known).

3.2 Rheological properties of oxidized starches before and after cationization

Tab. 2 shows the effect of pH on the apparent viscosity of oxidized starch samples before and after cationization when the oxidation was carried out using 1% H₂O₂ in presence and absence of FeSO₄ at various rates of shear.

Obviously, the apparent viscosity decreases by increasing the shear rate. This is observed regardless of the conditions used including the pH value, the presence of FeSO₄ and cationization. Implication of this is that all the pastes under investigation are characterized by a non-Newtonian behavior.

A close examination of the results of Tab. 3 would indicate that for a given shear rate the apparent viscosity is lower at pH 11 than at pH 4. This is observed before and after cationization indicating higher molecular degradation of starch via oxidation and subsequent reactions at pH 11. Oxidation by H₂O₂ at pH 4 seems to proceed according to

Tab. 3. Apparent viscosity (mPas) of printing pastes thickened with a mixture of oxidized starch and 4% sodium alginate.

Shear rate [s ⁻¹]	Oxidation at pH 4			Oxidation at pH 11		
	Mix. I	Mix. II	Mix. III	Mix. I	Mix. II	Mix. III
11.2	2217	1817	1133	1890	1600	1450
12.1	2142	1773	1104	1808	1579	1430
13.0	2096	1729	1082	1812	1559	1434
14.0	2027	1677	1053	1777	1546	1424
14.9	1984	1634	1031	1746	1529	1413
15.8	1932	1588	1009	1717	1514	1409
16.7	1894	1553	989	1691	1500	1405
17.7	1853	1511	971	1668	1487	1336
18.6	1815	1473	950	1642	1475	1312
19.5	1779	1440	933	1621	1462	1289

All starch samples are oxidized without FeSO₄.

Mix. I = Mixture of 75% sodium alginate and 25% oxidized starch.

Mix. II = Mixture of 50% sodium alginate and 50% oxidized starch.

Mix. III = Mixture of 25% sodium alginate and 75% oxidized starch.

a free-radical mechanism [27]. This is rather substantiated when the oxidation was conducted in presence of FeSO₄ at pH 4. The Fe²⁺ forms a redox system with H₂O₂ and creates hydroxyl free radicals ([•]OH) as follows:



It is understandable that in absence of Fe²⁺ starch is involved with H₂O₂ to yield ultimately the hydroxyl free radicals ([•]OH). Once formed, the free radicals abstract hydrogen atoms from the starch to form starch macroradical. Atmospheric and/or occluded oxygen is added to the starch macroradical thereby giving rise to oxidized starch.

At pH 11, on the other hand, the mechanism of oxidation is different. H₂O₂ dissociates in an alkaline medium to give the peroxy anion (⁻OOH) which is responsible for oxidation of starch [27]. The role of Fe²⁺ (from FeSO₄) seems to enhance the formation of the oxidizing species, i.e., the peroxy anion (⁻OOH), thereby a higher molecular degradation of starch – as measured by the apparent viscosity – is observed in presence of FeSO₄ at pH 11. Further, the effect of cationization is to bring about decreased apparent viscosity. After cationization, the apparent viscosity decreases irrespective of the pH value.

Since cationization is carried out in an alkaline medium under ambient conditions, current data suggest that oxidized starch undergoes further oxidation during cationization by virtue of the alkaline medium in presence of atmospheric and/or occluded oxygen.

Tabs. 3 and 4 summarize the values of the apparent viscosity of printing pastes thickened with a mixture of sodium alginate and either oxidized starch or oxidized-cationized starch. Oxidation of starch was carried out using aqueous H₂O₂ (1%) at pH 4 and pH 11 in absence of FeSO₄. The ratio between sodium alginate and the said chemically modified starches in the printing pastes were 25:75, 50:50 or 75:25.

A comparison between Tabs. 3 and 4 reveals that for a given rate of shear and irrespective of the pH of the oxidation medium the apparent viscosity of pastes thickened with oxidized starch is much lower than their corresponding samples thickened with oxidized-cationized starch. This suggests that presence of bulky moieties of the quaternary ammonium salt, i.e., 2-hydroxypropyl trimethyl ammonium chloride in the molecular structure of oxidized starch enhances its molecular weight and, therefore, the apparent viscosity. Also formation of salt linkages between the quaternary ammonium groups in the oxidized-cationized starch and the carboxyl groups of sodium alginate is anticipated to increase resistance to flow; a point which is positively reflected on apparent viscosity.

It is further noted that the apparent viscosity of the samples examined (Tabs. 3 and 4) increases by increasing the ratio of the alginate in the mixture. This implies that the alginate thickener is the principal polymer, which essentially determines the value of apparent viscosity of the pastes under investigation. It is also seen (Tabs. 3 and 4) that the apparent viscosity of pastes containing starch

Tab. 4. Apparent viscosity (mPas) of printing pastes thickened with a mixture of oxidized-cationized starch and 4% sodium alginate.

Shear rate [s ⁻¹]	Oxidation at pH 4			Oxidation at pH 11		
	Mix. I	Mix. II	Mix. III	Mix. I	Mix. II	Mix. III
11.2	2478	2238	1670	4050	1900	1686
12.1	2281	2031	1656	3382	1763	1667
13.0	2207	1750	1618	2947	1658	1606
14.0	2161	1797	1578	2622	1650	1589
14.9	1938	1688	1530	2518	1600	1485
15.8	1922	1621	1470	2240	1469	1373
16.7	1921	1550	1391	2219	1460	1308
17.7	1845	1493	1123	2151	1483	1319
18.6	1719	1325	1109	2126	14300	1177
19.5	1702	1139	1087	2100	1290	1122

All starch samples are oxidized without FeSO₄.

Mix. I = Mixture of 75% sodium alginate and 25% oxidized-cationized starch.

Mix. II = Mixture of 50% sodium alginate and 50% oxidized-cationized starch.

Mix. III = Mixture of 25% sodium alginate and 75% oxidized-cationized starch.

oxidized at pH 4 is higher than of those containing starch oxidized at pH 11. An opposite situation is encountered after cationization of the oxidized starch. This could be interpreted in terms of the mechanisms involved in the oxidation at pH 4 and pH 11. It is understandable that a free-radical mechanism operates at pH 4 whereas oxidation of starch at pH 11 proceeds by the attack of perhydroxy anion (^-OOH) on the starch molecules as detailed above. The characteristics of the oxidized starches obtained at pH 4 and pH 11 with respect to creation of aldehyde (or carbonyl) and carboxyl groups in the molecular size of starch would certainly play a role in homogeneity and resistance to flow of the mixture when used along with the alginate. In other words, the physicochemical properties of oxidized starches prepared at pH 4 and pH 11 are different; consequently, their apparent viscosity would exhibit different values when used along with sodium alginate.

The finding that oxidized-cationized starch results in higher apparent viscosity when mixed with the alginate than starch oxidized at pH 4 is rather interesting. The presence of quaternary ammonium groups in the molecular structure of oxidized-cationized starch helps to establish salt linkages with the carboxyl groups of starch. Once this occurs, resistance to flow and, therefore, the apparent viscosity increases.

3.3 Sizing and desizing behavior of oxidized starches and oxidized-cationized starch

The sizability and desizability of oxidized and oxidized-cationized starch with respect to cotton textiles was studied by assessing the eight samples specified in

Tab. 1. Sizing and desizing were carried out as described in the experimental section and sized cotton strips were evaluated for breaking load, elongation at break, size add-on and percent size removal as well as viscosity of aqueous 10% (w/w) solution and the nitrogen content. The results are given in Tab. 5.

As can be seen the apparent viscosity of sample I has the highest value and that of sample IV the lowest, whereas samples II and III take a middle position, however, the apparent viscosity of sample II is certainly higher than that of sample III. This indicates that oxidation in alkaline medium at pH 11 is more effective in decreasing the apparent viscosity than oxidation in acidic medium (pH 4). Presence of FeSO_4 catalyst seems to enhance the molecular degradation of starch in alkaline medium compared to acid medium. Size add-on of the oxidized samples on the gauze amounts to 10% indicating that the nature of the oxidized starch plays no role in this regard. On the other hand, tensile strength increases strikingly but with the existence of the following order: sample 1 > sample II > sample III > Sample IV. Indeed sample I has a tensile strength, which is twice as high as that of the blank. The four oxidized starch sizes (samples I – IV) possess a decreased elongation at break, from 11% to an average of 7.5%. The amount of size removal ranges from 65 to 83% depending on the characteristics of the oxidized starch sample, particularly the apparent viscosity; the higher the apparent viscosity the lower the size removal.

Oxidized-cationized starches represented by samples V, VI, VII and VIII when applied as sizes enhance the tensile strength from about 220 N for untreated (unsized sample)

Tab. 5. Sizability and desizability of oxidized and oxidized-cationized maize starches.

Substrate	N [%]	Viscosity [mPas]	Size add-on [%]	Tensile strength [kgf]	Elongation at break [%]	Size removal [%]
Unsized gauze (blank)	–	–	–	22.10	11	–
Oxidized starches						
Sample I	–	180	10.30	45.30	8	65
Sample II	–	160	10.00	41.20	8	69
Sample III	–	130	10.20	39.50	7	78
Sample IV	–	120	10.00	36.20	7	83
Oxidized-cationized starches						
Sample V	0.73	173	9.98	46.70	8	93.50
Sample VI	0.91	155	10.00	49.30	8	95.70
Sample VII	1.20	110	10.00	47.20	7	100.00
Sample VIII	1.50	92	10.10	49.30	7	100.00

Viscosity was measured for aqueous 10.0% (w/v) solution at 80°C and at shear rate 516 s.⁻¹.

to about 470, 490, 470 and 490 N for samples V, VI, VII and VIII, respectively. These striking increases in the tensile strength are met by a very moderate decrease in elongation at break, which on average amounts to 7.5%. The salient feature here is the removal of the size, which reaches a value of 100% upon using samples VII and VIII. It could be concluded that sizing agents derived from combined oxidation and cationization of maize starch have proved to function as adequate and successful sizing agents.

The increased breaking load is unequivocally due to the extra strength brought about by the film of the sizing agent. It is understandable that during sizing a film-like coating is produced on the cotton strips, thereby increasing the tensile strength. At the same time, the film restricts movement of the yarns in the cotton fabric, as well as conferring certain rigidity on the fibers and as a result the elongation at break decreases.

3.4 Utilization of oxidized starches and cationized starches derived thereof as thickener in disperse printing

The aforementioned oxidized starches (samples I-IV) along with oxidized-cationized starches (samples V-VIII) were used alone or in admixture with sodium alginate to

thicken pastes for printing of polyester fabric using a disperse dye namely, Palanil Brilliant Violet 4REL. A thickening agent (commercial name Kelco print) was also used alone or in admixture with any of the eight modified starches samples for comparison. After printing, fixation and washing the printed goods were monitored for color strength and overall fastness properties. The color strength is expressed as K/S. The results obtained are listed in Tab. 6.

As Tab. 6 shows the K/S of the polyester fabrics printed using oxidized and cationized starch is lower than that of the sample printed using sodium alginate. Nevertheless, there is an improvement in overall fastness properties when the oxidized and oxidized-cationized starches were used. It is also observed that oxidized-cationized starch is compatible with sodium alginate as evidenced by the values of the K/S and overall fastness properties of the printed polyester fabrics in comparison to those printed using pure oxidized-cationized starch.

4 Conclusion

Oxidation of maize starch with H₂O₂ in absence and presence of FeSO₄ as an oxidation catalyst and in acidic or alkaline pH yield oxidized starches with different vis-

Tab. 6. Properties of the printed fabrics on using modified starch either alone or admixture with Kelco print and disperse dye Palanil Brilliant Violet 4 REL.

Thickener used	K/S	Rubbing fastness		Wash fastness at 60 °C		Perspiration fastness				Handle
		Wet	Dry	St.	Alt.	Acidic		Alkaline		
						St.	Alt.	St.	Alt.	
Kelco print 100%	9.10	5	5	4.5	5	5	5	4.5	5	Soft
Mixture of alginate with sample I	8.46	5	4–5	4.5	5	4.5–5	4.5	5	5	Soft
	7.75	4	4–4.5	4.5	4.5	4.5	4.5	4.5	5	Soft
	6.97	4–4.5	4	4	4.5	4	4–5	5	5	Soft
Mixture of alginate with sample II	8.83	4–4.5	5	5	4–5	5	5	4.5	4.5	Soft
	8.29	4–4.5	5	4–5	4–5	4.5–4–5	5	4.5	4.5	Soft
	7.65	3–4	4–4.5	3–4	4	4	4–5	4.5	4.5	Soft
Mixture of alginate with sample III	8.11	4.5–4.5	5	5	4.5	4.5–4.5	4.5	4.5	5	Soft
	7.88	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	Soft
	7.11	4	4	3–4	4	4.5	4.5	4.5	4.5	Soft
Mixture of alginate with sample IV	8.12	4.5	5	4.5	4.5	5	5	4.5	5	Soft
	7.75	3.5	4	4	4	4.5	4.5	4.5	4.5	Soft
	6.50	3–4	4	3–4	3.5	3–4	4	3.5	4	Soft
Cationized sample I	6.22	3–4	3–4	3.5	4	3.5	3.5	4	4	Soft
Cationized sample II	6.12	4	3–4	3	4	4–5	4	4	4	Soft
Cationized sample III	6.95	3–4	3–4	3.5	3.5	3.5	3.5	3–4	4	Soft
Cationized sample IV	5.60	4	3–4	4	4	3.5	3.5	4	4	Soft

St. = Staining, Alt. = Alteration.

cosity, carboxyl and carbonyl groups depending upon the presence and absence of FeSO_4 and pH of the oxidation medium. Starch samples oxidized at pH 4 in presence of FeSO_4 displays highest carboxyl content followed by those samples oxidized under the same conditions but in absence of FeSO_4 . Oxidation at pH 11 is more effective in decreasing the apparent viscosity than does the oxidation at pH 4. Presence of FeSO_4 catalyst seems to enhance molecular degradation of starch in alkaline medium than in acid medium. Starch samples oxidized in acidic medium is less susceptible to cationization than that oxidized in alkaline medium. Sizing agent derived from starch samples oxidized at pH 11 in presence or absence of FeSO_4 then cationized enhance the tensile strength and decrease the elongation at break of light cotton fabric sample compared with the other starch samples oxidized at pH 4 then cationized. The former show also 100% size removal. Although the K/S of polyester fabrics printed using oxidized and cationized starch is lower than that of the sample printed using sodium alginate, there is an improvement in overall fastness properties when the oxidized and oxidized-cationized were used.

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