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Application of germinated maize starch in textile printing

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ABSTRACT

Germinated maize is generally discarded as a waste material. In the present investigation starch obtained from germinated maize has been compared with the starch from non-germinated maize, as a thickener in textile printing. Extraction of starch was done by alkali steeping method. Analysis of both the starches was done by measuring swelling power, paste clarity, particle size, crystallinity and iodine binding. Printing of vat dyes on 100% cotton fabric was carried out using both the starches. The prints were analysed by measuring colour value (K/S and L^*, a^*, b^* value), bending length and fastness to washing and crocking. Results suggest that germinated maize starch can substitute the non-germinated maize starch partially if not fully, as a thickener in printing.

1. Introduction

The main objective of printing is to produce coloured patterns with sharp boundaries on textile materials without any dye spreading beyond the boundaries of the motif of design (Shenai, 1984). This is achieved by using proper thickeners which act as vehicles for carrying dyestuffs, chemicals and other printing assistants to the textile material during the process of printing (Narkar & Narkar, 1973). The printing thickener holds the dye particles in the desired place on the fabric until the printing and subsequent fixation processes are complete and the dye is permanently attached (Cooney, 1974). Thickeners used in textile printing are high molecular weight compounds giving viscous pastes in water (Shenai, 1990). There are a number of properties which a thickener is supposed to possess in order to give good quality prints and these properties are explained by a number of researchers (Shenai, 1990; Shrivastav & Gharia, 1980). Most of the natural polymers used as thickening agents in printing are polysaccharides (Thomas, 1981). Native starch is, after cellulose, the most abundant of the plant products and is therefore used as a low-cost readily available source of industrial materials (Miles, 2003). By far the largest source of starch is maize (corn) with other commonly used sources being wheat, potato, tapioca and rice. Starches contain amylose which is a straight (unbranched) chain polysaccharide and amylopectin which is a branched chain polysaccharide. It is the characteristic molecular sizes, amylose–amylopectin ratios and granular structures which impart each type of starch its unique properties (Daniel, Whistler, & Roper, 1997).

In India untimely rains and hail storms at harvest time and inadequate storage facility for the food-grains cause dampening of a lot of cereal grains such as wheat, sorghum, maize, rice, etc. The subsequent germination and microbial growth make them unacceptable for edible consumption (Pandey & Raja, 1992). The percentage of such waste is quite alarming i.e. 10–15%. Enzymatic hydrolysis of starch by enzymes produced in the sprouted grain persists in the flour and generates undesirable quantities of sugar. Hence germinated grains which are normally dumped can be effectively utilized for extraction of starch which in turn can find applications in textile printing as well as in sizing. Suitability of germinated wheat starch to substitute non-germinated wheat starch in printing of vat dyes on cotton has been reported earlier from our laboratory (Shanbhag V.S., M.Sc. Tech. Thesis 1994, TH 2296, University of Mumbai).

The present work looks in to the characterization and application of germinated maize starch as a substitute for non-germinated maize starch in printing of vat dyes on cotton.

2. Materials and methods

2.1. Materials

Maize cereals and jute sack used for extraction of starch were obtained from local grocery shop. 100% cotton fabric was used for printing with the fabric construction of E.P.I – 76 and P.P.I – 70. GSM of fabric used was 123.5 gm/m^2. Two hundred mesh nylon

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bolting cloth was used for the extraction of starch. All chemicals used were of laboratory grade. Vat dyes used were supplied by Atul (P) Ltd.

2.2. Equipment

Spectraflash SF300 was used to measure the K/S and L^*, a^*, b^* values of starch and printed samples. Particle size of germinated and non-germinated starch was determined by use of CILAS Particle Size Analyser and X-Ray Diffractometer (XRD-6000), Shimadzu was used to determine changes occurring in amorphous and crystalline structure of the starch granules. Thermal analysis of starches was carried out using Differential Scanning Calorimetry, Shimadzu DSC 60.

2.3. Methods

2.3.1. Germination

Germination of maize was done by imitating the actual poor conditions during storage. Maize grains were packed and allowed to suffocate in a jute sack. Sprinkling of water was done every 2 h for 24 h to keep it in a damp condition. After 24 h the grains were removed and without rinsing, they were completely dried in an oven at 50 °C.

2.3.2. Extraction of starch

Extraction of starch was done by alkali steeping method (Yanez & Walker, 1986). The grains were ground to coarse flour which was then treated with 5 times the volume of 0.25% NaOH for 4 h followed by draining. The treatment was repeated again for 3 h, which was followed by washing it thoroughly until free of NaOH. The grains were ground in a waring blender and the slurry obtained was then passed through a 200 mesh bolting cloth and squeezed to extract the crude starch. The extract obtained was kept overnight until separation of two layers. Upper layer was drained and lower layer was centrifuged at 4000 rpm for 10 min. The upper proteinous portion was then scrapped and starch obtained was dried in an oven at 50 °C. The starch was then ground to 60 mesh and stored in an air tight container under refrigeration to avoid microbial or fungal attack.

2.3.3. Analysis of starch

Analysis of germinated and non-germinated starch was done for comparison.

2.3.3.1. Estimation of colour of starch powders. The starch powder samples were taken in a small plastic sacks and placed against the measuring slit of spectrophotometer. Kubelka Munk function K/S and $L*$, $a*$, $b*$ values were measured using Spectraflash SF300, to determine its colour using 10 degree observer taking the mean of three readings at different interval after every time shaking the sample in the sack.

2.3.3.2. Swelling power. Swelling power was determined by the method reported by Subramanian, Hoseney and Bramel-Cox (1994). Starch (0.6 g) was heated with 30 ml of distilled water at 95 °C for 30 min. Lump formation was prevented by stirring this mixture at every 5 min interval. The mixture was then cooled and centrifuged (using CRU-5000 centrifuge) at 5000 rpm for 15 min. The supernatant liquid was carefully removed and the swollen starch sediment was weighed. Swelling power (g/g) was calculated as the ratio of the weight of the wet sediment to the initial weight of the dry starch.

2.3.3.3. Paste clarity. Measurement of paste clarity was carried out by method of Craig, Maningat, Seib, and Hoseney (1989). Starch sample (250 mg) was suspended in 20 ml of distilled water in a 40 ml test tube with plastic cap. The tubes were then placed in a boiling water bath for 30 min, shaken thoroughly every 5 min and then cooled to room temperature (25–30 °C) for about 10 min. The percent transmittance (% T) was determined at 650 nm against water as blank on a UV-1201 spectrophotometer (Shimadzu, Japan).

2.3.3.4. X-ray diffraction analysis. X-ray diffraction analysis was carried out to determine the changes occurring in amorphous and crystalline structure of the starch granules after germination. Analysis was done at an angular (2Φ) range of 4° to 32°20′ using XRD-6000 (Shimadzu, Japan). In order to have precise results XRD analysis was carried at four different places for both the starches and the average % crystallinity was calculated. From the radial scans of intensity versus 2Φ, the lateral order or the crystallinity index was determined using Shimadzu's crystallinity software.

2.3.3.5. Particle size analysis. Particle size analysis of both the starches was done on particle size analyser 1064 (CILAS) using water as a medium.

2.3.3.6. Thermal analysis using Differential Scanning Calorimetry. - Thermal analysis of starch was carried out by using Differential Scanning Calorimetry (Shimadzu DSC-60, Japan). Approximately 2.5 mg of sample and 12.5 μl of distilled water were weighed into sample pan and mixed by using pin. A stream of dry nitrogen was flushed through the DSC head at 60–70 ml/min throughout the study. Keeping the reference cell empty, the sample pan and reference pan were heated simultaneously at rate of 5 °C/min from 40 to 100 °C to analyse the thermal transition of starch. Onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c) and enthalpy of gelatinization (ΔH_g) were recorded by DSC-60, (Shimadzu). $T_o - T_c$ was calculated as the range of gelatinization (Bhosale & Singhal, 2007).

2.3.3.7. Estimation of Iodine binding. The amylose content of starch was measured colorimetrically using the iodine method (Juliano, 1971). The sample (100 mg) was weighed accurately and placed into a 50 ml Erlenmeyer flask, to which 1 ml of 95% ethanol and 9 ml of 1 N NaOH were added. The sample was heated for 10 mins in boiling water to gelatinize the starch. After cooling the gelatinized sample to room temperature, it was transferred to 100 ml volumetric flask; then the total volume made to 100 ml by adding distilled water. The starch solution (5 ml) was pipetted into a 100 ml volumetric flask and 1 ml of 1 N acetic acid and 2 ml of iodine solution (0.2 g of iodine and 2.0 g of potassium iodide in 100 ml of aqueous solution) were added. The solution was diluted to 100 ml with distilled water, shaken and then allowed to stand for 20 min. The absorbance was then measured at 620 nm using spectrophotometer (UV-1201 Shimadzu, Japan).

2.3.4. Printing

Printing of vat dyes was done by pre-reduction method: (Potash Rongalite Method)

Non-germinated maize starch thickener (10%) was prepared by taking 10 parts of starch and 90 parts of water. In case of germinated maize starch, paste of 11% solid content was used as a thickener and it was prepared by taking 11 parts of germinated maize starch and 89 parts of water. Starch powder was first pasted with little amount of water followed by addition of the remaining water.

The contents were then mixed and heated at boil for 30 min under continuous stirring.

Similar procedure was used for preparing binary blends of germinated and non-germinated thickeners. Binary blends of the germinated and non-germinated thickeners were made in the ratios of (w/w of the paste) 70:30, 50:50 and 30:70.

Formulation for printing using pre reduction method was made as follows:

Vat dye	2 parts
Glycerine + urea	5 parts
Solution salt B	3 parts
Potassium carbonate	12 parts
Sodium hydrosulphite	4 parts
Thickener paste	58 parts

The contents were then warmed at 60 °C and kept for 30 min at 60 °C. After cooling, 16 parts of Rongalite C was added to make a total of 100 parts. Samples were then printed with two strokes of squeeze, steamed at 102 °C for 4 min. This was followed by oxidation using 2 gm/l potassium dichromate and 5 gm/l acetic acid (30%) solution. The samples were washed with non-ionic soap (Auxipon NP) in hot water followed by washing with water and then dried in air.

2.3.5. Analysis of printed fabrics

2.3.5.1. Colour value by reflectance method. The printed samples were evaluated for the depth of colour by reflectance method using 10 degree observer. The absorbance of the printed samples was measured on "Pye Unicam SP 8-400 UV/Vis Spectrophotometer" equipped with reflectance accessories. The *K*/*S* values were determined using expression;

$$K/S = \frac{(1-R)^2}{(2R)}$$

where R is the reflectance at complete opacity, *K* is the absorption coefficient and *S* is the scattering coefficient.

2.3.5.2. Bending length. Bending length of printed samples, which is inversely proportional to the softness of the prints, was determined using a Shirley stiffness tester (Booth, 1983). To carry out the test, printed fabric strip of 6 × 1 inches was cut and then both the template and specimen were transferred to the platform with one end coinciding with the mark 'O' (zero) of the scale. The specimen and the template were moved until the tip of the specimen just touched the slanting side of the tester. At this position bending length could be directly read from the scale opposite to 'O' mark on the platform.

2.3.5.3. Washing fastness (ISO-III). The test for colour fastness to washing was carried out using ISO III methods (Trotmann, 1984).

2.3.5.4. Crocking fastness. The printed samples were tested for dry and wet crocking. The colour fastness to dry crocking and wet crocking (cloth impregnated with 70% expression of the same sample) was measured using "crock-meter" with 50 strokes of crocking.

3. Results and discussion

3.1. Properties of starch extracted from germinated and non-germinated maize grains

Not much difference was observed in *K*/*S* and *L*∗, *a*∗, *b*∗ values of both the starches (Table 1) and hence it is expected that the colour of starch would not play any role in affecting the final colour of prints.

Table 1
Analysis of starch extracted from germinated and sound maize grains

Characteristics of starch	Germinated	Non-germinated
Colour values of starch powder[a]		
K/*S*	0.0038 ± 2.15	0.0045 ± 1.81
L^*	94.69 ± 0.04	94.22 ± 0.02
a^*	0.31 ± 2.63	0.27 ± 3.02
b^*	7.33 ± 0.33	8.26 ± 0.20
Swelling power (gm/gm)[a]	3.57 ± 0.23	9.07 ± 0.27
Transmittance (%)[a]	2.13 ± 5.85	2.83 ± 1.67
Average crystallinity (%)[b]	29.2 1 ± 18.17	31.86 ± 14.38
Particle size (μm)[a]		
Diameter at 10%	1.92 ± 0.43	2.24 ± 0.73
Diameter at 50%	13.39 ± 0.12	14.00 ± 0.12
Diameter at 90%	21.49 ± 0.23	24.56 ± 0.13
Differential Scanning Clorimetry		
T_0 (°C)	65.30	66.16
T_c (°C)	75.53	75.35
T_p (°C)	71.04	70.33
Heat (mJ)	−487.16	−787.99
No. of peaks	2	1
Absorbance (%) (with iodine)[a]	0.10 ± 10.14	0.03 ± 22.58

[a] Values are means ± %SD of three determinations.
[b] Values are means ± %SD of six determinations.

Swelling power of non-germinated starch was about 2.6 times that of the germinated starch (Table 1). The major factor that controls the swelling behaviour of starch is the strength and character of the miscellar network within the granule, which in turn is dependant on the degree and kind of association. Also at the molecular level, many factors influence the degree of association, as well as the size, shape, composition and distribution of the miscellar areas in the internal lattice. These factors include the ratio of amylose to amylopectin, the characteristics of each fraction in terms of molecular weight and its distribution, degree of branching, conformation and the length of outer branches of the amylopectin (Whistler, Paschall, Bemiller, & Roberts, 1965). During germination α-amylase gets activated and catalyses the hydrolysis of α-1,4 glucosidic linkages in starch and gives rise to oligosaccharides of lower molecular weights such as dextrin, maltose and glucose which do not have any swelling power (Whistler et al., 1965). In maize starch the granular swelling during gelatinization is mainly a function of amylopectin content (Daniel et al., 1997). During germination the amylose content (%) increases and the starch granules with higher amylose content, are better reinforced and thus are more rigid causing swelling less freely when heated. This is also confirmed by the results obtained for determination of amylose by iodine. Hence, the swelling power of germinated starch is lower than that of non-germinated starch.

The transmittance (%) of non-germinated starch was higher than that of germinated starch (Table 1). The paste clarity is directly related to the state of dispersion and retrogradation tendency of the starch. The factors which increase granule swelling and solubilisation, or those factors that inhibit retrogradation increase in the paste clarity (Whistler et al., 1965). Since the swelling power of non-germinated starch was higher, its paste clarity was also higher than that of the germinated starch.

The crystallinity (%) of the starch was reduced on germination of maize, which may be attributed to activation of enzymes in presence of water which in turn would cause a gradual decrease in total crystallinity and degradation of the starch molecule.

Particle size of germinated starch was found to be lower than that of non-germinated starch (Table 1). In order to confirm the re-

Table 2
Analysis of samples printed with starch from non-germinated (NG) and germinated maize (G) and their blends

Std./batch name	*K/S*[a]	% Decrease in *K/S*	Bending length (cm)[b]	Washing fastness		Crocking fastness	
				Change in shade	Staining	Dry	Wet
Dye: Novatic Navy Blue RA (λ_{max} = 550 nm)							
100% N.G	3.74 ± 0.01	–	1.30 ± 2.72	4–5	5	5	5
30G: 70N.G	3.62 ± 0.02	3.21	1.25 ± 2.83	4–5	5	5	4–5
50G: 50N.G	3.56 ± 0.01	4.81	1.21 ± 3.60	4–5	5	5	4–5
70G: 30N.G	3.51 ± 0.03	6.15	1.20 ± 0.00	4–5	5	4–5	4
100% G	3.49 ± 0.25	6.68	1.19 ± 3.66	4–5	5	5	4
Dye: Novatic Red 3B (λ_{max} = 520 nm)							
100% N.G	3.80 ± 0.22	–	1.36 ± 3.20	4–5	5	5	5
30G: 70N.G	3.71 ± 0.08	2.37	1.31 ± 3.33	4–5	5	5	4–5
50G: 50N.G.	3.55 ± 0.08	6.58	1.27 ± 4.01	4–5	5	5	4–5
70G: 30N.G	3.40 ± 0.43	10.53	1.26 ± 3.46	4–5	5	4–5	4
100% G	3.30 ± 0.21	13.16	1.24 ± 3.51	4–5	5	5	4

[a] Values are means ± %SD of three determinations.
[b] Values are means ± %SD of four determinations.

sults, the test was repeated thrice and in all the cases it showed a similar trend. This may be attributed to 'pitting' of the granule caused due to the attack of enzymes released during germination which reduce the particle size.

It is evident that the Peak, Onset and Endset temperatures for gelatinization for both the germinated and non-germinated starches are very much close to each other (Table 1). On further analysis there is a single peak for non-germinated starch and a doublet found for germinated starch, which may correspond to gelatinization of degraded starch and second for non-degraded starch. The peak area for non-germinated starch is more than that for germinated starch. This states that the amount of heat required to gelatinize non-germinated starch is about 1.55 times that of germinated starch. Germination has thus lowered the molecular weight and degree of polymerisation of starch by forming lower molecular weight compounds

The iodine binding capacity of germinated starch was found to be 3.34 times that of non-germinated starch (Table 1). Helical amylose entraps iodine as an inclusion compounds and the amount of iodine binding is a property of amylose giving a deep blue complex (Daniel et al., 1997). The absorption of germinated starch at 620 nm in presence of iodine solution is about 3.34 times than that of non-germinated starch, which implies that the amylose content of the starch increased after germination. This is also supported in the literature that states that during germination the proportion of amylose in the starch increases and the composition of the amylopectin fractions alter and the average length of the polymer is reduced (Hough, Briggs, & Stevens, 1971).

3.2. Analysis of fabrics printed with vat dyes using starch extracted from germinated and non-germinated maize grains

K/S and L^*, a^*, b^* values for vat dye printed samples using germinated and non-germinated starches are summarized in Table 2. *K/S* values in case of germinated starch were lower than those for the starch from non-germinated maize. Blends of these two thickener pastes gave *K/S* values which increased with the increase in the proportion of starch from non-germinated or sound grains. The results show similar trend for both anthraquinone (Novatic Red 3B) and indigoid (Novatic Navy Blue RA) vat dyes. This may be attributed to higher swelling power, more clarity and relatively higher viscosity (10% solid content) of non-germinated maize starch as against that of germinated starch. The degradation of starch, to lower molecular weight compounds, on germination increases its solubility and washability, facilitating colour removal during washing and soaping.

Stiffness of prints which is determined by measuring the bending length of printed fabrics (Table 2) showed the presence of the starch in both the printed samples. It was observed that bending length of samples printed with starch from non-germinated maize was higher than that of germinated starch, which may be related to higher amount of starch left on the fabric contributing to the stiffness of the samples. This is mainly due to higher solubility of the germinated starch than that of sound starch.

Printed fabrics when tested for assessment of the washing fastness (IS0-III) showed similar fastness ratings for both the germinated and non-germinated starch printed samples and even for their binary blends (Table 2). Vat dyes are known for having all-round fastness properties (Shenai, 1990). The use of germinated maize starch had no effect on fastness properties. Analysis for dry and wet crocking fastness showed that although dry crocking fastness ratings for germinated and non-germinated starch printed samples were excellent and similar, in case of the wet crocking fastness, the germinated starch printed samples showed slightly but distinctly lower (1/2 grade) crocking fastness. This may be attributed to removal of the dye along with more soluble germinated starch during wet crocking.

4. Conclusions

Use of germinated starch against non-germinated can reduce the cost of the final print. Wash fastness and dry crocking fastness remain unaffected irrespective of the type of starch used, although 1/2 grade lowering of wet crocking fastness was observed in case of germinated maize starch. The results clearly indicate that there exists a very good potential for application of the germinated maize starch which is obtained from non-edible maize, as a full or partial substitute for non-germinated or sound maize starch.

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