Carbohydrate Polymers 76 (2009) 460–463

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Use of *Amaranthus* (Rajgeera) starch vis-à-vis wheat starch in printing of vat dyes

M.D. Teli [a,*], Pankaj Rohera [a], Javed Sheikh [a], Rekha Singhal [b]

[a] Department of Fibres and Textile Processing Technology, University Institute of Chemical Technology, Nathalal Parikh Marg, Matunga (E), Mumbai-400019, India
[b] Department of Foods and Fermentation Technology, University Institute of Chemical Technology, Matunga (E), Mumbai-400019, India

ARTICLE INFO

Article history:
Received 22 May 2008
Accepted 10 November 2008
Available online 18 November 2008

Keywords:
Amaranthus
Wheat starch
Vat dye printing

ABSTRACT

Wheat is the staple food and is widely consumed. *Amaranthus* (Rajgeera) has been proposed as an alternative to be used as a thickener in textile printing of vat dyes. Extraction of starch from *Amaranthus* (Rajgeera) and wheat was done by alkali steeping. In this paper detailed physical and chemical analysis of *Amaranthus* and wheat starch has been reported. Analysis of both the starches was done by measuring swelling power, paste clarity, crystallinity of starch using X-Ray diffraction and iodine binding. Printing of vat dye on 100% cotton fabric was done using *Amaranthus* (Rajgeera) and wheat starch pastes. The prints were then analysed by measuring *K*/*S* and L^*, a^*, b^* values by reflectance method, bending length, washing & rubbing fastness etc. Results suggest that *Amaranthus* (Rajgeera) can be used to substitute wheat starch in textile printing.

1. Introduction

Many of the under utilized crop species previously neglected by researchers and policy makers are now receiving greater attention. *Amaranthus* is one such crop species gaining recognition having lysine rich high protein grains with amino acid, vitamin and mineral composition similar to or even better than those of common cereals. These dual purpose plants supply not only nutrition grains but also tasty, leafy vegetables consumed all over the world as both human food and animal feed. About 50–60 members of the *Amaranthus* genus, spread throughout the world as pot-herbs, ornamentals, vegetables, grains and dye plants, grow under a wide range of climatic conditions with yields comparable to those of cereals.

Solubility of starch is one of the physicochemical properties which is influenced by the relative proportion of linear and branched fractions of the starch. As seen, *Amaranthus paniculatas* which comprises of 100% amylopectin has the maximum solubility as compared to that for starches from *A. polygamous* and *A. gracills*, which contain some amount of amylase (Rekha Singhal, M.Sc.Tech. thesis, University of Mumbai, TH1587, 1986).

Since this crop is underutilized and also available at cheaper rate, one could use the same for making thickeners for textile printing to substitute maize starch (Teli, Shanbag, Kulkarni, & Singhal, 1996). Suitability of *Amaranthus* (Rajgeera) starch to substitute conventional thickeners in printing of Indigosol (Solubilised Vat) and vat dyes on cotton has been reported from our laboratory (Teli et al., 1996). In order to investigate its applicability on shop floor, study with respect to rheological properties became quite important. An attempt was made by researchers to compare the rheological properties of the conventional thickener like Maize starch used in printing of Indigosol (Solubilised Vat) and vat dyes on cotton with those of *A. paniculates* (Rajgeera) starch (Teli, Shanbag, Dhande, & Singhal, 2007). The storage stability or shelf life of thickener paste becomes especially important since in textile printing the surplus colour paste is stored for a week or two depending upon the printing orders. Hence the storage stability of maize starch and Amarantus (Rajgeera) starch thickeners has been reported (Teli, Shanbag, Dhande, & Singhal, 2006).

Since wheat is a staple food and is widely consumed, in this work an attempt is made to replace wheat starch by the starch from *Amaranthus* as a thickener for printing.

2. Materials and methods

2.1. Materials

Wheat starch was purchased from the market. *Amaranthus* 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 & P.P.I–70. The GSM of fabric used was 123.5 gm/m^2. Nylon bolting cloth of 200 mesh was used for the extraction of starch. All chemicals used were of laboratory grade. Vat dyes used were supplied by Atul (P) Ltd, India.

2.2. Equipment

Spectraflash SF300 was used to measure the *K*/*S* & L^*, a^*, b^* values of starch and printed samples. X-Ray Diffractometer (XRD-

* Corresponding author. Tel.: +91 022 24145616x486; fax: +91 022 24145614.
E-mail address: textileudct@yahoo.com (M.D. Teli).

0144-8617/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2008.11.007

6000) from Shimadzu was used to determine changes occurring in amorphous and crystalline structure of the starch granules.

2.3. Methods

2.3.1. Extraction of starch

Extraction of starch from *Amaranthus* (Rajgeera) was done by alkali steeping method (Yanez & Walker, 1986). The cereals were obtained from local market and 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.

2.3.2. Analysis of starch

Analysis of *Amaranthus* (Rajgeera) and wheat starch was done for comparison.

2.3.2.1. Estimation of colour of starch powders. The starch powder samples were taken in a small plastic sacks and were 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.

2.3.2.2. 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.

2.3.2.3. Paste clarity. Measurement of paste clarity was carried out by method of Craig, Maningat, Seib, and Hoseney (1989). About 250 mg of starch sample 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 in UV-1201, spectrophotometer (Shimadzu, Japan).

2.3.2.4. X-Ray diffraction analysis. X-Ray Diffraction analysis was carried out to determine the changes in crystallinity of *Amaranthus* (Rajgeera) and wheat starch using XRD 6000, (Shimadzu, Japan) at an angular(2Φ) range of 4°–32°.20′. 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.

2.3.2.5. 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 min in boiling water to gelatinise the starch. After cooling the gelatinized sample to room temperature, it was transferred to 100 ml volumetric flask; then the total volume was made to 100 ml by adding distilled water. The starch solution (5 ml) was pippeted 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 UV-1201 spectrophotometer (Shimadzu, Japan).

2.3.3. Printing

Printing of vat dyes was done by pre-reduction method (Potash Rongalite Method). About 10% of *Amaranthus* (Rajgeera) thickener paste was prepared by taking 10 parts of thickener and 90 parts of water on weight basis. Thickener was first pasted with small amount of water followed by adding the remaining amount. The contents were then mixed and heated at boil for 30 min under continuous stirring. Similar procedure was used for preparing 10% wheat starch.

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

Vat dye	2parts
Glycerine + urea (1:1)	5parts
Solution salt B	3parts
Potassium carbonate	12parts
Sodium hydrosulphite	4parts
Thickener paste	55parts

The contents were then warmed and kept for 30 min at 60 °C. After cooling, 16 parts of Rongalite C and then thickener paste were 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 (Auxipon NP) soap in hot water followed by washing with water and then dried in air (Teli et al., 1996).

2.3.4. Analysis of printed fabrics

2.3.4.1. Colour value by reflectance method. The printed samples were evaluated for the depth of colour by reflectance method. The absorbance of the printed samples was measured on "Pye Unicam SP 8-400 UV/Vis. Spectrophotometer" equipped with reflectance accessories. The Kubelka Munk's function, *K*/*S* values were determined using the expression:-

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

where *R* is the reflectance at complete opacity, *K* is the Absorption cefficient & *S* is the Scattering coefficient.

2.3.4.2. Bending length. The bending length of printed samples was determined using a Shirley stiffness tester (Booth, 1983). To carry out the test, printed fabric strip of 6 × 1 in. was cut and then both the template and specimen were transferred to the platform with one end coinciding with the mark 'O' 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 the bending length could be directly read from the scale opposite to 'O' mark on the platform.

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

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

3. Results and discussion

3.1. Comparision of characteristics of Amrnthus (Rajgeera) and wheat starch

K/S values obtained for wheat starch purchased from the market were lower than that of *Amaranthus* (Rajgeera) (Table 1). Wheat starch appeared whiter as it was bleached during the manufacturing; however the difference in the two was not so significant to affect the final colour value of the prints.

Results in Table 1 indicate that swelling power of wheat starch is 2.8 times that of *Amaranthus* (Rajgeera) starch. This may be attributed to the fact that upon cooking pastes of ordinary wheat starch, it soon becomes opaque and sets to become gel like at concentrations greater than 4%; while waxy starches such as *Amaranthus* (Rajgeera) even at concentration of 20%, do not increase a great deal in viscosity and remain consistent and gummy for days (Baba, Arai, Yamanmoto, & Itoh, 1982). This behaviour is attributed to the presence of amylose (about 25%), the straight chain polysaccharide in wheat starch which is almost absent in the case of *Amaranthus* (Rajgeera) starch. The straight chain molecules of amylose add to increase in radius of gyration on hydration and their contribution towards thickening of the pastes becomes remarkable (Teli et al., 2007).

To determine the paste clarity of both the starches (Table 1), transmittance (%T) was measured. Transmittance value for *Amaranthus* starch was 1.1 times that of wheat starch. This was so because *Amaranthus* (Rajgeera) consists of approximately 98% of amylopectin which has higher solubility and thereby gives a clear stable solution (Miles, 2003) or its clarity of the paste is better than that for wheat starch paste.

X-Ray Diffraction analysis was done to determine the amorphous and crystalline structure of both the starches and Crystallinity (%) was calculated by using reported formula. The crystallinity of *Amaranthus* (Rajgeera) starch was 45.80% and that of wheat starch was 30.48% (Table 1). Higher crystallinity of *Amaranthus* (Rajgeera) is because of amylopectin (98%) being its major constituent and hence higher is the orientation. For wheat starch the presence of amylose along with amylopectin reduces the orientation and hence reduces the crystallinity too.

The iodine binding capacity of wheat starch was found to be 3.33 times that of *Amaranthus* (Rajgeera) starch (Table 1). Starches normally contain two polysaccharide components, amylose which consists of a straight (unbranched) chain polymer molecules which has a strong affinity for iodine with which it gives a deep blue complex and amylopectin which consists of a branched chain having little affinity for iodine with which it gives red colouration. The affinity for iodine varies inversely with degree of branching and directly with the length of chain. Rajgeera consists of about 98% amylopectin and hence gives reddish yellow colour, where as wheat starch contains 22% amylose which imparts blue colour and hence higher level of absorption.

Table 1
Analysis of wheat starch and starch extracted from *Amaranthus* (Rajgeera).

Characteristics of starch		*Amaranthus* (Rajgeera)	Wheat starch
Colour values of starch powder	*K/S*	0.0058	0.0017
	L^*	90.27	93.59
	a^*	−0.06	2.67
	b^*	0.59	0.37
Swelling power (g/g)		2.455	6.856
Transmittance (%)		1.945	1.752
Average Crystallinity (%)		45.08	30.48
Absorbence% (with iodine)		0.031	0.1035

Table 2
Analysis of samples printed with starch from *Amaranthus* (Rajgeera) and wheat using vat dye: Novatic Rubine 6BS (Λmax 540 nm).

Std./Batch name	% Shade of dye (cm)	*K/S*	Bending Length	Washing fastness		Rubbing fastness	
				Change in shade	Staining	Dry	Wet
Amaranthus	2	1.5081	1.14	4–5	5	5	5
Wheat	2	1.6609	1.23	4–5	5	5	5
Amaranthus	4	1.8131	1.18	4–5	5	5	5
Wheat	4	1.9523	1.3	4–5	5	5	5

3.2. Analysis of samples printed with starch from Amaranthus (Rajgeera) and wheat starch using Novatic Rubine 6BS (2% and 4%)

Rajgeera and wheat starch printed samples were then evaluated for their *K/S* values. Results in Table 2 indicate that *K/S* values for samples printed using *Amaranthus* (Rajgeera) starch were slightly lower than those for the samples obtained using wheat starch. This is because of higher transfer of colour from thickener film to the fabric in case of wheat starch, having higher swelling power and lower crystallinity as compared to that of *Amaranthus* (Rajgeera) starch. The higher content of amylopectin present in *Amaranthus* (Rajgeera) starch which has high solubility in water facilitates removal of dye during washing off process and other after treatments further leading to reduction in the *K/S* values.

Stiffness of printed samples was determined by measuring the bending length. Results in Table 2 indicate that bending length of samples printed using *Amaranthus* starch was lower than that of samples obtained using wheat starch. This may be due to higher amount of residual starch left on the fabric after printing in case of samples obtained using wheat starch. *Amaranthus* (Rajgeera) starch contains about 98% of amylopectin having higher solubility and hence gets easily washed off, thus giving relatively softer prints as compared to wheat starch, as reflected in the lower values of bending length.

Results from Table 2 indicate that the use of wheat starch or *Amaranthus* (Rajgeera) has no impact on the final wash fastness and rubbing fastness properties of the printed fabric.

4. Conclusion

Amaranthus (Rajgeera) which is an underutilized crop can be effectively used in textile printing, by extracting starch from it. This will decrease the load on consumption of wheat starch as thickener for printing in industrial application and will increase the availability of the same as staple food.

References

Baba, T., Arai, Y., Yamanmoto, T., & Itoh, T. (1982). Some structural features of amylomaize starch. *Phytochemistry, 21*(9), 2291–2296.
Booth, J. E. (1983). *Principles of textile testing*. London: Butterworths.
Craig, S. A., Maningat, C. C., Seib, P. A., & Hoseney, R. C. (1989). Starch paste clarity. *Cereal Chemistry, 66*, 173–182.
Juliano, B. O. (1971). A simplified assay for milled-rice amylase. *Cereal Science Today, 16*, 334–340.
Miles, W. C. (2003). *Textile printing*. Bradford: Society of Dyers and Colourists.

Subramanian, V., Hoseney, R. C., & Bramel-Cox, P. (1994). Shear thinning properties of sorghum and corn starches. *Cereal Chemistry, 71*, 272–275.

Teli, M. D., Shanbag, V., Dhande, S. S., & Singhal, R. S. (2006). Storage stability of *Amaranthus paniculates* (Rajgeera) starch thickener in textile printing. *Journal of Textile Association, 67*(3), 119–123.

Teli, M. D., Shanbag, V., Dhande, S. S., & Singhal, R. S. (2007). Rheological properties of *Amaranthus paniculates* (Rajgeera) starch vis-à-vis Maize starch. *Carbohydrate Polymers, 69*(1), 116–122.

Teli, M. D., Shanbag, V., Kulkarni, P. R., & Singhal, R. S. (1996). *Amaranthus paniculates* (Rajgeera) starch as a thickener in the printing of textiles. *Carbohydrate Polymers, 31*(11), 119–122.

Trotmann, E. R. (1984). *Dyeing and chemical technology of textile fibres*. England: Charles Griffin and Company Ltd..

Yanez, G. A., & Walker, C. E. (1986). Effect of tempering parameters on extraction and ash of prosomillet flours and partial characterization of proso starch. *Cereal Chemistry, 63*, 164–167.