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Rheological properties of *Amaranthus paniculates* (Rajgeera) starch vis-à-vis Maize starch

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Abstract

Amaranthus paniculates (Rajgeera) is abundantly available at a lower cost and hence the attempt was made in our earlier work to study the suitability of *Amaranthus paniculates* (Rajgeera) starch in substituting conventional thickener, Maize starch used in the printing of Indigosol (solubilised Vat) and Vat dyes on cotton. Having observed the promising performance of Rajgeera starch, it is important to know its rheological behaviour. Therefore, in the present work the effect of solid contents of thickener and the shearing time on the viscosity of paste over a wide range of shear rates has been studied. The shear thinning index (STI) and the values of viscosity at 1 rpm shear rate (i.e., *K* value) were used to compare the behaviour of thickeners. Keeping in mind the applicability of these two thickeners in the printing of Indigosol (solubilised Vat) and Vat dyes on cotton, their rheological properties were compared, which throw light on the print performance.

Keywords: Amaranth (Rajgeera) starch; Rheological properties; Maize starch

1. Introduction

Textile printing is a complex process as the printing pastes, besides colorants and thickeners consists of special chemicals and processing media which can influence the rheological behaviour of the pastes and consequently their capability of penetrating into the fabric. Therefore, it is very important to understand the effect of shear rate on deformation/flow behaviour of thickening agents. Rheology has been gaining more and more importance in the quality optimization and control in the textile printing process (Bandyopadhyay & Bhattacharya, 1998; Sostar, 1997). The rheology of the paste affects the amount of the paste applied as well as the spread of paste on the surface and into the structure of textile material. The viscosity of most the thickener pastes does not remain constant, but decreases with shear rate. Such substances are called non-Newtonian, pseudoplastic, or shear thinning and the viscosity values of pseudoplastic materials are called ''apparent'' viscosities, meaning that they correspond to a given shear rate. Since pseudoplastic material has as many apparent viscosities as there are shear rates, only a viscosity profile can thus display the wide range of attainable viscosities. Hence, to characterize a non-Newtonian fluid, it is necessary to make shear stress-shear rate determinations at many points. The pseudoplastic nature of printing pastes can best be studied by the Ostwald-de-wade equation, which is also called a 'power law'

$$\zeta = KD^n,$$

where ζ is shear stress, D is shear rate, K is constant, n is power, having value between 0 and 1 (Teli & Vyas,

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1990). Researchers have studied influence of electrolytes and investigated some of the relationships between the rheological behaviour of printing pastes and the performance of resulting prints (Dang & Prasil, 2001). The influence of temperature, concentration of dyes and thickeners on the rheological behaviour of printing pastes both experimentally and mathematically has also been studied (Prasil & Dang, 1996). However, so far no detailed identification of rheological properties of printing thickeners and printing pastes has been made during the process of textile printing (Sostar, 1997).

While exploring the potential of *Amaranth* starch in the printing of Indigosol (Solubilised Vat) and Vat dyes, 15–25% of decrease in the depth of print (K/S values) in the case of Indigosol dyes and 7% of decrease in the case of Vat dyes was observed when the *Amaranth* starch substituted the maize starch fully in the printing of these dyes. The performance properties such as wash fastness and rubbing fastness of the prints obtained using *Amaranth* starch were quite comparable with those of the prints obtained using conventional thickener, i.e., maize starch. However, the softness of the print was distinctly better as reflected in the lower values of bending length in the case of *Amaranth* starch. It has also been reported that if the partial substitution of the maize starch is done by the *Amaranth* starch, the decrease in the depth of the print could be reduced and at the same time it was possible to improve the softness of the prints. Hence, it was very clear that 50:50 composition of the blend paste would give better retention of the depth while giving improved performance properties. This work has been already reported from this laboratory which showed promising performance of *Amaranthus paniculates* (Rajgeera) starch vis-à-vis Maize starch (Teli, Shanbag, Kulkarni, & Singhal, 1996).

In order to investigate its applicability on shop floor, study with respect to rheological properties became quite important. In present work, thus the effect of solid content of thickeners and shearing time on the viscosity over a wide range of shear rates is studied. An attempt is made 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, which is abundantly available at much lower cost, in order to understand the potential of *A. paniculates* (Rajgeera) starch in substituting the conventional thickener-Maize starch.

2. Materials and methods

2.1. Materials

2.1.1. Thickeners

Maize starch was obtained from local market and used as a thickener. Amaranth seeds were obtained from the local market and grounded to powder flour. The *A. paniculates* (Rajgeera) starch was isolated from grain flour by alkali steeping method (Yanez & Walker, 1986), wherein Rajgeera flour was extracted with 0.25% NaOH solution in 1:5 ratio, till it became free of protein, as indicated by Biuret reagent. The extracted Rajgeera flour was washed thoroughly till it was free of NaOH. Further, it was ground in a warring blender and the slurry was passed through a 200 mesh bolting cloth and squeezed to remove crude starch. It was then centrifuged at 6000 rpm for 15 min and sludge was allowed to settle. Sludge thus obtained was dried at room temperature for overnight and then at 50 °C till it was dried completely. Finally, it was ground to 60 mesh and stored in an air tight container as Rajgeera starch. This starch was used as thickener in comparison with Maize starch.

2.2. Methods

2.2.1. Preparation of thickener pastes

2.2.1.1. Maize starch paste. The various solid content used were 8.0%, 9.0%, 10%, 11% and 12%. The thickener paste for 10% solid content was prepared as follows. Maize starch powder, 10 parts; water, 90 parts. The dry powder of Maize starch was pasted with small amount of water followed by addition of the remaining amount of water. This milky dispersion was heated to boil with continuous stirring for 30 min. The heating was stopped when the dispersion got converted into a translucent paste. The contents were then cooled with continuous stirring.

2.2.1.2. Rajgeera starch paste. The various solid content used were 4.0%, 5.0%, 6.0%, 7.0%, 8.0%, 9.0% and 10%. The procedure used remained similar to that of preparation of Maize starch paste.

2.2.2. Measurement of viscosity of thickener pastes

The various factors affecting the viscosity of these thickener pastes were studied, namely; shear rate, solid content of thickener, time of shearing (shear sensitivity), etc. using a "Brookfield Syncrolectric Viscometer (Model RV)". The thickener pastes were prepared at different solid contents and viscosity was measured by changing the shear rate at each concentration of thickener. The readings were taken in triplicate and its mean is reported. The standard deviation in general was in the range of ±0.25 to ±2.47. Shear sensitivity was measured by shearing the thickener pastes over a period of time continuously.

3. Results and discussion

3.1. Rheology of A. paniculates (Rajgeera) starch paste

Having explored the potential of *Amaranth* starch in print performance (Teli et al., 1996), it was thought appropriate to study rheology of the pastes at varying shear rates and solid contents. The results in Table 1 indicate that, with increase in the solid content the viscosity of the thickener increased. When solid content was increased from 4% to 6%, viscosity increased gradually and between 6% and

Table 1
Effect of solid content on viscosity of *Amaranth* starch at different shear rates

RPM	Viscosity at different solid content of thickener (poise)						
	4%	5%	6%	7%	8%	9%	10%
0.5	120	130	160	360	400	720	1200
1.0	75	120	120	220	280	460	600
2.5	55	64	64	112	160	240	328
5.0	29.5	32	40	72	104	148	244
10.0	8	12	28	48	64	96	152
20.0	6	12	18	30	42	62	102
50.0	4	6.4	10.8	16	22.5	36.8	55.8
100.0	2.4	4	7.2	10.8	15.6	25.4	35.4

8% solid content, the increase in the viscosity was enhanced. Beyond 8% solid content, the increase in viscosity was quite rapid. Such an increase in viscosity with increase in solid content was hyperbolic type and it is peculiar with most of natural thickeners. The data also indicate that, with an increase in shear rate, the viscosity reduced drastically and such a reduction in viscosity with an increase in shear rate seemed to be leveled off in the range of 80–100 rpm. This property of a thickener is termed as pseudoplastic behaviour and most of the thickeners do behave in this fashion. When automatic flat-bed screen printing or rotary screen printing machine is used in textile printing, the thickener paste thins down due to the shearing action of the squeegee with thickener and the printing operation is carried out smoothly facilitating the transfer of printing paste through the screens to the fabric. However, during the stoppage of the machine when the shear-rate is reduced the viscosity of the paste is more or less regained making the paste difficult to penetrate through the screen on to the fabric and thus it protects the fabric from undue staining. Hence, the pseudoplastic behaviour of the thickener is best used in the printing operation.

In order to see the effect of shearing time on viscosity of the *Amaranth* starch paste, experiments were carried out on paste with 8% and 9% solid content and the results are given in Tables 2 and 3, respectively.

It is not sufficient to know only the influence of shearing rate on the thickener paste, but it is also necessary to study the extent of such an influence when shearing is continued at a fixed rate. From this point of view, the results when analysed indicated that, although from the start there was a gradual decrease in viscosity, but after shearing time of about 3 min the viscosity of the paste at any given rpm remained unaltered. When at a particular shearing rate, the paste is sheared the polymer chain molecules are increasingly displaced from one plane to the other breaking

Table 2
Effect of shearing time on viscosity of *Amaranth* starch at different shear rates for 8% solid content

RPM	Viscosity at different shearing time (poise)									
	0.5 min	1.0 min	1.5 min	3.0 min	4.0 min	5.0 min	8.0 min	10.0 min	12.0 min	15.0 min
1.0	330	320	320	320	320	320	320	320	320	320
2.5	184	172	168	164	164	164	164	164	164	164
5.0	104	106	104	104	102	102	102	100	100	100
10.0	71	68	66	63	63	62	62	62	62	62
20.0	46	43.5	42	40.5	40.5	40.5	40	40	40	40
50.0	26	25.2	24.4	24.6	24.6	24.4	24.4	24.4	24.4	24.4
100.0	17.4	17.3	17.6	17.2	17	16.9	16.9	16.9	16.9	16.9

Table 3
Effect of shearing time on viscosity of *Amaranth* starch at different shear rates for 9% solid content

RPM	Viscosity at different shearing time (poise)									
	0.5 min	1.0 min	1.5 min	3.0 min	4.0 min	5.0 min	8.0 min	10.0 min	12.0 min	15.0 min
1.0	464	460.5	460	460.5	459.8	458.2	458	458	458	458
2.5	240.8	240	240	238.6	238.2	238	236	236	236	236
5.0	148	148	146	146	148	148.2	144	144	140	144
10.0	96	98	98	96.8	96.2	96	95.8	95	95	95
20.0	62	60	60.2	60.6	60	60	60	60	60	60
50.0	36.8	36.2	36	36	36	35.8	35.8	35.4	35.4	35.4
100.0	25.4	25.2	25	25	24.8	24.8	24.8	24.8	24.8	24.8

Table 4
Effect of solid content on viscosity of Maize starch at different shear rates

RPM	Viscosity at different solid content, (poise)				
	8%	9%	10%	11%	12%
0.5	300	1880	4880	6200	7800
1.0	170	1280	2800	3000	4000
2.5	80	496	1200	1440	1820
5.0	52	264	688	820	1000
10.0	31	153	320	470	220
20.0	20	90	116	285	305
50.0	12	52	72	140	152
100.0	8	30.8	36	81	90

the intermolecular H-bonding bringing down the viscosity. Such an operation when continued, it is overall shear rate and time for which shearing is being carried out, which finally governed such displacement of layers of the thickener and once the whole system gets properly stirred, the viscosity does not show any more influence of thixotrophic nature of the thickener. The higher solid content of 9% also showed the similar trend as observed in the earlier case, although the actual values of viscosity were higher than those when solid content was lower (8%).

3.2. Rheology of Maize starch thickener

Since the Maize starch was used as a reference thickener in printing during investigation of *Amaranth* (Rajgeera) starch (Teli et al., 1996), it was thought appropriate to study the rheology of Maize starch and compare the same with that of Amaranth (Rajgeera) starch. Hence similar set of experiment was repeated on Maize starch paste at varying solid content levels. The results in Table 4 indicates that, the trend observed was similar to that observed in case of *Amaranth* rajgeera starch paste. With increase in the solid content the viscosity of thickener increased hyperbolically. The higher the shearing rate, lower was the viscosity at a given solid content. It should be noted that the Maize starch paste showed very high viscosity as compared to *Amaranth* (Rajgeera) starch paste especially at higher solid contents. This may be possibly due to the presence of amylase (i.e., about 25%), the straight chain polysaccharide, which is almost absent in the case of *Amaranth* starch. The amylopectin being branched one, is almost 100% in case of *Amaranth*, whereas the content of the same is of the order of 75% in Maize starch. The straight chain molecules of amylase on hydration, having higher radius of gyration than that of amylopectin, contribute towards thickening quite significantly. Thus Maize starch is responsible for giving higher degree of viscosity values as compared to *Amaranth* starch. The viscosity of the Maize starch paste was found to be decreasing drastically when shear rate was increased up to 10 rpm. However, such a decrease became gradual and finally leveled off at around 80–100 rpm. This pseudoplastic behaviour was more or less similar to that of *Amaranth* (Rajgeera) starch paste.

In order to study the effect of shear-rate on lowering of viscosity in more detail log-viscosity versus log-shear rate relations were plotted for *Amaranth* (Rajgeera) and Maize starch (Figs. 1 and 2, respectively). The shear thinning index (STI) values calculated from graphs and the K values, i.e., viscosity at 1 rpm, which gives an indication of flow property (since more is the K value, less flowing will be the thickener paste) are given in Table 5. It is clear from this data that, with increase in the solid content, STI values initially increased and subsequently leveled off in case of Maize starch. In the case of *Amaranth* (Rajgeera) starch too, the similar trend was observed. It is clear from this data that, while Maize starch gave maximum value of STI at 10% solid content and subsequently leveled off, *Amaranth* (Rajgeera) starch gave the maximum value of STI at 8% solid content. It is for this reason these two solid content levels could be considered as optimum solid content levels for making their thickener paste for the printing. As far as the K values were concerned, it could be said that

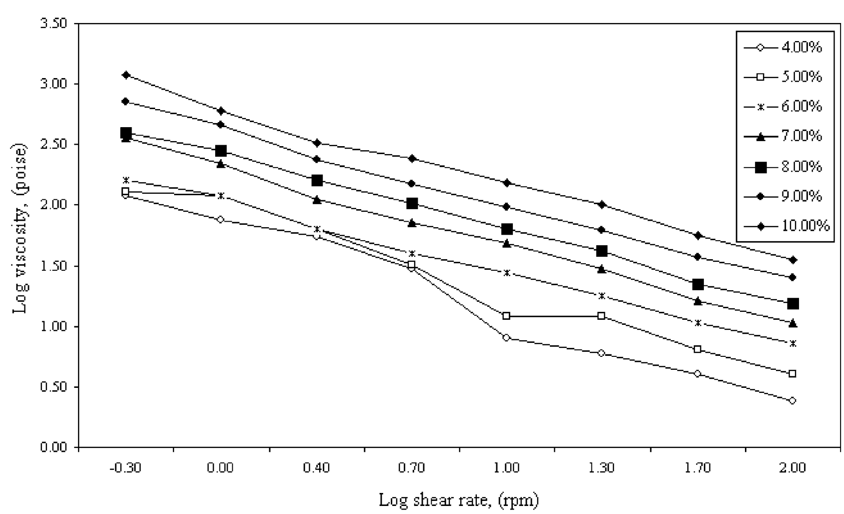

Fig. 1. Relation between viscosity and shear rate on log–log scale at various solid contents for *Amaranth* starch.

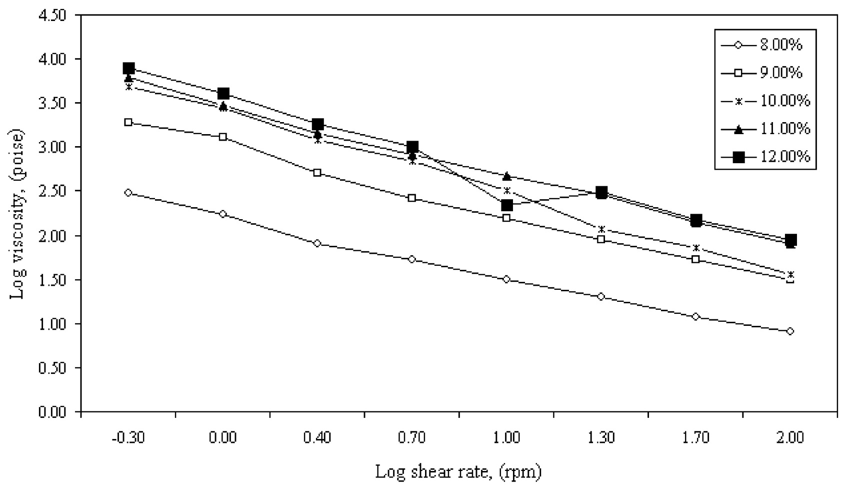

Fig. 2. Relation between viscosity and shear rate on log–log scale at various solid contents for Maize starch.

Table 5
Shear-thinning index (STI) and *K* values for Rajgeera and Maize thickeners at different solid contents

Solid content (%)	4.0	5.0	6.0	7.0	8.0	9.0	10.0	11.0	12.0
Amaranth starch									
STI	0.500	0.525	0.564	0.548	0.645	0.600	0.600	–	–
K value	25.750	85.250	91.200	151.360	257.000	346.700	478.600	–	–
Maize starch									
STI	–	–	–	–	0.645	0.772	0.803	0.806	0.806
K value	–	–	–	–	128.820	831.700	2238.700	2630.300	2884.000

at the identical solid content levels *K* values of Maize starch paste were higher than the same for *Amaranth* starch paste. Reverse would be the trend in case of flow properties. However, when the paste of 8% solid content level of *Amaranth* starch was compared with the paste of 10% solid content of Maize starch, it is clear that the shear-thinning index was much higher in case of Maize starch than that of *Amaranth* starch. The presence of straight chain and branched chain of amylase and amylopectin polymer chain molecules, respectively in Maize starch is responsible for such behaviour (Kerr, 1950; Wolfoarm, 1965). The flow properties were much low in the case of Maize starch paste as compared to that of *Amaranth* starch paste and in printing, this property is also of tremendous importance for printing of longer length of fabric or continuous printing. In this case too, it could be said that *Amaranth* starch paste had an edge over the Maize starch paste. Also the solid content level was lower in the case of *Amaranth* starch than that in the Maize starch paste. Since *Amaranth* starch is containing amylopectin fully (100%), the problem of retrogradation is also almost absent which is of concern in the case of Maize starch, originated due to presence of amylase to the tune of 20–25% (Blanshard, 1979; Kulkarni & Singhal, 1988; Modi & Kulkarni, 1976).

When effect of shearing time on the Maize starch paste was studied, the results obtained are given in Tables 6 and 7. The data indicate that up to about 4 min time of shearing, the viscosity of Maize starch paste was found to be decreasing at any given shear rate. However, beyond this span of time, it seemed to be leveled off. Such an influ-

Table 6
Effect of shearing time on viscosity of Maize starch at different shear rates for 9% solid content

RPM	Viscosity at different shearing time (poise)									
	0.5 min	1.0 min	1.5 min	2.0 min	2.5 min	3.0 min	3.5 min	4.0 min	5.0 min	10.0 min
1.0	1280	1160	1080	1050	1040	1040	1030	1020	1020	1020
2.5	496	480	472	468	464	456	456	456	452	452
5.0	264	258	256	256	254	254	254	254	254	254
10.0	153	151	150	149	148	147	147	147	146	146
20.0	90	86	86	86	84	83	83	83	82	80
50.0	52	48.8	48	48	47.2	46.4	46.4	46.4	45.6	45
100.0	30.8	30	29.2	28.8	28.6	28.4	28.6	28.4	28	28

Table 7
Effect of shearing time on viscosity of Maize starch at different shear rates for 10% solid content

RPM	Viscosity at different shearing time (poise)									
	0.5 min	1.0 min	1.5 min	2.0 min	2.5 min	3.0 min	3.5 min	4.0 min	5.0 min	10.0 min
1.0	2880	2320	2280	2240	2200	2180	2160	2160	2160	2160
2.5	1200	1120	1136	1120	1080	1072	1056	1048	1040	1040
5.0	688	664	656	624	608	600	600	600	600	600
10.0	320	308	300	280	272	264	264	260	260	260
20.0	136	126	120	120	118	128	127	126	124	124
50.0	72	71.2	68	62.4	61.6	60.8	60	59.2	58.4	58
100.0	37.2	37.2	38.4	38.0	37.2	36.8	36.6	36.0	36.0	36.0

ence, although is more apparent at low shear rate, at higher shear rate, is quite negligible.

This thixotropic nature is more or less common in most of the natural thickeners and the reason behind this has been already discussed.

3.3. Rheology of blend of Maize and Amaranth starch

In our earlier work it was found that the blend of the two thickener pastes also gave commendable results in terms of print performance (Teli et al., 1996). Hence, in the next set of experiments, the blends of thickener pastes using their optimum solid content levels were taken for study of viscosity. At varying shearing rates these viscosities were found out. It is apparent from the results given in Tables 8, 9 and Fig. 3 that, as the *Amaranth* starch (less viscous) substituted the Maize starch (more viscous), viscosity of the blend pastes was found to be decreasing as reflected in lowering of K values. It is obvious that its effect was also seen in flow property of the blend paste accordingly. STI values also decreased as more and more maize starch was substituted by Amaranth starch. In general, lower the viscosity, better was the flow property as was the case observed in case of *Amaranth* starch paste. However, these blend pastes also exhibited thinning down with increase in the shear rate. In other words, the trend observed was a gradual one causing changes in viscosity as a result of blending of the respective thickener pastes and it reflects good compatibility of the thickener pastes. This may be attributed to both the thickeners being starch based.

Amaranth starch paste used for printing giving lower value for optimum solid content (8%) as compared to Maize starch paste (10%) clearly indicates as to why the prints in case of the former are softer (less bending length) than that in case of latter as reported earlier (Teli et al., 1996). Also the flow properties in case of *Amaranth* starch are better than that of Maize starch paste, and thus it is natural that the former thickener paste will print longer length fabric as compared to the latter one. In other words, the rheological behaviour seemed to be in conformity with the performance of the prints obtained using individual

Table 8
Effect of composition on viscosity of blend of Maize starch (10% solid content) and *Amaranth* starch (8% solid content) at different shearing rates

RPM	Viscosity at different blend composition, Maize:*Amaranth* (poise).				
	100:00	80:20	50:50	20:80	00:100
0.5	4400	4000	3400	900	660
1.0	2500	2400	2000	500	370
2.5	1320	1040	960	280	188
5.0	840	660	560	160	114
10.0	480	420	320	100	71
20.0	300	275	185	65	42
50.0	154	136	92	35	23.2
100.0	90	86	57.5	23.5	15.1

Table 9
Shear-thinning index (STI) and K values for various blend compositions of Maize starch (10% solid content) and Amaranth starch (8% solid content)

Blend compositions (Maize:*Amaranth*)	100:00	80:20	50:50	20:80	00:100
STI	0.800	0.750	0.600	0.604	0.640
K value	2238.300	2170.720	1940.085	490.180	257.050

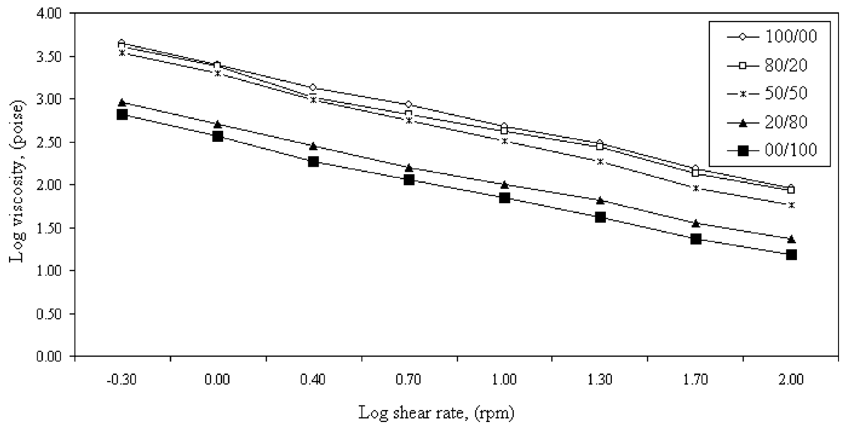

Fig. 3. Relation between viscosity and shear rate on log–log scale at various blend compositions of Maize starch (10% solid content) and *Amaranth* starch (8% solid content).

thickener pastes and their blends, as reported earlier (Teli et al., 1996).

4. Conclusion

The rheological properties of Amaranth and Maize starch indicated that, both the pastes exhibited pseudoplastic and thixotropic behaviour. However, Maize starch paste showed higher viscosity as compared to *Amaranth* starch paste at an identical solid content. The STI and K values for Maize starch paste were found to be higher than those for Amaranth starch paste. In other words, flow properties of Amaranth starch paste were better than that of Maize starch paste. Thus it could be said that, rheological properties of the two thickeners revealed that *Amaranth* starch has very good potential to substitute Maize starch in textile printing.

References

Bandyopadhyay, B. N., & Bhattacharya, N. (1998). Carboxymethyl starch as an alternative to alginate for reactive printing. *Colourage, 45(annual)*, 141–151.

Blanshard, J. M. V. (1979). *Polysaccharides in foods*. London: Butterworth, pp. 127–132.

Dang, T. L., Prasil, M. (2001). Rheological behaviour of reactive printing pastes and its effects on print parameters, Texsc' 98, 3, 508–511, vide WTA (2001), 3660.

Kerr, R. W. (1950). *Chemistry of industrial starch*. New York: Academic Press, 167 pp.

Kulkarni, P. R., & Singhal, R. S. (1988). Composition of the seeds of some *Amaranthus* species. *Journal of Science of Food Agriculture, 42*, 325–331.

Modi, J. D., & Kulkarni, P. R. (1976). New starches: The properties of the starch from *Amaranthus paniculates* linn. *Acta Alimenta, 5*(4), 399–402.

Prasil, M., & Dang, T. L. (1996). Rheological behaviour of disperse dye printing pastes. *Vladkha a Textl, 3*(3), 89–91.

Sostar, S. (1997). Rheologic properties of printing pastes-bases of rheology-I. *Texstilec, 40*(3–4), 59–65.

Teli, M. D., & Vyas, U. V. (1990). Rheological behaviour of textile thickeners. *American Dyestuff Reporter, 79*(2), 15–18.

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

Wolfoarm, M. L. (1965). In R. L. Whistler & P. F. Eugene (Eds.), *Starch: chemistry and technology* (pp. 257). New York and London: Academic Press.

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