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Rheology of Broken Rice-Foxtail Millet-Maize Flour Blends Related to Extrusion Cooking

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Rheological properties of the various flours from the broken rice, foxtail millet and maize used during extrusion conditions were investigated for pasting properties and dynamic oscillation using Rheometer. Results pointed out that each of the different flour might be utilized for specific applications in food processing. In addition, the functional properties of individual flours were measured. The swelling power of broken rice flour showed the highest values, indicated that the viscoelastic properties of pastes were dependent on the swelled starch–protein complex granules and the formation of new cross-links in the network. All formulation flours exhibited variable pasting behavior, among different temperatures and formulations at 90°C and 20:60:20 had the highest peak viscosity 6741 MPa.s and final viscosity 6842 MPa.s and was found to be more effective than other temperature and formulation combinations. Viscosity decreased with the increase of temperature and formulation combinations. The storage modulus was invariably higher than loss modulus at all stages during heating, holding and cooling of the sample, showing that the paste has a tendency to behave like weak gel. G´ was the most primary dynamic rheological parameter that reflected rheological properties, G´ represented the elastic properties of rice starch paste.

Keywords: Rheology, Viscoelasticity, Broken rice, Functional properties.

Rice (*Oryza sativa*) is one of the major cereal crops worldwide and it is consumed principally as a grain obtained from specific varieties. The understanding of their rheological behavior is very important for optimizing industrial applications and allowing consumer to select appropriate types for different culinary recipes (Correa *et al.,* 2013). In the food industry, starch based products like cereal flours are cooked during extrusion processes. Therefore, the knowledge of their viscous behaviour is required to process them because the choice of the optimal processing conditions and the quality of end products depends on the rheological properties of the material.

During extrusion, protein structures are disrupted and altered under high shear, pressure, and temperature. Protein solubility decreases and cross-linking reactions occur possibly due to some covalent bonds formed at high temperature as well as protein denaturation and formation of complexes between starch and lipids and between protein and lipids. Among all flour components, starch plays a key role. The extrusion of starchy foods results in gelatinization, partial or complete destruction of the crystalline structure and molecular fragmentation of starch polymers (Perez *et al.,* 2008).

The rheological properties of extruded blend dispersions, which influence the breakfast porridge-making process, are essential for producing high-quality products. Recent studies concentrated on extrusion cooking processing effects for creating new products and evaluation of physical and chemical properties. However, there are very few literatures investigating thoroughly on dynamic rheological properties of extruded product pastes.

The objective of this work was to examine the effects of temperature (90-110°C) and formulation combinations [broken rice flour: foxtail millet: maize flour, 10:80:10 (Mix 1); 20:60:20 (Mix 2); 30:40:30 (Mix 3); 10:60:30 (Mix 4) and 30:60:10 (Mix 5)] on the rheological properties of flours used during the extrusion study (employing a dynamic rheometer). The purpose of this study was to investigate the use of temperatures and formulation combinations used during extrusion cooking on flours and to provide basic information for the further application of broken rice, millets and maize in food extrusion industry.

Materials and Methods

Raw materials

Raw materials, broken rice IR-20 (procured from modern rice mill, Kangayam, Tirupur District, Tamil Nadu), foxtail millet Co (Te)7 (purchased from Department of Millets, Tamil Nadu Agricultural University, Coimbatore) and maize Co-7 (from Department of Maize, Central Farm, Tamil Nadu Agricultural University, Coimbatore). These grains were cleaned, washed, dried and milled into flour in

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a flourmill. The flour was sieved in ISS 40 sieve and used in the experiments.

Swelling power and solubility index

The flour samples of (broken rice flour, foxtail millet flour and maize flour) at 1 % w/v (dry basis) were prepared in a centrifuge tubes with closed screw caps and heated in a water bath for 30 min at 80°C with minimum shear condition. After heating, the centrifuge tubes were immediately immersed in an ice bath to quickly cool the dispersion to room temperature. After cooling in ice for 5 min, samples were centrifuged at 4500 rpm at 5°C for 15 min and then the supernatant was removed for the measurement of solubilized starch. The supernatant was dried to constant weight in a hot air oven at 105°C. Precipitated paste and dried supernatant were weighed. All measurements were done in triplicate. The swelling power (SP) and solubility index (SOL) were calculated as follows (Abdel-Rahman *et al.,* 2008).

$$\text{Swelling power (g/g)} = \frac{\text{Weight of sedimented starch (g)}}{\text{Weight of sample (g) (100- \% Soluble (d.b.))}}$$

$$\text{Soluble Index (\% d.b.)} = \frac{\text{Residue Weight (g) x water weight (g)}}{\text{Aliquot volume (ml) x sample weight (g)}} \text{x 100}$$

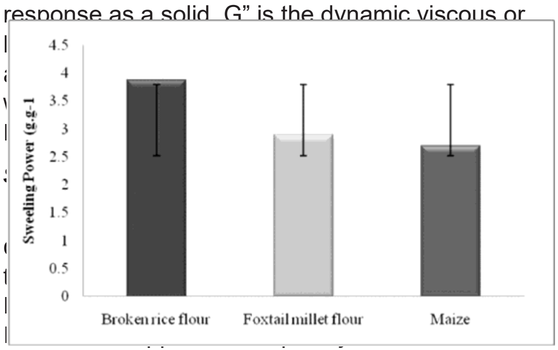
Rheological studies

Pasting properties

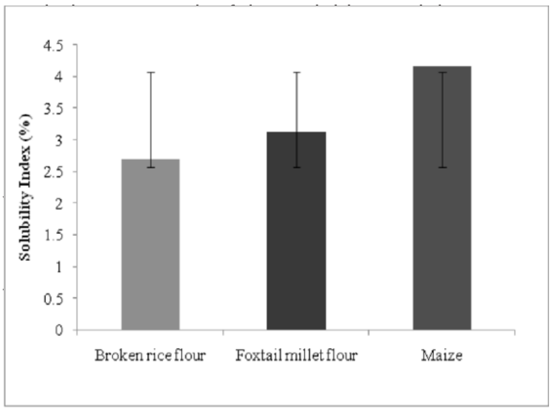
Pasting properties were determined using a starch cell C-ETD 160/ST (Physica Smart, Starch analyzer-Anton Paar) attached to a rheometer (MCR 52, Anton Paar, GmbH, Germany) and established methodology (Jayakody *et al.,* 2007). A sample (7% w/w) was equilibrated at 50°C for 1 min, then heated from 50 to 90°C, 100°C, 110°C at 6°C/min, held at 90°C, 100°C, 110°C for 5 min, cooled to 50°C at 6°C/min, and held at 50°C for 2 min. The speed was 960 rpm for the first 10s, then 160 rpm for the reminder of the experiment. The pasting properties of each sample were inferred from acquired diagrams including the peak time, peak viscosity, holding strength, setback, and final viscosity.

Viscoelastic behavior

Fresh pastes obtained from the Rheometer were used for dynamic oscillatory rheological measurement by a rheometer (Physica MCR 52, Anton Paar GmbH, Stuttgart, Germany). Samples were placed into the rheometer measuring system (cone and plate geometry, 24.983 mm diameter, 1.993° cone angle, and 0.106 mm gap) which was equilibrated to 25°C. All samples were subjected to a shear rate sweep at 20°C, from 0.01 to 100/s. Two steps of rheological measurements were performed: (a) amplitude sweeps at a constant frequency (10 rad/s) to determine the maximum deformation attainable by a sample in the linear viscoelastic range and (b) frequency sweeps at a constant deformation (0.5% strain) within the linear viscoelastic range. The mechanical spectra were obtained recording the dynamic moduli G', G" and tan ä as a function of frequency. G' is the dynamic elastic or storage modulus, related to the material response as a solid. G" is the dynamic viscous or



Design with Analysis of Variance (ANOVA) was



Vertical bar represents ± SD from the mean

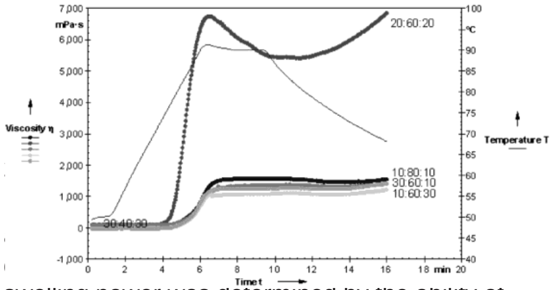
Fig. 1. Swelling power of broken rice flour, foxtail millet flour and maize flour.

ability of broken rice flour to swell in the presence of excess water was different significantly from foxtail millet and maize flours. The broken rice flour (3.88

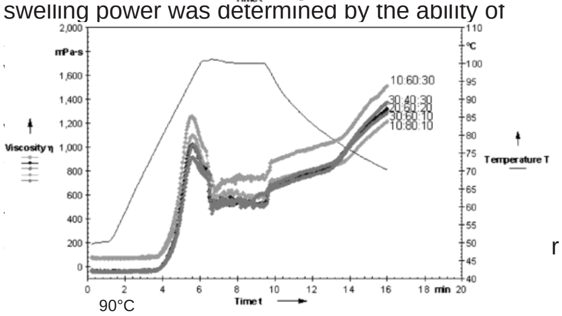
Vertical bar represents ± SD from the mean

Fig. 2. Solubility index of broken rice flour, foxtail millet flour and maize flour.

g/g) showed the highest swelling power compared to foxtail millet flour (2.90 g/g) and maize flour (2.69 g/g) with less difference between foxtail millet flour

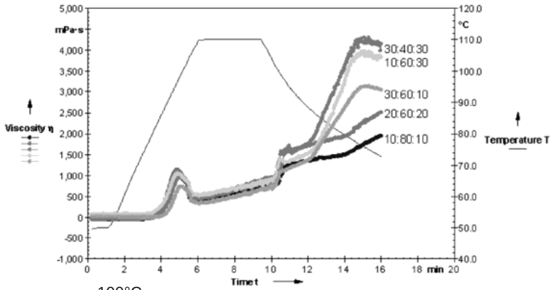


swelling power was determined by the ability of



r

90°C



100°C

110°C

Fig. 3. Rheometer viscosity profiles for formulations of broken rice flour: foxtail millet: maize flour (10:80:10; 20:60:20; 30:40:30; 10:60:30 and 30:60:10) at different temperatures 90°C, 100°C and 110°C

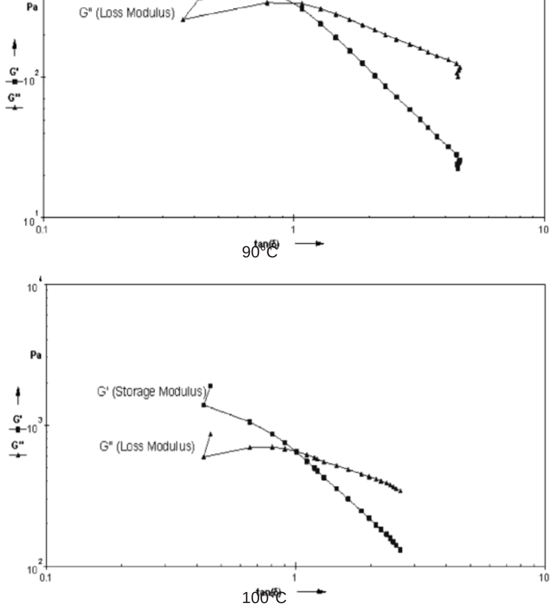
extent. The apparent viscosity of starch dispersions in water is strongly influenced by the extent of swelling of starch granules. Starch granules swell radially in the beginning of heat induced pasting, and when the temperature is increased, the amylopectin-rich granules swell tangentially. As a consequence, the granules get deformed and lose their original shape. The presence of amylose in the continuous phase surrounding the swollen granules results in the formation of a gel on cooling.

Data from the present solubility studies revealed significant difference (Pd”0.05) between broken rice flour, foxtail millet flour and maize flour. Most previous researchers have suggested a relationship between swelling power and solubility. Statistical analysis was performed comparing SP and SOL values of flours. The SP and SOL profiles of flours were nearly the same. The broken rice flour, however, exhibited a significantly (Pd”0.05) higher SP and lower SOL values than those of the foxtail millet flour and maize flour tested. This result demonstrated that broken rice flour inhibited starch swelling and prevented amylose leach out, whereas foxtail millet flour and maize flour seemed to have no effect on these properties.

Pasting profiles

The pasting behavior of samples is reported in terms of degree of gelatinization, gelatinization temperature, PV, BDV, setback and final paste viscosities, and the set back and breakdown ratios (Table 1). The data obtained from the rheograms indicated that viscosity of all temperature and formulation combination flours studied increased during heating, started decreasing just before holding, and increased again during the cooling cycle (Fig. 3). The viscosity values observed ranged from 111.6 to 1552, 384.5 to 6741, 56.07 to 1348, 30.27 to 1260 and 283.7 to 1242 MPa.s, for the formulations of broken rice flour: foxtail millet flour: maize flour combinations 10:80:10, 20:60:20, 30:40:30, 10:60:30 and 30:60:10, respectively. The changes taking place during heating of starch in excess water have been studied in detail by Shinoj*et al.* (2006). Starch granules are insoluble in water, but when a starch suspension in water is heated above critical temperature, the hydrogen bond responsible for structural integrity of the granules weakens allowing the penetration of water, and hydration of the linear segments of amylopectin.

In this study, the increase in temperatures, broken rice and maize flours synergistically increased the viscosity observed during pasting (Fig.3) reflected the contribution of media viscosity, these observations were in good agreement with the results obtained from the extrusion of rice flour (Li *et al.,* 2011) for mung bean starch. This can also make the shear forces exerted on granules much larger than those encountered in starch–water suspensions. This significantly affects the breakdown of granules leading to a significantly (*P*d”0.05) higher breakdown viscosity of 20:60:20 formulation combination systems as compared with all temperatures but formulation combinations are not significantly different at the 5% level by DMRT. Breakdown viscosity measures the tendency of swollen starch granules to rupture when held at high temperatures and continuous shearing. The maximum rise observed before the completion of heating cycle for all the temperature, formulation combinations of flours was due to the changing temperatures and behavioural characteristics of starch and protein components present in flours.

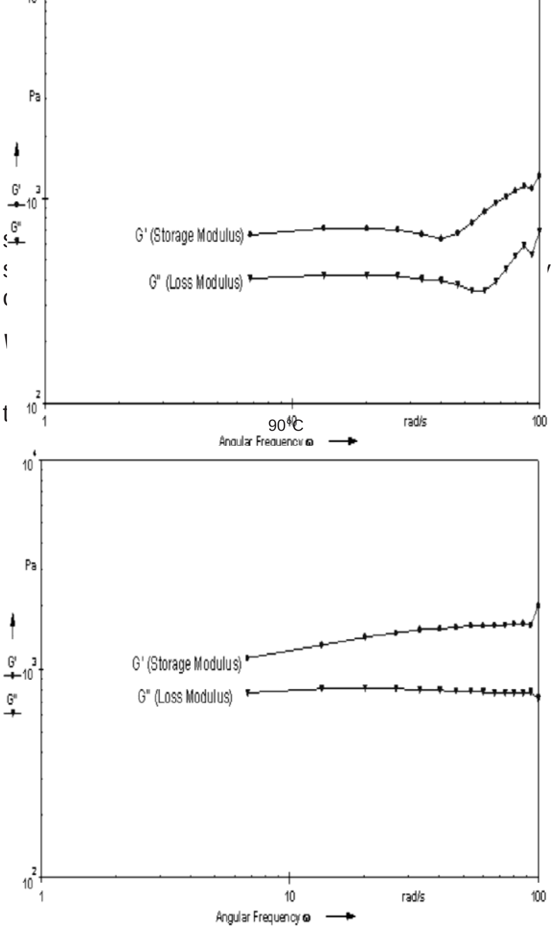


110°C

Fig. 4. Amplitude sweep test profiles for formulation of broken rice flour: foxtail millet: maize flour (20:60:20) at different temperatures 90°C, 100°C and 110°C

During the isothermal holding at 90, 100 and 110°C, all flours exhibited a reducing tendency in viscosity, which has been reported for minor millets flours (Shinoj *et al.,* 2006). Again during cooling, an increase in viscosity was observed, which can be related to the retrogradation tendency of starch. This behaviour is largely determined by the affinity of hydroxyl groups of one molecule to another. The amylose molecules being randomly dispersed can orient themselves in parallel fashion to form aggregates at low solubility leading to gel formation. The peak viscosity, peak time, pasting temperature, holding strength, breakdown, final viscosity, setback from peak and setback from trough were obtained (Table 1).

From the results it is seen that the peak viscosity and final viscosity of broken rice flour: foxtail millet flour: maize flour with the ratio of 20:60:20 at 90°C were higher than that of corresponding holding, breakdown, set back from peak and trough. A similar trend was reported by Musa *et al.* (2011) for rice



100°C

110°C

Fig. 5. Frequency sweep test profiles for formulation of broken rice flour: foxtail millet: maize flour (20:60:20) at different temperatures 90°C, 100°C and 110°C

Table 1. Pasting properties of broken rice flour blended with foxtail millet flour and maize flour formulations used for the extrusion process

Temperature (°C)	Formulations (%) Broken rice flour (%)	Foxtail millet flour (%)	Maize flour (%)	Peak Viscosity (mPa.s)	Peak Time (s)	Pasting temperature (°C)	Holding strength (mPa.s)	Break down (mPa.s)	Final viscosity (mPa.s)	Set back from peak (mPa.s)	Setback from trough (mPa.s)
90	10	80	10	1552	481.2	79.36	1441	111	1539	12.86	98.14
90	20	60	20	6741	390.4	78.20	5408	1333	6842	-101.0	1434
90	30	40	30	1348	502.1	78.74	1292	56.07	1401	-53.04	109.1
90	10	60	30	1076	395.3	80.88	1046	30.27	1201	-125.4	155.7
90	30	60	10	1242	461.9	84.56	1226	15.37	1414	-172.4	187.8
100	10	80	10	1100	335.8	82.17	568.7	530.9	1216	-116.6	647.4
100	20	60	20	1019	335.4	82.06	507.4	511.4	1321	-302.0	813.4
100	30	40	30	911.7	337.5	82.38	527.9	383.9	1375	-463.2	847.1
100	10	60	30	1260	333.9	80.49	695.1	565.0	1512	-251.6	816.6
100	30	60	10	1019	338.6	82.64	493.1	525.7	1289	-270.3	796.0
110	10	80	10	934.1	310	79.80	523.5	410.6	1943	-1009	1420
110	20	60	20	1007	310	82.38	622.3	384.5	2506	-1499	1883
110	30	40	30	943.6	310	81.14	565.9	377.6	4145	-3202	3579
110	10	60	30	971.7	310	84.43	638.8	332.9	3843	-2871	3204
110	30	60	10	738.7	310	87.59	455.0	283.7	3055	-2316	2600

combinations are shown in Fig. 4 and 5. Viscoelastic properties can be used to characterize the three dimensional network structure of five formulation flour combinations. Dynamic moduli involves two parameters viz. storage modulus G' and loss modulus G", showing initial increase during heating cycle, followed by decrease during holding, then rise during cooling and remain near constant (Fig. 4 and 5). The storage modulus was invariably higher than loss modulus at all stages during heating, holding and cooling of the sample, showing that the paste has a tendency to behave like weak gel. G' was the most primary dynamic rheological parameter that reflected rheological properties, G' represented the elastic properties of rice starch paste. These observations were in agreement with the results obtained from Indica rice flour (Qin-lu *et al.,* 2011).

In the dynamic measurement with rheometer, the changes of G' can reflect the changes of hardness and strength of the gel, and the higher G' means higher hardness and strength (Lawal *et al*. 2011). The rheological parameters, G' and G" showed significant variation among three temperatures and five formulation flour combinations when subjected to oscillatory rheological assays of both amplitude and frequency sweep testing ranging from 1 to 100 rad/s under a deformation of 0.5% strain. For all samples, the magnitudes of G' were higher than those of G" over a range of oscillatory amplitudes and frequencies studied. The increase in G' was accompanied by a corresponding increase in G". The G' and G" curves of all combinations were almost parallel in the frequency range studied. Decreased temperatures and increased flour combinations the G' values of starch paste up to 14- and 5-fold at an angular frequency of 1 rad/s, respectively.

Fig. 5 shows that except formulation 20:60:20 at 90°C others resulted in a decrease of the tan ä values from 0.261 for 20:60:20 to 0.290 at 1 rad/s frequency and remained roughly constant across the range of angular frequencies; and 0.217 to 3.76 at 10 rad/s angular frequency; whereas,other temperature and flour combinations exhibited slightly lower tan ä at low frequencies but higher at high frequencies due to the reduction of tan ä of formulation flours at high frequencies (Fig. 4). Therefore, the 20:60:20 formulation exhibited seemingly more solid like behavior than the other remaining formulation combinations.

The main properties of weak gels are given by Wu *et al.* (2010) as G'>G" throughout the accessible amplitude and frequency range, both G' and G" are slightly increased with increasing frequency and the separation of the two moduli (tan ä=G"/G') is smaller than 0.1 for typical polysaccharide gels. The increase of G' values were also related with the rate of amylose and amylose–gum associations that occurred during cooling. The increase of G' cannot be attributed to the aggregation of amylopectin because amylopectin retrogradation occurs over long time periods. From the rheological point of view, the decrease of tan ä corresponded to a more solid like behavior, that is, a stronger three-dimensional network was constructed by amylose and amylose–gum system.

Conclusion

The formulation 20:60:20 at 90°C increased viscosity and viscoelasticity of broken rice flour: foxtail millet flour: maize flour suspensions during and after heating, respectively. The ionic interactions between starch and protein molecules play an important role on these properties. The strong electrostatic interactions between three temperatures and five formulation combination flours resulted in an instantaneous aggregation of granules. These observations can be related to the increase in swelling power, decrease in solubility index of broken rice flours, decrease in peak viscosity, and loss tangent (tan ä) but increase in pasting temperature and rheological parameters G' and G" of formulation 20:60:20 at 90°C with respected to the other temperature and formulation combinations.

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