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Research Paper

Effect of Concentration and Hydrocolloids Formation on Rheological Properties of Gelatinized Cassava Starch and Jackfruit Seeds Starch Dispersions

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ABSTRACT

Rheological properties of gelatinized cassava starch dispersions at different starch concentrations (5.0, 10.0, 15.0, 20.0, and 25.0% w/v) with hydrocolloids i.e. sorbitol and glycerol were experimentally determined using a Brookfield Viscometerat various shear rate 0.08, 0.4, 0.66, 1.6, 2.66, 3.192, 5.32, 7.98, 13.3, 15.96 and 26.6(1/s). Starch dispersions showed shear-thinning behavior. All the fluid exhibited pseudoplastic nature (n<1) Herschel-Bulkley model was well fitted to the experimental data with $r^2 \geq 0.986$ & MSE ≤ 134269.230. The corresponding parameters were correlated with starch concentration. Rheological properties of gelatinized jackfruit seed starch dispersions at different concentrations (5.0, 10.0, 15.0, 20.0, and 25.0% w/v) with hydrocolloids i.e. sorbitol and glycerol were experimentally determined using a Brookfield Viscometer at various shear rate 0.08, 0.4, 0.66, 1.6, 2.66, 3.192, 5.32, 7.98, 13.3, 15.96 and 26.6 (1/s). Starch dispersions showed shear-thinning behavior. All the fluid exhibited pseudoplastic nature (n<1) Herschel-Bulkley model was fitted to the experimental data with $r^2 \geq 0.900$ & MSE ≤ 2.4316×10^5 and the corresponding parameters were correlated with starch concentration.

Keywords: Cassava starch, Jackfruit seeds starch, viscosity and rheology.

Starch has a number of uses in the food industry and for film formation, gelling, and thickening. The rheology of starch hydrocolloids is the most important for industrial use of starch and its mixtures with different nature additives (Whistler and Miller, 1997). The behavior of 3–10% modified potato starch pastes is strictly related to the magnitude of shear stress and it can be of thixotropic and antithixotropic behaviour (M. Harrod, 1989). The rheological properties are very sensitive to the solvent system, sample treatment, and starch composition (Ikeda, S., and Nishinari, K. 2001). They were more stable in 0.2 N solutions of sodium hydroxide and the mixtures of dimethyl sulfoxide with water. Starch samples containing large amounts of amylopectin were able to form networks in water. Amylopectin molecules might adopt a random conformation and prevent intramolecular associations in aqueous solutions. The wheat starch in aqueous solution showed

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non-Newtonian flow behavior and dynamic visco elasticity. The extended heating or vigorous stirring of samples generally destroyed the ability of starch to formshear-thickening fluids. Cluster formation in the 2.6%cross-linked starch dispersion was observed by the light microscopic method, and scanning electron microscopy (Singh *et al.* 2007). Gelatinized starch dispersions exhibit specific rheological properties, depending on source, temperature, and concentration (Rao, 2007). Particularly, potato starch dispersions, usually employed in the food industry, can provide low or high (Wang *et al.* 2011) apparent viscosity values depending on the selected potato variety. These changes in viscosity values may be attributed to differences in the degree of polymerization of amylopectin, whose values vary significantly among the starches from different potato cultivars, and this fact influences greatly the rheological data (Singh *et al.* 2008). On the other hand, dispersions of other starches like waxy maize displayed both shear thinning (downwards) and shear thickening (upwards) properties (Wang *et al.* 2011). These facts show that it is necessary to obtain experimentally the rheological properties of starch dispersions. The influence of starch concentration and temperature is also important because these systems can be subjected to different conditions during processing of starch-based products (Kim and Yoo, 2009).

Starches are the main source of carbohydrates in the human diet and have great nutritional and technological importance in processed foods, as well as a wide range of non-food applications, including pharmaceuticals, fertilizers, paper, adhesives, textiles, and oil drilling. Functional properties, such as gelatinization temperature, gel formation and paste viscosity define their industrial use. The composition and structure of starch granules vary with botanical source, affecting its properties and functionality (Peroni *et al.* 2006; Singh *et al.* 2007). As the industry demands for new technological properties, several nonconventional starch sources have been studied due to the interest in using native starches for food production instead of using chemically modified starches (Copeland *et al.* 2009).

Starch is a reserve carbohydrate in the plant kingdom that worldwide 70–80% of the calories consumed by humans and is generally deposited in the form of minute granules or cells ranging from 1 to 100 mm or more in diameter (Buleon *et al.,* 1998; Whistler and xcBeMiller, 1997; Wurzburg, 1986; Zobel and Stephen, 1995). One of the reasons for choosing cassava starch is its low cost due to the large production in India. India produces around 80.6 lakh tonnes of cassava production. Jackfruit (*Artocarpus heterophyllus L.*) is a shrub belonging to the family Moraceae and is widely distributed in tropical countries such as India, Brazil, Thailand, Indonesia, Philippines, and Malaysia (Chowdhury, Raman, and Mian, 1997). In India, it is generally found in the west and south regions of the country. Fruit is rich source of carbohydrates, fibre, and total minerals. Jackfruit are composed of several berries of yellow pulp and brown seeds encased in a hard shell and are rich in carbohydrates, complex B vitamins, and minerals. However, only 15–20% of the fruit is used as food, which can be cooked, baked, or roasted on coals (Silva *et al.* 2007). Jackfruit seeds are from 2 to 4 cm long, and fruit can contain from 100 to 500 seeds, which represent 8–15% of the total fruit weight. The seeds usually are consumed roasted, boiled, steamed, and eaten as a snack. However, fresh seeds have a short shelf-life. The addition of jackfruit seed flour in the preparation of biscuits, sweets, and bread has been investigated as an alternative use of this by-product. Also jackfruit seeds are waste product in jackfruit processing industries in konkan (Nisha, 2015).

Amylose is essentially a linear polymer in which the theanhydro glucose units are linked through a-D-(1 - 4) glucosidic bonds, whereas amylopectin is a branched polymer with a-D-(1 - 4) glucosidic bonds, having periodic branches at the O-6 position (Buleon *et al.* 1998; Wurzburg, 1986). The influence of starch concentration and temperature is also important because these systems can be subjected to different conditions during the processing of starch-based products (Kim and Yoo, 2009).

A useful review of this aspect is very well documented in Parker and Ring (2001) and Tester *et al.* (2004). Addition of different solutes, such as sugars, salts, acids, and bases, has been used to modify the gelatinization temperature (Chiotelli *et al.* 2002; Roberts and Cameron, 2002; Wootton and Bamunuarachchi, 1979) can be very useful regarding the baking process.

This investigation aimed to examine the rheological properties of gelatinized cassava and jackfruit seed starch and to obtain the model of the rheological behavior at the starch concentration 5, 10, 15, 20, and 25 % w/v; the rheological study of gelatinized starch will help to develop an edible film from these materials. So there is a huge opportunity to use jackfruit seeds starch in many food and non-food industries. Therefore, there is a great interest in providing more information about the rheological properties of gelatinized cassava and jackfruit seeds starch.

MATERIALS AND METHODS

Materials

Cassava for experimentation was procured from the university farm at Central Research Station, Wakawali Dr. B.S.K.K.V. Dapoli. The freshly harvested cassava roots were used for the extraction of starch. Cassava starch was prepared according to the method of Aseidu (1989). Peeled cassava tuber was washed, surface moisture was removed, and slices were beaten into small fragments and mixed with water with 1:2 proportion. Then, wet grinding was done. The mixture was screened by using muslin cloth, starch was allowed to settle and decanted. Then supernatant water was removed, and starch was collected. The starch was then dried in a tray dryer at 45 °C temperature up to 8 hrs. The moisture content of the starch was 11.41 % (d.b.).

Jackfruit seeds for experimentation were procured from the farmer's field at Kudal in the jurisdiction of Dr. B.S.K.K.V Dapoli. The seeds of jackfruit were washed with tap water, and surface water was removed. The seeds were soaked in Sodium hydroxide (5g/100 ml) and citric acid (5g/100 ml) water for 2 minutes and washed with water. The seeds were removed from the solution, and the brown spermoderm covering the cotyledon was removed by peeling it. The cotyledon portion of the seeds, after washing in tap water were sliced around 2 mm thickness and mixed with water with 1:2 proportion. The mixture was wet grounded in a food processor (Make: Jaipan Industries Ltd, Model: CK-2541). The mixture was screened through a muslin cloth and allowed to settle and decanted. After removing the water, the decanted starch was washed 2-3 times with distilled water. The washed starch was taken into a pettry dish and dried at 45^0C in a tray dryer for up to 7.5 h. The moisture content of the starch was 7.94 %(d.b.).

Preparation of gelatinized cassava and jackfruit seeds starch dispersions

Starch dispersions were prepared as per the procedure reported by Kim and Yoo (2009) using suspensions of binary polyol mixtures i.e., glycerol and sorbitol (food grade), Starch, aqueous acetic acid 0.1N (food grade) and distilled water. Initially binary polyol mixtures (glycerol 5 % (w/v) + sorbitol 5 % (w/v) of water) dissolved into distilled water (100 ml), and starch was added into it (5%, 10%, 15%, 20%, and 25% (w/v) of water) to obtain a suspension. The solution at various concentrations of starch (5%, 10%, 15%, 20%, and 25% w/v) was heated in a water bath at 90±2 °C for 20 minutes. The mixture was stirred continuously by hand till the sample was gelatinized, the process was continued till the milky gel was formed. The mixture was kept up to 5 minutes for proper gelatinization at 90±1 °C. The sample was allowed to cool up to 50 °C then dispersion was tested under the Brookfield Viscometer(Model: DV-II + Pro) to carry out rheological tests.

Measurement of Viscosity of starch by Brookfield Viscometer

A Brookfield Viscometer (Model: DV-II + Pro) was used to determine the viscosity of cassava and Jackfruit seeds starch suspensions. Spindle 07 of the Brookfield viscometer was used for the study at different rotational speeds, such as 0.3, 0.6, 1.5, 2.5, 4, 6, 10, 12, 20, 30, 50, 60, and 100 rpm. The viscosity was measured using 500 ml of gelatinized starches filled in a 500 ml beaker. The spindle was dipped in the sample up to the mark at the center of the beaker. The torque required to rotate the spindle in the sample, at a given revolution per minute, was recorded for different speeds. Four replications for each treatment were performed. Brookfield viscometer was leveled on the platform and the spindle 07 was attached to the viscometer by screwing them onto the lower shaft. The above-mentioned starches were filled in a 500 ml beaker. The rheological data were recorded at the speed mentioned above by pressing the enter keys on the equipment. The viscosity was displayed in centipoise (cP), and torque was displayed in percentage. This viscosity was converted into shear stress (Pa.s)as per procedure (Razavi *et al.* 2007).

Shear rate and shear stress calculation

The shear rate (q) was calculated as per the procedure described by Razavi *et al.* (2007). The average shear rate, q_{av}, was computed using Equation (1).

$$q_{av} = (8/\pi)\,\Omega \quad \text{…(1)}$$

where,

q_{av} = shear rate, s^{-1};

Ω = angular speed, rad sec^{-1}.

The average shear stress, τ_{av}, imposed on the fluid by the rotating spindle was calculated using;

$$\tau_{av} = (8/\pi)\,\Omega\eta \quad \text{…(2)}$$

where,

τ_{av} = Shear stress, Pas; η = Viscosity, (cP); Ω = angular speed, rad sec^{-1}

Flow behavior index was described by fitting the experimental data (Shear rate-Shear stress) with the Herschel-Bulkley (1926) model by the following Equation (3) (Razavi *et al.* 2007);

$$\eta = k(\rho)^{n-1} + \frac{\sigma}{\rho} \quad \text{…(3)}$$

where,

k = Consistency index, Pa

n = Flow behavior index.

ρ = Shear rate, (s^{-1})

σ = Fitting parameter

If $n<1$, the nature of the fluid is pseudoplastic (shear thinning), and if $n>1$, the fluid is dilatant (shear thickening). Generally pseudoplastic nature is observed in syrups, juices, food products such as cassava starch (Charles *et al.* 2004; Freitas *et al.* 2004), sesame paste/date syrup blend (Razavi *et al.* 2007), tomato paste (Heidarinasab and Nansa, 2010), totapuri mango juice, kesar mango juice (Dak *et al.* 2007), strawberry, raspberry, peach, prune puree (Maceiras *et al.* 2007).

Statistical analysis

The effect of cassava and jackfruit seeds starch concentration on the fitting parameters of the employed model was studied by analysis of variance (ANOVA). The flow behavior index (n), consistency coefficient(k), and correlation coefficient (r^2) were calculated by fitting the shear stress-shear rate data to the Herschel-Bulkley (Eq. (3) model using Microsoft Office Excel 2007 software.

RESULTS AND DISCUSSION

Steady shear behaviour

Fig. 1 shows the shear stress (pa) versus shear rate (1/s) of gelatinized cassava starch at 5%, 10%, 15%, 20%, and 25% (w/v) cassava starch incorporation. The shear stress increases with an increase in shear rate. As the cassava starch incorporation increases the shear stress increases. The shear stress vs. shear rate data shows the shear thinning behavior. Table 1 shows the model parameter of Herschel-Bulkley model is well fitted to the experimental data of cassava starch suspension with $r^2 \geq 0.986$, MSE≥134269.230. As the cassava starch incorporation increases from 5% to 25%, the K value increases from 4815.350 to 412125.00. 'K' value is a consistency coefficient that increased

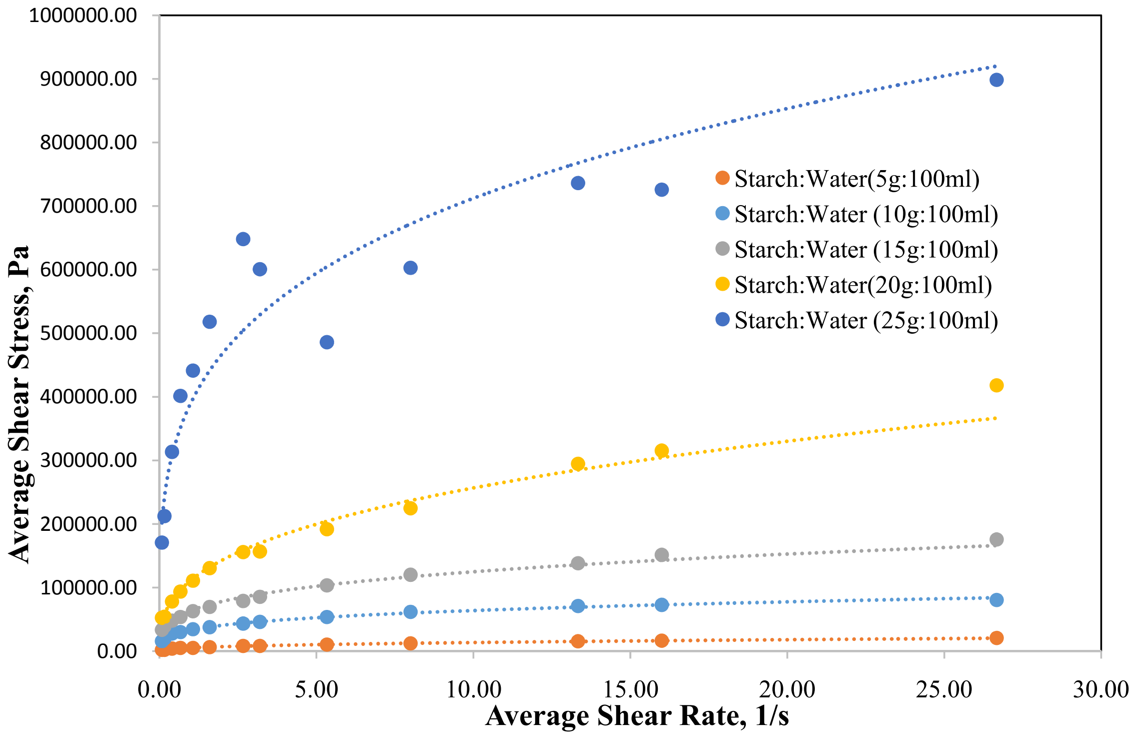

Fig. 1: Shear Stress (Pa) versus Shear rate (1/s) for Cassava starch

Table 1: Parameters of Herschel-Bulkley model of cassava starch

Starch	Proportion (g:ml)	Parameters of Herschel-Bulkley model				
		Y_S	K	n	r^2	MSE
	5:100	463.634	4815.350	0.437	0.999	134269.230
	10:100	0.0001000	33854.80	04134	0.999	1980520.0
Cassava	15:100	0.0001000	61684.30	0.3161	0.997	1.12725×10^7
	20:100	0.0001000	102414.00	0.2731	0.997	1.36160×10^8
	25:100	0.0001000	412125.00	0.2252	0.986	4.94214×10^9

Significant p≤0.01.

with increases in cassava starch incorporation. The flow behavior index n≥0.225 indicates that the gelatinized cassava starch is pseudoplastic in nature and exhibits shear thinning behavior. Y_S is the yield stress 463.63 Pa.s at 5% (w/v) starch concentration and decreases up to 0.0001 Pa.s as the concentration increases 5% to 10% w/v & no change after that. It means it requires a minimum 0.0001 Pa.s force to create deformation in the material. Shear-thinning behavior is related to the progressive orientation of molecules in the direction of flow and the breaking of H-bonds formed in the amylose-amylopectin-water structure during shearing (Cornell, 2004). Flow curves of cassava starch dispersions at the studied concentrations displayed shear thinning behaviour without significant variations between viscosities when shear rate decreases viscosity increases.

Fig. 2 shows the shear stress (pa) versus shear rate (1/s) of gelatinized jackfruit seed starch at 5%, 10%, 15%, 20%, and 25% (w/v) jackfruit seed starch incorporation. The shear stress increases with an increase in shear rate as the jackfruit seed starch

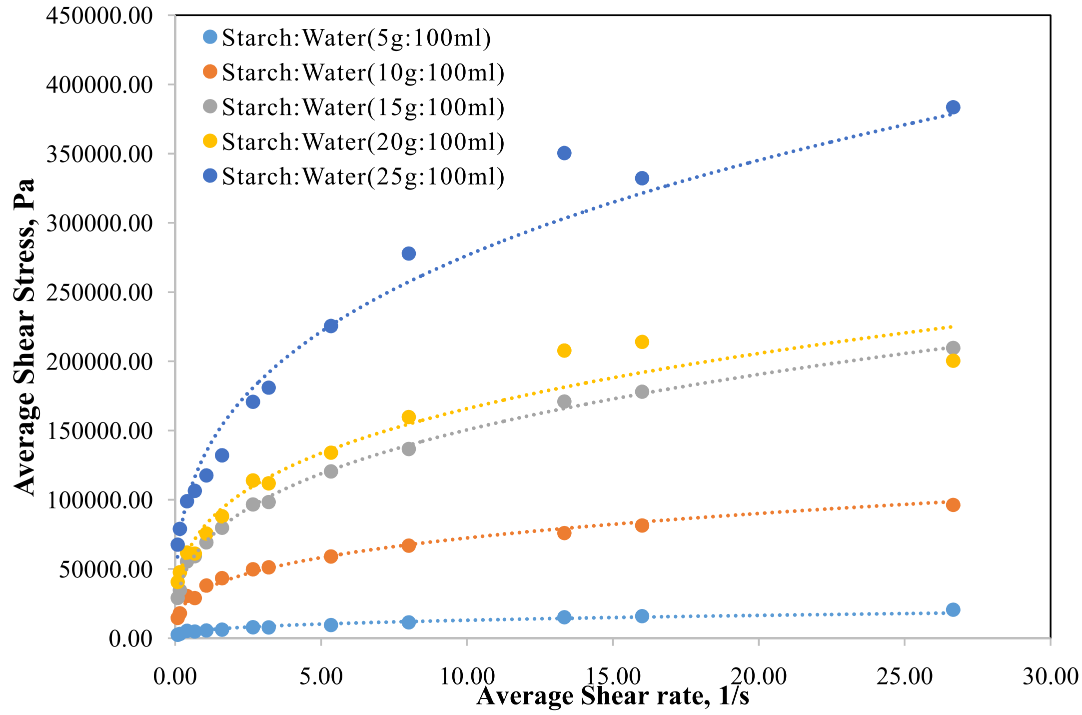

Fig. 2: Shear stress versus Shear rate of Jackfruit seed starch

Table 2: Parameters of Herschel-Bulkley model of jackfruit seeds starch

Starch	Proportion (g:ml)	Parameters of Herschel-Bulkley model				
		Y_S	K	n	r^2	MSE
Jackfruit seeds	5:100	2359.21	3069.89	0.5433	0.998	2.4316×10^5
	10:100	0.0001000	35961.70	0.3501	0.998	1.84463×10^6
	15:100	0.0001000	68384.20	0.3432	0.999	3.92834×10^6
	20:100	0.0001000	81074.30	0.3159	0.900	7.58653×10^6
	25:100	0.0001000	127182.00	0.2978	0.995	2.63143×10^8

Significant p≤0.01.

incorporation increases from 5% (w/v) to 25% (w/v). The shear stress vs. shear rate data shows the shear thinning behavior. Table 2 shows the model parameter of the Herschel-Bulkley model. The Herschel-Bulkley model is well fitted to the experimental data with $r^2 \geq 0.900$, MSE $\geq 2.4316 \times 10^5$. As the jackfruit seed starch incorporation increases from 5% to 25% the K value increases from 3069.89 to 127182.000. 'K' value is a consistency coefficient that increased with increases in jackfruit seed starch incorporation. The flow behavior index $n \geq 0.297$ indicates that the gelatinized jackfruit seed starch is pseudoplastic in nature and exhibits shear thinning behavior. Y_S is the yield stress was 2359.21 Pa.sat jackfruit seed starch concentration 5 w/v, it decreases as the concentration of jackfruit seed starch increases up to 10% w/v and no change after that.

Determination of rheological parameters

The flow behavior index of cassava and jackfruit seeds starch decreased from 0.437 to 0.2389 and 0.5433 to 0.29783. The consistency index of cassava and jackfruit seeds starch dispersion increased from 4815.350 to 412125.00 and 3069.89 to 127182.00. Correlation coefficient of all treatments of cassava and jackfruit seeds starch dispersions was greater than 0.986. Moreira *et al.* (2012) reported that the flow behavior index of chestnut starch decreased from 0.21±0.01 to 0.15±0.01. Also, the consistency index of chestnut starch dispersion increased from 1.75±0.01 to 8.00±0.01 as concentration increases from 4% to 7%. Correlation coefficient of all treatments of chestnut starch dispersions was greater than 0.964.

The cassava and jackfruit seeds' starch dispersions showed non-Newtonian behaviour. The similar results were observed in previous studies performed with sesame paste/date syrup blend (Razavi *et al.* 2007), tomato paste (Heidarinasab and Nanas, 2010), tota puri mango juice (Dak *et al.* 2006), strawberry, raspberry, peach, and prune puree (Maceiras *et al.* 2007). Fig. 1 and 2 shows the effect of starch content on therheological parameters of cassava and jackfruit seeds starch dispersions. The correlation coefficient of index cassava and jackfruit seeds starch dispersion was decreased from 0.999 to 0.986 and 0.999 to 0.900. The cassava and jackfruit seeds starch dispersion shows the pseudoplastic (shear thinning).

CONCLUSION

Rheological (shear rate and shear stress) properties of cassava and jackfruit seeds starch dispersion were dependent on the starch concentration. Gelatinized cassava and jackfruit seeds starch dispersions showed shear-thinning, non-Newtonian behavior. Steady shear flow curves of cassava and jackfruit seeds starch dispersions were satisfactorily fitted by means of the Herschel-Bulkley model. The flow behavior index of cassava and jackfruit seeds starch dispersions decreased from 0.437 to 0.225 and 0.5433 to 0.29783. The consistency index of cassava and jackfruit seeds starch dispersion increased from 4815.35 to 412125.00 and 3069.89 to 127182.00. Correlation coefficient of all treatments of cassava starch and jackfruit seeds starch dispersions was greater than 0.900. The correlation coefficient of index cassava and jackfruit seeds starch dispersion was decreased from 0.999 to 0.986 and 0.999 to 0.900. Model parameters were correlated with cassava and jackfruit seeds starch concentration. The found results indicate that cassava and jackfruit seeds starch could be used as viscosity enhances suitable as an additive in the food industry and used for several purposes.

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