ELSEVIER

Carbohydrate Polymers 47 (2002) 365–371

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Effect of succinylation on the rheological profile of starch pastes

Praful N. Bhandari, R.S. Singhal*, D.D. Kale

Department of Chemical Technology, Food and Fermentation Tech. Div., University of Mumbai, Matunga, Mumbai 400 019, India

Received 14 September 2000; revised 16 January 2001; accepted 16 February 2001

Abstract

Rheological properties of native corn and amaranth starches, and the changes therein on succinylation have been evaluated. The degree of substitution (DS) was varied from 0.05 to 0.20 at concentrations up to 5%. A strong shear thinning behavior was observed in all the starch pastes, as described by the power law parameters, i.e. the consistency index, *K*, and the flow behavior or power law index, *n*. The effect of concentration and DS on the apparent viscosity is described. Amaranth starch succinates showed a greater shear thinning behavior vis-à-vis corn starch succinates. The bulky hydrophilic succinate group seem to influence the rheological properties.

Keywords: Succinylation; Rheology; Corn starch; Amaranth starch; Non-newtonian flow

1. Introduction

Texture, pasting properties, appearance and viscosity of starch pastes are the important factors for choosing it as an ingredient in processed foods. A study of the rheological properties of the starch pastes enables the assessment of its behavior during processing, which is crucial to successful product formulation and engineering scale up (Islam, Azemi & Manan, 1999). Rheological properties of starch containing foods are widely dependent on the nature and the type of molecular arrangement of starch and its chemical structure, conformation and the forces acting between them. A small change in molecular conformation and structure of starch can bring about dramatic change in functional and rheological properties of starch (Djakovic & Dokic, 1972).

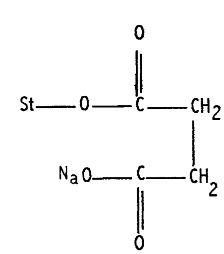
The pasting properties of starch are believed to be sensitive to energy input and shear rate. Swelling of the starch granules at and above the gelatinisation temperature opens and weakens the granule structure, resulting in an increase in the paste viscosity and the susceptibility of the granules to shear damage. The degree of swelling and the granule integrity are directly related to the viscosity of the starch paste (Borwankar, 1992).

Pasting properties of starch were first characterized using a consistometer (Caesar, 1932). Since then, numerous types of apparatus have been developed and are being used. The Brabender amylograph has undoubtedly been the most popular instrument used by starch manufacturers and food processors. Presently, Haake viscometers, Brookefield viscometers, Ostwald rheometers, and rapid viscosity analyzers are used in determining the viscosity with respect to shear rate and shear stress.

In food processing, starch dispersions are often heated, cooled and pumped at a wide range of shear rates. For instance batch mixing, pumping, plate heat exchanger, atomization and extrusion cooking generally employ shear rates of 10–100, 30–500, 50–500, 1000–1,00,000 and 500–50,000 s^{-1}, respectively (Borwankar, 1992).

Starch granules are susceptible to shear damage that can cause a loss in viscosity of the cooked paste. In addition, the rheology of the cooked starch paste becomes increasingly non newtonian. This further complicates the assessment of the effect of shear rate and strain on the viscosity (Bohlin & Eliasson, 1986). Therefore, to ensure the engineering scalability, it is desirable to evaluate the pasting property of starch at appropriate or specific shear rates.

Starch reacts with succinic anhydride in presence of the catalyst pyridine to form the half ester, represented as follows (Trubiano, 1987).



starch succinate

Starch succinates are cleared for food use by the US Food and Drug Administration (FDA) up to 4% treatment level. The major properties of starch succinate are a lower gelatinisation

* Corresponding author.

0144-8617/02/$ - see front matter
PII: S0144-8617(01)00215-6

Table 1
Effect of shear rate on the viscosity (mpa s) of 3, 4, and 5% native corn modified corn starch succinate at 30°C (each value is the mean of three determinations)

Shear rate (s^{-1})	Native			Corn starch succinate of DS											
				0.05			0.10			0.15			0.20		
	3%	4%	5%	3%	4%	5%	3%	4%	5%	3%	4%	5%	3%	4%	5%
27.05	437	*657*	950	427	*630*	924	468	*630*	940	458	*649*	960	476	*660*	1540
44.9	400	*584*	720	410	*595*	735	427	*600*	743	435	*610*	768	443	*625*	892
75.2	379	*521*	639	376	*538*	642	385	*552*	660	396	*570*	681	408	*580*	760
125.5	334	*469*	533	338	*473*	525	358	*489*	589	368	*500*	629	379	*527*	689
245.1	298	*405*	448	301	*420*	460	315	*432*	524	328	*448*	568	339	*460*	575
349	258	*348*	368	268	*380*	370	270	*390*	475	287	*398*	479	300	*400*	485
583.2	210	*298*	315	224	*331*	340	238	*340*	410	254	*347*	425	269	*355*	439
971.6	175	*238*	260	181	*248*	278	200	*267*	300	220	*271*	310	236	*280*	348
1621	147	*170*	228	150	*179*	240	159	*186*	261	164	*194*	270	180	*210*	284
2702	115	*125*	135	120	*135*	145	130	*145*	170	135	*160*	200	150	*170*	210

temperature, its ability to swell in cold water, its excellent viscosity stability, improved paste clarity and freeze–thaw stability, reduced tendency to retrograde and stability in acidic and salt containing medium. These properties enable starch succinates to be a good candidate for a number of applications. They have been recommended (Trubiano, 1987) as binders and thickening agents in soups, snacks, canned and refrigerated food products, as tablet disintegrants in the pharmaceutical industry, and as a sizing agent and coating binder in paper manufacture.

The objective of the present study was to probe into the complexity involved in the shear rate and concentration effects on the pasting property of native corn and amaranth starch, and the change encountered therein after succinylation.

2. Materials and methods

2.1. Materials

Corn starch used in the study was procured from M/S Raptakos Brett and Co Ltd., Thane. Amaranth starch was isolated in the laboratory by the alkali steeping method (Yanez & Walker, 1986). Corn and amaranth starch succinate of DS 0.05–0.2 (Bhandari & Singhal, unpublished work) were chosen for rheological studies and compared with their native counterparts.

2.2. Methods

2.2.1. Rheological properties of starch succinates

The procedure adopted was as per the literature reports (Islam & Azemi, 1997; Islam et al., 1999; Navarro, Martino & Zaritzky, 1992). Dry samples (3–5%) were suspended in 75 ml distilled water and heated at 95°C for 30 min, in order to gelatinize the starch, with constant stirring to avoid sedimentation and agglomeration. The starch paste so obtained was then cooled to room temperature (30 ± 2°C).

Rheological behavior of the starch paste was studied by the Haake Rotoviscometer (VT 500) using the sensor system NV (cup) and NV (rotor) in the shear rate range of 27.05–2701 s^{-1}. Flow behavior characteristics were analyzed from the apparent viscosity and shear rate relationship data. Apparent viscosity measurements were taken at different shear rate ranges (27.05–2701 s^{-1}). Variation in apparent viscosity as a function of solid concentration was also investigated. A Power law model that relates the apparent viscosity to shear rate was used to characterize the flow behavior index (n) of the starch paste (Islam et al., 1999).

$$\eta = \kappa\gamma^{n-1}$$

The effects of concentration on flow parameters were examined at all the shear rates used in the study. The following power law equation, suggested by Rao, Cooley and Vitali (1984) was used for the present study.

$$\eta_a = MC^a$$

Where η_a is the apparent viscosity, C is the concentration of the starch gel (%), and M and a are constants to be determined from the log–log plot of apparent viscosity vs. starch concentration.

3. Results and discussions

The flow behavior characteristics are influenced by shear rate and starch concentration. Table 1 shows the viscosity values (mPa) of corn starch and its succinate derivatives of varying DS at different shear rates (27.01– 2701 s^{-1}) and concentrations of 3, 4 and 5%, respectively. Table 2 shows similar data for amaranth starch. A decrease in viscosity with increase in shear rates for both the starches and their modified derivatives were observed (Eliasson, 1986). The highest viscosity values were obtained at lowest shear rate (27.01 s^{-1}) and the lowest for highest shear rate (2701 s^{-1}). This suggests that the starch dispersion is susceptible to shear thinning behavior or is pseudoplastic nature (Islam & Azemi, 1997; Isalm et al., 1999; Kim & Eliasson, 1992). The magnitude of the increase in viscosity at a

Table 2
Effect of shear rate on the viscosity (mpa s) of 3, 4 and 5% native amaranth modified amaranth starch succinate at 30°C (each value is the mean of three determinations)

Shear rate (s^{-1})	Native			Amaranth starch succinate of DS											
				0.05			0.10			0.15			0.20		
	3%	4%	5%	3%	4%	5%	3%	4%	5%	3%	4%	5%	3%	4%	5%
27.05	460	*690*	1000	465	*590*	1090	470	*600*	1120	482	*627*	1140	490	*640*	1180
44.9	359	*620*	824	385	*548*	832	394	*554*	860	401	*560*	827	424	*588*	890
75.2	272	*540*	615	349	*509*	740	360	*487*	752	375	*477*	770	390	*537*	794
125.5	215	*490*	465	301	*458*	684	334	*438*	700	330	*420*	724	358	*472*	730
245.1	149	*325*	312	270	*403*	524	291	*370*	560	299	*365*	593	310	*412*	617
349	122	*240*	270	210	*240*	476	248	*367*	500	250	*321*	571	271	*292*	541
583.2	91	*204*	232	160	*293*	380	180	*290*	410	200	*242*	438	209	*298*	459
971.6	71	*160*	184	110	*210*	299	134	*232*	338	140	*194*	360	170	*210*	374
1621	68	*124*	160	75	*145*	201	90	*160*	210	100	*157*	240	124	*167*	257
2702	50	*90*	120	50	*90*	120	58	*105*	135	67	*105*	141	91	*120*	150

fixed shear rate for both corn starch succinates (CSS) and amaranth starch succinates (ASS) was found to be in the order of

$$0.2 > 0.15 > 0.10 > 0.05 > \text{Native}$$

i.e. the viscosity increased progressively with an increase in the DS. The shear thinning behavior of starches with increasing shear rates can be described on the basis of a starch network entanglement mechanism during shearing. In an entangled network system, viscosity remains constant at lower shear rates or may decrease slightly. Increasing shear rate progressively disentangles the arrangement of long chain molecules and helps to overcome the intermolecular resistance to flow i.e. the rate of re-entanglement falls behind the rate of disruption of existing entanglement. On the other hand the highly solvated molecules or particles present in the dispersion medium may be progressively sheared away with increasing shear rate causing a reduction in effective size of particles and hence the reduction in apparent viscosity. The decrease in viscosity indicated that the breakage of the intra and intermolecular associative bonding system in the starch network micelles was higher at higher shear rates (Evans & Haisman, 1979; Holdworth, 1977; Sandhya Rani & Bhattacharya, 1989).

The data from Tables 1 and 2 was utilised to calculate the flow behavior index, n and the consistency indices, K by a

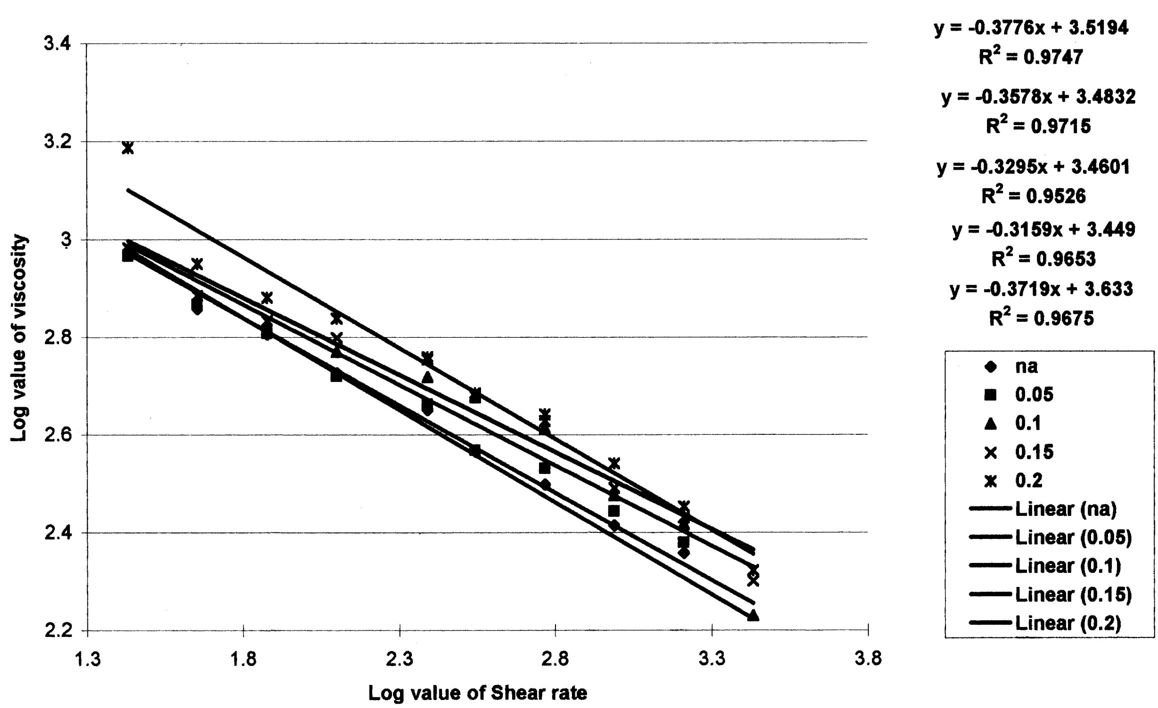


Fig. 1. Effect of shear rate on the viscosity of 5% native and corn starch succinates.

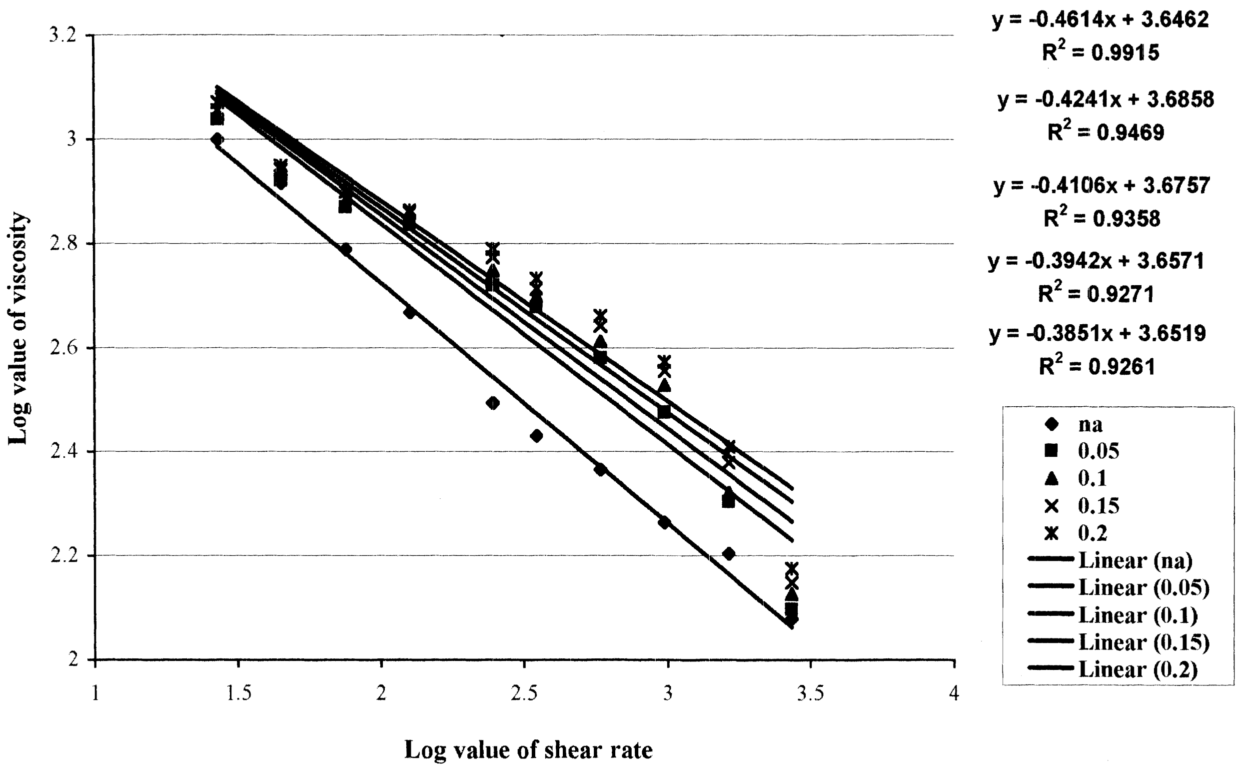


Fig. 2. Effect of shear rate on the viscosity of 5% native and corn starch succinates.

log–log plot of shear rate vs. viscosity. Figs. 1 and 2 shows the representative log–log plot of viscosity vs. shear rate for native corn starch and CSS pastes, and for native amaranth starch and ASS pastes at 5%. Similar profiles were also obtained at 3 and 4% starch pastes (figures not given). Table 3 compiles the result so obtained and shows that the values of flow behavior indices for both native and modified starch dispersions were always less than unity and fall in the wide range of 0.512–0.757 indicating that the starch paste are pseudoplastic in nature.

Succinylation affected the flow behavior index as a function of concentration and DS for both the starches, as can be seen in Table 3. It is interesting to note that at a given concentration, the power law index, n, increased with increasing DS of the starch succinates, indicating a reduction in the degree of shear thinning. A power law index of 1 denotes Newtonian behavior; a decreasing n value indicates a stronger shear thinning behavior. Similarly, at a given DS, the starch pastes showed increasing shear thinning behavior with an increase in concentration. At any concentration and DS, ASS pastes were more viscous and also underwent greater shear thinning than their corn starch counterparts.

An increase in viscosity with increasing DS for both starches as seen from the values of consistency index, K can be explained as follows. Increased bulky hydrophilic groups in the starch molecule caused it to imbibe more water leading to an enhanced water binding capacity. These micelles remain intact and hold the granule in enormously swollen networks (Tessler & Wurzburg, 1983). These may cause an increase in hydration volume

Table 3
Effect of succinylation on flow behavior indices,n and consistency index K of corn and amaranth starches at various concentration

Concentration (%)	Native		0.05		0.103		0.15		0.20	
	n	K	n	K	n	K	n	K	n	K
Corn starch										
3	0.71	1227	0.72	1226	0.73	1266	0.74	1225	0.76	1173
4	0.66	2325	0.68	2166	0.69	2085	0.70	2059	0.71	2027
5	0.62	3307	0.64	3042	0.67	2885	0.68	2812	0.63	4295
Amaranth starch										
3	0.51	2230	0.53	2633	0.57	2349	0.60	2160	0.65	1794
4	0.54	3682	0.62	2587	0.65	2240	0.63	2412	0.64	2448
5	0.54	4428	0.58	4851	0.59	4739	0.61	4540	0.61	4486

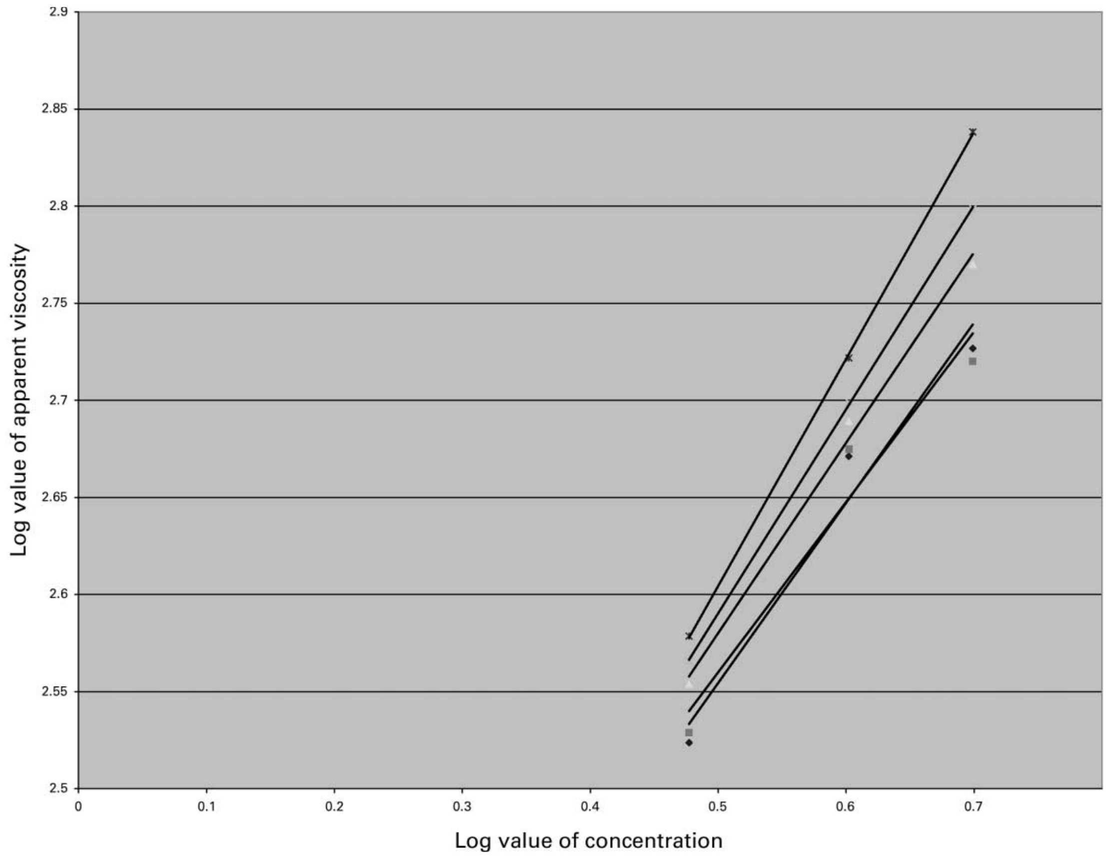


Fig. 3. Log–log plot of apparent viscosity vs. starch concentration for native corn starch and its succinate derivatives of different DS.

of the starch granules in the paste resulting in higher viscosity. The relationship of apparent viscosity with the concentration was estimated from the power law model described earlier by the equation (Islam & Azemi, 1997; Rao et al., 1984).

$$\eta_a = MC^a$$

The constants M and a were determined from the log–log plot of apparent viscosity vs. starch concentration. This is depicted at a fixed shear rate of 125 s^{-1} for both native and modified derivatives of corn and amaranth starches in Figs. 3 and 4, respectively. The values of M and a were determined as the intercept and the slope of the lines obtained from the plot. These values were also calculated for the entire range of shear rates used in the study (figures not shown). Tables 4 and 5 record these values for both native and modified derivatives of corn and amaranth starches.

Viscosity of native and succinate derivatives for both the starches increased with an increase of DS and starch concentration. It is well known that viscosity is directly proportional to starch concentration. At higher concentrations, starch molecules agglomerate by overlapping and interpenetrating into one another forming an entangled network in the paste via hydrogen bonding. This limits the water penetration and restricts the mobility and fluidity of starch pastes. Consequently, higher viscosity was observed at higher concentrations (Eliasson & Kim, 1992; Kim, Muhrbeck & Eliasson, 1993; Sugimoto, Sakamoto, Yamada & Fuwa, 1981). In the case of modified derivatives of both the starches, the viscosity was found to be higher and follows the order

$$\text{Native} < 0.05 < 0.10 < 0.15 < 0.20$$

This may be due to the bulky hydrophilic nature of starch succinate, which disrupts the ordered structure and keep the molecules in expanded or extended form and inhibit its coiling in the solution. As a result, effective hydration volume of the molecule increases. Consequently, higher viscosity was observed than that of native starches.

M did not show any particular trend with respect to DS for both modified corn and amaranth starches at different shear rates. However, values showed a definite decreasing trend with an increase in shear rates. Similar results were also observed for amaranth starch and its derivatives (Islam & Azemi, 1992; Loh, 1992). As the shear rate increases, the starch molecules often get oriented in the direction of the shear, thereby decreasing the viscosity. Hence, the dependence of viscosity on concentration at high shear rates is always weak. This correlation between viscosity and concentration could find valuable applications for setting guidelines for estimating the rheological behavior of formulated foods containing starch succinates.

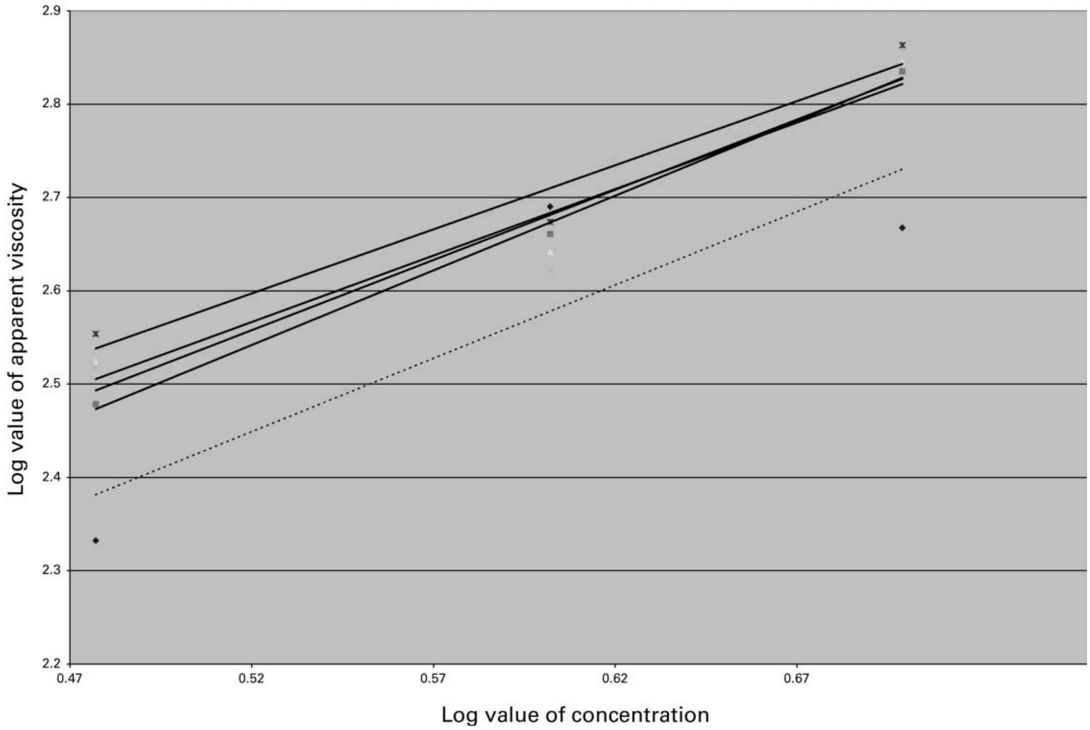


Fig. 4. Log–log plot of apparent viscosity vs. starch concentration at a shear rate of 125 s^{-1} for amaranth starch and its succinate derivatives of different DS.

Table 4
Effect of succinylation of corn starch on the apparent viscosity as a function of concentration at 30°C (Regression coefficient in all cases was 0.9 or greater)

Shear rate (s^{-1})	Native	Corn starch succinates of DS			
		0.05	0.103	0.15	0.2
27.01	**1.515**[a]	**1.503**	**1.349**	**1.473**	**2.243**
	1.913[b]	1.907	2.014	1.66	1.565
44.9	**1.158**	**1.584**	**1.089**	**1.115**	**1.361**
	2.055	2.055	2.114	2.108	1.99
75.2	**1.026**	**1.056**	**1.064**	**1.071**	**1.218**
	2.09	2.078	2.084	2.094	2.029
125.5	**0.927**	**0.876**	**0.979**	**1.050**	**1.168**
	2.090	2.12	2.09	2.06	2.020
245.1	**0.810**	**0.845**	**1.000**	**1.075**	**1.035**
	2.09	2.086	2.024	2.00	2.037
349	**0.711**	**0.658**	**1.091**	**1.000**	**0.943**
	2.080	2.13	1.901	1.981	2.029
583.2	**0.813**	**0843**	**1.073**	**1.011**	**0.959**
	1.949	1.967	1.87	1.925	1.975
971.6	**0.788**	**0.852**	**0.803**	**0.673**	**0.752**
	1.925	1.860	1.877	2.00	2.022
1621	**0.842**	**0.905**	**0.950**	**0.957**	**0.875**
	1.752	1.732	1.732	1.743	1.824
2702	**0.312**	**0.372**	**0.518**	**0.761**	**0.648**
	1.910	1.90	1.861	1.760	1.858

[a] Slope of the regression line (*a*).
[b] Constant (η_1).

Table 5
Effect of succinylation of amaranth starch on the apparent viscosity as a function of concentration at 30°C (Regression coefficients in all cases was 0.9 or greater)

Shear rate (s^{-1})	Native	Amaranth starch succinates of DS			
		0.05	0.103	0.15	0.2
27.01	**1.514**[a]	**1.628**	**1.659**	**1.648**	**1.683**
	1.935[b]	1.860	1.840	1.868	1.858
44.9	**1.639**	**1.495**	**1.511**	**1.404**	**1.436**
	1.782	1.861	1.861	1.923	1.930
75.2	**1.634**	**1.463**	**1.423**	**1.381**	**1.378**
	1.683	1.838	1.862	1.894	1.923
125.5	**1.574**	**1.599**	**1.424**	**1.505**	**1.374**
	1.63	1.702	1.824	1.775	1.882
245.1	**1.506**	**1.302**	**1.260**	**1.309**	**1.330**
	1.50	1.813	1.846	1.827	1.843
349	**1.592**	**1.548**	**1.372**	**1.581**	**1.301**
	1.355	1.542	1.739	1.616	1.772
583.2	**1.878**	**1.712**	**1.613**	**1.493**	**1.525**
	1.098	1.401	1.487	1.556	1.581
971.6	**1.909**	**1.971**	**1.815**	**1.815**	**1.505**
	0.975	1.111	1.260	1.250	1.480
1621	**1.694**	**1.946**	**1.674**	**1.706**	**1.402**
	1.03	0.959	1.167	1.180	1.407
2702	**1.729**	**1.729**	**1.659**	**1.461**	**0.977**
	0.885	0.885	0.987	1.132	1.492

[a] Slope of the regression line (*a*).
[b] Constant (η_1).

4. Conclusions

Rheological behavior of native and modified derivatives of corn and amaranth starches are markedly influenced by shear rates and concentration of the starch. Both natïve and modified derivatives of corn and amaranth starch showed shear thinning behavior indicating their pseudoplastic nature. However, viscosity was found to be a function of the DS of the starch succinates. Bulky hydrophilic groups of the modified derivatives seems to be responsible for its improved and stable viscosity characteristics.

References

Bohlin, L., & Eliasson, A. C. (1986). Shear stress relaxation of native and modified potato starch gels. *Starch/Stärke*, *38* (4), 120–124.

Borwankar, R. P. (1992). Food texture and rheology. In R. P. Borwankar & C. F. Shoemaker, *Rheology of foods* (pp. 1–16). New York: Elsevier.

Caesar, G. V. (1932). Consistency changes in starch paste. *Industrial and Engineering Chemistry*, *24*, 1432–1439.

Djakovic, L. J., & Dokic, P. (1972). Rheological characteristics of starch gels. *Starch/Stärke*, *24* (6), 195–201.

Eliasson, A. C. (1986). Viscoelastic behavior during the gelatinisation of starch and comparison of wheat, maize, potato and barley starches. *Journal of Texture Studies*, *17*, 253–265.

Eliasson, A. C., & Kim, H. R. (1992). Changes in rheological property of hydroxypropyl potato starch pastes during freeze–thaw treatments I: a rheological approach for evaluation of freeze–thaw stability. *Journal of Texture Studies*, *23*, 279–295.

Evans, I. C., & Haisman, D. R. (1979). Rheology of gelatinised starch suspension. *Journal of Texture Studies*, *10*, 347–370.

Holdsworth, S. D. (1977). Applicability of rheological models to the interpretation of flow and processing behaviour of fluid food products. *Journal of Texture Studies*, *2*, 393–418.

Islam, N., & Azemi, B. M. N. M. (1992). Effect of molar substitution on calcium binding by hydroxypropyl rice starches. *Starch/Stärke*, *44* (9), 332–334.

Islam, N. M., & Azemi, B. M. N. M. (1997). Rheological properties of calcium treated hydroxypropyl rice starches. *Starch/Stärke*, *49* (4), 136–141.

Islam, N., Azemi, B. M. N. M., & Manan, D. M. A. (1999). Rheological behaviour of sago (*Metronylon Sago*) starch paste. *Food Chemistry*, *64*, 501–505.

Kim, H. R., & Eliasson, A. C. (1992). Changes in rheological property of hydroxypropyl potato starch pastes during freeze–thaw treatments II: effect of molar substitution and cross-linking. *Journal of Texture Studies*, *24*, 199–213.

Kim, H. R., Muhrbeck, P., & Eliasson, A. C. (1993). Changes in rheological properties of hydroxypropyl potato starch pastes during freeze thaw treatments III: effect of cooking conditions and concentration of the starch paste. *Journal of the Science of Food and Agriculture*, *61*, 109–116.

Loh, J. (1992). The effect of shear rate and strain on the pasting behavior of food starches. In R. P. Borwankar & C. F. Shoemaker, *Rheology of foods* (pp. 75–90). New York: Elsevier.

Navarro, A. S., Martino, M. N., & Zaritzky, N. E. (1992). Rheological behavior of gelatinised starch paste stored at low temperature. *Science et Technique du Froid*, 274–280 (Cited from Chem Abstr, 122, 104235*j* (1992)).

Rao, M. A., Cooley, M. J., & Vitali, A. A. (1984). Flow properties of concentrated juices at low temperatures. *Food Technology*, *38*, 113–119.

Sandhya Rani, M. R., & Bhattacharya, K. R. (1989). Rheology of rice flour paste: effect of variety, concentration and time and temperature of cooking. *Journal of Texture Studies*, *20*, 127–137.

Sugimoto, Y., Sakamoto, S., Yamada, K., & Fuwa, H. (1981). Some properties of normal and waxy type starches of *Amaranthus hypochondriacus* L. *Starch/Stärke*, *33* (4), 112–116.

Tessler, M.M., & Wurzburg, O.B. (1983). Starch sulfomaleate half ester and their use to prepare starch disulfosuccinate half ester. *US patent* US 4379 919 [Cited from Chem. Abstr, 98, 217532 *h* (1983)].

Trubiano, P. C. (1987). Succinate and substituted succinate derivatives of starch. In O. B. Wurzburg, *Modified starches: properties and uses* (pp. 131–148). Boca Raton, FL: CRC Press.

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