Effect of Emulsifiers on the Physical Properties of Native and Fermented Cassava Starches

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The effect of the emulsifying agents, glycerol monostearate (GMS), sodium steroyl lactylate (SSL), and konjac flour (KF, a texture modifier which releases an aggregated glucomannan polymer in water), on the thermal and physical properties of native, naturally fermented (NF), and mixed-culture fermented (MCF) cassava starches was investigated. GMS and SSL decreased hot water-mediated granule swelling and amylose leaching thereby further increasing internal stability of the starches via formation of an emulsifier−amylose complex and granule surface coating. KF had little effect on the rheological behavior of starch pastes. Both the fermentation process and addition of the emulsifying agents would likely also influence the textural properties of cassava starch or flour pastes.

Keywords: *Glycerol monostearate; sodium steroyl lactylate; konjac flour; gelatinization; swelling power*

INTRODUCTION

In many parts of West and Central Africa, cassava (*Manihot esculenta* Crantz) roots are processed into a fermented flour and consumed in the form of a hot water paste called "fufu". The product exhibits undesirable cohesiveness not appreciated by many nontraditional consumers. This is restricting the expansion of consumption of the product outside its traditional base to the detriment of local agriculture (Numfor and Lyonga, 1987; Okezie et al., 1988; Hahn, 1989).

Emulsifiers have become established as agents for the modification of the textural properties of a wide range of starch-based products including pasta, baked goods, and mashed potato products (Krog, 1973; Hoover and Hadziyev, 1981). Some of the properties that these agents are able to control include cohesiveness, or stickiness, and viscosity. In dehydrated mashed potato production, their use is primarily aimed at controlling stickiness.

The success of some emulsifying agents in modifying the texture of potato and baked goods suggests that they could be used to decrease the cohesiveness of pastes made from cassava flour and cassava starch. However, the addition of an emulsifier to starches from diverse plant sources may not result in a similar rheological response. Krog (1973) showed that when distilled monoglycerides were added to potato starch, there was a decrease in viscosity, whereas, when the same emulsifier was added to wheat starch, an increase in viscosity was observed. Eliasson (1986) studied the effects of various emulsifiers on many starches and concluded that the viscoelastic changes during their gelatinization were because of a combination of the properties of the emulsifier, those of the starch to which it was added, and a wide range of other factors such as pH, salts, and heat/shear regimes.

Information concerning the effects of emulsifiers on cassava starch and flour, particularly when fermented, is not abundant. Phan and Mercier (1984) investigated the effects of monoglycerides on native cassava flour paste made from sweet (absence or low concentrations of cyanogenic glycosides) varieties. Moorthy (1985) investigated the effect of several emulsifiers (surfactants) on the properties of commercial cassava starch. In neither investigation was starch from fermented cassava studied. The "bitter" cassava varieties (containing high concentrations of cyanogenic glycosides) are much more commonly used, and their roots must be fermented before they are consumed so that the toxic cyanide concentration can be reduced to innocuous levels. Thus, it is essential to understand how starches which have been fermented interact with commonly used emulsifying agents.

Emulsifiers we selected for this study were of the small molecule and polysaccharide types (Narishman, 1992). Among the small molecule surfactants, we selected glycerol monostearate (GMS) and sodium steroyl lactylate (SSL). Monoglycerols such as GMS form lamellar liquid crystalline structures on food surfaces, thereby reducing van der Waals attraction and enhancing surface mechanical properties (Narishman, 1992). SSL, consisting of the sodium salt of a long-chain fatty acid containing an esterified hydroxyl group, has detergent-like properties in that it is attracted to both nonpolar and polar surfaces. The polysaccharide type we selected was konjac flour. This material is composed of oval sacs 100−500 μm in diameter which swell in water releasing a high molecular weight acetylated glucomanan (Tye, 1991). Suspensions of konjac flour at neutral or slightly acidic pH values is made up of molecular agglomerates which can impart fat-like mouthfeel to food products. This material also interacts with starch and has been used to decrease starch leaching from noodles during heating (Tye, 1991).

The objective of this study was to investigate the effects of two types of emulsifiers on the thermal and physical properties of pastes made from native and fermented cassava starches.

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MATERIALS AND METHODS

Fresh cassava roots of the "red-skin" variety and commercial cassava starch (for comparison purposes) were purchased from a local supermarket. *Bacillus subtilis*, ATCC 33712, and *Candida krusei* were purchased from American Type Culture Collection (Rockville, MD), while *Lactobacillus plantarum* strain LA102 no. 83 was supplied by the USDA Food Fermentation Laboratory (Raleigh, NC). GMS and SSL were supplied by Specialty Industrial Products, Inc., (Spartanburg, SC), while KF was bought from FMC Corporation (Rockland, ME). All other chemicals were of laboratory grade.

Starch Preparation. "Red skin" cassava roots were fermented naturally and by inoculation with a mixed culture containing *B. subtilis*, *L. plantarum*, and *C. krusei* each at 10^6 cells/mL (Numfor et al., 1995). Starch was isolated from unfermented and fermented cassava roots as described by Numfor et al. (1995).

Preparation of Starch−Emulsifier Systems. The method described by Eliasson (1986) was used. GMS was mixed with water (1:10) and allowed to swell at 70 °C for 30 min before being added to the starch at 0, 0.5, 1.0, and 2.0% levels, based on starch dry weight. SSL was also mixed with distilled water (1:10), but allowed to swell at room temperature for 6 h and added to the starch in the same proportions. KF was added to the starches at the same levels, but in the dry state.

Calorimetry. Onset, peak gelatinization temperatures, and enthalpy of the starches were determined using a differential scanning calorimeter Model DSC 4 (Perkin-Elmer Corp., Norwalk, CT). Thermograms were run in sealed, stainless steel DSC pans containing 10 mg of starch mixed with 40 mg of water. Where emulsifiers were used, the required amount of emulsifier was added as a dispersion in the water. A sealed DSC pan containing an equivalent amount of water served as the reference.

Average Granule Diameter. Average granule diameter of starch was measured using a light microscope. A sample (100 mg) of starch was dispersed in 9.9 mL of distilled water and held at 25, 60, or 85 °C in a constant temperature water bath (with constant stirring) for 15 min. Two drops of the suspension were placed on a slide, stained with two drops of 3% iodine solution, and observed using a 40× objective and a micrometer eye piece. Twenty granules were randomly selected and their diameters measured. Each reading was multiplied by 2.75, the constant for the 40× lens to convert to micrometers. Three determinations were made for each sample.

Solubility and Swelling Power. Solubility and swelling power of starch at 85 °C were determined by the method of Leach et al. (1959). Briefly, weighed samples were mixed with a measured volume of water and heated in a temperature-controlled water bath for 30 min with intermittent stirring. After heating, the slurries were centrifuged, dissolved solids measured, and the weight of the residue measured. Swelling power was calculated as the percent weight increase of the swollen starch. Determinations were run on replicates at several water bath temperatures.

Amylography. Amylograms were obtained with a Brabender amylograph Model VAV 3113/67 (C. W. Brabender Instruments, Inc., Hackensack, NJ), as previously described (Numfor et al., 1995) except that emulsifiers were included in the water at the desired levels.

Each procedure described above was conducted on duplicate lots, with the exception of amylography, which was conducted once. For each duplicate lot, three determinations were done. From these data, the mean and standard deviation were calculated for each parameter.

RESULTS AND DISCUSSION

Differential Scanning Calorimetry. No differences in gelatinization peak temperatures were observed when the emulsifiers were added to the starches (Table 1). There was an apparent decrease in the gelatinization onset temperature when GMS was added to the starches. However, it is likely that this was because of an overlap of the emulsifier melting temperature with the gelatinization onset temperature of the starch (Figures 1 and 2). Observed gelatinization enthalpies increased (Table 1) possibly because the melting curve of GMS was superimposed on the gelatinization endotherm of the starch (Figure 2).

The decrease in the gelatinization endotherm in the presence of SSL has been explained as being due to heat uptake during the formation of the amylose−SSL complex that occurs at the starch gelatinization range. The decrease in the gelatinization endotherm was found to be linearly related to the melting endotherm that occurred at around 100 °C. This observation is in agreement with earlier studies (Krog, 1973).

The glucomannan of KF did not interact directly with any of the starches as shown by the absence of any change in enthalpy when KF was heated through the temperature range studied (Figure 2, Table 1). This high molecular weight polymer of glucose and mannose in a molar ratio of 2:3 with β 1,4-linkages (Tye, 1991) apparently is too large to penetrate the starch granule and complex with amylose. Its essentially linear con-

Table 1. Gelatinization Onset Temperatures[a] and Gelatinization Enthalpies of Native and Fermented Cassava Starches in the Presence of Glycerol Monostearate (GMS), Sodium Steroyl Lactylate (SSL), or Konjac Flour (KF)

	type of cassava starch		
emulsifier	native	fermented naturally	fermented with culture
Gelatinization Onset Temperatures (°C)			
none	67.7 ± 0.5	66.8 ± 0.2	69.1 ± 0.9
GMS[b]	62.6 ± 0.5	64.4 ± 2.2	64.9 ± 1.1
SSL	68.2 ± 0.5	67.3 ± 0.5	69.2 ± 1.0
KF	67.8 ± 0.4	67.0 ± 0.5	68.2 ± 0.4
Gelatinization Enthalpies (mJ/mg)			
none	12.8 ± 0.6	14.4 ± 0.8	14.5 ± 0.7
GMS[b]	25.7 ± 3.4	27.4 ± 2.8	27.2 ± 0.6
SSL[b]	9.7 ± 1.2	10.9 ± 0.5	10.7 ± 0.3
SSL (melting)[b,c]	1.8 ± 0.8	1.9 ± 0.2	2.1 ± 0.3
KF[b]	12.5 ± 0.8	13.3 ± 3.1	12.8 ± 0.3

[a] Each value represents the mean and standard deviation for two samples each measured three times. [b] Each emulsifier was added at 1% of starch dry weight. [c] These values represent the melting enthalpies near 100 °C of the amylose−SSL complex formed at the gelatinization temperature range. Amylose−GMS complex did not melt over the temperature range (25−120 °C) studied.

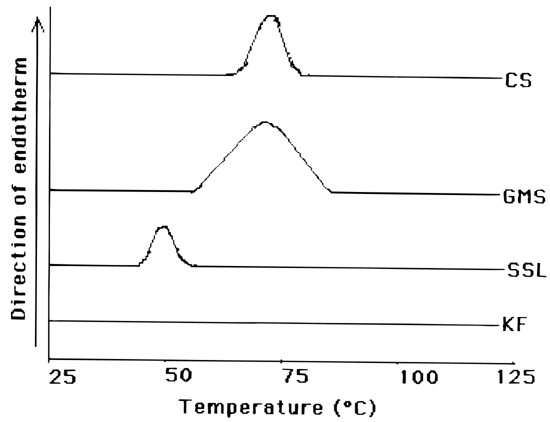

Figure 1. Schematic representation of differential scanning calorimetry (DSC) thermograms of native cassava starch (CS), glycerol monostearate (GMS), sodium steroyl lactylate (SSL), and konjac flour (KF). At a weight fraction of 0.2, melting enthalpies were found to be 12.75, 150.36, 53.63, and 0.00 mJ/mg for CS, GMS, SSL, and KF, respectively.

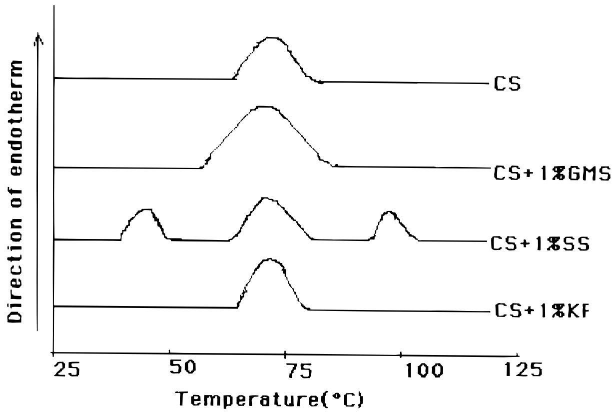

Figure 2. Schematic representation of differential scanning calorimetry (DSC) thermograms of native cassava starch (CS) alone and in the presence of glycerol monostearate (GMS), sodium steroyl lactylate (SSL), or konjac flour (KF).

Table 2. Swelling Power (w/w)[a] at 85 °C of Native and Fermented Cassava Starches in the Presence of Glycerol Monostearate (GMS), Sodium Steroyl Lactylate (SSL), or Konjac Flour (KF)

		type of cassava starch		
emulsifier[b] type	concentration (%)	native	fermented naturally	fermented with culture
none	0.0	28.7 ± 1.5	25.2 ± 0.3	24.3 ± 0.6
GMS	0.5	19.0 ± 0.6	15.9 ± 0.9	13.6 ± 0.2
	1.0	16.4 ± 0.8	14.9 ± 0.6	12.4 ± 0.2
	2.0	13.9 ± 0.6	12.5 ± 0.4	10.0 ± 0.8
SSL	0.5	17.2 ± 0.2	14.0 ± 0.7	15.1 ± 0.1
	1.0	12.6 ± 0.9	13.2 ± 0.5	14.3 ± 0.5
	2.0	11.6 ± 1.3	9.6 ± 1.8	13.4 ± 1.3
KF	0.5	25.9 ± 1.1	22.8 ± 2.9	22.8 ± 1.1
	1.0	24.6 ± 3.4	22.6 ± 2.4	20.6 ± 0.4
	2.0	27.2 ± 2.5	22.7 ± 5.6	17.7 ± 1.1

[a] Each value represents the mean and standard deviation for two samples each measured three times. [b] Percent emulsifier is expressed on starch dry weight basis.

formation (β linkages) would also not allow for intermolecular bonding and resulting optimum alignment with either amylose or amylopectin since α linkages have a tendency to form helices.

Swelling Power, Solubility, and Granule Size. The effect of fermentation and emulsifiers on the swelling power of the starches at 85 °C is shown in Table 2. Native laboratory starch had a swelling power at 85 °C of 28.7%. This is similar to the results obtained by Rasper (1969) and Soni et al. (1985). Moorthy and Ramanujam (1986) have suggested that the swelling power of granules reflect the extent of the associative forces within the granule. The addition of 0.5% of either GMS or SSL dramatically depressed the swelling power of all the starches by over one-third, the effect being greater for SSL and for the fermented starches. Further depression of swelling power was observed with increasing concentrations of GMS and SSL. Hoover and Hadziyev (1981) reported an 80% depression of the swelling power of 0.25% potato starch dispersion when treated with 0.7 mM/100 g (dry starch) of GMS at 85 °C for 30 min. We found that KF had no effect on this parameter.

Solubility values at 85 °C of the native and fermented cassava starches treated with different levels of the emulsifiers are shown in Table 3. Since leaching of amylose is responsible for most of the solubility of starch (Dengate, 1981), lower solubility implies less leaching, which in the fermented product means either that some of the amylose was hydrolyzed and lost during the fermentation process or that its leaching is hindered by new internal bonding. A similar depression of solubility upon addition of both GMS and SSL was observed for the three types of starch. This similar level of complex formation suggests that any loss in amylose during fermentation could have been compensated for by fragments formed by hydrolysis in the amorphous region of amylopectin. These fragments would also be capable of interacting with the emulsifier, thus decreasing solubility.

Table 3. Solubilities (%)[a] at 85 °C of Native and Fermented Cassava Starches in the Presence of Glycerol Monostearate (GMS), Sodium Steroyl Lactylate (SSL), or Konjac Flour (KF)

		type of cassava starch		
emulsifier[b] type	concentration (%)	native	fermented naturally	fermented with culture
none	0.0	29.7 ± 1.3	21.8 ± 2.3	18.5 ± 1.0
GMS	0.5	16.0 ± 0.9	12.0 ± 0.5	13.4 ± 3.7
	1.0	14.2 ± 0.6	6.1 ± 1.1	9.4 ± 1.0
	2.0	8.3 ± 1.1	4.0 ± 0.6	7.5 ± 0.2
SSL	0.5	11.8 ± 0.4	8.5 ± 0.7	13.3 ± 0.8
	1.0	6.3 ± 1.4	6.8 ± 0.8	9.4 ± 1.4
	2.0	6.3 ± 1.4	6.8 ± 0.8	9.4 ± 1.3
KF	0.5	25.2 ± 2.4	17.9 ± 0.6	18.4 ± 1.4
	1.0	18.8 ± 1.7	16.5 ± 1.5	19.0 ± 0.8
	2.0	20.2 ± 2.9	14.9 ± 0.9	17.4 ± 1.6

[a] Each value represents the mean and standard deviation for two samples each measured three times. [b] Percent emulsifier is expressed on starch dry weight basis.

Table 4. Average Granule Diameter (μm)[a] at 85 °C of Native and Fermented Cassava Starches in the Presence of Glycerol Monostearate (GMS), Sodium Steroyl Lactylate (SSL), or Konjac Flour (KF)

		type of cassava starch		
emulsifier[b] type	concentration (%)	native	fermented naturally	fermented with culture
none	0.0	68.5 ± 4.1	54.1 ± 6.8	58.5 ± 3.6
GMS	0.5	40.2 ± 2.6	41.6 ± 5.1	39.9 ± 2.2
	1.0	40.4 ± 2.0	40.1 ± 3.9	36.9 ± 1.8
	2.0	39.6 ± 2.2	40.6 ± 3.8	36.1 ± 2.0
SSL	0.5	41.7 ± 2.4	39.3 ± 5.5	35.3 ± 2.1
	1.0	33.7 ± 1.8	30.2 ± 4.0	29.1 ± 2.0
	2.0	31.5 ± 2.0	29.2 ± 3.4	27.9 ± 1.7
KF	0.5	58.9 ± 4.6	64.3 ± 8.6	56.9 ± 1.8
	1.0	54.6 ± 3.1	50.6 ± 6.8	57.2 ± 4.1
	2.0	53.6 ± 3.5	51.4 ± 6.6	51.8 ± 5.3

[a] Each value represents the mean and standard deviation for two samples each measured three times. [b] Percent emulsifier is expressed on starch dry weight basis. [c] Standard deviations from the mean of granule sizes at 85 °C were adjusted to those at 25 °C to account for natural granule size variation.

The average starch granule diameter of native "redskin" cassava at 60 °C was 41 μm, while diameters of starch from natural and mixed fermentations were lower, being 37 and 35 μm, respectively (data not shown). Addition of GMS and SSL to the starches also at 60 °C resulted in decreased granule diameters ranging from 5 to 30% (data not shown). In this case, however, there was no clear concentration effect in that granule diameter did not decrease in a predictable manner with increased emulsifier concentration. KF addition did not affect starch granule diameters. Since 60 °C is below the gelatinization temperature range of cassava starch and our DSC study indicated that the amylose–emulsifier complex forms only in this temperature range, the only way in which emulsifiers could restrict granule diameter increase with increasing temperature is to coat the granule surface and, thereby, restrain granule expansion. When the temperature of

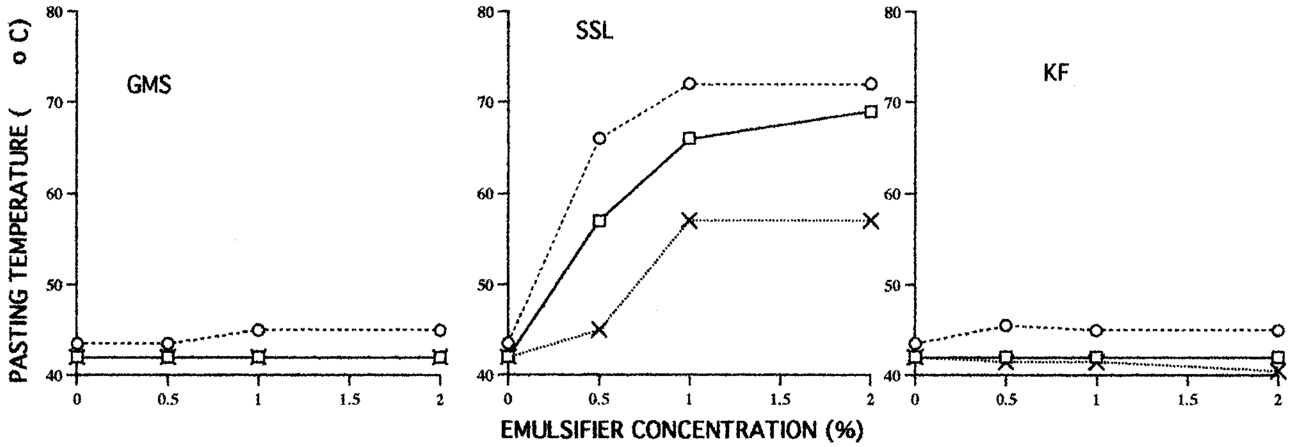

Figure 3. Pasting temperatures of native cassava starch (CS) and fermented cassava starches in the presence of glycerol monostearate (GMS), sodium steroyl lactylate (SSL), or konjac flour (KF): (square) native, (cross) natural, (circle) mixed.

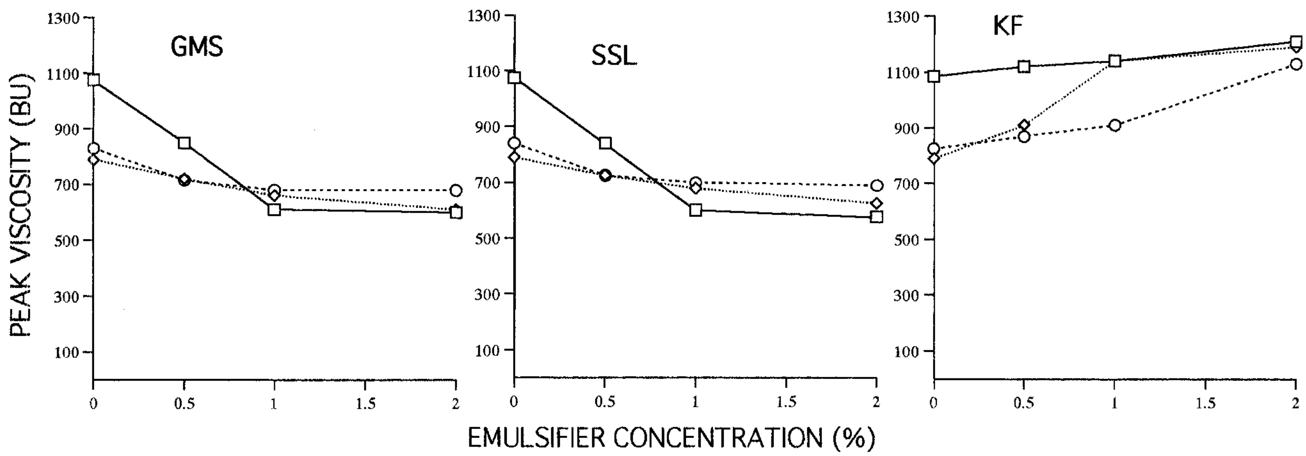

Figure 4. Peak viscosities in Brabender units (BU) of native cassava starch (CS) and fermented cassava starch in the presence of glycerol monostearate (GMS), sodium steroyl lactylate (SSL), or konjac flour (KF): (square) native, (tilted square) natural, (circle) mixed.

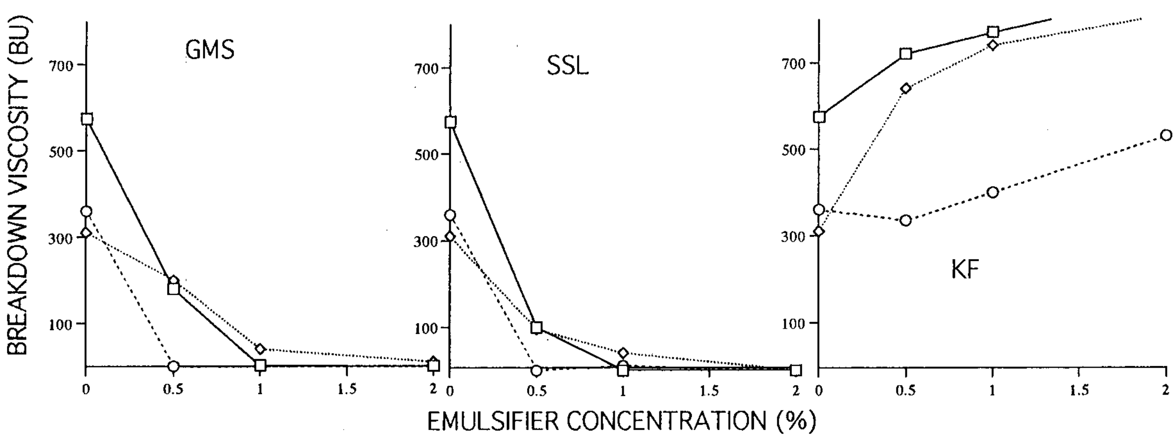

Figure 5. Breakdown viscosities in Brabender units (BU) of native cassava starch (CS) and fermented cassava starch in the presence of glycerol monostearate (GMS), sodium steroyl lactylate (SSL), or konjac flour (KF): (square) native, (tilted square) natural, (circle) mixed.

the mixture was 85 °C, which is above the gelatinization range, increased restriction of granule diameter was observed for starches treated with both GMS and SSL (Table 4) could be the result of both granule coating and formation of the amylose–emulsifier complex. This phenomenon has been verified in photomicrographs by Hoover and Hadziyev (1981) which showed the surface of a potato starch granule heated to 85 °C in the presence of monoglycerides to be coated with the agent, while at the same time no leached amylose was visible.

Brabender Amylography. Brabender amylography showed that only SSL caused increased pasting temperatures (Figure 3). The two emulsifiers, GMS and SSL, form complexes with amylose and also coat the surface of the granules reducing both granule swelling and amylose leaching both of which account for viscosity development. Alternatively, Ghiasi et al. (1982) showed the SSL enters the granule itself and complexes amylose, thereby reducing granule swelling and amylose leaching. Perhaps both phenomena occur. The ease of dispersion of SSL in water compared to GMS would likely account for its greater effectiveness. Increasing

GMS and SSL concentrations decreased peak viscosities (Figure 4) and breakdown viscosities (Figure 5). Increasing concentrations of konjac flour, on the other hand, caused an increase in the breakdown viscosity probably due to the water-binding nature of this polymer. For both peak and breakdown viscosities, the initial values of native starch were more strongly affected by both GMS and SSL than were fermented starches (Figures 4 and 5). This was most likely because the capacity of the fermented starches to swell and for amylose to be leached had been curtailed somewhat by the fermentation process.

Although GMS and SSL are small molecule surfactants, they have very different hydrophile−lipophile balances (HLB). According to Dickinson and Stainsby (1982) HLB values for GMS and SSL are 3.8 and 21.0, respectively. Emulsifiers having values from 3 to 6 function as water/oil emulsifiers and those from 15 to 18 are classified as solubilizers (Tadros and Vincent, 1983). This research has shown that in spite of the differences in the HLB ratios and with the single exception of the pasting temperature, SSL and GMS cause similar changes in the physical properties of native and fermented cassava starch.

Conclusions. The study has shown that for fermented cassava greater internal stability of starch granules, resulting in reduced swelling and decreased amylose solubility during heat treatment, was increased in the presence of GMS and SSL. On the other hand, the glucomannan of KF did not exert any influence on the granules. More studies are necessary to better understand the changes that occur in the cassava starch granule during the fermentation process. Moreover, there is a need to better understand the relationship between the observed rheological changes and textural and sensory properties of the starch and flour pastes.

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