

A Rheological Characterization of Cereal Starch-Galactomannan Mixtures¹

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ABSTRACT

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Wheat and corn starch dispersions with concentrations ranging between 1.5 and 7% were pasted in the presence of guar gum or locust bean gum. These mixtures were characterized by means of a coaxial cylinders viscometer. Flow curves of these starch-galactomannans mixtures were compared with the curves obtained from starch or galactomannan alone. A strong synergistic effect was observed, resulting in a dramatic increase in the viscosity of the mixtures compared with starch or galactomannan alone. A simple model is proposed to interpret such effects. Because starch pastes are described as suspensions of swollen particles dispersed in a macromolecular medium, it is suggested that galactomannans are located within the continuous phase. Thus, the volume of this phase, accessible to

the galactomannan, is therefore reduced. This yields an increase of the galactomannan concentration within the continuous phase and a dramatic increase in the viscosity of the continuous medium owing to the thickening properties of this polysaccharide. Because the overall viscosity of a suspension depends upon the viscosity of the continuous phase as well as on the volume fraction of the dispersed phase, the respective contribution of each phase can be estimated. Validity of this model was supported by experiments where the galactomannan concentration in the continuous medium was kept constant (1%) while the volume fraction of the dispersed phase was varied between 0.1 and 0.9.

Starch/hydrocolloid mixtures are widely used to modify and control the texture of foodstuffs. From a rheological point of view, it is well known that addition of a hydrocolloid (e.g., guar gum, locust bean gum, xanthan gum, carrageenans, carboxymethylcellulose) strongly influences the gelatinization and retrogradation of starch. Understanding such properties will lead to improvements in the formulation of starch based foods. So far, in studies undertaken on starch/hydrocolloid blends, synergistic effects were observed that resulted in a spectacular increase in the viscosity of the mixtures compared with starch or hydrocolloid alone (Crossland and Favor 1948, Sandstedt and Abbott 1964). Christianson (1982) assumed that such effects, as observed by means of viscograph studies, result from at least two phenomena. First, there are interactions between the solubilized starch, amylose, and the other polysaccharide. Second, addition of the thickening agent increases the forces exerted on the granules, thus affecting granule breakdown and the amount of solubilized starch. Recently, Sajjan and Rao (1987) reported on rheological properties of starch/hydrocolloid blends using a concentric cylinders viscometer. The flow curves they obtained were interpreted assuming the hydrocolloid interacts with amylose. Cereal starch pastes can be described as suspensions of swollen particles dispersed in a macromolecular medium (Doublie et al 1987). Swollen particles are mainly composed of amylopectin, whereas the continuous phase contains mostly amylose. The rheological behavior of such a system has been shown to result from a concomitant effect of both the continuous phase and the dispersed phase. The aim of the present investigation is to describe the rheology of cereal starch/galactomannan mixtures on a similar basis, assuming the hydrocolloid to be located mainly inside the continuous phase.

Mero-Rousselot-Satia (France) for experiments with corn starch. The characteristics of the gums are shown in Table I, where M/G is the mannose/galactose molar ratio and $[\eta]$ is the intrinsic viscosity of the gums.

Gum solution was prepared by sprinkling the gum onto the sides of a water vortex. Stirring was continued at slow speed for 1 hr at room temperature; then the solution was heated to 80°C for 0.5 hr while stirring. Finally, the solution was filtered.

Procedures

Starch powder was dispersed in the previously prepared aqueous gum solution. Starch concentrations were within the range 1-5.5% (w/w). The wheat starch/gum dispersions were poured in the bowl of the Brabender Viscograph and heated from 30 to 96°C, kept at this temperature for 15 min, and then cooled to 80°C. The rate of heating and cooling was 1.5°C/min. The rotation speed of the bowl was 75 rpm. In the present experiments, the viscograph was used only as a cooking instrument to prepare pastes. These conditions correspond to those defined in Doublie (1981) as "low (heating) rate, low stirring rate" (LR-LS).

The corn starch/gum dispersion was prepared in a different way: it was heated in a double-walled, round-bottom vessel. Stirring was achieved with an anchor-shaped blade rotating at 200 rpm. The maximum temperature (96°C) was reached in about 15 min. This procedure is characterized by a "high (heating) rate, low stirring rate" (HR-LS). It was shown in a previous study that corn starch pastes are much less susceptible to the heating rate than wheat starch pastes; the HR-LS procedure is in this case comparable to the LR-LS one and preferred to it for practical reasons.

Concentrations of the starch pastes and of the blends were determined by drying aliquots overnight at 103°C.

Viscosity Measurements

Viscosity measurements (on starch pastes, gum solutions, and

MATERIALS AND METHODS

Starch

Wheat and corn starch were obtained from Roquette Frères. They were commercial starches with less than 0.4% protein.

Galactomannans

Pure guar and locust bean gum were supplied by Meyhall-Chemical (Switzerland) for experiments with wheat starch and by

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TABLE I
Characteristics of the Gums

Gum/ Source	% H ₂ O	% Protein (N × 6.25)	M/G ^a	$[\eta]$ ^b (ml/g)
Guar gum				
Meyhall ^c	nd ^d	<1	nd	1,000
MRS ^e	8.32	0.25	1.68	1,200
Locust bean gum				
Meyhall	nd	<1	nd	1,000
MRS	3.37	<0.1	3.8	946

^aMannose/galactose molar ratio.

^bIntrinsic viscosity.

^cMeyhall-Chemical, Switzerland.

^dNot determined.

^eMero-Rousselot-Satia, France.

blends) were performed using a coaxial-cylinders viscometer (Rheomat 30, Contraves, Zurich) with the following specifications for the cylinders: internal radius, 22.9 mm; external radius, 24.2 mm; height, 56.5 mm.

Measurements were carried out at 70°C on pastes immediately transferred from the cooking device. Each sample was submitted to shear rate scans from 0 to 6.60 sec⁻¹ and back to 0 sec⁻¹, and then from 0 to 660 sec⁻¹ and back to 0 sec⁻¹ (in 2 min). So, time dependency ("thixotropy") could be estimated when a loop was obtained between the "up" and the "down" curves. Then the same sample was submitted to stepwise measurements of decreasing shear rates from 660 to about 1 sec⁻¹ (each step was maintained until equilibrium of the shear stress was reached). This procedure allowed the apparent viscosity to be determined with accuracy over almost three decades of shear rates.

RESULTS AND DISCUSSION

Viscograms displayed in Figure 1 illustrate the modification of the consistency profile induced by the presence of galactomannans. The difference between guar gum and locust bean gum can be partly explained by a lower molecular weight of locust bean gum with respect to guar gum.

Figure 2 shows flow curves of a 4% corn starch paste (curve 1), the 0.352% galactomannan solutions (curves 2 and 3) and 4% starch/0.352% galactomannan mixtures (curves 4 and 5). Curve 1 is typical of a cereal starch paste with a pronounced shear-thinning behavior and a thixotropic loop (Doublier 1981). Similarly, curves 2 and 3 were usually displayed by galactomannans in solution with a slight shear-thinning behavior at this concentration and no thixotropy. Curves 4 and 5 exhibit a shape quite similar to starch alone but with a much higher apparent viscosity, which is, at the upper shear rate (660 sec⁻¹), about three times that of starch. Thixotropy appears to be less pronounced in the presence of the hydrocolloid as seen by the area of the loop between the up and down curve; this area is almost the same for curves 1, 4, and 5, whereas the apparent viscosity is more important for the blends. This is related to the absence of thixotropy in galactomannan solutions. Guar and locust bean gum behaved differently. The guar gum mixture exhibited a higher degree of shear-thinning and thixotropy than locust bean gum. However, surprisingly, at upper shear rates their apparent viscosity became of the same order.

A logarithmic plot of these flow curves obtained in the same experiment is shown in Figure 3. The curve for starch alone displays the classical tendency to a yield stress at low shear rates (Evans and Haisman 1979, Wong and Lelievre 1982). Existence of such a yield stress is typical of suspensions and has been ascribed by these authors to the presence of highly deformable swollen particles in the medium. The flow curves for guar gum and locust bean gum are also typical of galactomannans in aqueous solution. Slopes are less than 1, indicating a shear-thinning behavior; the

Newtonian region displayed by such types of solutions towards low shear rates cannot be evidenced due to the low sensitivity of the viscometer, but it does exist. The flow curves of the blends seem to exhibit both types of behaviors. At high shear rates they resemble curves for galactomannans alone, in contrast to the low shear rates where a tendency to a yield stress is exhibited.

Although controversial, microscopic observations (Bowler et al 1980, Williams and Bowler 1982, Varriano-Marston 1985) also give some evidence that a cereal starch paste can be described as a suspension of swollen particles dispersed in a macromolecular medium. Such a biphasic system can be described as follows (Doublier et al 1987): 1) a dispersed phase that is composed of swollen particles mainly constituted of amylopectin is described by the volume fraction of particles, Φ , which depends on their size,

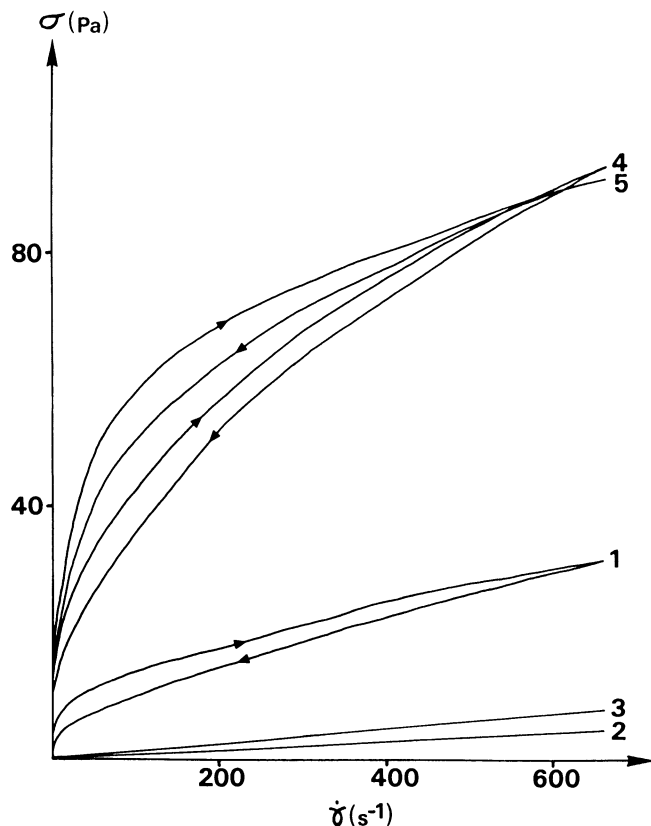


Fig. 2. Flow curves of corn starch-galactomannan blends (in normal coordinates). Temperature: 70°C. 1, Corn starch (4%); 2, locust bean gum (0.35%); 3, guar gum (0.35%); 4, corn starch (4%)/locust bean gum (0.35%); 5, corn starch (4%)/guar gum (0.35%).

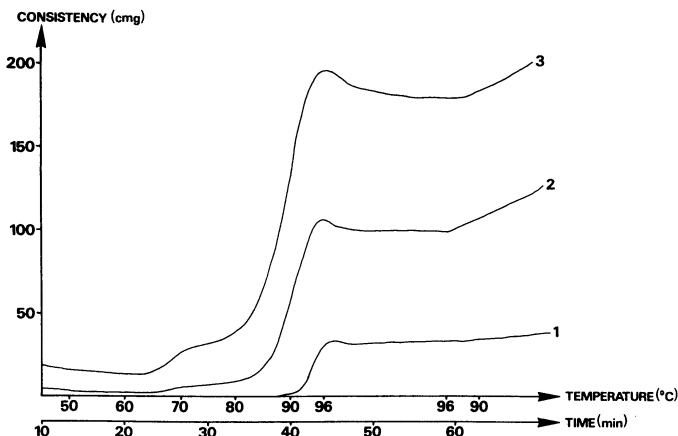


Fig. 1. Brabender viscograms of corn starch-galactomannan blends. 1, Corn starch (4%); 2, corn starch (4%)/locust bean gum (0.35%); 3, corn starch (4%)/guar gum (0.35%).

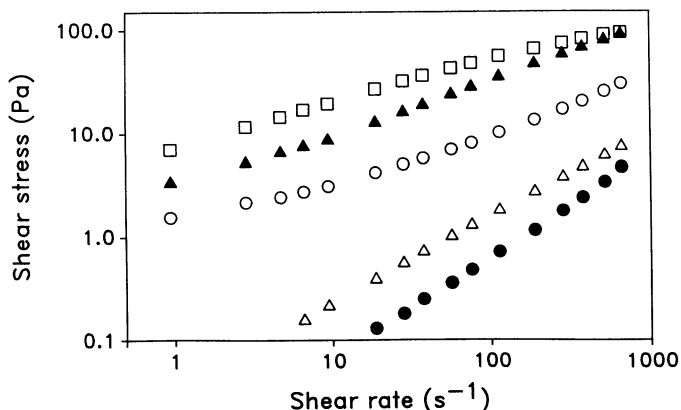


Fig. 3. Flow curves of corn starch-galactomannan blends (in logarithmic coordinates). Temperature: 70°C. o, Corn starch (4%); ●, locust bean gum (0.35%); △, guar gum (0.35%); ▲, corn starch (4%)/locust bean gum (0.35%); □, corn starch (4%)/guar gum (0.35%).

shape and deformability; 2) a continuous phase that contains the soluble macromolecules of the system. During the gelatinization process, starch components, mainly amylose but sometimes a certain amount of amylopectin, diffuse from the granule into the continuous medium. This phase is characterized by C_s , the concentration of soluble macromolecules within this phase.

On the basis of a description initially proposed by Bagley and Christianson (1982), it has been shown that Φ and C_s can be estimated from swelling-solubility experiments on 0.5% starch dispersions (Doublier 1987, Doublier et al 1987):

$$\Phi = (1 - S/100) \times C \times G \quad (1)$$

$$C_s = 1/(1 - \Phi) \times C \times S/100 \quad (2)$$

where S is the solubility index, expressed in g/100 g; C is the starch concentration, in g/g; and G is the swelling index, in g/g.

Thus, in the example given in Figure 2 (starch concentration 4%), we obtain $\Phi = 0.65$ and $C_s = 2.7\%$, with $G = 22$ g/g and $S = 22\%$ for the corn starch sample in HR-LS conditions. The viscosity of a suspension can be roughly written as:

$$\eta = \eta_c \times f(\Phi) \quad (3)$$

The value for η_c , the viscosity of the continuous phase, should be a direct function of C_s . The $f(\Phi)$ function depends on the characteristics of the dispersed phase and is not known yet. Moreover, η_c and $f(\Phi)$ are functions of the shear rate. Hence, equation 3 can only be taken as a useful tool for a qualitative description of starch paste rheology (Doublier 1987).

The same description is proposed for starch/galactomannan mixtures. Using the examples in Figures 1, 2, and 3, before gelatinization takes place the volume fraction is very low ($\Phi < 0.1$) and C_s is negligible. Viscosity of the suspension is thus governed by the concentration of the galactomannan in the continuous phase ($C_h = 0.352\%$). At such a concentration, and owing to the thickening capacities of galactomannans, η_c is not negligible. During the pasting process, we assume that starch swelling and solubilization are not affected by the galactomannan. Also, it is likely that galactomannan molecules remain in the continuous phase, their diffusion inside granules being impossible for

hydrodynamic reasons. Hence, as soon as starch granules swell above the gelatinization temperature (around 60°C), the volume available to galactomannan molecules decreases and their concentration (C_h) in the continuous phase increases up to 0.8% during the first swelling step (between 60 and 85°C). Because viscosity of galactomannans in solution is strongly concentration dependent ($\eta \propto C_h^3$), it is clear that the first swelling at 60°C yields an important increase of the viscosity of the continuous phase, η_c , and then of the medium by way of equation 3. This explains the appearance of the first swelling step on viscograms at around 60°C.

The second swelling step above 85°C is characterized by the solubilization of most of the amylose. Then the final characteristics of the starch/galactomannan mixtures of Figures 1-3 would be: volume fraction of swollen particles, $\Phi = 0.65$; amylose concentration in the continuous phase: $C_s = 2.7\%$; galactomannan concentration in the continuous phase: $C_h = 1\%$.

From η_{sp0} versus concentration curves at 75°C reported by Kalichevsky et al (1986) for amylose (with $\eta_{sp0} = [\eta/\eta_s] - 1$; η_s is the viscosity of the solvent) we can estimate that (η_0) the viscosity at very low shear rate is of the order of 2 mPa·sec for amylose at 2.7%. The viscosity at low shear rate (η_0) of the gums (concentration 1%) is about 0.2 Pa·sec at 70°C, that is two orders of magnitude higher. Thickening properties of amylose thus being very low compared to the galactomannans, we assume that η_c , viscosity of the continuous phase, is mainly determined by the galactomannan viscosity, η_h . It nevertheless remains to be demonstrated that the presence of amylose does not affect the galactomannan rheology.

In order to verify the validity of our assumption, we performed

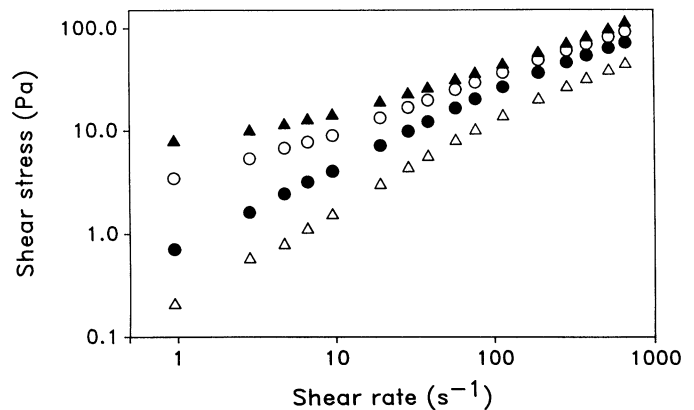


Fig. 4. Flow curves of corn starch - locust bean gum blends (in logarithmic coordinates). Temperature: 70°C. Gum concentration in the continuous phase: 1% (Table II). Δ , Locust bean gum (1%); \bullet , starch (2%)/locust bean gum (0.68%); \circ , starch (4%)/locust bean gum (0.35%); \blacktriangle , starch (5.5%)/locust bean gum (0.11%).

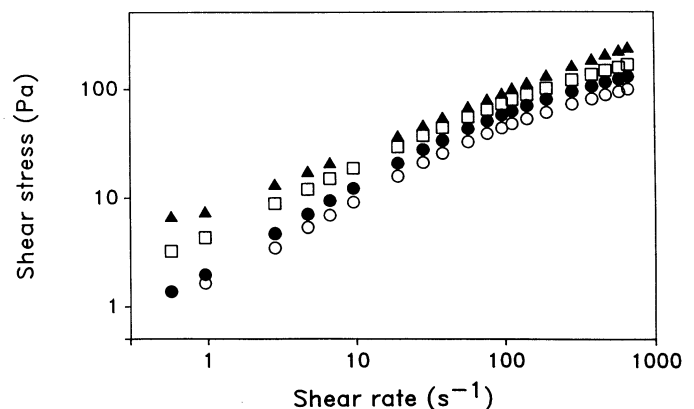


Fig. 5. Flow curves of wheat starch-locust bean gum blends (in logarithmic coordinates). Temperature: 70°C. Gum concentration in the continuous phase: 1% (Table III). \circ , Locust bean gum (1%); \bullet , starch (1.5%)/locust bean gum (0.84%); \square , starch (5%)/locust bean gum (0.47%); \blacktriangle , starch (7%)/locust bean gum (0.26%).

TABLE II

Estimation of Gum Concentration in Corn Starch/Gum Mixtures^a

Corn Starch Concentration (%)	Φ Predicted	C_i Initial Gum Concentration (%)
1	0.162	0.838
2	0.324	0.676
3	0.486	0.514
5	0.647	0.352
5.5	0.890	0.110
6	0.971	0.029

^aWith $C_i = (1 - \Phi) C_h$.

TABLE III

Estimation of Gum Concentration in Wheat Starch/Gum Mixtures^a

Wheat Starch Concentration (%)	Φ Predicted	C_i Initial Gum Concentration (%)
1	0.105	0.895
1.5	0.160	0.840
2	0.210	0.790
3	0.315	0.685
4	0.420	0.580
5	0.520	0.475
7	0.735	0.265

^aWith $C_i = (1 - \Phi) C_h$.

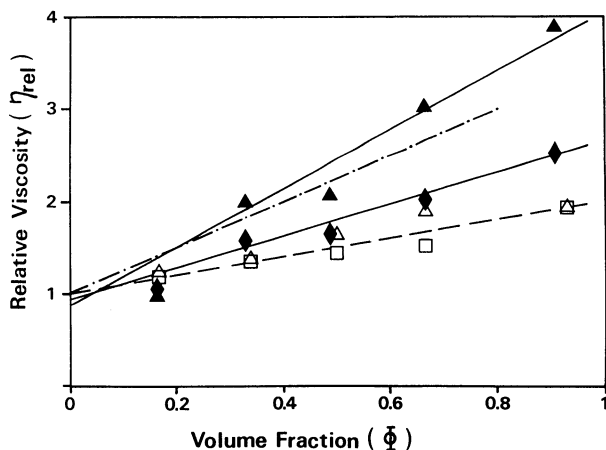


Fig. 6. Relative viscosity η_{rel} as a function of the volume fraction Φ (see text). Locust bean gum: —▲—, 57 sec^{-1} ; —◆—, 660 sec^{-1} . Guar gum: --△--, 57 sec^{-1} ; - -□- -, 660 sec^{-1} ; - · - · - ·, Einstein relation.

two series of experiments in which the final galactomannan concentration in the continuous phase was predicted constant at 1%, while Φ was varied. For this purpose, starch/galactomannan mixtures were prepared in which starch concentration was varied between 1 and 6%. In the meantime, the initial gum concentration was chosen in order to yield 1% of gum in the continuous phase after pasting. This is illustrated in Table II for corn starch. These predictions arise from equation 1, the swelling-solubility parameters (S and G) being obtained on 0.5% starch dispersions. Figure 4 shows the results obtained with corn starch and locust bean gum in this way. The flow curves are compared to that of locust bean gum at 1% to estimate the effect of the swollen particles on the viscosity of the mixture. It is clear that all curves of the blends are located above the curve for the locust bean gum alone. Furthermore, these curves are in increasing order when increasing corn starch concentration, that is when increasing Φ . The volume fraction and the viscosity of the mixture vary in the same way. Wheat starch/galactomannan mixtures resulted in a similar pattern. This is illustrated in Figure 5 for wheat starch/locust bean gum systems. Since the swelling-solubility values are different for wheat starch, these experiments were performed for starch concentrations given in Table III, with the locust bean gum concentration in the continuous phase predicted to be 1%. Figure 6 shows the relative viscosity ($\eta_{rel} = \eta_{blend}/\eta_{1\%}$) at two shear rates (56.7 and 660 sec^{-1}) as a function of Φ for guar gum and locust bean gum with corn starch. Even if there is not an excellent correlation between η_{rel} and Φ , it is observed that η_{rel} seems indeed to tend to 1 when Φ tends to 0. This is expected when dealing with a suspension of particles. Then, the η_{rel} variations give an indication of the $f(\Phi)$ function. These variations are low when compared to what is classically reported on the rheology of suspensions. As an indication, the well-known Einstein relation ($\eta_{rel} = 1 + 2.5 \Phi$) would yield the curve shown as the line of dashes and dots in Figure 6. This relation is valid for a limited Φ range ($\Phi < 0.1$), and variations of η_{rel} of most suspensions are reported to be more important. The slight Φ dependence displayed by these starch/hydrocolloid mixtures may originate from a high deformability of the starch particles in the suspensions. These are highly hydrated and thus highly swollen and deformable.

There is, however, a point that ought to be discussed further. As illustrated in Figures 2 and 3, guar gum and locust bean gum yield quite different flow curves in the presence of starch. The rheological properties of these two galactomannans are known to be similar, although their chemical structure is slightly different via their mannose/galactose ratios. The difference in their rheological behavior in blends thus suggests that synergistic effects are also influenced by the chemical structure of the galactomannan in the continuous phase. Christianson et al (1981) suggested the existence of amylose-galactomannan interactions; their strength would

depend on the chemical structure of the galactomannan, and the mannose/galactose ratio particularly. Another interpretation can be based on the possibility of an incompatibility between amylose and galactomannan macromolecules. Such a phenomenon, which was described by Kalichevsky et al (1986, 1987) for amylose/dextran and amylose/amylopectin mixtures, would yield a further phase separation and then a modification in the rheology of the "continuous" phase. Also, structural parameters, particularly molecular weight, may be involved in the overall process.

CONCLUSION

This work deals with the description of the dramatic synergistic effect of galactomannans on the rheology of starch pastes. The basic assumption is that the hydrocolloid is present only in the continuous phase of the medium, which yields an artificial concentration of the gum in this phase. We suppose that the presence of the gum does not affect the swelling-solubility characteristics of starch. Based on viscosity measurements, we showed that such an assumption seems to be valid. Vicinity of amylose and galactomannan molecules in the same phase and possible interactions between these two components are, however, to be taken into account in the overall phenomena and could explain the differences observed between the flow behaviors of starch-guar gum and starch-locust bean gum systems. Then, although the present study allows a basis for the study of starch/hydrocolloid mixtures, further work is required to describe more completely such intricate macromolecular systems.

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