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Steady flow and viscoelastic behavior of crosslinked waxy corn starch-κ-carrageenan pastes and gels

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Abstract

The steady and small-deformation shear behaviors of 2–4 wt.% cross-linked waxy corn starch (CWCS) and 0.5 wt.% κ-carrageenan (κC) mixtures have been studied. In some cases κC gelation was induced by the addition of 20 mM KCl and cooling to 25°C. Rheological behavior was interpreted considering swelling-solubility as well as laser diffraction particle size and size distribution data. CWCS was chosen because it lacks amylose and its granules can swell without disruption under appropriate thermal conditions; thus the condition of particles dispersed in a continuous phase can be best fulfilled. Dispersions were heated (1.5°C/min) to 96°C, held for 10 min, then cooled (1.5°C/min) to 80°C. Steady tests were carried out at 60°C and oscillatory tests were carried out at 60 and 25°C. Only more concentrated dispersions displayed an anticlockwise up–down shear loop, which was enhanced by κC and KCl. Hysteresis disappeared with continuous shearing, and shear-thinning was observed with CWCS + κC being more viscous than CWCS + κC + KCl and CWCS. Oscillatory tests at 60°C showed that dispersions exhibited a predominantly solid-like behavior which was attenuated at lower starch concentrations and when κC and KCl were added. At 25°C, trends were similar but with slightly greater G' and accentuated elastic character at higher starch concentrations. KCl-containing media formed gels whose rigidity depended on starch concentration. Solubility was low ($<2\%$) and swelling increased from 25.3 g/g up to 29.6 g/g when κC was added, irrespective of starch concentration. Particle size data also showed higher swelling power in κC-containing media. Results could be interpreted in terms of two types of systems; particles suspended in a macromolecular solution and composite gels of particles embedded in a network matrix when both κC and KCl were added.

Keywords: Crosslinked waxy corn starch; κ-carrageenan mixture; Starch–hydrocolloid mixtures

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1. Introduction

Blends of cereal starches and other polysaccharide molecules have been used for many years in the food industry (Descamps, Langevin & Combs, 1986). Arabic, guar, xanthan, carboxymethylcellulose, locust bean and carrageenan gums are some of the macromolecules commonly combined with either wheat or corn starch. One of the appealing aspects of starch–hydrocolloid mixtures is that they show a variety of rheological and texture-imparting properties not only suitable for, but also helpful to decide different applications in food products (Eidam, Kulicke, Kuhn & Stute, 1995). For this reason their rheological behavior has deserved increasing attention; however, a large deal of work has focused on mixtures with native corn starch because of its technological importance.

It is generally accepted that cooked starch aqueous media can be described as biphasic systems formed by a continuous and a disperse phase. In the case of native starch, the former is essentially an aqueous solution of amylose leached during granule swelling, while the latter is constituted by swollen normal starch granules (Bagley and Christianson, 1982; Doublier, 1987; Ellis, Ring & Whittam, 1989). When severe cooking and shear conditions are employed, the resulting paste can be a mixture of swollen and fragmented granules, starch molecules in solution and in colloidal dispersion, then the suggested simplified two-phase picture may not be appropriate to describe the cooked starch paste (Loh, 1992). However, in many practical situations swollen starch particles are the dominant structural feature (Steeneken, 1989). In mixed systems, the picture remains the same but a further complication arises from the fact that the continuous phase is itself an aqueous mixture of amylose

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and added hydrocolloid; this, without considering the possible solubilization of amylopectin during pasting. This situation complicates further the analysis and characterization of these mixtures.

The rheology of starch–hydrocolloid combinations is particular to each mixture and depends on experimental conditions, namely, those involved in paste preparation. Therefore, it is necessary to determine it for each particular case. The literature on the rheology of starch–hydrocolloid systems is less abundant than that on starch alone and is dominated by the study involving native corn or wheat starch mixed with thickening hydrocolloids (Appelqvist & Debet, 1997). The most important aspects examined are their steady flow and dynamic viscoelastic behavior. Depending on its thickening capacity, addition of a given hydrocolloid usually results in a noticeable increase of starch alone viscosity. This behavior proved to be the result of an increase in hydrocolloid concentration in the continuous phase, derived from starch swelling, in hot native starch–galactomannan (guar or locust bean gums) dispersions (Alloncle, Lefebrve, Llamas & Doublier, 1989). However, in uncrosslinked and crosslinked waxy maize starch–xanthan mixtures, the observed increase of dynamic moduli upon progressive addition of starch to solutions of xanthan could not be completely explained by this continuous-phase-increased-concentration scheme and it has been speculated that depletion flocculation mechanisms might be involved (Abdulmola, Hember, Richardson & Morris, 1996b).

The dynamic viscoelastic properties of starch–hydrocolloid systems change in a more subtle way. Unlike viscosity, moduli do not necessarily show spectacular changes when different amounts of hydrocolloid are added and starch concentration is kept constant as observed in native maize starch–xanthan systems (Alloncle & Doublier, 1991). Further, sometimes partial substitution of starch by a given hydrocolloid even results in lower storage and higher loss modulus than starch alone dispersions of equal total concentration (Eidam et al., 1995).

Considering the two-phase picture mentioned earlier, one important fact is that the rheological properties of these systems are determined by both the concentration (or volume fraction) of the disperse phase and the rheological behavior of the continuous phase. In this sense, the behavior of the latter becomes more complex when two macromolecules are present; it has been shown that interaction (or lack of it) between amylose and galactomannans plays an important role in the rheological response of pastes and gels, and also on the kinetics of gel formation (Alloncle & Doublier, 1991). While in general, addition of hydrocolloid accelerates gel formation of native maize starch, some of them (i.e. iota carrageenan) have been reported to retard it (Eidam et al., 1995). Interactions are thus complex, and it has been recognized that modifications resulting from hydrocolloid addition to starch ought to be considered in the light of thermodynamic incompatibility phenomena at least when amylose is present. While it has been possible to get valuable information on the rheological behavior of native starch–hydrocolloid mixtures, interpretation of results on a structural basis is far more complex.

On the contrary, modified starches also find important industrial applications but their rheological properties either alone or mixed with another component have deserved less attention than their native counterpart. As pointed earlier, only few reports deal with crosslinked waxy corn starch (CWCS) mixed with gelatin (Abdulmola, Hember, Richardson & Morris, 1996a) or xanthan (Abdulmola et al., 1996b). CWCS is an interesting material because it is free of amylose and because chemical modification makes it more resistant to thermal and mechanical treatment. Therefore, it is possible to use conditions that promote granule swelling without destruction, avoiding the presence of amylopectin in the continuous phase. Actually, partial solubilization of this component may occur during pasting, but it is in general so low that it is not expected to influence the rheology of this phase. With this type of starch, it can be reasonably considered that swelled granules are dispersed in a phase constituted only by either water or an aqueous solution of the added hydrocolloid. It has proved to be appropriate for studying the application of polymer blending laws because the volume fraction of each phase is easier to determine than in non-particulate systems (Abdulmola et al., 1996a). It also offers the possibility of studying the effect of the added hydrocolloid without having the complexities normally existing when amylose is present. Considering this, and the technological importance of its combination with κ-carrageenan (κC) in the food industry, it is the aim of this work to study the rheological behavior of CWCS–κC mixtures, which form an amylose-free two-phase system, in order to get a better understanding of the interaction between components under gelling and non-gelling conditions of κC. For such purposes we combined rheological measurements with techniques providing the degree of granule swelling as well as particle size and size distribution.

2. Materials and methods

2.1. Materials

The CWCS (Clearam® CH10, lot E9887) was an adipate/acetate starch supplied by Roquette Frères. The κC sample was a gift from SKW Biosystems (France); it contained (mg/g) 121.2 Na^+, 65.2 K^+, and less than 1.0 of Ca^{+2} and Mg^{+2} (provided by the supplier) and was used as is. Analytical grade KCl (Merck) and deionized water were used throughout.

2.2. Pasting procedure

Starch was slurried in water at room temperature (∽20°C) with continuous stirring with a spatula to avoid settling. In

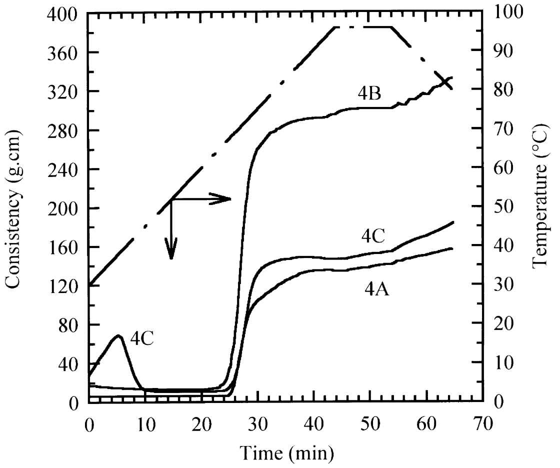

Fig. 1. Brabender profiles of 4% starch pastes (see Table 1 for sample identification). The discontinuous line shows the thermal history of pasting. The earlier peak of sample 4C was due to carrageenan solubilization; it appeared for all starch concentrations, but only when KCl (20 mM) was present and components were dry mixed before slurrying and pasting.

the case of mixtures, two procedures were tested: (1) κC was first dispersed in water with or without KCl under magnetic stirring, heated to 60°C for 45 min and cooled to ambient temperature; then, starch was slurried in the κC solution; (2) all components were well dry blended prior to slurrying in water. In both cases slurries were stirred with a spatula as long as needed to avoid formation of lumps. Both procedures resulted in equal pasting profiles (Fig. 1) with the only difference of a peak that always appeared at about 38°C when procedure (2) was used, but only when KCl was present. The peak was the result of an increase of viscosity due to κC solubilization followed by a decrease produced by increasing temperature; DSC traces showed 38°C to be the temperature at which a conformational transition of κC took place. Either (1) or (2) resulted in equal rheological properties, therefore, they were considered equivalent. A total mass of 485 g of the resulting slurries was pasted in the Brabender® Viscograph-E (Mod. 8 025) at a bowl speed of 75 rpm, and was gradually heated (1.5°C/min) to 96°C, then held at this temperature for 10 min and cooled (1.5°C/min) to 80°C. The viscograph was only used as a cooker and to monitor consistency changes during pasting. Dry-weight concentrations were: CWCS 2, 3 and 4%; κC 0.5%. In some slurries, 20 mM KCl was added to induce κC gelation upon cooling. Pastes were prepared at least in duplicate. Starch preparations were identified as indicated in Table 1.

Table 1
Identification of starch pastes

Preparation	2%[a]	3%	4%
CWCS	2A	3A	4A
CWCS + κC[b]	2B	3B	4B
CWCS + κC[b] + KCl[c]	2C	3C	4C

[a] Indicates starch concentration in the mixture.

[b] κC concentration = 0.5%.

[c] KCl concentration = 20 mM.

2.3. Solubility-swelling determination

Terminal swelling and solubility were determined in quadruplicate by taking a mass of the starch dispersion pasted under the above conditions and diluting with hot solvent (either water or 20 mM KCl at ~ 60°C) to a final weight concentration of 0.5%. After cooling, 8 ml of dilution were centrifuged at 2200 rpm (700 g) for 15 min (Leach, McCowen & Schoch, 1959), and 8 ml were dried overnight at 100°C to get the dry mass of starch. Solubility, *S*, was referred to the mass of dry starch and determined from the concentration of soluble starch in the total volume of supernatant (Doublier, 1981) which was quantified by the orcinol-sulphuric method (Tollier & Robin, 1979). As this method quantifies total sugars, *S* was corrected when required by running a blank of κC. Granule swelling, *G*, was calculated from the mass of centrifuged residue and the mass of dry starch corrected by the amount of soluble material and the presence of κC.

2.4. Particle size and size distribution

Particle size determination was run at least in duplicate at room temperature using a Malvern Master SizerS (Malvern Instruments, Ltd.) laser diffraction analyzer with a 300 mm Fourier cell (range 0.5–878.7 μm) and the Small Volume Sample Dispersion Unit (SVSDU). At the end of pasting, the starch dispersion was diluted (1/2) in hot solvent and cooled to ambient temperature. Then, 0.1 ml was dispersed in 100 ml of water in the SVSDU, stirred for few seconds and fed to the measuring cell. Thus, depending on the initial amount of starch, final concentrations ranged from 1×10^{-3} to 2×10^{-3} (w/v)%. The instrument outputs a volume distribution as the fundamental measurement, as well as standard mean $D[4,3]$ (Herdan), $D[3,2]$ (Sauter), and median $D[v,0.1]$, $D[v,0.5]$, $D[v,0.9]$ diameters. However, it is also possible to get a number distribution and a number mean diameter $D[1,0]$. These derived outputs are numerical transformations of diffracted light angles using Mie's theory and assuming spherical particles (Malvern Insruments Ltd., 1990). In this work the median diameter, $D[v,0.5]$; the size at which 50% of particles by volume are smaller and 50% are larger, was chosen simply to allow comparisons with literature data (Ziegler, Thompson & Casasnovas, 1993). Laser diffraction requires media of different refractive indices. We used 1.5295 and 1.3300 as the refractive index of starch and liquid phase, respectively, with 0.1 absorption for starch particles. These figures have proved to yield reproducible and consistent results in starchy materials (Loisel, Fayolle, Cantoni & Doublier, 1997) and were assumed not to change even by the presence of carrageenan because of sample dilution.

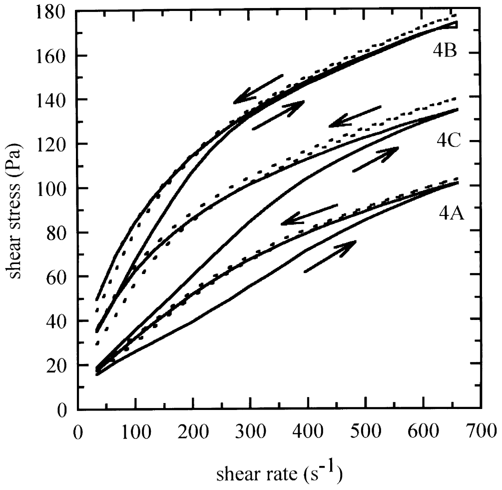

Fig. 2. Flow curves of 4% starch pastes at 60°C. Dotted lines indicate the second up–down shear scan.

2.5. Rheological measurements

Steady shear tests were carried out at 60°C with a rotational viscometer (Rheomat 120, Contraves) in a coaxial-cylinders fixture (diameters: bob = 46 mm, cup = 49 mm, height: 78 mm). Two consecutive up–down shear scans from 0 to 660 s^{-1}, followed by a descent from 660 to 0.1 s^{-1} were applied in a total time of 12 min. Low amplitude oscillatory shear tests were carried out in a stress rheometer (Carrimed CS50, Carri-Med) using either cone/plate (diam. 6 cm, angle 4°) or grooved parallel plates (diam. 4 cm, gap 1 mm). Some samples were tested in a strain rheometer (Fluids Spectrometer RFS II, Rheometrics) using either cone and plate (diam. 5 cm, angle 0.04 rad) or parallel plates (diam. 5 cm, gap 1 mm). Gap adjustment considered thermal expansion and the fixture rim was covered with paraffin oil to prevent evaporation. Strain sweeps were carried out to determine the zone of linear viscoelasticity. The following in-sequence protocol was used for each preparation: (1) a mechanical spectrum at 60°C, (2) a gel-cure experiment at 25°C, and (3) a mechanical spectrum at 25°C. Samples were quenched from 60 to 25°C using the Peltier element of the rheometer.

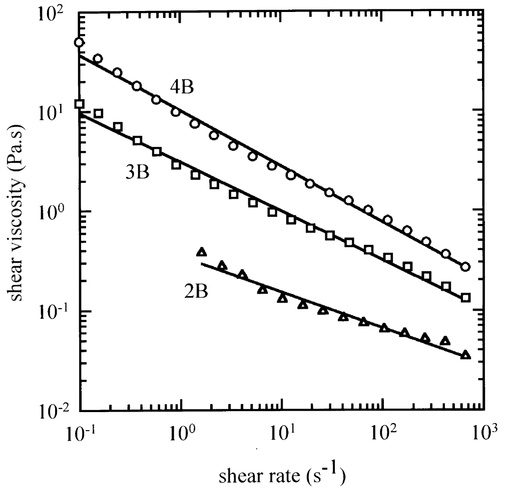

Fig. 3. Shear viscosity at 60°C of CWCS + κC mixtures with different starch concentration. Lines represent power-law regressions with values of K and n given in Table 2.

Table 2
Power-law parameters of starch dispersions at 60°C. Percentage indicates starch concentration in the mixture

Dispersion	K (Pa s^n)	n	r^2
4% A	5.02	0.41	0.9819
B	10.26	0.44	0.9941
C	5.30	0.52	0.9936
3% A	0.57	0.54	0.9983
B	3.11	0.51	0.9921
C	1.76	0.48	0.9707
2% A	0.01[a]	1.0	–
B	0.25	0.71	0.9817
C	0.11	0.79	0.9765

[a] Viscosity in Pa s.

3. Results

3.1. Pasting profiles

Brabender profiles, though not rigorously representing viscosity, are useful to obtain qualitative information on the behavior of starch dispersions during pasting. Pastes B and C had higher consistencies than paste A, irrespective of starch concentration. Fig. 1 shows the differences observed in 4% starch pastes. The swelling temperature, taken as that at which consistency began to increase, was slightly lower (~64°C) in B than in A and C (~66°C). All pastes displayed a rapid swelling, followed by a smooth transition to a slowly increasing zone that extended up to the holding and cooling periods indicating good thermal stability. Pastes with 3 and 2% starch had lower consistencies but their traces kept the same relative position and shape as those shown in Fig. 1.

3.2. Flow behavior of hot pastes

Except 2A, all pastes exhibited non-Newtonian behavior the extent of which depended on their composition. Fig. 2 shows the flow properties of 4% starch pastes. The first up–down scan (continuous line) resulted in an anti-clockwise loop. This behavior was also observed in pastes 3B and 3C, but it was not present in 3A and all 2% starch pastes. In fact, 2A exhibited a Newtonian behavior with a viscosity of about 10 mPa s at 60°C. The relative position of flow curves was similar to that observed in the Brabender regardless of starch concentration. The degree of hysteresis was particular to each mixture; 4C exhibited higher hysteresis than 4A and 4B, while 3B did it over 3A and 3C. Hysteresis essentially disappeared upon continuous shearing as shown by the

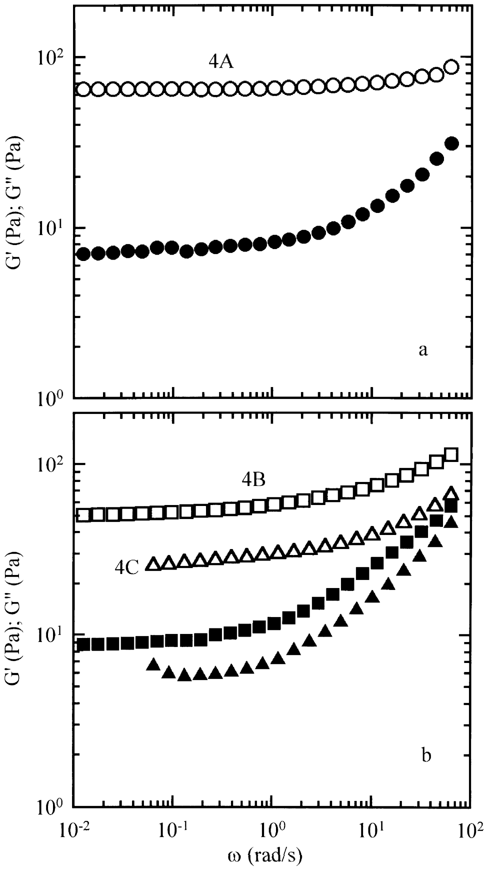

Fig. 4. Mechanical spectra of 4% starch pastes at 60°C and 4% strain. G' (hollow), G'' (solid).

second scan (dotted line), which always lay on the descending portion of the first one. In pastes formed from starch alone, a limit starch concentration seemed to exist beyond which hysteresis developed; results suggest the limit to lie above 3% starch. In the mixtures the limit was shifted to lower starch concentrations and under the conditions tested it was closer to 2%. This simply means that in the absence of κC, hysteresis appeared at higher starch concentrations, while in its presence it did it at lower concentrations. Therefore, the viscosity of the continuous phase played a role in the appearance of such behavior. After the two consecutive up–down scans shear-thinning behavior was observed as shown in Fig. 3. However, the power law relationship $\eta = K\dot{\gamma}^{n-1}$ did not fit the data satisfactorily as shown by the regression lines in Fig. 3 and the r^2 values in Table 2. The upward curvature observed at low shear rates is typical of starch suspensions which normally exhibit high viscosities in this region. Some authors (Giboreau, Cuvelier & Launay, 1994) have described the behavior of hot (60°C) modified starch pastes in terms of a “pseudo-yield stress” on the basis of dynamic and creep experiments. The latter revealed the existence of incipient Newtonian flow at long times, while the former exposed a gel-like behavior at short times. Whether a yield value actually exists is not a clear matter, not only because of the difficulties in determining it, but also because it is not possible to generalize it even for the same material. This is especially true for starch pastes whose properties are very sensitive, among other things, to pasting conditions. Nevertheless, it is clear that for a given constant starch concentration, K of the B pastes was higher than for C and A, while as the starch concentration increased in the mixture, fluids were more shear-thinning.

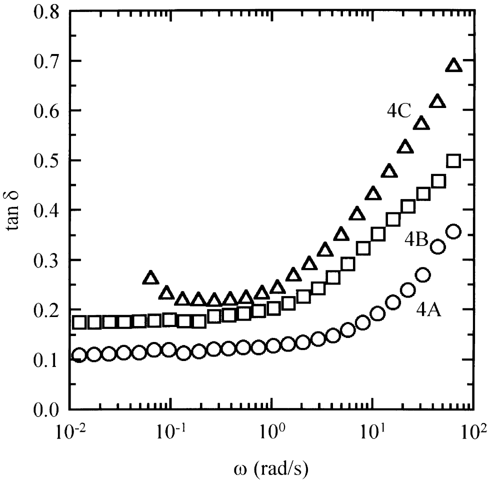

Fig. 5. Loss angles of 4% starch pastes at 60°C and 4% strain.

3.3. Viscoelastic behavior at 60°C

The viscoelastic properties of hot pastes were sensitive to both the starch concentration and the presence of carrageenan and KCl. Such sensitivity depended, however, on their relative proportion in the mixture. Fig. 4 illustrates the viscoelastic behavior of 4% starch dispersions. All of them were pourable materials with a liquid more than solid aspect, yet 4A and 4B exhibited seemingly a solid-like behavior with $G' > G''$ and both independent of frequency below 1 and 0.1 rad/s, respectively. Unlike Brabender and steady shear flow behavior, dynamic oscillation revealed that addition of carrageenan did not increase the moduli of mixtures over that of starch alone. In fact, 4C displayed lower and more frequency-dependent moduli. The overall behavior of 4A was dominated by the elastic component, while 4B and 4C had higher and more frequency-dependent loss angles as shown in Fig. 5. Significant differences were observed in 3% starch dispersions as depicted in Fig. 6. Pastes 3A still exhibited a seemingly solid-like behavior mainly at low frequencies. However, G' exhibited a rather unexpected behavior, decreasing first and then increasing continuously with frequency. The predominant elastic response of pastes 4A and 3A can be attributed to swollen granules; however, in 3A the loss angles were higher because of the lower starch concentration. Addition of carrageenan with or without KCl modified substantially the viscoelastic properties of 3% starch alone dispersions. Dispersions 3B exhibited very well defined spectra showing an over-crossing of moduli at about

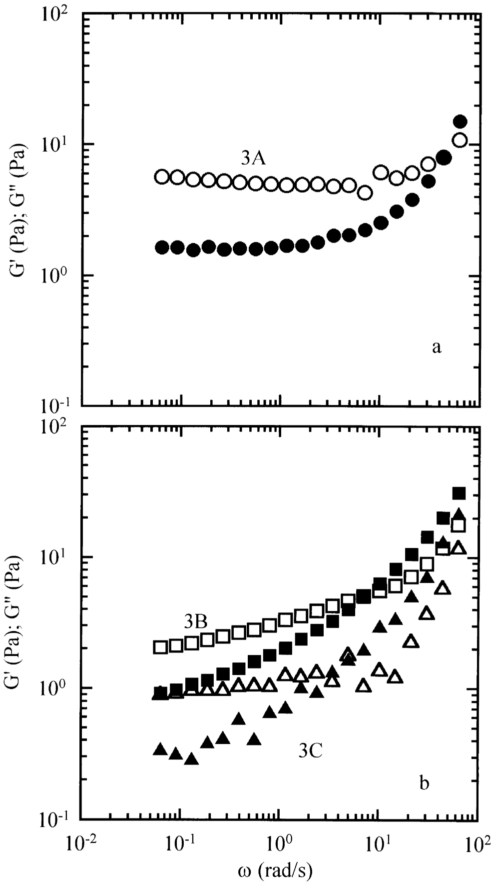

Fig. 6. Mechanical spectra of 3% starch pastes at 60°C and 4% strain. G' (hollow), G'' (solid).

7.0 rad/s; below this value $G' > G''$, while at higher frequencies G'' predominated slightly over G'. The overall higher dependence of moduli with frequency suggests a more fluid than rigid system. In the presence of KCl the same general trend was observed although with lower moduli and rather dispersed values at lower frequencies. The loss angles of 3A dispersions were similar to those of 4A (Fig. 5). The corresponding loss angles of the mixtures were much dependent on frequency with values superior to starch alone. The spectra of 2A dispersions could not be

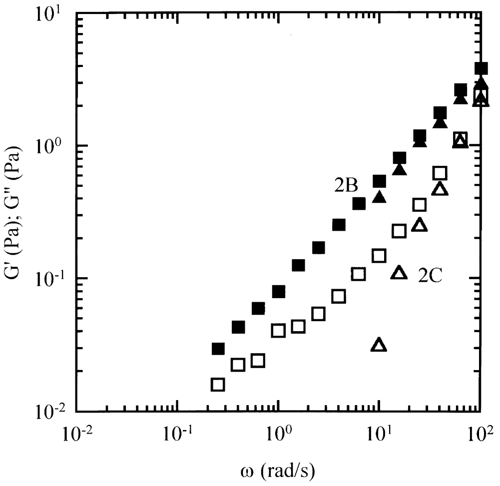

Fig. 7. Mechanical spectra of 2% starch pastes at 60°C and 20% (2B), 4% (2C) strain. G' (hollow), G'' (solid).

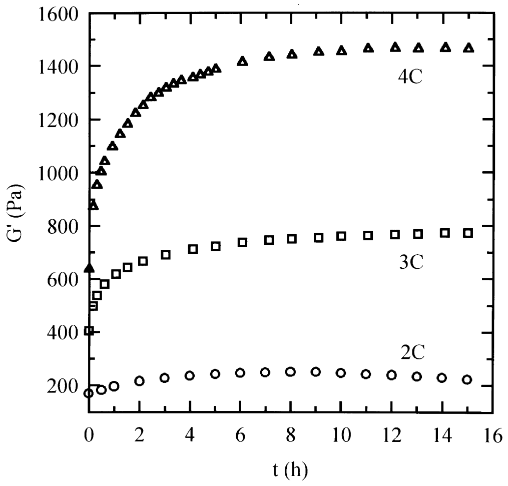

Fig. 8. Change with time of dynamic moduli of CWCS + κC + KCl dispersions with different starch concentration. Strain 4%, frequency 6.28 rad/s.

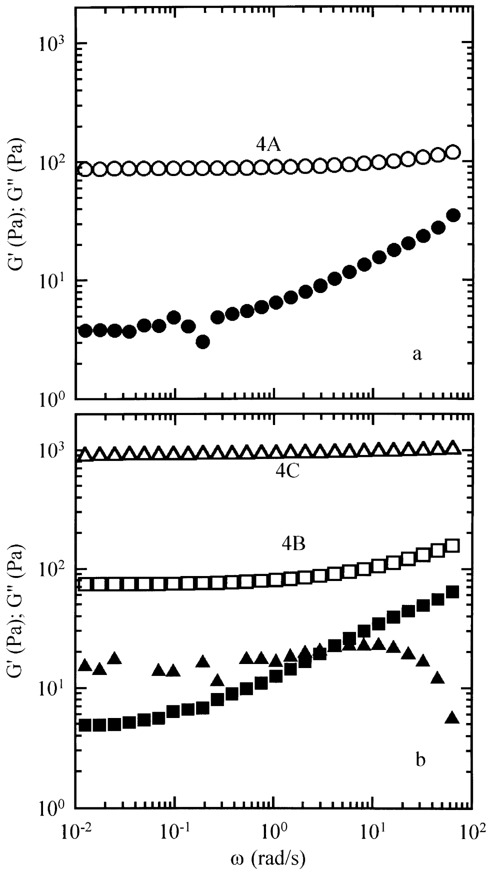

Fig. 9. Mechanical spectra of 4% starch pastes at 25°C and 4% strain. G' (hollow), G'' (solid).

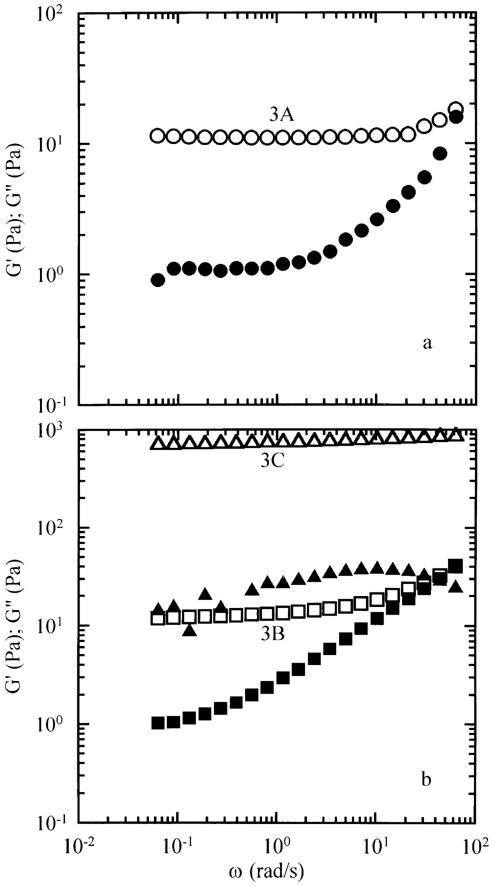

Fig. 10. Mechanical spectra of 3% starch pastes at 25°C and 4% strain. G' (hollow), G'' (solid).

determined because of their low viscosity. Nevertheless, the mechanical spectra of 2% starch systems revealed liquid-like behavior, as illustrated in Fig. 7 for 2B and 2C. The overall response in this case was clearly dominated by the continuous phase. However, owing to the low thickening ability of carrageenan at 60°C it was difficult to get a neat spectra even at higher deformations.

3.4. Time evolution of dynamic moduli at 25°C

Moduli of preparations A and B did not exhibit an appreciable evolution with time; the maximum observed increase of G' was about 10 Pa over 15 h in 4% starch pastes. This behavior is normal considering the absence of amylose, but it also shows that concentration of ions already present in κC and possibly its concentration in the continuous phase were not enough to induce gelation upon cooling. It was only when KCl was added that time evolution was observed. Fig. 8 illustrates the change with time of G' in C mixtures of different starch concentration. An early increase was followed by a region where G' essentially levelled off. The initial rate of increase of G' increased with the starch concentration. 4C and 3C exhibited a faster rate than 2C; however, the latter reached the plateau zone earlier. The ratio between the final and the initial G' was more than double at higher starch concentrations.

3.5. Viscoelastic behavior at 25°C

The viscoelastic behavior of cooled starch pastes was in some cases similar to those of the hot ones. Figs. 9–11 show the mechanical spectra of preparations A, B and C for different starch concentrations. Spectra of 4A and 4B were very similar to their corresponding ones at 60°C; however, G'' was more dependent on the frequency at 25°C. The loss angle was lower indicating a greater predominance of the elastic character. Storage moduli were presumably greater only because of the low temperature as these dispersions did not form gels upon cooling. Dispersions 3A (Fig. 10) exhibited a solid-like behavior even if they were still non-gelling materials, while 2A (Fig. 11) were definitely quite fluid; moduli were highly dependent on frequency with $G'' > G'$ and beyond 40 rad/s a cross-over occurred, but G' was not overwhelmingly superior to G''. The behavior of 2B and 3B was also different with respect to their hot counterparts; they were more solid-like at 25°C, but 3B had a stronger elastic behavior than 2B. It is worth noting that for 2B the hot pastes (squares in Fig. 7) changed substantially their behavior upon cooling (squares in Fig. 11). This can be attributed to the presence of κC which, although did not form a self-standing gel, certainly contributed to the behavior of the cold paste. Such affirmation is also supported by the different behavior exhibited by 2A (Fig. 11(a)) and 2B (Fig. 11(b)); both were at 25°C but the former did not contain carrageenan, which showed that the behavior of 2B cannot be attributed to starch particles. On the contrary, as expected, all dispersions C formed self-standing gels with characteristic spectra; G' almost two orders of magnitude greater than G'' and both independent of frequency. All gels were tested in a grooved parallel plate geometry to avoid sample slippage, however, in 4C, G'' showed some dispersion at low frequencies. The loss angles ranged from 0.02 to 0.04, although in 2C they increased to 0.08 at higher frequencies. Preparations showed, however, an essentially elastic response characteristic of true gels.

3.6. Solubility-swelling

Swelling-solubility data were very similar at different starch concentrations. Starch solubility ranged from 1.1 to 2%, while swelling was 25.9 ± 0.82, 27.3 ± 0.76 and 29.3 ± 1.90 g/g for A, C and B, respectively. Although not being very large, differences were significant ($P \leq 0.05$), showing that the presence of κC and KCl had some effect on the degree of granule swelling. Even though different swelling was observed, the volume fractions of swollen granules, calculated using the formula (Doublier, 1987): $\phi = (1 - S/100)\,CG$, where S is the solubility (1.5 g/g), C the initial starch concentration and G the swelling (25.9 g/g), and were essentially 1.00, 0.75 and 0.50 for 4, 3 and 2% starch dispersions, respectively. This showed that 4% starch dispersions

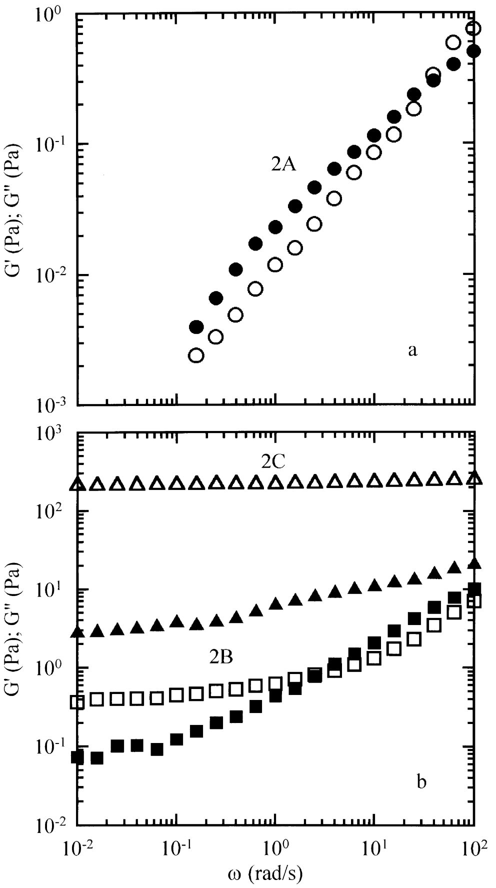

Fig. 11. Mechanical spectra of 2% starch pastes at 25°C and 4% strain. G' (hollow), G'' (solid).

were systems with a high volume fraction while 2% were rather diluted.

3.7. Particle size and size distribution

Laser diffraction results were expressed as median diameter and size distributions. Table 3 summarizes the median 50% diameter, *D*[v,0.5], when starch dispersions were prepared at 2 and 4% starch. The median diameter of uncooked starch slurries was also included; it was essentially the same when KCl was present in uncooked starch. The maximum swelling power defined as the ratio of the maximum volume to the initial volume, calculated as the cubed ratio of the maximum diameter to the initial diameter, $(D_{\max}/D_{\mathrm{i}})^3$ (Ziegler et al., 1993), with both being *D*[v,0.5], is also given. Pasting at 96°C resulted in a significant increase of diameter, but unlike swelling values (*G*) presented in the preceding section differences among diameters were clearly larger. The median diameters of 4 and 2% starch dispersions differed by about 2% and can be considered practically the same. Ziegler et al. (1993) measured the granule swelling during gelatinization in the sample cell of a laser diffraction analyzer of the same type as used by us, and reported a maximum swelling power of 10.3 for a cross-linked waxy starch sample from a different supplier treated at a maximum temperature of 80°C. This value is in excellent agreement with our results (Table 3), which was calculated using the *D*[(v,0.5] of pastes after preparation in the Brabender, even though temperature and shear conditions were not the same. Presence of κC and KCl resulted in higher swelling powers. Laser diffraction results agreed quite well with swelling-solubility data with both registering the same tendency; greater swelling (or median diameter) in B than in C and A dispersions.

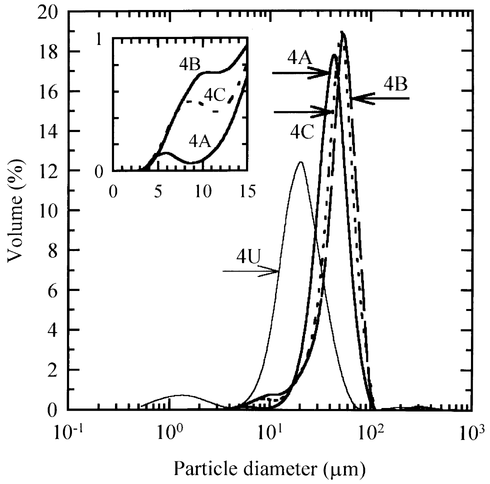

Fig. 12. Volume size distribution of 4% starch pastes. 4U denotes uncooked CWCS. The insert shows an amplification, in linear scales, of the volume distribution for particle diameters in the range 5–15 μm.

Volume size distributions of 2 and 4% starch dispersions were essentially similar. This showed that the cooking process leads to essentially the same extent of swelling, and displayed a similar behavior independent of the starch concentration and the presence of other components. Fig. 12 shows the volume distributions of 4% starch samples. Curve

Table 3
Median volume diameters and swelling powers of starch dispersions

Dispersion	*D*[*v*,0.5] (μm) 4% starch	*D*[*v*,0.5] (μm) 2% starch	Swelling power[a]
Uncooked starch	18.6 ± 0.79	18.6 ± 0.45	1.0
A	41.2 ± 0.07	42.2 ± 0.09	10.9
B	50.6 ± 0.10	49.7 ± 0.06	20.1
C	47.9 ± 0.05	48.8 ± 0.11	17.1

[a] Based on 4% starch diameters.

4U is the size distribution of uncooked starch; it consisted of a minor fraction of particles smaller than 4 μm and a rather wide distribution from 4 to 80 μm. Pasting also resulted in relatively wide distributions that included a small fraction of particles under 10 μm in 4A and around 15 μm in 4B and 4C (insert of Fig. 12). This last fraction, however, represented less than 1% of the total volume of particles. As can be seen in the insert, the effect of carrageenan and KCl was apparent. Distributions of dispersions 4B and 4C were slightly shifted to the right of 4A and 4U, but were very similar in shape.

4. Discussion

Using the same type of steady-shear experiments carried out here, other authors (Dintzis, Bagey & Felker, 1995) have pointed out the presence of "anti-thixotropy" in dispersions of normal waxy starch in 90% DMSO-water. Based on observations of phase contrast microscopy they considered this behavior as an indication of a flow-induced structure. The behavior illustrated in Fig. 2 indicates some type of dependence of viscosity on time that could also be qualitatively identified as "anti-thixotropy" because of the presence of an anti-clockwise hysteresis loop. Anti-thixotropy is defined as the increase of viscosity with time at a constant shear rate (Barnes, Hutton & Walters, 1993). Its rigorous characterization involves determining the variation of viscosity with time at different but constant shear rates. Therefore, considering the type of experiment we carried out, in which shear rate increased continuously with time, the term cannot be rigorously applied. However, it is well known that the type of experiment from which anti-thixotropy can be formally characterized is difficult to perform in hot starch pastes because sample evaporation, possible further granule swelling and granule sedimentation can lead to spurious results mainly if long experiments are involved. While evaporation is relatively simple to control, the other two factors are not and represent a challenge because neither the sensitivity of viscosity to shear nor the time required for it to achieve a constant value are known a priori. This without considering that several shear rates have to be used. Therefore, experiments of the type performed here are normally preferred. What is clear is that addition of carrageenan and KCl had a noticeable effect on viscosity as well as on flow behavior. It is not apparent, however, why when KCl was not added viscosity was greater. This feature was observed in all starch concentrations but its intensity depended on the amount of starch; in more concentrated pastes the increase of viscosity over starch alone was higher. A possible explanation is that in the absence of salt, carrageenan random chains are more expanded and occupy a greater hydrodynamic volume than in the presence of salt. It is well known that the intrinsic viscosity of polyelectrolytes decreases with ionic strength with the effect being more noticeable at higher molecular weights (Snoeren, 1976).

Hot dispersions were not true gels but pourable materials. In some cases, however, their mechanical spectra showed the features of a structured medium with a predominant elastic response. Dispersions with 4% starch behaved as thick systems of swollen particles suspended in a continuous phase. At this starch concentration, the nominal volume fraction was practically unity indicating highly concentrated systems allowing a low volume to the continuous phase. This does not necessarily agree with the actual physical situation, because it is obvious that there is still place for such a phase. However, in 4A the system was so concentrated that starch granules dominated the overall response exhibiting a predominantly elastic behavior as illustrated in Fig. 5. The loss angle increased very slowly at lower frequencies, then at frequencies higher than about 3 rad/s it went upwards noticeably. This frequency sets the boundary between the elastic response given by the swollen granules and the viscous response of the aqueous phase. We are not, however, implying that each phase responded separately as if the other was absent. It is obvious that the whole profile is the result of the overall behavior of the starch dispersion, but such a profile contains the features of both phases, which become apparent when the frequency was varied. Dispersions 4B and 4C also behaved as concentrated systems, but in this case the continuous phase was a macromolecular solution. Dispersions with 3% starch were less viscous simply because the nominal volume fraction of swollen starch was lower (0.75). Thus, at this particular fraction, the behavior of the continuous phase was less masked than at 4%, and this resulted in the mechanical spectra shown in Fig. 6. Systems were less concentrated than at 4% and the overall behavior of dispersions was dominated by the continuous phase with the response of the dispersion phase becoming gradually fainter, which is particularly observable in Fig. 6(b). At 2% starch, volume fraction was 0.5 and this was reflected in the viscoelastic properties of pastes. At this volume fraction they were diluted enough to make their rheological characterization at 60°C difficult. Despite this, a completely liquid-like behavior with a marginal contribution of the disperse phase to the mechanical spectra of the samples was observed (Fig. 7).

At 25°C dispersions and true gels were obtained. In general, preparations A and B exhibited a more solid- than liquid-like behavior when cooled. This change upon cooling is particularly noticeable for dispersions 2B (squares in Figs. 7 and 11(b)) and 3B (squares in Figs. 6 and 10(b)) whose spectra were those of a suspension of particles in a more viscous macromolecular solution. Dispersions 2A, however, exhibited the behavior of a diluted suspension of particles in a still low viscosity continuous phase (Fig. 11(a)). The differences between 60 and 25°C for a constant given starch concentration are associated to the increase of viscosity of the continuous phase that occurred upon cooling. Nevertheless, it is apparent that in contrast to the viscous behavior, addition of carrageenan with or without KCl did not result in an enhancement of viscoelastic properties of hot dispersions irrespective of starch concentration. In cold dispersions the same was true except under gelling conditions. When KCl was present gels were formed but their rigidity depended on starch concentration. Gel-cure results suggest that gelation occurred faster in more concentrated starch dispersions possibly because carrageenan concentration in the continuous phase increased as the volume fraction increased.

According to the scheme proposed by Alloncle et al. (1989), the concentration of carrageenan in the continuous phase would increase on starch granule swelling as a result of volume reduction. Considering an initial concentration of 0.5%, we obtained 1 and 2% as the concentrations of carrageenan corresponding to volume fractions of 0.5 and 0.75, respectively. At 60°C we observed a very low thickening power of 2% carrageenan solutions either with or without KCl. They exhibited a large Newtonian plateau with a shear viscosity of 0.11 Pa s and an incipient shear-thinning behavior beyond 100 s^{-1}. Lower concentrations are expected to have lower viscosities and probably show Newtonian behavior at all shear rates. This situation, combined with a low starch concentration, could explain for example the spectra shown in Fig. 7 and the predominance of the liquid-like behavior easier to detect at higher starch concentrations as seen in Figs. 4(b) and 6(b). It is worth noting that such a scheme has only been used as a rough estimate of carrageenan concentration in the continuous phase. However, it is much less apparent when applied to cooled dispersions; if carrageenan concentration in the continuous phase was effectively close to either 1 or 2%, dispersions 2B and 3B would be expected to gelify upon cooling because at these concentrations κC alone formed gels upon cooling even without KCl. Therefore, it is likely that carrageenan concentration did not increase as much as predicted by Alloncle and coworkers's scheme. However, at present, such a question remains unclear. Nevertheless, it is clear that the change observed between 2B at 60°C (Fig. 7) and 2B at 25°C (Fig. 11) can be attributed to the presence of carrageenan in the continuous phase and its gelation.

Starch pastes prepared in the presence of hydrocolloids exhibit higher viscosities and normally higher dynamic moduli than starch alone preparations. Such an effect is frequently called synergism and is defined, in a rather simplistic way, as an increase of viscosity (or moduli) over that of components alone. In systems like ours, it depends mainly on the type of starch and hydrocolloid and also on their concentration in the mixture as observed by several authors (Alloncle & Doublier, 1991; Christianson, Hodge, Osborne & Detroy, 1981; Descamps et al., 1986; Eidam et al., 1995; Sajjan & Rao, 1987). In this context, Brabender and steady flow results show a synergistic effect between CWCS and carrageenan, the extent of which varied with starch concentration. Viscoelastic properties either of hot or cold preparations did not show the same trend, except in the case of KCl-containing mixtures where the gels were formed upon cooling, and 2% starch dispersions (i.e. 2A and 2B at 25°C) moduli of mixtures were lower than the moduli of starch alone at a given temperature. However, at this point it is not possible to say that viscoelastic synergism was non-existent because only one carrageenan concentration was tested. Synergism observed from viscosity data has been explained on a rheological basis (Alloncle et al., 1989), while that observed from viscoelastic data has been presumed to be the result of complex interactions between amylose and hydrocolloid (Alloncle & Doublier, 1991). In our case no amylose was present and this may explain the lack of such an effect on dynamic moduli. Another factor to consider is the superior thickening ability of gums that have been mixed with starch (i.e. guar, locust bean, xanthan) over that of carrageenan. The apparent lack of moduli enhancement due to the low thickening ability of carragenan or an insufficient concentration of it in the continuous phase cannot at present be proved because only one concentration was used.

All the foregoing results point to the existence of systems of particles suspended in aqueous media of different rheological properties in which the contribution to the overall behavior of either the disperse or the continuous phase prevails one over the other depending on starch concentration and presence of KCl. According to the swelling-solubility and particle size distribution data, 4% starch dispersions can be considered as a close-packing of swelled granules which leaves only a reduced volume to the continuous phase. These systems had a very high volume fraction and this may explain the initial “anti-thixotropic” behavior, the extent of which depended on the viscosity of the fluid phase. However, at 60 and 25°C, except for dispersions C, the increasing dependence of moduli with frequency can be attributed to the response of the continuous phase which is to some extent overwhelmed by that of starch particles. Systems behaved as highly concentrated suspensions of starch particles in water (dispersions A at 60 and 25°C) and in a macromolecular solution (dispersions B at 60 and 25°C and dispersions C at 60°C), and as composite gels of swollen particles embedded in a macromolecular network (dispersions C at 25°C).

5. Conclusions

Combination of CWCS with carrageenan and KCl resulted in mixtures possessing different rheological behaviors. Such behaviors could be revealed clearly only when starch concentration was sufficiently low to produce volume fractions below unity. In all cases systems showed responses associated with the characteristics of a dispersion of starch particles in aqueous media of different compositions. Under the thermal and mechanical conditions used, CWCS proved to be a useful material and treated starch dispersions as a two-phase system that comprised a disperse and a continuous phase.

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