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Phase separation and rheology of aqueous starch/galactomannan systems

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Abstract

Phase behaviour (at 25°C and 60°C), phase separation kinetics and rheological properties of aqueous starch/galactomannan systems were studied. Pure, soluble amylopectin and waxy maize starch dispersions with varying degrees of granule disintegration were employed to investigate the effect of starch granules and aggregation of starch polysaccharides. Polysaccharide blends were made by either mixing starch and galactomannan stock solutions (solution-based preparations) or by dry blending starch and galactomannan powders prior to dispersion in water (powder-based preparations). In phase diagrams for soluble amylopectin, the binodal is not symmetrical but displaced towards the axis of amylopectin, i.e. the lower molecular weight polysaccharide. The binodals of the waxy maize starch systems nearly coincide with the axes representing the polysaccharide concentrations, which reflects the influence of the high molecular weight and limited solubility. Near infrared reflection analysis was employed to determine the phase separation kinetics in samples of standard volume. Phase separation in a 5 ml sample was completed after 8 h for most systems, the exception being powder-based systems containing waxy maize starch granules in the swollen state and galactomannan at high concentrations ($> 3\%$ starch/ $> 0.3\%$ galactomannan). In this latter system the separation of the phases proceeded more slowly than in the systems with a lower degree of supermolecular organisation, such as soluble amylopectin and molecularly dispersed waxy maize starch. Likewise, the rheological properties of the blends were largely determined by the extent of starch granule disintegration and polymer degradation. Rheological characterisation revealed the greater structural rigidity, indicated by the increase in measured G' and G'' values, of the powder-based preparations. Marked frequency dependence of the dynamic moduli in the frequency range 0.1 rad s^{-1}–10 rad s^{-1} was found for all blends under study. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

As both ingredients and additives, starch/non-starch hydrocolloid systems are important texture agents in many food products. It is well known that the addition of a non-starch hydrocolloid (named ‘hydrocolloid’ hereafter, e.g. locust bean gum, guar gum, xanthan) strongly influences the gelatinisation and retrogradation of starch. The combination of starch and hydrocolloids can lead to a considerable viscosity increase.

Starch is a storage carbohydrate; it is isolated from plant sources as discrete granules which are insoluble in water at room temperature owing to hydrogen bonding and crystallinity. Although the solubility of starch in water increases as temperatures approach 95–100°C, starch still exists largely as highly swollen granules and granule fragments. Starch is composed of two macromolecular entities, the essentially linear α-(1 $\rightarrow$ 4)-glucan amylose, and the branched amylopectin, a α-(1 $\rightarrow$ 4)-glucan containing α-(1 $\rightarrow$ 6)-branch points leading to short, α-(1 $\rightarrow$ 4)-chains (Galliard & Bowler, 1987). Starches are commonly used in the food industry as a thickener in foods such as soups, sauces and dairy desserts.

Galactomannans are water-soluble polysaccharides found in a variety of legume seed endosperms. The galactomannans from carob (*Ceratonia siliqua*) and guar (*Cyamopsis tetragonoloba*) seeds find widespread application as thickeners and gelling agents in food systems. Galactomannans consist of a β-(1 $\rightarrow$ 4)-linked mannopyranosyl backbone with α-(1 $\rightarrow$ 6)-linked single unit galactopyranosyl side branches. Mannose:galactose ratios vary between ~1:1 and ~4:1, depending upon the botanical source of the polysaccharide (Grant Reid, 1985).

The mechanism of the interaction between starch and hydrocolloids has not yet been fully explained. Previous studies have focused on starch solubles or dispersions approaching complete starch granule disintegration, simplifying the system for valuable in-depth studies (Christianson et al., 1981, Kulicke et al., 1996), but passing over the role of starch granules as important contributors to the functionality of starch (Bagley & Christianson, 1982). Alloncle et al. (1989) described the starch/hydrocolloid system as a

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suspension of swollen starch particles dispersed in a solution of hydrocolloid. The existence of a thermodynamic incompatibility between the starch polysaccharides and the hydrocolloid biopolymer has been suggested (Kulicke et al., 1996, Alloncle & Doublier, 1991, Conde-Petit et al., 1997). Information on the phase behaviour of polysaccharide blends is scarce: phase diagrams describing thermodynamic incompatibility were established for the two starch polysaccharides amylose and amylopectin (Kalichevsky & Ring, 1987) and for dextran and amylose (Kalichevsky et al., 1986). Investigating approximately 80 aqueous polysaccharide blends for their thermodynamic incompatibility, Antonov et al. (1987) found their results to be in agreement with the Kalichevsky data. In spite of the industrial significance of starch/hydrocolloid blends, the phase behaviour of these systems has not been studied.

As starch/hydrocolloid blends are being used as texture agents, their flow properties and rheology are the most frequently studied aspects. Sudhakar et al. (1995) employed a Brabender Viscoamylograph to study the influence of inorganic salts on the gelatinisation or 'pasting' behaviour of starch/xanthan systems. In later work, Sudhakar et al. (1996) employed the same technique to study the pasting characteristics of corn starch and waxy maize starch with guar gum and locust bean gum. To extend the accessible shear rate range both studies were performed in conjunction with rotational viscometers. Flow curves, obtained from conventional steady shear measurements have been combined with Brabender measurements (Alloncle et al., 1989) and with dynamic rheological measurements (Alloncle & Doublier, 1991, Annable et al., 1994, Eidam et al., 1995, Kulicke et al., 1996) for rheological characterisation of the viscoelastic properties of starch/hydrocolloid systems. The latter two studies investigated the influence of hydrocolloid nature and concentration on different starches, with the level of starch swelling and solubilisation assumed to be constant.

In the study reported herein, starch/guar galactomannan systems were investigated in terms of phase behaviour and phase composition, liquid–liquid phase-separation kinetics and rheology. Waxy maize starch was chosen since it consists of almost only amylopectin. This limited the experiments to ternary systems composed of two polysaccharides, amylopectin and galactomannan, and the solvent, water. To investigate the effect of starch granules as well as granule disintegration and solubilisation of starch polysaccharides on the starch/galactomannan mixtures, three starch systems with different levels of amylopectin solubility and starch granule disintegration were employed by using pure, partially degraded amylopectin (A), pregelatinised waxy maize starch (PWM) and native waxy maize starch (WM). This resulted in a true macromolecular amylopectin solution, a mostly macromolecular dispersion of amylopectin and a suspension of gelatinised starch granules, respectively. Two methods of blend preparation were compared: blends were made by either mixing amylopectin or starch and galactomannan stock solutions (solution-based preparations) or combining amylopectin or starch and galactomannan powders prior to the addition to water (powder-based preparations).

2. Materials and methods

Pure amylopectin A-7780 (A) which was partially degraded and, therefore, water-soluble was supplied by Sigma Chemical Co. Drum-dried pregelatinised waxy maize starch (PWM) and native waxy maize starch (WM) were obtained from Roquette Frères, and purified guar galactomannan (GM) was kindly provided by Systems Bio Industries.

2.1. Sample preparation

Amylopectin stock solutions or waxy maize starch (PMW, WM) stock suspensions for the solution-based preparations were prepared on a weight percentage basis. True amylopectin solutions were prepared by dispersing pure, partially degraded amylopectin (A) in distilled water at 85°C for 15 min. Molecular dispersions of waxy maize starch were prepared by solubilisation of pregelatinised waxy maize (PWM) starch in distilled water at 85°C for 15 min. Finally, suspensions of gelatinised waxy maize starch (WM) granules were obtained by heating native waxy maize starch in distilled water under mild conditions (85°C, 15 min, low shear). In order to obtain a homogeneous and liquid product, the possible maximum concentration for amylopectin stock solutions was 7.5% (w/w) and 3.0% (w/w) for the starch suspensions, respectively. Guar galactomannan stock solutions were prepared in distilled water and heated to 85°C for 15 min to hydrate the galactomannan. Solution-based polysaccharide blends were made by weighing out the appropriate masses of amylopectin solution or waxy maize starch (PMW, WM) suspension, galactomannan solution and distilled water into a beaker. All blends and their initial constituents showed weak viscoelastic or Newtonian liquid behaviour, which facilitated the mixing of the system. For the powder-based preparations the appropriate amounts of amylopectin, starch and guar galactomannan powder were weighed out and the powders were dry blended prior to dispersion in distilled water at 85°C for 15 min, resulting in liquid blends. All blends were mixed vigorously for a minimum of 2 h with a magnetic stirring bar and held either at room temperature or, where applicable, in a water-bath at 60°C (60°C being the consumption temperature of possible applications like soups and sauces).

2.2. Microscopy

The extent of starch granule disintegration and gelatinisation in the waxy maize starch systems (PWM, WM) was assessed by light microscopy. Phase separation of starch/galactomannan blends was visualised by phase contrast microscopy. Both techniques were performed using a Leitz Orthoplan light microscope equipped with a Leica Wild MPS52 camera device. The samples were placed between a slide and a cover slip and sealed to prevent dehydration.

2.3. Determination of relative molecular weight distribution

Gel permeation chromatography was performed on a Pharmacia HR 1/60 column packed with Sephacryl S-1000 gel (Pharmacia). The columns were eluted with degassed 0.01 M NaOH. Photometric detection (Gilson Holochrome) was carried out after post-column orcine-sulphuric acid derivatisation (Tollier & Robin, 1979).

2.4. Phase diagrams

The blends were transferred to plastic centrifuge tubes, the tubes were sealed and left to liquid–liquid bulk phase separate overnight at room temperature (25°C) or in a water-bath at 60°C. Preliminary experiments indicated that after 5 h of centrifugation at 100*g* the polysaccharide concentration in the phases remained constant. To ensure complete phase separation, the samples were, therefore, centrifuged at 100*g* for 5 hs. The tube was sliced at the interface of the two phases, thereby allowing the isolation of the individual upper and the lower phases. Polymer concentrations in both the initial blends and the separated phases were determined by high performance anion exchange chromatography coupled with pulsed amperometric detection (HPAE-PAD, Dionex Co. USA) after weak hydrolysis in 0.5 M H_2SO_4 at 130°C for 75 min (Jørgensen & Jensen, 1994).

2.5. Kinetics of phase separation

The kinetics of liquid–liquid phase separation were determined at room temperature (25°C) from vertical scan near infrared (NIR) analysis using a Turbiscan MA 1000 vertical scan macroscopic analyser. Aliquots of 5 g were filled into glass tubes of 12 mm diameter and back-scattered, as well as transmitted light at a wavelength of 850 nm, was measured along the entire height (~50 mm, instrument resolution: 0.01 mm) of the sample, starting from the bottom of the tube. The polysaccharide blends were measured within 5 min after mixing and periodically thereafter for up to 200 hs.

2.6. Rheology

Previous work (Closs et al., 1997) has emphasised the structurally weak properties of the polysaccharide blends of interest. Accordingly, small amplitude dynamic oscillatory testing was undertaken using a Rheometrics RFSII controlled strain rheometer, equipped with a 10GM FR torque transducer (0.002–10 g cm^{-1}). A Couette geometry (34 mm outer diameter, 32 mm inner diameter, 33 mm immersion depth) with a sample volume of 13 ml was employed. During sample loading care was taken to ensure that the sample meniscus was level with the upper surface of the inner cylinder, thereby guaranteeing constant immersion height. Measurements were performed within 5 min after completion of blend preparation at a temperature of 25°C.

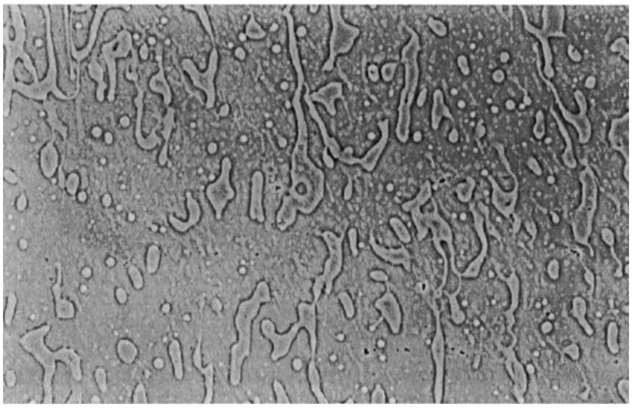

Fig. 1. Phase contrast light micrograph of 3% PWM/0.3% GM, powder-based preparation, magnification 100×.

The following test procedure was adopted: conventional strain sweep tests, involving incremental increases in applied strain at a constant frequency (0.02–0.5, at 3.14 rad s^{-1}) were performed to determine the limits of the linear viscoelastic region of each sample. Sequential, incrementally increased frequency measurements (frequency sweeps) were performed in the range 10 rad s^{-1} to 0.1 rad s^{-1} and repeated employing at least two different strain levels, thereby allowing a further check for linearity across the frequency range. The results of these tests are discussed in terms of the storage and loss moduli, G' and G'', respectively, and the phase angle δ ($\delta = \tan^{-1}(G''/G')$; $0° < \delta < 90°$). Note that for a Newtonian liquid $\delta = 90°$ and for a pure elastic solid $\delta = 0°$.

3. Results and discussion

For the discussion of the results, it is important to keep in mind the different levels of amylopectin solubility and starch granule disintegration and solubilisation studied in this work: the true macromolecular amylopectin solution, the mostly molecularly dispersed PMW and the suspension of gelatinized waxy maize-starch granules. Only in the latter system were swollen starch granules detected by phase contrast microscopy. Under examination by polarized light microscopy the starch granules showed no birefringence (micrographs not shown).

Blends of initially translucent amylopectin and galactomannan solutions become cloudy immediately after mixing, providing a first indication of the immiscibility of the two

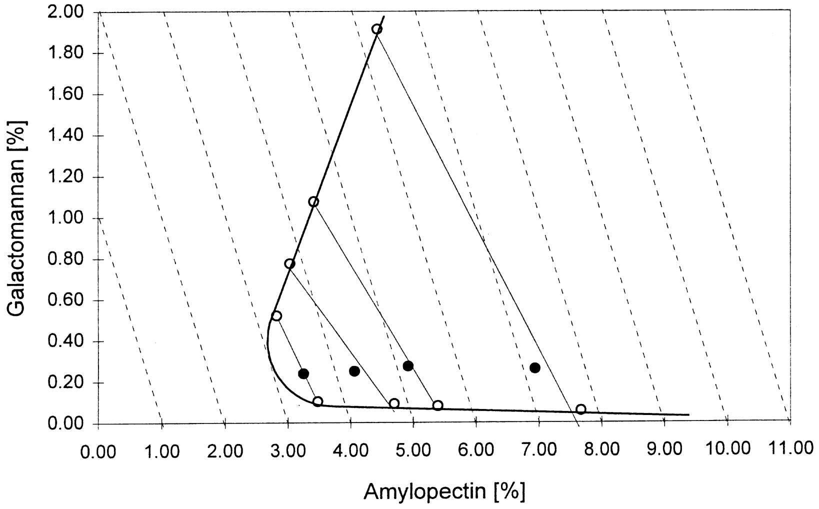

Fig. 2. Phase diagram of amylopectin/galactomannan (A/GM) blends at room temperature (————, tie lines; - - -, water distribution lines; ●, initial blends; ○, bulk phases).

solutions. Examination of a phase contrast light micrograph of a blend within 5 min after sample preparation reveals clearly visible continuous and dispersed phases (Fig. 1). This again implies thermodynamic incompatibility between the starch polysaccharides and the galactomannan. The suggestion, based on the phase-volume ratio after bulk phase separation, is that the continuous phase is starch-based and the dispersed phase galactomannan-based.

With the exception of the high concentration powder-based preparations of WM(> 3%)/GM(> 0.3%), the polysaccharide blends were found to separate into two visually distinct phases within a period of 8 hs. Phase diagrams of mixed aqueous biopolymer systems containing amylopectin or waxy maize starch and guar galactomannan at 25°C prepared by the solution-based method are given in Figs. 2–4. Bulk phase separation occurred, resulting in a galactomannan-rich upper phase and an amylopectin/starch-rich lower phase. The points on the curves represent the polysaccharide weight concentrations as determined by HPAE-PAD. The binodal of the A/GM phase diagram in Fig. 2 is not symmetrical, but displaced towards the abscissa (representing the amylopectin concentration) and the slope of the tie lines is not parallel with the slope of the water distribution lines. In these polysaccharide blends the amylopectin (A) has a lower molecular weight than the galactomannan (GM), resulting in two distinct peaks on the gel permeation chromatogram (Fig. 5). The binodal computed from the Flory–Huggins theory for typical flexible chain polymers is shifted towards the lower molecular weight polymer with decreasing molecular weight of one of the polymers (Hsu & Prausnitz, 1974). The shift of the binodal towards the abscissa in Fig. 2 indicates that the theory developed for flexible chain polymers can be applied to the more polydisperse macromolecules of polysaccharides. The binodal branch representing the total composition of the galactomannan-rich upper phase shows a slant towards higher amylopectin

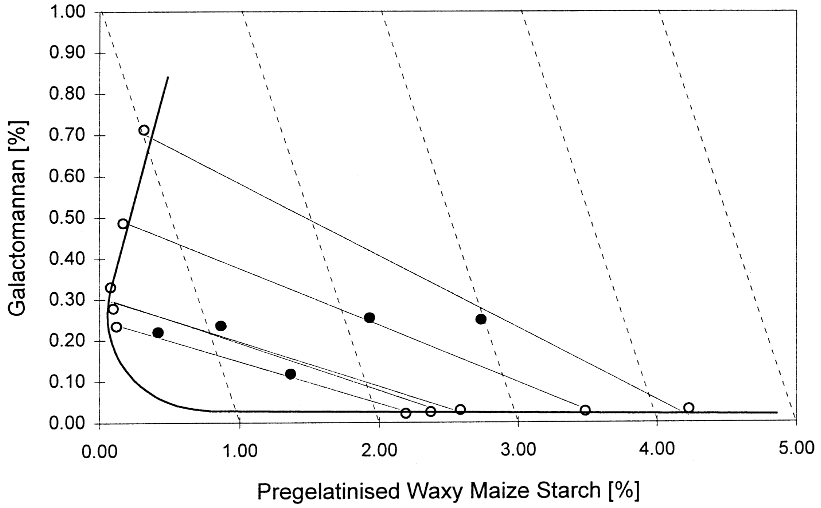

Fig. 3. Equilibrium phase diagram of pregelatinised waxy maize starch/galactomannan (PWM/GM) blends at room temperature (————, tie lines; - - -, water distribution lines; ●, initial blends; ○, bulk phases).

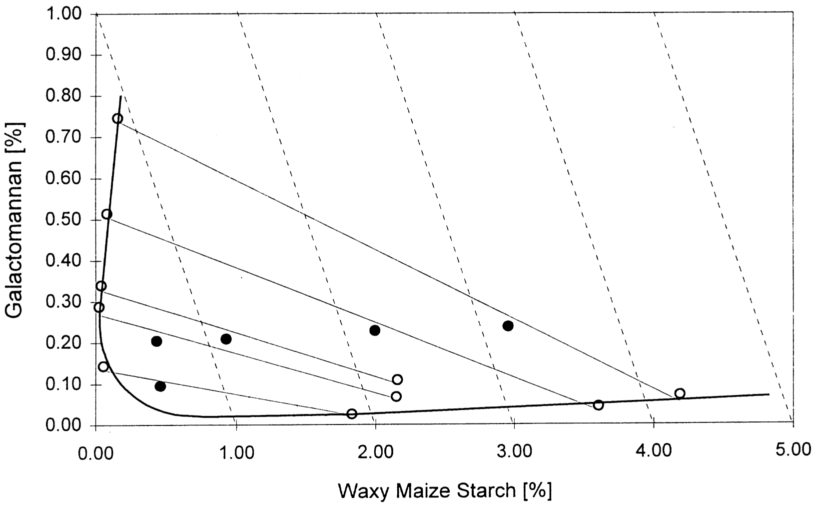

Fig. 4. Equilibrium phase diagram of waxy maize starch/galactomannan (WM/GM) blends at room temperature (————, tie lines; - - -, water distribution lines; ●, initial blends; ○, bulk phases).

concentrations. This difference between equilibrium and actual phase diagrams is because of the galactomannan enrichment in the upper phase leading to an approximately sixfold increase in galactomannan concentration in the upper phase (i.e. ~1.8%) for the highest blend concentration (7.5% A/0.3% GM). As a result of the increased galactomannan concentration the upper phase is gel-like. This is in agreement with the work of Dea et al. (1977), who found that galactomannans form weak gels at concentrations $>$ 0.75%. The gelled upper phase does not permit complete phase separation by entrapping remainders of the lower amylopectin-rich phase. This means that the A/GM phase diagrams presented here are non-equilibrium by nature and can be regarded as diagrams of state, showing the critical gelation concentration of the galactomannan-rich upper phase at ~0.8% GM. Fig. 3 shows a phase diagram for a blend of PWM/GM, in which the single phase region under the binodal is reduced to a minimum and the binodal nearly coincides with the concentration axes of the polysaccharides. This reflects the fact that by gel filtration the molecular weight of amylopectin in PWM was found to be higher than that of the pure amylopectin (A) (Fig. 5), which results in a molecular dispersion of amylopectin and not in a true solution like the amylopectin solutions described above. The displacement of the binodal towards lower concentrations of polymers with increasing molecular weight has been described by Albertsson (1971). The high molecular weight of the PWM amylopectin and the colloidal character of the system and, therefore, the inherent thermodynamic instability, promote depletion flocculation in these systems at low polysaccharide concentrations (e.g. 0.5% PWM/0.3% GM). Note that this is in the

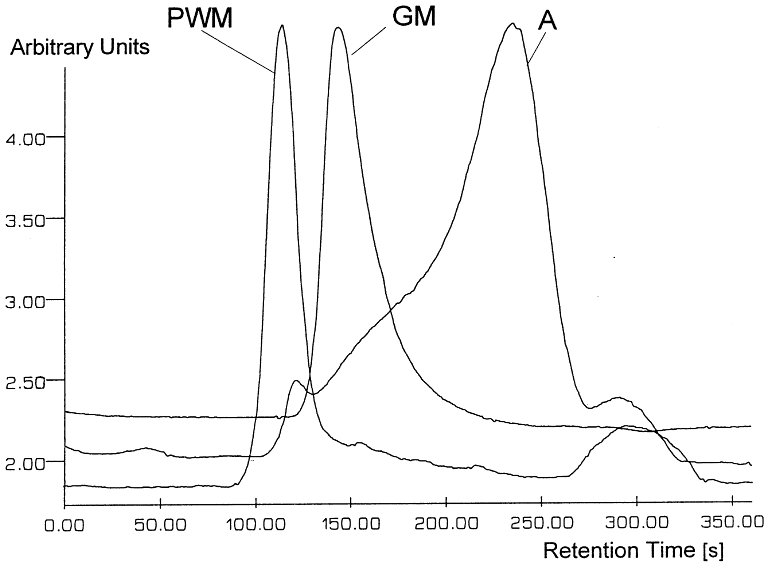

Fig. 5. Gel permeation chromatogram representing relative molecular weights of amylopectin (A), pregelatinised waxy maize starch (PWM) and galactomannan (GM).

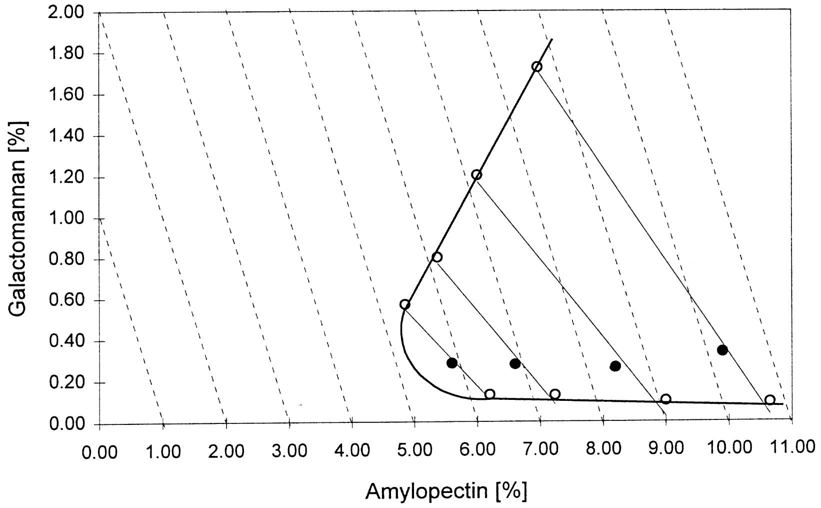

Fig. 6. Phase diagram for amylopectin/galactomannan (A/GM) blends at 60°C (————, tie lines; - - -, water distribution lines; ●, initial blends; ○, bulk phases).

absence of starch granules which may flocculate, thereby increasing the biphasic region above the binodal. The phase diagram of a WM/GM system containing swollen starch granules (Fig. 4) is, therefore, practically identical to that of PWM/GM described above. In contrast to the A/GM phase diagram in Fig. 2, the PWM/GM and WM/GM phase diagrams represent equilibrium conditions, since both phases are liquid and separation can, therefore, take place without limitation by a gelling phase. Phase diagrams established at 60°C showed a displacement of the binodal towards higher polysaccharide concentrations (compared to Fig. 2), with a corresponding increase of the single phase region for the A/GM system (Fig. 6). There is no displacement of the binodal for the PWM/GM (Fig. 7) and WM/GM systems, which further emphasises the immiscibility of these blends. Indeed, a temperature rise of 35°C is insufficient to influence miscibility. It should be noted that the location of the binodal was found to be independent of preparation procedure (powder- or solution-based). For this reason, only diagrams for the solution-based preparations are depicted.

Vertical scan NIR analysis of biphasic systems in the process of phase separation was employed to study the phase separation kinetics of the A/GM, PWM/GM and WM/GM systems. The difference in turbidity between the initial biphasic blends and the separated phases makes this method sensitive to the changes occurring during separation. Fig. 8 shows that for an A/GM system the first remarkable changes in turbidity are registered after 1 h and constant values are reached 8 h after preparation of the initial blends. Once separation is completed, the amylopectin-rich lower phase becomes translucent and allows transmission of up to 59% of light at NIR wavelengths. The transparency of the galactomannan-rich upper phase is considerably lower and transmission of light through this phase does not exceed 5%. From these measurements it can be

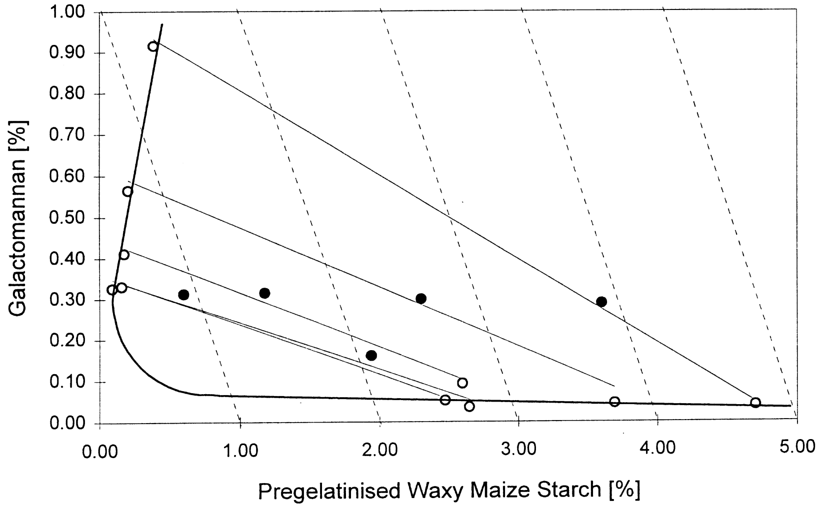

Fig. 7. Equilibrium phase diagram for pregelatinised waxy maize starch/galactomannan (PWM/GM) blends at 60°C (————, tie lines; - - -, water distribution lines; ●, initial blends; ○, bulk phases).

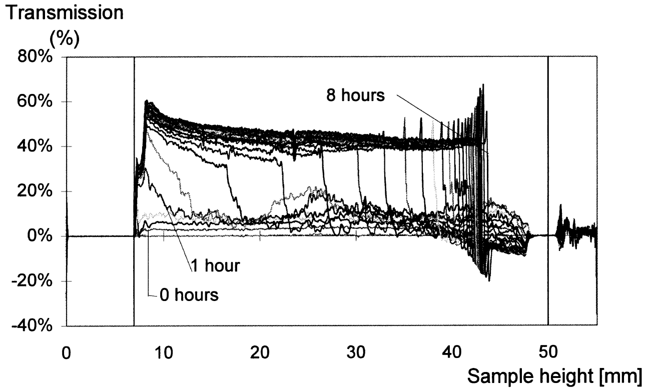

Fig. 8. Changes in NIR transmission through a 7.5% amylopectin/0.3% galactomannan (A/GM) blend with time (solution-based preparation).

seen that liquid–liquid bulk phase separation is completed after 8 hs, resulting in two discrete phases separated by a well-defined interface with almost no meniscus, owing to the low interfacial tension between the two chemically and physically similar phases.

In Fig. 9 vertical scan NIR measurements for a PWM/GM system are depicted. The kinetics of bulk phase separation are similar, with the first signs of changes in turbidity apparent after 1 h and measurements of NIR light transmission reaching constant values after 8 hs. However, the opaque lower starch phase and the translucent (30% of NIR light transmitted) galactomannan upper phase are not separated by a clear boundary, but by a region of increasing light transmission. This is consistent with the behaviour observed in vertical scan NIR studies of suspensions (Meunier, 1995), where it is attributed to a sedimentation process, thereby suggesting that the behaviour observed in the work described herein may be associated with the sedimentation of starch polysaccharide aggregates rather than actual bulk phase separation. These results underline again the colloidal and suspension-like character of the PWM and WM systems, respectively. Once more, with the exception of the higher concentration powder-based preparations of WM($>$ 3%)/GM($>$ 0.3%), the preparation method of the polysaccharide blends was found to have no influence on the separation kinetics of the phases determined by vertical scan NIR analysis.

For the WM/GM system, however, the preparation mode at concentrations $>$ 3% WM/ $>$ 0.3% GM influences the kinetics of separation. Fig. 10 shows the growth of the upper phase layer thickness with time as determined by vertical scan NIR analysis. From this it can be seen that the solution-based preparation undergoes complete bulk phase separation after approximately 8 hs, whereas the powder-based preparation presents a stable dispersion for up to 80 h prior to phase separation being observed. Further, comparison of the upper phases resulting from phase separation of 3% WM/0.3% GM reveals a ~90% decrease in the upper phase layer thickness when the powder-based preparation is employed rather than the solution-based alternative. These studies confirm the suggested existence of incompatibility between the starch polysaccharides and galactomannan as well as demonstrating the phase behaviour of these systems in a simplified model. We suggest that this behaviour is also present in real food systems, although, because of the complexity of the matter, the separation into galactomannan-rich areas will be very localized rather than bulk separation.

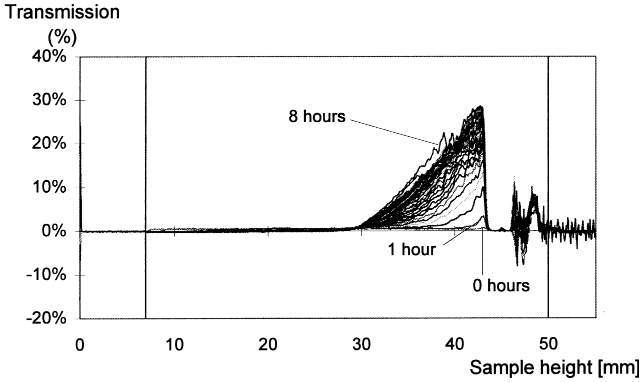

Fig. 9. Changes in NIR transmission through a 3% pregelatinised waxy maize starch/0.3% galactomannan (PWM/GM) blend with time (solution-based preparation).

Of particular interest, in the context of this study, is a comparison of the rheological properties of the systems with different levels of starch granule disintegration and amylopectin solubilisation. In addition, the rheology of the different blends prepared via the powder-based and the solution-based techniques was compared. Results of strain sweep measurements performed across the strain range $0.02 < \gamma < 0.5$ at a frequency of 3.14 rad s^{-1} are displayed in Figs. 11 and 12, depicting powder-based preparation and solution-based preparation respectively. Given the structurally weak properties of the blends, systematic rheological characterisation was confined to the blends at the highest polysaccharide concentrations (i.e. 7.5% A/0.3% GM, 3.0% PWM/0.3% GM, 3.0% WM/0.3% GM). Considering the solution-based blends (Fig. 11), the low values of G' and G'' ($G',G'' < 2.5$ Pa) indicate the structurally extremely

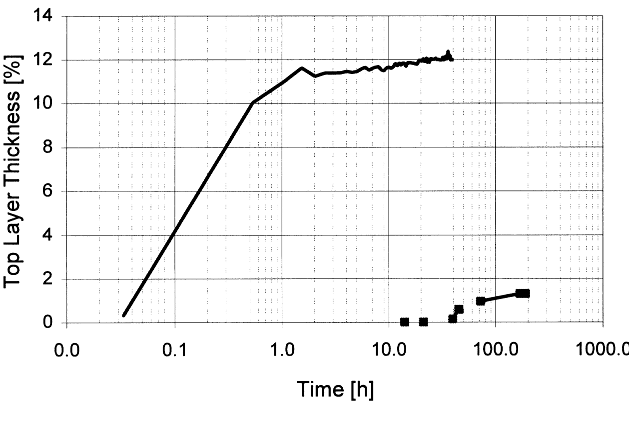

Fig. 10. Development of upper phase layer thickness with time for a 3% native waxy maize starch 70.3% galactomannan (WM/GM) blend (————, solution-based preparation; ■, powder-based preparation).

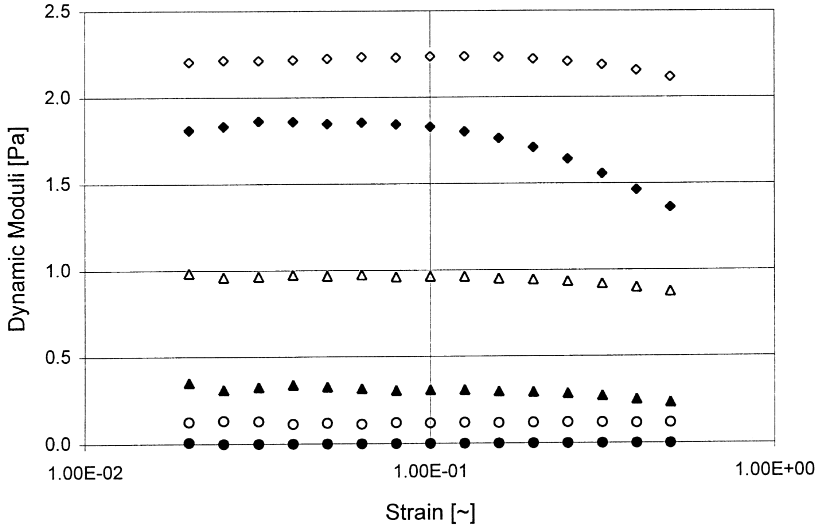

Fig. 11. Strain sweep of solution-based preparations performed at a frequency of 3.14 rad s^{-1} (filled and open symbols represent G' and G'', respectively; ◆/◇, 3% WM/0.3% GM; ▲/△, 3% PWM/0.3% GM; ●/○, 7.5% A/0.3% GM).

weak nature of all these polysaccharide blends with the WM/GM system displaying markedly greater structural rigidity ($G' \approx 1.8$ Pa, $G'' \approx 2.2$ Pa, $\delta \approx 50°$) than the PWM/GM and A/GM blends. Of the latter the A/GM blend displays near-Newtonian characteristics with $G' \approx 0$ Pa (i.e. outside the instruments measuring range) and G'' (≈ 0.2 Pa) giving a phase angle of $\approx 90°$. The PWM/GM blend displays viscoelastic behaviour with G'' (≈ 0.9 Pa) dominant compared to G'(≈ 0.3 Pa) giving $\delta \approx 70°$. Although no clear viscoelastic limit is observed (conventionally a decrease in a previously 'constant' G' may be taken as an indication of the critical strain, γ_c, being exceeded), a gradual decline in G', with an accompanying marked decline in G'', is observed for the 3% WM/0.3% GM blend for $\gamma > 0.1$. This value was used thereafter as a guide to maximum strain setting for this system.

From examination of Fig. 12 it is evident that there is a slight increase in both G' and G'' resulting from the powder-based preparation. An increase in both G' and G'' of $\approx 10\%$ and $\approx 20\%$ respectively, is observed for the powder-based WM/GM blend and $\approx 60\%$ and 20% for the PWM/GM blend. For the A/GM blend a small increase in G'' is accompanied by an increase in G' from ≈ 0 Pa to ≈ 0.1 Pa at $\gamma = 0.1$. The resulting phase angle of $\approx 65°$ reflects a clear departure from the near-Newtonian behaviour observed in Fig. 11. Interestingly, although G' and G'' are slightly greater for the powder-based preparations, the general behaviour of each blend across the strain range $0.02 < \gamma < 0.5$ is remarkably consistent with that displayed in Fig. 11. Similarly to Fig. 11 only the WM/GM blend displays significant strain dependence.

Frequency sweep data is displayed in Figs. 13 and 14 for

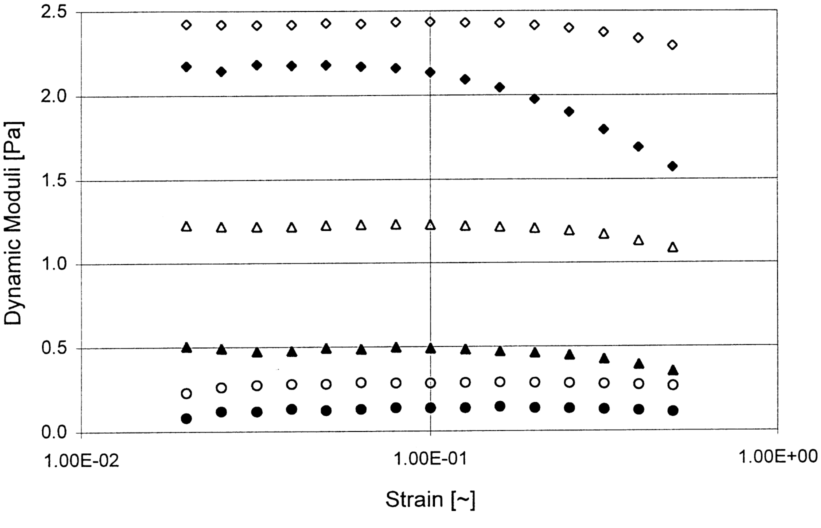

Fig. 12. Strain sweep of powder-based preparations performed at a frequency of 3.14 rad s^{-1} (filled and open symbols represent G' and G'', respectively; ◆/◇, 3% WM/0.3% GM; ▲/△, 3% PWM/0.3% GM; ●/○, 7.5% A/0.3% GM).

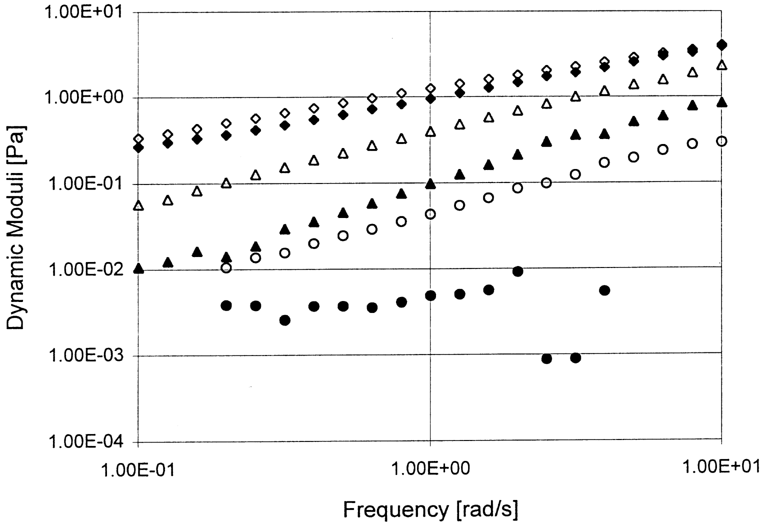

Fig. 13. Frequency sweep of solution-based preparation (filled and open symbols represent *G′* and *G″*, respectively; ◆/◇, 3% WM/0.3% GM; ▲/△, 3% PWM/0.3% GM; ●/○, 7.5% A/0.3% GM).

each of the previously discussed blends. Values of *G′* and *G″* are greater for the powder-based blends across the frequency range 0.1 rad s^{-1} to 10 rad s^{-1}. The three blends (regardless of preparation technique) display marked frequency dependence with both *G′* and *G″* increasing with frequency. For the WM/GM and PWM/GM blends *G′* and *G″* converge with increasing frequency, thereby displaying viscoelastic liquid characteristics (i.e. δ decreasing with increasing frequency). Although it is worth noting that the measurements on the A/GM blend are performed at the limits of the operational range of the torque transducer, a situation which may be further complicated by the influence of inertial effects at higher frequencies, the trends in blend behaviour can clearly be observed.

Strain and frequency sweeps were also performed to characterize each of the individual components of the blends. Solutions of 7.5% A and 0.3% GM fell outside the range of the instrument torque transducer and thereby defied characterisation. The structurally extremely weak 3% PWM displayed frequency-dependent behaviour of *G″*, which increased with increasing frequency from 0.0089 Pa at 0.1 rad s^{-1} to 0.43 Pa at 10 rad s^{-1}. The measured value of *G′* ($>$ 0.028 Pa) is inconsistent particularly at higher frequencies. The 3% WM represents a structurally stronger system with *G′* increasing from 0.22 Pa to 1.32 Pa, and *G″* from 0.22 Pa to 1.55 Pa, for a frequency increase from 0.1 rad s^{-1} to 10 rad s^{-1}. Across this range δ increases with increasing frequency from 40° to 50°, a behaviour generally associated with viscoelastic solid characteristics, which, it should be noted, is in direct contrast to the behaviour of the WM/GM blend.

As expected, the rheological characterisation of starch/galactomannan systems reveals a greater structural strength

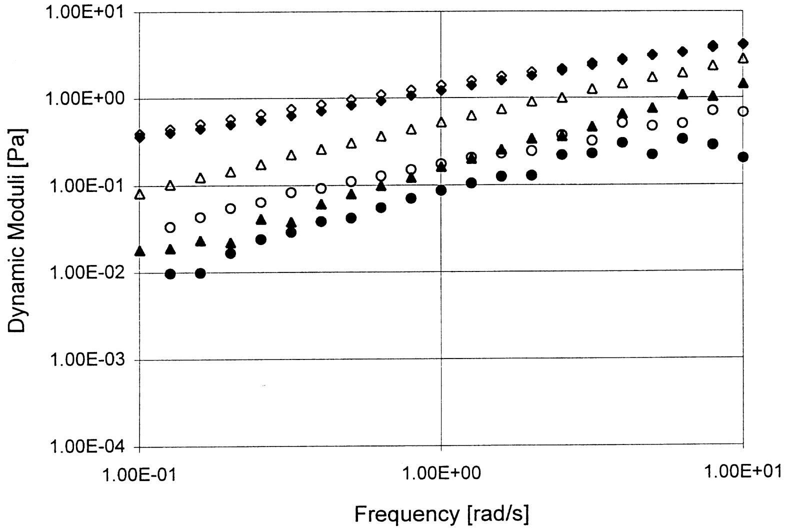

Fig. 14. Frequency sweep of powder-based preparation (filled and open symbols represent *G′* and *G″*, respectively; ◆/◇, 3% WM/0.3% GM; ▲/△, 3% PWM/0.3% GM; ●/○, 7.5% A/0.3% GM).

of the blends than of their individual components. The large differences in the viscoelastic properties of the blends, ranging from weak gel behaviour for the blends containing waxy maize starch in the granular state, to near Newtonian behaviour for the blends containing partially degraded and, therefore, soluble amylopectin, clearly shows that the rheological properties of the blends are largely determined by the extent of starch-granule swelling, disintegration and polymer degradation. This supports the hypothesis that the enhanced structural strength of the blends is caused by volume exclusion effects rather than by true synergistic interaction between amylopectin and galactomannan. The higher viscoelasticity of blends prepared by the powder-based method could be explained by a reduced swelling of waxy maize starch granules and reduced disintegration of starch granules when heating WM and PWM, respectively, in the presence of galactomannan. However, this does not explain the differences in the rheological properties of solution- and powder-based A/GM blends, where no supermolecular starch structure exists. It is conceivable that the preparation procedure of the A/GM blends, which may be described as water-in-water emulsions before bulk phase separation occurs, influences the structure, e.g. the droplet size of the dispersed phase or the kinetics of phase separation below the resolution limits of the vertical-scan NIR analysis.

4. Conclusions

Phase diagrams show that for water-soluble A/G blends the binodal is not symmetrical but displaced towards the lower molecular weight amylopectin. Owing to the high molecular weight and the aggregation of the non-degraded amylopectin in waxy maize starch, the binodals for the PWM/GM and WM/GM systems nearly coincide with the axes representing the polysaccharide concentrations; this we attribute to the inherent instability of these systems. Vertical scan NIR analysis reveals a different nature of separation between the A/GM systems (clear interfaces) and the waxy maize starch blends (sedimentation-like spectra). For the ‘stable’ powder-based preparations of $> 3\%$ WM/ $> 0.3\%$ GM the sedimentation-like NIR transmission spectra for these systems suggest a stabilising influence of the higher viscosity, rather than improved miscibility of the polysaccharides. The rheological studies displayed the importance of the extent of starch swelling, disintegration and degradation, resulting in systems of different structural strength and viscoelastic behaviour. The preparation method (powder-based or solution-based) influences the rheological properties of the blends, with a clear increase in both G' and G'' following the powder-based preparation. The structural strength of the blends is clearly greater than that of any of the individual components. The implications to the food industry of this enhanced structural strength merit further consideration.

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