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Phase and rheological behaviors of xanthan/amylose and xanthan/starch mixed systems

I. Mandala[1], C. Michon*, B. Launay

ENSIA, Food Science Department, 1 avenue des Olympiades, F-91744 MASSY Cedex, France

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Abstract

Phase separation and rheological properties of wheat starch (2 wt%) or amylose (0.3 wt%) with xanthan (0.1 or 0.5 wt%) mixtures were investigated at two salt levels (less than 0.01 M equivalent NaCl and 0.1 M NaCl). Mixed systems were prepared with pre-heated solutions and/or dispersions. Appearance of two or more phases upon time, followed using a technique based on multiple light scattering, occurred at both salt concentrations. However, it was faster and more pronounced at higher salt concentration. Generally, a transparent upper phase, an intermediate diffuse turbid zone (amylose aggregates) and an opaque down phase (granules and/or aggregated amylose sedimentation) were observed. According to their dynamic rheological properties, xanthan and mixed systems behave like viscoelastic fluids with xanthan dominating the overall behavior. Spectra obtained at various xanthan concentrations may be shifted along modulus and frequency axis for both salt conditions and the shift factors dependence on xanthan concentration is discussed.

Keywords: Xanthan; Starch; Amylose; Mixed system; Phase behavior; Viscoelasticity

1. Introduction

Starch and non-starch hydrocolloids are used together in many foods to improve texture, stability, to facilitate processing and generally to improve overall quality. Xanthan is used to enhance the texture in bakery products, sauces, dry mix formulations, confectionary, dairy products as binder, thickener, stabilizer, bodying agent, etc. It has many advantages such as high solubility in hot or cold water, high viscosity, excellent stability in acid systems, thermal or freeze-thaw stability (Kang & Petitt, 1993; Nussinovitch, 1997) and it is the most widely used stabilizer for salad dressings (Brand, 1999). Typically, its level is 0.05–1% (Morris, 1995): 0.1–0.3% in bakery products (Pomeranz, 1991), 0.1–0.2% in instant mixes, e.g. soups, sauces or 0.5% in starch-jelly candies (Nussinovitch).

Starch is a polysaccharide of major importance, with many functional properties, due to granules' swelling, disintegration and amylose leaching out depending on thermo-mechanical treatment (gelatinisation). Gelatinized starch consists of a continuous phase enriched in amylose and a dispersed phase (more or less ruptured starch granules containing mainly amylopectin). On cooling and further storage, a composite gel can be formed. The properties and structure of this composite are determined by size, shape, distribution, rigidity of granules and by interactions among them and with the amylose/amylopectin matrix (Clegg, 1995; Eliasson & Gudmundsson, 1996; Hermansson & Svegmark, 1996).

In such a mixture, phase separation may occur, with the classical distinction between associative and segregative phase separation. In an associative phase separation one of the phases is enriched in both polymers, whilst, in a segregative phase separation, each phase is enriched in one of the polymers (Piculell, Bergfeld, & Nilsson, 1995). The underlying reasons for the segregative phase behavior of

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* Corresponding author. Tel.: +33-169-935-127; fax: +33-169-935-005.
E-mail addresses: michon@ensia.fr (C. Michon), imandala@aua.gr (I. Mandala).

[1] Present address: Department of Food Science and Technology, Laboratory of Engineering, Processing and Preservation of Foods, Agricultural University of Athens, 75 Iera Odos, 11855 Votanikos, Athens, Greece.

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mixed biopolymer systems may be attributed to either a low affinity of polymers to each others (thermodynamic incompatibility) or to a very low affinity of one polymer for the solvent (Piculell et al.).

In starch dispersion, granules are dispersed in an amylose rich phase, which may contain also some amylopectin molecules. In this later case a segregative phase separation may occur due to the thermodynamic incompatibility between amylose and amylopectin (Kalichevsky & Ring, 1987). Amylose gelation takes place through association of ordered amylose chains that allows the formation of aggregates, which, at low concentrations, precipitate (Miles, Morris & Ring, 1984; Ellis & Ring, 1985; Eliasson & Gudmundsson, 1996). Gelation may be followed by turbidity development related to the number, size and compaction of aggregates and by the evolution of the storage modulus depending on the number of junctions and on the overall rigidity of the network (Clark, Gidley, Richardson, & Ross-Murphy, 1989; Doublier & Choplin, 1989; Eliasson & Gudmundsson, 1996; Miles, Morris, & Ring, 1984; Leloup, Colonna, Ring, Roberts, & Wells, 1992). The presence of swollen granules increases the effective concentration of dissolved amylose and amylopectin chains and favors their mutual exclusion, which in turn promotes the aggregation of the highly concentrated amylose located between the starch granules (Conde-Petit & Escher, 1995).

Adding another biopolymer, like xanthan, in starch dispersion modifies the structure of the continuous phase, resulting in a marked change in the rheological properties of the mixture. Starch pastes and amylose gels are dominantly elastic and their storage modulus is strongly dependent on their concentration (Ellis & Ring, 1985; Evans & Lips, 1992). On the other hand, xanthan solutions can be considered as highly structured liquids with much longer relaxation times compared to classical entangled macromolecular solutions (Giboreau, Cuvelier, & Launay 1994; Doublier & Cuvelier, 1996). Moreover, phase separation phenomena may play an important role on the behavior of such systems as interactions between chain segments of the same type can be favored energetically and exclusion effects may occur (Closs, Conde-Petit, Roberts, Tolstoguzov, & Escher, 1999; Eidam, Kulicke, Kuhn, & Stute, 1995; Mandala & Palogou, 2003). Different types of phase behavior of starch or amylose/biopolymer mixed systems have been described in the literature. Either segregative interactions (Alloncle & Doublier, 1991; Appelqvist, Brown, Goff, Lane, & Norton, 1996), or, on the contrary, associative phase interactions with amylose molecules leached from granules (Shi & BeMiller, 2002) have been assumed.

The present investigation was undertaken to investigate phase separation phenomena of wheat starch/xanthan mixtures, in ‘low’ (less than 0.01 M) and ‘high’ (0.1 M NaCl) salt concentrations. Heat treatment under stirring was chosen in order to leach amylose chains out of the granules. The phase and rheological behaviors of both starch/xanthan and amylose/xanthan mixed systems were studied in order to understand the respective contribution of amylose and starch.

2. Material and methods

2.1. Materials

Wheat starch from Merck (Darmstadt, Germany) and xanthan gum from Sigma (St Louis, MO, USA) were used for the experiments. The moisture content of xanthan powder was 11.2 ± 0.1% (105 °C, 24 h, 3 replications). The amylose content of starch determined by the method of Gilbert and Spragg (1964) was 20 ± 0.2%. The starch moisture content was 11.5 ± 0.4% (105 °C, 24 h, 3 replications).

2.2. Sample preparation

Water (no addition of NaCl) or salt (NaCl 0.1 M) solutions of xanthan (1 or 0.8 wt%) were prepared and heated in a water bath at 90 °C for 20 min. Samples were stirred with a propeller stirrer at 500 rpm. After heating, xanthan solutions were filtered under vacuum (3 μm filter) to obtain clear solutions and were degassed. According to Cuvelier (1988) filtering in such conditions does not modify the rheological properties of xanthan solutions.

Wheat starch dispersions (5 wt%) were prepared in water according to the above heating procedure, but samples were stirred at 200 rpm for avoiding granules’ rupture. For samples containing 0.1 M NaCl, the appropriate quantity of NaCl was added after mixing with xanthan.

Amylose used in all experiments corresponded to the amount leached from 2 wt% wheat starch following heating at 90 °C as described above. After centrifugation (10 min, 2000 *g*) the supernatants were collected. Amylose purity (control of amylopectin leached out during granules’ heating) and concentration were determined with a spectrophotometer (Cary 100, Varian, France; optical density accuracy 0.001). Supernatants were scanned according to the method of Jarris and Walker (1993) in a range of a wavelength of 400–800 nm, in which both amylose and amylopectin absorb. Amylopectin presents a peak value at 548 nm and amylose at 630 nm. The spectra obtained were compared with those of pure amylose (Merck, Darmstadt, Germany) solutions of known concentration. Similar spectra were obtained with a peak value around 630 nm and no peak detection at lower wave lengths, where amylopectin absorb. Thus, it was confirmed that amylopectin was not leached out from granules during heating, mainly because granules were stirred gently and their disruption was avoided.

Mixed systems of wheat starch (2% w/w) or amylose (0.30 ± 0.06%w/w) and xanthan at 0.1 or 0.5 wt% were prepared by mixing the corresponding mother preparations in appropriate proportions. Hot mixtures were stirred with a magnetic stirrer during 10 min and were immediately used for phase separation observations and rheological experiments. For microbiological stability 0.04 wt% NaN_3 was added in all samples.

2.3. Phase separation behavior

For phase separation observations, samples (5 ml) were poured in glass tubes (inner diameter 6.1 mm) and stored at 25 °C. Light transmission at 850 nm was measured with a Turbiscan MA 1000 (Formulaction, France; accuracy 0.05 nm) during storage. Samples were scanned at different time intervals and transmission values along sample height were obtained. For each mixture two or three replicates were used.

2.4. Amylose and total solids determination

At equilibrium, amylose concentration in water was calculated in each separated phase. A reference curve was plotted, using nine different concentrations of pure amylose solution (2–3 replica at each concentration) and measuring the absorption at 630 nm.

A second reference curve was also used for amylose solutions in 0.1 M NaCl (5 concentrations, 2 replicates at each concentration). During storage a shift of peak absorption at lower wave length and an underestimate of amylose concentration were noticed. This underestimate was large, e.g. 50% in a starch/xanthan mixture after 6 days of storage in 0.1 M NaCl. In consequence, only amylose concentrations in water will be evaluated and, in few cases, values in 0.1 M NaCl when they were obtained after the same ageing time.

The total solid contents were calculated in each separated phase. Samples from each phase were weighted and dried at 120 °C for 24 h. Total solids content (%) was determined as the dry weight divided by the initial weight of samples.

Xanthan amount was calculated by subtracting from the weight of total solids, the weight of amylose according to its distribution in each phase plus the weight of NaN_3 added. In samples containing salt, the weight of salt, assuming that its distribution was uniform along sample height, was also subtracted.

2.5. Rheological measurements

Dynamic viscoelastic measurements were performed with a RFSII (Rheometrics Scientific, Inc., NJ) fitted with coaxial cylinders ($R_1/R_2=0.97$, $R_1=24$ mm). Samples were degassed after preparation and were poured at hot in the pre-heated apparatus. A thin layer of paraffin oil was put at the surface to avoid water evaporation and the measurement started immediately at 25 °C. The storage modulus, G', and the loss modulus, G'', were determined between 10^{-3} and 15 Hz, with two replica.

In a preliminary step, the linear viscoelastic domain was determined at 0.1 and 10 Hz (2–3 replica): maximum strain amplitude used were 20–50% for xanthan solutions and 2–8% for mixed systems.

3. Results and discussion

3.1. Phase behavior of starch/xanthan and amylose/xanthan mixed systems

In reference starch dispersions (2 wt%) stored at 25 °C, granules' sedimentation was completed within 2 h. The upper transparent phase occupied 67% of the total sample volume. One can assume that the upper phase contains dissolved amylose chains that had been leached out of the granules during the thermomechanical pre-treatment. In water the same volume of upper phase was obtained for a starch (1 wt%)/xanthan (0.1 wt%) mixture but after almost 7 days. Addition of xanthan leads to an increase of the viscosity of the continuous phase which delays granules sedimentation. In such starch/xanthan mixtures stored at 25 °C, a single turbid phase was observed during more than 1 day. After this time, an upper, semi-transparent phase appeared. This phase occupied 10% of the total sample volume and its transmission values (about 15%) remained approximately constant after the first 3 days of storage (Fig. 1). In further storage, an intermediate diffuse opaque zone was created (Fig. 2). Following addition of iodine, the absorbance spectrum between 350 and 800 nm corresponding to this intermediate zone was typical of amylose. The increase in turbidity of this amylose rich phase indicates the presence of large semi-crystalline domains comparable in size to the wavelength of light as described by Miles et al. (1984). Unlike the initial turbidity of starch/xanthan mixtures due to the presence of granules, amylose/xanthan mixtures, at the beginning of storage, were transparent (transmission value of almost 90%) (Fig. 1). Amylose was completely dissolved in the medium and no apparent phase separation was observed. During the first 22 h of storage the percentage of transmitted light was almost constant, and was followed by a fast turbidity increase (i.e. decrease of the percentage of transmission). After 5 days of storage (120 h), the transmission value was reduced by 67% and after 18 days (432 h) by 92% in comparison to the initial value. The aggregation of polymer molecules takes place

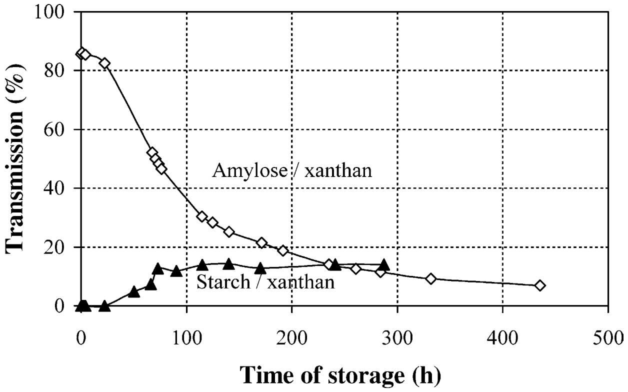

Fig. 1. Transmission values of the upper phase of aqueous amylose (0.3 wt%)/xanthan (0.1 wt%) or starch (2 wt%)/xanthan (0.1 wt%) systems in water.

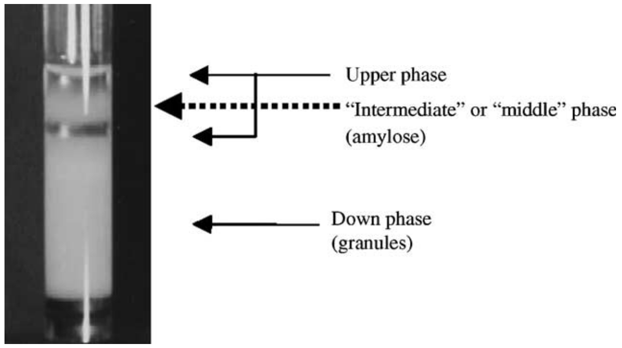

Fig. 2. Phase separation in a starch (2%)/xanthan (0.1%) mixture after extensive storage (≈one month) at 25 °C in water.

before any turbidity development because the first aggregates are totally solvated, and, when sufficiently large aggregates are formed, turbidity develops (Doublier & Choplin, 1989). A pure amylose 0.45 wt% solution shows an increase of turbidity (decrease of transmission signal measured by Turbiscan) during time of ageing (Fig. 3). At the beginning the transmission signal is almost constant all along the sample. However, rapidly, the transmission level decreases in the bottom of the tube, when it increases slightly at the top of the sample: amylose aggregates sink in the bottom of the tube whenever density is high enough.

In a qualitatively similar way the transmission signal of amylose/xanthan system decreases continuously and uniformly along the height of the sample during 3.5 days (Figs. 4 and 7A). After that delay, a turbid precipitate is formed at the bottom of the tube (about 5% of transmission after 6.5 days) and a clearer upper phase reappears. After 10 days, the aggregates on the bottom of the tube are more compact and the upper phase became rather transparent except around 30 mm of the height of the sample where a diffuse white ring is observed. This would be explained by fast amylose aggregation, which occurs either in presence or not of xanthan. However, in presence of xanthan it seems that amylose aggregation is faster and insoluble amylose aggregates are formed faster.

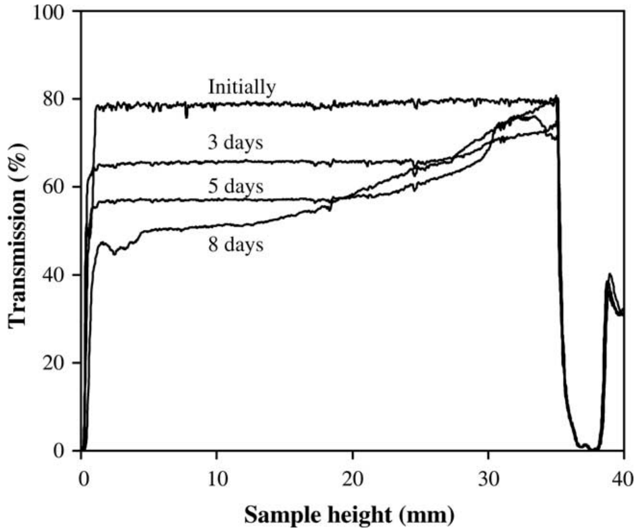

Fig. 3. Transmission values of amylose (0.45%) in water along its height in a glass tube during storage at 25 °C.

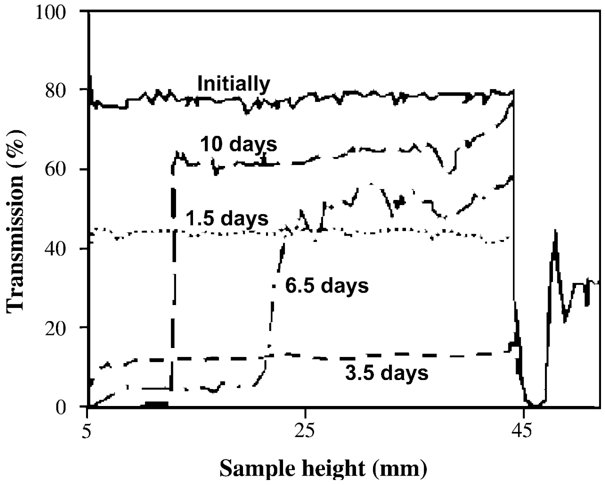

Fig. 4. Transmission values of amylose (0.3%)/xanthan (0.1%) mixture in water along its height in a glass tube during storage at 25 °C.

Like in starch/xanthan samples (Fig. 2) three phases were created: an upper phase, more transparent than the other two, a middle one occupying the greatest volume and a small turbid one at the bottom of the sample (Fig. 4). It seems, in that case, that the aggregation of amylose during time leads to the appearance of aggregates, some of them, being insoluble, sinking, the other ones remaining in, more or less solvated, in suspension in the middle phase. The upper phase would also contain mostly xanthan.

In conclusion, it seems that amylose 0.3 wt%/xanthan 0.1 wt% mixed systems, containing no added salt, do not lead to segregative phase separation whenever the amylose remains in solution. Aggregates appear after a rather long time of ageing (more than 1 day) and may be attributed to amylose aggregation decreasing strongly its affinity for the solvent. This phenomenon leads to a segregative phase separation, due at least to a low affinity of amylose for the solvent. Thermodynamic incompatibility between xanthan and amylose probably also exists and may explain either the increased speed of amylose aggregation (turbidity increase) and the rather rapid precipitation of amylose aggregates in amylose/xanthan systems despite the increase of viscosity of the continuous phase by xanthan. The thermodynamic incompatibility between amylose and xanthan should be increased by amylose aggregation.

In presence of 0.1 M NaCl, phase separation of both starch/xanthan and amylose/xanthan mixed systems was accelerated (Fig. 5). In both starch and amylose/xanthan mixtures a minimum transmission value was noticed at approximately the same storage time (≈4 days) (Fig. 5).

According to transmission values, in starch/xanthan mixtures, a semi-transparent upper phase appeared within less than 1 day of storage (Fig. 6a). The height of this

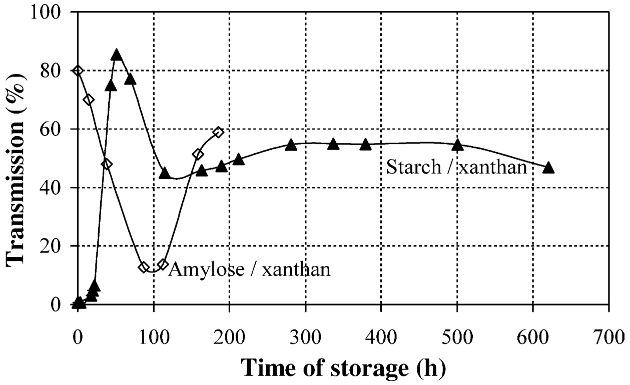

Fig. 5. Transmission values of the upper phase of amylose (0.3%) or starch (2%)/xanthan (0.1%) systems in 0.1 M NaCl.

upper phase increased upon time for at least 10 days. It was initially very transparent (transmission of about 80%), then an intermediate diffuse opaque zone (amylose aggregates) appeared resulting in a minimum in the transmission signal of the upper phase (see the scan obtained after 10 days in Fig. 4a). The volume of the upper phase after 10 days of ageing was 27% of the total volume versus 10% obtained in water solution, indicating a more complete phase separation or a less swollen bottom phase. The evolution of the state of the upper phase (height and transmission level) is the result of two phenomena having different kinetics: (a) Fast granules sedimentation producing an increase in transparency of the upper phase, (b) Association of amylose chains and decrease in transparency after about 4 days (Fig. 5).

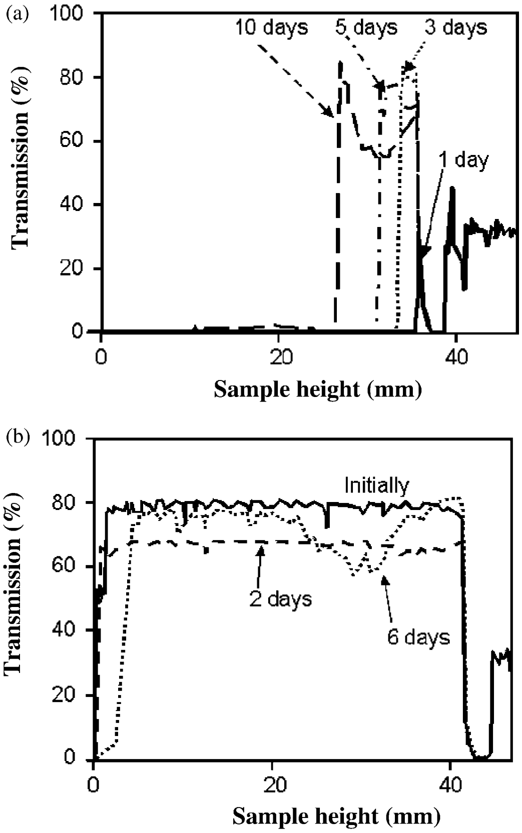

Fig. 6. Transmission values of (a) starch (2%)/xanthan (0.1%), (b) amylose (0.3%)/xanthan (0.1%) mixture in 0.1 M NaCl along their height in a glass tube during storage at 25 °C.

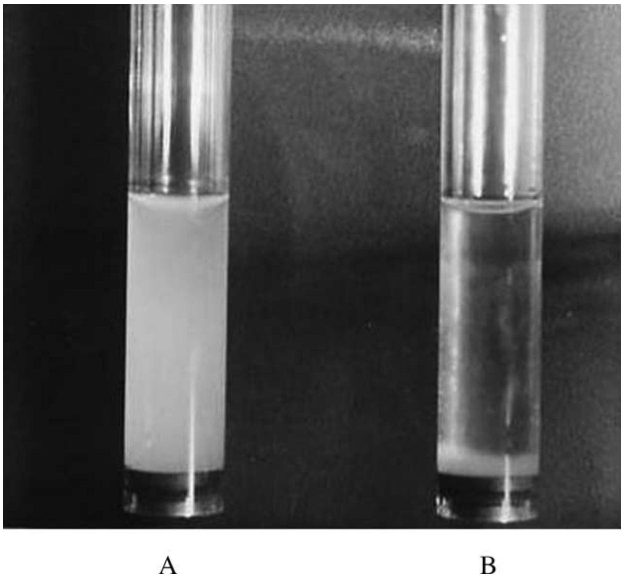

Fig. 7. Turbidity change of an amylose (0.3%)/xanthan (0.1%) mixture (A) in water and (B) in 0.1 M NaCl stored 4 days at 25 °C.

In case of amylose/xanthan mixtures in 0.1 M NaCl, a gradual but faster decrease in transmission values was noticed as in water solutions: a minimum is reached after 100 h instead of 300–400 h in low salt conditions. The decrease of transmission corresponds to the appearance of interconnected filaments (observed by naked eyes) in the upper phase, which look like the amylose network described by Leloup et al. (1992). After this minimum of transmission, a significant transmission increase was noticed corresponding to sedimentation of more compact aggregates. These phenomena lead to the formation of three phases (Figs. 6b and 7B):

- A small upper transparent one containing mainly xanthan, its transmission value increasing upon time and reaching a value of 80% after 10 days,
- A middle one with partially solvated amylose aggregates,
- An opaque phase at the bottom containing mostly compacted amylose aggregates. In this phase, the transmission is low and decreases with time as the compaction of amylose aggregates increases. However, its height increases too with time, as the number of amylose aggregates, which sediment, increases.

After a long storage time (more than 30 days), the volume of each phase for both starch/xanthan and amylose/xanthan mixtures is constant and gives additional information about amylose distribution when thermodynamical equilibrium is reached (Fig. 8).

In amylose/xanthan systems in water the volume of the down phase (2.6%) corresponds to a very small amount of

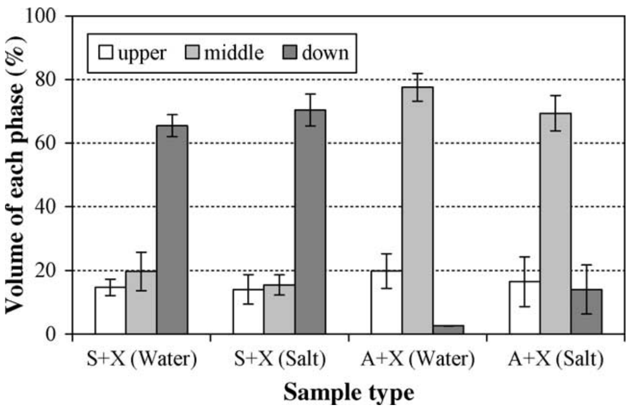

Fig. 8. Volume of separated phases at equilibrium of starch (S, 2%) or amylose (A, 0.3%)/xanthan (X, 0.1%) mixtures in water and salt solution at 25 °C.

precipitated amylose. In starch/xanthan mixtures, the bottom phase contains starch granules and few amylose aggregates. Starch granules would occupy about 64% of the total sample volume and amylose 2.6%. In 0.1 M NaCl, the volume of the bottom phase of starch/xanthan mixture was greater (70%) indicating that besides starch granules, the contribution of precipitated amylose aggregates to the volume of the bottom phase is larger. In amylose/xanthan mixed systems in 0.1 M NaCl the volume of the bottom phase containing amylose aggregates is about 14%. This result confirms the hypothesis of the composition of the bottom phase in starch/xanthan mixed systems: swollen starch granules and amylose aggregates.

The amylose content was determined by spectrophotometry. Even if the method was not totally quantitative (see Section 2), it could give information on the location of amylose in the phase separated sample. Amylose aggregates were concentrated in the diffused ring of the upper phase. As an example after 8 days of storage of an amylose/xanthan in 0.1 M NaCl mixed system, 71% of amylose was located in the turbid ring (‘middle phase’). However, the amylose concentration of the bottom phase is always higher than the upper one.

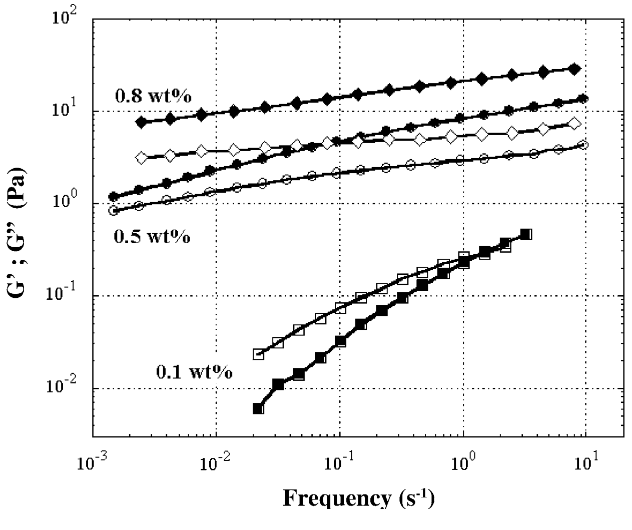

Fig. 9. Spectra of solutions of xanthan 0.1 wt% (□, ■), 0.5 wt% (○, ●) and 0.8 wt% (◇, ◆). Closed symbols G', open symbols G''. 0.1 M NaCl, 25 °C, maximum strain amplitude: 20–50%.

In conclusion, amylose and xanthan are probably thermodynamically incompatible but it could not be demonstrated in the present study. The association of amylose chains leads to a decrease of their solvent (water) affinity and then to their precipitation. However, aggregates may remain in suspension due to partial solvatation and/or low density due to high swelling. In addition, precipitation is slowed down by the high viscosity of the upper xanthan rich phase. Apart from phase separation, the high volume occupied by the swollen starch granules increases amylose

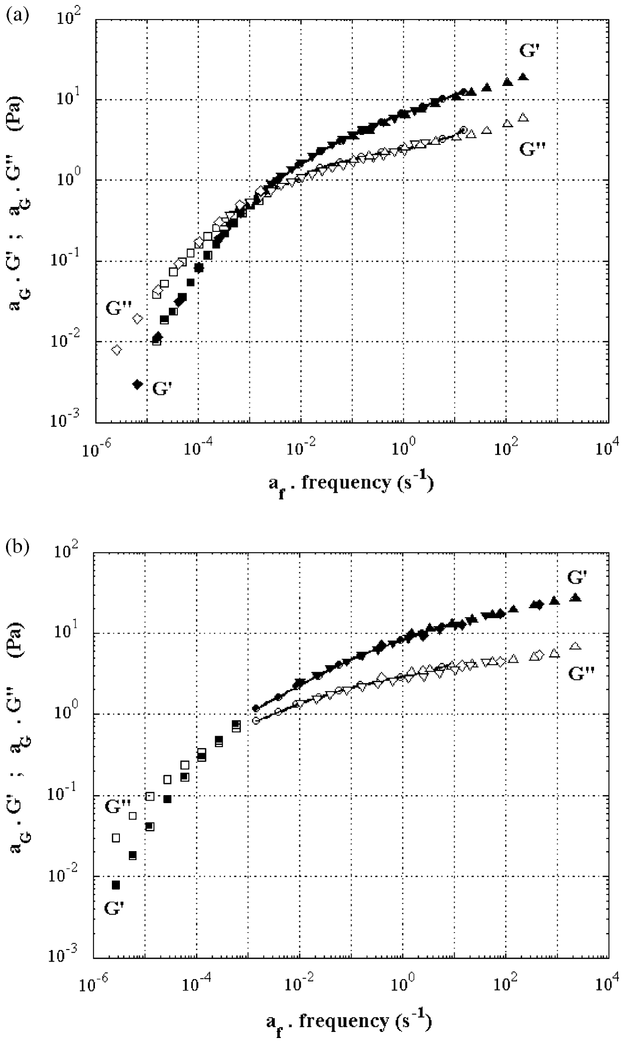

Fig. 10. Superimposed shifted spectra. (a) In water of xanthan 0.1 wt% (□, ■) and 0.5 wt% (○, ●), starch 2 wt%/xanthan 0.5 wt% (△, ▲), amylose 0.3 wt%/xanthan 0.1 wt% (◇, ◆), amylose 0.3 wt%/xanthan 0.5 wt% (▽, ▼). (b) In 0.1 M NaCl of xanthan 0.1 wt% (□, ■), 0.5 wt% (○, ●) and 0.8 wt% (◇, ◆), starch 2 wt%/xanthan 0.5 wt% (△, ▲), amylose 0.3 wt%/xanthan 0.5 wt% (▽, ▼). Reference curve: xanthan 0.5 wt%; closed symbols G', open symbols G''. 25 °C, maximum strain amplitude: 20–50% for xanthan solutions, 2–8% for mixed systems.

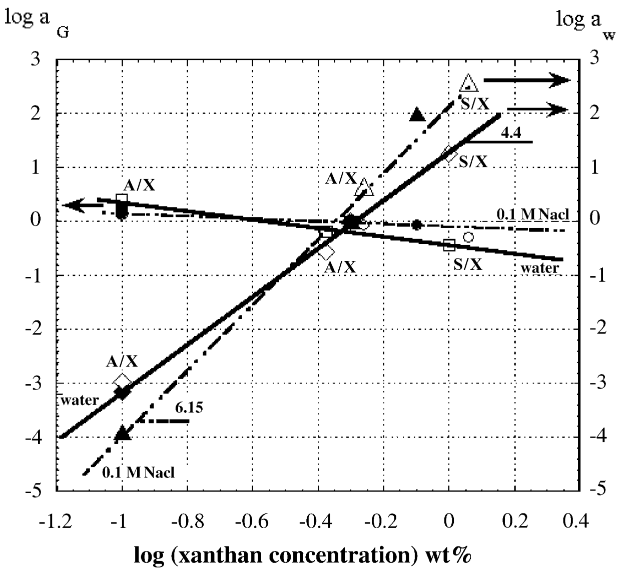

Fig. 11. Concentration dependence of modulus (α_G) and frequency (α_ω) shift factors of xanthan solutions and amylose/xanthan and starch/xanthan mixed systems: ((□, ■, ◇, ♦) in water, (△, ▲, ○, ●), in 0.1 M NaCl. Filled symbols: xanthan solutions, open symbols: amylose/xanthan and starch/xanthan mixed systems for which the apparent xanthan solution is chosen so that α_ω value fit the log α_ω − log(xanthan concentration) straight line obtained for 0.1 and 0.5% xanthan concentrations.

concentration in the continuous phase and promotes aggregates formation.

3.2. Rheological properties

The variation of G' and G'' with frequency shows that the viscoelastic behavior of xanthan solution changes from a weakly elastic to a rubber-like liquid, when its concentration increases (Fig. 9). These results are comparable to those obtained by Cuvelier and Launay (1986) in the range of concentrations 0.08–0.7 wt%. A time-concentration superimposition was applied successfully for both salt concentrations: no salt added (Fig. 10a) and 0.1 M NaCl (Fig. 10b). The spectra obtained for all mixed systems were also all shifted in order to try to fit them to the curve corresponding to 0.5 wt% xanthan (Fig. 10a and b). The values of frequency shift factors (α_ω) and G' modulus shift factor (α_G) were collected and reported in Fig. 11 as a function of xanthan concentration in logarithm scale. As frequency shift factor α_ω seemed to be the most sensible parameter the equivalent concentration of xanthan was determined so that α_ω α_f points of mixed systems were on the line obtained for xanthan alone. The equivalent xanthan concentrations obtained for amylose 0.3 wt%/xanthan 0.5 wt% mixed systems were 0.42 and 0.55 wt% in water and 0.1 M NaCl, respectively. If an increase of the equivalent xanthan concentration (0.55 wt%) in presence of amylose in 0.1 M NaCl is easily understandable from the hypothesis of an excluded volume effect, its decrease in water (0.42 wt%) is surprising. In water, the xanthan entanglements may structure differently the solution in comparison to 0.1 M NaCl conditions. A decrease of salt concentration may favor the packing in parallel of xanthan chains leading to a less entangled xanthan solution. In that case, addition of amylose may increase the packing of xanthan chains by excluded volume effect resulting in a small apparent xanthan concentration decrease. The variation of the modulus shift factor α_G is very small (α_G varies as $C^{-0.22}$ and $C^{-0.72}$ for water and 0.1 M NaCl solvent, respectively) compared to the frequency shift factors α_ω one (α_ω varies as $C^{4.4}$ and $C^{6.15}$ for water and 0.1 M NaCl solvent, respectively). The value of 6.15 is of the same order of magnitude as the value found by Cuvelier and Launay (1986): 7.4. This phenomenon could be explained by the high extension of xanthan, which would bring about parallel packing of chain segments. Adding new chains could only reinforce existing junction zones without creating any new ones. However, such a mechanism would also bring about a large increase in the lifetime of these junction zones and therefore could explain the very high dependence of the time shift factor α_ω. The higher the salt concentration, the higher the frequency shift factor dependence on concentration. In that later case the reinforcement of existing junctions zones is more efficient on the lifetime as packed chain segments may be more rigid. Some additional junction may also appear in that case.

Addition of amylose to xanthan solution does not seem to change the rheological spectra in comparison to those obtained with xanthan alone, which indicates that xanthan behavior dominates. It is also in good agreement with the fact that xanthan/amylose mixed systems seemed to be able to stay in the same phase at the beginning of ageing time (a few hours, see Fig. 3). Addition of starch modifies the spectra but they are closely similar to those obtained at higher xanthan concentration. As starch is assumed to play only a role of filler, the hypothesis of a dominating effect of excluded volume phenomenon may be inferred for both salt conditions.

The equivalent concentrations of xanthan showing the same behavior than starch 2 wt%/xanthan 0.5 wt% found from Fig. 11 are 1 and 1.15 wt% in water and in 0.1 M NaCl, respectively. Assuming from the results on amylose /xanthan in 0.1 M NaCl results that amylose takes 10% of the volume in the amylose/xanthan continuous phase, the increase in the xanthan concentration from 0.5 to 1.15 wt%, means that starch granules occupy 52% of the volume, which is a lower value than the one obtained by measuring the height of the phases after decantation. However, in that later case swollen granules may have not been packed in the bottom of the tube and the height of the bottom phase is probably an overestimate of the volume occupied by starch granules in the mixed systems.

4. Conclusion

In starch/xanthan systems a sedimentation of starch granules is observed, only slowed down by the presence of xanthan. Amylose/xanthan mixed systems show evidence of segregative phase separation type after some delay: sedimentation of amylose aggregates is shown to occur. It should be slowed down by the increase of viscosity of the continuous phase due to xanthan. However it is not the case in low salt conditions. To the contrary, xanthan accelerates the amylose aggregates formation and their sedimentation. Thermodynamic incompatibility, which would accelerate phase separation, may be invoked to explain such a phenomenon. When the mixed systems are still macroscopically homogeneous, phenomena of excluded volume are clearly observed, resulting in an increase of the equivalent concentration of xanthan in the continuous phase. In the studied mixed systems, xanthan dominates the viscoelastic behaviour and the main effect of adding starch is an increase of its effective concentration.

The shift of viscoelastic spectra is shown here to be an interesting way to evidence a segregative phase separation phenomenon. The volumes occupied by the dispersed phase may be evaluated from shift factors α_G. It is probably more accurate than the study of bulk phase separation

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