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Gel formation in mixtures of amylose and high amylopectin potato starch

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Abstract

The influence of amylopectin (Ap) (in the form of high amylopectin potato starch, HAPP) on the rheological properties of its mixtures with amylose (Am) has been studied in small-deformation oscillatory rheometry during relatively long times (6 h). The absence of HAPP granule remnants in the samples has been considered important; therefore HAPP, Am, and HAPP–Am mixtures have been prepared at 140 °C.

A higher amount of HAPP in the HAPP–Am mixture resulted in a lower value of G' of the formed systems. This trend was stronger at 10 and 8%, than at 6% total polysaccharide concentration. The rheological properties of the mixtures with the lowest amount of Am resulted in a rheological behaviour that was similar to that of HAPP at identical concentration. With increasing Am concentration in the Am–HAPP mixtures, the behaviour was comparable to pure Am. HAPP did not seem to increase the effective concentration of Am and act as a precipitator. The frequency dependence of $G'(n')$ strongly drop with increasing Am concentration until a certain ratio of Am:HAPP was reached, approaching zero. This implied a drastic liquid–solid transition, which was clearer at higher total polysaccharide concentrations.

The values of G' for pure Am increased more rapidly and at considerably lower concentrations than for pure HAPP. For HAPP the decrease in n' with increasing concentration was gradual, in three different stages. First a strong decrease in n' and n'' to a more or less constant value (~ 0.5) and then, at the highest concentration, n' decreased even further, and approached zero. For Am, the values of n' decreased abruptly from ~ 1 to ~ 0 with increasing concentration, which implies a distinct liquid to solid transition.

Keywords: High amylopectin potato starch; Amylose; Gel

1. Introduction

The rheological behaviour of several types of starch has been characterised to understand the role of the starch and its constituents in mixed systems. The effects of morphology, temperature, water/starch ratio, granule size distribution, shear, and amylose–amylopectin ratio (Am:Ap) on starch gel structure and its viscoelastic properties have been studied (Chedid & Kokini, 1992; Evans & Haisman, 1979; Kokini, Lai, & Chedid, 1992; Myers, Knauss, & Hoffman, 1962; Rosalina & Bhattacharya, 2002). For instance, in studies of starch gelation, a linear relationship between the storage modulus (G') and concentration has been reported for gelled corn and potato starches (Evans & Haisman, 1979), potato and waxy maize starches (Keetels, van Vliet, & Walstra, 1996; Steeneken, 1989), and slightly sheared potato starch dispersions (Svegmark & Hermansson, 1991). On the other hand, a non-linear relationship was found for highly sheared potato starch dispersions (Svegmark & Hermansson, 1991). Low fracture stress and strain for high amylose maize starch gels prepared at 121–166 °C were attributed to a low ability for Am to phase separate during cooling (Case et al., 1998). The effects of granular structures on the rheological behaviour have also been studied for rice and corn starch (cross-linked and uncross-linked) pastes (Tsai, Li, & Lii, 1997). The time-dependence of the ordering of Am and Ap has been related to changes in the gel's mechanical behaviour (Miles, Morris, Orford, & Ring, 1985; Miles, Morris, & Ring, 1985). The association and crystallization of Ap chains and branches in the gel has also been described (Ring et al., 1987). Rheopectic and shear thickening behaviours have been reported for waxy maize starch, whereas gels of normal native maize starch showed shear thickening behaviour after short heating times (Dintzis & Bagley, 1995). However, these characteristics changed slowly to shear thinning with increasing heating time. Modified waxy maize starch had faster and broader swelling, showing rheopectic time-dependence and shear

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thinning with yield stress (da Silva & Oliveira, 1997; Doublier, 1981; Evans & Haisman, 1979).

Although many studies have been performed to understand the viscoelastic properties of starch gels, it is yet not clear how Am and Ap contribute to the properties of the mixed system. Phase separation and the ratio of Am to Ap have been used to describe the effects of increasing Am or Ap content on the gel behaviour (Doublier & Llamas, 1993; Kalichevsky & Ring, 1987; Klucinec & Thompson, 2002; Leloup, Colonna, & Buleon, 1991). Although phase separation of Am and Ap at 80 °C (Kalichevsky & Ring, 1987) has been invoked to explain the rheological properties of gels of Am–Ap mixtures, the conditions for that phenomenon are not well established.

The intention of the present study was to investigate how Ap (in the form of high Ap potato starch, HAPP) contributes to the rheological characteristics in a mixture with amylose. The rheological behaviour of Am, dissolved HAPP granules, and their mixtures, was investigated using small-deformation oscillatory measurements. A study of the behaviour of mixed systems during long times (6 h) was included as well.

2. Materials and methods

2.1. Materials

Amylose (potato amylose, [9005-82-7], $\gg 95\%$ amylose) was purchased from ICN AB (Malmö, Sweden). Amylopectin (high amylopectin potato starch, $\ll 1\%$ amylose) was provided by Lyckeby-Stärkelsen Food and Fibre AB (Lyckeby, Sweden).

2.2. Methods

2.2.1. Rheological measurements

The gelling behaviour of Am was studied by preparing Am suspensions at different concentrations (1.5, 1.62, 1.65, 1.7, 1.8, 2 and 3% (w/w)). Am–HAPP blends at several concentrations (6, 8 and 10% w/w, total polysaccharide concentration) at different Am:HAPP ratios (from 100:0 to 0:100) were heated in water (see below). Samples were prepared according to the previously published preparation procedure for HAPP (Ortega-Ojeda, Larsson, & Eliasson, 2003) to reduce the amount of granular remnants in the mixture. This means that all suspensions were heated at 140 °C for 20 min, and then quenched for 4 s in a water bath at 60 °C. Afterwards, the samples were transferred to the cone-plate geometry of a StressTech controlled stress rheometer (Reologica AB, Lund, Sweden), where the measurements were carried out at 10 °C. The storage and loss moduli (G' and G'') as function of time (t) with 0.025 strain at a frequency (f) of 0.2 Hz were recorded. From the power law relationships shown by G' and G'' in a frequency sweep experiment, $G' = G'_0 f^{n'}$ and $G'' = G''_0 f^{n''}$, where G'_0 and G''_0 are the intercepts, the slopes of $\log(G', G'')$ vs. $\log f(n'$ and $n'')$ were calculated. It should be mentioned and taken into account that after preparation and prior the actual rheological measurements started, the HAPP samples were left to rest in the rheometer for 6 h for relaxation of residual stresses. Then, the rheological tests were performed for another 6 or 8 h (curing time). For pure Am and blends of Am–HAPP, which did not need a relaxation time, only 6 h are reported as curing time. All the reported values are the average of at least three different runs and sample preparations.

2.2.2. Microscopy

The sample preparation for the microscopy study was the same as for the rheological studies until the quenching to 60 °C. A drop of iodine (1% solution) was added to the starch suspension. An aliquot of the suspension was then placed on a microscope slide, observed and recorded on-line in an Olympus BX50 microscope (Tokyo, Japan), with a 530 nm Olympus U-TP530 polarised light filter (Tokyo, Japan).

3. Results

3.1. Individual components

3.1.1. Amylose

Fig. 1a shows the time dependence of G' during 8 h for Am solutions at 1.5–3% at 0.2 Hz. It can be seen that G' increased with Am concentration. The storage modulus also increased earlier with increasing concentration. The G' values corresponding to the 3% Am concentration, for instance, were thousand times higher than those of the 2% Am sample, which already were about hundred times larger than those of the lowest Am concentrations.

Fig. 1b shows the mechanical spectra of the Am solutions at different concentrations at the end of the measurements shown in Fig. 1a, after 8 h at 10 °C. The sample response in the mechanical spectra can be divided into two groups. Samples containing at least 1.7% Am always showed similar frequency dependence, with G' being independent of frequency. Besides, they showed solid-like behaviour ($G' > G''$). Below 1.7% Am, the frequency dependence was high, not influenced by Am concentration, and liquid-like behaviour was observed for all samples.

3.1.2. HAPP

Fig. 2a shows the time dependence of G' for HAPP solutions at 2–14%, after 6 h equilibrium time, and 6 h curing, at 0.2 Hz. One important feature of this system, which has been described in detail in a previous work (Ortega-Ojeda et al., 2003), is that there was no change in storage modulus during curing time. It is interesting to note that at the highest HAPP concentrations the registered G' values were lower than the values for normal potato starch

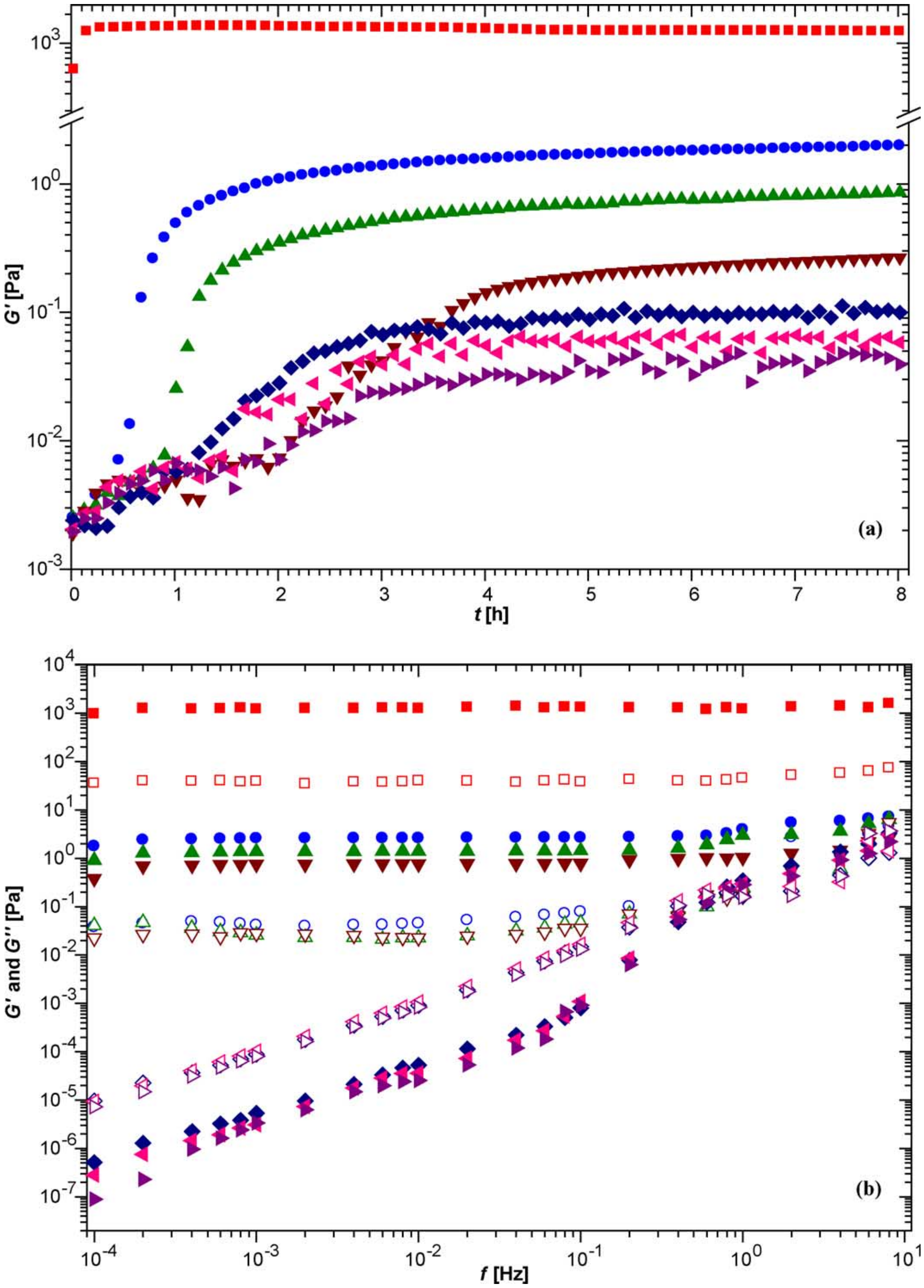

Fig. 1. (a) Storage modulus (G') against time for Am solutions at different concentrations; after heating at 140 °C, quenching to 60 °C and measured at 10 °C with 0.025 strain and at 0.2 Hz. (b) Mechanical spectra for the Am solutions. ■, □ = 3%; ●, ○ = 2%; ▲, △ = 1.8%; ▼, ▽ = 1.7%; ◆, ◇ = 1.65%; ◀, ◁ = 1.62%; ▷, ▶ = 1.5%. The closed symbols are G', and the open symbols in the frequency sweep are G''.

(<7 Pa) at the same concentrations (to be published). Nevertheless, both G' and G'' increased with concentration.

Fig. 2b shows the mechanical spectra for samples containing 2, 6, 10 and 14% HAPP, after the 6 h curing shown in Fig. 2a. The frequency dependence decreased with increasing concentration so that G' was independent of frequency at 14% HAPP. In addition, $G'/G'' \approx 1$ at the concentrations of 6 and 10%, over the entire frequency spectra.

3.2. Amylose–HAPP mixtures

Fig. 3a shows the values of G' versus time at 0.2 Hz during 6 h curing for Am–HAPP mixtures at a total polymer

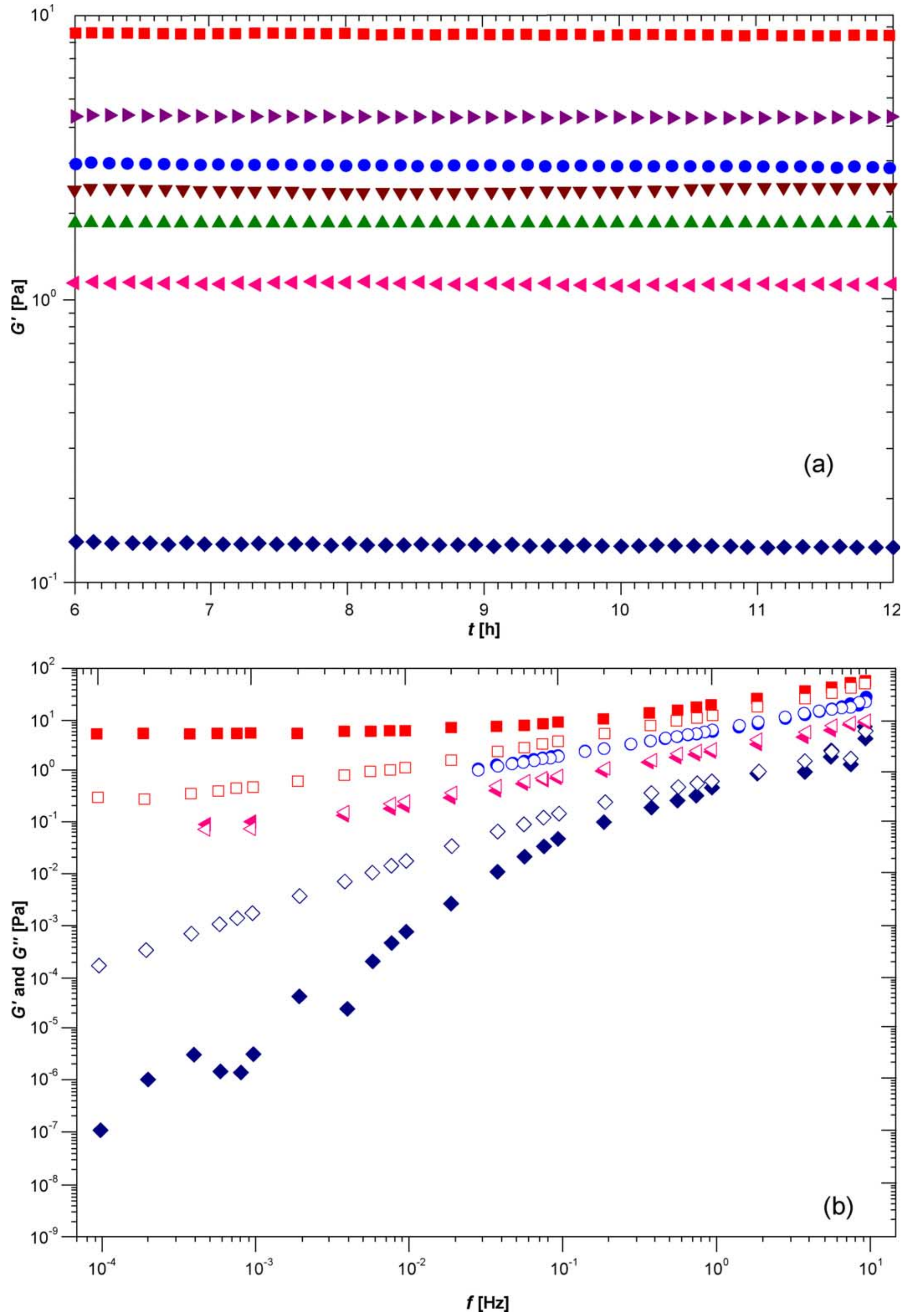

Fig. 2. (a) Storage modulus (G') against time for HAPP solutions at different concentrations; after heating at 140 °C, quenching to 60 °C and measured at 10 °C with 0.025 strain and at 0.2 Hz. Prior to 6 h curing, the sample had 6 h as relaxation time. ■ = 14%; ► = 12%; ● = 10%; ▼ = 9%; ▲ = 8%; ◄ = 6%; ◆ = 2%. (b) Mechanical spectra for the HAPP solutions. ■, □ = 14%; ●, ○ = 10%; ◄, ◁ = 6%; ◆, ◇ = 2%. The closed symbols are G', and the open symbols in the frequency sweep are G''.

concentration of 6% and different Am:HAPP ratios. The G' values for the 6% blends are on the same level as the G' values for HAPP, after curing (<10 Pa). However, the development of the gel for the mixture was more similar to the development of the Am gel. Moreover, the mixed system did not show the same stability in G' values with time as the HAPP G' values did. The storage modulus increased faster than the loss modulus (not shown), without reaching a steady

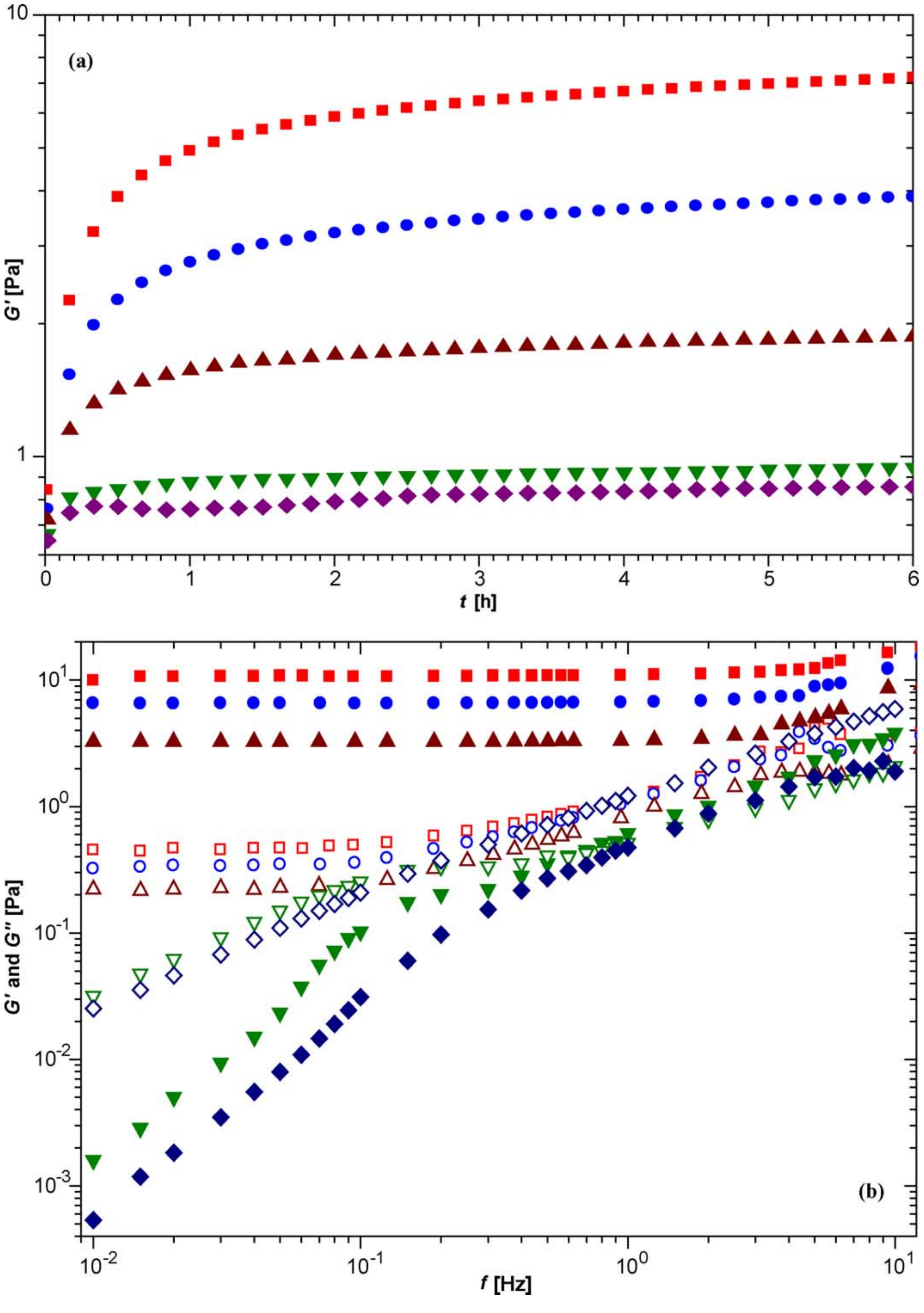

Fig. 3. (a) Storage modulus (G') against time for 6% Am–HAPP solutions with different Am:HAPP ratio; after heating at 140 °C, quenching to 60 °C and measured at 10 °C with 0.025 strain and at 0.2 Hz. (b) Mechanical spectra for 6% Am:HAPP solutions. Am:HAPP ratio: ■, □ = 60:40; ●, ○ = 50:50; ▲, △ = 40:60; ▼, ▽ = 30:70; ◆, ◇ = 20:80. The closed symbols are G', and the open symbols in the frequency sweep are G''.

value within the time of the experiment. The values of G' increased with increasing Am concentration. After the curing time, the G' values of the blends corresponding to the higher Am concentrations were almost 10 times larger than the G' values for the lowest Am concentrations.

Fig. 3b shows the mechanical spectra for Am–HAPP mixtures at 6% polysaccharide concentration, after 6 h curing. An increase in Am concentration in the blends reduced the frequency dependence of G' and G''. The frequency sweeps of the samples shown in Fig. 3b can be divided into two groups. For Am:HAPP ratios 60:40, 50:50 and 40:60 (Am concentrations approximately equal to or larger than 2.4%), G' showed almost no frequency dependence with $G' > G''$. For 20:80 and 30:70 Am–HAPP (below 2.4% total Am concentration) both G' and G'' showed a strong frequency dependence with $G'' > G'$. Similar to HAPP (Fig. 2b), the necessary relaxation time for the mixed system of Am and HAPP with highest Am concentration was long, of the order of al least 10^2 s (Fig. 3b).

Fig. 4a shows the storage modulus against time at 0.2 Hz during 6 h curing for 8% polysaccharide concentration of mixtures of Am–HAPP at different ratios. G' increased with Am concentration. The increase in G' during the first 2 h of curing was faster for the sample containing 8% polysaccharide compared with the blend with 6% polysaccharide

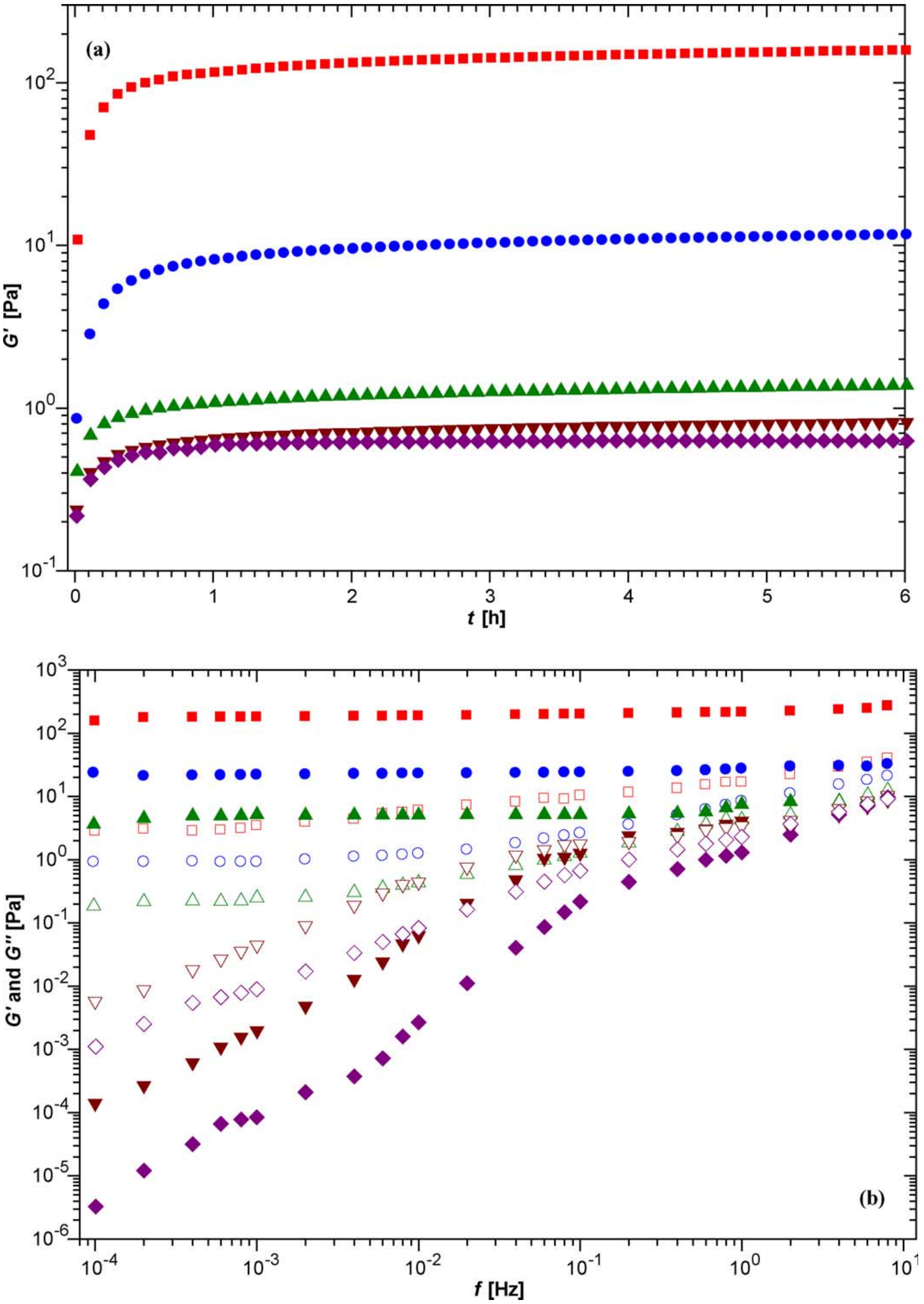

Fig. 4. (a) Storage modulus (G') against time for 8% Am–HAPP solutions with different Am:HAPP ratio; after heating at 140 °C, quenching to 60 °C and measured at 10 °C with 0.025 strain and at 0.2 Hz. (b) Mechanical spectra for the 8% Am:HAPP solutions. Am:HAPP ratio: ■, □ = 57:43; ●, ○ = 49:51; ▲, △ = 43:57; ▼, ▽ = 41:59; ◆, ◇ = 38:62. The closed symbols are G', and the open symbols in the frequency sweep are G''.

concentration. Furthermore, for the sample containing 8% polysaccharide similar to the sample at the 6%, G'' (not shown) increased slower than G' and reached a steady value with time. The development of G' with time resembled less the behaviour of HAPP and more the behaviour of Am. It can be noticed that the moduli values for the 8% samples were almost 20 times larger than the corresponding values of the 6% polysaccharide concentration.

Fig. 4b shows the mechanical spectra after 6 h curing for different ratios of Am–HAPP mixtures with 8% polysaccharide concentration. In general, the frequency dependence decreased with increasing Am concentration. The behaviour of the mixtures at a total polysaccharide concentration of 8%, similar to the 6% blend, may be divided into two groups. G' showed almost no frequency dependence for the 43:57, 49:51 and 57:43 Am:HAPP ratios ($\geq$3.44% Am concentration). When less than 43% of the total polysaccharide concentration was Am, both G' and G'' were strongly dependent on frequency, with $G'' > G'$. Moreover, the relaxation time for the system with the highest concentration of Am was of the order of at least 10^4 s.

Fig. 5a shows the G' values versus time for 10% polysaccharide concentration mixtures of Am–HAPP at different ratios during 6 h curing at 0.2 Hz. The G' values increased with Am concentration, similarly to the samples with 6 and 8% polysaccharide concentration. At 10% concentration, the values of G' increased even faster with time during the first 2 h of curing, compared with the other mixtures. The values of G' were larger than the values of G'' for the 38:62, 40:60 and 46:54 Am:HAPP ratios ($\geq$3.81% total Am concentration). Moreover, G' and G'' (not shown) values were larger than the values for 6 and 8% polysaccharide concentrations.

Fig. 5b shows the mechanical spectra after 6 h for the samples containing 10% polysaccharide concentration and different Am:HAPP ratios. Increasing Am concentration resulted in decreasing frequency dependence. The G' dependence on frequency could be separated into two groups as for the mixtures of 6 and 8% polysaccharide concentration. For the 35:65, 36:64, 38:62, 40:60 and 46:54 Am:HAPP ratios ($\geq$3.15% total Am), G' showed almost no frequency dependence with $G' > G''$ until around 1 Hz. The frequency dependence of the blend was strong at 33:67 Am–HAPP. The relaxation time of the system with the highest concentration of Am was at least 10^4 s.

4. Discussion

4.1. Comparison of amylose and HAPP

The different rheological behaviour of Am and HAPP is summarised in Fig. 6a and b. Fig. 6a shows the moduli of Am and HAPP as a function of concentration after the curing time in Figs. 1 and 2, respectively. The difference between the two polymers is evident. For Am both moduli increased much faster and at significantly lower concentrations than they did for HAPP. After reaching the concentrations where $G' = G''$ (1.6% Am), the value of G' for Am increased abruptly and faster than G''. The moduli for HAPP increased much slower than for Am. The strong increment in G' with concentration observed for Am has been explained with the fact that an Am solution phase separates first into polymer-rich and polymer-deficient regions, and its chains start to fold and crystallise, triggering the formation of a polymer network (Clark, Gidley, Richardson, & Ross-Murphy, 1989; Gidley, 1989; Gidley & Bulpin, 1989). Because HAPP is branched, its external chains will fold and reorder slowly (Miles, Morris, Orford, & Ring, 1985).

Fig. 6b shows the frequency dependence for G' and G'' (slope values of the frequency sweep, n' for G' and n'' for G'') as a function of Am and HAPP concentration. It can be seen that the values of n' and n'' for Am decreased suddenly and definitely, i.e. from $\sim$1 to $\sim$0 when the concentration increased from 1.65 to 1.75% Am, thus showing a very distinct liquid-like to solid-like transition. For HAPP this change was gradual and took place in three different, well defined stages (Ortega-Ojeda et al., 2003). First, with increasing concentration there was a drastic decrease in n' and n'' to a more or less constant value ($\sim$0.5) at concentrations of 6–10%. Finally, at the highest concentration n' decreased even further, and approached zero, thus a solid-like behaviour was more evident.

4.2. Mixtures of amylose and HAPP

The rheological behaviours of the Am–HAPP blends are summarised in Fig. 7a and b. Fig. 7a shows the moduli values at the end of the curing time against Am:HAPP ratio for the 6, 8 and 10% blends. The G' and G'' values for 6, 8 and 10% HAPP were added to the figure at 0% Am. Fig. 7a can be seen as a phase diagram where a gelled sample is described with $G' > G''$. In general, increasing Am concentration of the mixtures increased the value of the moduli. This was more evident for the samples prepared with 10 and 8%, than for the samples with 6% total polysaccharide concentration. These findings agree with a previous report (German, Blumenfeld, Guenin, Yuryev & Tolstoguzov, 1992) where it was suggested that increasing Ap concentration in an Am–Ap mixture leads to an increase in G' at low Am:Ap ratios. At the concentration of 6%, HAPP seemed not to be able to concentrate Am indirectly in the mixed systems which would result in an increase in the storage modulus. It should be noted that in every blend at the ratios with the lowest amount of Am, the behaviour and values of the moduli resemble more the rheological behaviour of pure HAPP at the corresponding concentration. For instance, the values and rheological behaviour of the 6% mixture with the lowest

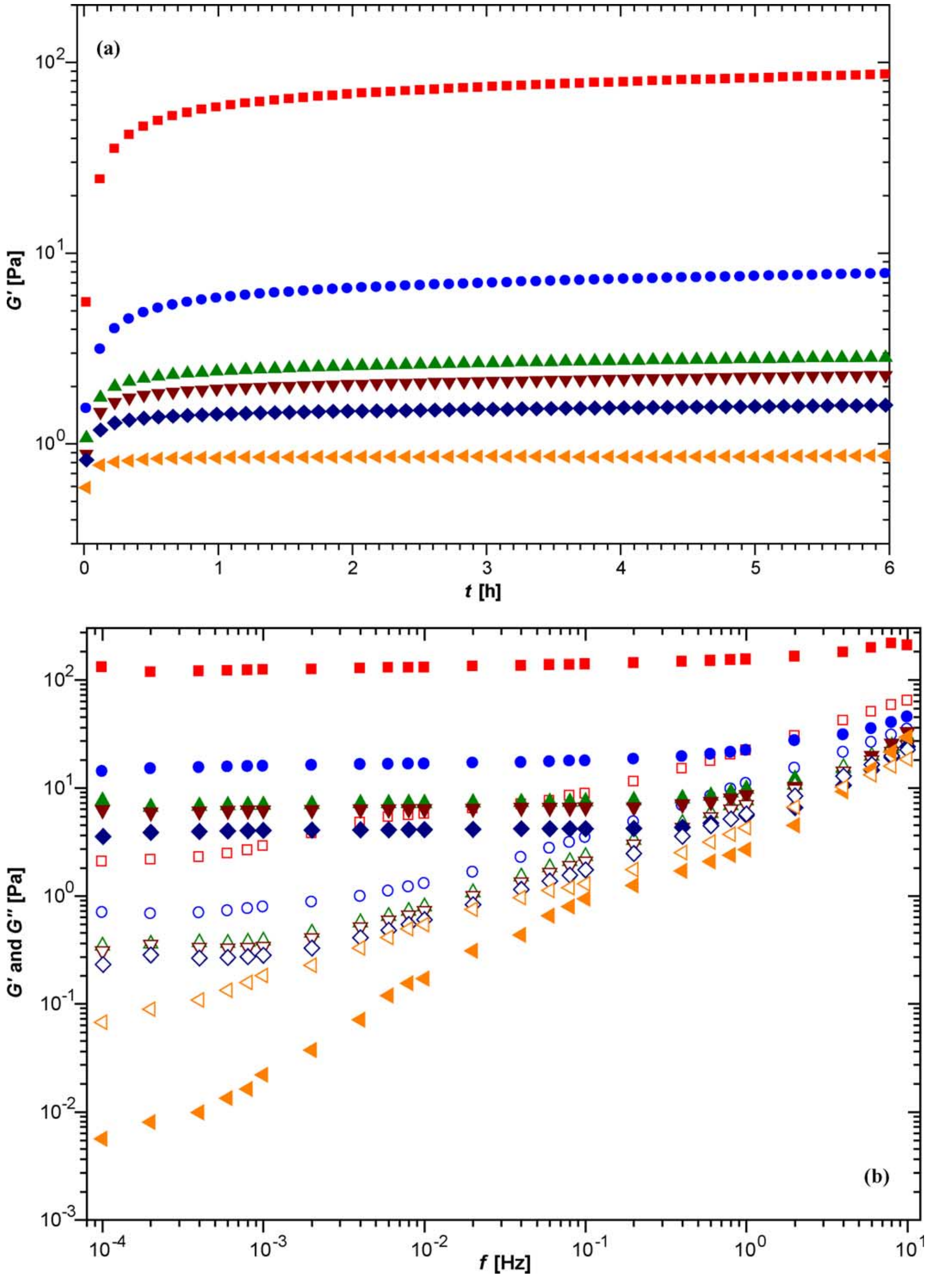

Fig. 5. (a) Storage modulus (G') against time for 10% Am–HAPP solutions with different Am:HAPP ratio; after heating at 140 °C, quenching to 60 °C and measured at 10 °C with 0.025 strain and at 0.2 Hz. (b) Mechanical spectra for the 10% Am:HAPP solutions. Am:HAPP ratio: ■, □ = 46:54; ●, ○ = 40:60; ▲, △ = 38:62; ▼, ▽ = 36:64; ◆, ◇ = 35:65; ◄, ◁ = 33:67. The closed symbols are G', and the open symbols in the frequency sweep are G''.

amount of Am (20:80 Am:HAPP ratio) resulted in moduli values very similar to those of 6% HAPP (Figs. 6a and 7a, 0% Am). When the proportion of Am was increased in the mixture, the behaviour started to resemble that of pure Am. Moreover, the mixture at 6% did not give $G' > G''$ until the Am:HAPP ratio was 40:60 (2.4% Am), even though the amount of Am was more than enough to give G' larger than G'', considering that an Am solution give $G' > G''$ at 1.6% Am (Fig. 6a). For the 8 and 10% mixtures the ratios of Am:HAPP necessary to give $G' \approx G''$ were 43:57 and 35:65 (roughly 3.4 and 3.5% on total Am concentration, respectively). These results confirm previous findings reporting a minimum amount of Am required to give $G' \approx G''$ (Doublier & Llamas, 1993). The presence of HAPP

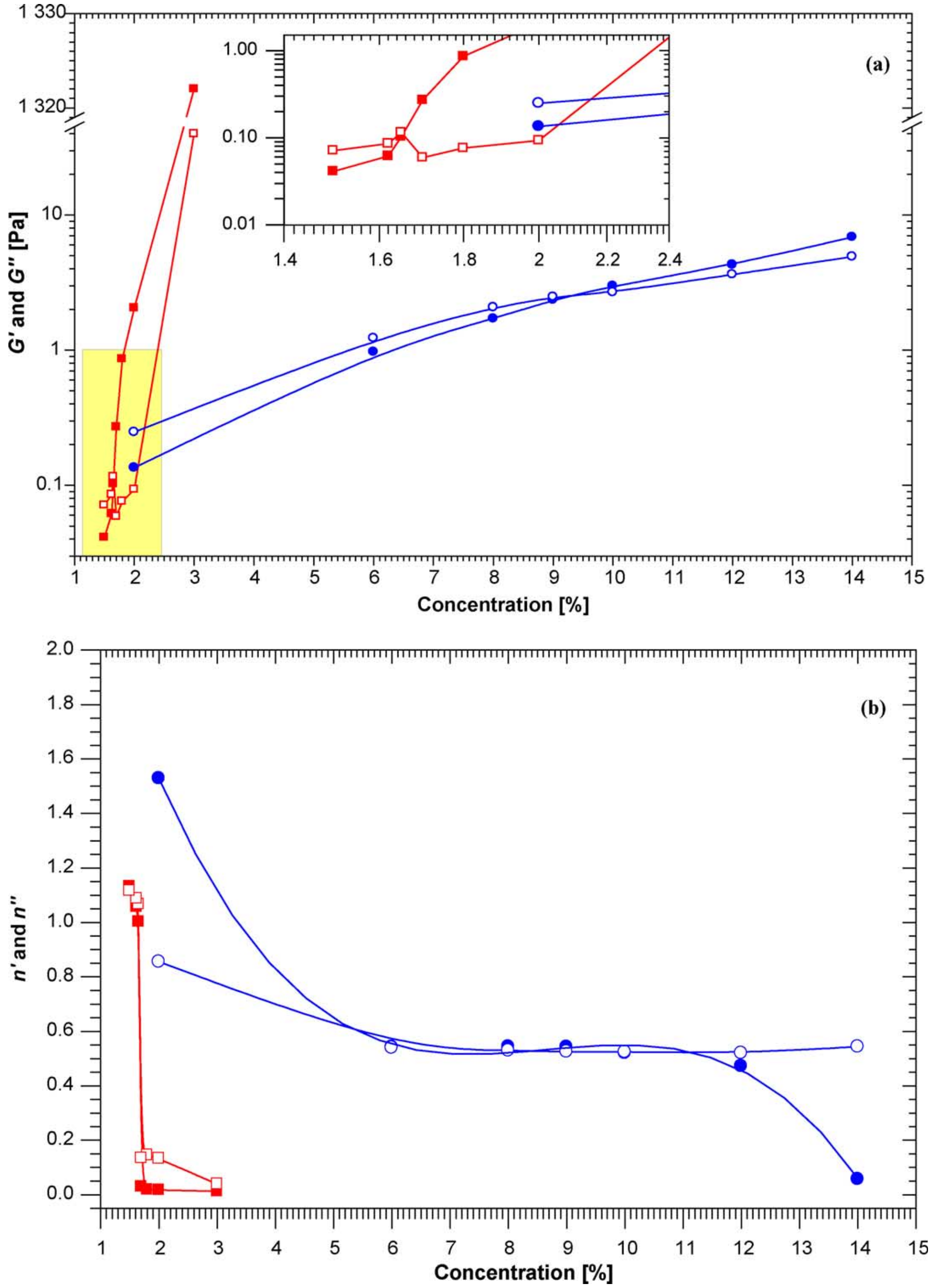

Fig. 6. (a) The moduli (after 6 or 8 h curing time) against polysaccharide concentration for Am and HAPP solutions at different concentrations. (b) n' and n'' versus polysaccharide concentration for the Am and HAPP solutions. ■, □ = Am; ●, ○ = HAPP. The closed symbols are G', and the open symbols are G''.

therefore precludes a concentration of Am into one phase and, thus, the formation of a continuous Am network. This phenomenon seemed to be enhanced with increasing total polysaccharide concentration (Fig. 7a).

In Fig. 7a it can be seen that the higher the total polysaccharide concentration the lower the proportion of Am was needed in the mixture to give $G' \gg G''$. When the polysaccharide concentration was increased, higher values of the moduli were obtained with less Am participating in the mixture. According to Leloup et al. (1991), an Am–Ap phase inversion was observed with a shift from an Ap-continuous phase with Am in the dispersed phase into an Am-continuous phase with Ap as dispersed phase at high Am concentrations. The phase inversion for

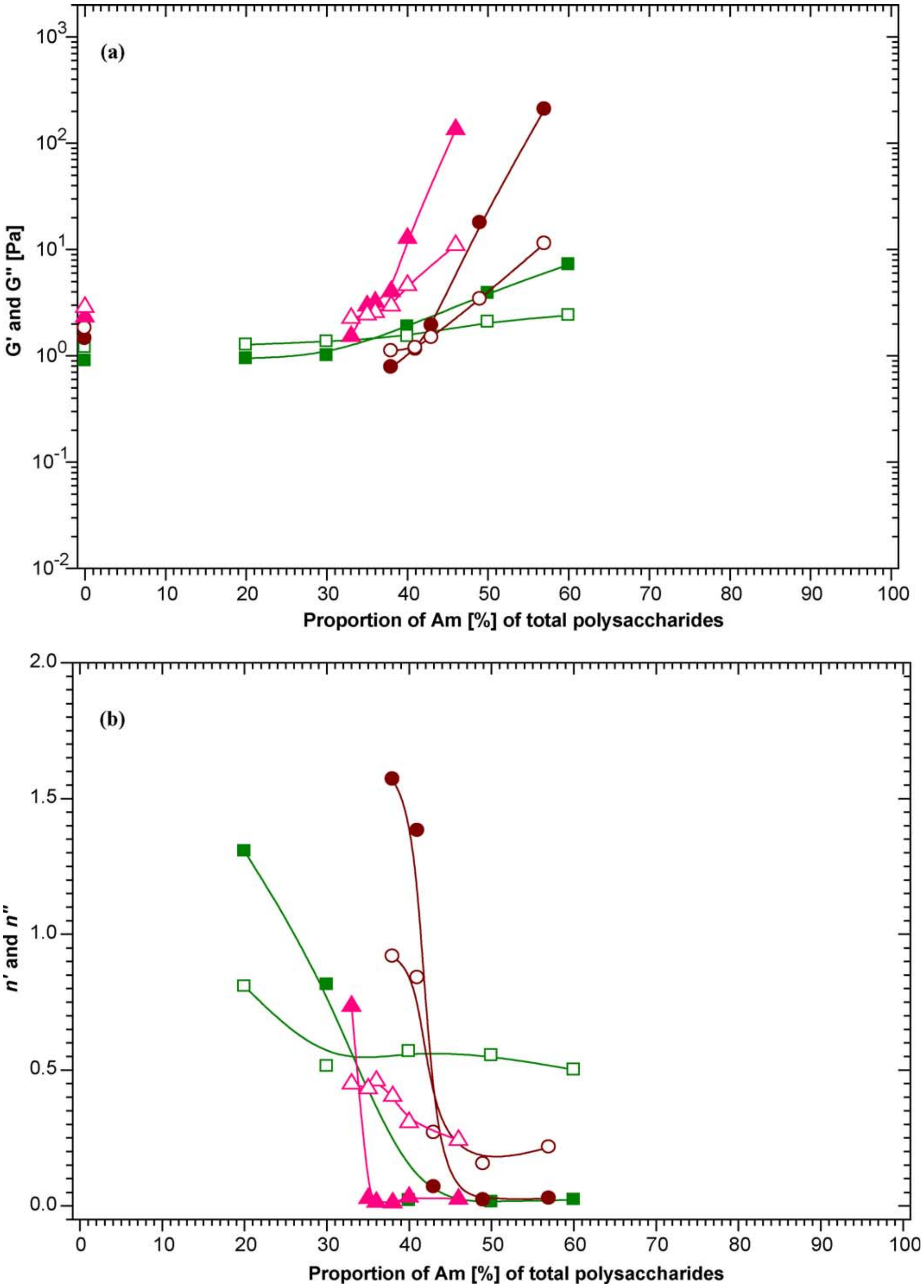

Fig. 7. (a) Phase diagram showing the moduli (after 6 or 8 h curing time) versus proportion of Am of total polysaccharides for Am–HAPP mixtures. The symbols at 0% Am represent ■, □ = 6%; ●, ○ = 8%; ◆, ◇ = 10% HAPP concentrations. (b) n' and n'' from the mechanical spectra against Am proportion in the Am–HAPP solutions. ■, □ = 6%; ●, ○ = 8%; ◆, ◇ = 10%. The closed symbols are G', and the open symbols are G''.

potato Am and waxy maize, which were dissolved with dimethylsulphoxide (DMSO), then recovered with pure ethanol, and dried by solvent exchange (acetone, diethylether), was reported to take place at around an Am:Ap ratio of 30:70 (Leloup et al., 1991). Our findings agree with that report. On the other hand, Doublier and Llamas (1993), who also dissolved potato Am and waxy maize with the method used by Leloup et al. (1991), reported that the critical Am:Ap ratio for a phase inversion of an Am–Ap system was between 15:85 and 22:78 (Doublier & Llamas, 1993). The difference in results may be attributed to the dissolution methods and the origin of the Am and Ap samples.

Fig. 7b shows the frequency dependence of the moduli at the end of the curing time against proportion of Am in the blend, for the 6, 8 and 10% Am–HAPP blends. It can be seen that for the 6% polysaccharide mixture, n' decreased strongly with increasing Am concentration until the 40:60 ratio was reached. After that, for larger amounts of Am in the mixtures, the values of n' were almost constant, and close to zero. For 8% polysaccharide concentration an even more distinct drop in n' was observed with increasing Am concentration until a ratio of 43:57 was reached. After that, the values of n' were roughly constant and close to zero. For 10% polysaccharide concentration, the n' value at the 33:67 ratio decreased with increasing Am concentration as fast as for 8% polysaccharide concentrations. After the drop in n', it reached an immediate stable value, as it did for the 8% samples. For the blend with 10%, the absolute values for G', at the minimum ratio where $n' \sim 0$ (35:65), still remained below 10 Pa. It can be seen that for the mixtures, gel-like properties can be observed at very low frequencies, which implies that the necessary relaxation times for these systems may be very long; of the order of at least 10^4 s (Figs. 3b, 4b and 5b).

Opposite to HAPP and similar to Am, the mixtures first showed a strong drop in n', and then a constant region with $n' \approx 0$. It should be noted that no intermediate region with $n' \approx n''$, resembling the one observed for HAPP between 6 and 10%, resulted for the blends. As for Am (Fig. 6b) the change in n' for 8 and 10% polysaccharide concentration was drastic, i.e. for a concentration increase of 1%, n' dropped from ~ 1.4 to ~ 0 for 8% Am–HAPP, and from ~ 0.8 to ~ 0 for 10% Am–HAPP. This may imply a tighter network due to the increment in total polysaccharide concentration and, thus, concentration of Am in those systems.

Fig. 8 shows the microscopy images for 6, 8 and 10% Am–HAPP mixtures, prepared in the same way as the samples used for the rheological measurements. Fig. 8a, d and g represent conditions where $G' < G''$ and $n' > n''$, Fig. 8b, e and h represent conditions where $G' \leq G''$ and $n' \approx n''$, and Fig. 8c, f and i represent conditions where $G' > G''$ and $n' \approx 0$. At the phase inversion ratio, neither HAPP nor Am form a continuous phase and the rheological behaviour is characterised by $n' \approx n''$, some small structures or conglomerates were found scattered in the sample (seen as dots in Fig. 8b, e and h). Below the phase inversion ratio, i.e. when $n' > n''$ (Fig. 7a, d and g), only few structures could be found in the samples showing that the system was homogeneous. When Am became the continuous phase and $n' < n''$ (Fig. 8c, f and i), darker (denser) ubiquitous groups of conglomerates were evident, possibly showing phase separation and thus, a concentration of the Am phase. In the present study we can conclude that the Am:HAPP ratio for phase inversion was

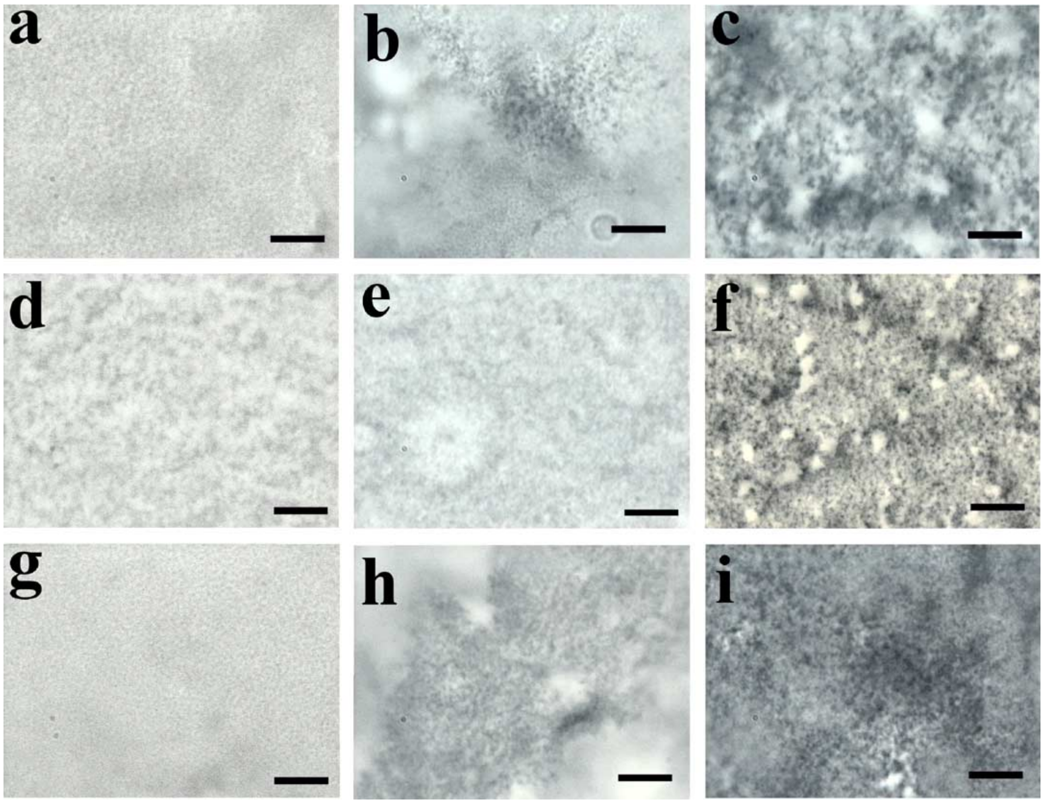

Fig. 8. Microscopy images for 6, 8 and 10% Am–HAPP mixtures; after heating at 140 °C, quenching to 60 °C and measured at ~20 °C with iodine staining. (a–c) 6%; (d–f) 8%; (g–i) 10%. (a), (d) and (g) represent conditions where $G' < G''$, for (a) 20:80, (d) 38:62, and (g) 33:67 Am:HAPP ratios, respectively. (b), (e) and (h) represent conditions were $G' \leq G''$, for the following Am:HAPP ratios: (b) 30:70; (e) 40:60; and (h) 30:70, respectively. (c), (f) and (i) represent conditions where $G' > G''$, for the following Am:HAPP ratios: (c) 50:50, (f) 50:50, and (i) 40:60. Scale bars 1 μm.

between 35:65 and 40:60, depending on total polysaccharide concentration (Fig. 7a).

5. Conclusion

In this work the rheological behaviour of potato amylose (Am), amylopectin (as high amylopectin potato starch, HAPP) and mixtures of Am and HAPP was investigated. Firstly, we would like to point out some important differences in the rheological behaviour between the pure Am and HAPP samples that were investigated. After the sample preparation the storage modulus (G') for Am increased faster with time and at significantly lower concentrations than for HAPP, while the loss modulus (G'') increased slowly with time for both Am and HAPP. Similarly, considerably higher values of G' were observed for Am (3%) than for HAPP (2–14%). The frequency dependence of G' and G'' (n' and n'', respectively) for Am decreased suddenly with increasing concentration, showing a very distinct liquid-like ($n' > n''$) to solid-like transition ($n' \approx 0$) at around 1.6% Am. For HAPP this change was steady and could be divided into three distinct concentration regions with the transition ($n' \approx n''$) observed between 6 and 10% HAPP.

Mixtures of Am and HAPP at different ratios were investigated at 6, 8 and 10% total polysaccharide concentration. Lower values of G' were found when the HAPP concentration was increased. This was more evident for the mixtures with 10 and 8%, than for the mixtures with 6% total polysaccharide concentration. When the mixtures were investigated at the lowest Am concentrations, the rheological behaviour was similar to the behaviour of pure HAPP at the same total polymer concentration. When the Am content of the mixtures was increased the rheological behaviour was more similar to pure Am. The higher the total polysaccharide concentration the smaller amount of Am was needed to give $G' \gg G''$ and higher values of the moduli. Similar to Am, the drop in n' for the mixtures with 8 and 10% was drastic and appeared at a well-defined polymer concentration. This behaviour may imply that a tighter network was formed.

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