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Gel formation in mixtures of hydrophobically modified potato and high amylopectin potato starch

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Abstract

The rheological properties of gels of hydrophobically modified potato starch (HMPot) and high amylopectin potato starch (HAPP) were studied by small deformation oscillatory rheometry. The hydrophobic modification consisted of octenyl succinate anhydride (OSA) chains grafted mainly on the amylopectin molecules. The rheological behaviour of HMPot was different from the behaviour of native potato starch and HAPP. At concentrations higher than ∼15%, the moduli for HMPot starch were higher than for native potato starch and HAPP. A higher level of OSA Substitution led to lower moduli values. The gel formation of HMPot was slower than the gel formation of native potato starch and HAPP. This was explained by the formation of amylose–OSA inclusion complexes and OSA–OSA hydrophobic interactions. Decreasing concentrations of HMPot in HMPot–HAPP mixtures led to reduced moduli values, and a rheological behaviour resembling that of HAPP. At HMPot concentrations lower than 50% in the HMpot–HAPP mixture, amylose or OSA seemed not to contribute to the network formation. Addition of sodium dodecyl sulphate (SDS) to HMPot reduced the moduli at lower concentrations (1%). Further increase in SDS concentration (2%) increased the moduli values. However, the moduli values were still lower than for pure HMPot. The decrease in the moduli when SDS was added is Suggested to be due to a replacement of OSA by SDS in the amylose–inclusion complex. The strengthening of the existing OSA–OSA hydrophobic interaction when further SDS was added, is explained by the formation of polymer-micelles. When SDS was added to native potato starch and HAPP the rheological behaviour was different from that observed for HMPot starch. The moduli increased when SDS was added to native potato starch and HAPP. With increasing SDS concentration, the storage modulus (G') of native potato starch and HAPP increased to the same value. Consequently, the rheological properties of native potato starch and HAPP were suggested to be dominated by amylopectin and not by amylose.

1. Introduction

Modified starches are native starches that have been altered chemically or physically in order to improve their properties (viscosity, surface activity, enzyme resistance, etc.) for a specific use in the industry. Chemically modified starches can be cross-linked, esterified or converted by acids or enzymes to have, for instance, greater viscosity, clarity, etc. Potato starch, among other starches, can be hydrophobically modified to become amphiphilic, and thus have surface active properties useful to stabilize oil/water systems. The properties of hydrophobically modified starches are based mainly on the fact that their hydrophobic interactions lead them to self-associate. Hydrophobically modified starches are created by grafting a low quantity of hydrophobic groups (∼1% of the monomers reacted) to both amylose and amylopectin, but preferably to the amylopectin (Sau & Landoll, 1989). Esters of starch alkenyl succinate are normally prepared by reacting granular starches and alkenyl succinic anhydrides with a base as catalyst (Bao, Xing, Phillips, & Corke, 2003; Jeon, Viswanathan Lowell, & Gross, 1999). The octenyl succinate anhydride (OSA) substitution occurs at the carbons 2, 3, and 6 in the glucose molecule (Jeon et al., 1999), and takes place mostly in the amylopectin branches (Shogren, Viswanathan, Felker, & Gross; 2000; Tesch, Gerhards, & Schubert, 2002; Viswanathan, 1999).

Since the discovery of the amylose–iodine inclusion complex in 1814 (Thompson & Hamori, 1971), many studies have been published on inclusion complexes with

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amylose, and amylopectin. Research on inclusion complexes of amylose with hydrophobic ligand molecules (i.e. fatty acids, iodine, flavour compounds or emulsifiers) showed that hydrophobicity of the ligand chains could lead to coiling amylose around the complexing structures to form single amylose helices (Kuge & Takeo, 1967; Thompson & Hamori, 1971; Yamagishi, Imamura, & Fujimoto, 1972). When the helices crystallise they show a V-diffraction pattern (Yamashita, 1965; Yamashita & Hirai; 1966; Yamashita & Monobe, 1971). Earlier studies showed that the complexation depends on the ligand molecular size (Kuge & Takeo, 1967). Mainly linear Structures are included in the helical cavity of amylose (Thompson & Hamori, 1971), while structures with a cyclic structure may be located between the helices in all amylose crystal (Helbert, Chanzy, Planchot, Buléon, & Colonna, 1993). Amylopectin was believed not to form inclusion complexes (French, Pulley, & Whelan, 1963), however, during the last decades a number of studies on amylopectin complexes have been reported (Batres & White, 1986; Gudmundsson & Eliasson, 1990; Lundqvist, Eliasson, & Olofsson, 2002a,b). The amount of the ligand complexed to starch depend on the structure of the ligand molecule (French et al., 1963; Kuge & Takeo, 1968; Osman-Ismail & Solms, 1973; Schierbaum, 1959; Ulmann & Schierbaum, 1958). The formation of starch inclusion complexes influences the colloidal properties of the starch dispersions. The interaction between complexed amylose and water induces local phase separation which leads to turbidity and changes of the rheological properties that range from bulk phase separation to gelation (Batres & White, 1986; Karkalas & Raphaelides, 1986; Kuge & Takeo, 1968; Nuessli, Handschin, Conde-Petit, & Escher, 2000; Osman-Ismail & Solms, 1973; Raphaelides, 1992).

Hydrophobically modified polymers like OSA-modified starches and others, are called associative thickeners because they are able to modify the rheological properties of a sample by interacting with other compounds, *e.g.*, surfactants and other polymers. The interactions between surfactants and hydrophobically modified homopolymers in aqueous solution have been broadly studied. In a hydrophobically modified polymer, the hydrophobic tails which are grafted on the polymer backbone are hydrophobically attracted to other neighbour hydrophobic chains grafted on the same or another polymer. These hydrophobic tails may also be attracted to the hydrophobic tails of surfactant micelles (Thuresson, Nystroem, Wang, & Lindman, 1995). Surfactant micelles are formed at surfactant concentrations above the critical micelle concentration (*cmc*)(KIevens, 1946). The concentration of surfactant below which no surfactant/polymer cooperative binding takes place is called the critical association concentration (*cac*) (Herzfeld, Corrin, & Harkins, 1950). Cooperative binding occurs in this case when the surfactant binding, is initiated by hydrophobic interactions between a surfactant tail and a hydrophobic chain in the modified polymer. In this way, the hydrophobic polymer chain works as a template for the first surfactant molecule. This is followed by the binding of next surfactant to the initial complex at an adjacent site, driven by the hydrophobic interaction with the already bound surfactant chain. The *cac* is usually lower than *cmc*, and depends on the type of hydrophobic modification present on the polymer and temperature (Hoff, Nyström, & Lindman, 2001; Singh & Nilsson, 1999; Thuresson et al., 1995), and it is almost independent of polymer molecular weight and concentration (Patist, Oh, Leung, & Shah, 2001). The formation of mixed micelle-like aggregates with the hydrophobic polymer chains occurs above *cac*, until the grafted hydrophobic chains are saturated with surfactant. This occurs at a surfactant saturation concentration (c_{sat},), which depends on the polymer concentration, molecular weight, hydrophobic modification, and temperature. The only additional self-assembled structures formed when the surfactant concentration is increased above c_{sat} are micelles binding only one hydrophobic polymer chain at a time (Jönsson, Lindman, Holmberg, & Kronberg, 1999; Piculell, Thuresson, & Lindman, 2001).

The aim of the present work was to study the influence of hydrophobic (OSA) chains on the rheological behaviour of mixtures of high amylopectin potato starch (HAPP) and hydrophobically modified potato starch (HMPot). HMPot starch was mixed with sodium dodecyl sulphate (SDS) to study the effect on the rheological properties of the OSA chains. SDS has a linear chain similar to OSA and might compete for the formation of an inclusion complex. The gelation of the different systems was investigated using small deformation oscillatory rheometry.

2. Materials and methods

2.1. Materials

Amylopectin (high amylopectin potato starch (HAPP, $\ll$1% amylose) and hydrophobically modified potato starches (HMPot) were provided by Lyckeby Stärkelsen (Nöbbelöv, Sweden). The two HMPot starches used in this study had nominally 1 and 2% octenyl succinate anhydride (OSA) substitution degrees. They are refereed to as HMPot1 and HMPot2, respectively. Sodium dodecyl sulphate (SDS; $M=288.38$) was purchased from BDH Laboratory Supplies (Poole, England). The critical micelle concentration (*cmc*) of SDS is ~0.24% w/v (8.3 mM)(Tanford, 1973).

2.2. Methods

2.2.1. Microscopy

A drop of iodine solution (0.6 g I_2 in 50 mL ethanol, plus 0.6 g KI in 500 mL water, diluted to 1 L with water) was added to a 2% HMPot starch sample. An aliquot of the suspension was then placed on a microscope slide, observed and recorded on-line in an Olympus BX50 microscope (Olympus, Tokyo, Japan), with a 530 nm Olympus U-TP530 polarised light filter (Olympus, Tokyo, Japan).

2.2.2. *Differential scanning calorimetry (DSC)*

The DSC measurements were carried out using a DSC 6200 (Seiko Instruments, Inc., Shizuoka, Japan). The samples (~10 mg of 20% starch concentration (w/w)) were prepared in coated aluminium pans (TA Instruments, New Castle, USA), and were allowed to equilibrate for at least 30 min before the DSC run. $A1_2O_3$ was used as reference. The heating temperature range was 10–140 °C, the heating rate was 5 °C min^{-1}, and the data-collecting rate was 0.2 points s^{-1}. The following parameters were evaluated for the gelatinisation study: onset temperature ($T_{o,\mathrm{gel}}$), peak temperature ($T_{p,\mathrm{gel}}$), final temperature ($T_{f,\mathrm{gel}}$), melting interval (ΔT_{gel}), and melting enthalpy (ΔH_{gel}). The Seiko standard software was used for the evaluation. The enthalpy values were calculated on in amylopectin basis. The standard deviation from two repetitions was ≤ 0.3 °C for all the temperature parameters, and ≤ 0.8 J g^{-1} for the enthalpy values.

2.2.3. *Rheological measurements*

The rheological behaviour of HMPot was studied at different starch concentrations (2–20% (w/w)). Mixtures of HAPP and HMPot were investigated with samples of 20% total polysaccharide concentration at different HAP-P:HMPot ratios (0:100; 20:80: 50:50; 80:20 and 100:0 HAPP:HMPot). Mixtures of native potato starch and HMPot were studied with samples of 20% total polysaccharide concentration at different native potato starch:HMPot ratios (0:100; 50:50 and 100:0 native potato starch:HMPot). Samples were prepared following the preparation procedure previously used for HAPP (Ortega-Ojeda, Larsson, & Eliasson, 2003) to reduce the amount of granular remnants in the sample. Therefore, the suspensions were heated at 140 °C for 20 min, and then quenched for 4 s in a water bath at 60 °C, prior the rheological measurements. For the measurements with SDS, SDS solutions were added at 60 °C to the previously dissolved samples, and gently mixed. The final SDS concentration in the samples was 1 or 2% w/w SDS on starch basis. The samples were then transferred to the cone-plate geometry of a StressTech controlled stress rheometer (Reologica AB, Lund, Sweden), and the analysis was carried out at 10 °C. The storage and loss moduli (G' and G'') as function of time (t) were measured at 0.025 strain and at a frequency (f) of 0.2 Hz. After the curing, a frequency sweep (0.001–10 Hz) at 0.025 strain was performed. The frequency dependence is illustrated by the slopes of $log(G', G'')$ vs. $\log\omega$ (n' and n''), where n' and n'' are calculated from the most linear segment at the lowest frequencies: $G' = G'_0\omega^{n'}$ and $G'' = G''_0\omega^{n''}$. G'_0 and G''_0 are the intercepts, $\omega = 2\pi f$ is the frequency in rad s^{-1}. The frequency dependence (n' and n'') is used to illustrate the liquid-to-solid transition of the systems. For n', values close to 2 or 0 represent liquid or solid behaviours, respectively, and for n'', values close to 1 or 0 represent liquid or solid behaviour, respectively (Barnes, 2000; Ferry, 1970). Before the actual rheological measurement was started, HAPP-containing samples were left to rest in the rheometer for 6 h for relaxation of residual stresses. Then, the rheological tests were performed for another 8 h; consequently, 14 h are reported as total curing time for those samples. All the presented data are the average of at least three different sample preparations. The coefficient variation was less than 10%.

3. Results

3.1. *Basic characterisation of HMPot*

The hydrophobically modified potato starches presented the Maltese-cross when investigated in the light microscope under polarized light. Fig. 1 shows the DSC thermogram for both HMPot, native potato and HAPP starches at 20% (w/w) concentration. Both HMPot showed a single gelatinisation endotherm (Table 1). For HMPot, the values of $T_{p,\mathrm{gel}}$ and $T_{f,\mathrm{gel}}$ were higher than for native potato starch, but lower than for HAPP. The values of $T_{o,\mathrm{gel}}$, $T_{p,\mathrm{gel}}$, $T_{f,\mathrm{ge}}$ and ΔH_{gel} were nearly the same for both HMPot.

3.2. *Gels of hydrophobically modified potato starch*

Fig. 2a shows the curing process during 8 h at 10 °C for 2–20% samples of HMPot1 at 0.2 Hz. The values of the storage modulus (G') increased with curing time, and much faster than the loss modulus (G'')(results not shown). The increase in the storage modulus was faster for the samples containing 15 and 20% HMPot1.

Fig. 2b shows the mechanical spectra at the end of the measurements shown in Fig. 2a, i.e., after 8 h at 10 °C. The values of G' and G'' showed frequency dependence,

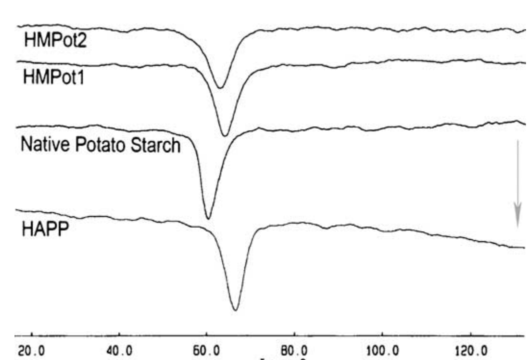

Fig. 1. DSC gelatinisation endotherms of 50% HAPP, HMPot, and native potato starches. The arrow indicates endothermic heat flow.

Table 1
DSC gelatinization parameters for HAPP, native potato, and HMPot starches at 20% (w/w) concentration

	$T_{o,\mathrm{gel}}$ (°C)	$T_{p,\mathrm{gel}}$ (°C)	$T_{f\text{-gel}}$ (°C)	ΔH_{gel} (J g A p^{-1})
Native potato	57.5	60.4	65.1	17.7
HAPP	62.3	66.6	70.4	16.5
HMPot1	60.0	64.2	69.0	17.9
HMPot2	57.7	63.1	68.6	18.1

σ_T, ±0.3 °C, and $\sigma\Delta H_{\mathrm{gel}}$, ±0.8 J g^{-1}.

which decreased with increasing concentration. For concentrations equal to or higher than 10% G' was higher than G'', and showed almost no frequency dependence. From and below 5% HMPot G' was lower than G'', and the moduli showed strong frequency dependence. For the samples with G' higher than G'', the terminal, or longest relaxation time ($\tau=(1/\omega)=(1/2\pi f)$) is expected to be at least 1.6×10^3 s.

Fig. 3a shows the curing process during 8 h at 10 °C for samples of 2–20% HMPot2 at 0.2 Hz. The values of the storage modulus increased with curing time, and with

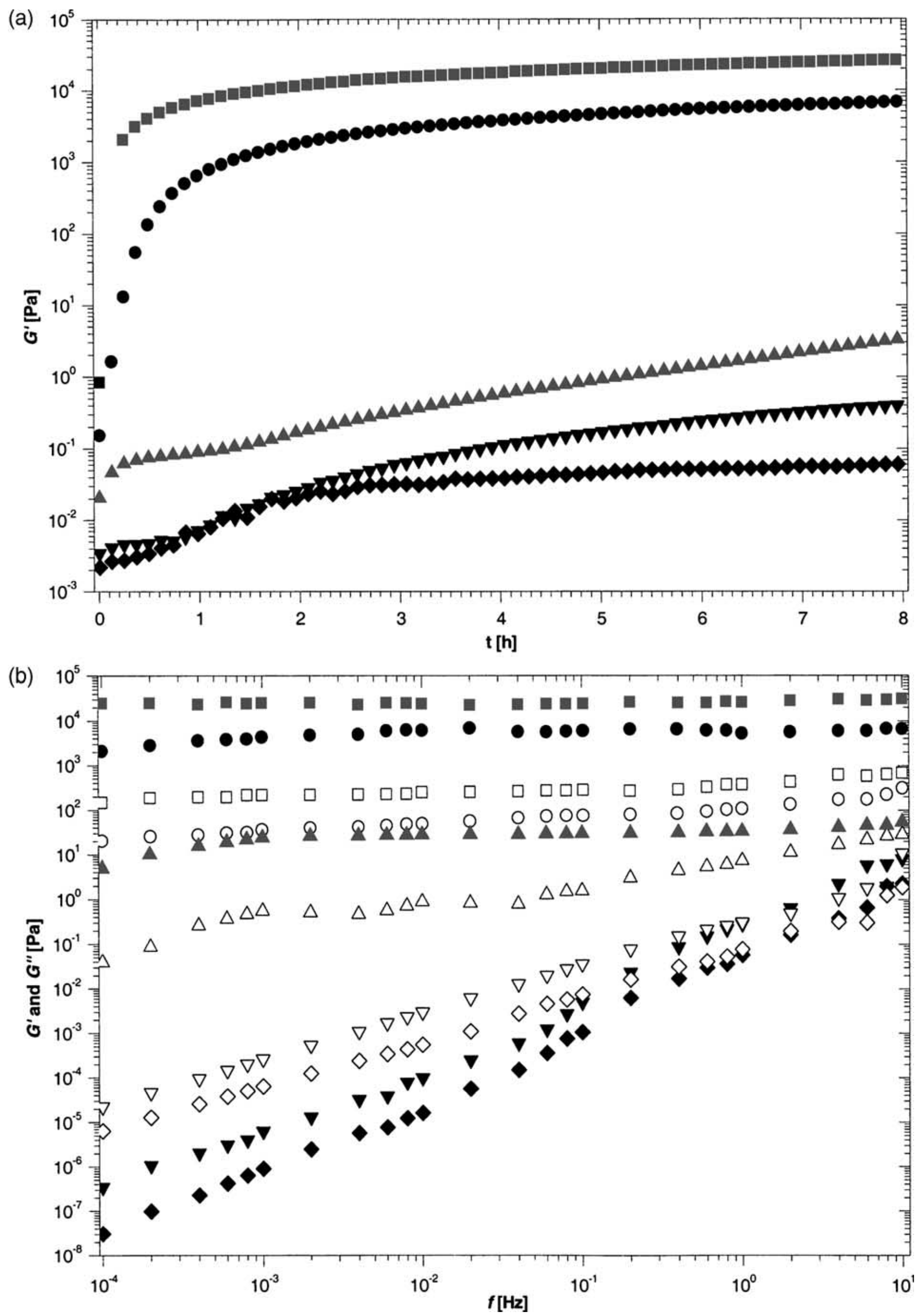

Fig. 2. (a) Storage modulus (G') against time for HMPot1 samples at different concentrations, after heating at 140 °C, quenching to 60 °C and measured at 10 °C at 0.025 strain and 0.2 Hz. (b) Mechanical spectra for the HMPot1 samples in Fig. 1a. ■, □ = 20%; ●, ○ = 15%;, ▲, △ = 10%; ▼, ▽ = 5%, ♦, ◇ = 2%. The closed symbols are G', and the open symbols are the loss modulus (G'').

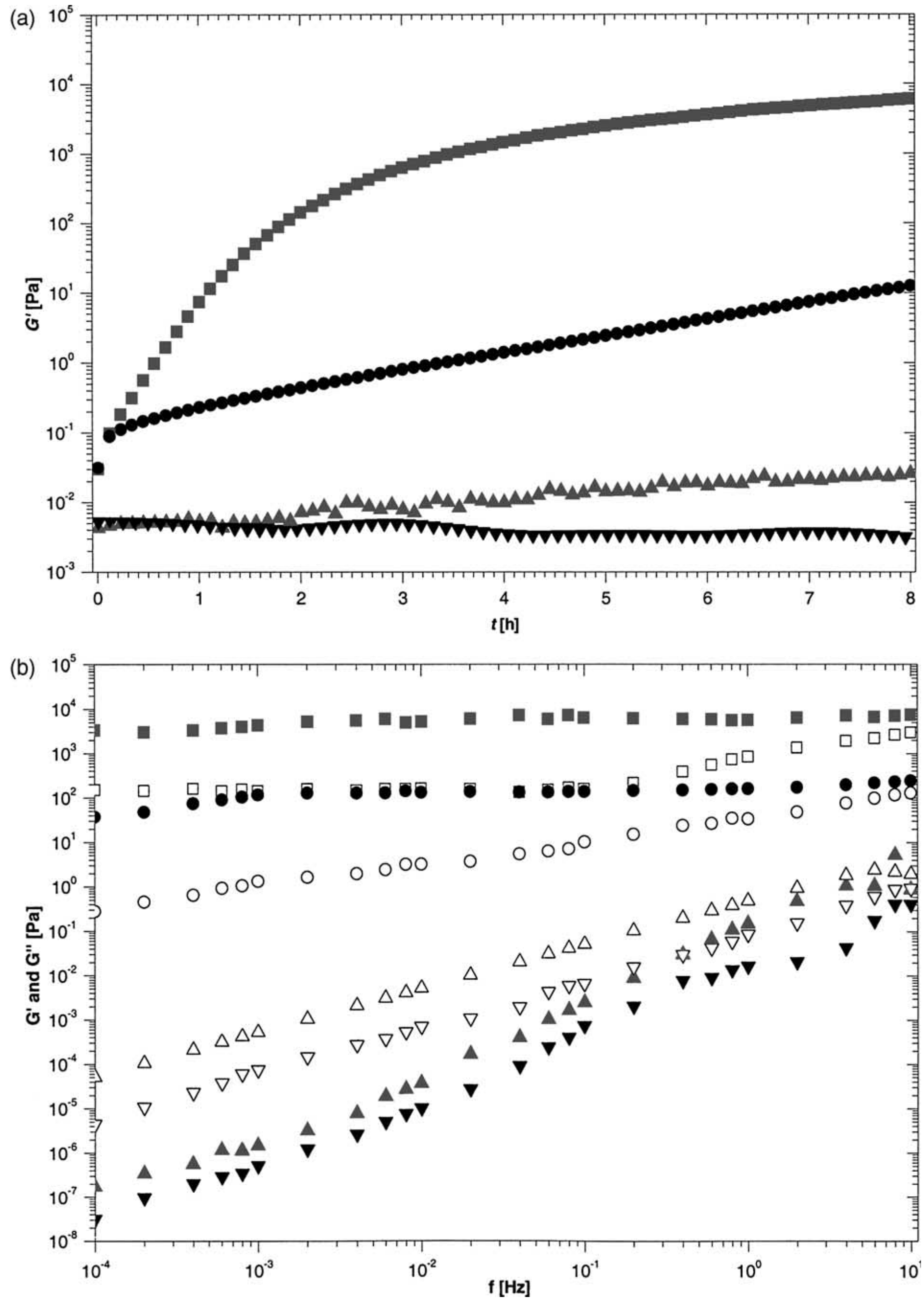

Fig. 3. (a) Storage modulus (G') against time for HMPot2 samples at different concentrations; after heating at 140 °C, quenching to 60 °C and measured at 10 °C with 0.025 strain and at 0.2 Hz. (b) Mechanical spectra for the HMPot2 samples shown in Fig. 2a. ■, □ = 20%; ●, ○ = 15%; ▲, △ = 10%; ▼, ▽ = 2%. The closed symbols are G', and the open symbols are the loss modulus (G'').

increasing HMPot concentration. The increase in G' with Curing time was most pronounced during the initial 20 min and 2 h for the 15 and 20% HMPot2, respectively. Similar to the HMPot1 starch, the values of G' increased much faster than G'' (results not shown).

Fig. 3b shows the mechanical spectra at the end of the measurements shown in Fig. 3a, i.e. after 8 h at 10 °C. The frequency dependence of the moduli decreased with increasing concentration. The viscoelastic behaviour illustrated by the frequency sweeps may be divided into two groups. At concentrations equal to or higher than 15%, G' was higher than G'', and G' showed no frequency dependence. Below 15%, G' was below G'', and the moduli were strongly frequency dependent. The longest relaxation time for the samples with G' higher G'' would be at least 1.6×10^3 s.

3.3. Mixed gels

3.3.1. Hydrophobically modified potato starch and HAPP

Fig. 4a shows the values of G' versus time at 0.2 Hz and 10 °C after 6 h of resting and during 8 h curing for 20% total

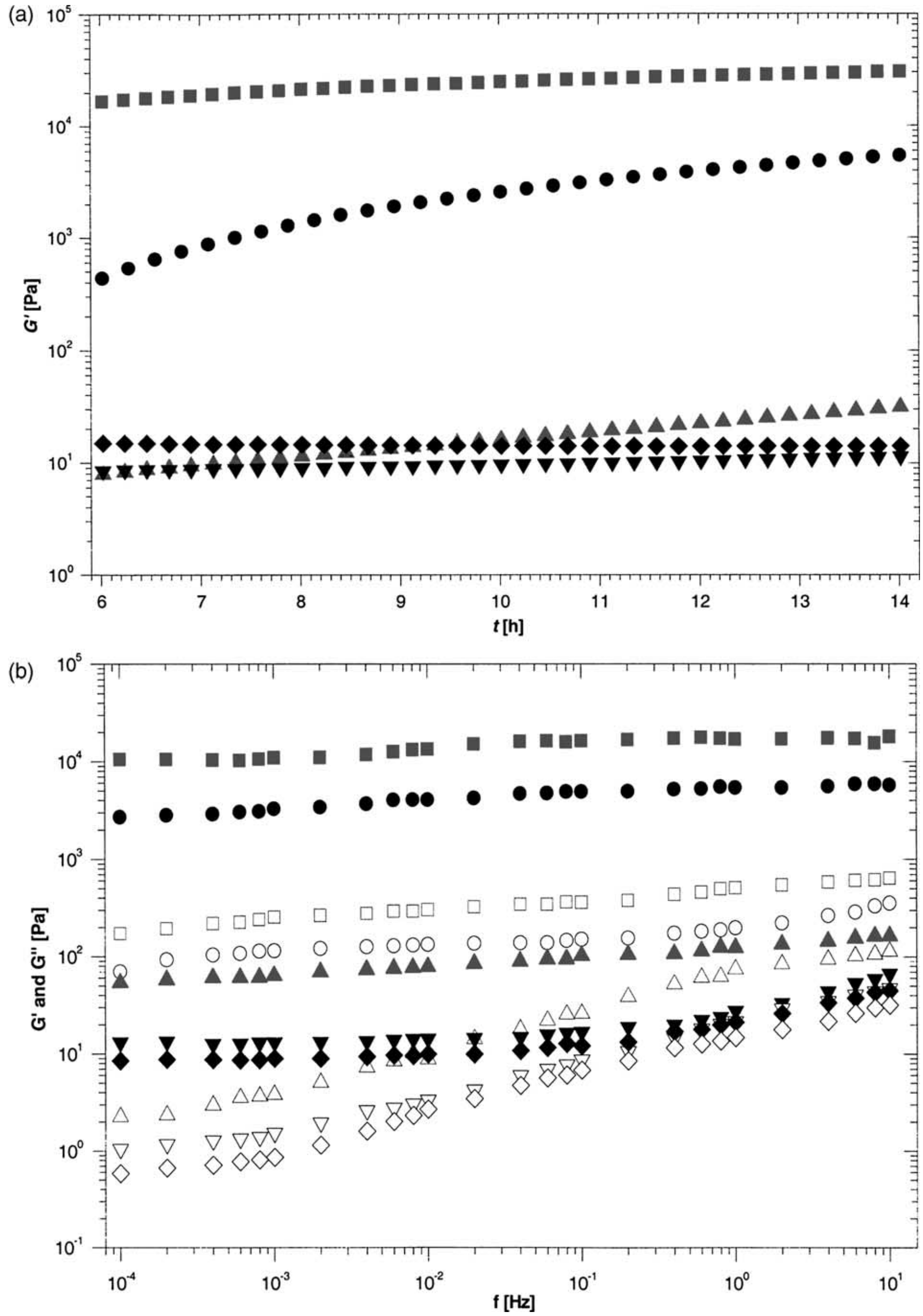

Fig. 4. (a) Storage modulus (G') against time for mixtures of 20% HAPP and HMPot1 with different HAPP: HMPot ratio. b) Mechanical spectra for 20% HAPP-HMPot1 samples. HAPP: HMPot1 ratio: ■, □, = 0: 100; ●, ○ = 20:80; ▲, △ = 50:50; ▼, ▽ = 80:20; ◆, ◇ = 100.0. The closed symbols are G', and the open symbols are the loss modulus (G'').

polysaccharide mixtures of HMPot 1 and HAPP at 0: 100, 20:80, 50:50, 80:20, and 100:0 HAPP:HMPot1. The mixtures showed large stability with time except for the mixtures containing 50 and 80% HMPot1. The values of G' increased with increasing HMPot1 concentration, except for 80:20 HAPP:HMPot1 which gave lower G' values than for the HAPP:HMPot1 mixture at a ratio of 100:0.

Fig. 4b shows the mechanical spectra for mixtures of 20% HMPot1 and HAPP at the end of the measurements shown in Fig. 4a. All samples showed solid-like behaviour ($G' > G''$) in most of the frequency range. The samples containing 50% HMPot1 or less showed a frequency dependence for G'' at higher frequencies. The frequency dependence for G' decreased to some extent with increasing HMPot1 concentration. The largest relaxation time was of the order of at least 1.6×10^3 S.

Fig. 5a shows the values of G' versus time at 0.2 Hz and 10 °C during, 8 h curing, for 20% total polysaccharide mixtures of HMPot2 and HAPP. The mixtures were investigated at the following HAPP:HMPot2 ratios: 0:100,

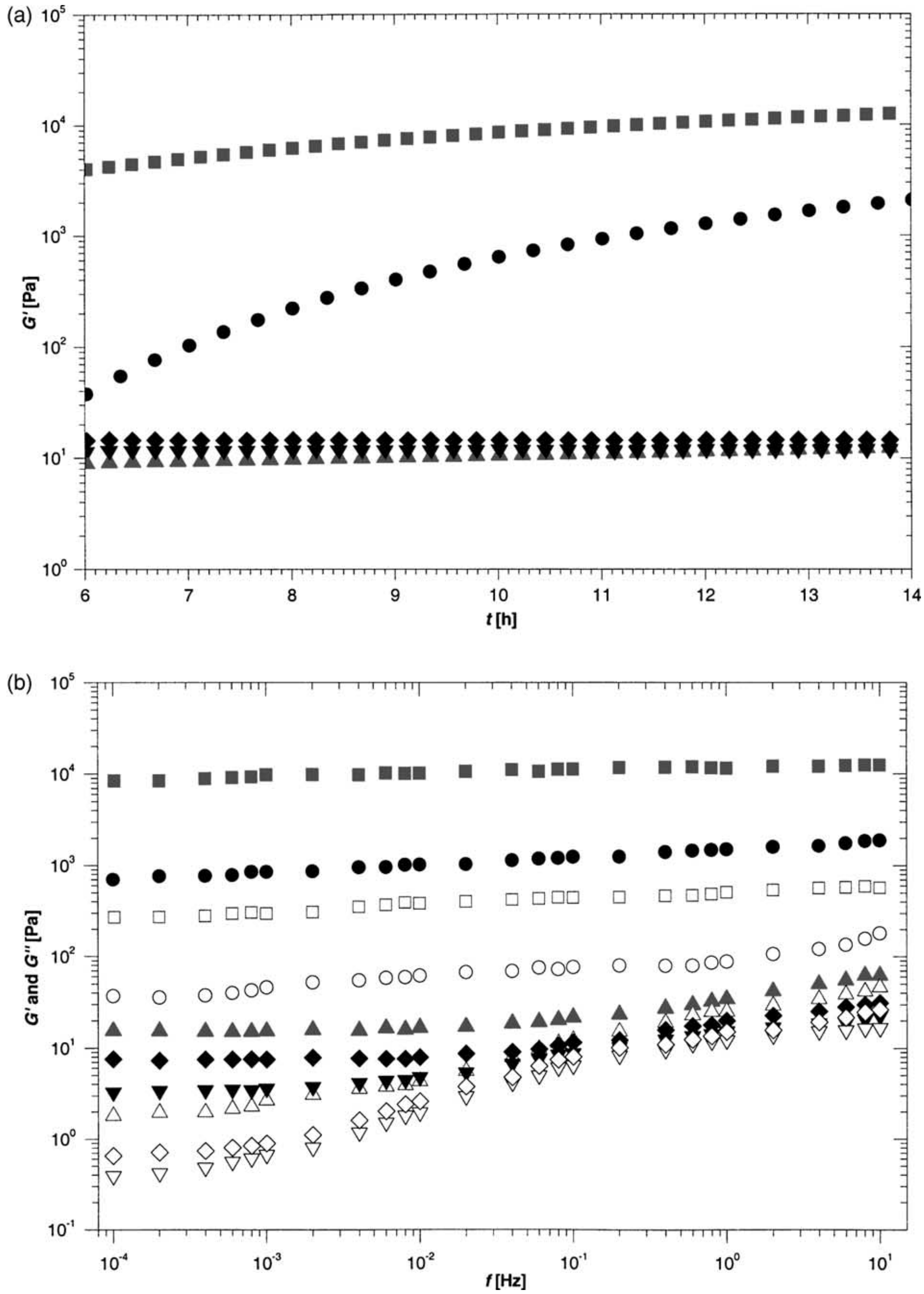

Fig. 5. (a) Storage modulus (G') against time for mixtures of 20% HAPP and HMPot2 with different HAPP: HMPot ratio. b) Mechanical spectra for 20% HAPP-HMPot2 samples. HAPP: HMPot1 ratio: ■, □, = 0: 100; ●, ○ = 20:80; ▲, △ = 50:50; ▼, ▽ = 80:20; ♦, ◇ = 100.0. The closed symbols are G', and the open symbols are the loss modulus (G'').

20:80, 50:50, 80:20, and 100:0. All mixtures exhibited large stability with time except the sample containing 20:80 HAPP:HMPot2. When 80% or more of HMPot2 was present in the sample, the moduli were relatively high (10^3–10^4 Pa), whilst at small amounts of HMPot2, lower values of G'($\sim$10 Pa) resulted.

Fig. 5b shows the mechanical spectra for mixtures of 20% HMPot2 and HAPP at the end of the measurements shown in Fig. 5a. All samples investigated showed solid-like behaviour ($G' > G''$) with an elastic plateau at low frequencies. When the samples contained 50% or less HMPot2, a frequency dependence was observed for G'' at higher frequencies. The frequency dependence decreased slightly with increasing HMPot2 proportion.

3.3.2. Gels with SDS

Fig. 6a shows the curing process for 20% of HMPot starches, with and without the addition of SDS. It can be seen that for HMPot1 the increase in G' with time was faster ($<$10 min) when SDS was present. This phenomenon was

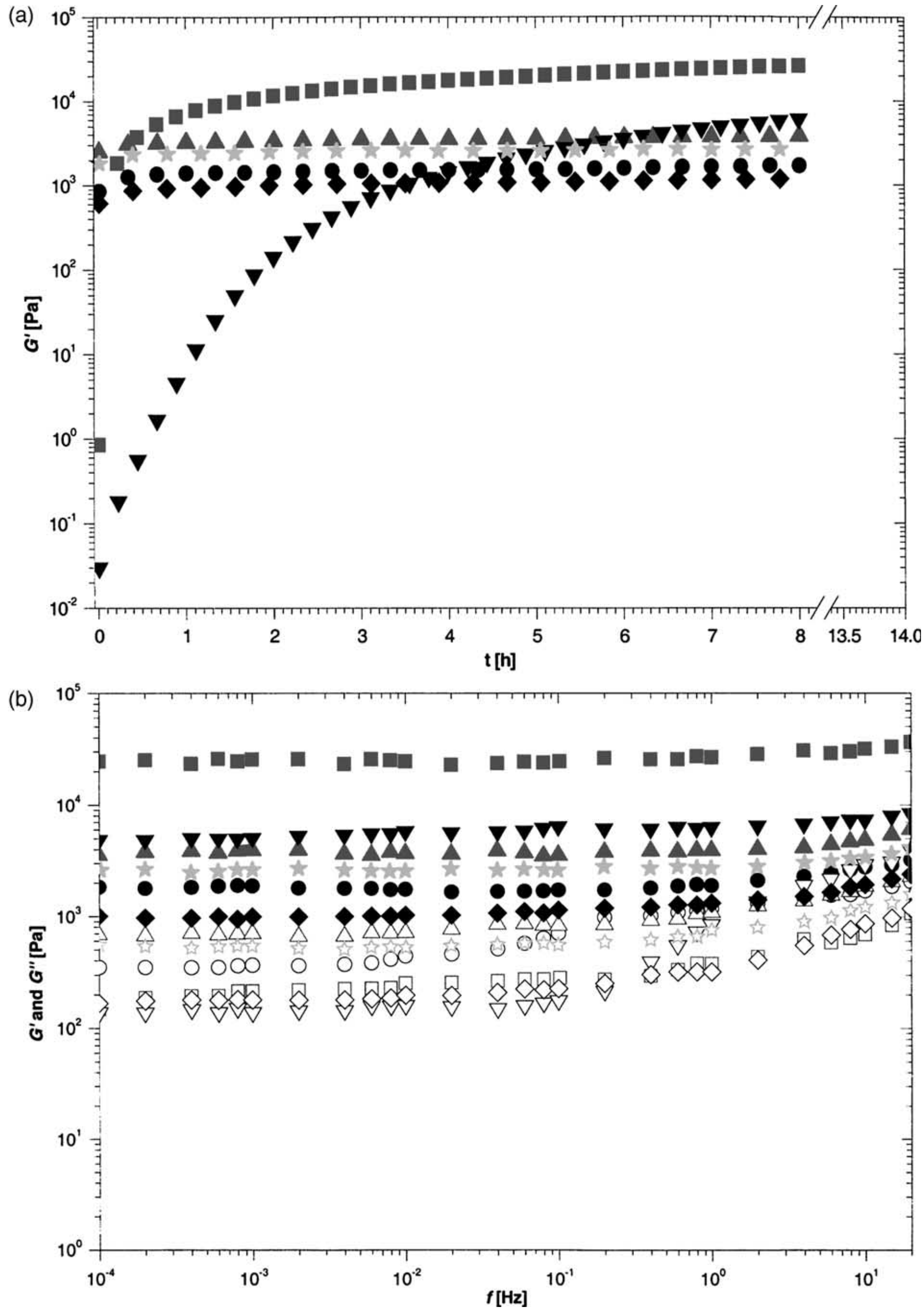

Fig. 6. (a) Storage modulus (G') against time for 20% HMPot with and without 1 or 2% SDS. b) Mechanical spectra for the samples shown in Fig. 6a: ■, □ = HMPot1; ●, ○ = HMPot1 with 1% SDS, ▲, △ = HMPot1 with 2% SDS; ▼, ▽ = HMPot2; ♦, ◇ = HMPot2 with 1% SDS; ★, ☆ = HMPot2 with 2% SDS. The closed symbols are G', and the open symbols are the loss modulus (G'').

enhanced when the SDS concentration was increased. After the initial increase, G' remained nearly constant. However, the G' values for pure HMPot1 were much higher than for the samples containing 1 and 2% SDS. The values of G' for the HMPot1 sample containing 2% SDS were higher than those for the sample containing 1% SDS. Qualitatively comparable behaviour was observed for the HMPot2 samples with addition of SDS. However, the effect of SDS on the initial increase in G' was even stronger for HMPot2 than for HMPot1. The values of G' for pure HMPot2 at the end of the curing time were higher than the values for the samples containing 1 and 2% SDS. The values of G' for the HMPot2 sample containing 2% SDS were higher than those for the sample containing 1% SDS. Samples containing 1% SDS had nearly the same values of G' whether they contained HMPot1 or HMPot2. The same was observed at 2% SDS concentration.

Fig. 6b shows the mechanical spectra for the samples shown in Fig. 6a. All samples showed solid-like behaviour with a plateau at lower frequencies, and a slight frequency dependence for G'' at higher frequencies. The samples largest relaxation time would be of the order of $\geq 1.6 \times 10^3$ s. For both HMPot, the phase angle (δ, $\tan \delta = (G''/G')$) was increased substantially when SDS was added.

Fig. 7a shows the curing process for 20% HAPP and native potato starch, with and without the addition of SDS. The values of G' for potato starch and HAPP samples containing SDS were much higher than for the sample without SDS, and increased with SDS concentration. It is evident that at 1% SDS concentration HAPP and native potato starch had similar values of G'. Similar rheological behaviour was found also at 2% SDS concentration.

Fig. 7b shows the mechanical spectra for the HAPP and native potato starch samples shown in Fig. 7a. The samples showed solid-like behaviour with a plateau at lower frequencies, and slight frequency dependence at higher frequencies. The samples largest relaxation time would be of the order of $\geq 1.6 \times 10^3$ s. For both native potato and HAPP, δ decreased when SDS was added, especially with 2% SDS.

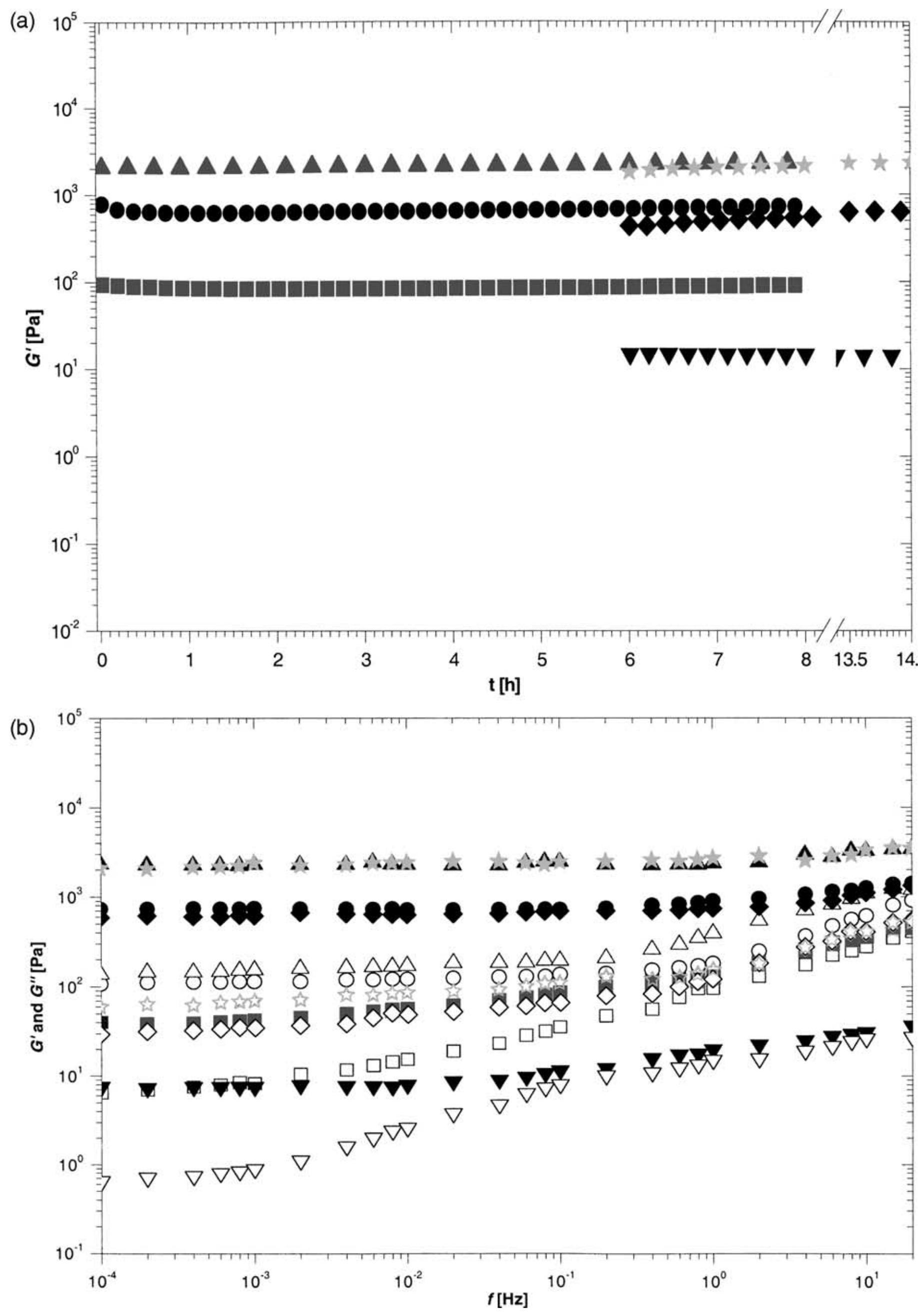

Fig. 7. (a) Storage modulus (G') against time for 20% HAPP and native potato starch with and without 1 or 2% SDS. (b) Mechanical spectra for the samples shown in Fig. 5a: ■, □ = native potato starch; ●, ○ = native potato starch with 1% SDS; ▲, △ = native potato starch with 2% SDS; ▼, ▽ = HAPP; ♦, ◇ = HAPP with 1% SDS; ★, ☆ = HAPP with 2% SDS. The closed symbols are G', and the open symbols are the loss modulus (G'').

4. Discussion

4.1. Basic characterisation of hydrophobically modified potato starches

Both HMPot starches dissolved fast at 140 °C in comparison with native potato starch and HAPP. Even at concentrations as high as 20% HMPot, 5 min heating was enough to produce a fluid sample. This fast dissolution of HMPot could be due to the derivatization process, which may have affected the granules and its crystalline structure, thus allowing them to swell and dissolve more easily than native potato starch and HAPP. However, the fast dissolution of HMPot granules remains controversial due to the fact that Maltese-crosses associated with the crystallinity order of native starch were observed in the granules. Moreover, the crystalline domains in OSA–starch were reported not to be significantly influenced by the derivatization process (Bao et al., 2003).

The fact that HMPot had higher $T_{p,\mathrm{gel}}$ than native potato agrees with a previous work (Bao et al., 2003). However, our results do not show a decrease in ΔH_{gel} with increasing degree of OSA substitution, as has been reported before for OSA starches at 13% starch concentration (Bao et al., 2003).

4.2. Hydrophobically modified potato, native potato and HAPP starches

The effect of total polysaccharide concentration on G' and G'' is compared for HMPot1, HMPot2, native potato starch and HAPP in Fig. 8. The rheological behaviour for HMPot is significantly different from that of native potato starch and HAPP. The moduli for both HMPot were lower than for native potato and HAPP at concentrations lower than ~10% HMPot1 and ~15% HMPot2. When the HMPot concentration was higher than ~15% for HMPot1 and ~20% for HMPot2 the moduli of the HMPot samples increased strongly to values higher than those of native potato starch and HAPP.

A relatively small difference in the degree of OSA substitution between HMPot1 and HMPot2 produced a large effect on the rheological behaviour compared to the difference in amylopectin content between native potato starch and HAPP. The moduli were higher for HMPot1 than for HMPot2 in the whole concentration range investigated. The different rheological behaviour of HMPot compared with native potato starch and HAPP, i.e. slow increase in G' with time, and higher G' values of the final gels at concentrations above ~14% for HMPot1 and ~20% for HMPot2, may be explained by two phenomena, i.e. the formation of amylose–OSA and amylopectin–OSA inclusion complexes, and the formation of hydrophobic associations between OSA chains.

The formation of amylose–OSA, and short outer amylopectin chains–OSA inclusion complexes is expected to be due to the presence of amylose, amylopectin and OSA hydrophobic tails (located mostly in amylopectin) in HMPot. The flexibility and length of amylose allow the amylose molecule to extend and form complexes over more than one amylopectin molecule domain. In this way, the amylose–OSA complex could join neighbour amylopectin branches and hence form an extended network. Due to the limited length of the outer amylopectin branches, amylopectin–OSA inclusion complexes should be shorter and more local, therefore only neighbour amylopectin chains which are close enough would be joined by amylopectin–OSA inclusion complexes. Amylose–OSA inclusion complexes would thus be more efficient in forming, networks than amylopectin–OSA inclusion complexes. A similar slow development in G' observed in Figs. 2a and 3a for the two hydrophobically modified starches has also been observed for the formation of inclusion complexes with other grafted polymers, like for example, amylose-hydrophobically modified ethyl(hydroxyethyl) cellulose (HM-EHEC) (Egermayer, Karlberg, & Piculell, 2004).

Hydrophobic interactions between OSA chains located in neighbour amylopectin branch chains may also lead to the formation of a network. Network formation by hydrophobic interactions has been described for other hydrophobically modified graft-polymers like hydroxyethyl cellulose (HMHEC) (Sau & Landoll, 1989), hydrophobically modified pullulan (Kuroda, Kazushi, & Junzo, 2002), ethoxylated alkali-soluble associative polymers (HASE) (Tam, Farmer, Jenkins, & Bassett, 1998), hydrophobically modified polyacrylamide (HMPAM) (Panmai, Prud'homme, & Peiffer, 1999), hydrophobically modified hydroxypropyl cellulose (HMHPC) (Taylor & Nasr-El-Din, 1998), and polystyrene-block-polyethylene oxide associative water-soluble polymers (PS-block-PEO) (Ballard, Buscall, & Waite, 1988; Boschet, Branger, & Margaillan, 2003). With increasing OSA modification, the ability of HMPot to form a network at short times was reduced especially at lower polysaccharide concentrations (10% and less) (Figs. 2a and 3a). This may be due to substantial intramolecular associations between the hydrophobic OSA tails present in the same amylopectin molecule at higher degree of OSA substitution. Because of this, the amylopectin molecules would contract and the possibility to form an extended network may be reduced. In this case, G' will decrease. An increase in G' would be observed only above a certain polymer concentration, when the contact points between polymers increase due to inter-molecular associations via OSA–OSA hydrophobic interactions and entanglements. Similar behaviour where an increase in the degree of hydrophobic modification induced intra-molecular associations has been reported for other grafted polymers like hydrophobically modified pullulan (Kuroda et al., 2002), hydrophobically modified dextrans (Zhang, Pelton, & Waagberg, 1998), pyrenesulfonamide-labeled model associative polymers (Ezzell & McCormick, 1992), (Ballard et al., 1988), HMPAM (Panmai et al., 1999), HMHPC

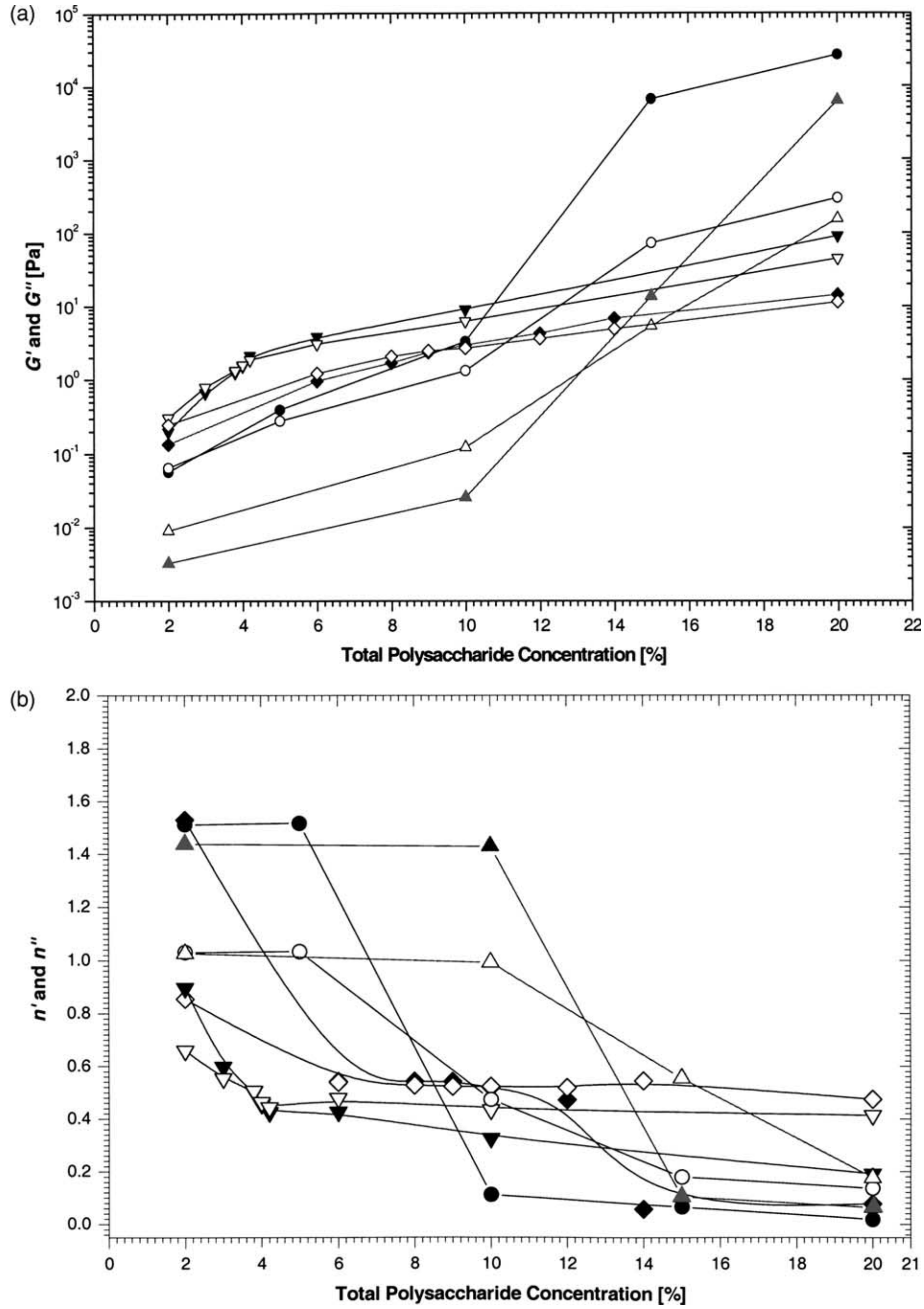

Fig. 8. (a) Limiting moduli (after 8 h curing time) against total polysaccharide concentration for HMPot, native potato starch and HAPP samples. b) Frequency dependence of the samples shown in Fig. 6a. ●, ○ = HMPot1; ▲, △ = HMPot2; ▼, ▽ = native potato starch (Ortega-Ojeda et al., 2004b); ♦, ◇ = HAPP (Ortega-Ojeda et al., 2003). The closed symbols are G', and the open symbols are G''.

(Taylor & Nasr-El-Din, 1998), HASE (Tam et al., 1998), and HMHEC (Sau & Landoll, 1989).

The transition from liquid to solid can be illustrated by the frequency dependence of G' (n') for the samples, where a liquid is characterised by n' approaching 2 whilst for a solid, n' approaches zero. Fig. 8b shows the frequency dependence of G' and G'' (n' and n'', respectively) for the samples in Fig. 8a. Thus, the liquid to solid transition for native potato starch (Ortega-Ojeda, Larsson, & Eliasson, 2004b) was observed at lower polysaccharide concentrations, compared with HAPP (Ortega-Ojeda et al., 2003). This may be due to the presence of amylose in potato starch. Compared to native potato and HAPP, the values of n' and n'' for HMPot1 and HMPot2 were higher, at concentrations lower than $\sim$10 and $\sim$15%, respectively. HMPot1 showed a distinct liquid-to-solid transition between 5 and 10% total polysaccharide concentration, whereas for HMPot2 this transition was observed between 10 and 15% HMPot2. For both HMPot starches the values of n' and n'' became almost zero after the transition, at the highest concentrations, showing a well defined solid behaviour. The HMPot starches had similar frequency dependence at low ($n' \approx 1.5$) and high ($n' \approx 0.1$) concentrations. The main differences between the two HMPot starches were first, that the increase in the moduli with time and concentration for HMPot1 was faster than for the HMPot2, and second, the liquid-to-solid transition took place at a higher polysaccharide concentration when the degree of OSA substitution was higher.

4.3. HMPot–HAPP mixtures

When mixing HMPot with HAPP, a different rheological behaviour was obtained, compared to the mixtures of HAPP and native potato starch. For the latter system, an increase in the moduli with increasing concentration of native potato starch was almost linear and less pronounced (Ortega-Ojeda et al., 2004b). The HMPot–HAPP mixtures containing HMPot1 showed higher moduli values than the mixtures

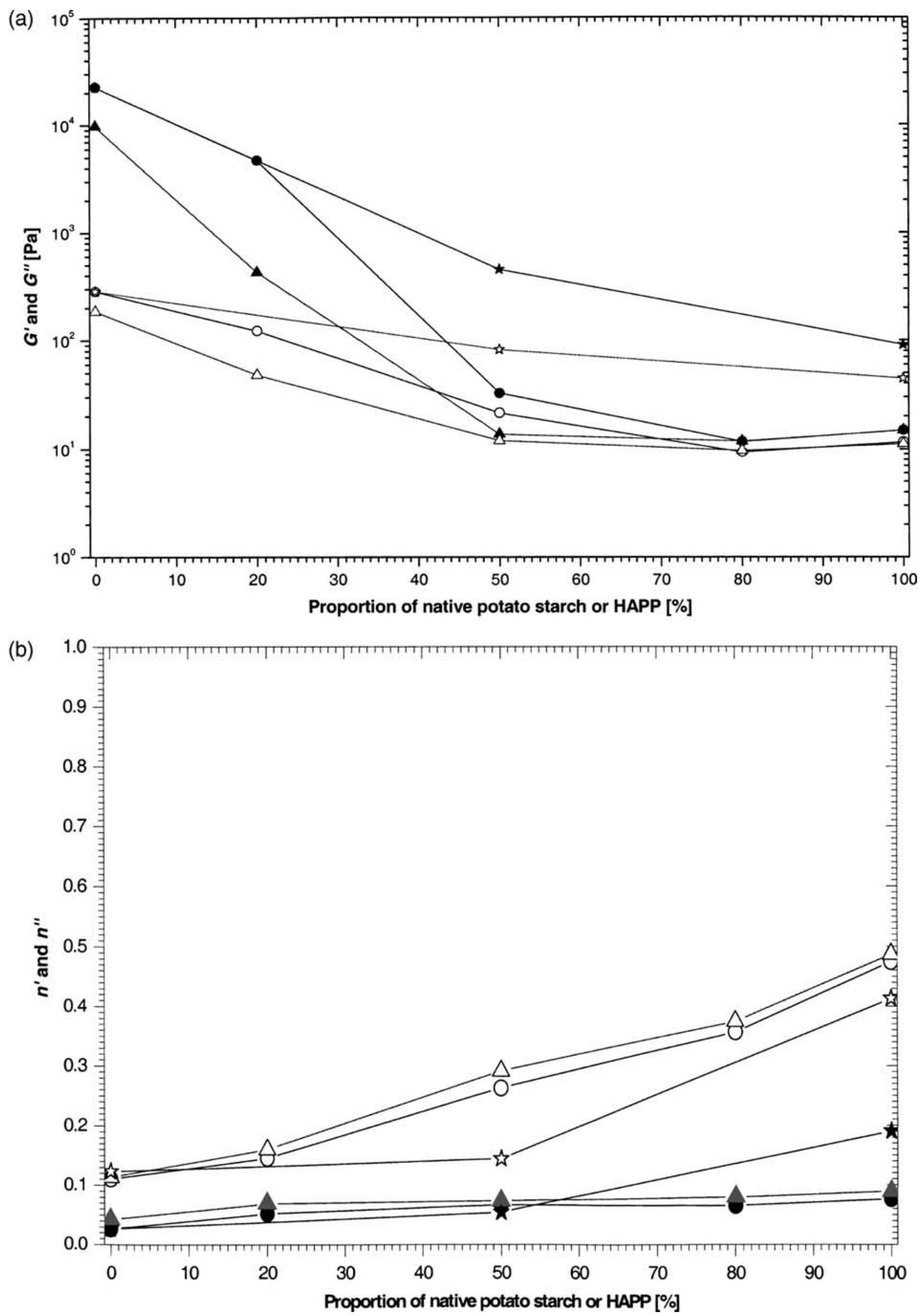

Fig. 9. (a) Limiting moduli (after 8 h curing time) against proportion of native potato starch or HAPP, for different HMPot-HAPP and HMPot1-native potato starch mixtures. (b) Frequency dependence of the samples shown in Fig. 9a. ●, ○ = HMPot1-HAPP; ▲, △ = HMPot2-HAPP; ★, ☆ = HMPot1-native potato starch. The closed symbols are G', and the opened symbols are G''.

with HMPot2. For the HMPot–HAPP mixtures, decreasing the proportion of HMPot reduced the moduli significantly until the mixture consisted of 50% HMPot (Fig. 9a). Thereafter, further decrease in HMPot proportion affected less the moduli values of the mixtures. Thus, in these mixtures it seemed like when HMPot was present in amounts lower than 50% neither the amylose nor the OSA hydrophobic tails contributed to the structure of the network. The rheological behaviour of the HMPot–HAPP mixtures was thus similar to the rheological behaviour of the amylose–HAPP mixture (Ortega-Ojeda, Larsson, & Eliasson, 2004a). When the amount of amylose decreased in mixtures containing HAPP, the rheological behaviour became more similar to the behaviour of HAPP. From these results it is not possible to say wheather amylose is contributing or not to the network. When mixing HMPot1 with native potato starch a slightly different rheological behaviour was evident. The moduli decreased with decreasing proportion of HMPot, but the decrease was not as steep as for the HMPot–HAPP mixtures. Thus, the behaviour of the HMPot–native potato starch mixtures indicated that both amylose and OSA did contribute to the network formation of these samples.

Fig. 9b shows the frequency dependence for G' and G'' (n' and n'', respectively) as a function of proportion of native potato starch or HAPP in the sample for the mixtures shown in Fig. 9a. For both HMPot n' was always lower than n'' (Fig. 9b). The values of n' for HMPot1 were always lower than for HMPot2 showing a more liquid behaviour. For all mixtures, n' increased slightly with increasing the proportion of native potato starch or HAPP in the sample. This increase in n' for the HMPot–HAPP mixtures, is due to the decreasing amount of OSA chains as the concentration of HAPP increased. For the HMPot1–native potato starch mixtures, the increase in n' is related to the lower concentration of both OSA chains and amylose.

4.4. Mixtures with SDS

Whereas the HMPot, native potato starch, and HAPP samples without SDS were transparent, the addition of SDS induced turbidity in all samples, which indicates that aggregation had occurred. The addition of SDS to the HMPot samples resulted in an immediate gel formation. The moduli values for the samples containing SDS were lower than for the pure HMPot samples (Fig. 6a). Further increase in SDS concentration produced gels with higher values of the moduli; although still lower than for pure HMPot. The immediate formation of a stable gel (no time-dependence) when SDS was added to all starches may be due to the presence of micelle–polymer interactions, which are known to induce fast gel formation and stable gel networks (Axberg, Wennerburg, & Stenius, 1980; Goddard, Faucher, Scott, & Turney, 1975; Myers, 1988; Nagarajan, 1980). Mobile SDS molecules may replace immobile OSA in the existing amylose–OSA and amylopectin–OSA complexes. In addition, the alkyl chains of OSA and SDS may self-associate by hydrophobic interactions. Therefore, it is expected that one or a few OSA chains become part of a SDS micelle, and the polymer chains become “cross-linked” or bridged by the SDS micelles (Fig. 6). With further SDS addition (up to 2%), the dissociation of amylose–OSA or amylopectin–OSA complexes is expected to continue. At the same time, the added SDS may interact strongly with the hydrophobic OSA chains, which form hydrophobic bridges between amylopectin branches, leading to an increase in G'.

The addition of SDS to both native potato starch and HAPP produced a different rheological behaviour compared to when SDS was added to HMPot. Adding SDS increased the values of G', which increased further when more SDS (2%) was added. The fact that adding SDS to native potato starch and HAPP samples resulted in almost the same G' values, may indicate that amylose did not participate in the actual network formation. This may result from a separation of the amylose–SDS complexes. In this case, only relatively few inclusion complexes between SDS and the amylopectin side chains would result in higher moduli values. A similar rheological behaviour where the moduli increased due to the formation of inclusion complexes resulting from few interactions between a polymer and a host molecule has been described for other polymers like starch–lactone (Heinemann, Escher, & Conde-Petit, 2003) and cyclodextrin-grafted chitosan and adamantly derivatives (Auzély-Velty & Rinaudo, 2002).

5. Conclusion

The influence of hydrophobic modification on the rheological properties of gels of hydrophobically modified potato starch (HMPot) and high amylopectin potato starch (HAPP) was studied using small deformation oscillatory rheometry. Two HMPot starches with different octenyl succinate anhydride (OSA) substitution degrees were investigated; HMPot1 and HMPot2, respectively. The rheological behaviour of HMPot starch was different from the behaviour of native potato starch and HAPP. The storage moduli (G') for HMPot starch were higher than for native potato starch and HAPP at concentrations higher than ~15%. Higher levels of OSA substitution resulted in lower moduli values. The gel formation of HMPot was slower than for native potato starch and HAPP. This was explained by a formation of both amylose–OSA inclusion complexes, and hydrophobic interactions between the OSA chains located mostly at the amylopectin branches.

For mixtures made with HMPot and HAPP, decreasing concentrations of HMPot resulted in reduced moduli values, and rheological behaviour resembling that of HAPP. In these mixtures, amylose and OSA seemed not to contribute to the network formation when the HMPot concentration was lower than 50%.

The addition of 1% SDS to HMPot first caused a decrease in the moduli. Further increase in SDS concentration from 1 to 2% resulted in higher values of the moduli; yet lower than for pure HMPot. A possible explanation for the decrease in the moduli is that SDS is replacing OSA chains in the amylose–inclusion complexes. With no amylose participation in the network, the moduli would initially decrease. Further addition of SDS would strengthen the still existing OSA–OSA hydrophobic interactions by polymer–micelles interactions, thus the moduli would increase.

The addition of SDS to native potato starch and HAPP had a different effect on the rheological properties compared with the addition of SDS to HMPot starch. For native potato starch and HAPP, an increase in the moduli was observed when 1 and 2% SDS was added. The storage modulus of both native potato starch and HAPP increased to the same value when SDS concentration was increased to 2%. This was suggested to indicate that amylopectin dominated the effect on G' observed for the gel formation of those networks.

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