Film-forming properties of a modified starch/κ-carrageenan mixture in relation to its rheological behaviour

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Abstract

The mechanical and calorimetric properties of acid hydrolyzed hydroxypropylated pea starch (HPPS)/κ-carrageenan (κC) cast films were investigated in relation to the rheological behaviour of the gelled film-forming dispersions. The mixture was prepared by mixing HPPS (25%, w/w), an easily slurried non-gelling polysaccharide, and a K^+κ-carrageenan ($\leqslant$1% w/w) used for its gelling properties. Whatever the κ-carrageenan content, the total ionic concentration (K^+) was maintained constant to control the transition temperatures. Compared to individual components, the rheological properties of the hot mixtures at 60 °C showed a dramatic increase of the viscosity. Upon cooling, stronger gels were formed compared to those of the pure κ-carrageenan in similar ionic conditions. Meanwhile, these gels set and melted at temperatures around 10 and 20 °C higher than those of the κ-carrageenan alone in the same conditions. These phenomena were attributed to excluded volume effects between κ-carrageenan and starch resulting in the increased concentration of the carrageenan forming the network. Drying was performed under controlled conditions at 25 °C and 40% relative humidity. The glass transition temperature T_g of HPPS at different water contents was obtained by calorimetry. The properties of the cast films were evaluated on the basis of mechanical and calorimetric measurements. Overall, the final film properties of the blends were similar to those of the films with starch alone. This means that the influence of the κ-carrageenan on the solid-state behaviour of the blends was hidden, in spite of the strong influence of κ-carrageenan on the rheological behaviour in the solution and in the gel state.
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1. Introduction

Polysaccharides are known for their film-forming properties which have been intensively investigated for food and non-food applications. It has been shown that a wide range of film properties can be obtained owing to the diversity of available polysaccharides (Nisperos-Carriedo, 1994).

Starch, an abundant natural polysaccharide, has been widely studied to achieve renewable and biodegradable films thanks to its wide availability, its low cost, and its functional diversity. Mechanical properties of starch films are highly dependent on the amylose/amylopectin ratio, the two main macromolecular components of starch. Amylose, the linear component, favours good film properties compared to amylopectin, the highly branched macromolecule (Bader & Goritz, 1994; Lourdin, Della Valle, & Colonna, 1995). Starch films contain residual water which also plays a significant role for their mechanical properties by reducing the glass transition temperature (Bizot et al., 1997; Zeleznak & Hoseney, 1987). However, the industrial application of starch films for non-food uses is limited due to their brittleness and their hydrophilic nature. Plasticizers such as glycerol can be used to overcome these limitations by improving the processing and the flexibility of starch films (Krogars et al., 2003; Lourdin, Coignard, Bizot, & Colonna, 1997; Mehyar & Han, 2004). Another way to reduce these drawbacks is the use of modified starch or the incorporation of another biopolymer. Studies have been carried out to develop modified starches to improve the processing and extend their film-forming ability. These

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modifications, which can be chemical, physical or enzymatic, enable to change the physico-chemical properties of the dispersions and of the films. Reduction of the molecular weight and/or chemical substitution yield a lowering of the gelatinization temperatures or delay retrogradation (BeMiller, 1997). This also improves the transparency and the flexibility of the films (Vorwerg, Dijksterhuis, Borghuis, Radosta, & Kroger, 2004).

Composite films from mixed polysaccharides can be produced to combine the intrinsic properties of the components to obtain an enhancement of the properties. Cellulose and its derivatives (such as ethers and esters) (Psomiadou, Arvanitoyannis, & Yamamoto, 1996), pullulan (Biliaderis, Lazaridou, & Arvanitoyannis, 1999), chitosan (Rueda, Secall, & Bayer, 1999) and pectin (Fishman, Coffin, Unruh, & Ly, 1996) have been shown to reinforce the mechanical properties of the starch films.

Although a great interest has been focussed on polysaccharides films, film-forming properties of starch/κ-carrageenan mixtures have not been investigated despite κ-carrageenan itself is known for its good film forming ability (Briones et al., 2004; Choi et al., 2005; Park, Lee, Jung, & Park, 2001). κ-Carrageenan is usually employed in the food industry for its gelling properties and its stabilizing role. The gelling properties of the κ-carrageenan in the K^+ form are well known and especially the sol–gel transition temperature dependence on the K^+ content (Piculell, 2006; Rochas, 1982; Rochas & Rinaudo, 1980; te Nijenhuis, 1997).

The characteristics of biopolymer-based films depend strongly on the composition and also on the process of film formation. The casting process consisting in drying a solution or a gel is a simple method for producing films with controlled thickness. This technique is also useful to mimic some industrial processes for forming free-standing polysaccharide films as is the case for dip-moulding. In this method used for food coatings (Cisneros-Zevallos & Krochta, 2003) as well as for non-food applications (Santacruz, Ferrari, Nieto, & Moreno, 2004), the gelled state is usually preferred to set hot solutions on a surface upon cooling. Tailor-made polysaccharides films for dip-moulding processes are however still difficult to achieve and require accurate knowledge of the rheological behaviour of the film-forming components in solution and in the gel state (Peressini, Bravin, Lapasin, Rizzotti, & Sensidoni, 2003).

The purpose of the present work was to combine the intrinsic properties of two polysaccharides in order to prepare films for dip-moulding applications. A non-gelling modified starch easily dispersible in water at high concentration was mixed with the κ-carrageenan in the K^+ form. The aim was to take advantage of the film forming properties of starch and of the gelling ability of the κ-carrageenan. This allowed one to easily control the sol–gel transition upon cooling and also to obtain a thermoreversible material. The properties in hot mixtures and upon cooling have been investigated by rheological measurements. Then, mechanical and calorimetric properties of the films obtained under controlled drying conditions have been studied.

2. Experimental

2.1. Materials

Hydroxypropylated pea starch (HPPS) with a moisture content of 10.2% was manufactured and provided by Roquette Frères (Lestrem, France). The sample has been hydrolyzed by acid treatment and the mean molecular weight $\overline{M}_w$ determined by HPSEC-MALLS by the manufacturer was of about 720,000 g/mol. The molar substitution of the whole modified sample was 0.23. The K^+ κ-carrageenan (κC) sample was supplied by Cargill Texturizing Solutions (Baupte, France); it contains 191.8 mequiv/100 g of K^+ (7.5%), 87 mequiv/100 g of Na^+ (2%), 0.6% of chloride ions, 10 mequiv/100 g of Ca^{2+} (0.4%) and 1.23 mequiv/100 g of Mg^{2+} (0.03%). Its mean molecular weight $\overline{M}_w$ was 780,000 g/mol and its moisture content was about 10%.

2.2. Solutions preparation

HPPS pastes were prepared at a constant concentration of 25% (w/w); some flow curves have also been measured for HPPS concentrations at 27% and 30%. First of all, the starch powder was slurried in deionised water at room temperature and then heated to 90 °C during 30 min. To avoid air bubbles, the solutions were stored at this temperature under low stirring. The K^+κ-carrageenan powder [1%, 0.75%, 0.5%, 0.25% or 0.1%] was slowly dispersed in deionised water under agitation with the corresponding KCl concentration (0, 3.24, 6.49, 9.73, 11.70 mM) (Table 1) and heated to 80 °C during 40 min. As far as the mixtures were concerned, components were well dry blended prior solubilisation in deionised water with or without KCl at 90 °C under stirring during 40 min. To achieve a good film elaboration, bubbles had to be removed by keeping hot solutions at 70 °C during at least 1 h.

When dealing with κ-carrageenan, it is possible to monitor the coil to helix temperature and hence the gelling–melting temperature by adjusting the total K^+ content (C_T) in the system according to the following relationship (Rochas & Rinaudo, 1980):

Table 1
Compositions of the HPPS–κC mixtures with varying the κ-carrageenan/KCl ratio

Compositions of the mixtures (% of HPPS and of κ-carrageenan)	κ-Carrageenan concentrations C_P (%)	κ-Carrageenan concentrations $C_P \times 10^3$ (equiv/l)	KCl salt concentrations $C_s \times 10^3$ (equiv/l)[a]
HPPS25–κC1	1	23.58	0
HPPS25–κC0.75	0.75	17.69	3.24
HPPS25–κC0.5	0.5	11.79	6.49
HPPS25–κC0.25	0.25	5.90	9.73
HPPS25–κC0.1	0.1	2.36	11.70

[a] The KCl content is varied in order to keep the total K^+ content C_T constant according to Eq. (1) (see text).

$$C_T = C_S + \overline{\gamma} \cdot C_P \qquad (1)$$

where C_S is the concentration of the added salt, C_P is the concentration of the counterions from the polymer, and $\overline{\gamma}$ is a mean activity coefficient taken to 0.55 (Rochas, 1982). The logarithm of the total K^+ concentration C_T is a linear function of the inverse of the gelling transition temperature. It has been shown that a gel can be formed at concentrations above the critical concentration $C_T = 7$ mM corresponding to a gelation temperature of about $T = 20$ °C (Rochas & Rinaudo, 1980). Beyond this critical concentration a thermal hysteresis in the conformational transitions was evidenced. Our own rheological and microcalorimetric measurements performed on the κ-carrageenan sample demonstrated the same transition temperatures dependence upon the total K^+ concentration (results not shown).

In the present work, we chose to maintain the total K^+ content C_T at 1.3×10^{-2} equiv/l corresponding to a gel temperature of around 25 °C for pure carrageenan. Whatever the κ-carrageenan content, the total K^+ content (C_T) was maintained constant thanks to the κ-carrageenan/KCl ratio on the basis of Eq. (1), as indicated in Table 1.

2.3. Rheological measurements

Rheological measurements were carried out using either an AR2000 controlled-stress rheometer (TA Instruments) equipped with a stainless steel cone plate geometry (diameter: 40 mm; angle: 4°; truncation: 98 μm) or an ARES-LS (TA Instruments) controlled strain rheometer equipped with a plastic cone plate geometry (diameter: 40 mm; angle: 2°; truncation: 55.6 μm). Both instruments were equipped with a Peltier temperature controller. The samples were covered with paraffin oil to prevent evaporation during measurements.

Dynamic oscillatory measurements were carried out in the linear viscoelasticity domain, from 100 to 0.1 rad/s with a strain amplitude of 0.1%. First, mechanical spectra were obtained at 50 °C. Temperature ramp sweep tests (1 °C/min) were then performed from 60 to 20 °C, and from 20 to 60 °C at an angular frequency of 1 rad/s and a strain of 1%. Flow properties were determined at 50 °C. Two consecutive up–down shear scans from 0 to 100 s^{-1}, followed by a descent from 100 to 0 s^{-1} were performed during a total time of 2 min to detect an eventual hysteresis. For gel cure experiments, the storage modulus G' and the loss modulus G'' variations as a function of time were performed at 1 rad/s obtained after quenching from 70 °C down to 20 °C. Finally mechanical spectra were performed at 20 °C at the end of the gel cure experiment.

2.4. Film preparation and characterization

After 30 min of stabilization at 50 °C, the suspension was poured on Teflon® plates. The original thickness was adjusted with a spreader from 800 to 1300 μm depending on the desired final thickness. For κC solutions, rectangular polystyrene Petri dishes (120×120 mm) were used. In this case, the final thickness of the film depended on the mass of solution. Solutions were dried in a cabinet (ERATIS, Bouloc, France) under controlled conditions of storage at 25 °C and 40% of relative humidity (RH). Drying kinetics were followed using an interfaced balance (Sartorius, ±0.01 g). To limit fluctuations of mass during the drying process, we deliberately limited the air velocity at ∼0 m/s.

2.5. Water content determination

Prior experiments, equilibrated samples were conditioned at the relative humidity of 58% for 2 weeks, in order to obtain complete equilibrium. The thermogravimetric method was used to measure the water content of the samples (wet basis) after storage at controlled relative humidity. Water was extracted and evaluated from the samples at 130 °C for 90 min.

2.6. Mechanical properties measurements

Elongation (ϵ_R) and tensile stress at break (σ_R) together with Young's modulus (E) were measured with an Instron machine, model 1122 with a 100 N tensile load cell. These mechanical properties were evaluated on 5A type dumbbell-shape specimens according to the ISO-527-2 standard ($l_o = 20$ mm). Film thickness was determined in five points with a micrometer Mitutoyo (±1 μm). The distance between the supports was set at 50 mm, and the crosshead speed was fixed at 1 mm/min. Each measurement was performed at least five times until sample failure.

2.7. Differential scanning calorimetry

Glass transition temperatures of the cast films were determined by differential scanning calorimeter either on DSC121 (SETARAM, France) and on Q100 (TA Instruments). The films were previously reduced to powder by a cryogrinder and stored at a constant RH before being placed in pressure-tight cells. After a first scan from 5 to 155 °C, to delete any thermal event caused by ageing phenomena which could occur during storage, the samples were quickly cooled to 5 °C (60 °C/min) to maintain the material in an amorphous state. A second scan was then performed from 5 to 155 °C at 3 °C min^{-1}.

3. Results

3.1. Flow behaviour at 50 °C

The flow behaviour at 50 °C of pure κ-carrageenan at 0.5% (κC0.5), and of pure hydroxypropylated starch at 25%, 27%, and 30%, (HPPS25, HPPS27, HPPS30, respectively), is shown in Fig. 1 as a linear plot. The curve corresponding to the HPPS25-κC0.5 mixture is also reported in this figure. These curves show the variations of the shear

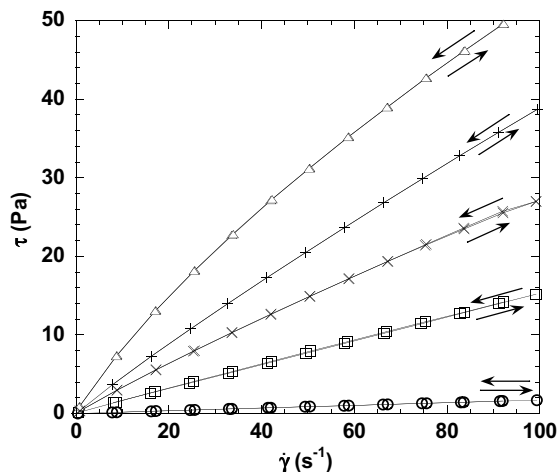Fig. 1. Flow curves of the κ-carrageenan solution at 0.5% (κC0.5, ⊖), starch dispersions (HPPS), (25% ⊟, 27% ✕ and 30% +) and the HPPS25-κC0.5 mixture (△). Measurement temperature, 50 °C.

stress as a function of the shear rate during two consecutive up and down shear ramps. The κC0.5 solution exhibited a Newtonian behaviour with a viscosity of about 16 mPa s. This behaviour was also observed for all κC concentrations studied from 0.1% to 1% with the viscosity ranging from 5 to 65 mPa s (not shown). For HPPS, the non-linear dependence and the superposition of the up and down curves in Fig. 1 demonstrated a shear-thinning and non-thixotropic behaviour with the viscosity of the paste increasing with the HPPS concentration. The HPPS25-κC0.5 mixture exhibited a more pronounced shear-thinning behaviour while the lack of hysteresis demonstrated that the non-thixotropic character persisted. The viscosity of the mixture was dramatically increased in comparison to the individual components at equivalent concentrations. It was still higher than HPPS30. The equivalent flow curves in logarithmic scales, apparent viscosity (η_A) versus shear rate ($\dot{\gamma}$), are shown in Fig. 2 for HPPS25 and the

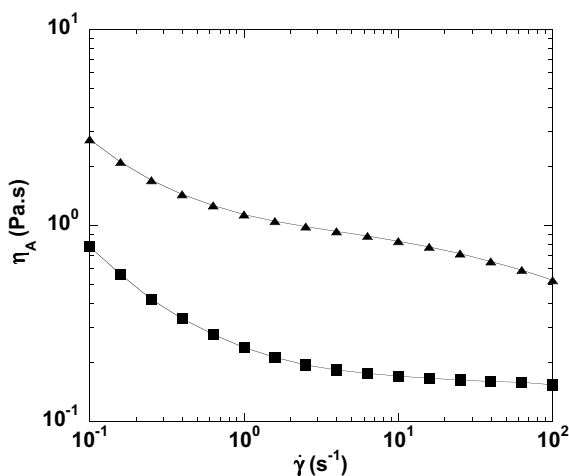Fig. 2. Flow curves, apparent viscosity as a function of shear rate, of the starch dispersion HPPS25 (■), and of the HPPS25–κC0.5 mixture (▲). Measurement temperature: 50 °C.

HPPS25-κC0.5 mixture. The shear-thinning behaviour and the dramatic increase of the viscosity for the mixture are clearly illustrated in this figure. The upward curvature observed at low shear rates for HPPS25 and also for the mixture is typical of starch suspensions which normally exhibit high viscosities in this region. This phenomenon may be ascribed to a "pseudo-yield stress" (Giboreau, Cuvelier, & Launay, 1994). The addition of a small amount of κ-carrageenan thus contributes to a dramatic increase of the viscosity together with a more pronounced shear-thinning behaviour. However, we could note that for HPPS25-κC0.1, corresponding to 0.1% of κ-carrageenan in the mixture, the flow curve was superimposed to that of HPPS25 alone (not shown). At this low concentration, the κ-carrageenan did not have any influence on the flow properties of the mixture at 50 °C.

3.2. Temperature sweep experiments

The variations of G' and G'' between 20 and 60 °C are illustrated in Fig. 3 for κC0.5 and the HPPS-κC0.5 mixture. The cooling and the heating ramps are reported separately in Fig. 3a and b, respectively. For κC0.5, it was not possible to determine G' modulus values above 27 °C upon cooling and 36 °C upon heating owing to the sensitivity limit of the equipment. Upon cooling pure κC0.5 (Fig. 3a), as long as the temperature was above 27 °C, G'' was constant and G' was negligible reflecting the liquid-like behaviour. Both moduli sharply increased at around 27 °C and reached the same values of about 1 Pa at 20 °C. The liquid-like behaviour was also exhibited for the HPPS25-κC0.5 mixture but at higher temperatures and with higher moduli values than for κC0.5. However, at high temperature, the G''/G' ratio (tan δ) was lower compared to pure carrageenan due to the contribution of starch to the rheology of the mixture. The moduli dramatically increased between 35 and 30 °C and crossed each other at 33 °C. At 20 °C, G' and G'' were about 480 and 28 Pa, respectively. Upon heating (Fig. 3b), G' and G'' moduli of κC0.5 and of the mixture at 20 °C were higher compared to the values at 20 °C at the end of the cooling ramp. This reflects the evolution of the gel while staying at 20 °C during around 1 h. At 20 °C, G' and G'' of κC0.5 were of about 10 and 3 Pa, respectively. Upon heating, both moduli progressively decreased and crossed over at 33 °C to finally reach a constant value at high temperature. G' and G'' of the HPPS25-κC0.5 mixture at 20 °C were close to 830 and 40 Pa, respectively. Both moduli decreased as the temperature increased and over crossed at 52 °C to finally reach identical values as those obtained before cooling. Thermoreversibility was exhibited for all the mixtures, like for pure carrageenan. The transition temperatures T_{GEL} and T_{MELT}, defined by $G' = G''$ on cooling and heating ramps, respectively, are presented in Table 2. The temperature dependence of the gels was strongly sensitive to the presence of carrageenan. Theoretically, for an identical total ionic concentration C_T, the transition temperatures
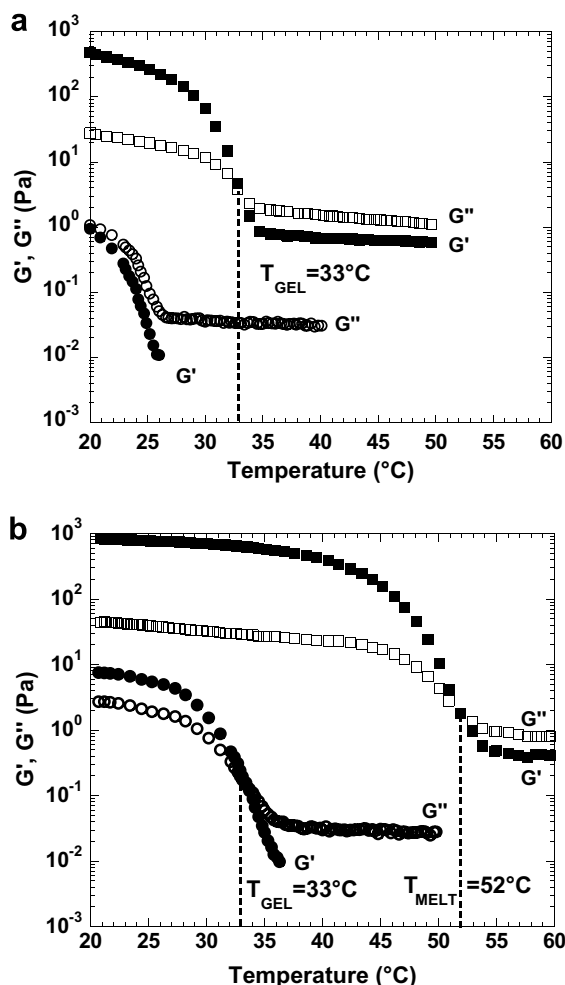
Fig. 3. Storage modulus G' and loss modulus G'' variations as a function of temperature for κC0.5 (●, ○), and HPPS25–κC0.5 (■, □). G', filled symbols, G'', empty symbols. Temperature ramp, 1 °C/min; frequency, 1 rad/s; strain amplitude, 1%. (a) cooling ramp from 60 to 20 °C. (b) heating ramp from 20 to 60 °C.

Table 2
Gelation temperature (T_{GEL}) and melting temperature (T_{MELT}) from the cooling and the heating ramp for κ-carrageenan alone and the HPPS–κC mixtures

Samples	T_{GEL} (°C)	T_{MELT} (°C)	Storage modulus G'^a (Pa)	Loss modulus G''^a (Pa)
κ-Carrageenan				
κC1	23	34	47.0	9.9
κC0.75	22	33	13.2	4.3
κC0.5	22	33	3.3	1.5
κC0.25	NG[b]	NG[b]	NG[b]	NG[b]
κC0.1	NG[b]	NG[b]	NG[b]	NG[b]
Mixtures				
HPPS25–κC1	34	53	2680	110
HPPS25–κC0.75	33.5	52.5	1135	88.3
HPPS25–κC0.5	33	52	803	28.7
HPPS25–κC0.25	32	52	332	12.6
HPPS25–κC0.1	31	52	20.3	2.0

The storage modulus (G') and the loss modulus (G'') values at 0.1 rad/s from mechanical spectra at 20 °C are also given.
[a] Values obtained from mechanical spectra at 20 °C and at 0.1 rad/s.
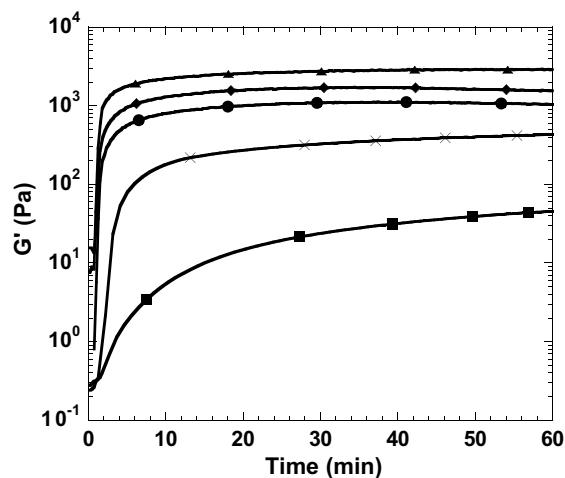[b] Not gelified at 20 °C.

Fig. 4. G' variations as a function of time for HPPS25–κC1 (▲), HPPS25–κC0.75 (♦), HPPS25–κC0.5 (●), HPPS25–κC0.25 (×), and HPPS25–κC0.1 (■). Measurement temperature, 20 °C; strain amplitude, 0.1%.

should be similar. For pure κ-carrageenan the gelation transition occurred at around 25 °C as it was predicted. For the low concentration of κC0.1 and κC0.25, no transition was detected by rheology. In the case of the mixtures, the transitions were shifted to higher temperatures but stayed approximately constant whatever the carrageenan concentration. As seen in Fig. 3a and b, G' and G'' of the mixtures strongly increased compared to the individual components.

3.3. Gel cure at 20 °C

The G' variations as a function of time after quenching from 70 °C down to 20 °C are shown in Fig. 4 for different mixtures. This illustrates that gelation was a time-dependent process. The initial rate of gelation increased with the carrageenan concentration. For HPPS25-κC0.1, G' steadily increased and never reached a constant value, G' being of the order of 45 Pa after 1 h. For HPPS25-κC0.25, G' increased more rapidly and reached a plateau

value of about 450 Pa beyond 30 min. For HPPS25-κC0.5, HPPS25-κC0.75 and HPPS25-κC1, G' increased as a function time more and more sharply and tended to plateauing to 1000, 1300 and 2900 Pa, respectively. Clearly, the mixed gels were strengthened with increasing the κ-carrageenan concentration in the mixture.

3.4. Viscoelastic properties at 20 °C

The mechanical spectrum at 20 °C of the mixture HPPS25–κC0.5 is shown in Fig. 5 together with those of pure κC0.5 and HPPS25, taken as references. For κC0.5, the storage modulus G' was higher than the loss modulus G'' within all the frequency range. G' and G'' slightly increased with frequency and G' displayed a plateau at low frequency at 3.3 Pa. The slight frequency dependence
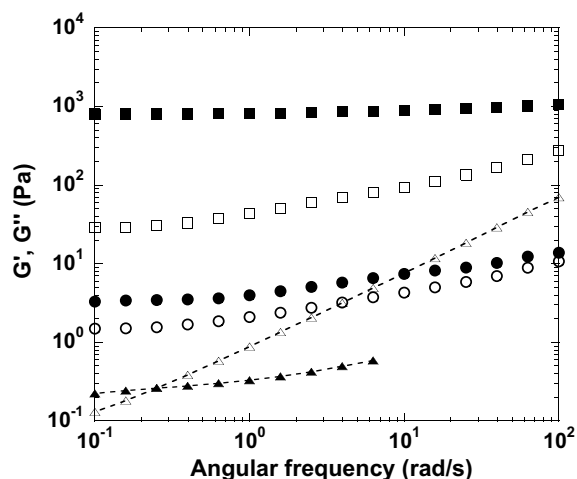
Fig. 5. Mechanical spectra of κC0.5 (●, ○), HPPS25 (dashed lines with ▲, Δ), and of the HPPS25–κC0.5 mixture (■, □). Measurement temperature, 20 °C; strain amplitude, 0.1%. G', filled symbols; G'', empty symbols.

of the moduli and also the fact that G' was higher than G'' over all the frequency range indicate a solid-like behaviour. However, the fact that G'' was close to G' over nearly the whole frequency range demonstrates that at this concentration the system was close to the gelation temperature. Indeed, at a lower carrageenan concentration (κC0.1 and κC0.25), no gelation was detected (see Table 2). On the other hand, for HPPS25, that is 25% of starch, a strong frequency dependence of G'' was observed ($G'' \sim \omega^{0.92}$) while G' was less frequency dependent. Above 7 rad/s, G' could not be measured because of the resolution limit of the rheometer. A crossover of moduli took place at about 0.2 rad/s although the HPPS is a non-gelling material. Below this value $G' > G''$ whereas at higher frequency G'' predominated. Despite this atypical frequency dependence of G', the frequency dependence of G'' suggests that the behavi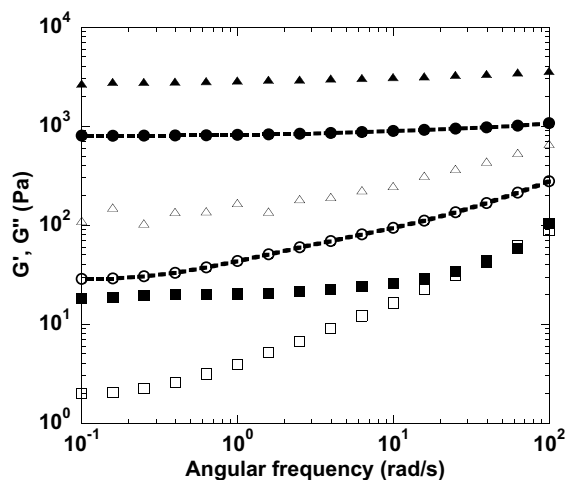our is not so far from that of a macromolecular solution composed of soluble molecules of HPPS. Regarding the HPPS25-κC0.5 mixture, the viscoelastic behaviour was dominated by the elastic component G' with $G' > 10G''$ and a flat frequency independence of G' typical of a true gel (Clark & Ross-Murphy, 1987). The moduli were much higher than of pure carrageenan as reported in Table 2: 800 Pa for G' and 29 Pa for G'' at 0.1 rad/s instead of 3.3 Pa for G' and 1.5 Pa for G' in the case of κC0.5 alone.

Fig. 6 illustrates the viscoelastic behaviour of two other mixtures HPPS25–κC1 and HPPS25–κC0.1. HPPS25–κC0.5 is shown for comparison. The HPPS25–κC0.1 mixture exhibited a solid-like behaviour, with G' plateauing at low frequency ($G' \sim 20$ Pa) and a slight frequency dependence of G' and G''. The HPPS25–κC1 mixture exhibited a true gel behaviour with a very slight frequency dependence of G' reaching a value of 2680 Pa at 0.1 rad/s.

From all these experiments, it is clear that the viscoelastic behaviour of the mixtures was modified even at the lowest concentrations of carrageenan studied suggesting the predominant role of this polysaccharide on the rheological properties.

3.5. Drying process

Fig. 7 shows the drying kinetics of the HPPS25 and of the HPPS25–κC0.5 mixture. The total weight/dry weight ratio, that is the inverse of the polymer concentration, is plotted as a function of time for a duration of 10 h. For both film-forming compositions, the water loss as a function of the drying time was linear in the initial part of the curve; then after this constant rate region, the drying rate slowly decreased leading to a plateau at the end of the drying process. In these experimental conditions (25 °C and 40% RH), the film from the blend exhibited the fastest drying rate. At equilibrium, HPPS25 and the blend had approximately the same water content at around 11% (Table 3). This drying profile is typical of the two stage mechanism observed in the drying process of films

Fig. 6. Mechanical spectra of the mixtures: HPPS25–κC1 (▲, Δ), HPPS25–κC0.5 (dashed lines with ●, ○), and HPPS25–κC0.1 (■, □). Measurement temperature, 20 °C; strain amplitude, 0.1%. G', filled symbols; G'', empty symbols.
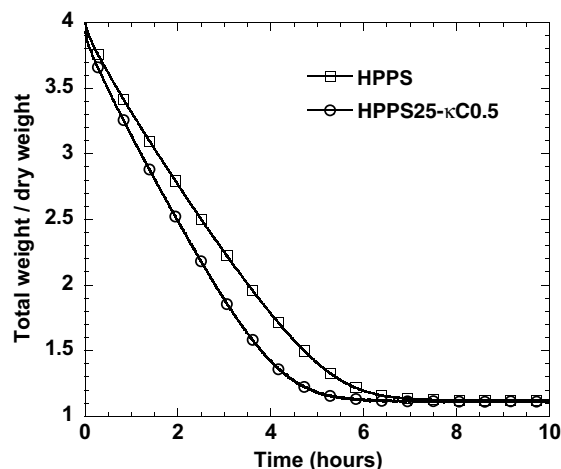

Fig. 7. Drying kinetics for HPPS (⊟) and the mixture HPPS25–κC0.5 (⊖) at 25 °C and 40% RH.

Table 3
Water content of the samples stored under two different relative humidity conditions and two different states

Relative humidity (%)	Films[a]			Powders[b]		
	HPPS	κC	Mixtures	HPPS	κC	Mixtures
40[c]	10.8	17.3	11.0	11.1	17.5	–
58[d]	13.1	19.5	13.3	13.2	20.0	13.5

[a] For tensile tests.
[b] For DSC measurements.
[c] Obtained after the drying process: desorption.
[d] Obtained after storage: sorption.

(Menagalli, Sobral, Roques, & Laurent, 1999; Steward, Hearn, & Wilkinson, 2000). Due to the high initial water content, the water can move relatively freely from the medium in this linear part. As the polymer concentration increases during the drying time, the polymer structure (entanglement) and the drop of molecular mobility affect the drying rate explaining the decrease of the drying rate in the non-linear region (Gu & Alexandridis, 2005).

3.6. Mechanical behaviour of the films

Tensile stress-elongation curves of the films for κC, HPPS25 and the mixtures are shown in Fig. 8. κ-Carrageenan films displayed a fragile behaviour (rupture in the elastic domain) with a Young's modulus (E) of 1.1 GPa, a tensile strength at break (σ_R) of around 57 MPa and an elongation (ϵ) of around 7% as reported in Table 4. HPPS films exhibited a ductile behaviour (rupture in the plastic domain) with a lower Young's modulus of around 0.9 GPa, a lower tensile strength at break close to 32 MPa and a higher elongation at break of 9 % compared to κC film. Whatever the κC content in the blend, the tensile properties of the blend were not significantly different from those of individual HPPS25. The ductile behaviour was also demonstrated for the mixtures.
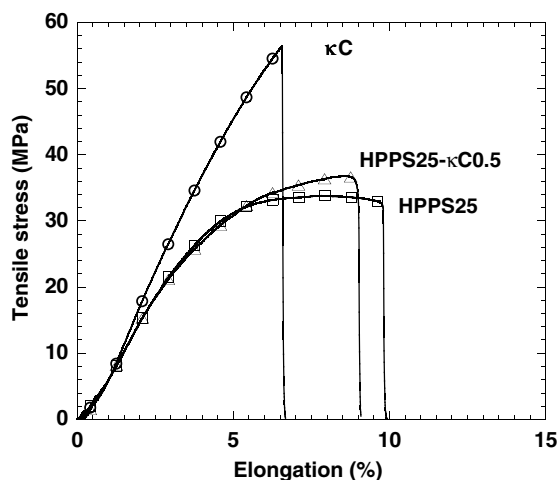
Table 4
Mechanical characteristics of the films from tensile tests

Samples	Young's modulus, E (GPa)	Stress at break σ_R (MPa)	Strain at break, ϵ_R (%)
HPPS	0.89 (±0.08)	32.4 (±2.2)	10.2 (±1.2)
κC	1.11 (±0.04)	57.2 (±1.3)	6.8 (±2.1)
Blends			
HPPS25–κC1	0.90 (±0.02)	35.7 (±2.2)	9.2 (±2.0)
HPPS25–κC0.1	0.91 (±0.02)	35.3 (±1.8)	9.4 (±2.5)

3.7. Thermal transitions

The DSC thermograms of HPPS25 and of the HPPS25–κC0.5 blend are shown in Fig. 9. Sub-T_g endotherms were observed at around 45 °C during the first scan on HPPS and blended films. This phenomenon observed on all samples studied corresponds to an enthalpy relaxation due to physical ageing during storage of the samples (Lourdin, Colonna, Brownsey, Noel, & Ring, 2002; Shogren, 1992). A second endothermic peak appeared at around 100–120 °C and was more pronounced for the blend. This endotherm has already been observed for amylose and amylopectin blend films (Rindlav-Westling, Stading, & Gatenholm, 2002) and was simultaneously attributed to the melting of cocrystallized amylose and amylopectin and of crystallized amylopectin. In preliminary X-ray diffraction measurements (not shown) performed on the samples, the occurrence of a B-type crystallization during casting was found consistent with the melting temperature detected by DSC. Both endotherms disappeared during the second scan. T_g was defined as the inflexion point on the thermograms obtained on the second scan to eliminate the enthalpy relaxation pre-peak, as well as to control the thermal history of the samples. For HPPS25 and for the blends, T_g was similar at around 67 °C with a very similar water content at around 13.5% (see Table 3). Other T_g measurements have been performed on HPPS25 at water

Fig. 8. Tensile stress–strain curve of κC films (⊖), HPPS films (⊟), and HPPS25–κC0.5 (△) films at 25 °C after a storage at 25 °C and 58% RH.
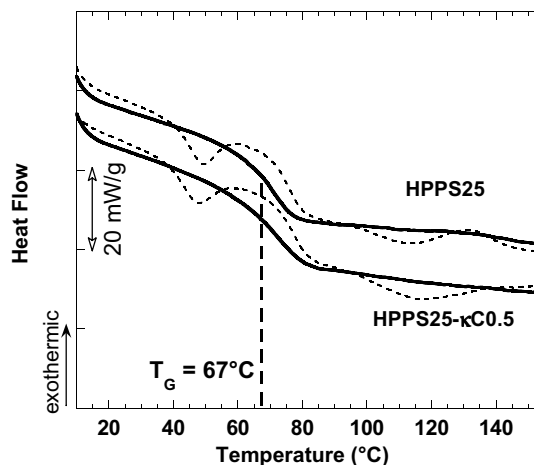
Fig. 9. DSC thermograms of HPPS films and HPPS25–κC0.5 stored at 25 °C and 58% of relative humidity. First scan, dotted lined; second scan, continuous line.

contents of 11% and 19% yielding to T_g values of 97 and 27 °C, respectively.

4. Discussion

4.1. Dominant role of κ-carrageenan in the solution and in the gel state

Before discussing the properties of the mixtures, it is important to consider the behaviour of individual components. Starch (HPPS), which accounted for 25% (w/w) or even more, was the major macromolecular component of the different mixtures we investigated. It displayed at 50 °C as well as at 20 °C the behaviour of a concentrated solution (Fig. 5). The viscoelastic behaviour at 20 °C, with the G'' frequency dependence ($G'' \sim \omega^{0.92}$), as well as the clarity of the concentrated HPPS pastes, suggest the components are almost totally solubilised. As a matter of fact, some starch remnants were still present in the dispersion as it has been observed by microscopy (not shown). This may explain the yield stress observed in Fig. 2 and also the unusual frequency dependence of G' at 20 °C. The HPPS dispersion can therefore be regarded as a fluid and non-gelling system whatever the temperature. As known, the κ-carrageenan exhibited a newtonian behaviour at 50 °C. On the other hand, by adjusting the KCl content, we managed in order that individual κ-carrageenan gelled at 23 °C and melted at 34 °C, whatever the carrageenan content (Table 2). The results are consistent with those of the phase diagram as reported by (Rochas & Rinaudo, 1980).

The rheological behaviour of the mixtures at 50 °C, in solution, and at 20 °C, in the gelled state, was strongly influenced by a small amount of κ-carrageenan. These effects were experienced whatever the carrageenan concentration, even at a low amount, the total K^+ concentration (C_T) being kept constant at 1.3×10^{-2} equiv/l.

The apparent viscosity of the mixtures was considerably higher than that of individual components and the shear-thinning behaviour already exhibited in individual HPPS was accentuated. However, due to the high concentration of HPPS in the system, the flow curves of the mixtures reflected the dominant contribution of the HPPS in hot solution. The extensive modifications of the flow behaviour of the mixtures in hot pastes might be ascribed to a local concentration of the added hydrocolloid. This phenomenon can be related to excluded volume effects due to the incompatibility between the soluble amylose and amylopectin components of starch and the κ-carrageenan which mutually concentrate each other in solution as it has been discussed by several authors (Morris, 1990; Zasypkin, Braudo, & Tolstoguzov, 1997). Moreover, the existence of thermodynamic incompatibility between starch components and other polysaccharides was extensively described in previous studies (Chaudemanche & Budtova, 2005; Closs, Conde-Petit, Roberts, Tolstoguzov, & Escher, 1999; Kalichevsky, Orford, & Ring, 1986; Kalichevsky & Ring, 1987; Tecante & Doublier, 2002).

Upon cooling the binary mixtures, a true gel was formed. From the mechanical spectra at 20 °C, the G' and G'' moduli of the gel were more than tenfold higher than individual κ-carrageenan in similar ionic conditions (see Fig. 3). A shift of T_{GEL} and T_{MELT} from 22 to 34 °C upon cooling and from 32 to 53 °C upon heating compared to individual κC was observed. Another interesting result was the dramatic decrease of the minimum concentration of gelation of the mixture compared to κ-carrageenan alone as shown in Table 2. These effects can be explained by an increase of the total ionic concentration (C_T) in the medium. From Eq. (1), C_T depends on the added salt as well as on the carrageenan concentration. Since the total ionic concentration was kept constant, the more likely explanation is that this increase of the transition temperatures in the mixtures is ascribed to the carrageenan concentration effect. Based on the K^+ κ-carrageenan phase diagram of Rochas and Rinaudo (1980), such temperature transitions correspond to carrageenan concentrations of 2% on cooling and 2.5% on heating. This concentration effect also explains the lowering of the gelation threshold as compared to the individual κ-carrageenan as reported in Table 2.

Such enhancement effect in gels composed of binary mixtures of polysaccharides may be attributed to intermolecular binding between the dissimilar macromolecules (Cairns, Miles, Morris, & Brownsey, 1987; Morris, 1990). However, thermodynamic incompatibility between polysaccharides would also result in such enhancement effects by mutually concentrating each polysaccharide in the system (Zasypkin et al., 1997).

The phenomena outlined above from rheological measurements are typical of those described in the literature for binary mixtures of dissimilar polysaccharides with excluded volume effects (Morris, 1990; Zasypkin et al., 1997). From these assumptions and in agreement with the rheological behaviour of HPPS–κC mixtures described in the solution state, we suggest that the gelled κ-carrageenan macromolecules are excluded from the volume occupied by the much more concentrated HPPS. This results in the concentration of the κ-carrageenan in the medium assuming that it was concentrated in one separated phase as it was described in previous studies dealing with starch/κ-carrageenan mixtures (Tecante & Doublier, 2002). Since the κ-carrageenan is able to dominate the rheology of the phase separated system, despite being the minor component, and HPPS components are non-gelling molecules, the carrageenan would form a percolating network finely structured. The overall behaviour of the binary gels of HPPS–κC would be regarded as that of a filled gel. The κ-carrageenan three-dimensional network forming the continuous phase is filled and reinforced with the highly concentrated HPPS.

4.2. Phenomena occurring during film formation

The complex macromolecular interactions in the system during the gelation process also influence the drying process via the gel state. Incompatibility between compo-

nents inside the gel may contribute to the increase of the drying rate of the mixtures compared to HPPS alone as shown Fig. 7. A decrease of the drying time has previously been observed on proteins gels (Menagalli et al., 1999) which has been attributed to the presence of heterogeneities in the system. This hypothesis may be consistent with the presence of local concentrated zones of κ-carrageenan in the continuous phase favoured by the excluded volume effect with HPPS. From the T_g values for HPPS we obtained at three water contents (11%, 15% and 19%) by DSC, it is possible to estimate T_g variations as a function of the water content below to 30% (Fig. 10). Because of ice formation, the measurement of T_g is impossible at water contents higher than 30% (Jouppila & Roos, 1997). In this figure, data from Bizot et al. (1997) on amylopectin films are also reported as a comparison. The T_g variations from 0% to 30% of water content were calculated using the Couchman's model (Couchman, 1987), on the basis of the following equation usually employed to predict the influence of the water content on the T_g of biopolymers:

$$T_g(Y^w) = \frac{Y^w T_g^w + (1 - Y^w)(\Delta C_p^p / \Delta C_p^w) T_g^p}{Y^w + (1 - Y^w)(\Delta C_p^p / \Delta C_p^w)} \qquad (2)$$

where Y^w is the weight fraction water, ΔC_p^p and ΔC_p^w are the respective specific heat changes of polymer and water at the respective glass transition temperatures: T_g^p and T_g^w. The glass transition of water (T_g^w) was −139 °C (Sugisaki, Suga, & Seki, 1968). The glass transition of HPPS25 T_g^p at 0% of water content was calculated at 272 °C and the $\Delta C_p^p / \Delta C_p^w$ ratio obtained was 0.169. Despite our data are slightly higher than those reported by Bizot et al. (1997) on amylopectin films, the T_g variations with the water content are comparable. These values are also in agreement with other studies on starch and amylopectin films (Jouppila & Roos, 1997; Zeleznak & Hoseney, 1987). Beyond

the experimental domain situated between 5% and 20%, T_g can be easily calculated from the model. From the T_g variations of HPPS as a function of the water content below 30% (Fig. 10) and the variations of the water content as a function of drying time (Fig. 7), we can plot T_g variations of HPPS films during the drying process. This is illustrated in Fig. 11. The continuous line shows T_g variations at water contents below 20% while the dotted line corresponds to the calculated values at water contents above 20%. The results from Bizot et al. (1997) are also reported in this figure. Quite obviously, T_g increases as a function of time during the drying process as a result of the decrease of the water content in the system. At equilibrium, corresponding to the end of the drying process, the water content in the film was 11% and T_g was about 97 °C. From T_g variations as a function of the drying time, we can determine the critical water content for which T_g of HPPS is equal to 25 °C, the drying temperature. This critical value corresponds to a water content of 20%. It was reached at a drying time of around 5h40min (indicated by arrows in Fig. 11). It could be argued that concentration gradients during drying may yield skin formation with impermeable glassy layer at the surface, while the core of the film is still rubbery (Crank, 1958). Owing to the relative low initial thickness and the low drying rate, we assume that skin formation is minimized. The water content of 20% represents an average water content inside the film. A similar critical water content of around 20% was reported for starch and amylopectin (Jouppila & Roos, 1997; Slade & Levine, 1995). It can be inferred that at this drying time of 5 h 40 min, the system experiences a transition from a liquid state to a glassy state freezing the molecular mobility in
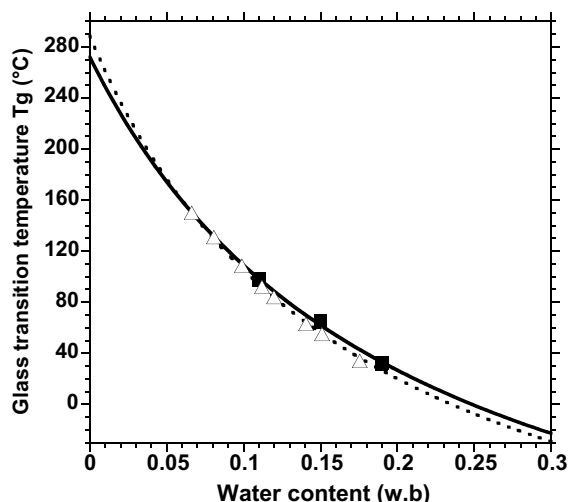

Fig. 10. Glass transition temperature T_g as a function of water content for HPPS (■) fitted with the Couchman's model (continuous line) (see text). T_g of amylopectin films (△) at different water contents also fitted with the Couchman's model (dotted line) from Bizot et al. (1997) are reported as a comparison.
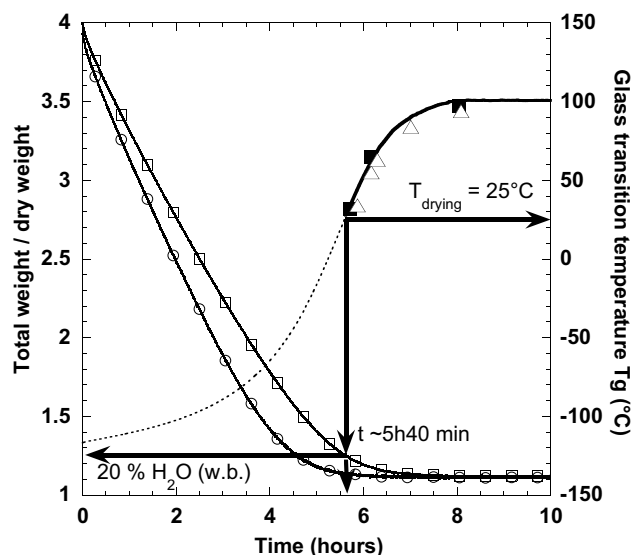
Fig. 11. T_g variations as a function of the drying time. Experimental data of the present study (■), data from Bizot et al. (1997) (△); the curve fitted from the Couchman's model Eq. (2) is plotted in continuous line for water contents lower than 20% and in dashed line above 20% (see text). The critical water content and the transition time occurring during the drying process at 25 °C are shown with arrows. The drying kinetics displayed in Fig. 7 are also shown.

HPPS. It is noteworthy that it is within this time period that the water loss is slowed down probably due to a drastic reduction of the mobility. The T_g values of the HPPS25–κC blends as a function of the water content have not been determined. However, we can attempt to apply the same approach to determine, in this case, the transition from the gel state to the glassy state. Although the κ-carrageenan does not influence the T_g at 13% of water content ($T_g = 67$ °C) as shown by DSC data (Fig. 9), the increase of the drying kinetics illustrated in Fig. 7 indicates that the transition to the glassy state would occur one hour earlier during the casting process.

4.3. Dominant role of starch in the solid state

The predominant role of κ-carrageenan previously described in the solution and in the gel state is not found in the dry state for which the physical properties of the film are governed by HPPS. According to water vapor sorption isotherms previously published, the water content of carrageenan (Mitsuiki, Yamamoto, Mizuno, & Motoki, 1998) is higher than HPPS due to its chemical structure known to advantage tightness of binding of water (Table 3). Mechanical properties measured on κ-carrageenan films reported in Table 4 are in agreement with data previously published (Briones et al., 2004; Park et al., 2001). HPPS films exhibit a ductile behaviour with lower Young's modulus (E), lower maximum stress at break (σ_R), and higher elongation at break compared to κ-carrageenan films. The tensile properties of the blend were slightly modified compared to HPPS with a slight increase of the tensile strength and the small decrease of the elongation at break. But on the basis of standard deviations measurements reported in Table 4, theses differences were not statistically significant. From the calorimetric experiments (Fig. 9), no significant change in the T_g values of the blends was observed compared to individual HPPS. Despite the strong role of the carrageenan in the solution and in the gelled state, its effect on blend films is hidden by the major component (HPPS) which governs the overall physical properties in the solid state.

We previously suggested that the second endothermic event observed at around 110 °C (Fig. 9) for the films can be simultaneously attributed to the melting of cocrystallized amylose and amylopectin and of crystallized amylopectin (Rindlav-Westling et al., 2002). The shift of this melting temperature in the case of the blend may be due to the incompatibility of carrageenan with amylose and amylopectin macromolecules which would hinder the crystallization process. Although hydroxypropylation should prevent gelation of starch, we observed by X-ray measurements that crystallisation mechanism occurs during film formation in these drying conditions (work in progress).

5. Conclusions

From the rheological behaviour of the film-forming HPPS–κC mixtures, a dramatic increase of the viscosity of the mixtures was evidenced in the hot paste. The behaviour in solution is influenced by the presence of highly concentrated HPPS and the mutually self-concentration of the incompatible components in the system. As HPPS by itself is a non-gelling polysaccharide, network formation is to be ascribed to the gelling κ-carrageenan. The strengthening of the gel, as well as the lowering of the gelation threshold and the increase of the transition temperatures compared to individual carrageenan are to be ascribed to an increase of the carrageenan concentration in the continuous phase. Excluded volume effects due to the thermodynamic incompatibility between the HPPS and the carrageenan can explain these phenomena. From this macromolecular statement, the system can be regarded as a filled gel in which carrageenan molecules form a three-dimensional network filled and strengthened by HPPS. The reduction of the drying time under controlled conditions for the mixtures is to be ascribed to the presence of these heterogeneities in the system. The transition from the liquid or the gelled state to the glassy state could be determined during the drying kinetics. This enables one to predict the modifications of the macromolecular state occurring during the process of film formation. Mechanical and calorimetric experiments showed that the enhancement of the properties in the solution and in the gel brought about by the carrageenan disappears in the solid state. The carrageenan does not significantly influence the HPPS film properties.

Finally, this study demonstrates that thanks to the addition of a low amount of the gelling carrageenan to HPPS, we are able to monitor the macromolecular behaviour of film-forming mixtures from the solution and the gel state to the final film properties. The contribution of the gelation with enhanced solution properties and thermoreversibility without modifying the film properties might be beneficial to design tailor-made films.

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