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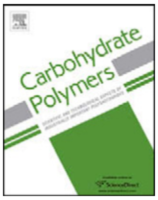

Effect of oat spelt and beech xylan on the gelling properties of *kappa*-carrageenan hydrogels☆

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ABSTRACT

Mixed hydrogel samples of commercially important food hydrocolloid, viz. *kappa*-carrageeenan (kC) with abundantly available oat spelt (OSX) and beech (BX) xylan were investigated using dynamic oscillatory measurements, thermal (DSC), syneresis measurement in gel samples, moisture content, morphological (SEM), and swelling measurements on the dried samples. At total polymer concentrations of 1% (w/w), a kC concentration in the interval between 10 and 50% (w/w), and OSX or BX concentrations 50–90% (w/w, w.r. to dry kC), were used. Syneresis in kC gels was decreased significantly, while swelling ability was increased radically, after mixing with xylans. Gelling and melting temperatures of kC were increased in kC/BX$_{50-90}$ hydrogels, while decreased in kC/OSX$_{50-90}$. SEM analysis indicated that kC formed porous and compact hydrogels with OSX and BX, respectively. Frequency dependence result indicated that kC$_{10}$ solution behaves like gel materials when mixed with 90% (w/w) OSX or BX.

1. Introduction

The viscous and gelling properties of polysaccharides in water with and without additives have found broad applications in the food industry because these are very important in the texturing of foodstuffs (Nishinari, Miyoshi, Takaya, & Williams, 1996). Mixed polysaccharide systems, solutions and their gels, have been widely studied by many authors due to their wider industrial applications (Amici, Clark, Normand, & Johnson, 2001; Kasapis, Morris, Norton, & Clark, 1993; Michon, Cuvelier, Launay, & Parker, 1996; Tolstoguzov, 1995). Products without fat or low-fat can have similar body texture and flavor to its full fat counterpart, by using at least one food grade, polyanionic gum selected from xanthan, alginate, carrageenan, cellulose gums and their mixtures (Adamany, Henry, Moore, & Filkouski, 1999). Meena, Prasad, and Siddhanta (2009) have reported stable hydrogel material based on cross-linked agar-*kappa*-carrageenan blend.

Carrageenans are anionic biopolymers extracted from *Gigartina*, *Chondrus*, *Iridaea* and *Eucheuma* spp. Mainly three types of carrageenan (*kappa*-, *iota*-, and *lambda*-) are obtained from these red seaweeds. Among them, *kappa*-carrageenan is forming the strongest gel in presence of potassium salt, and has been characterized by its repeating disaccharide units of 3-linked β-D-galactose 4-sulphate and 4-linked 3,6-anhydro-α-D-galactose. The gelation process occurs through an aggregation step after undergoing a coil-helix transition. The mechanism of gelation involves coil–helix transition of *kappa*-carrageenan molecules (Morris, Rees, & Robinson, 1980). Mixing of galactomannan with food hydrocolloids namely agarose or *kappa*-carrageenan is known to improve their mechanical properties and reduce brittleness or syneresis of the gels (Morris, 1986). Morris (1986) has also reported that the synergistic effects between galactomannan and above hydrocolloids lead to gels with enhanced elasticity and strength under conditions where the pure polysaccharide does not form gel. Mixtures of galactomannan and xanthan formed gels despite the fact that they neither form gels separately. Blend systems of polysaccharides including hydrocolloids are normally used in the food industry to impart 'smart test' to the food products, modify their rheological properties and simplify industrial procedures (Norziah, Foo, & Karim, 2006). The mixed gel systems of *kappa*-carrageenan with *lambda*-carrageenan and locust bean gum have been reported with improved gelling properties (Baker, 1949; Christensen & Trudsoe,

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1980; Goycoolea, Richardson, Morris, & Gidley, 1995; Igoe, 1982; Kohyama, Iida, & Nishinari, 1993; Turquois, Rochas, & Taravel, 1992). Potassium *kappa*-carrageenan formed a stronger gel when mixed with locust bean gum than sodium- and calcium-*kappa*-carrageenan (Tako & Nakamura, 1986).

The current trend of using environmental friendly products has resulted in an extensive exploitation of new materials obtained from renewable resources. Preparation of polysaccharide based composites, blends or mixtures represent a new category of environmentally safe materials for newer applications, due to their water solubility and biodegradability. Numerous synthetic polymers are used for composite preparation prior to polysaccharides, which may create environmental problems due to the use of organic solvents and the limited degradability of the products. Further, there is a need to explore the behavior of abundantly available hemicelluloses and seaweed polysaccharides based composites to form a supreme choice, and needs to optimize the composition of these polysaccharides (Ivan, 2008). The important plant materials are cellulose, hemicelluloses and lignin. The term "hemicelluloses" is used for polysaccharide which normally occurs in the plant tissues together with cellulose, and hemicelluloses. They can be isolated from many raw materials by extraction with water or aqueous alkali solution (Gabrielii, Gatenholm, Glasser, Jain, & Kenne, 2000). As reported by Prade (1996), xylan accounts approximately for one third of all renewable organic carbon available on the earth. The hydrogel formation of hemicelluloses with chitosan under acidic conditions has been reported (Gabrielii & Gatenholm, 1998; Gabrielii et al., 2000; Tanodekaew, Channasanon, & Uppanan, 2006). Up to date hemicelluloses from lignocelluloses have been investigated for application as paper additives, for film formation, various derivatives as well as blends with chitosan, carboxymethyl xylan, and for synthesis of graft copolymers (Ebringerova & Heinze, 2000; Gabrielii & Gatenholm, 1998; Petzold, Schwikal, & Heinze, 2006; Ramírez, Puls, Zúñiga, & Saake, 2008; Tanodekaew, Channasanon, & Uppanan, 2006).

Commercially available xylans are used mainly after degradation as a source for xylitol and furfural (Mansilla et al., 1998; Parajo, Dominguez, & Dominguez, 1996). In small quantities sulfated xylo oligosaccharides from beech wood are used as an anti-thrombotic pharmaceutical (Tromocid, Bene, Munich, Germany). In the present investigation, arabinoxylans were extracted from oat spelt and 4-O-methylglucuronoxylan from beech wood. Both were utilized to form smart new materials as showing enhanced gelling, swelling and pH resistance properties in comparison to the native components, using greener composite techniques and water as a greener solvent, as well as explore their uses as hydrogel modifying agent. Resultant hydrogel samples were characterized systematically using rheometry, DSC, and SEM techniques.

2. Materials and methods

2.1. Materials

A commercially important hydrocolloid namely *kappa*-carrageenan (kC) was extracted in the pilot plant (CSMCRI, Bhavnagar, India), using 10 kg *Kappaphycus alvarezii* of Indian waters following the patented method (Ghosh, Prasad, Siddhanta, Meena, & Bhattacharya, 2006). Arabinoxylan, from oat spelts (OSX) was obtained by sodium hydroxide extraction and precipitation as published previously (Saake, Erasmy, Kruse, Schmekal, & Puls, 2004). 4-O-methylglucuronoxylan from beech wood (BX) was obtained analogously by extraction of beech wood holocellulose. The holocellulose was prepared by treatment of the starting material with 4.5% sodium chlorite for 120 h at room temperature (Dietrichs & Zschirnt, 1972).

Specification of kC, OSX, and BX were as follows (carbohydrates calculated in mol% based on the polymer backbone):

OSX: Mw 27,200 g/mol, 3.8 mol% 4-O-MeGlcA, 71.9 mol% xylose, 11.3 mol% arabinose, 0.2 mol% rhamnose, 2.0 mol% galactose, 2.8 mol% glucose.
BX: Mw 18,700 g/mol, 9.4 mol% 4-O-MeGlcA, 63.6 mol% xylose, 0.6 mol% arabinose, 0.9 mol% rhamnose, 1.2 mol% galactose, 1.1 mol% glucose.
kC: Mw 1,508,600 g/mol; sulphate content 16% mol%, 64.5 mol% galactose, 9.6% mol% mannose & 16.5 mol% arabinose.

Technical grade isopropanol (IPA) was used as received from Sigma–Aldrich Ltd., Germany, without further purification.

2.2. Preparation of mixed hydrogel

Blend hydrogel samples of kC with OSX and BX were prepared as follows: the kC, OSX and BX sols in 1% aqueous KCl were prepared separately by heating on a hot plate under shearing at 9500 rpm and 13,500 rpm during addition and mixing, using IKA T25 Digital ULTRA TURRAX (Germany). The sols were then mixed in required proportions under shearing rate of 9500 rpm at 80 °C for 60 s. Six blend hydrogel (three of each xylan) samples with total polysaccharide concentration 1% (w/w), were prepared using the following ratios of kC/OSX or BX: (I) kC/OSX or BX = 10/90 (w/w); (II) kC/OSX or BX = 30:70 (w/w), and (III) kC/OSX or BX = 50/50 (w/w). The resulting mixed sols were kept at room temperature followed by storage at 10 °C overnight to obtain soft to hard gels, which were then divided into two parts. One part was used for rheological, DSC, and syneresis measurements under identical conditions. Another part was cut into small pieces and dehydrated with isopropanol (IPA) for 24 h. Dehydrated gels were dried in air followed by oven drying at 50 °C for 2–4 h, to avoid thermal decomposition. The dried hydrogel samples were used for swelling ratio, and moisture content measurements. The parent hydrogel samples without xylans were prepared by similar methods having only 0.1%, 0.3% and 0.5% kC concentrations, which are present in the above 10/90, 30/70 and 50/50 (w/w) mixed hydrogel samples. These kC hydrogels were used for syneresis, and rheological measurements as the reference samples. Hereafter, mixed gels prepared with 10% (w/w) kC and 90% (w/w) OSX or BX were named as kC/OSX_{90} and $kC/BX_{90,}$ similarly hydrogels prepared with 30/70 (w/w) and 50/50 (w/w) kC and xylan ratios, are named as kC/OSX_{70}, $kC/BX_{70,}$ kC/OSX_{50} and kC/BX_{50}, respectively. Analogous, the parent gels of 0.1%, 0.3% and 0.5% kC were called kC_{10}, kC_{30}, and $kC_{50.}$

2.3. Swelling ratio and weight loss measurements

The preweighed (0.1 g of each) hydrogel sample (W_1) were immersed in different pH solutions [e.g. pH 1.2 (adjusted using HCl) and pH 7.0 (distilled water)] (50 ml for each 0.1 g dry hydrogel sample) separately at room temperature (25 ± 1 °C). At certain times, the swollen gel samples were removed from swelling medium, quickly wiped dry to remove excess liquid on the surface, and weighted (W_2). The swelling ratio (%) was calculated using the following Eq. (1). Swelled hydrogels were dried after reaching at equilibrium swelling and weighted (W_3) for measuring the weight loss ratio (%) during soaking, using the following Eq. (2) (Meena et al., 2009). Total durations for the soaking were 4 and 7 h in the neutral and acidic pHs. Results are the mean and standard deviation of 3 replicates.

$$\text{Swellingratio}(\%) = (W_2 - W_1)\cdot 100/W_1 \tag{1}$$

$$\text{Wtlossratio}(\%) = (W_1 - W_3)\cdot 100/W_1 \tag{2}$$

2.4. Syneresis

The amount of exuded water from the parent and mixed hydrogel samples after standing for a certain period of time was determined and quantified using a modified method (Fiszman & Duran, 1992; Meena, Prasad, & Siddhanta, 2006). 10 g hot solution (in 1% KCl; 1.0 wt% concentration; pH = ca. 7.0; ca. 50 °C) of kC, kC/OSX_{50-90} and kC/BX_{50-90} was poured into test tubes (21 mm diameter), allowed to gel at room temperature (25 °C), and kept at 10 °C for 24 h. The initial weight of these gel samples was measured before placing them on dry Whatman filter papers at room temperature. The gel was weighed after 2 h and the weight loss due to water was calculated. The extent of syneresis was estimated by the amount of water (ΔW) separated from the gel phase after 2 h under ambient conditions.

2.5. Chemical analysis

Weight average molecular weight (Mw) was analysed by SEC in DMSO/H_2O/LiBr according to Saake, Kruse, and Puls (2001). The carbohydrate compositions of xylans were analysed according to Puls, Poutanen, Körner, and Viikari (1985) and the 4-O-MeGlcA by ^{1}H NMR (Varian Mercury 400 MHz) according to Saake, Russler, Lebioda, and Puls (2003). The Mw of kC was analysed by gel permeation chromatography (GPC; Waters Alliance 2695 machine with RI 2414 detector) in 0.1 M $NaNO_3$. The composition of kC was determined by GC–MS (Shimadzu GCMS-QP2010), using an SGE BP-225 capillary column and helium as carrier gas as reported previously (Mehta, Meena, Prasad, Ganesan, & Siddhanta, 2010; Siddhanta, Goswami, Ramavat, Mody, & Mair, 2001).

2.6. Preparation of sample for DSC measurement

Differential scanning calorimetry (DSC) measurements were carried out using DSC 821^e, Mettler Toledo, Switzerland. About 28 ± 1 mg of gel sample was sealed into the 40 μl DSC pan. For each sample, an empty 40 μl pan was used as a reference pan. The two pans were then placed inside the calorimeter, heated to 90 °C and kept for 1 min to annihilate the thermal history. Then the temperature was lowered to −10 °C at 5 °C/min and raised again at the same rate up to 90 °C. The experiments were repeated twice and the peaks for peak temperature of sol–gel ($T_{p,s-g}$) and peak temperature of gel–sol ($T_{p,g-s}$) transition were observed on the same positions. The difference in thermal hysteresis (ΔH) was also measured.

2.7. Dynamic rheological measurements

Shear thinning experiments were performed in a TA instruments AR2000 Rheometer (TA Instruments, 109 Lukens Drive, New Castle Delaware 19720, USA) using a cone-plate (diameter 4 cm, 52 μm) shear mode. Steady state flow and viscosity curves were determined in the range between 0 and 100 1/s. Rheological behavior of the sol–gel transition of the parent kC_{30-50}, kC/OSX_{50-90} and kC/BX_{50-90} mixed hydrogels were investigated by measuring the temperature dependence of the moduli at 0.05% strain. The hot sample solutions were loaded on to the pre-heated plate (ca. 90 °C) of the rheometer and allowed to equilibrate for 1 min. The rheometer was equipped with a solvent trap in order to minimize the water evaporation. Temperature dependence of storage (G′) and loss (G”) moduli as well as loss tangent (tan δ) were observed by cooling the system from 90 °C to 10 °C, and then reheating to 90 °C after 5 min equilibration time. The temperature gradient was 1.5 °C/min both on cooling and heating scan, while the frequency was 1.0 Hz and strain was 0.05%. For this measurement plate–plate geometry (40 mm diameter, 1000 μm gap) was used. The temperature of sol–gel (T_{s-g}) and temperature of gel–sol transition (T_{g-s}) were determined as described in the literature (Hsieh, Regenstein, & Rao, 1993; Meena et al., 2007; Norziah et al., 2006; Sarabia, Gomez-Guillen, & Montero, 2000).

The solution of the hydrogel samples was loaded on to the pre-heated rheometer plate at 90 °C, which was then rapidly quenched to 25 °C. After an equilibration time of 5 min at 25 °C the effect of oscillatory frequency on the dynamic rheological properties of the final gel obtained was determined. The mechanical spectra were characterized by G′ and G″ and complex viscosity as a function of frequency in the range of 0.0–20 Hz, using parallel plates (diameter = 4 cm, gap 1000 μm). The stress and time dependency of storage modulus (G′) were performed evaluating the linear viscoelastic regions (LVR) and firmness of kC hydrogels with and without xylan content, using parallel plates (diameter = 4 cm, gap 1000 μm) at 25 °C.

2.8. Scanning electron microscopy

For scanning electron microscopy (SEM), vacuum oven-dried samples were mounted on aluminum stubs covered with double-coated carbon conductive adhesive tabs. After sputter-coating with gold, the samples were examined with a field emission scanning electron microscope (Type FEI Quanta 250 FEG) under high vacuum at an accelerating voltage of 10 kV.

2.9. Statistical analyses

Data were evaluated using the analysis of variance (ANOVA) method. Results were considered statistically significant when $p < 0.05$. Calculations were performed using Origin Software, Version 6 (Microcal Software Inc., MA, USA).

3. Results and discussion

3.1. Physical properties

The effect of OSX and BX on the properties of the parent kC_{10-50} gels was first studied through syneresis measurements. The amount of exuded water from the reference kC gels were significantly greater than those of the mixed kC/OSX_{50-90} and kC/BX_{50-90} gels ($p < 0.05$), where the extent of syneresis is greater in kC/OSX_{50-90} compared to kC/BX_{50-90} gels. The syneresis was increased when increasing the amount of xylans in the mixed gels. For the kC reference gel samples the exuded water decreased with increasing the concentration of kC starting from 98 (±1%) (kC_{10}) over 72 (±1%) (kC_{30}) reduced to 56 (±1%) in kC_{50} hydrogel. In the mixed hydrogels, the greatest 82 (±1%) for kC/OSX_{90} and lowest 50 (±1%) for kC/BX_{50} and kC/BX_{70}, extents of the exuded water were obtained. kC/OSX_{50} and kC/OSX_{70} hydrogels exhibited intermediated performance with 60 (±1%) exuded water, while 69 (±1%) was obtained for kC/BX_{90} hydrogel. This result indicated that the xylans can replace kC in high proportions in order to produce stable blend hydrogel networks.

The results of swelling experiments of kC/OSX_{50-90} and kC/BX_{50-90} blend hydrogels in acidic (pH 1.2) and in neutral (pH 7.0) media are presented in Fig. 1a and b. The maximum duration of soaking was 7 h in pH 1.2 and 4 h in pH 7.0 solution. kC/OSX_{50-90} and kC/BX_{50-90} hydrogels attained equilibrium swelling faster in the pH 7.0 (1–2 h) solution than in pH 1.2 medium (3.5–6 h) (Fig. 1a and b). The mixed kC/OSX_{50} and kC/BX_{50} hydrogels showed greatest swelling ratio in acidic (13,500 ± 42%, 7600 ± 32%) and neutral media (8200 ± 25%, 5000 ± 25%). It is important to note that kC, OSX and BX dispersed rapidly (Meena, Prasad, Mehta, & Siddhanta, 2006) in above pH media, while the mixed kC/OSX_{50-70} and kC/BX_{50-70} hydrogels exhibited significantly greater swelling ($p < 0.05$) in above pH media and were almost steady up to total

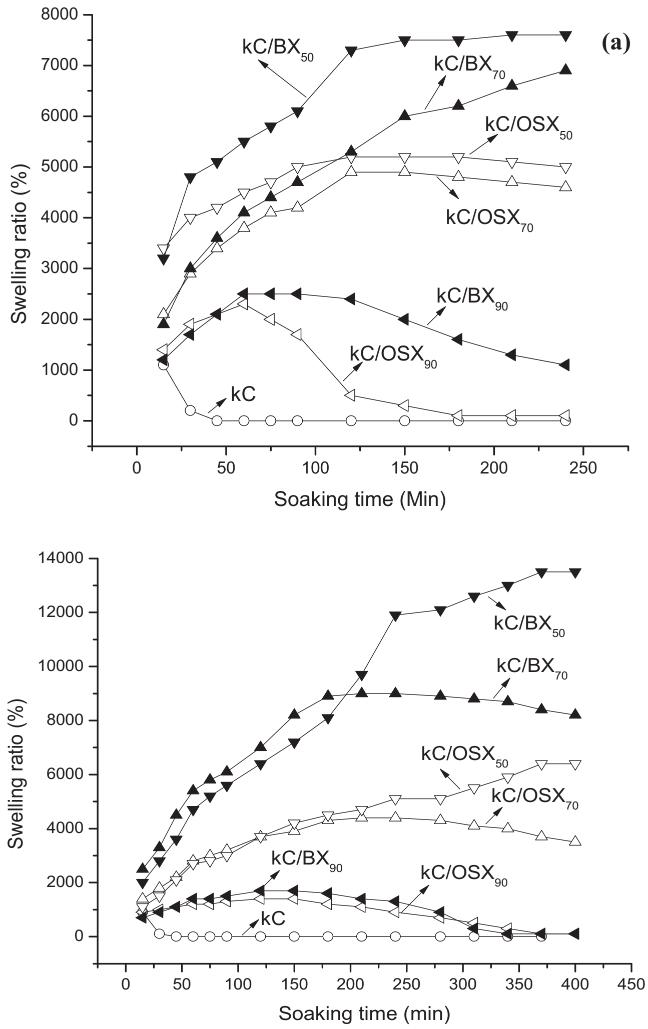

Fig. 1. Swelling ability of the parent kC, kC/OSX$_{50–90}$ and kC/BX$_{50–90}$ hydrogel samples (a) in pH 7.0 and (b) in pH 1.2.

soaking time studied herein (Fig. 1a and b). kC/OSX$_{50–90}$ hydrogels attained equilibrium swelling already between 1 and 2 h, while those of kC/BX$_{50–90}$, exhibited slower swelling and attained equilibrium between 3.5 and 6 h in the swelling media studied herein (Fig. 1a and b). The steady swelling ability of the mixed kC/OSX$_{50–70}$ and kC/BX$_{50–70}$ hydrogel samples indicated negligible mass losses with soaking time in the different media. Improved swelling of most mixed samples compared to the kC might be explained on the basis of network stability due to the formation of an interpenetrating network of both polymers. The slower swelling ability and lower syneresis of kC/BX$_{50–90}$ hydrogels could be explained on the basis of the surface morphology, as kC/OSX formed porous structures and kC/BX formed a more compact product (SEM). This may be the results of different molecular arrangement during the gel network formation as expected from the different structural features of OSX and BX (Ebringerova, 2006). They indicated a more stable gel network formation in kC/BX$_{50–90}$ compared to kC/OSX$_{50–90}$ may be due to different porosities and binding abilities of OSX and BX. Further, stability and swelling ability of these xylans may be the results of chemical heterogeneity, as BX has smaller molar mass and higher amounts of 4-O-MeGclA (9.4 mol%, NMR). Especially the 4-O-MeGlcA might favor the formation of a strong gel network by improved interaction through more stable hydrogen bonding in the kC/BX hydrogel, as well as this may be due to the electrostatic interaction between potassium ion and carboxyl ions of BX. These results are in good agreement with the previous report that interaction and gel forming properties of xylans mainly depend on the structural features (Ebringerova, 2006). It can be suggested that the increased stability of kC/BX hydrogels might be due to the hydrogen bonding between carboxyl groups in BX and hydroxyl groups in carrageenan, analogous to the literature reports on the interaction of gelatin and carrageenan mixed gels (Kobayashi & Nakahama, 1986).

The moisture content of the parent kC was 12.4 (±0.2) and increased when mixed with OSX or BX. The greatest moisture content was obtained for kC/BX$_{50–90}$ hydrogel samples indicating greater association property of BX with water. The moisture content in mixed kC/OSX$_{50–90}$ and kC/BX$_{50–90}$ was increased when the xylan contents were reduced. Accordingly the minimum 16.3 (±0.2) and maximum 19.2 (±0.2) moisture contents were obtained in the kC/OSX$_{90}$ and kC/BX$_{50}$ hydrogels. The moisture contents of kC/OSX$_{50}$ and kC/OSX$_{70}$ were 16.7 (±0.2%) and 17.3 (±0.2%), while kC/BX$_{70}$ and kC/BX$_{90}$ exhibited 18.4 (±0.2%) and 18.0 (±0.2%), respectively. This difference might be explained on the basis of the greater hydrophilicity of BX, as a result of carboxyl functional groups in the form of 4-O-MeGlcA. This moiety might result in improved hydrogen bonding with hydroxyl group of water as well as with hydroxyl groups of carrageenan. The observation regarding the syneresis for kC/BX$_{50–90}$ hydrogels is in accordance with this hypothesis.

3.2. DSC studies

Fig. 2a,a′–c,c′ shows cooling and heating DSC curves of parent kC with and without OSX and BX of various ratios. Cooling and heating rate was chosen as 5 °C/min in all experiments. The cooling and heating curves for parent kC with and without xylans showed always a single exothermic peak and a single endothermic peak at different temperatures. The temperature of the endothermic peak in the heating DSC and the temperature of the exothermic peak in the cooling DSC curve will be called peak temperature of gel–sol ($T_{\mathrm{p,g–s}}$) and peak temperature of sol–gel transition ($T_{\mathrm{p,s–g}}$). Generally, peak temperature of sol–gel ($T_{\mathrm{p,s–g}}$) and peak temperature of gel–sol transition ($T_{\mathrm{p,g–s}}$) shifted towards the lower temperatures for kC/OSX$_{50–90}$ hydrogels, while they shifted towards the higher temperatures in kC/BX$_{50–90}$ hydrogels (Fig. 2). The greatest (61 °C) and lowest (44.5 °C) $T_{\mathrm{p,s–g}}$ were observed in kC/BX$_{50}$ and kC/OSX$_{90}$, respectively. Analogous, the greatest (82.9 °C) and lowest (64 °C) $T_{\mathrm{p,g–s}}$ temperatures were also observed in kC/BX$_{50}$ and kC/OSX$_{90}$ hydrogels, respectively. Fig. 2 shows that the $T_{\mathrm{p,g–s}}$ of the parent kC was 73.5 °C. In this study, variations in $T_{\mathrm{p,g–s}}$ value of kC in the mixture were considered as a measure of mixture compatibility. Similar findings have been described for chitosan/PVA blend hydrogels by Kumar et al. (2010).

From the cooling curve, it is clear that the trend of decreasing and increasing $T_{\mathrm{p,s–g}}$ was similar to that of $T_{\mathrm{p,g–s}}$ in the hydrogels (Fig. 2). The $T_{\mathrm{p,s–g}}$ of the parent kC was 55 °C. Significant decrease in $T_{\mathrm{p,s–g}}$ from 55 °C to 44.5 °C and significant increase from 55 °C to 61 °C were observed in kC/OSX$_{90}$ and kC/BX$_{50}$ hydrogel samples, respectively (Table 1). The maximum decrease in $T_{\mathrm{p,s–g}}$ of kC gel was observed in kC/OSX$_{90}$ (10.5 °C), and the greatest increase in $T_{\mathrm{p,s–g}}$ was observed in kC/BX$_{50}$ hydrogel (6.0 °C) (Table 1). Similarly, the greatest decrease in $T_{\mathrm{p,g–s}}$ of parent kC gel (9.5 °C) was observed in kC/OSX$_{90}$ and the greatest increase in $T_{\mathrm{p,g–s}}$ was observed in kC/BX50 hydrogel (9.4 °C) (Table 1). The thermal hysteresis of the parent kC gel was improved with all ratios of OSX and BX (Table 1). The thermal hysteresis is defined as $\Delta T = T_{\mathrm{p,g–s}} - T_{\mathrm{p,s–g}}$. For the parent kC gel ΔT amounted to 18.5 °C (Table 1). For the mixed hydrogels ΔT was obtained between 19.5–23.3 °C in kC/OSX$_{50–90}$ and 18.8–21.9 °C in kC/BX$_{50–90}$ hydrogels (Table 1). The maximum and minimum enhancement in the thermal hysteresis was obtained

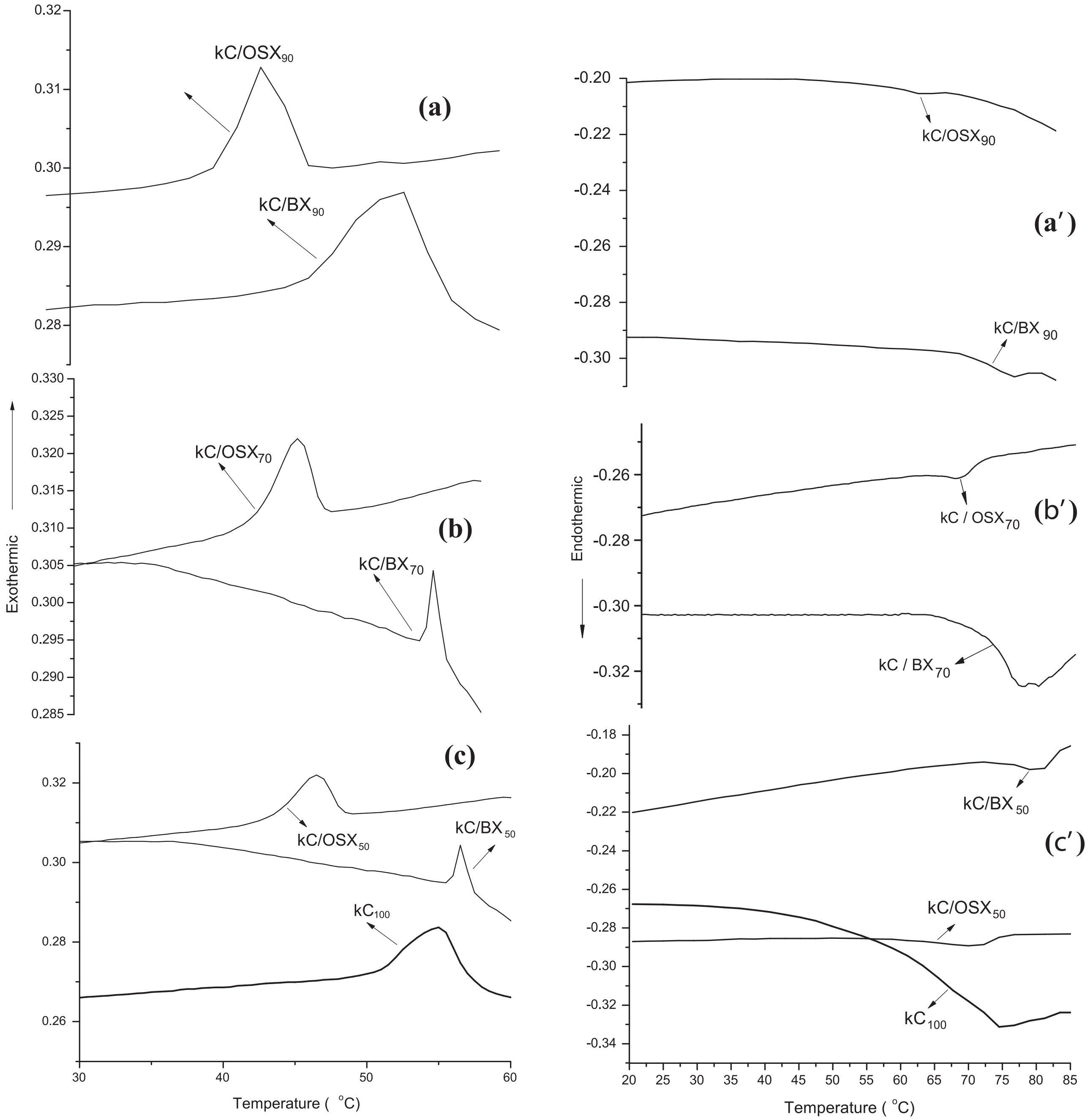

Fig. 2. Cooling and heating DSC curves of (a,a′) kC/OSXorBX$_{90}$, (b,b′) kC/OSXorBX$_{70}$, and (c,c′) kC/OSXorBX$_{50}$ hydrogel samples.

Table 1
Effect of oat (OSX) and beech (BX) xylan on the peak temperature of sol–gel ($T_{p,s-g}$) and gel–sol ($T_{p,g-s}$) transition, as well as extent of thermal hysteresis (ΔH) of *kappa*-carrageenan (kC).

Systems	$T_{p,s-g}$ (in °C)	$T_{p,g-s}$ (in °C)	ΔH (in °C)	Effect of xylan on $T_{p,s-g}$ (in °C)	Effect of xylan on $T_{p,g-s}$ (in °C)	Effect of xylan on ΔH (in °C)
kC	55.0	73.5	18.5	–	–	–
kC/OSX$_{90}$	44.5	64.0	19.5	−(10.5)	−(9.5)	+(1.0)
kC/OSX$_{70}$	46.5	69.5	23.0	−(8.5)	−(4.0)	+(4.5)
kC/OSX$_{50}$	50.0	73.3	23.3	−(5.0)	−(0.2)	+(4.8)
kC/BX$_{90}$	55.9	74.7	18.8	+(0.9)	+(1.2)	+(0.3)
kC/BX$_{70}$	57.1	76.8	19.7	+(2.1)	+(3.3)	+(1.2)
kC/BX$_{50}$	61.0	82.9	21.9	+(6.0)	+(9.4)	+(3.4)

$T_{p,s-g} = (T_{p,s-g-kC} - T_{p,s-g-kC/OSXorBX})$; $T_{p,g-s} = (T_{p,g-s-kC} - T_{p,g-s-kC/OSXorBX})$; $\Delta H = (\Delta H_{kC} - \Delta H_{kC/OSXorBX})$

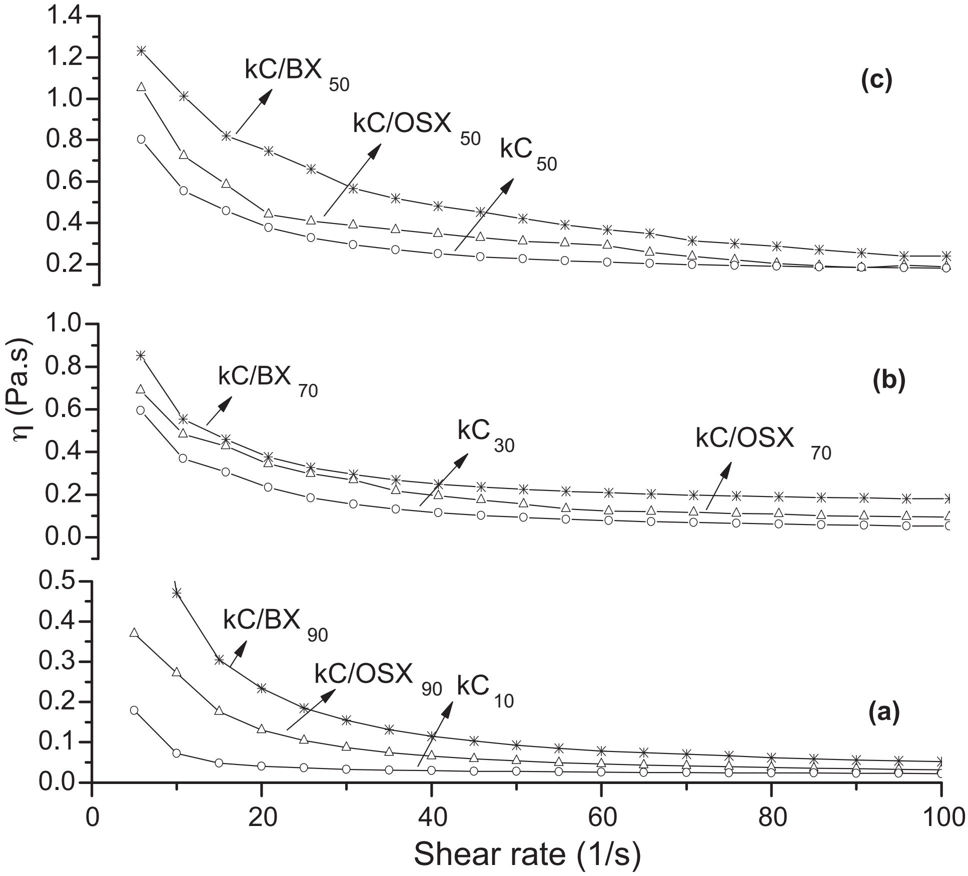

Fig. 3. Flow curves of (a) kC/OSXorBX$_{90}$, (b) kC/OSXorBX$_{70}$, and (c) kC/OSXorBX$_{50}$ hydrogel samples*. *kC$_{10}$, kC$_{30}$, and kC$_{50}$ represented 0.1, 0.3 and 0.5% kC gels in 1% KCl solution without xylans, using as the reference hydrogel samples.

in kC/OSX$_{50}$ (4.8 °C) and kC/OSX$_{90}$ (1.0 °C) hydrogel, respectively (Table 1). Further, these finding in the mixed hydrogel samples revealed interaction, compatibility and formation of mixed network (Kumar et al., 2010). The decrease of $T_{\mathrm{p,s-g}}$ and $T_{\mathrm{p,g-s}}$ in kC/OSX hydrogels, suggests, that the structure of kC gels became less thermally stable with OSX. This may be due to the increase of rotational freedom by the addition of OSX (Watase, Kohyama, & Nishinari, 1992). The decreases and increases in the gelling temperatures on the addition of OSX and BX xylans could also be explained on the basis of the required energy for the gelation process. This indicates that lower values are need for kC/OSX gel formation compared to those of kC/BX hydrogels. Similar observations have been described by Medina-Torres, Brito-De La Fuente, Gomez-Aldapa, Aragon-Pina, and Toro-Vazquez (2006). The effect of xylans on the gelling and melting points could be explained by their structural features. The large molar mass and neutral arabinose unit of OSX will disfavor the formation of more junction zones and hydrogen bonding, while the 4-O-methyl-glucuronic acid content of BX might result in interaction of higher bonding energy. Analogous results have been reported for agarose and *kappa*-carrageenan mixed gels (Watase et al., 1992). This will be further discussed for the gelation results.

3.3. Rheological studies

3.3.1. Flow properties

The gelling properties of the parent kC, kC/OSX$_{50–90}$, and kC/BX$_{50–90}$ hydrogels were first studied through flow experiment using shear rate from 0 to 100 s^{-1} (Fig. 3a–c). The flow curves of the parent kC, kC/OSX$_{50–90}$ and kC/BX$_{50–90}$ obtained at 25 °C, are characteristic for shear thinning or pseudoplastic liquids. The shear thinning of kC was decreased when mixed with OSX and BX. This decrease was greater in presence of BX for all mixing ratios (Fig. 3a–c). The parent kC, kC/OSX$_{50–90}$, and kC/BX$_{50–90}$ hydrogels showed shear thinning behavior under the applied shear rate, as viscosity was decreased with increasing the shear rate (Fig. 3a–c). Similar results have been reported in the previous studies on the mixtures of different agars in the presence of sugars (Meena, Prasad, & Siddhanta, 2006).

3.3.2. Viscoelastic properties

The frequency dependence of moduli (G′ and G″) and viscosity provides information about weak or strong structure of the hydrogel samples, which was fashioned when mixing kC with OSX and BX. The spectra of parent kC$_{10–50}$ (e.g. 0.1, 0.3, and 0.5% gels), kC/OSX$_{50–90}$ and kC/BX$_{50–90}$ hydrogel samples are depicted in Fig. 4a–c. The parent kC$_{10}$ sol exhibits a liquid like behavior, as the G′ and G″ has greater dependency of frequency (Fig. 4a) and viscosity values remains almost independent of frequency (Fig. 4a′). kC$_{30}$ sol showed solid like behavior, as the storage modulus (G′) and the loss modulus were slightly frequency dependent (Fig. 4b), while the viscosity of the gel was decreased with increasing the frequency (Fig. 4b′). kC$_{50}$ exhibit a strong gel behavior, as G′ and G″ remained almost independent of frequency (Fig. 4c), while a significant decrease in viscosity occurred under the applied frequency (Fig. 4c′).

Similarly, kC/OSX$_{50–90}$ and kC/BX$_{50–90}$ hydrogels showed weak to strong (true) gels like behavior, with improved values of moduli (Fig. 4a–c). The values of G′ and G″, and viscosity were significantly greater for kC/OSX$_{50–90}$ and kC/BX$_{50–90}$ than those of the

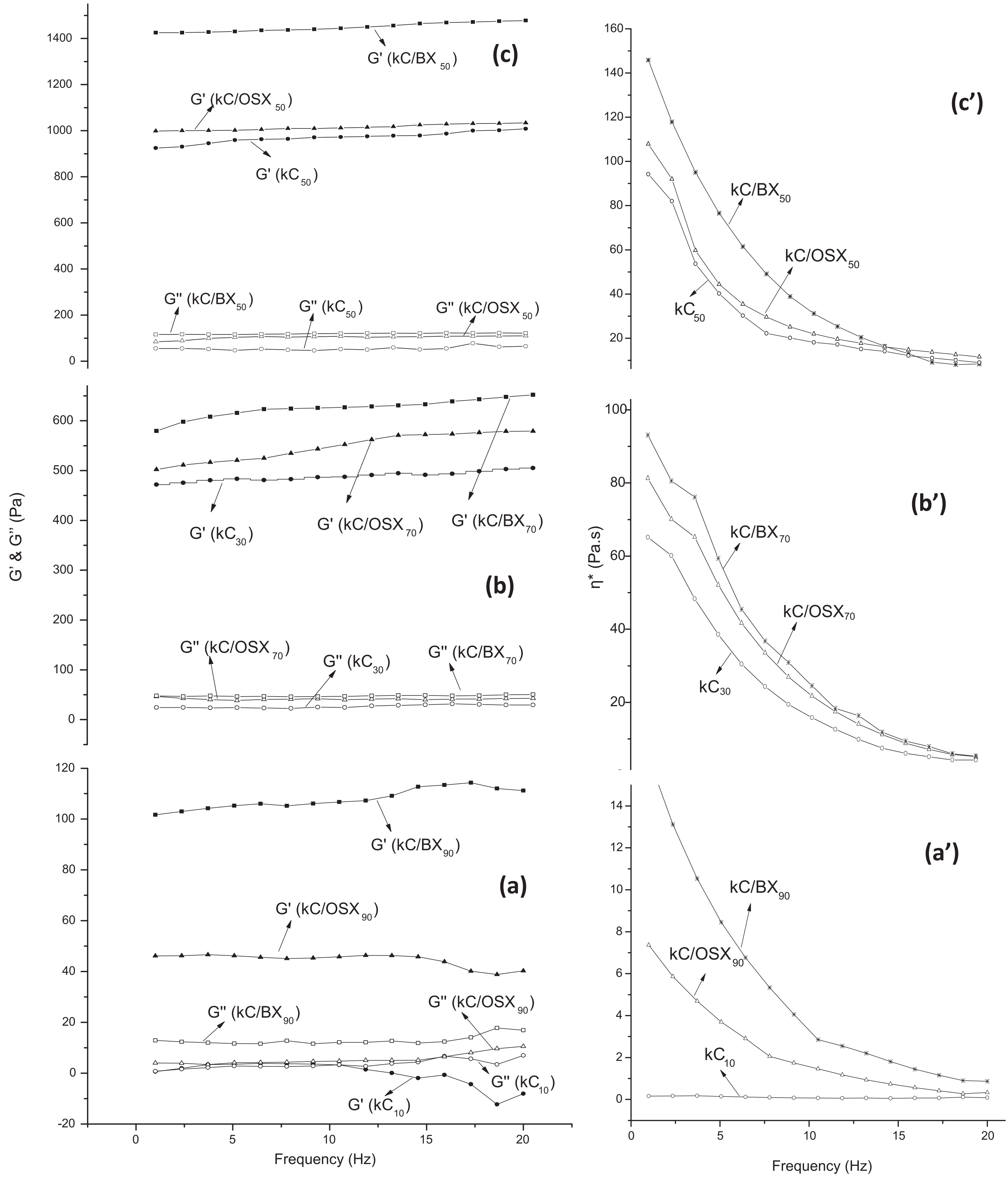

Fig. 4. Frequency dependence of moduli (G′ and G″) and viscosity of (a,a′) kC/OSXorBX$_{90}$, (b,b′) kC/OSXorBX$_{70}$, and (c,c′) kC/OSXorBX$_{50}$ hydrogel samples*. *kC$_{10}$, kC$_{30}$, and kC$_{50}$ represented 0.1, 0.3 and 0.5% kC gels in 1% KCl solution without xylans, using as the reference hydrogel samples.

respective parent kC gel samples over the applied frequency ranges from 0.0 to 20.0 Hz. Further, the moduli (G′ and G″) and the viscosity were significantly greater for kC/BX$_{50–90}$ compared to kC/OSX$_{50–90}$ hydrogels (Fig. 4a,a′–c,c′). This result revealed that more elastic and ordered structures were formed in kC/BX$_{50–90}$ than in kC/OSX$_{50–90}$ hydrogels (Khondkar, Tester, Hudson, Karkalas, & Morrow, 2007). These significant variations in the values of moduli and viscosity could be explained by the different structural features, self-association capacity and molecular size of the two xylans (Turquois & Doublier, 1994).

This study revealed that a very dilute solution of kC$_{10}$ with 90% (w/w) OSX or BX would yield a gel like network. Similar results have been reported for carrageenan and galactomannan (Khondkar et al., 2007). The greater overall independence or dependence of moduli on the frequency revealed the more viscoelastic or fluid like characteristics of the parent kC$_{10}$, kC/OSX$_{90}$ and kC/BX$_{90}$ hydrogels. It is also suggested that xylan requires only the presence of a very low content of kC in order to produce hydrogels, which may have some specific applications in the areas of digestive and non-digestive products and bio-medical application (Tanodekaew, Channasanon, & Uppanan, 2006).

The mechanical spectra of kC/OSX$_{70-90}$ and kC/BX$_{70-90}$ hydrogel samples is typical for solid-like or strong gel structures (Clark & Ross-Murphy, 1987; Khondkar et al., 2007), where G′ is greater than G″ throughout the measured frequency range and G′ remains almost independent of frequency (Fig. 4b and c). Further, viscosity of these hydrogel samples was decreased significantly with frequency also indicating the formation of strong hydrogel networks. For kC/OSX$_{50-90}$ hydrogels, the values of moduli were significantly lower than those of kC/BX$_{50-90}$ hydrogel samples, indicating that under the same experimental conditions OSX developed a weaker network or less number of junction zones with kC than BX. The results revealed that the elastic component of all kC gels increased by mixing with OSX and BX. This increase was significantly greater with BX compared to OSX. Amongst all the kC/OSX and kC/BX ratios used, the kC/OSX$_{50}$ and kC/BX$_{50}$ showed relatively high G′ and G″ demonstrating the greatest degree of elasticity and structural integrity, as well as more ordered structures. Similar results have been reported by Yoneya, Ishibashi, Hironaka, and Yamamoto (2003) for cross-linked potato starch. These observations suggest that kC and xylans are forming more ordered structures in the gel networks. Khondkar et al. (2007) have reported similar results in starch and pectin mixed gels.

3.3.3. *Linear viscoelastic region (LVR) and firmness*

The native kC, kC/OSX$_{50-90}$ and kC/BX$_{50-90}$ hydrogel samples were subjected to dynamic oscillation stress ramping tests (Fig. 5a–c). The stress range over which G′ is independent of the applied stress is called the linear viscoelastic (LVR) region. The end point of LVR is named as critical stress. At this point the structure of the material was disturbed as a result of the mechanical stress (Fig. 5a–c). As shown in the graph, the LVR of parent kC was increased on addition of OSX and BX. At each mixing ratio kC/BX$_{50-90}$ hydrogel samples exhibited the longer LVR range and significantly greater G′ values compared to the respective kC/OSX$_{50-90}$ samples. This revealed more elastic and stronger hydrogel formation with BX. kC/OSX$_{50-90}$ hydrogel samples exhibited a weaker structure (↓G′) at each mixing ratio, resulting in a shortened LVR and a lower critical stress (Fig. 5a–c). Rudraraju and Wyandt (2005) have reported similar data for microcrystalline cellulose and sodium carboxymethyl cellulose hydrogels.

The time dependence of the storage modulus (G′) for kC$_{10-50}$ hydrogels with and without OSX and BX are depicted in Fig. 5a′–c′. Again it is apparent that the G′ value of kC gel was significantly increased by both xylans in all mixing ratios. kC/BX$_{50-90}$ hydrogel samples exhibited significantly greater G′ values in the time series than the respective kC/OSX$_{50-90}$ hydrogels (Fig. 5a′–c′). The time dependence of G′ also confirms that the network formation of kC/BX$_{50-90}$ hydrogels is more rigid than those of kC/OSX$_{50-90}$ samples. The greater G′ values of kC/BX hydrogels indicated a greater firmness of these hydrogels. Beech xylan due to its low molecular weight might have a more flexible molecular geometry and could be favorably accommodated in the kC gel network, resulting in increased hydrogen bonding and increased number of junction zones (Meena, Prasad, & Siddhanta, 2006; Rees, 1969).

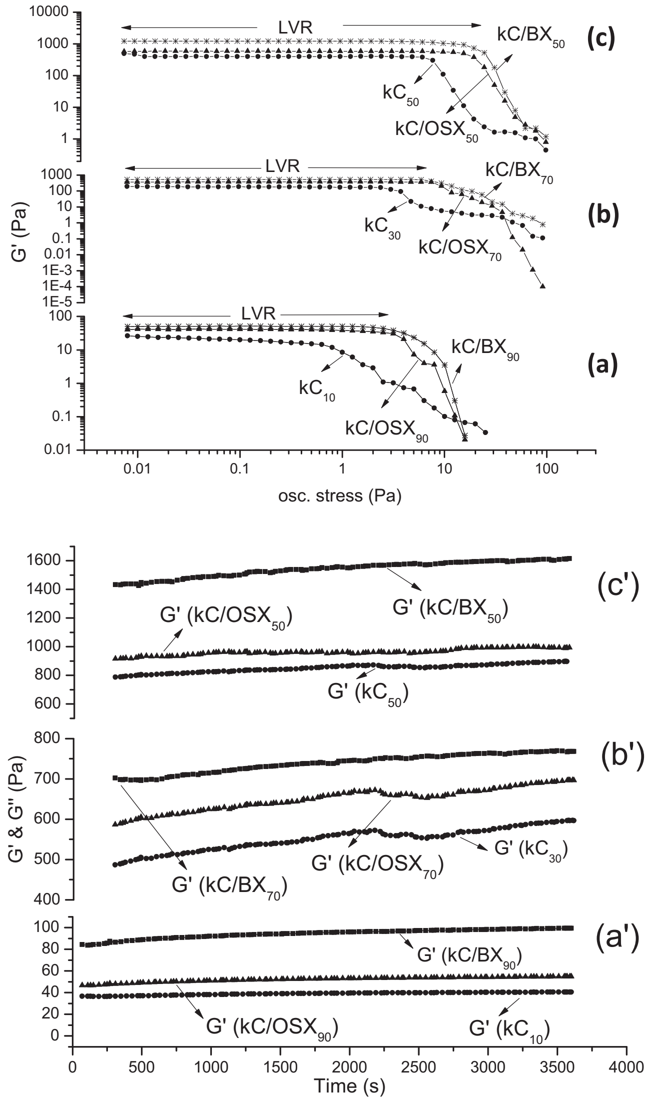

Fig. 5. Stress and time dependence of storage (G′) modulus of (a,a′) kC/OSXorBX$_{90}$, (b,b′) kC/OSXorBX$_{70}$, and (c,c′) kC/OSXorBX$_{50}$ hydrogel samples*. *kC$_{10}$, kC$_{30}$, and kC$_{50}$ represented 0.1, 0.3 and 0.5% kC gels in 1% KCl solution without xylans, using as the reference hydrogel samples.

3.3.4. *Gelation studies*

Fig. 6a,a′–c,c′ shows the gelation of the parent kC, kC/OSX$_{50-90}$ and kC/BX$_{50-90}$ hydrogel samples. The viscoelastic experiments of parent kC$_{30\text{ and }50}$ (e.g. 0.3 and 0.5%, w/w) and the mixed kC/OSX$_{50-90}$ and kC/BX$_{50-90}$ hydrogels were carried out using a constant polysaccharide concentration of 1.0%. Temperature dependence of moduli (G′ and G″) during cooling from 90 to 10 °C of kC/OSX$_{50-90}$ and kC/BX$_{50-90}$ mixtures and of the parent kC$_{30\text{ and }50}$ is depicted in Fig. 6. The viscoelastic measurements on all hydrogel samples showed a maximum in the storage (G′) modulus and loss (G″) modulus as temperature was decreased from 90 °C to 10 °C. The beginning of the aggregation is indicated by the increase in G′ and G″ and the decrease of the phase angle δ. This phenomenon occurred at ca. 56 °C in the parent kC$_{30\text{ and }50}$ hydrogel samples. The greatest (ca. 58 °C) and lowest (ca. 45 °C) gelling temperatures were observed in rheological measurements for kC/BX$_{50}$ and kC/OSX$_{90}$ hydrogel samples, respectively. The trends of increase or decrease in the gelling temperatures with BX and OSX addition are in good agreement with those observed by DSC experiments (Fig. 2a–c). A maximum in G′, during the cooling curve of the parent kC$_{50}$ hydrogel sample was observed. Similar

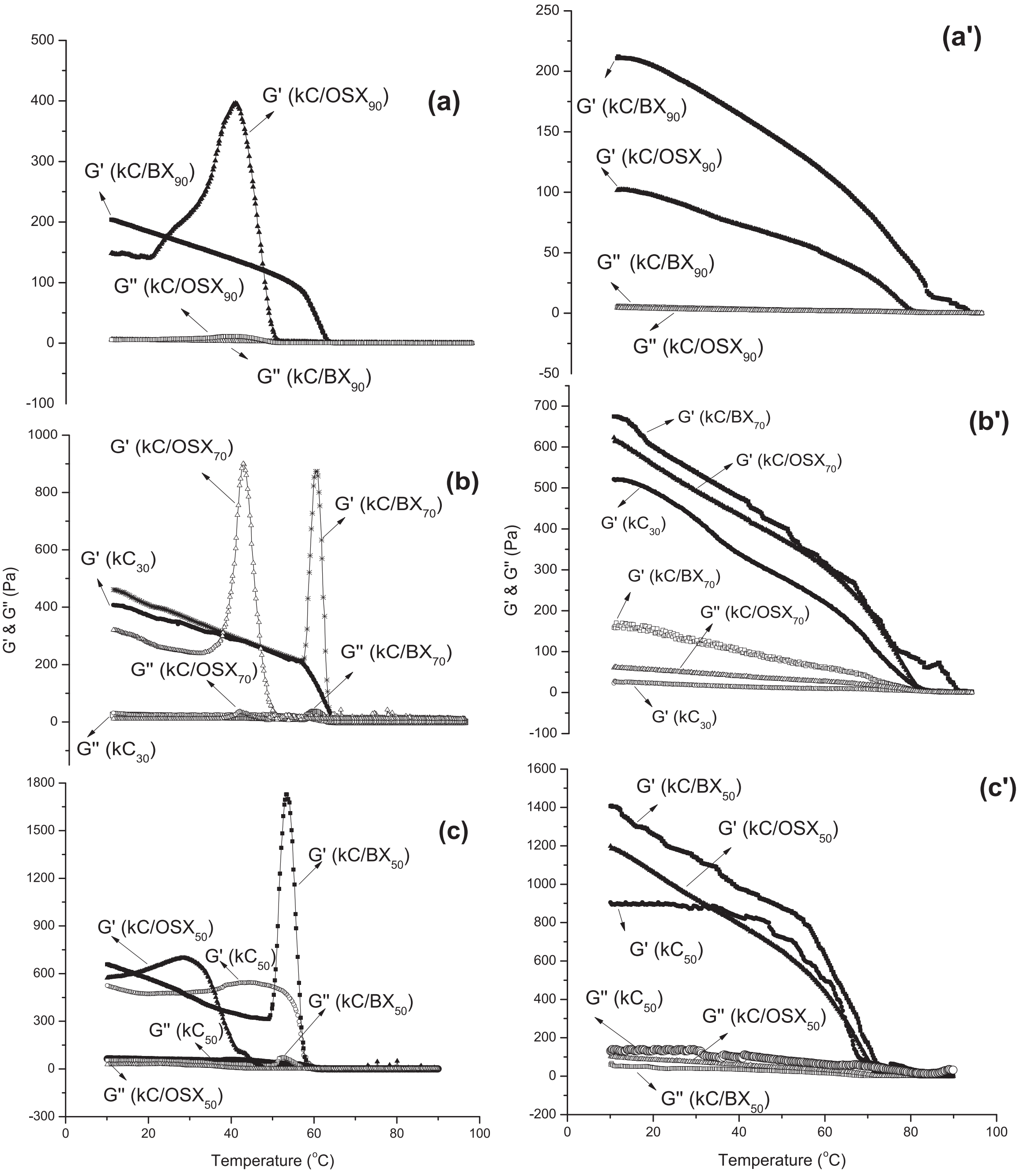

Fig. 6. Temperature dependence of moduli (G′ and G″) of (a,a′) kC/OSXorBX$_{90}$, (b,b′) kC/OSXorBX$_{70}$, and (c,c′) kC/OSXorBX$_{50}$ hydrogel samples*#. *kC$_{30}$ and kC$_{50}$ represented 0.3 and 0.5% kC gels in 1% KCl solution without xylans, using as the reference hydrogel samples. #Data of 0.1% kC solution was not given in this experiment.

trend in G′ maximum at various temperatures were also obtained in the hydrogel samples of kC/OSX$_{50–90}$ and kC/BX$_{50\text{ and }70}$. However, kC/BX$_{90}$ does not exhibit such maximum during the cooling study (Fig. 6a). Similar observation, during the sol–gel transition of κ-carrageenan and mixed gels of carrageenan has been reported (Hermansson, 1989; Hermansson, Ericksson, & Jordansson, 1991; Stading & Hermansson, 1993). This could be explained on the basis of the formation of transient state, consisting of a fine network structure (Ould Eleya & Turgeon, 2000). The further decrease in G′ after the peak value could also be explained on the basis of partial breakdown of this transient structure and the formation of coarse supermolecular network during the gelation of kC$_{50}$ and other mixed hydrogel samples studied herein (Hermansson, 1989; Ould Eleya & Turgeon, 2000). Hydrogels kC$_{50}$, kC/OSX$_{50–90}$ and kC/BX$_{50\text{ and }70}$ exhibited this characteristic, while kC$_{30}$ and kC/BX$_{90}$ did not (Fig. 6). Similar results have been reported for potassium dominant form of *kappa*-carrageenan, but this is not possible in the all commercially available carrageenans (Ould Eleya & Turgeon, 2000).

The effect of subsequent heating up to 90 °C on the parent and mixed hydrogels has been depicted in Fig. 6a,a′–c,c′. The results of the heating and cooling study exhibited that the parent kC and mixed hydrogels formed thermoreversible gels. On heating, only a single thermal transition was obtained in the parent kC and all mixed hydrogel samples. Fig. 6 shows that on the heating the significant decrease in G′ was obtained and led to complete meltdown of the parent kC$_{30\text{ and }50}$ networks at about 75 °C, as cooling induced gel formation, at about 55 °C. This indicates hysteresis in the rheological measurements between the heating and cooling curves (Hermansson et al., 1991; Kohyama, Sano, & Nishinari, 1996;

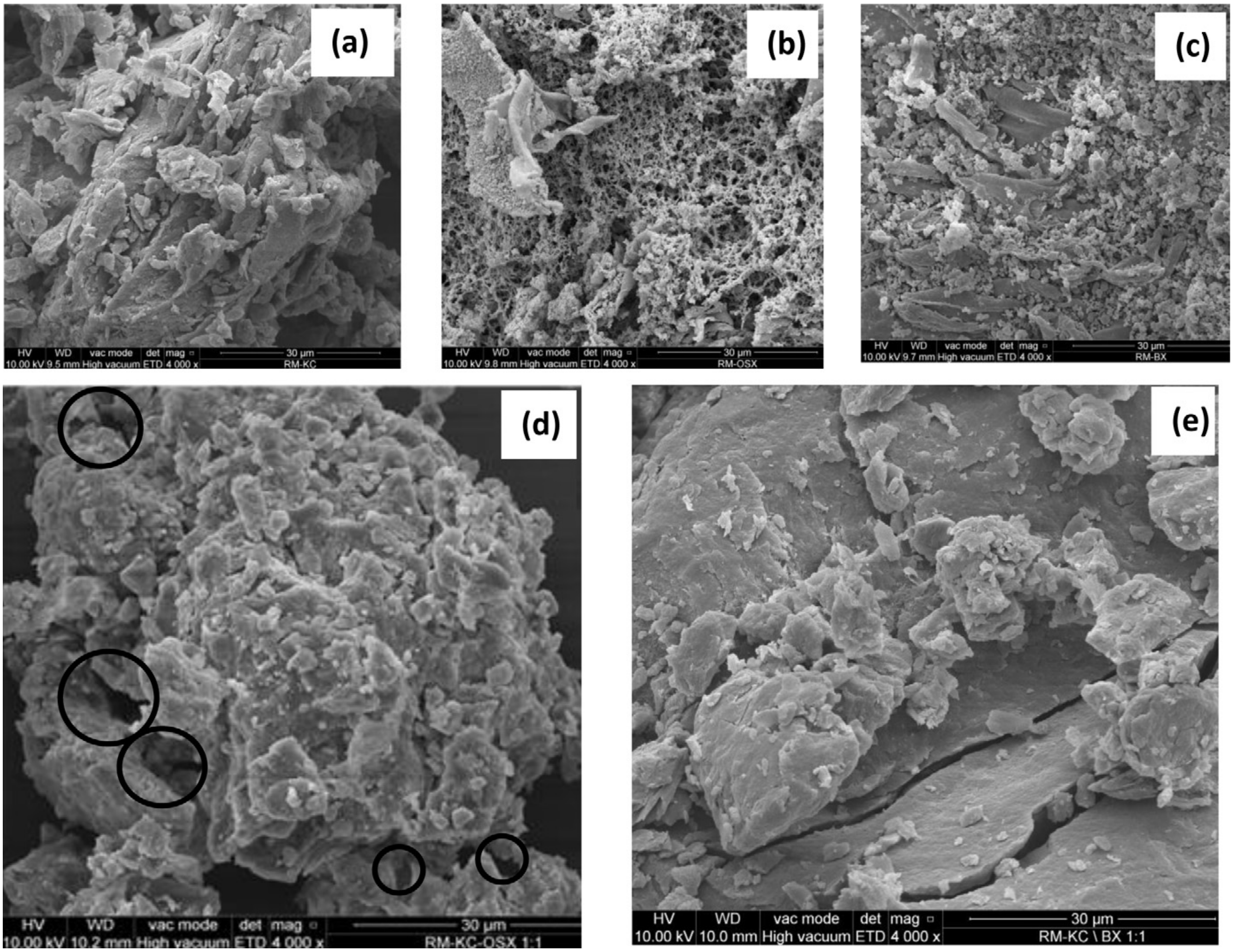

Fig. 7. SEM images of (a) kC, (b) OSX, (c) BX, (d) kC/OSX$_{50}$, and (e) kC/BX$_{50}$ hydrogel samples.

Rochas & Rinaudo, 1980). A maximum of G′ was only observed during the cooling, but not on the heating of the hydrogels. This result was in good agreement with the previous report (Hermansson, 1989). Further, there was a significant change in the melting temperatures of the parent kC, when mixed with different xylans. The melting temperature of the parent kC was increased in the kC/BX$_{50–90}$ hydrogels but decreased significantly in kC/OSX$_{50–90}$ hydrogels (Fig. 6).

The greatest and lowest melting temperatures about 81 °C and 64 °C were obtained in kC/BX$_{50}$ and kC/OSX$_{90}$ hydrogel samples, respectively, and are in good agreement with that of DSC results (Fig. 2). The effect of xylans on the gelling and melting points could be explained on the basis of their structural features. OSX has a larger molar mass and the neutral arabinose side groups which may disfavor the formation of junction zone and the number of hydrogen bonds (Yoshimura & Nishinari, 1999). This effect tends to delay the development of gel structures during the cooling curve through interhelical association in the kC/OSX hydrogel samples (Ould Eleya & Turgeon, 2000), but may be needs lower temperatures to meltdown completely during the heating (Fig. 6). Further, variations in the gelling and melting temperatures can also be explained on the basis of Zipper model approach. By this model, the appearance of different gelation points in the mixed kC/OSX$_{50–90}$ and kC/BX$_{50–90}$ hydrogels suggests that the zippers with different bonding energies or different rotational freedoms may be formed in the mixtures of kC and xylans. The lower melting temperatures for kC/OSX$_{50–90}$ hydrogels may be the result of the formation of zippers with lower bonding energies or higher rotational freedom. Correspondingly the higher melting values in kC/BX$_{50–90}$ hydrogels might indicate zippers with higher bonding energies or lower rotational freedoms most likely as a result of the higher uronic acid content (Norziah et al., 2006).

3.4. Surface morphology

The scanning electron micrographs (SEM images) of the parent kC, OSX and BX, as well as the mixed kC/OSX$_{50}$ and kC/BX$_{50}$ hydrogels are depicted in Fig. 7a–e. The morphology of kC appears fibrous and particulate (Fig. 7a), while the morphology of OSX is porous, and BX is a mixture of particulate and cloudy structures (Fig. 7b and c). The SEM images indicated significant changes on the surface morphology of kC when blended with OSX or BX. The kC/OSX$_{50}$ blend exhibited a more porous structure of the particles. Some of the pores have been denoted with circles in Fig. 7d. This may be the results of different molecular arrangement during the gel network formation as expected from the different structural features and morphologies of OSX and BX. In contrast to that kC/BX$_{50}$ exhibited a more solid structure (Fig. 7e). The finding on surface morphology could be related to the observation of faster swelling and greater syneresis as well as stability of kC/OSX$_{50–90}$ hydrogels. SEM images of the other mixed products were as well recorded and exhibited identical structural patterns (data not shown).

4. Conclusion

This work presented novel results on the interactions between *kappa*-carrageenan (kC) and either oat spelt (OSX) or beech (BX) xylan. Result of SEM and DSC indicated that OSX and BX might be used in order to introduce a more porous structure and higher thermal stability into the parent kC gels, respectively. The mechanical properties of these mixed gels showed significantly improved properties compared to kC. Mixed kC/OSX or kC/BX gels were strong and elastic. Results of this study, suggested that the effect of xylans on the gelling properties of kC depends on structural diversity of xylans. The interaction between kC and OSX is weaker than that between kC and BX, but strong enough to produce elastic and stable hydrogels. Results of syneresis, swelling and moisture measurements indicated strong binding and association tendencies of the BX. Consequently the resulting kC/BX$_{50-90}$ hydrogel samples exhibited the greatest water retention, swelling capacity, and water content for a given xylan ratio. In kC/BX mixtures, the more ordered structure may be formed by BX, resulting in a significant increase in the elastic properties of the parent kC. These results suggest that we can tailor gel structures or textures by mixing the gelling kC polymer with the non-gelling OSX or BX in adequate concentrations and ratios. In kC/OSX$_{50-90}$ and kC/BX$_{50-90}$ hydrogel samples, the thermo-reversible hysteresis was slightly increased compared to the parent kC hydrogel (DSC and Rheology). The blends of kC with OSX or BX produced a stable hydrogel network assembly, resulting in remarkable swelling capacity and solution stability in wide range of pH. This property can be utilized in specific food applications as well as other fields which demand pH-resistance.

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