Available online at www.sciencedirect.com

ScienceDirect

Carbohydrate Polymers 67 (2007) 586–595

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Viscoelastic properties of dispersed chitosan/xanthan hydrogels

A. Martínez-Ruvalcaba [a,*], E. Chornet [b], D. Rodrigue [c]

[a] Departamento de Ingeniería Química, Universidad de Guadalajara, Guadalajara, Jalisco 44430, Mexico
[b] Department of Chemical Engineering, Université de Sherbrooke Sherbrooke, Que., Canada J1K 2R1
[c] Department of Chemical Engineering, Université Laval Québec, Que., Canada G1K 7P4

Received 13 February 2006; accepted 28 June 2006
Available online 17 August 2006

Abstract

In this work a gel was formed by complexation of two natural polyelectrolytes, chitosan and xanthan. Changes in the hydrogels rheological properties have been studied in terms of hydrogel concentration (7–10% w/w), chemical media used for the hydrogel dispersion, and 'test lag time'; i.e., the time between hydrogel dispersion in the chemical media and the start of the rheological test (up to 390 min). The viscoelastic properties of this polysaccharide system were characterized by oscillatory shear measurements under small-deformation conditions and the results show that chitosan/xanthan hydrogels behave like weak gels. The shear modulus increased almost linearly with frequency in the range studied (0.1–65 s^{-1}). The effects of hydrogel concentration and dispersion medium have been related to electrostatic equilibrium and by the presence of counter-ions modifying the internal structure of the hydrogel.

Keywords: Chitosan; Xanthan; Rheology of hydrogels

1. Introduction

1.1. Chitosan–xanthan hydrogel formation

Chitosan is a linear polyether of high molecular weight which has unique properties including bioactivity, biocompatibility, and biodegradability favourable for a broad variety of industrial and biomedical applications (Gupta & Majeti, 2000; Majeti, 2000). It is a hydrophilic polyelectrolyte of *N*-acetyl-D-glucosamine, obtained from partial deacetylation of chitin using a concentrated (~50%) solution of sodium hydroxide.

The properties of chitosan are related to average molecular weight (from 10^4 to 10^6 g/mol), molecular-weight distribution, extent of deacetylation, and chain degradation that occurs in the alkaline hydrolysis of chitin. One of the most important parameter in the characterization of chitosan is the degree of acetylation (DA), defined as the ratio of the number of formed NH_2 groups to the initial number of $NHCOCH_3$ groups present in chitin (Martínez-Ruvalcaba, 2001).

Xanthan gum is the extracellular polysaccharide obtained from *Xanthomonas campestris*. Its chemical structure is composed of glucose, mannose, glucuronic acid acetate and pyruvate. Its molecular weight is in the range of several million. Xanthan gum will not form a rigid gel by itself but will give a thermoreversible physical gel when mixed not only with carob gum or tara gum, but also with chitosan. The resulting gel has a fascinating texture, being very elastic and having high rupture strength (Mitchell, 1976).

Polyelectrolytes, like chitosan or xanthan in solutions, are polymers with potentially ionizable groups. In polar solvents they dissociate into polyions and counter-ions. Strong electric interactions between them are the source of their characteristic properties in solution. Hydrogels are usually formed by the covalent cross-linking of linear hydrophilic polymers to form a network of material capable of absorbing water, yet still remaining insoluble. Heterogeneous polymer mixtures may also be used to form

---

[*] Corresponding author. Tel./fax: +52 33 3650 3401.
E-mail addresses: agustinm@ccip.udg.mx, agustin21@gmail.com (A. Martínez-Ruvalcaba).

0144-8617/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2006.06.033

hydrogels without the need for covalent cross-linking (Noble, Gray, Sadic, & Uchegbu, 1999).

Chitosan hydrogels are usually covalently cross-linked. Cross-linking agents such as glutaraldehyde and glyoxal have been used in the production of chitosan hydrogels (De Angelis, Capitani, & Crescenzi, 1998; Nakatsuka & Andrady, 1992). In addition, semi-interpenetrating polymer network hydrogels and co-network of two cross-linked polymers have been produced (Noble et al., 1999); such hydrogel materials have limited biocompatibility and biodegradability due to their complex structure and, sometimes, for the presence of synthetic polymers. Cho, Heuzey, Bégin, and Carreau (2004) studied the gelation of chitosan/β-glycerophosphate solutions. In their work, the physical properties of the sol–gel transition were characterized by dynamic mechanical testing under different polymer and urea concentration. In gelation tests, the evolution of the elastic and viscous moduli was monitored as a function of temperature and results for the sol–gel transition at a critical temperature (gelation temperature) were reported.

Non-covalent cross-linked chitosan gel mixtures can be prepared from polyelectrolyte complexes of chitosan and polymers such as carrageenan or xanthan. When two oppositely charged polyelectrolytes are mixed in an aqueous solution, a polyelectrolyte complex is formed by electrostatic attraction. Polyelectrolyte complexes are highly hydrophilic materials and form highly swollen systems in water. Chitosan has been used for the preparation of various polyelectrolyte-complex products with natural polyanions as alginate (Takka & Acartürk, 1999), carboxymethyl-cellulose (Argüelles-Monal, Hechavarria, Rodríguez, & Peniche, 1993; Fukuda, 1980), dextran sulfate (Sakiyama, Takata, Toga, & Nakanishi, 2001), carboxymethyl-dextran (Fukuda & Kikuchi, 1978), heparin (Kikuchi & Noda, 1976; Kratz, Back, Arnander, & Larm, 1998), carrageenan (Sakiyama, Chu, Fujii, & Yano, 1993), pectin (Chang & Lin, 2000; Mireles, Martino, Bouzas, & Torres, 1992), collagen (Zhang, Liu, Ren, & Wang, 1997), and xanthan (Chelat et al., 2000; Chu, Sakiyama, & Yano, 1995; Dumitriu & Chornet, 1996, 1998, 2000; Dumitriu, Magny, Montane, Vidal, & Chornet, 1994; Ikeda, Kumagai, Sakiyama, Chu, & Nakamura, 1995).

Dumitriu et al. (1994) presented a method for the preparation of hydrogels from the complexation of chitosan and xanthan. Stable hydrogels are able to retain between 65% and 95% of their weight in water. Water retention and hydrogel properties are function of the degree of acetylation (DA) of chitosan and the ratio chitosan–xanthan used in gel preparation.

1.2. Viscoelastic properties of chitosan-based hydrogels

With respect to chemically cross-linked gels formed via covalent association of chitosan, Argüelles-Monal, Goycoolea, Peniche, and Higuera-Ciapara (1998) reported a dynamic oscillatory study of chitosan–glutaraldehyde chemical gels. They focused on the viscoelastic characteristic as well as the mechanical properties as a function of cross-linking degree of the formed gels. For the same systems Cheng et al. (1998) reported that the effect of water content on the polymer network can be correlated with the relaxation of the hydrogel network.

Rheological studies on semi-interpenetrating networks are also available. Khalid, Ho, Agnely, Grossiord, and Couarraze (1999) reported swelling properties and rheological characterization of a semi-interpenetrating chitosan–polyethylene oxide network. They showed how the network displayed a high capacity to swell via pH modification. The rheological properties showed that the semi-interpenetrating network had increased elastic properties from the presence of the polyethylene oxide physical network.

The rheology of chitosan gel systems used in the pharmaceutical field has been studied. Bodek (2000) reported on the rheological properties of microcrystalline chitosan hydrogels prepared by adding a methylcellulose hydrogel to aqueous chitosan dispersions. The results showed that a pseudoplastic or plastic system can be obtained depending on the kind and content of the pharmaceutical substances and on the interactions between the polymer and these pharmaceutical substances. Ruel-Gariepy, Chenite, Chaput, Guirguis, and Leroux (2000) for the case of chitosan/glycerophosphate thermosensitive solution, which gels at 37 °C, evaluated the in vitro release profiles of different pharmaceutical model compounds and showed the effect of temperature, chitosan deacetylation degree, molecular weight, and substances present.

The understanding of rheological phenomena is based on two types of theories. Phenomenological theories use macroscopic stress–strain–time relationships; while molecular theories provide evidence of viscoelastic behavior from molecular structure and conformation. For synthetic polymers, both theories have been successfully applied in practice. However, biological systems, which are ‘‘heterogeneous dispersions’’, exhibit considerable variability in their rheological properties because of their inherent complexity. This is why the application of classical rheological models is limited (Zoon, Roefs, De Cindio, & Van Vliet, 1990).

Many weak gels and complex dispersions can be treated as three-dimensional networks where weak interactions ensure structure stability. In structured materials such as gels, the most relevant theory is probably the one proposed by Winter (1989): at the gel point, not only the longest relaxation time diverges but the relaxation modulus follows a power–law:

$$G(t) = At^{-n}, \qquad (1)$$

where n is a relaxation exponent and A is the gel strength. The relation is valid for $\lambda_0 < t < \infty$, λ_0 being a characteristic time for cross-over to small-scale dynamics. Eq. (1) can be transformed for the case of oscillatory tests at fixed frequency (ω) as:

$$G(\omega) = A\omega^n \tag{2}$$

for $0 < \omega < 1/\lambda_0$. The critical gel is assumed to correspond to a solid. Therefore it does not flow, the viscosity being infinite.

Winter and Chambon (1986) developed a constitutive equation based on the existence of an intermediate state of the material at which the dynamic moduli, $G'(\omega)$ and $G''(\omega)$, are congruent functions in the entire range $0 < \omega < \infty$. This work defined a new material property, the strength or stiffness (S), easily measures in a single oscillatory shear experiment during the cross-linking reaction. In this case, the shear stress (τ) is expressed as:

$$\underline{\underline{\tau}}(t) = S\int_{-\infty}^{t}(t-t')^{-0.5}\dot{\underline{\underline{\gamma}}}(t')\,\mathrm{d}t'. \tag{3}$$

Dynamic mechanical data near the gel point allow easy determination of the parameters of the critical gel. The parameters n and S can be obtained as follows (Winter & Mours, 1997):

$$n = \frac{2}{\pi}\tan^{-1}\left(\frac{G''}{G'}\right), \tag{4}$$

$$S = \frac{G'(\omega)}{\omega^n\cos(n\pi/2)\Gamma(1-n)}, \tag{5}$$

where $\Gamma(1-n)$ is the Gamma function of $1-n$. Eqs. (4) and (5) are generally valid for viscoelastic liquids and solids. For $n \to 1$, the material is purely viscous; and for $n \to 0$, the material is purely elastic. The case $n = 0.5$ was called an ideal gel (Chambon & Winter, 1987).

Weak gels and dispersions behave like three-dimensional networks and have limited flowability. This suggests that weak gels behave like critical gels as described earlier and must be considered as gel-like networks able to flow because they show a finite relaxation time. Gabriele, De Cindio, and D'Antona (2001) weak gel model suggests that the structure of a material corresponds to a cooperative arrangement of flow units forming interacting strands. Their model introduces the coordination parameter (z) which is the number of flow units interacting with one another. During dynamic oscillatory experiments, gel strands may be considered as a combination of flow units where z is the number of rheological units interacting with one another in a three-dimensional structure. The complex modulus can be expressed by:

$$G^*(\omega) = \sqrt{G'(\omega)^2 + G''(\omega)^2} = A_\mathrm{F}\omega^{1/z}, \tag{6}$$

where A_F is the gel strength and can be interpreted as the strength of the interactions between flow units. Eq. (6) is a simple relationship but provides good qualitative representations of the relationships between microscopic and macroscopic properties of physical gels. This approach gives useful information about the rheological structure of hydrogels, considering the existence of a three-dimensional network in which flow units are linked by more or less weak interactions. However, when the loss modulus is small ($G'' \ll G'$), $G^* \approx G'$ and the model simplifies to:

$$G'(\omega) = A_\mathrm{F}\omega^{1/z}. \tag{7}$$

In this work a study of the rheological behavior of chitosan/xanthan gels is presented. The effect of the chemical media used in dispersion, hydrogel concentration, and lag time on gel rheology is presented and the results are analyzed using the models of Winter and Chambon (1986) and Gabriele et al. (2001).

2. Materials and methods

2.1. Materials

The chitosan used was prepared from chitin obtained from shrimp's shells and produced by Kemestrie Inc., Sherbrooke (Canada). A chitosan sample with degree of acetylation (DA) of 28%, polydispersity of 4.7, and weight average molecular weight (M_w) of 8.2×10^5 g/mol was used. The xanthan was supplied by Kelko Inc. Xanthan gum is a high molecular weight (approximately 1×10^6 g/mol) polysaccharide produced by a pure culture fermentation of a carbohydrate with *X. campestris*, then purified by recovery with isopropyl alcohol, dried, and milled.

To prepare hydrogel dispersions, three different chemical media were used: distilled water, a buffer solution (0.05 M potassium phosphate monobasic–sodium hydroxide buffer with pH 7.00 at 25 °C by Fisher Scientific), and 0.05 M NaCl aqueous solution (analytical-grade sodium chloride by Sigma). Analytical-grade hydrochloric acid (BDH) and sodium hydroxide (Anachemia) were used for chitosan solubilisation and neutralization. Further details can be obtained from Martínez-Ruvalcaba (2001).

2.2. Samples preparation

2.2.1. Chitosan solutions preparation

Chitosan solutions were prepared as follows: 6.5 g of chitosan were dissolved in 300 ml of 0.1 N HCl. The solution was then neutralized with 0.2 N NaOH and distilled water was added for a total volume of 1000 ml at pH 5.6. To obtain good solutions, the chitosan powder was dispersed by agitation with a magnetic stirrer until total solubilisation. The chitosan solutions were kept at 4 °C until gel formation was performed.

2.2.2. Xanthan solutions preparation

A xanthan solution was prepared by adding 6.5 g of xanthan to 1000 ml of distilled water and dispersion was done with a magnetic stirrer until total solubilisation.

2.2.3. Hydrogel formation

Mixing 1000 ml of the chitosan solution with 1000 ml of the xanthan solution formed the hydrogel. Agitation was conducted for 10 min at room temperature and the hydrogel formed was separated out by filtration. The hydrogel was washed repeatedly with water to remove free chitosan and xanthan. The washed hydrogel was then lyophilized in a freeze dry system (LABCONCO). The study used a controlled xerogel particle size: 55–75 μm. In order to obtain this fraction, the dried hydrogel was grounded using a Pulverisette 14 by Fritsch; and sifted using two USA standard testing sieves by Fisher Scientific: #200 (75 μm) and #270 (55 μm).

2.2.4. Rheological samples preparation

For each dispersion media (distilled water, buffer solution at pH 7.0, and 0.05 M NaCl solution), different hydrogel concentrations (7–10 %) were prepared. As soon as the hydrogel was weighted, it was dispersed in the selected media until a homogeneous dispersion of the gel was obtained. For better dispersion, it was necessary to perform manual agitation. For this reason only small quantities, between 8 and 15 g, were prepared for each batch.

2.3. Rheological tests

The rheological tests were performed using a controlled rate Carri-Med Weissenberg rheogoniometer R20 to measure the dynamic properties of the hydrogels: frequency sweep and time sweep tests. Flow measurements were carried out at a temperature of 25 °C. In order to preserve hydrogel moisture, a special setup was adapted allowing circulation of water saturated air. For the oscillatory shear rheology measurements, parallel plate geometry was used: plates diameter = 40 mm, gap = 1500 μm, and strain = 3.0%. Logarithmic frequency sweeps were carried out over frequencies between 0.1 and 65 s^{-1}. Preliminary strain sweeps test confirmed that the tests were in the linear viscoelastic regime. Time sweep measurements were performed for 1000 s at a constant angular frequency of 1 and 10 Hz with a sequence of one experimental point each 60 s.

2.4. Determination of the degree of swelling

The hydrogel degree of swelling (α) was determined by weighing the dry hydrogels before and after immersion in the different chemical solvent media used in this study. The degree of swelling is defined as:

$$\alpha = \{[(\text{weight of hydrated gel}) - (\text{weight of dry gel})]/(\text{weight of dry gel})\} \times 100. \tag{8}$$

3. Results and discussion

The gels were prepared by mixing two oppositely charged polyelectrolytes, chitosan and xanthan. The network structure of these gels was maintained by ionic cross-linking between polyelectrolytes (the gels are dispersed in water or in aqueous solutions). The charged state of the polyelectrolytes functional groups contributes to the gel network structure. The rheological properties of these complex gels are now analyzed in terms of hydrogel concentration (7%, 8%, 9%, and 10% w/w), chemical media used for the hydrogel dispersion (distilled water, buffer solution at pH 7.0, and 0.05 M NaCl solution), and lag time (up to 390 min).

3.1. Hydrogel concentration effect

The concentration range was selected as the hydrogel capacity to swell. The degree of swelling (α) was determined by weighing the dry hydrogels before and after immersion in each chemical media used for dispersion. Chu et al. (1995) showed that chitosan–xanthan gels are sensitive to the swelling medium and Table 1 presents that it is the case for the hydrogels prepared in this work. For example, chitosan–xanthan hydrogels dispersed in water have a degree of swelling of 1521, meaning that this hydrogel can absorb water 15.21 times its weight. In other words, no free water will be present in hydrogels, when the hydrogel concentration is 6.57% or higher.

Fig. 1 presents the effect of concentration on the storage modulus of chitosan–xanthan hydrogels dispersed in water after a lag time of 90 min. For the frequency range available, the storage modulus (G') increases with hydrogel concentration and frequency. There was no experimental evidence for G' being constant (reaching a plateau) in this case.

3.2. Effect of the dispersion medium and test lag time

Three chemical media were used to disperse the hydrogels: distilled water, buffer solution at pH 7.0, and 0.05 M NaCl solution. The effect of these media on the rhe-

Table 1
Degree of swelling for chitosan–xanthan hydrogels

Dispersion medium	α
Distilled water	1521
Buffer solution	1162
0.05 M NaCl solution	1028

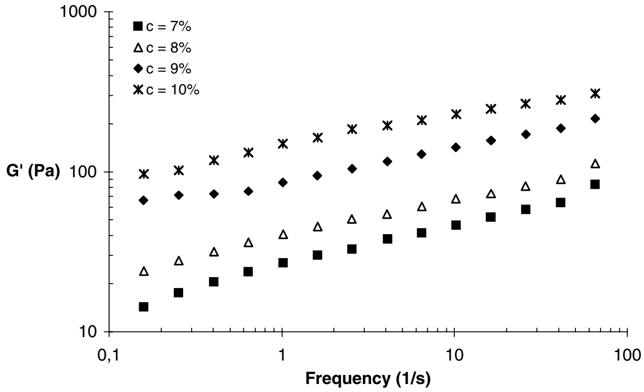

Fig. 1. Storage modulus (G') for chitosan–xanthan hydrogels dispersed in water at different hydrogel concentrations and 25 °C. Test lag time = 90 min.

ology of the hydrogels is presented in Fig. 2 for concentrations of 7% and 10%, the lag time being constant at 90 min. Fig. 2 shows that higher moduli are obtained for systems having ionic nature: the buffer solution (phosphate anions) and the sodium chloride solution (chloride anions); with phosphate giving higher moduli. For chitosan solutions, it is known that the presence of salts decreases viscosity because of interactions between charged chains and small ions in solution (Martínez-Ruvalcaba, Chornet, & Rodrigue, 2004; Martínez, Chornet, & Rodrigue, 2004). For chitosan–xanthan hydrogels, a reverse trend is observed: the modulus (viscosity) is higher for hydrogels dispersed in ionic media.

Some hydrogels change their equilibrium characteristics responding to external conditions such as pH, ionic strength, temperature, and electric fields. For chitosan–xanthan hydrogels, two ionizable functional groups are present: the free carboxyl group of xanthan and the free amino group of chitosan. Just before gel preparation, these functional groups are considered to be oppositely charged and both molecules can link electrostatically to each other. During gel formation not all the ionizable functional groups are neutralized. When the gel is dispersed in an ionic medium, the un-neutralized amino group interacts with the anion of the ionic medium, while the carboxyl group holds the negative charge. Therefore, electrostatic equilibrium between both functional groups will change. In addition, counter-ions (like Na^+) attracted by the negatively charged carboxyl groups may modify the internal structure of the hydrogel and this effect is observed as an increase of the moduli (viscosity) of the hydrogel.

The dispersion medium has also an effect when we analyze the "test lag time", defined as the time between the moment when the hydrogel is dispersed and the moment when the rheological test is started. Fig. 3 shows the effect of test lag time for 7% chitosan–xanthan hydrogel dispersed in water and buffer solution. In this plot, storage moduli are higher for systems dispersed in the buffer solution as in Fig. 2. In addition, the slope is higher for hydrogels dispersed in water vs. hydrogels dispersed in the buffer solution. There is also a point where both curves almost superimpose. This can be explained by the effects of counter-ions in a polyelectrolyte system: decreased electrostatic interactions strength by means of salt addition. For hydrogels dispersed in water, links formed between both polyelectrolytes and water preserve the electrostatic interactions preventing to attain constant moduli values at different test lag times. Systems dispersed in NaCl solutions have an intermediate behavior between the systems dispersed in water and others dispersed in buffer solutions. However, storage moduli are always greater with respect to hydrogels dispersed in water because of electrostatic interactions due to the salt addition.

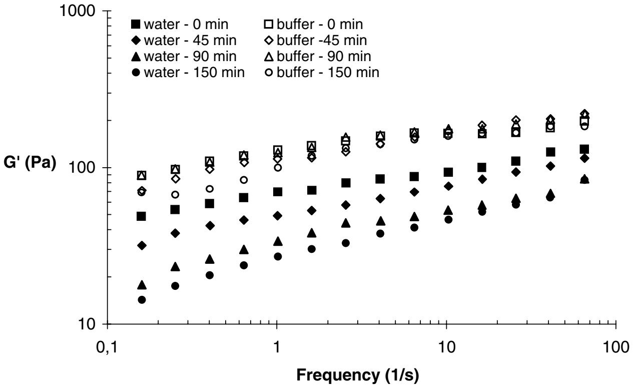

Fig. 3. Storage modulus of chitosan–xanthan hydrogels at different test lag times. The hydrogels were dispersed in water and buffer solution at a concentration of 7%.

Fig. 3 also shows that G' decreases with increase in test lag time. In general, a hydrogel system recently prepared has higher moduli than one that has been rheologically tested at longer times after its preparation. This effect is more pronounced for systems dispersed in distilled water than in buffer solutions. Fig. 4 presents how storage moduli, at constant angular frequency, change with test lag times for the systems presented in Fig. 3. It is clear that

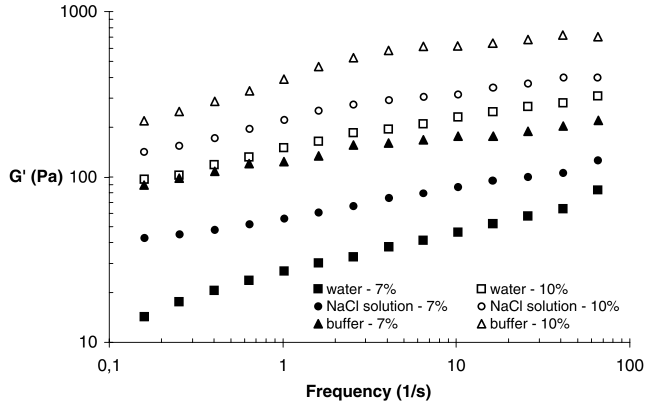

Fig. 2. Storage modulus of chitosan–xanthan hydrogels in different dispersion media at two hydrogel concentrations (7% and 10%). Test lag time = 9 min.

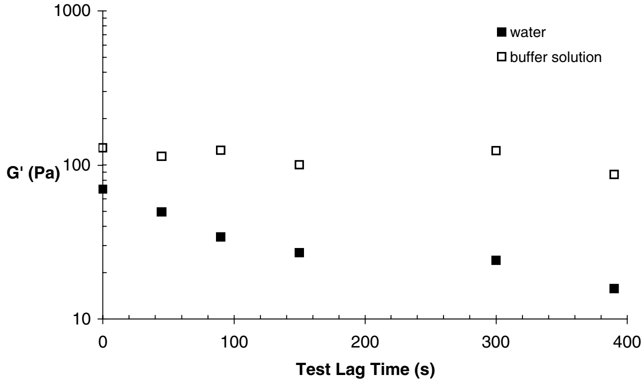

Fig. 4. Storage modulus as a function of test lag time at constant frequency (1 Hz) for chitosan–xanthan hydrogels dispersed in water and buffer solution at a concentration of 7%.

the modulus is almost constant for buffer solutions; while for hydrogels dispersed in water the moduli decreases with increasing test lag time, tending to a constant value as time increases. This different behavior indicates a faster equilibrium stabilization of the buffer solution. This kinetic effect is discussed next using time sweep tests.

3.3. Time sweep tests

Oscillatory time sweep tests enabled to follow the evolution of the hydrogel rheology at a constant frequency. In general, the effects observed in a time sweep test are similar to the ones observed in a frequency sweep experiment. Fig. 5 presents the evolution of the storage modulus of chitosan–xanthan hydrogels dispersed in 0.05 M NaCl solutions for a lag time of 120 min. The storage modulus (G') increases with hydrogel concentration but the effect of time is negligible: constant G' value.

Fig. 6 presents the effect of the dispersion medium on the hydrogel in a time sweep test. The systems presented are 7% and 10% chitosan–xanthan hydrogels for a test lag time of 120 min. The curves show similar results as for frequency sweep tests: the storage modulus is higher for systems with ionic strength (buffer solution and NaCl solution). The dependence of the moduli with time is almost insignificant; but for some systems, an increase at larger times (nearly 1000 s after test initiation) was observed. This can be explained by the elastic character of these systems (relaxation effect). Although small, possible evaporation effects leading to higher hydrogel concentration with time may be present.

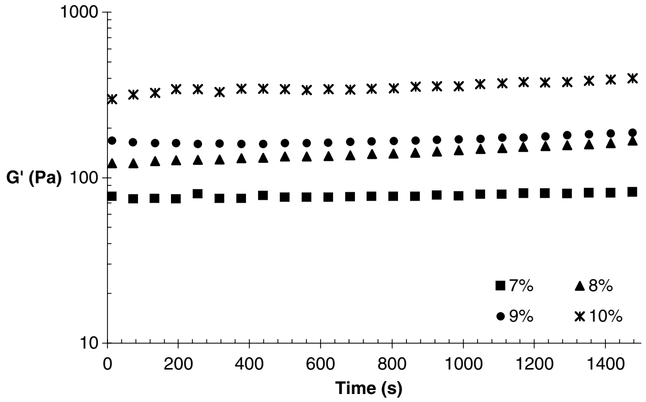

Fig. 5. Storage modulus as a function of time at constant frequency (1 Hz) for chitosan–xanthan hydrogels dispersed in 0.05 M NaCl solution at different hydrogel concentrations. Test lag time = 120 min.

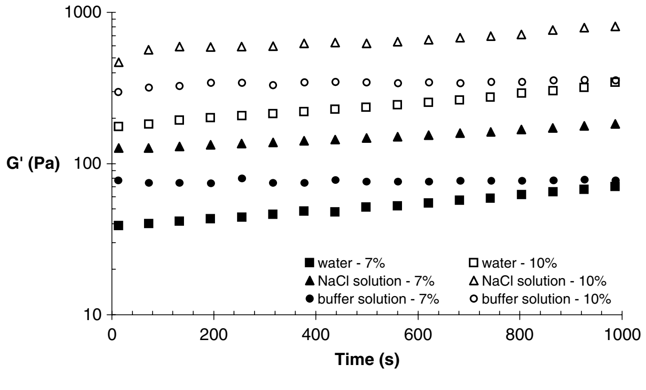

Fig. 6. Storage modulus as a function of time at a constant frequency (1 Hz) for chitosan–xanthan hydrogels dispersed in different media and concentrations. Test lag time = 120 min.

3.4. Comparison of the rheological properties between chitosan–xanthan hydrogels and other polysaccharide gels

Chitosan–xanthan hydrogels are a special case of gels among polysaccharide gels as they are formed by the complexation of natural polyions: the interaction of acidic polysaccharide (xanthan) and polycationic polysaccharide (chitosan). Very little rheological information exists for polysaccharide complexes formed by anion–cation interactions. However, a comparison of the rheological behavior of our system with the rheological properties reported for other polysaccharide-containing hydrogels like carrageenans, alginates, pectins or starch gels is made here.

Carrageenan gels are one of the most rheologically studied polysaccharide gels because of their dependence on ionic strength. Carrageenan gels are sulphated polysaccharide polymers that can be extracted from various genera of marine algae of the *Rhodophyceae* class. Carrageenan gels form strong gels in the presence of K^+ or Ca^{2+} ions but almost no gelation occurs in the presence of Li^+ or Na^+ (Clark & Ross-Murphy, 1987). Morris and Chilvers (1981, 1983) made shear modulus measurements on carrageenan gels and have plotted modulus–concentration relationships for gels made in the presence of different cations. They have also considered the effect of temperature range. Their results confirmed the increase of gel rigidity (rigidity modulus, GR) with K^+ ions, but they also showed that these gels can be obtained in presence of Li^+ or Na^+ under high polymer and electrolyte concentrations. Moduli in the order of 10–20 Pa at low polymer concentrations were obtained. The modulus approaches 200 Pa for polymers gelled with K^+ ions and 600 Pa for carrageenans gelled with Na^+ ions. The concentration range studied was from 0.25% to 3.0% in weight.

Strong and weak gels are classified on the basis of their mechanical spectra. Typical strong gel spectrum consists of two nearly horizontal straight lines; G' typically 1–2 orders of magnitude higher than G''. Weak gels have both moduli showing a slight frequency dependence G' exceeding G'' at all frequencies. Chitosan–xanthan hydrogels can be considered as weak gels because their G' are function of frequency. However, the rheology of chitosan–xanthan hydrogels can be compared to strong gel such as alginates gels.

Alginates are salts of alginic acid found as intercellular material in brown algae. Their function as structure-forming components appears to result from their capacity to gel in the presence of certain divalent cations. Unlike carrageenans gels, alginates do not form thermoreversible gels.

But, like carrageenan gels, gel strength is function of the cation used. Segeren, Boskamp, and van den Tempel (1974) reported the rheological properties of Ca^{2+} alginate gels (1.4% w/w). As in the case of our chitosan–xanthan hydrogels, the dynamic analysis was restricted to the storage modulus G' because the ratio G''/G' was lower than 10^{-2}. G' values reported for these alginate gels were slightly higher than 10^3 Pa and were essentially constant over all the frequency range studied (10^{-1}–10^1 rad/s).

The strong gel behavior in most of the strong polysaccharide gels is frequently associated with high values of the storage modulus. For alginate gels, they exhibit an equilibrium shear modulus that is characteristic of viscoelastic solids such as chemically cross-linked networks. For chitosan–xanthan hydrogels, it is assumed that chain associations result in three-dimensional networks having various levels of connectivity and junction zones of different length and strength. The frequency dependence of the storage modulus can be approximated with simple models such as the power–law. Some cases of polysaccharide strong gels having moduli similar to values obtained with chitosan-xanthan hydrogels have been reported. One example is starch that is a complex polysaccharide present as energy reserve in plants. Starch consists of two different polysaccharides: amylose and amylopectin. The structural and rheological data for both components are generally reported separately.

Doublier and Choplin (1989) reported the mechanical spectra of two amylose gels at low concentration (1.03% and 1.33%). Like strong gels, they observed no variation of G' profiles within the experimental frequency range and G' was 1–2 orders of magnitude greater than G''. For dilute gels, values of G' lower than 10 Pa were measured. These values are evidence that rigidity of these strong gels is similar to the behavior observed for the chitosan–xanthan hydrogels, but our hydrogels were prepared at a concentration having as a minimum 7%. The concentration dependence of strong gels can be investigated more easily since G' is almost frequency independent and can therefore be approximated by the equilibrium shear modulus. For typical alginate gels, G' shows a C^2 dependence whereas for κ-carrageenan in 0.1 M KCl it shows a $C^{3.4}$ dependence (Lapasin & Pricl, 1995). A special case was observed with amylose gels. Ellis and Ring (1985), working with pea amylose samples over the concentration range 1.5–7.0% w/w, found on average that G' varies as C^n, with n comprised between 7 (high degree of polymerization) and 4.4 (low degree of polymerization). This behavior has been related with high elasticity of the amylose gels.

Another case of polysaccharide gels of commercial importance is pectins. Pectins are substances that originate from plants, contain pectinic acid as a major component. They are water soluble and are able to form gels under suitable conditions, by temperature changes, by the introduction of specific counter-ions or pH variations (Lapasin & Pricl, 1995). Commercial pectins are divided into high ester (HM) pectins and low ester (LM) pectins according to the degree of methyl esterification. G' modulus of LM-pectins gels is 10 times that of G'' and independent of frequency over a wide frequency range, which indicates that the solid character is predominant like a strong gel. An increase in temperature leads to a sharp decrease in G' (Durand, Bertrand, Clark, & Lips, 1990). Watson (1966) found in HM-pectin gels the presence of plastic flow, indicating the existence of an elastic limit defined as the greatest stress a material can sustain without any permanent strain.

Another comparison can be made with xanthan alone which behaves almost like a gel for concentrations higher than 1%. Since xanthan is a polyelectrolyte its rheological properties are expected to change with ionic strength and concentration. In the case of chitosan–xanthan hydrogels, dissolution in electrolyte medium increases viscosity and moduli; while for xanthan alone at low concentration (0.15% w/w), the addition of an electrolyte such as NaCl reduces slightly viscosity. Xanthan thus behaves like a solution as it is the case for chitosan solutions (Martínez-Ruvalcaba, 2001). However, at higher xanthan concentrations, the presence of an electrolyte has the opposite effect: a weak gel behavior is observed. Moduli and viscosity increase with ionic strength is similar to chitosan–xanthan hydrogels (Pettitt, 1982). For 1.0% w/w xanthan with 0.02 M KCl, a weak gel behavior was observed: it was not possible to obtain G' independent of frequency. Moduli values were of the order of $G' \sim 10^2$ Pa and $G'' \sim 10^1$ Pa (Lapasin & Pricl, 1995). G' values were similar to values obtained for chitosan–xanthan hydrogels but the difference is that the G'' values were closer to G' values and were measured. In our case it was impossible to measure G'' because of rheometer sensitivity.

We know that in weak gels there is no evidence for G' to converge to a finite value at high frequency. In the case of xanthan hydrogels, Carnali (1992), based on the fact that the frequency dependence changes with polymer concentration, took into account a series of reference frequency in order to analyze the effects of concentration. He found that in the 0.3–3.0% w/w concentration range, G' was proportional to C^n, where n decreases with increasing frequency, tending to a limiting value of 1.9. In general, n values extrapolated for weak gels are very small in comparison with values obtained directly for strong gels.

After comparing the characteristics of several polysaccharide gel systems, we can conclude that chitosan–xanthan gels have moduli values similar to values observed in other polysaccharide weak gels. However, some strong gels also show similar values. The dependence of G' with concentration is clearly that of a weak gel.

3.5. Oscillatory shear flow modeling

Eq. (7) was first used to fit our experimental data and some results are presented in Fig. 7 for chitosan–xanthan gels dispersed in the three different media, for 7% and 10% hydrogel concentration (lag time = 90 min). The results reported in Table 2 and Fig. 7 reveal that the final

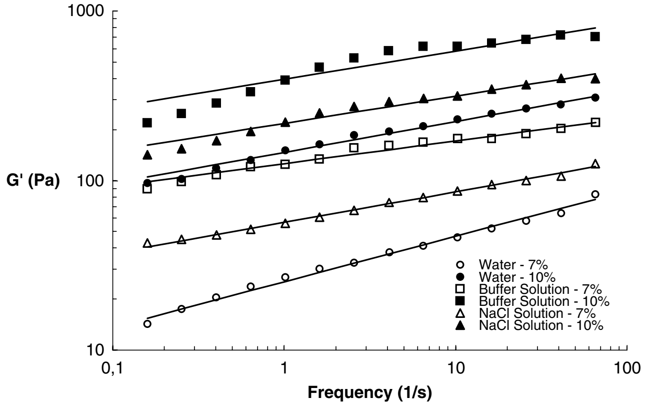

Fig. 7. Storage modulus of chitosan–xanthan hydrogels dispersed in different media for concentrations of 7% and 10%. Lines represent the model of Gabriele et al. (Eq. (7)). Test lag time = 90 min.

structure and the final properties of these hydrogels are function of hydrogel concentration and dispersion media, but some interaction exists between both parameters.

3.5.1. Effect of hydrogel concentration

As expected, gel strength (A_F) increases with increasing concentration: G' increases over the entire concentration range. This means that independently of the number of interactions (z value) the systems turns out to be stronger when concentration increases.

3.5.2. Effect of the dispersion media

Hydrogels dispersed in distilled water were found to have lower z and A_F values. This means a lower number of interactions with lower networks strength with respect to systems dispersed in NaCl and buffer solutions. When compared to similar systems dispersed in NaCl and buffer solutions the differences in z are not important; i.e., a similar number of interactions. However, interactions in systems dispersed in buffer solutions are stronger (higher values of A_F).

The results were also analyzed using the model of Winter and Chambon (1986), as presented in Eq. (5). In our case, since G'' was not measured (below the rheometer sensibility), it was impossible to evaluate the relaxation exponent (n) from Eq. (4). In this case, a non-linear regression procedure using only Eq. (5) enabled us to obtain the relaxation exponent (n) and the gel stiffness (S). The resulting parameters are reported in Table 3.

A comparison between the numerical values reported in Tables 2 and 3 indicates a clear relation between both sets of parameters. The exponent (n) in the Winter and Chambon model is the inverse of the number of flow units (z) in the Gabriele et al. model; while gel stiffness (S) is similar to the gel strength (A_F); both series of values reflects analogous tendencies. Therefore, both models are similar for this particular hydrogel: the strength of the interaction between flow units in the hydrogel is mainly function of hydrogel concentration and dispersion media. A comparison between A_F and S is presented in Fig. 8 for different hydrogel concentration and a test lag time of 90 min. The plot shows a similarity between both parameters which are increasing with hydrogel concentration. As reported previously, a simple power–law relation can be used to determine the effect of concentration on A_F and S as:

$$A_F = aC^b \quad \text{or} \quad S = aC^b. \tag{9}$$

Table 4 reports the values for our hydrogels at a test lag time of 0 and 90 min. The exponent b is comprised between 0.3 and 0.6 depending on dispersion media and lag time. The value changes slightly for a lag time of 0 min. However, for longer lag time, b decreases when the dispersion media is a salt solution. These values are in accordance with comparisons made in Section 3.4 between the rheological properties of chitosan–xanthan hydrogels and other polysaccharide gels. For weak gels, b values (0.3–0.6) are small in comparison with values obtained for strong gels (1–4).

4. Conclusion

Hydrogels formed by complexation of chitosan and xanthan have been rheologically characterized by oscillatory

Table 2
Model parameters of Eq. (7) for chitosan–xanthan hydrogels

Dispersion media	Test lag time (min)	Hydrogel concentration (%)			
		7	8	9	10
Distilled water	0	$A_F = 66.8$ $z = 6.30$	$A_F = 67.0$ $z = 5.05$	$A_F = 161.7$ $z = 6.07$	$A_F = 197.2$ $z = 5.75$
	90	$A_F = 25.3$ $z = 3.73$	$A_F = 38.9$ $z = 4.18$	$A_F = 87.6$ $z = 4.78$	$A_F = 146.9$ $z = 5.50$
Buffer solution	0	$A_F = 125.1$ $z = 9.20$	$A_F = 203.0$ $z = 7.02$	$A_F = 302.9$ $z = 8.10$	$A_F = 534.2$ $z = 7.66$
	90	$A_F = 126.2$ $z = 7.48$	$A_F = 198.5$ $z = 5.88$	$A_F = 249.3$ $z = 5.56$	$A_F = 396.5$ $z = 6.02$
0.05 M NaCl solution	0	$A_F = 85.3$ $z = 9.85$	$A_F = 143.6$ $z = 7.76$	$A_F = 169.1$ $z = 6.27$	$A_F = 247.1$ $z = 5.79$
	90	$A_F = 56.5$ $z = 5.48$	$A_F = 93.0$ $z = 5.92$	$A_F = 134.4$ $z = 6.21$	$A_F = 217.7$ $z = 6.23$

Table 3
Model parameters of Eq. (6) for chitosan–xanthan hydrogels

Dispersion media	Test lag time (min)	Hydrogel concentration (%)			
		7	8	9	10
Distilled water	0	$S = 61.5$	$S = 60.6$	$S = 148.4$	$S = 180.3$
		$n = 0.159$	$n = 0.198$	$n = 0.165$	$n = 0.174$
	90	$S = 22.1$	$S = 34.5$	$S = 78.8$	$S = 133.8$
		$n = 0.268$	$n = 0.239$	$n = 0.209$	$n = 0.182$
Buffer solution	0	$S = 117.9$	$S = 188.3$	$S = 283.7$	$S = 498.4$
		$n = 0.109$	$n = 0.143$	$n = 0.123$	$n = 0.131$
	90	$S = 117.6$	$S = 181.7$	$S = 227.2$	$S = 363.8$
		$n = 0.134$	$n = 0.170$	$n = 0.180$	$n = 0.166$
0.05 M NaCl solution	0	$S = 80.8$	$S = 134.1$	$S = 155.7$	$S = 225.9$
		$n = 0.102$	$n = 0.129$	$n = 0.159$	$n = 0.173$
	90	$S = 51.5$	$S = 85.2$	$S = 123.6$	$S = 200.3$
		$n = 0.182$	$n = 0.169$	$n = 0.161$	$n = 0.161$

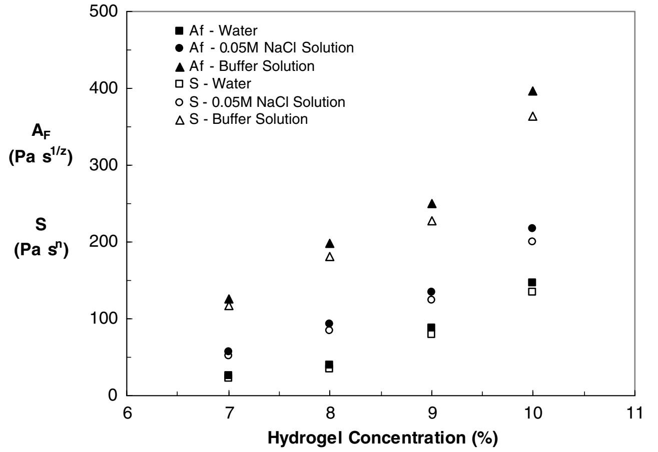

Fig. 8. Gel strength (A_F) and gel stiffness (S) as a function of hydrogel concentration for different dispersion media. Test lag time = 90 min.

Table 4
Power–law concentration model parameters for the chitosan/xanthan hydrogels

Test lag time (min)	Dispersion media	$A_F = aC^b$		$S = aC^b$	
		a	b	a	b
0	Distilled water	3.63	0.403	3.32	0.403
	0.05 M NaCl solution	9.78	0.322	9.96	0.311
	Buffer solution	3.60	0.499	3.39	0.498
90	Water	0.37	0.599	0.30	0.611
	0.05 NaCl solution	2.55	0.444	2.29	0.446
	Buffer solution	9.18	0.375	8.53	0.373

shear measurements under small-deformation conditions. The complex moduli are frequency dependent, increasing slightly with frequency. Since G' was always greater than G'', chitosan–xanthan hydrogels are mainly elastic materials (negligible viscous effects). Finally, G' was found to increase with chitosan–xanthan hydrogel concentration.

In comparison with systems dispersed in distilled water, higher moduli were obtained in systems with ionic strength: buffer solution and sodium chloride solution. Higher moduli were obtained for the phosphate anion than the chloride anion. This can be explained by electrostatic equilibrium changes induced by the counter-ions; the ionic strength modifies the internal structure of the hydrogel leading to increased moduli of the hydrogel. It was shown in that case that G' decreases with test lag time, reaching a constant value later on.

Modelling of the hydrogels rheological properties was done using the Gabriele et al. model, which was established for weak gel systems. The model parameters obtained are dependent on hydrogel concentration, dispersion medium and test lag time. The structure of the hydrogel system is explained as a combination of flow units with parameters related to the number of rheological units correlated with one another in a three-dimensional structure and to the strength of the interactions between these flow units. The results reveal that the final structure and the final properties of these hydrogels are functions of varying factors (such as hydrogel concentration and nature of dispersion medium), and that interactions between these factors must be considered in order to prepare hydrogels with desired properties. These results were confirmed using the Winter and Chambon model, which is a more general model in relation with the critical gel theory of Winter.

References

Argüelles-Monal, W., Goycoolea, F. M., Peniche, C., & Higuera-Ciapara, I. (1998). Rheological study of the chitosan/glutaraldehyde chemical gel system. *Polymer Gels and Networks, 6*, 429–440.

Argüelles-Monal, W., Hechavarria, O. L., Rodríguez, L., & Peniche, C. (1993). Swelling of membranes from the polyelectrolyte complex between chitosan and carboxymethyl cellulose. *Polymer Bulletin, 31*, 471–478.

Bodek, K. H. (2000). Study on the rheological properties of microcrystalline chitosan hydrogels used as drug carriers. *Polimery, 45*(11–12), 818–825.

Carnali, J. O. (1992). Gelation in physically associating biopolymer systems. *Rheologica Acta, 31*, 399–412.

Chambon, F., & Winter, H. H. (1987). Linear viscoelasticity at the gel point of crosslinking PDMS with unbalanced stoichiometry. *Journal of Rheology, 31*(8), 683–697.

Chang, K. L. B., & Lin, J. (2000). Swelling behavior and the release of protein from chitosan-pectin composite particles. *Carbohydrate Polymers, 43*, 163–169.

Chelat, F., Tabrizian, M., Dumitriu, S., Chornet, E., Magny, P., Rivard, C. H., et al. (2000). In vitro and in vivo biocompatibility of chitosan–xanthan polyionic complex. *Journal of Biomedical Materials Research, 51*, 107–116.

Cheng, G., Liu, J., Zhao, R., Yao, K., Sun, P., Men, A., et al. (1998). Studies on dynamic behavior of water in crosslinked chitosan hydrogel. *Journal of Applied Polymer Science, 67*, 983–988.

Cho, J., Heuzey, M.-C., Bégin, A., & Carreau, P. J. (2004). Gelation study of chitosan/β-glycerophosphate solutions by rheological measurements. In *Proceedings of the XIVth international congress on rheology (FB09). Seoul, Korea*.

Chu, C., Sakiyama, T., & Yano, T. (1995). pH-sensitive swelling of a polyelectrolyte complex gel prepared from xanthan and chitosan. *Bioscience, Biotechnology and Biochemistry, 59*(4), 717–719.

Clark, A. H., & Ross-Murphy, S. B. (1987). Structural and mechanical properties of biopolymer gels. *Advances in Polymer Science, 83*, 60–192.

De Angelis, A. A., Capitani, D., & Crescenzi, V. (1998). Synthesis and ^{13}C CP-MAS NMR characterisation of a new chitosan-base polymeric network. *Macromolecules, 31*, 1595–1601.

Doublier, J. L., & Choplin, L. (1989). A rheological description of amylose gelation. *Carbohydrate Research, 193*, 215–226.

Dumitriu, S., Magny, P., Montane, D., Vidal, P. F., & Chornet, E. (1994). Polyionic hydrogels obtained by complexation between xanthan and chitosan: their properties as supports for enzyme immobilization. *Journal of Bioactive and Compatible Polymers, 9*, 184–209.

Dumitriu, S., & Chornet, E. (1996). Functional versatility of polyionic hydrogels. In R. A. A. Muzzarelli (Ed.). *Chitin enzymology* (Vol. 2, pp. 543–564). Italy: Atec Edizioni.

Dumitriu, S., & Chornet, E. (1998). Inclusion and release of proteins from polysaccharide-based polyion complexes. *Advanced Drug Delivery Reviews, 31*, 223–246.

Dumitriu, S., & Chornet, E. (2000). Polyionic hydrogels as support for enzyme immobilization. *Chitin Enzymology, 2*, 527–542.

Durand, D., Bertrand, C., Clark, A. H., & Lips, A. (1990). Calcium-induced gelation of low methoxy pectin solutions–thermodynamic and rheological considerations. *International Journal of Biological Macromolecules, 12*, 14–18.

Ellis, H. S., & Ring, S. G. (1985). A study of some factors influencing amylose gelation. *Carbohydrate Polymers, 5*, 201–213.

Fukuda, H. (1980). Polyelectrolyte complexes of chitosan with sodium carboxymethyl cellulose. *Bulletin of the Chemical Society of Japan, 53*, 837–840.

Fukuda, H., & Kikuchi, Y. (1978). Polyelectrolyte complexes of chitosan with carboxymethyldextran. *Bulletin of the Chemical Society of Japan, 51*, 1142–1144.

Gabriele, D., De Cindio, B., & D'Antona, P. (2001). A weak gel model for foods. *Rheologica Acta, 40*, 120–127.

Gupta, K. C., & Majeti, N. V. R. K. (2000). An overview on chitin and chitosan applications with an emphasis on controlled drug release formulations. *Journal of Macromolecular Science: Polymer Reviews, 40*, 273–308.

Ikeda, S., Kumagai, H., Sakiyama, T., Chu, C., & Nakamura, K. (1995). Method for analyzing pH-sensitive swelling of amphoteric hydrogels – Application to a polyelectrolyte complex gel prepared from xanthan and chitosan. *Bioscience, Biotechnology and Biochemistry, 59*(8), 1422–1427.

Khalid, M. N., Ho, L., Agnely, F., Grossiord, J. L., & Couarraze, G. (1999). Swelling properties and mechanical characterization of a semi-interpenetrating chitosan/polyethylene oxide network. Comparison with a chitosan reference gel. *S. T. P. Pharma Sciences, 9*(4), 359–364.

Kikuchi, Y., & Noda, A. (1976). Polyelectrolyte complexes of heparin with chitosan. *Journal of Applied Polymer Science, 20*, 2561–2563.

Kratz, G., Back, M., Arnander, C., & Larm, O. (1998). Immobilised heparin accelerates the healing of human wounds in vivo. *Scandinavian Journal of Plastic and Reconstructive Surgery and Hand Surgery, 32*, 301–307.

Lapasin, R., & Pricl, S. (1995). *Rheology of industrial polysaccharides: Theory and applications*. Blackie Academic & Professional.

Majeti, N. V. R. K. (2000). A review of chitin and chitosan applications. *Reactive and Functional Polymers, 46*, 1–27.

Martínez-Ruvalcaba, A. (2001). Rhéologie des solutions de chitosane et des hydrogels de chitosane-xanthane. Ph.D. Thesis. Québec, Canada: Université de Sherbrooke.

Martínez-Ruvalcaba, A., Chornet, E., & Rodrigue, D. (2004). Dynamic rheological properties of concentrated chitosan solutions. *Applied Rheology, 14*, 140–147.

Martínez, A., Chornet, E., & Rodrigue, D. (2004). Steady-shear rheology of concentrated chitosan solutions. *Journal of Texture Studies, 35*, 53–74.

Mireles, C., Martino, M., Bouzas, J., & Torres, J. A. (1992). Complex formation of chitosan and naturally occurring polyanions. In *Chitin and chitosan* (pp. 506–515). London: Elsevier Applied Science.

Mitchell, J. R. (1976). Rheology of gels. *Journal of Texture Studies, 7*, 313–339.

Morris, V. J., & Chilvers, G. R. (1981). Rheological studies on specific ion forms of ι-carrageenan gels. *Journal of the Science of Food and Agriculture, 32*, 1235–1241.

Morris, V. J., & Chilvers, G. R. (1983). Rheological studies of specific cation forms of kappa-carrageenan gels. *Carbohydrate Polymers, 3*, 129–141.

Nakatsuka, S., & Andrady, A. L. (1992). Permeability of vitamin-B12 in chitosan membranes – effect of cross-linking and blending with poly(vinyl alcohol) on permeability. *Journal of Applied Polymer Science, 44*, 17–28.

Noble, L., Gray, A. I., Sadic, L., & Uchegbu, I. F. (1999). A non-covalently cross-linked chitosan based hydrogel. *International Journal of Pharmaceutics, 192*, 173–182.

Pettitt, D. (1982). Xanthan. In *Food hydrocolloids* (Vol. 1, Chapter 5). Boca Raton, FL: CRC Press.

Ruel-Gariepy, E., Chenite, A., Chaput, C., Guirguis, S., & Leroux, J.-C. (2000). Characterization of thermosensitive chitosan gels for the sustained delivery of drugs. *International Journal of Pharmaceutics, 203*, 89–98.

Sakiyama, T., Chu, C., Fujii, T., & Yano, T. (1993). Preparation of a polyelectrolyte complex gel from chitosan and κ-carrageenan and its pH-sensitive swelling. *Journal of Applied Polymer Science, 50*, 2021–2025.

Sakiyama, T., Takata, H., Toga, T., & Nakanishi, K. (2001). pH-sensitive shrinking of a dextran sulfate/chitosan complex gel and its promotion effect on the release of polymeric substances. *Journal of Applied Polymer Science, 81*, 667–674.

Segeren, A. J. M., Boskamp, J. V., & van den Tempel, M. (1974). Rheological and swelling properties of alginate gels. *Discussions of the Faraday Society, 57*, 255–263.

Takka, S., & Acartürk, F. (1999). Calcium alginate microparticles for oral administration: I. Effect of sodium alginate type on drug release and drug entrapment efficiency. *Journal of Microencapsulation, 16*, 275–290.

Watson, E. L. (1966). Stress-strain and creep relationships of pectin gels. *Journal of Food Science, 31*, 373–380.

Winter, H. H. (1989). Gel point. In *Encyclopedia of polymer science and engineering* (2nd ed., pp. 343–351). New York: Wiley Science.

Winter, H. H., & Chambon, F. (1986). Analysis of linear viscoelasticity of a crosslinking polymer at the gel point. *Journal of Rheology, 30*(2), 367–382.

Winter, H. H., & Mours, M. (1997). Rheology of polymers near liquid-solid transitions. *Advances in Polymer Science, 134*, 165–234.

Zhang, Q. Q., Liu, L. R., Ren, L., & Wang, F. J. (1997). Preparation and characterization of collagen-chitosan composites. *Journal of Applied Polymer Science, 64*, 2127–2130.

Zoon, P., Roefs, S., De Cindio, B., & Van Vliet, T. (1990). Rheological properties of skim milk gels at various temperatures; interrelation between the dynamic moduli and the relaxation modulus. *Rheologica Acta, 29*, 223–230.