Investigation of Linear Viscoelastic Properties of Xanthan-Carob Mixture in Sol and Gel States

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Abstract Synergistic interactions between xanthan (X) and carob (C) were investigated by studying the linear viscoelastic behavior of X, C, and X/C mixtures at sol and gel states. At the solution state, storage modulus (G') dominates the linear viscoelastic properties of X/C mixtures. The gelation temperature (52 to 57°C) was weakly dependent on the xanthan fraction (ϕ_X) in the mixture. The ϕ_X also had a strong effect on G' until $\phi_X=0.5$. The elastic active network concentration (EANC) of X/C gels was estimated from the pseudo-equilibrium modulus. The EANC for systems with $\phi_X=0.25$, 0.5, 0.75, and 1 at 1% total concentration was 2.3, 4.4, 4.1, and 0.32 ($\times 10^{-3}$ mol/m^3), respectively. The maximum synergistic effect was observed at about $\phi_X=0.5$. The G' at the transition state of X/C mixed gel was proportional to $\omega^{3/2}$ at $\omega > \omega_{tr}$ (the onset transition frequency) compared to the theoretical limit of $\omega^{1/2}$.

Keywords: xanthan and carob, elastically active network concentration, equilibrium modulus, linear viscoelasticity, frequency spectrum

Introduction

Biopolymers were defined as proteins and polysaccharides from plant, animal, and microbial origin, in this study. Some biopolymers show an ability to form an infinite 3-dimensional network entrapping water and other constituents. In fact, without using such biopolymers it is difficult to control processing conditions, composition, and physicochemical properties of several food products, such as dairy products, processed meat products, and surimi based seafood products. One recent trend in the use of biopolymers is mixing two or more biocompatible polymers to modify physical properties of the resultant gels. The synergistic interactions between the biopolymers result in novel biocompatible gels with desirable viscoelastic properties. Mixtures of biopolymers may result in the gelation of mixture at concentrations below the minimum concentration required for gelation of the component biopolymer(s) or may even promote gelation in otherwise non-gelling systems (1). Studies of mixed biopolymer gel systems are more realistic models for foods (2).

Rheological and thermal behavior are considered as macroscopic properties of a material, and chemical structure or configuration changes of molecules are considered as microscopic properties (3). The changes in microscopic properties significantly affect the macroscopic properties of polymeric materials. Especially, rheological behavior of polymeric materials regardless of sol or gel state, are strongly dependent on the changes in structure

and configuration of molecules (3). In sol state, due to low molecular interactions, no self-supporting networks exist and material properties are characterized by viscosity. However, after gelation, due to strong molecular interactions, macromolecules are able to resist flow, and material properties are characterized by elasticity (2).

Xanthan and carob gums enhance the solution viscosity in dispersed state and are commonly used as stabilizers/thickeners in food formulations (1,4,5). Though they do not form stable gels independently, they synergistically form a stable gel network when used together. Many molecular models have been proposed to describe the synergistic interactions between xanthan and carob (6). However, due to the complicated structure of xanthan and carob mixture, these interactions are not well understood. Especially, the elastic properties of the mixed gel have not been thoroughly studied. The elastic properties of biopolymer gels, such as gelatin, are important to add commercial values into the processed foods because of its contribution on texture of final products. The elastic properties mechanically measured reflect the molecular interactions between biopolymers included in the final food product. The rubber elasticity theory is widely used to quantify the contribution of structure to the mechanical modulus (3).

The objectives of this study were to: 1) investigate dynamic rheological behavior of xanthan-carob mixture in sol and gel states and 2) determine effect of mixing ratio on the synergistic effect during gelation.

Materials and Methods

Sample preparation Laboratory grade xanthan (X) and carob (C) were used (Sigma-Aldrich, St. Louis, MO, USA). The xanthan and carob powders were solubilized separately in water at 90°C by stirring for 30 min. To

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minimize the effect of ionic compounds in water, the solutions were prepared using de-ionized water. They were blended at 85°C and mixed for 30 min at selected xanthan-to-carob (X/C) ratios, 1:3, 1:1, and 3:1. The ionized water was used as a solvent. The total polymer concentration of 0.5% (0.5 g/100 mL of 0.1 M NaCl solution) was maintained for all mixtures.

Rheological measurement Oscillatory shear (SAOS) tests were performed using the cone-and-plate (4°/40 mm) geometry in a dynamic rheometer (CVO; Bohlin Instruments Ltd., Cranberry, NJ, USA). To prevent moisture loss during experiments, mineral oil was applied around the sample edge. Temperature sweep tests were conducted at 0.1 Hz to obtain the viscoelastic properties during gelation by *in situ* cooling of the gel mixture from 75 to 25°C at a rate of –1°C/min. Frequency sweep tests were performed at 10^{-2} to 10^{1} Hz to characterize the rheological behavior of solution and gel states at isothermal conditions at 75 and 25°C, respectively. The storage (G') and loss (G'') moduli were recorded. All experiments were performed in the linear viscoelastic region by setting a target strain (1.5%), determined experimentally by stress sweep tests. All experiments were 3 times, and the average values were selected and used for further analysis.

Results and Discussion

Rheological behavior at solution state before cooling According to the polymer dynamics theory, for a prototypical liquid-like material, i.e., G'<<G'', the frequency dependence of the moduli is governed by power law relations, $G'(w) \propto \omega^m$ and $G''(\omega) \propto \omega^n$, where m=2 and n=1 (7). Our results indicate that at 75°C, C and X/C solutions exhibited a typical linear viscoelastic behavior of a diluted polymer solution with m=2.0 (R^2=0.99) and 1.7 (R^2=0.99), and n= 1.1 (R^2=0.98) and 0.9 (R^2=0.94), respectively in the frequency region studied (Fig. 1). However, G' and G'' of X was relatively independent of frequency (m=0.83, n= 0.28), compared to those of X/C and C. This relative frequency independence implies that at high temperatures, xanthan solution behaves more like a pseudo-gel than like a dilute polymer solution, even without any crosslinks present in the system. This 'weak' gel behavior may be due to the highly stiff xanthan backbone in contrast to the flexible coil structure found in other polysaccharide solutions (8). In addition, the exponents value of X/C showed more deviation from the prototypical value than that of C. It might be due to the increase of X portion in the solution.

At some high frequency range, the G' values are higher than G'' for X, C, and X/C solutions (Fig. 1), although the prototypical rheological behavior of liquid-like fluid is known to be dominated by G'' (i.e., G''>>G'). According to the molecular theory, when the molecular weight (Mw) of polymer is sufficiently high, i.e., >20,000, G' may dominate a high frequency region because molecular ends do not influence the monomeric friction coefficient (7,9,10). Because of the high Mw of X (about 500,000) and C (about 300,000), respectively (11), the G'-dominated rheological behavior was observed in this study.
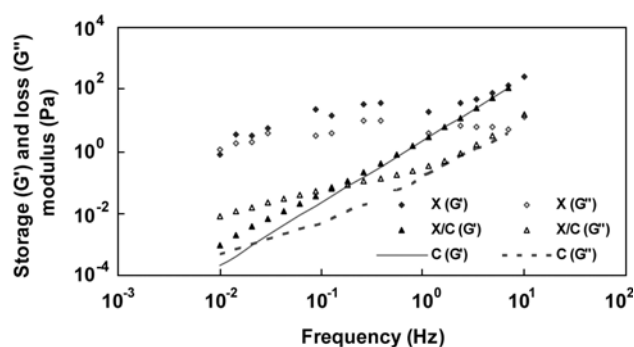

Fig. 1. Frequency spectrum of pre-gel solutions of xanthan (X), and carob (C) and 1:1 xanthan-carob (X/C) mixture at 75°C.
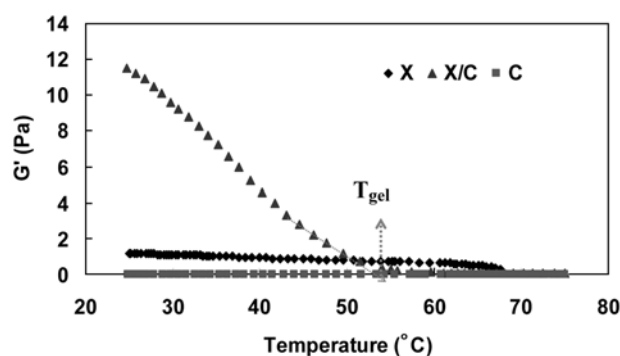

Fig. 2. Storage modulus (G') of xanthan (X) and carob (C), and 1:1 xanthan-carob (X/C) mixture during cooling from 75 to 25°C at 1 Hz. T_{gel}=gelation temperature.

Changes in G' during cooling During the temperature sweep from 75 to 25°C, G' of xanthan and carob solutions did not show any appreciable increase (Fig. 2). However, G' of the X/C mixture began to increase substantially at about 55°C. The interactions between X and galactomannan groups of C have been described by a junction-zone model (12). This invokes a direct association between the double helix of X and unsubstituted regions of C. Since the conformational transition temperature of X molecules in 0.1 M NaCl has been estimated to be about 55°C (2), the gelation due to the association of X and C occurs immediately after the conformational transition of X. The significant increase in G' of the X/C mixture indicates that the junction zone association between X and C may begin at about 55°C.

Rheological behavior at gel state after cooling At 25°C, C maintained the typical linear macromolecular solution behavior, i.e., m=2, and the pure xanthan and X/C mixture exhibited a 'weak gel' and a gel behavior, respectively, with some plateau region where the modulus is independent of frequency (Fig. 3). According to molecular dynamics, the modulus at plateau indicates a pseudo-equilibrium modulus (G_e) of entanglement or lightly cross-linked network. The G_e is considered the most important parameter to explain the conceptual scheme of entanglement coupling and to quantify the structural contribution to mechanical modulus (7). It is defined as:
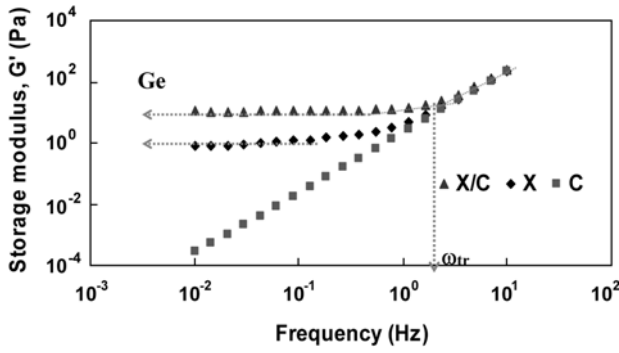
Fig. 3. Frequency spectrum of xanthan (X), carob (C), and 1:1 xanthan-carob (X/C) gel at 25°C. G_e=pseudo-equilibrium modulus, ω_{tr}=onset transition frequency.

$$G_e = g\nu_e RT = g\left(\frac{\rho}{M_e}\right)RT \qquad (1)$$

where, G_e=pseudo-equilibrium modulus; g=a numerical factor; ν_e=the moles of network strands/unit volume, ρ =density, M_e=the average molecular weight between coupling loci or crosslinks, R=universal gas constant, and T=absolute temperature.

The Eq. 1 describes the relation between the concentration (microscopic contribution) and the mechanical modulus (macroscopic property). This equation, called the rubber elasticity theory, is derived based on the entropic elasticity. According to this, the modulus increases with temperature due to an increase in entropy. Although biopolymer gels do not follow such temperature dependency, this relation is useful to interpret the concentration or structural effects on the mechanical modulus at the isothermal state.

The ν_e, also called the elastic active network concentration (EANC), is directly proportional to the equilibrium modulus, and it quantitatively indicates the structural contribution to the mechanical modulus. In general, g is assumed to be unity. Then, from Fig. 3, G_e and EANC of X/C and X were estimated to be about 10.90 and 0.98 Pa and 4.4 and 0.4 ($\times 10^{-3}$ mol/m^3), respectively. Based on these values, it is clear that EANC of the X/C mixture increases several folds compared to that of X alone just by virtue of adding C, although the total polymer concentration was 0.5% for all systems. This EANC increment, calculated as below, was about 21.

$$\text{EANC increment} = \frac{(\text{EANC of X/C}) - (\phi_X)(\text{EANC of X})}{(\phi_X)(\text{EANC of X}) + (\phi_C)(\text{EANC of C})}$$

where, ϕ_x and ϕ_c=the mass fraction of X and C, respectively in the X/C mixture.

A 'transition zone' may be observed in the frequency spectrum of X and X/C (Fig. 3). This indicates that, as time or frequency is varied, the magnitude of modulus changes from rubberlike to glasslike (7). In the high frequency region (>0.785 and >0.183 Hz for X/C and X, respectively), the modulus is strongly dependent on frequency (Fig. 3). The position of the transition zone in time or frequency scale is the most striking feature that varies for different polymers, because the position is directly related to the monomeric friction coefficient (ζ_0) whose magnitude sets

the time scale according to the molecular dynamic theory (14). The upper level of the onset point, i.e., from glasslike consistency to the beginning of the transition zone, has been somewhat arbitrarily selected to be the frequency where G'=10^7 Pa (7). However, our biopolymer gel system did not exhibit such a high G' value over the frequency region studied. An graphical estimation based on the extrapolation indicates an extremely high frequency, i.e., approximately 10^7-10^8 Hz. It implies that a glasslike region was not obtained for our system at 25°C due to its low glass transition temperature. Therefore, the onset of the transition zone was estimated to be at the boundary between the transition zone and the rubberlike plateau region. The onset frequency, ω_{tr}, was defined at the intersection of lines representing the plateau and increasing modulus regions, as illustrated for X/C curve in Fig. 3. The ω_{tr} values were determined to be 0.95 Hz for X/C and 0.22 Hz for X. According to the Rouse-Mooney theory, the ω_{tr} is inversely proportional to the longest relaxation time in the transition zone (τ_{tr}) (7):

$$\omega_{tr} = \frac{8}{\pi^2 \tau_{tr}} \qquad (2)$$

The longest relaxation times of X/C and X in the transition zone were estimated to be 7.4 and 1.7 sec, respectively. Compare to τ_{tr} of X, higher values of τ_{tr} of the X/C mixture might be because of the higher EANC structurally contributing to increase the solid-like property in the gel. In addition, t_{tr} is related to other parameters shown in the Eq. 3 (7):

$$\tau_{tr} = \frac{a^2 P_e^2 \xi_0}{6\pi\, KT} \qquad (3)$$

where, K=Boltzman constant, a=characteristic length, and ζ_0=monomeric friction coefficient. The number of monomers between crosslinks (P_e) is defined as (6):

$$P_e = \frac{M_e}{M_0} = \frac{1}{M_0}\left(\frac{\rho}{\nu_e}\right) \qquad (4)$$

where, M_0=molecular weight of monomer. If the differences in M_0, r, and a of X, C, and X/C are not significant, then the ζ_0 expressed as:

$$\zeta_0 = A\frac{\tau_{tr}}{\nu_e^{-2}}, \text{ where } A = \frac{6\pi^2 M_0^2 KT}{a^2 \rho^2} \qquad (5)$$

Then, the difference between X and X/C solely depends on the ratio of τ_{tr} to $(\nu_e)^{-2}$. Thus, the monomeric friction coefficient of X/C is about 526 times of that of X. That is,

$$\frac{\zeta_0 \text{ of X/C}}{\zeta_0 \text{ of X}} = \frac{(\tau_{tr} \text{ of X/C})/(\nu_0 \text{ of X/C})^{-2}}{(\tau_{tr} \text{ of X})/(\nu_0 \text{ of X})} = 526$$

Based on the above derivation procedure to obtain the monomeric friction coefficient, it should be noticed here that the monomeric friction coefficient is proportional to the second power of EANC.

In addition, the magnitude of G' of the X/C gel was substantially higher compared to that of the X/C solution at
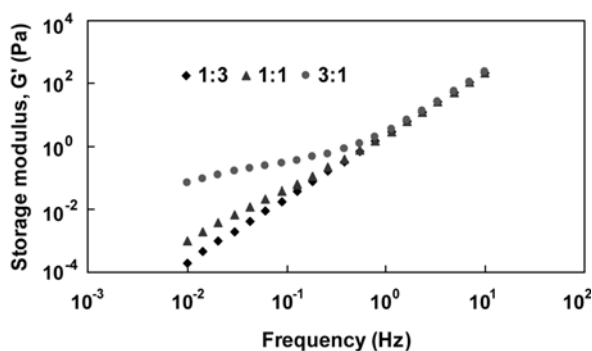
Fig. 4. Frequency spectrum of X/C mixture (1:3, 1:1, and 3:1) in solution state at 75°C.

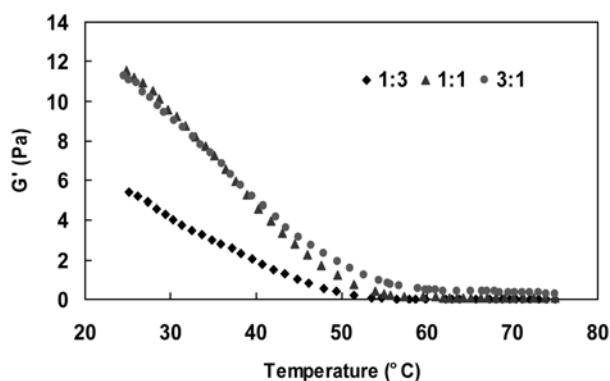Fig. 6. Frequency spectrum of X/C mixture (1:3, 1:1, and 3:1) in gel state at 25°C.

Fig. 5. Change in storage modulus (G') of different X/C mixture (1:3, 1:1, and 3:1) during temperature sweep from 75 to 25°C.

75°C (Fig. 1 and 3). The G' of xanthan and carob did not change appreciably after the cooling process. It clearly indicates that although xanthan and carob do not form a gel, when mixed together, they synergistically interact and form a gel, and there exists a phase transition from sol to gel state at about 55°C.

Effect of mixing ratio The dependence of rheological properties on X/C ratio before, during, and after cooling, are shown in Fig. 4, 5, and 6, respectively. At 75°C, rheological behavior of most of X/C mixtures, beside 3:1 X/C, showed linear viscoelastic properties of macromolecular solution. However, the frequency dependence of modulus was strongly dependent on the X/C ratio (Fig. 4). In the low frequency region (0.01-1.0 Hz), the higher the mass fraction of xanthan (ϕ_X), the higher the G'. In general, modulus in low frequency region, equivalent to the long time scale, indicates the equilibrium behavior of molecules. In the case of X/C mixture, the rigid properties of xanthan chain apparently dominates the mechanical properties of the solution state.

At all X/C ratios studied, the typical gelation behavior described earlier was observed-increasing moduli with a phase transition at slightly lower than the configurational transition temperature of xanthan 55°C (Fig. 5). The ϕ_X had a strong effect on the synergistic interaction (as measured by increasing G') as the ϕ_X changed from 0.25 to 0.5 (i.e., 1:3 to 1:1 X/C ratio). When $\phi_X>0.5$, the ϕ_X fraction did not seem to positively contribute to the gel strength beyond
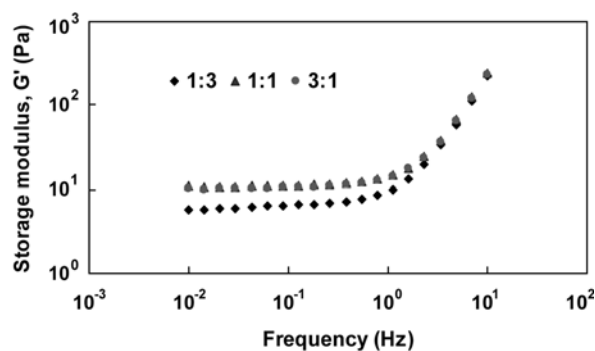
what was observed at $\phi_X=0.5$. Thus, 1:1 mixing of xanthan and carob can be considered optimal to facilitate the most synergistic interactions (7).

According to Eldridge and Ferry (14), the gelation temperature (or melting temperature) is dependent on polymer concentration and molecular weight. In case of melting of gelatin gels, the melting temperature increased with higher molecular weight and polymer concentration (14). In this study, the difference of gelation temperature of different ratio of X/C was slightly dependent on the X/C ratio. Higher ϕ_x shows higher gelation temperature, i.e., 56.6, 55.1, and 51.9×C ($p<0.05$) at $\phi_x=0.75$, 0.5, and 0.25, respectively. It may be because the higher xanthan portion has higher probability to find a suitable molecular pair to form X/C association.

The G' values of different ratio of X/C at the gel state (25°C) are compared in Fig. 6. Although the modulus of 1:1 gel was higher than that of 3:1 gel, the difference was not significant ($p<0.01$, ANOVA). All mixtures showed both plateau and transition zones in the frequency spectrum. The EANC and τ_{tr} for different X/C ratios, calculated using Eq. 1 and 2, respectively, were fitted to second-order polynomial trend lines (Fig. 7). The dotted lines on Fig. 7 represent extrapolations for a system of pure C. Since no plateau regions were observed for C (Fig. 3), the EANC was assumed zero. The τ_{tr} of C is not measurable by the onset frequency, but it must be much longer than that of pure X. Higher interactions between X and C result in higher EANC, so that the elastic portions in X/C mixed gel have to be the maximum at the highest interaction. Consequently, since the relaxation time is the ratio of the viscosity to elasticity (7), the τ_{tr} of X/C mixed gel must be the shortest at the maximum interaction. Then, obviously, the highest interaction or synergistic effect between X and C is observed at just beyond $\phi_x=0.5$. The highest interaction between X and C in X/C mixed gels have been evaluated in other ways. Williams *et al.* (15), used the breaking force of the X/C mixed gel. They reported that the highest synergistic effect was obtained for the 1:1 X/C gel at 1.2% of total concentration. This synergistic effect has also been shown to be a function of total polymer concentration. According to Tonton *et al.* (16), the highest synergistic effect was observed at $\phi_x=0.4$, 0.6, and 0.6 for X/C gels prepared using total polymer concentrations of 0.5, 0.4, and 0.3%, respectively.
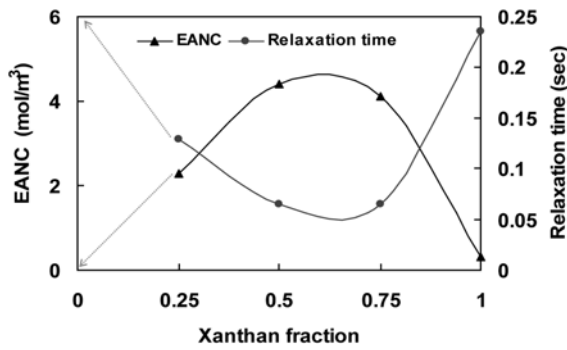
Fig. 7. Effect of xanthan fraction (ϕ_x) on the elastic active network chain (EANC) concentration and the longest relaxation time. The dotted lines are extrapolated at $\phi_x = 0$.

Fig. 8. Comparison with the modified Rouse theory. The G' values (X/C = 1:1) are normalized dividing by the equilibrium storage modulus, and the frequency is normalized by multiplying with the longest relaxation time. The dotted line indicates the Rouse limit, i.e., $G' \approx \omega^{1/2}$. The symbol i indicates the ith element of relaxation time in Eq. 7.

Estimation of viscoelastic property of solutions The molecular motions are directly related to the macroscopic properties. The theory of Rouse is based on the change in free energy associated with the entropy decrease for nonrandom configurations and the tendency of the system to diffuse toward a random state (7). According to the Rouse theory, the macroscopic property, G', of dilute polymer solution is defined as:

$$G' = nKT \sum_{i=1}^{N} \left(\frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} \right) \qquad (6)$$

where, n=the number of polymer molecules/cubic centimeter and τ=relaxation time. The Eq. 6 represents the relation between G' and the number density of polymer in the frequency spectrum. However, when the polymers have crosslinks, there is a plateau region in a certain frequency region, and the equilibrium modulus is defined per Eq. 1. Thus, the number density of polymer in the Eq. 6 can be replaced with the EANC defined as Eq. 1. Accordingly, the Rouse theory for the crosslinked system was modified from the Eq. 6 (7):

$$G' = \nu RT \left[1 + \sum_{i=1}^{N} \left(\frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} \right) \right] \qquad (7)$$

The first term of right hand side of Eq. 7 represents the plateau region, and the second term the transition zone between rubberlike plateau and glassy regions in the frequency spectrum.

Figure 8 is a double logarithmic plot of the normalized G' of 1:1 X/C gel against the normalized frequency. Theoretically, the modified Rouse theory shows square root dependence in double logarithmic scale as frequency increases above the onset frequency (i.e., G' proportional to $\omega^{1/2}$ for $\omega > \omega_{tr}$) (7,17). However, we observed a big deviation between theoretical and experimental data (Fig. 8). A model with 3 relaxation elements, such as $\tau_1 = 5.104$, $\tau_2 = 5.101$, $\tau_3 = 5.101$ ($\times 10^{-2}$ sec), showed the limiting behavior of the modified Rouse model. The G' of X/C gel at frequencies above ω_{tr} showed higher frequency dependence (G' proportional to $\omega^{2/3}$). According to the cluster model of van der Vorst *et al*. (17), the cluster connecting with 6 neighboring beads was able to describe higher frequency de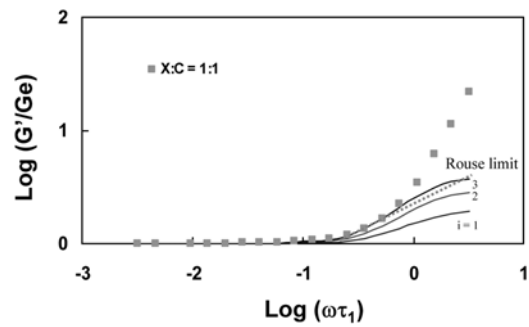pendence of G' values of weakly aggregating or ordering colloids. Stronger frequency dependence of G' of X/C gel may be due to the influence of coordination number used in the Rouse theory. The coordination number for the linear Rouse chain is 2, because every bead is connected to 2 neighboring beads (7). In our study, the limiting behavior of the X/C gel is in agreement with the predicted values derived (17). It may be because X/C mixed gels form clusters due to intermolecular interactions between unsubstitued mannan backbone and xanthan helices as well as the self-association of xanthan molecules.

In conlcusion, the xanthan (X) and carob (C) gums interact synergistically forming a stable gel network. The frequency spectrum at 75°C showed nearly viscoelastic solution state, for C and X/C. During cooling, only X/C mixture increases the modulus. Higher gelation temperature was observed at higher ϕ_x. Based on rheological properties (i.e., the pseudo-equilibrium modulus, EANC, and the longest relaxation time), the optimal interaction between X and C occurs at about 1:1 X/C ratio. The optimal interaction observed 1:1 ratio might be because of the highest probability to form the junction zone between the helical structure of xanthan and the carob gums. Such junction zones formed by interaction of 2 polymers increased the mechanical modulus. The structural contribution to the mechanical modulus by mixing 2 components was estimated and compared based the EANC. The G' at the above the onset frequency was proportional to $\omega^{2/3}$.

Acknowledgment

References

1. Higiro J, Herald TJ, Alavi S, Bean S. Rheological study of xanthan and locust bean gum interaction in dilute solution: Effect of salt. Food Res. Int. 40: 435-447 (2007)
2. de Jong S, van de Velde Fred. Charge density of polysaccharide controls microstructure and large deformation properties of mixed gels. Food Hydrocolloid 21: 1172-1187 (2007)
3. Sperling LH. Introduction to Physical Polymer Science. John Wiley & Sons, Inc., New York, NY, USA. pp. 382-457 (1992)

4. Rao MA. Phase transition, food texture, and structure. Vol.1, pp. 36-62. In: Texture in Food: Semi-solid Food. McKenna B (ed), Woodhead Publishing Ltd. and CRC Press LLC., Cambridge, England (2003)

5. Nishinari K, Zhang H, Ikeda S. Hydrocolloid gels of polysaccharides and proteins. Curr. Opin. Colloid In. 5: 195-201 (2000)

6. Urlacher B, Noble O. Xanthan gum. pp. 284-311. In: Thickening and Gelling Agents for Food. 2nd ed. Imeson A (ed). Blackie Academic and Professional, New York, NY, USA (1992)

7. Ferry JD. Viscoelastic Properties of Polymers. John Wiley & Sons, New York, NY, USA. pp. 177-263 (1980)

8. Morris ER. Mixed polymer gels. pp. 327-344. In: Food Gels. Harris P (ed). Elsevier Applied Science, New York, NY, USA (1990)

9. Ferry JD, Landel RF, Williams ML. Extension of the Rouse theory of viscoelastic properties to undiluted linear polymers. J. Appl. Phys. 26: 359-362 (1955)

10. Berry GC, Fox TG. The viscosity of polymers and their concentrated solutions. Adv. Polym. Sci. 5: 261-357 (1968)

11. Lapasin R, Pricl S. Rheology of Industrial Polysaccharide-Theory and Application. Blackie Academic and Professional, New York, NY, USA. pp. 76-78 (1995)

12. Rees DA. Structure, conformation, and mechanism in the formation of polysaccharide gels and networks. Adv. Carbohyd. Chem. Bi. 24: 267-332 (1969)

13. Graessley WW. The entanglement concept in polymer rheology. Adv. Polym. Sci. 16: 1-179 (1974)

14. Eldridge JE, Ferry JD. Studies of the cross-linking process in gelatin gels. III. Dependence of melting point on concentration and molecular weight. J. Phys. Chem.-US 58: 992-995 (1954)

15. Williams PA, Day DH, Langdon MJ, Phillips GO, Nishinari K. Synergistic interaction of xanthan gum with glucomannans and galactomannans. Food Hydrocolloid 4: 489-493 (1991)

16. Tonon C, Cuvelier G, Launay G. Rheological properties of xanthan/carob mixture in the diluted and semidiluted concentration regimes. pp. 335-344. In: Physical Networks, Polymers, and Gels. Burchard W, Ross-Murphy SB (eds). Elsevier Applied Science, London, UK (1990)

17. van der Vorst B, Toose EM, van den Ende D, Mellema J. Generalized rouse model for a dilute solution of clustered polymers. Rheol. Acta 34: 274-280 (1995)