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Rheological study of xanthan and locust bean gum interaction in dilute solution

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Abstract

An oscillatory capillary rheometer was used to investigate visco-elastic properties of xanthan and locust bean gum (LBG) blends in dilute solution. Gums were evaluated for intrinsic viscosity and the elastic component. Molecular conformation of the complex of xanthan–LBG was assessed by the power law and the Huggins equations. A 60% xanthan–40% LBG blend exhibited the strongest attraction between xanthan and LBG molecules as evidenced by a greater intrinsic viscosity, the polymer miscibility coefficient α, the elastic component, and a positive Huggins coefficient K_m. The power-law model was successfully applied to predict the molecular conformation of xanthan and LBG alone in dilute solution and was exhibited as rod-like and random coil conformation. The power-law coefficient b increased as the LBG fraction increased in the blends, suggesting a more flexible xanthan–LBG complex dependent on LBG.

Keywords: Gums; Rheology; Viscosity; Intrinsic viscosity; Elasticity

1. Introduction

Xanthan gum is a microbial heteropolysaccharide composed of a 1-4-linked β-D-glucose backbone substituted with a trisaccharide side chain that is composed of two mannoses and one glucuronic acid at every second residue (Nussinovitch, 1997). The side chains bind to the helical backbone and stabilize the helical structure (Moorhouse, Walkinshaw, & Arnott, 1977), thus making the molecule a rather stiff rod with extraordinary stability to heat, acid, and alkali (Whistler & BeMiller, 1997). Greater viscosity and pseudoplasticity result from xanthan gum solutions due to formation of high-molecular-weight aggregates of stiff rod molecules (Whistler & BeMiller, 1997).

Locust bean gum (LBG) is a plant seed galactomannan, composed of a 1-4-linked β-D-mannan backbone with 1-6-linked α-D-galactose side groups (Dea & Morrison, 1975). Physico-chemical properties of galactomannans are strongly influenced by the galactose content (Morris, 1990) and the distribution of the galactose units along the main chain (Launay, Doublier, & Cuvelier, 1986). Longer galactose side chains yield stronger synergistic interactions with other polymers (Morris, 1990) and greater functionality (Launay et al., 1986).

Xanthan gum is well known to yield a strong interaction with galactomannans, and this property is exploited in food applications in which thickening or gelling is desired. The synergistic interaction between xanthan and

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galactomannans (LBG and guar gum) was first pointed out by Rocks (1971), who reported that xanthan gum formed thermoreversible gels with LBG but not with guar gum. In further studies, Morris, Rees, Robinson, and Young (1980) confirmed that the interaction between xanthan and galactomannans arose from intermolecular binding rather than from mutual exclusion of incompatible molecules. Tako, Asato, and Nakamura (1984) studied the interaction between xanthan and LBG by using rheological procedures, and suggested that the interaction occurs between xanthan side chains and the LBG backbone as in a lock-and-key model, in which one xanthan chain could associate with one, two, or more LBG molecules. Cairns, Miles, and Morris (1986) and Cairns, Miles, Morris, and Brownsey (1987) used an X-ray diffraction method to study xanthan–LBG interaction, and suggested the necessity to denature xanthan at temperatures exceeding the helix–coil transition temperature for binding to occur. Cuvelier and Launay (1988) studied the interaction between xanthan and LBG at very low concentrations and in the presence of 0.1 mol dm^{-3} NaCl by using low-shear rheometry, and they concluded that super aggregates formed into a network structure. Cairns et al. (1986) suggested that association between xanthan and LBG occurred because of disordered xanthan chains. In contrast, Williams, Clegg, Day, Phillips, and Nishinari (1991), using DSC and rheological methods, reported that the association xanthan–LBG is triggered by xanthan conformational change. Wang, Wang, and Sun (2002), using texture analysis and Ubbelohde capillary viscometry, recently investigated the effect of xanthan chain deacetylation on the interaction between xanthan and LBG. The authors observed a conformational change for xanthan in the presence of LBG, despite the stabilization of the xanthan helical structure with salt.

Although many efforts continue to elucidate xathan–LBG synergistic interaction, the research findings are under debate (Wang et al., 2002). To date, much work has been accomplished on the gelling properties of gums and their inherent visco-elastic properties, as evidenced by many published papers; evaluation of gums in solution has been studied to a lesser extent (Casas & Garcia-Ochoa, 1999; Cuvelier & Launay, 1986), and most of the research was performed by using the Ubbelohde or rotational viscometer. Advancements in capillary rheometry now allow for improved, reproducible observation of the elastic component in a dilute solution, which could not be measured with an Ubbelohde or rotational viscometer (Yaseen, Herald, Aramouni, & Alavi, 2005). In this study, a sensitive oscillatory rheometry technique was employed to determine to what extent xanthan and LBG interaction occurs in dilute solution. To capture this interaction, different intrinsic viscosity models and the elastic component for the gum blends were used to determine if any conformational change or interaction occurred between xanthan and LBG in dilute solution.

2. Materials and methods

2.1. Materials and solutions preparation

Xanthan gum and locust bean gum (LBG) were purchased from Sigma (Sigma–Aldrich, St. Louis, MO). The stock solutions (0.1% m/v) were prepared by mixing 0.1 g of dry sample with deionized distilled water while continuously stirring at ambient temperature. The solutions were heated for 30 min at 80 °C in a water bath to completely solubilize the gums, then were cooled and immediately dialyzed against deionized distilled water for 72 h with a dialyzing tube (Snakeskin TM Pleated Dialysis Tubing, Pierce, Rockford, IL), which was designed to let through compounds with a molecular weight of 10 kDa or less.

To study the interaction between gums, the following treatments were considered: xanthan 100%, xanthan 80%–LBG 20%, xanthan 60%–LBG 40%, xanthan 20%–LBG 80%, and LBG 100%. Stock solutions were stirred at room temperature after dialysis, diluted with deionized distilled water to a final concentration of 0.025% (m/v), and blended as previously stated. The concentration of each solution was determined by the phenol–sulfuric method (Dubois, Giles, Hamilton, Rebers, & Smith, 1956).

2.2. Density measurement

The densities of the solutions were determined with a standardized 10-mL pycnometer (Bradly, 1998). The mass of the solution was calculated from the weight difference between the empty pycnometer (Kmax®, Kimble Glass Inc., Vineland, NJ) and the filled vessel. The pycnometer filled with each respective gum solution was incubated at 20 °C for 1 h (Equatherm, Lab-Line Instruments Inc., Melrose Park, IL) to equilibrate the sample before density determinations (Yaseen et al., 2005).

2.3. Rheological properties

The elastic and viscous components of each gum solution and of the blends were measured as a function of oscillating shear rate by using an oscillating capillary rheometer (Viscoelasticity Analyzer, Vilastic 3, Vilastic Scientific Inc., Austin, TX), which is specifically engineered to measure the oscillatory viscosity of fluids. The viscoelasticity analyzer is based on the principles of generating oscillatory flow at a selected frequency within a straight, cylindrical, stainless steel tube (0.0504 cm radius and 6.038 cm length).

The fluid in the capillary tube is forced into oscillatory flow at a selected frequency, during which the pressure gradient and the volume flow are monitored. Precise resolution of magnitude and phase of the pressure and volume flow allows calculation of the viscous and elastic components of the shear stress, shear rate, and shear strain at the tube wall (Thurston, 1960, 1996).

The viscosity and elasticity were determined at a frequency of 2 Hz (Thurston, 1996) within a shear-rate range of 0.8–20 s^{-1}. Morris and Taylor (1982) reported that oral perception of solution viscosity correlated well with viscosity measurements at 10 s^{-1}. Thus, all viscosity and elasticity measurements were statistically assessed at 10 s^{-1}. Rheological measurements were carried out at 20 °C by using a temperature-controlled circulating water bath (Haake DC5, Gebr. Haake GmbH, Karlsruhe, Germany). The viscoelasticity analyzer was calibrated with deionized distilled water at 20 °C, followed by the verification procedure to further ensure that the rheometer was operating at optimum conditions.

Microsoft Excel 2000 (Microsoft Corporation, Seattle, WA) was used to plot viscosities against concentrations, as well as to obtain linear regression lines with the corresponding equations and correlation coefficients (R^2) in order to assess the best model.

2.4. Intrinsic viscosity determination

The intrinsic viscosity $[\eta]$ is a measure of the hydrodynamic volume occupied by a macromolecule, which is closely related to the size and conformation of the macromolecular chains in a particular solvent (Lai & Chiang, 2002). The intrinsic viscosity $[\eta]$ is determined experimentally from measurements of the viscosity of very low concentration (C) solutions. Denoting solution and solvent viscosity as, respectively, η_{solution} and η_{solvent}, $[\eta]$ is defined by the following relationships:

$$\text{Relative viscosity:}\quad \eta_{\text{rel}} = \eta_{\text{solution}}/\eta_{\text{solvent}}. \tag{1}$$

$$\text{Specific viscosity:}\quad \eta_{\text{sp}} = \eta_{\text{rel}} - 1. \tag{2}$$

$$\text{Intrinsic viscosity:}\quad [\eta] = \lim_{C\to 0} \frac{\eta_{\text{sp}}}{C}. \tag{3}$$

The intrinsic viscosity can be obtained by measuring specific viscosities at different concentrations at the same shear-rate, and extrapolating the course of specific viscosity to infinite dilution (Heitmann & Mersmann, 1995). The intrinsic viscosity $[\eta]$ is, therefore, obtained by extrapolating data to zero concentration by using a linear regression, which will be called the graphic double-extrapolation procedure (GDEP) in this study. McMillan (1974) showed that $\frac{\eta_{\text{sp}}}{C}$ could be written in the form of Huggins' equation (Huggins, 1942):

$$\frac{\eta_{\text{sp}}}{C} = [\eta] + k'[\eta]^2 C, \tag{4}$$

where k' is the Huggins constant. The determination of the intrinsic viscosity is, therefore, the extrapolation of $\frac{\eta_{\text{sp}}}{C}$ to the value at zero solute concentration. The extrapolations are usually done for relative viscosity values between 1.2 and 2.0, the corresponding specific viscosities being between 0.2 and 1.0 (Da Silva & Rao, 1992). In the present work, gum solutions were therefore diluted to be within the described range. In addition, McMillan (1974) reported that the intrinsic viscosity could be obtained from the Kraemer's equation (Kraemer, 1938) by extrapolation to zero concentration (C):

$$\frac{\ln \eta_{\text{rel}}}{C} = [\eta] + k''[\eta]^2 C, \tag{5}$$

where k'' is the Kraemer constant. For very dilute solutions, however, Eq. (5) can be shortened by retaining only the first-order term, and $[\eta]$ can be determined from the slope of a plot of C against $\ln \eta_{\text{rel}}$ (Sornsrivichai, 1986). McMillan (1974) showed that methods of determination of the intrinsic viscosity that were based on slopes of plots had higher correlation coefficients and lower standard errors, compared with those based on intercepts of plots. On the basis of such findings, Tanglertpaibul and Rao (1987) used the following equations to obtain the intrinsic viscosity of tomato serum:

$$\eta_{\text{rel}} = 1 + [\eta]C. \tag{6}$$

The intrinsic viscosity $[\eta]$ is the slope obtained by plotting η_{rel} vs. C

$$\eta_{\text{rel}} = e^{[\eta]C}. \tag{7}$$

The intrinsic viscosity $[\eta]$ is the slope obtained by plotting $\ln \eta_{\text{rel}}$ vs. C

$$\eta_{\text{rel}} = \frac{1}{1 - [\eta]C}. \tag{8}$$

The intrinsic viscosity is the slope obtained by plotting $1 - \frac{1}{\eta_{\text{rel}}}$ vs. C.

The intrinsic viscosity $[\eta]$ was estimated based on the slope of η_{sp} vs. C for polyelectrolytes, as suggested by Chou and Kokini (1987), this is similar to the method discussed in Eq. (6). Chou and Kokini (1987) reported that when there is essentially no molecular interaction, as in dilute solutions, the second term of the Huggins equation (Eq. (4)) is negligible, and a plot of η_{sp} against concentration is linear. Particularly in this study, the intrinsic viscosity in the dilute domain was estimated on the basis of Eqs. (3), (6), (7) and (8), and the four methods were statistically compared for a better fit.

2.5. Determination of the molecular conformation and polymer interaction

The power-law equation:

$$\eta_{\text{sp}} = aC^b \tag{9}$$

was used to estimate the exponent b from the slope of a double logarithmic plot of η_{sp} against concentration, and provides an indication of the conformation of polysaccharides (Lai, Tung, & Lin, 2000). To determine xanthan–LBG interaction, the verified theory (Chee, 1990; Sun, Wang, & Feng, 1992), based on the classical Huggins equation expressing the specific viscosity (η_{sp}) of a polymer as a function of polymer concentration C, was used:

$$\frac{\eta_{sp}}{C} = [\eta] + bC \tag{10}$$

and

$$b = K[\eta]^2, \tag{11}$$

where $[\eta]$ is the intrinsic viscosity, and b and K are Huggins parameters.

According to this theory, the following equation applies to a ternary polymer–polymer–solvent dilute solution, in which there is no aggregation between molecules:

$$\alpha = b_m - (\sqrt{b_1}W_1 + \sqrt{b_2}W_2)^2, \tag{12}$$

where b_m, b_1, and b_2 are the Huggins coefficients for blend, polymer 1 and polymer 2, respectively. W_i is the weight fraction of polymer i in the polymer blend ($i = 1$ or 2). The equation may be used to provide qualitative information on polymer–polymer interaction: two polymers are attractive in solution when $\alpha \geqslant 0$, whereas they are repulsive when $\alpha < 0$ (Wang, Sun, & Wang, 2001). Three types of interaction contribute to the value of b_m for a ternary polymer–polymer–solvent interaction (Cragg & Bigelow, 1955):

1. Long-range hydrodynamic interaction of pairs of single molecules:

$$b_{m1} = b_1W_1^2 + b_2W_2^2 + 2\sqrt{b_1b_2}W_1W_2 = \left(\sqrt{b_1}W_1 + \sqrt{b_2}W_2\right)^2, \tag{13}$$

   where b_i is the Huggins parameter b for component i ($i = 1$ or 2). W_i is the weight fraction of polymer i in the blend.
2. The formation of double molecules. This assumes actual contact:

$$b_{m2} = K'([\eta]_2 - [\eta]_1), \tag{14}$$

   where $[\eta]_1$ and $[\eta]_2$ are intrinsic viscosities of double- and single-molecule species, respectively, and K' is a constant. In the absence of aggregation between molecules and at sufficiently low concentrations, this term is neglected.
3. Intermolecular attraction or repulsion:

$$b_{m3} = \alpha, \tag{15}$$

   where $\alpha \geqslant 0$ means attraction, whereas $\alpha < 0$ means repulsion.
   Therefore,

$$b_m = b_{m1} + b_{m2} + b_{m3} \approx b_{m1} + b_{m3}, \tag{16}$$

$$b_m = (\sqrt{b_1}W_1 + \sqrt{b_2}W_2)^2 + \alpha, \tag{17}$$

$$\alpha = b_m - (\sqrt{b_1}W_1 + \sqrt{b_2}W_2)^2. \tag{18}$$

By measuring b_m from the Huggins equation for polymer–polymer–solvent solution, α was calculated and the interaction was characterized.

2.6. Statistical analysis

Intrinsic viscosity data was used to generate the best-fitting model by using a two-way factorial design. The gum blends were compared for their elastic component, the miscibility coefficient α, and the Huggins coefficient K_m by using a completely randomized design. In each instance, three replications were made. The analysis of variance and means comparison were conducted by the general linear models procedure (Proc GLM), with Statistical Analysis System software (version 8.2, SAS Institute, Inc., Cary, NC). Comparisons among treatments were analyzed by using Fisher's least significant difference (LSD), with a significance level at $P < 0.05$.

3. Results and discussion

3.1. Intrinsic viscosity

In general, for all blends of xanthan and LBG, an increase in specific viscosity was observed as the concentration decreased (Fig. 1), but a more pronounced increase in specific viscosity was evident for concentrations less than 0.008 g/dl. The GDEP therefore failed to generate the intrinsic viscosity for xanthan gum and xanthan–LBG blends. The data did not fit with the linear regression model. Lapasin and Pricl (1995) reported that neutral polysaccharides (i.e., LBG) exhibited linear plots of lower slope, whereas ionic polysaccharides (i.e., xanthan) displayed a sharp increase of the slope, possibly due to expanded coil dimensions and electrostatic repulsion between chain segments. Pals and Hermans (1952) reported that $\frac{\eta_{sp}}{C}$ increased rapidly at greater dilutions in sodium pectate without salts. Our results showed an increase of $\frac{\eta_{sp}}{C}$ for xanthan and xanthan–LBG blends as gum concentration decreased. This observation may be due to the removal of counterions during dialysis.

For LBG, the Huggins and Kraemer plots (Fig. 2) provided a better fit and, therefore, were selected as the best methods for intrinsic viscosity estimation. From Eq. (4), the Huggins constant k' theoretically should lie between 0.3 and 0.8, and values larger than 1 imply

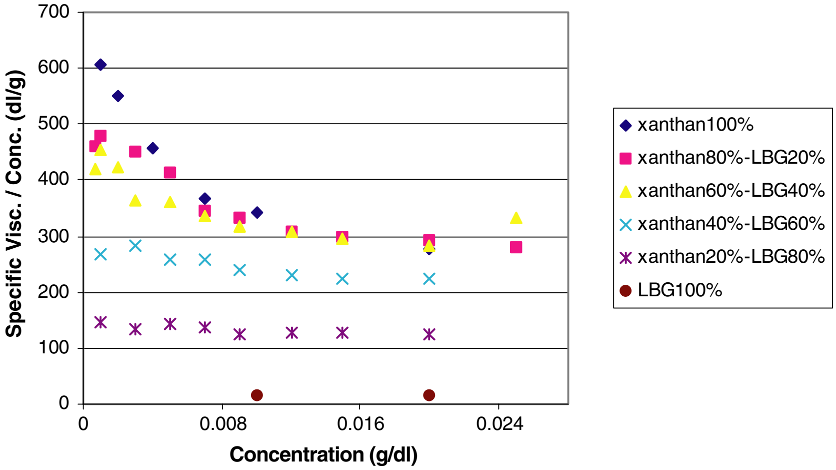

Fig. 1. Reduced viscosity of xanthan, LBG, and their blends as a function of gum concentration.

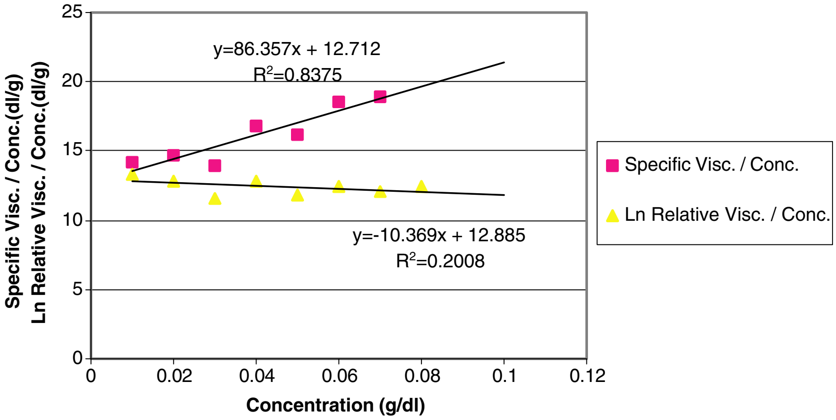

Fig. 2. Reduced viscosity and ln (relative viscosity)/concentration for LBG as a function of gum concentration.

polymer–polymer aggregation (Morris, 1995). The sum of the Huggins constant k' and Kraemer constant k'' should equal $0.5 \pm 10\%$, and larger or smaller values are attributed to molecule association (Morris, Cutler, Ross-Murphy, & Rees, 1981). Values from this study fall within this range, meaning the absence of molecular association. Furthermore, the intrinsic viscosity obtained (12.5 dl/g) was comparable to the 13.4 dl/g obtained by Launay, Cuvelier, and Martinez-Reyes (1997).

The nonlinear relationship between $\frac{\eta_{sp}}{C}$ and gum blend concentration observed at low xanthan and xanthan–LBG blend concentrations, thus making impossible the determination of the intrinsic viscosity by extrapolating experimental data, prompted the use of slope models (Chou & Kokini, 1987; Tanglertpaibul & Rao, 1987) to determine the intrinsic viscosity by plotting η_{sp} vs. C (similar with Eq. (6)), $\ln \eta_{rel}$ vs. C (Eq. (7)), and $1 - \frac{1}{\eta_{rel}}$ vs. C (Eq. (8)). Straight-line relationships with large linear regression coefficients were obtained for xanthan and xanthan–LBG blends (Figs. 3–6). McMillan (1974) reported that methods of determination of intrinsic viscosity based on slopes of plots had larger correlation coefficients and smaller standard errors than those based on intercepts of plots. The values of the intrinsic viscosities resulting from these models differed, but showed similar trends (Table 1). Intrinsic viscosity values calculated by using Eq. (6) were larger than those obtained by using Eqs. (7) and (8). Tanglertpaibul and Rao (1987) successfully implemented the model from Eq. (6) in the intrinsic viscosity determination of tomato serum. The authors reported higher correlation coefficients and fewer errors. Xanthan intrinsic viscosity values in water solvent and without dialysis calculated by using the Huggins model (intercept of a straight-line) and reported elsewhere ranging from 44.93 to 168 dl/g (Launay et al., 1997; Wang et al., 2001, 2002). These values were less than those found in this study by using Eq. (6), but greater than those in Eqs. (7) and (8). Significant differences between gum blends were detected with Eqs. (6) and (7), whereas Eq. (8) showed no significant differences among gum blends. Therefore, Eq. (6) was chosen as the best model for intrinsic viscosity determination

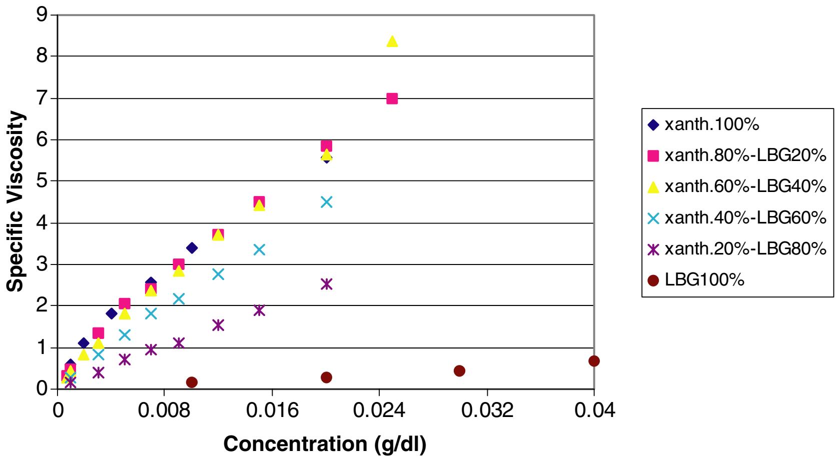

Fig. 3. Specific viscosity vs. concentration for xanthan, LBG, and their blends.

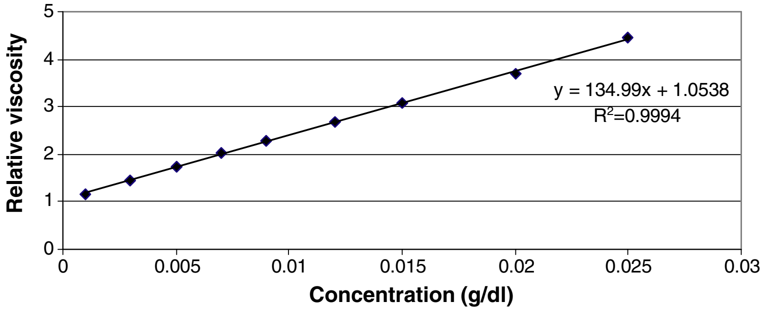

Fig. 4. Relative viscosity for xanthan 20%–LBG 80% blend as a function of gum concentration.

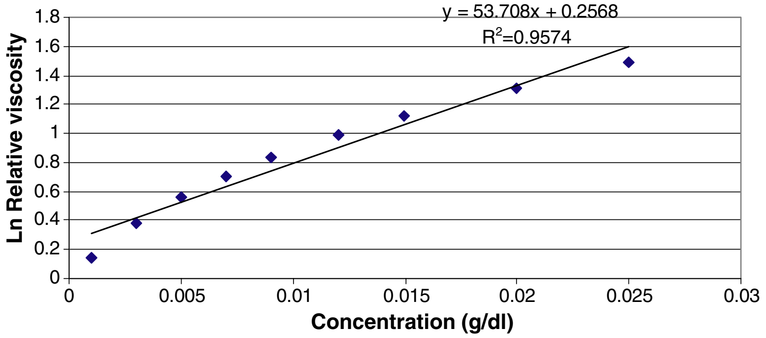

Fig. 5. Ln relative viscosity for xanthan 20%–LBG 80% blend as a function of gum concentration.

because it showed a better linear fit, with higher correlation (R^2) for all blends, and the results were similar with other findings (Tanglertpaibul & Rao, 1987).

Larger intrinsic-viscosity values from this study may be due to the dialysis process that removed most counterions, thus facilitating molecular expansion. The aggregation effects may have been suppressed by blending the two gums at 0.025 g/dl. Launay et al. (1997) reported that xanthan at 0.025 g/dl or less corresponded to the Newtonian viscosity. The dilute Newtonian domain was evidenced by the plot of $\log(\eta_{sp})$ against $\log C[\eta]$, known as the ''master curve'' (Fig. 7) (Launay et al., 1997; Morris et al., 1981), as well as by the independence of gum viscosities from shear rate. The slope of the master curve was 0.9 for all gum blends, close to the findings from Morris et al. (1981) who determined the slope to be around 1.4 for several food gums in dilute dispersion.

The intrinsic viscosity calculated from Eqs. (6) and (7) significantly increased as the proportion of LBG increased to reach the largest value at 60% xanthan–40% LBG (Table 1). The intrinsic viscosities of the gum

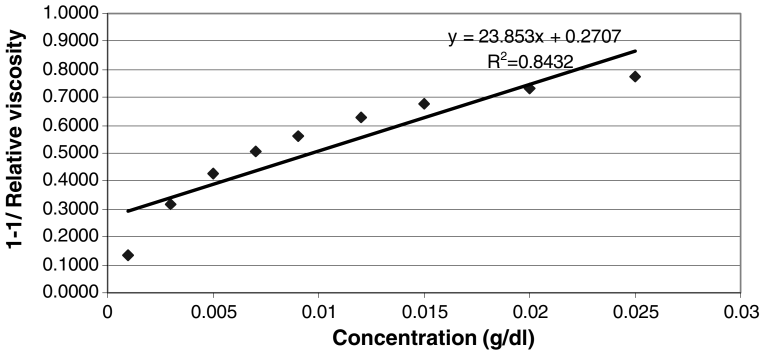

Fig. 6. Plot of (1 − 1/relative viscosity) as a function of gum concentration for xanthan 20%–LBG 80% blend as a function of gum concentration.

Table 1
Intrinsic viscosity values (dl/g) obtained for xanthan, LBG, and their blends

Gum	Model				
	Huggins	Kraemer	Tanglertpaibul and Rao		
	1	2	3	4	5
LBG 100%	12.7 ± 0.19	12.8 ± 0.1	$21.12_e^a \pm 1.05$	$10.75_f^b \pm 1.3$	$6.54_b^c \pm 1.8$
Xanth.20%–LBG80%	–	–	$134.47_d^a \pm 1.54$	$53.47_e^b \pm 1.08$	$23.92_a^c \pm 1.9$
Xanth.40%–LBG60%	–	–	$216.89_c^a \pm 2.5$	$68.68_c^b \pm 2.3$	$25.26_a^c \pm 1.3$
Xanth.60%–LBG40%	–	–	$306.61_a^a \pm 2.8$	$76.90_a^b \pm 1.5$	$24.17_a^c \pm 0.8$
Xanth.80%–LBG20%	–	–	$272.91_b^a \pm 2.5$	$72.90_b^b \pm 1.04$	$24.27_a^c \pm 1.8$
Xanth.100%	–	–	$214.21_c^a \pm 2.8$	$62.38_d^b \pm 1.6$	$21.36_a^c \pm 1.2$

Results are expressed as means ± SD for three replications.

[a] Means followed by the same letters in the same row are not significantly different ($P < 0.05$).

[b] Means followed by the same letters in the same column are not significantly different ($P < 0.05$).

–: Not estimated by Huggins and Kraemer equations.

1. $\frac{\eta_{sp}}{C} = [\eta] + k'[\eta]^2 C$.
2. $\frac{\ln \eta_{rel}}{C} = [\eta] + k''[\eta]^2 C$.
3. $\eta_{rel} = 1 + [\eta]C$.
4. $\eta_{rel} = e^{[\eta]C}$.
5. $\eta_{rel} = \frac{1}{1-[\eta]C}$.

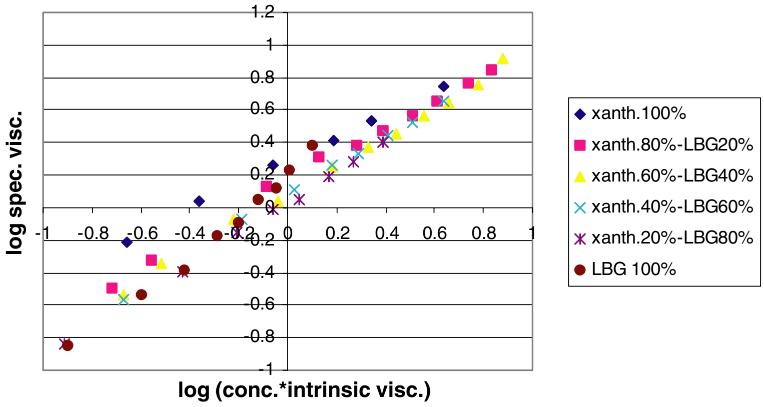

Fig. 7. Log (specific viscosity) as a function of log (concentration*intrinsic viscosity) for xanthan, LBG, and their blends.

blends were greater than those calculated from the weight average of the individual gums. These results suggest an intermolecular synergism between xanthan and LBG, which was greater at 60% xanthan and 40% LBG blend. The optimum intrinsic viscosity value was reached at 306.61 dl/g, which suggests that Eq. (6) is the best equation to estimate the intrinsic viscosity. A similar trend was reported from studies at higher

Table 2
Slope (b) of $\log \eta_{sp}$ versus $\log C$ from the power-law equation for xanthan, LBG, and their blends

Gum	Slope (b)
LBG 100%	1.234^{a}
Xanthan20%–LBG80%	$0.941^{b–d}$
Xanth.40%–LBG60%	$0.905^{b–d}$
Xanth.60%–LBG40%	0.884^{cd}
Xanth.80%–LBG20%	0.885^{cd}
Xanth.100%	0.786^{c}

[a] Means followed by the same letters in the column are not significantly different ($P < 0.05$).

xanthan and LBG concentration, in which the measured viscosities passed through a maximum when the two polymers were present in roughly equal concentrations (Goycoolea, Morris, & Gidley, 1995). From a molecular viewpoint, LBG may have destabilized the xanthan helical structure and rendered a more flexible xanthan chain, thus facilitating formation of heterotypic junctions with xanthan (Wang et al., 2002; Zhan, Ridout, Brownsey, & Morris, 1993). Whether this synergism is accompanied by a change in molecular weight of both species remains unclear, and is subject to further investigations.

3.2. Molecular conformation and polymer interaction

The power-law model (Eq. (9)) was used to estimate the exponent b from the slope of a double logarithmic plot of η_{sp} against concentration (Table 2). Results showed that the b value for LBG 100% was significantly larger than that of either xanthan–LBG blends or xanthan alone. The slope of the power-law equation was used to determine the molecular conformational structure of polymers. In this study, the slope value of LBG alone was greater than unity. In dilute regimes, slope values greater than unity have been reported to be associated with random coil conformation (Lapasin & Pricl, 1995) or entanglement (Morris et al., 1981). In dilute regimes, slope values less than 1 have been reported to be associated with rod-like conformation (Lai & Chiang, 2002). Lai and Chiang (2002) found slopes in the dilute regime ranging from 0.78 to 0.8 while investigating on hsian-tsao leaf gum. They concluded that the molecular conformation of hsian-tsao gum was more rod-like than random coil. In this study, the slope value for the gum blends and xanthan alone was less than unity. The data in this study is in agreement with the hypothesized molecular conformation of xanthan as a rod molecule (Whistler & BeMiller, 1997) and that of LBG as a random coil (Robinson, Ross-Murphy, & Morris, 1982). The increase in slope values with the addition of LBG to the gum blends may suggest a possible conformational change of xanthan–LBG complex molecules from rod-like to random coil.

Huggins parameters b, K, and α were used to determine the presence or absence of interaction between polymers. The Huggins parameters were estimated for xanthan and LBG alone, and for the blends. Results (Table 3) showed positive and increasing b values with the addition of xanthan. This may suggest that the addition of xanthan gum assists with the miscibility of LBG. Chee (1990) studied different polymers in different solvents and reported that the miscibility of polymers can be determined with the Huggins parameter b; positive values indicated miscibility, whereas negative values corresponded to polymer immiscibility. Morawetz (1965) suggested that polymer systems in which polymers interact with each other might show very large values of b, compared with the average b value of the two polymers. The increase was not observed in the present study. Sun et al. (1992) reported that parameter b should not be regarded as the only criterion for determining the presence of intermolecular interaction between polymers. The authors pointed out that because b is a measure of the interaction between attractive molecules, this term may erroneously be estimated when repulsive molecules interact due to shear forces.

The K value indicates the ability for the polymers to aggregate. A K value greater than unity indicates aggregates, whereas K values less than unity indicate no aggregation (Millard, Dintzis, Wilett, & Klavons, 1997). The results in this study (Table 3) showed that the K values are all less than unity, suggesting no aggregation of the gums in the solution. In contrast, Wang et al. (2001) reported that the K value determined for a xanthan–starch solution was greater than 0.3. In this

Table 3
Huggins parameters b, K, and α for xanthan, LBG, and their blends

Gum blends	b (l^2/g^2)	K	α
LBG100%	$0.012^{a} \pm 0.005$	$0.0077^{a} \pm 0.003$	–
Xanth.20%–LBG80%	$0.041^{b} \pm 0.013$	$0.00023^{b} \pm 0.00007$	$0.0005^{b} \pm 0.00001$
Xanth.40%–LBG60%	$0.130^{c} \pm 0.02$	$0.00027^{b} \pm 0.00004$	$0.0196^{b} \pm 0.001$
Xanth.60%–LBG40%	$0.270^{d} \pm 0.014$	$0.00028^{b} \pm 0.00001$	$0.0545^{a} \pm 0.002$
Xanth.80%–LBG20%	$0.356^{e} \pm 0.012$	$0.00048^{b} \pm 0.00002$	$0.0235^{b} \pm 0.001$
Xanth.100%	$0.481^{f} \pm 0.009$	$0.0011^{b} \pm 0.00002$	–

Results are expressed as means ± SD for three replications.

[a] Means followed by the same letters in the same column are significantly different ($P < 0.05$).

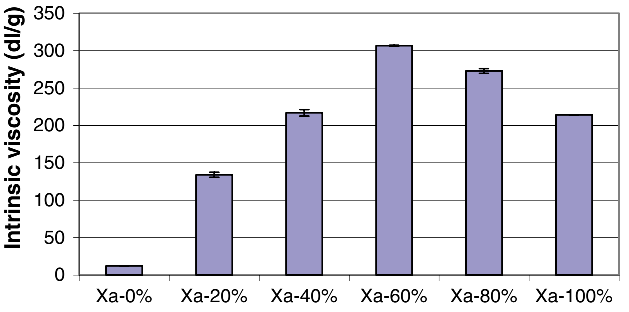

Fig. 8. Intrinsic viscosity as a function of increasing xanthan (Xa) fraction in xanthan–LBG blends.

study, however, removal of counterions was performed through dialysis; that may have made the gum molecules more flexible, and may not have reduced the propensity to aggregate.

Polymer interaction was assessed by calculating α (Eq. (18)) and results are shown in Table 3. Sun et al. (1992) reported that α values greater than zero indicate a strong attraction between polymers. The α values for each of the gum blends in this study were all greater than zero suggesting that a strong attraction between xanthan and LBG was present. Wang et al. (2002) reported that deacetylation of xanthan chains increases xanthan side chain flexibility, thus making possible xanthan–LBG interaction. The authors pointed out that salts reduce xanthan interaction with LBG due to electrostatic shielding. The strong attraction observed in this study may have resulted from the increase in xanthan side chains flexibility due to removal of counterions (see Fig. 8).

3.3. Elastic component of gum solutions

The elastic component of xanthan, locust bean gum, and their blends as a function of gum concentration are shown in Fig. 9. Launay et al. (1997) reported that the Newtonian viscosity of xanthan corresponded to a xanthan concentration of 0.025 g/dl or less. The results in this study showed that, at a gum concentration of 0.025 g/dl, the elastic component for LBG alone approached zero, whereas xanthan alone showed an elastic component around 10 mPa s. Between gum blends, xanthan 60%–LBG 40% blend showed the largest elastic component (22 mPa s), followed by xanthan 40%–LBG 60% blend (17 mPa s). By definition, fluids that do not contain an elastic component are considered purely viscous. According to that criterion, LBG was viscous at 0.025 g/dl range, whereas xanthan and xanthan–LBG blends were visco-elastic. The presence or absence of gum synergy may be established by comparing the elastic component of gum blends and gums alone at a given gum concentration. A greater gum synergy was noticed with xanthan 60%–LBG 40%, as evidenced by an elastic-component value two to three times larger than the average elastic-component value of the two gums. These results agree with our viscosity data, in which this blend exhibited greater intrinsic viscosity, significantly different from that of the rest of the blends.

Thurston (1996) reported that the elastic component of 0.05% (w/v) xanthan was about 1.25 mPa s by using the oscillatory flow method. No other elastic-component values were found in the literature for gum solutions. A 100% xanthan and xanthan 60%–LBG 40% blend from our results had a larger elastic component, 10 and 19-fold larger, respectively, compared with the value reported by Thurston (1996). In as much the gum solutions were Newtonian, these results suggest a critical role is played by the elastic component of the polymers in xanthan–LBG synergism.

4. Conclusion

A strong interaction occurred between xanthan and LBG, even in dilute gum solution. The methods, while characterizing the molecular conformation of xanthan and LBG alone, suggested a conformational change of

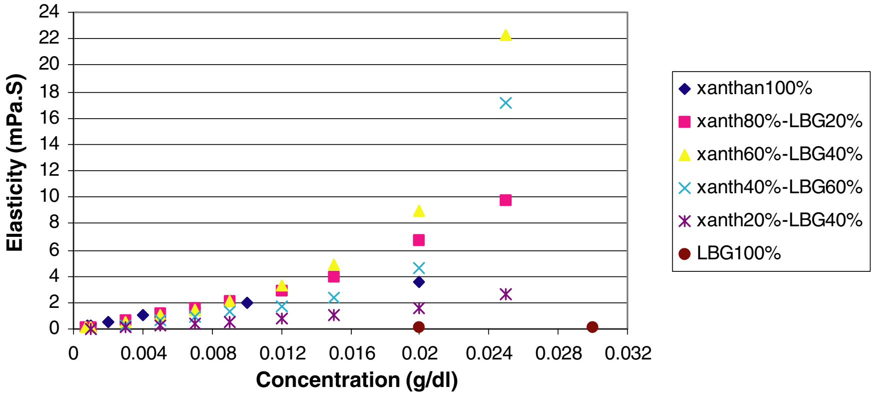

Fig. 9. Elastic component as a function of concentration for xanthan, LBG, and their blends.

the complex xanthan–LBG in which LBG may play a significant role. Findings also suggest changes in molecular conformation that may coincide with an increase in the elastic component.

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