Carbohydrate Polymers 92 (2013) 1151–1158

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Characterization of non-linear rheological behavior of SPI–FG dispersions using LAOS tests and FT rheology

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ARTICLE INFO

Article history:
Received 9 September 2012
Received in revised form 11 October 2012
Accepted 28 October 2012
Available online 3 November 2012

Keywords:
Rheological behavior
Flaxseed gum
Soy protein isolate
Fourier transform rheology
Time–temperature superposition

ABSTRACT

The effect of flaxseed gum (FG) on the rheological and nonlinear stress response behaviors of mixed soy protein isolate (SPI)–flaxseed gum (FG) dispersions were studied. Results showed that the viscosity of the SPI–FG mixed dispersions increased significantly with increase in the FG concentration. Both the shear stress and the apparent viscosity values as a function of shear rate were fitted well using Power law model as expected. The frequency dependence of G', G'' and $\tan\delta$ of soy protein isolate decreased as the FG concentration increased. The large amplitude oscillatory shear (LAOS) test and Fourier transform (FT) rheology analysis showed that the addition of flaxseed gum strongly affected the structure of the SPI–FG mixed dispersion system as shown by deformation of the nonlinear stress response curve and significantly altered magnitude of higher harmonic curve. The addition of FG increased the instantaneous strain softening effect of the SPI–FG mixed dispersion system.

1. Introduction

Proteins and polysaccharides play an important role in manufactured foods due to their unique functional and textural properties. When proteins and polysaccharides are mixed, it is expected that the behavior of one is affected by the presence of the other (Tolstoguzov, 1997). It has been found that the charged polysaccharides readily interact with other macromolecules such as lipids and proteins (Samat, Singhal, Kulkarni, & Rege, 1993). The understanding of the protein–polysaccharide interaction is very important in developing novel foods with tailored textural properties (Cain, Jones, & Norton, 1987; Tolstoguzov, 2003).

The demand for soy protein is continuously growing because of its nutritional as well as functional (emulsifying, gelling and foaming) properties (Maltais, Remondetto, Gonzalez, & Subirade, 2005; Molina, Papadopoulou, & Ledward, 2001; Renkema, Knabben, & van Vliet, 2001). Because of these reasons, the soy protein isolates are commonly used in food formulation as functional ingredients. The specific functional properties of soy protein isolate can be improved through some conscious modifications. In this context, the effect of various treatments and presence of additives on structural and functional properties of soy proteins has been studied to considerable details (Petruccelli & Añón, 1994a, 1994b; Puppo & Añón, 1999; Puppo, Lupano, & Añón, 1995).

The flaxseed gum is a natural carbohydrate polymer and is extracted from flaxseed (*Linum usitatissimum*). It comprises approximately 8% of the flaxseed by weight. As flaxseed gum is composed of xylose, arabinose, fucose, galactose, rhamnose and galacturonic acid, it is regarded as a heterogeneous polysaccharide (Chen, Xu, & Wang, 2004; Cui, Mazza, & Biliaderis, 1994; Erskine & Jones, 1957; Hunt & Jones, 1962; Muralikrishna, Salimath, & Tharanathan, 1987). Because of its unique thickening, emulsification and water holding properties, the flaxseed gum can be used as an effective thickener, stabilizer and emulsifier in food industry (Chen, Xu, & Wang, 2006; Wang et al., 2008; Wang, Wang, Li, Xue, & Mao, 2009). As the proteins and polysaccharides are used together in manufactured foods, the composition of both the proteins and polysaccharides can affect the structure, stability and textural properties of the foods in which both the proteins and polysaccharides are incorporated (Galazka, Dickinson, & Ledward, 2000).

The nonlinear regimes in flow, structure deformation and other rheological properties are commonly observed in food processing operations. The complex dispersion systems containing protein and other hydrocolloids show nonlinear rheological properties (Larson, 1999; Macosko, 1994). The understanding of non-linear behavior in shear-induced structure–function relationship is essential in developing foods with desired textural properties. In this context, the

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http://dx.doi.org/10.1016/j.carbpol.2012.10.067

Nomenclature

A	pre-exponential constant
E_a	activation energy (kJ mol^{-1})
f	angular frequency (rad/s)
G'	storage modulus (Pa)
G''	loss modulus (Pa)
I_n	magnitude of nth harmonic wave
I_1	magnitude of fundamental wave
K	consistency coefficient (Pa s^n)
K'	power law constant (Pa s$^{n'}$)
K''	power law constant (Pa s$^{n''}$)
n	power law index (dimensionless)
n'	frequency exponent (dimensionless)
n''	frequency exponent (dimensionless)
R	universal gas constant (Pa s)
R^2	correlation coefficient (dimensionless)
$\dot{\gamma}$	shear rate (s^{-1})
δ_n	phase of nth harmonics (°)
η	apparent viscosity (Pa s)
σ	stress amplitude (Pa)
ψ	additional parameter (dimensionless)
ω_n	angular frequency of nth harmonics (rad/s)

Fourier transform rheology (FT rheology) can be applied in analyzing the higher harmonics in the oscillatory shear stress response (Craciun, Carreau, Heuzy, Moan, & Ven, 2003; Kallus et al., 2001; Wilhelm, 2002). The large amplitude oscillatory shear tests (LAOS) can be used to understand the non-linear behavior in rheology in complex macromolecular food systems (Hyun, Kim, Ahn, & Lee, 2002; Klein, Spiess, Calin, Balan, & Wilhelm, 2007; Sim, Ahn, & Lee, 2003).

In the past, a series of studies have been undertaken to investigate various aspects of protein–polysaccharide interactions (Hua, Cui, & Wang, 2003; Ipsen, 1995; Wang, Li, Wang, & Adhikari, 2011a). Most of these studies used carrageenan or xanthan gum as model polysaccharides. To our knowledge there are no studies reporting the effect of addition of flaxseed gum on rheological properties of soy protein isolate. There are many interesting aspects in the soy protein isolate–flaxseed gum (SPI–FG) interactions which have not yet elucidated. Therefore, this study was undertaken in order to measure and predict rheological properties of SPI–FG mixed dispersions and to elucidate the structural changes in soy protein dispersion in the presence of flaxseed gum.

2. Materials and methods

2.1. Soy protein isolate

Commercial soy protein isolate (7S 31 ± 1%, 11S 41 ± 1%) was obtained from Messenger Biotechnology Co. Ltd. (Beijing, China).

2.2. Flaxseed gum extraction

Flaxseed, with 6.50% (w/w) moisture content was purchased from Hebei province of China. One hundred grams of flaxseed was mixed with 900 mL deionized water (pH 6.4–7.0) and was washed to remove the dust. The flaxseed gum was extracted according to the method proposed by Cui (2001) and Cui et al. (1994). Briefly, the slurry of flaxseed and water was stirred at 300 rpm for 5 h and the temperature of the mixture was maintained at 60 °C using a water bath. The extracted solution was filtered through a 40-mesh screen to remove any remaining solid impurities. The 95.00% (v/v) ethanol (in two volumes) was added into the extracted solution to precipitate flaxseed gum and it was collected by centrifugation for 10 min at 3000 rpm using a centrifuge (LG10-2.4A, Beijing Medical Centrifuge Corporation, Beijing, China). The collected flaxseed gum was dried in a hot air oven at 80 °C for 4 h, according to the method proposed by Wang, Li, Wang, Wu, and Özkan (2011b).

2.3. Solution preparation

For rheological tests, the soy protein isolate (8.00%, w/w)–flaxseed gum (0.30–0.70%, w/w) mixtures were prepared as follows. Flaxseed gum (0.06 g, 0.1 g, 0.14 g) was added into 20 mL water, and the soy protein isolate (1.6 g) was subsequently added while stirring. When the flaxseed gum and the soy protein isolate powders were completely dissolved in water, the resultant dispersions were heated to boil for 1 min while stirring and then cooled down to ambient temperature (25 °C). These dispersion samples were equilibrated at 25 °C for 2 h before the test (pH = 6.8 ± 0.2). The soy protein isolate dispersions without gum and the flaxseed gum dispersion without protein were also prepared in the same way and were used as control samples. All of the experiments were performed in triplicate and their average values are reported in ensuing sections.

2.4. Rheological tests

AR2000ex rheometer (TA Instruments Ltd., Crawley, UK) with aluminum parallel plate geometry (40 mm diameter, 1 mm gap) was used to carry out rheological measurements. The AR2000ex is a stress controlled rheometer equipped with a force rebalance transducer. The transducer is capable of measuring torque values ranging from 0.03 μN m to 200 mN m. The high resolution motor of this rheometer can generate and control angular frequencies from 7.5×10^{-7} rad/s to 628 rad/s. The temperature of the sample was maintained as desired using a water bath connected to a Peltier system in the bottom plate. To prevent evaporation, a thin layer of silicone oil was used on the surface of the samples.

2.4.1. Frequency sweep tests

The frequency sweep tests were performed at 25 °C, 50 °C, and 75 °C over the angular frequency range of 10–100 rad/s. In order to keep the strain amplitude in the linear viscoelastic region for all samples, the strain amplitude of the frequency sweep tests was selected to be 2% based on the strain sweep test results (data not shown).

2.4.2. Steady state flow tests

The steady shear tests were performed at 20 °C, 30 °C, 40 °C, 50 °C and 60 °C over the shear rate range of 1–100 s^{-1}. The shear rates used this study were within the shear rates prevailing in extrusion (1–100 s^{-1}), pipe flow (1–1000 s^{-1}) and agitation (10–1000 s^{-1}) in food process operations (Steffe, 1996). The variation in apparent viscosity and shear stress as a function of shear rate were measured using this test.

2.4.3. Large amplitude oscillatory shear tests (LAOS)

Samples of 8.00% SPI dispersion and 8.00%SPI + 0.70% FG mixed dispersion were used in these tests. The large amplitude oscillatory shear test was performed using strain sweep mode at 1 Hz over a strain duration of 10–1000%. The strain, stress and angular frequency outputs were connected to a computer, where the data for FT rheology analysis was required. The transformation of the stress respond data from time domain to frequency domain was processed with Origin Pro v8.0725 software (OriginLab Corporation).

2.5. Theory

2.5.1. Frequency sweep test

The loss modulus (G'') values calculated using the Kronig–Kramers relationship were compared to the measured values to insure all the data recorded during the frequency sweep test were within the linearity regime of the gel system during the entire frequency range (data not shown). The approximation equation was (Tschoegl, 1989)

$$G''(f) = \frac{\pi}{2}\frac{d(G'(f))}{d\ \ln(f)} \quad (1)$$

The variation of storage modulus (G') and loss modulus (G'') with the angular frequency for soy protein isolate–flaxseed gum mixtures can be fitted using Eqs. (2) and (3) given below (Ikeda & Nishinari, 2001).

$$G' = K' \cdot f^{n'} \quad (2)$$

$$G'' = K'' \cdot f^{n''} \quad (3)$$

where K' and K'' are power law constants and the n' and n'' values are considered as frequency exponents, f is the angular frequency.

2.5.2. Steady state flow test

The experimental apparent viscosity versus shear rate data were fitted using Power law model (Eq. (4)) which is commonly used in modeling steady shear properties of non-Newtonian liquids (Steffe, 1996). Once the power law parameters, i.e. consistency coefficient (K) and flow behavior index (n) are obtained, the relationship between the measured apparent viscosity and shear rates can be expressed using Eq. (4), given below.

$$\eta = K \cdot \dot{\gamma}^{n-1} \quad (4)$$

where η is the apparent viscosity (Pa s), $\dot{\gamma}$ is the shear rate (1/s), and K is consistency coefficient (Pa s^n), and n is known as flow behavior index (dimensionless).

2.5.3. Analysis using FT rheology

Besides the common rheological properties measured from the small amplitude oscillation test within the linear viscoelastic region, the stress response outside the linear viscoelastic regime provides useful information when LAOS is applied on the sample (Grand & Petekidis, 2008). Therefore, a newly developed approach (FT rheology), which considers the superposition of different overtone spectra of typical nonlinear effects in the entire frequency spectrum, is applied. The LAOS test was used to generate the G' and G'' data and to describe the non linear behavior (Wilhelm, Maring, & Spiess, 1998).

The time domain stress response signal was transformed into the frequency domain signal, and the stress was represented by the sum of higher harmonics:

$$\sigma = A\ \sin(\omega_1 t + \delta_1) + B\ \sin(\omega_2 t + \delta_2) + C\ \sin(\omega_3 t + \delta_3) + \cdots \quad (5)$$

where σ is the stress amplitude (Pa), ω_n is the angular frequency (rad/s) of each harmonics, and δ_n is the phase (degree) of each harmonics. The experimental σ versus t data show more than 2 higher harmonics and the FT rheology takes these higher harmonics into consideration.

At low strains, the stress signal is sinusoidal, whereas, when the strain amplitude is increased outside the linear viscoelastic region, the stress response gets distorted as the dispersion start to deform or flow. Outside the linear regime, the stress response curve becomes strongly non-linear and out of phase. For simplicity, only four characteristic stress response curves were considered, and the non-linear effect was described by a superposition of these stress response curves by using sine, triangular, rectangular and saw tooth functions (Klein, Venema, Sagis, & Van Der Linden, 2008). These four functions represent four types of rheological contributions from higher harmonics: linear, strain hardening, strain softening, and wall slip or shear bands (Klein et al., 2007). These non-liner effects become very important under LAOS conditions. In FT rheology, the analysis of LAOS data is based on the magnitude I_n/I_1 (Klein et al., 2007). The quantification of the non-linear response regarding the rheological phenomenon is based on the measurement and analysis of the magnitude of the higher harmonics (I_n/I_1).

3. Results and discussion

3.1. Rheological properties

3.1.1. Frequency sweep test

The variation of storage modulus (G'), loss modulus (G'') and the loss tangent ($\tan\delta$) as a function of angular frequency measured at 25 °C is shown in Fig. 1. It can be seen from this figure that both the storage and loss moduli increase as the angular frequency increases. The variation of G' and G'' with angular frequency in the case of soy protein isolate is significant as both the moduli are found to increase by approximately two orders of magnitude. The increase of G' value with the increase in the angular frequency slows down distinctly when the flaxseed gum is added. This observation suggests that the addition of flaxseed gum decreases the frequency dependence of the rheological parameters of the soy protein isolate.

It can also be seen from Fig. 1 that the $\tan\delta$ values of soy protein isolate decrease sharply with the increase in angular frequency and the addition of flaxseed gum. The addition of flaxseed gum especially within 0.50% (w/w) and 0.70% (w/w) concentration has made the trend steadier. This suggests that the $\tan\delta$ of soy protein isolate–flaxseed gum mixtures have less frequency dependence than that of the dispersions having only soy protein isolate.

The viscoelastic nature of foods can be represented by Power law type model (Özkan, Xin, & Chen, 2002). The frequency exponents (n' and n'') of SPI–FG mixed dispersions (Table 1) were distinctly different compared to those of soy protein isolate dispersions. Both the n' and n'' values of SPI–FG mixed dispersions at 25 °C, 50 °C, and 75 °C were lower than those of soy protein isolate dispersions at the same temperature. The values of the power law constants (K' and K'') of SPI–FG mixed dispersions were much higher than those of soy protein isolate dispersions This might be due to the fact that the addition of small amount of flaxseed gum helps to form more rigid SPI–FG mixed dispersions.

Fig. 2 shows the variation of G', G'' and $\tan\delta$ with angular frequency at three different temperatures (25 °C, 50 °C, and 75 °C) in the case of 8.00% (w/w) soy protein isolate dispersion. This figure also presents the variation of these rheological parameters in 8.00% (w/w) (SPI)–0.70% (w/w) FG mixed dispersions. It can be seen from this figure that the temperature dependence of soy protein isolate dispersion is much stronger than that of the SPI–FG mixed dispersions. Both the G' and G'' values of the 8.00% (w/w) SPI–0.70% (w/w) FG mixed dispersions are much higher compared to those of the soy protein isolate dispersions. These data suggest that the addition of flaxseed gum contributes to the increase in both the moduli of the mixed dispersions. When the temperature of these dispersions increased, the G' and G'' values of both the soy protein isolate dispersions decreased, as well as the SPI–FG mixed dispersions. A similar trend of temperature dependence of these rheological parameters was reported previously in the case of carrageenan–soy protein mixed dispersions (Baeza, Carp, Pérez, & Pilosof, 2002). The magnitude of $\tan\delta$ values and its variation with angular frequency in the case of 8.00% (w/w) soy protein isolate dispersion were quite different compared to that of 8.00% (w/w) SPI–0.70% (w/w) FG mixed dispersions. The $\tan\delta$ values of 8.00% (w/w) soy protein isolate

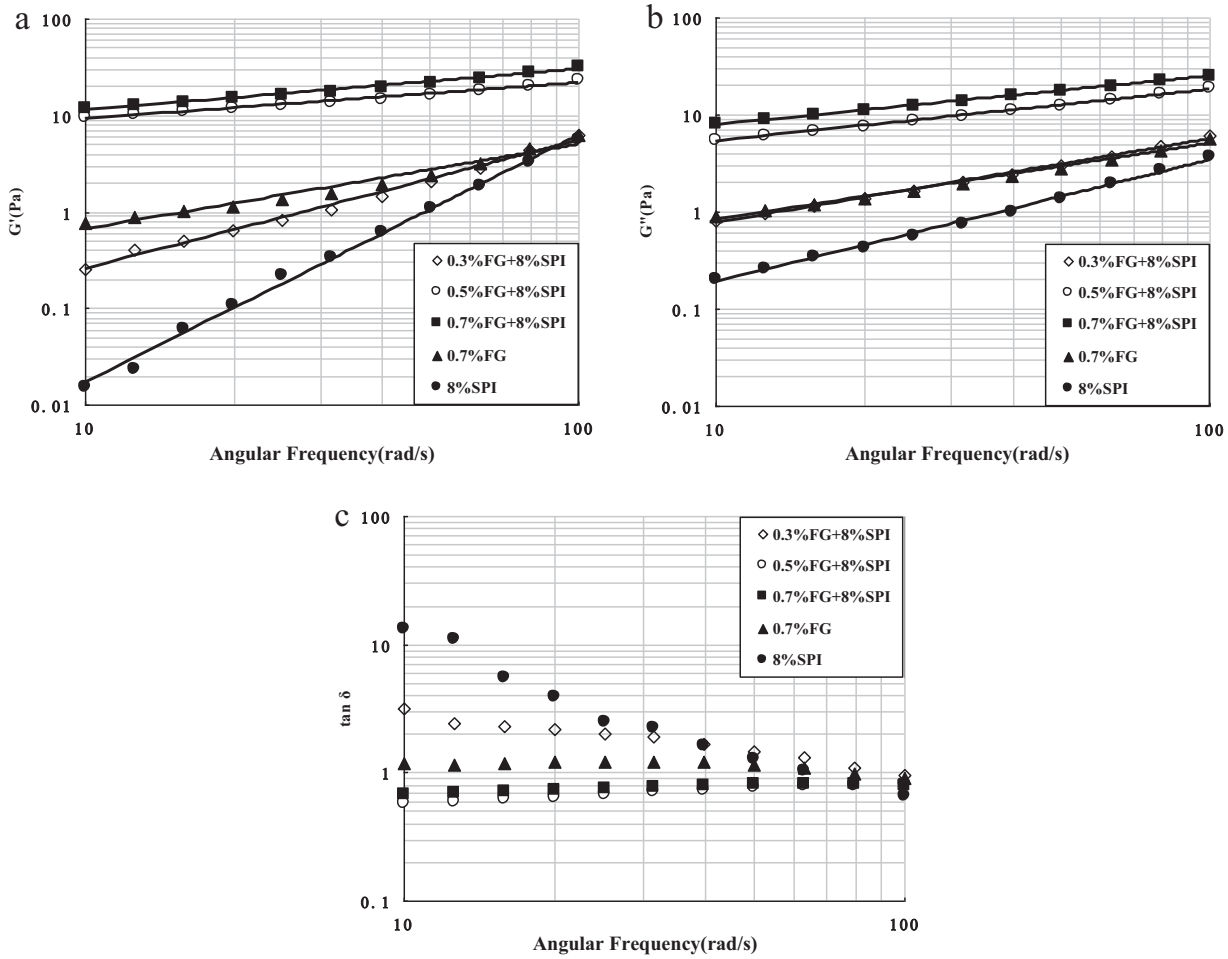

Fig. 1. Angular frequency dependence of G', G'' and tan δ for 8.00% (w/w) of soy protein isolate dispersions, 0.70% (w/w) flaxseed gum dispersion and SPI–FG mixed dispersions (at 25 °C).

dispersion increased with the increase in the temperature. However, the effect of temperature on the tan δ values of 8.00% (w/w) SPI–0.70% (w/w) FG mixed dispersion was almost negligible.

3.1.2. Steady state shear flow test

Fig. 3 presents the variation of apparent viscosity of 8.00% (w/w) soy protein isolate, 0.70% (w/w) flaxseed gum and their mixed dispersions. It can be seen from this figure that the apparent viscosity of all these dispersions decreases with increase in the shear rate. The shear thinning behavior can be observed in all samples and the steady shear curves are almost parallel to each other. This type of steady shear behavior is widely observed in biopolymers (Lu, Liu, & Tong, 2006). It can also be seen from Fig. 3 that the addition of flaxseed gum sharply increases the viscosity of SPI–FG mixed dispersions suggesting that the flaxseed gum promotes the interaction and network formation between soy protein and flaxseed gum which results into mixed dispersions with stronger molecular level networks.

The experimental apparent viscosity versus shear rate data in all the SPI–FG mixed dispersions at different flaxseed gum concentrations and different temperature shows a good accord with the Power law model Eq. (4) with $R^2 \geq 0.950$. Fig. 4 shows the effect

Table 1
Effect of temperature and flaxseed gum (FG) concentration on the Power law parameters (K' and n') and (K'' and n'') of SPI–FG mixed dispersions.

FG conc. (%)	Temperature (°C)	$G' = K' f^{n'}$			$G'' = K'' f^{n''}$		
		K'	n'	R^2	K''	n''	R^2
0	25	8E−5 ± 2E−6	2.41 ± 0.03	0.9961	0.01 ± 3E−4	1.26 ± 0.07	0.9986
0.3	25	7.6E−3 ± 3E−4	1.47 ± 0.05	0.9879	7.8E−2 ± 5E−4	0.95 ± 0.02	0.9902
0.5	25	3.03 ± 0.02	0.45 ± 0.03	0.9653	1.45 ± 0.02	0.56 ± 0.009	0.9976
0.7	25	3.33 ± 0.06	0.50 ± 0.06	0.9758	2.41 ± 0.008	0.51 ± 0.008	0.9995
0	50	2E−5 ± 1E−7	2.64 ± 0.02	0.9917	6.5E−3 ± 9E−5	1.29 ± 0.01	0.9988
0.3	50	1.2E−3 ± 5E−5	1.77 ± 0.01	0.9811	2.7E−2 ± 4E−4	1.11 ± 0.04	0.9868
0.5	50	1.75 ± 0.02	0.45 ± 0.007	0.9804	0.91 ± 0.006	0.57 ± 0.01	0.9927
0.7	50	1.63 ± 0.03	0.53 ± 0.002	0.9630	1.35 ± 0.05	0.52 ± 0.009	0.9979
0	75	3E−5 ± 4E−7	2.56 ± 0.009	0.9961	3.8E−3 ± 8E−5	1.36 ± 0.03	0.9989
0.3	75	3E−4 ± 1E−6	2.10 ± 0.02	0.9939	1.1E−2 ± 4E−4	1.26 ± 0.07	0.9916
0.5	75	0.46 ± 0.004	0.71 ± 0.05	0.9205	0.56 ± 0.005	0.57 ± 0.01	0.9894
0.7	75	0.21 ± 0.006	0.87 ± 0.05	0.9510	0.61 ± 0.003	0.55 ± 0.007	0.9990

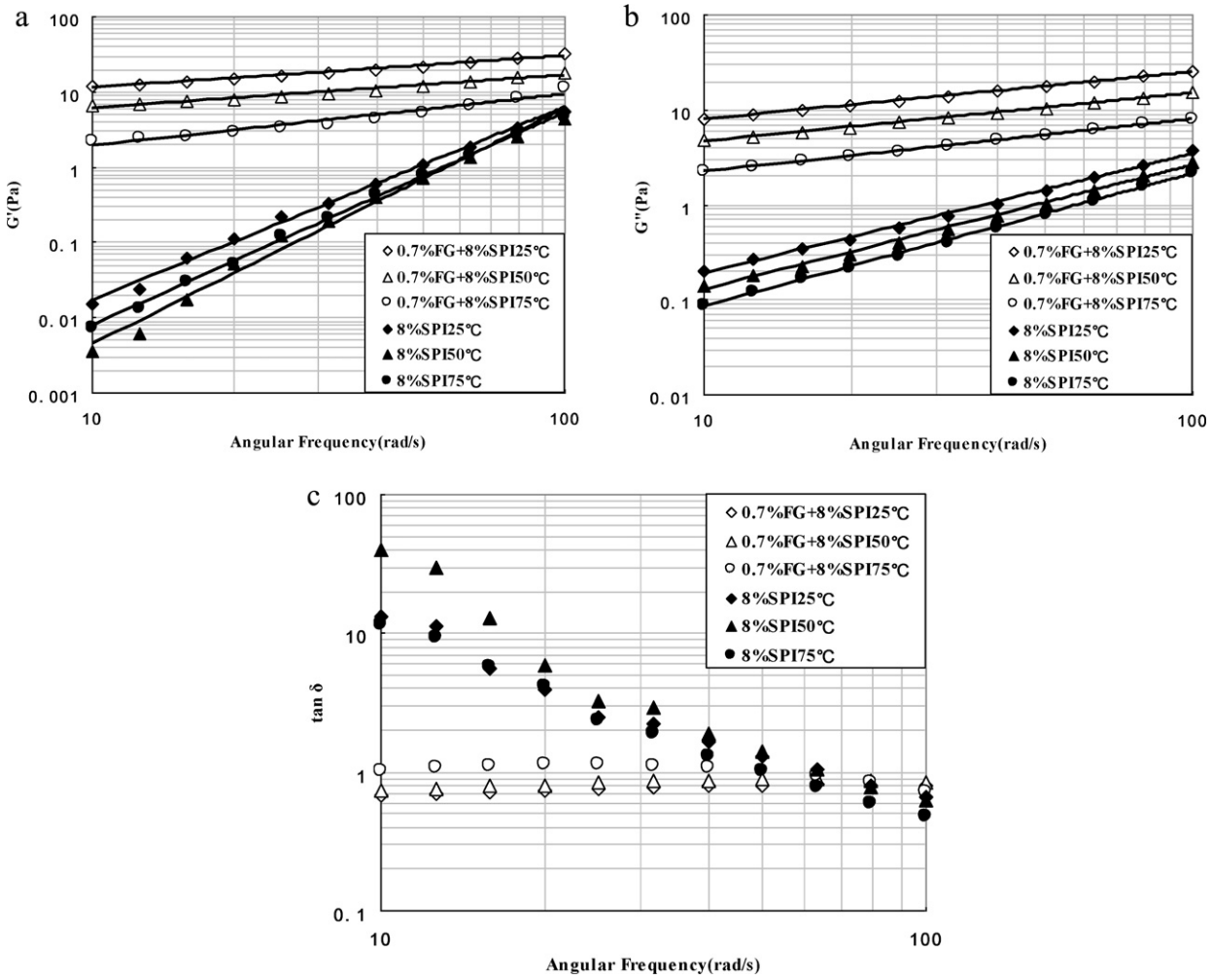

Fig. 2. Angular frequency dependence of G', G'' and tan δ at 25, 50, and 75 °C for 8.00% (w/w) soy protein isolate dispersions and 8.00% (w/w) SPI–0.70% (w/w) FG mixed dispersions.

of flaxseed gum concentration and temperature on the consistency index (K) for the SPI–FG mixed dispersions. As shown in Fig. 4, the K values decrease with the increase in temperature for given flaxseed gum concentration and increase with the increase in the flaxseed gum concentration at a given or set temperature.

The effect of temperature on apparent viscosity can be presented in a unified form by means of master curve (shear stress σ vs. γ/α_T). In our study, the shift factor (α_T) was obtained as the ratio of the

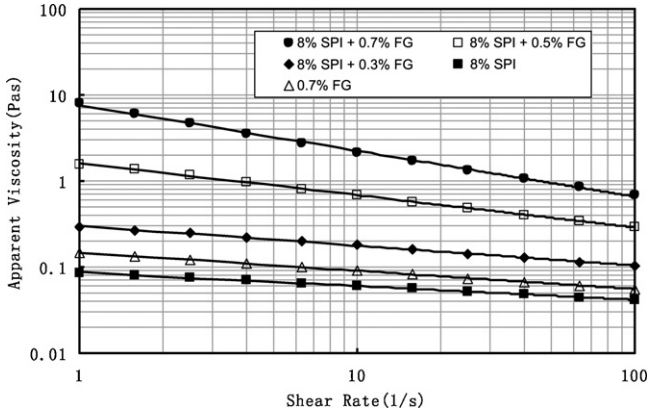

Fig. 3. Variation of apparent viscosity of 8.00% (w/w) soy protein isolate dispersion, 0.70% (w/w) flaxseed gum dispersion and SPI–FG mixed dispersions at 20 °C.

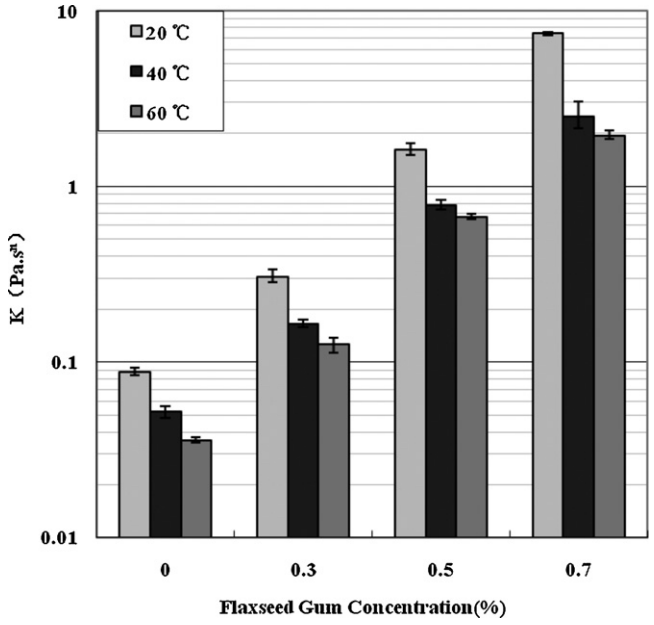

Fig. 4. The effect of flaxseed gum concentration and temperature on the consistency coefficient (K) of the SPI–FG mixed dispersions.

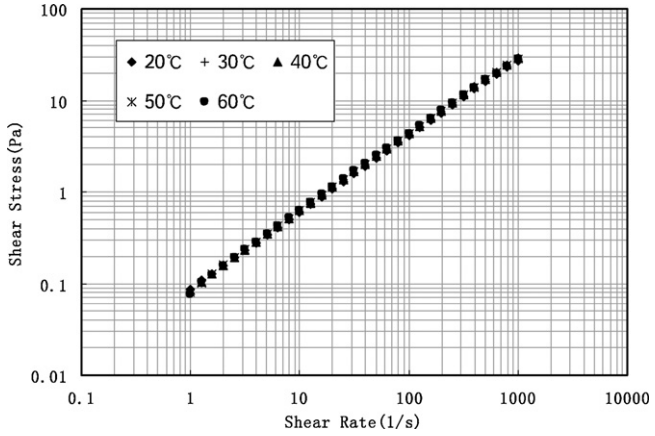

Fig. 5. Superimposed shear rate versus temperature master curve of 8.00% (w/w) soy protein isolate dispersions using 20 °C as a reference temperature.

shear rate at a given temperature (γ_T) to the shear rate at a reference temperature (γ_{Tr}) at the same shear stress. Fig. 5 shows the master curve, using 20 °C as reference temperature. The flow curves at each temperature were satisfactorily superimposed to the reference flow curve. The flow curves of SPI (8.00% w/w)–FG (0.70% w/w) mixed dispersion were also satisfactorily superimposed into a master curve (results not shown). It has been generally accepted that the master curve is a valid tool to investigate the flow behavior of fluids which have experimental limitation in terms of shear rates and temperatures (Steffe, 1996). In this study, the superposition of all the flow curves into a maser curve suggested that no chemical change or structural alteration had occurred in the samples during the measurements.

An additional parameter (ψ, as shown in Eq. (6)) is proposed in this work in order to model the apparent viscosity data of SPI (8.00%, w/w)–FG (0.70%, w/w) mixed dispersions from the viscosity data of corresponding binary systems (soybean–water, gum–water) within the shear rate and flaxseed gum concentration ranges investigated in this study.

$$\eta_i = \eta_p(1+\psi) + \eta_g - \eta_w \tag{6}$$

where η_i is the apparent viscosity of SPI (8.00%, w/w)–FG(0.70%, w/w) mixed dispersion at each shear rate. η_p is the apparent viscosity of soy protein dispersion (8.00%, w/w) at each shear rate and η_g is the viscosity of flaxseed gum solution. η_w is the viscosity of water and ψ (dimensionless) is the additional fitting parameter.

The η_w is taken to be the viscosity of water (1.52×10^{-3} Pa s) at 5 °C. In both cases, the parameter ψ was correlated with flaxseed gum concentration using a power function given by Eq. (7), below.

$$\psi = c \cdot w_g^d \tag{7}$$

where w_g (w/w) is flaxseed gum concentration, c and d are dimensionless fitting parameters. The values for parameter c were found to be 206.8, 96.6 and 42.71 at the shear rates of 1, 10 and 100 s^{-1}, respectively. Similarly the values for the parameter d were found to be 4.04, 3.44 and 3.20 for the shear rates of 1, 10 and 100 s^{-1}, respectively. These values were obtained through the least square fitting of the data ($R^2 > 0.980$). The effect of flaxseed gum concentration in increasing the apparent viscosity of these ternary systems, compared to the viscosity of the soy protein dispersions, can be evaluated through η_p and ψ as given by Eqs. (6) and (7).

3.1.3. The analysis using FT rheology

The non-linear stress response of the dispersions beyond the linear viscoelastic region provides useful information. Fig. 6 shows the stress response as a function of strain amplitude in time domain for SPI–FG mixed dispersions at 1 Hz. It can be seen from this figure that at low strain, the stress signal is sinusoidal. When the amplitude of the strain increases, the samples begin to yield and deform which gives rise to non-linear stress response as a function of strain amplitude. It is interesting to note that the stress response becomes out of phase due to the deformation and flow of the dispersions. For all samples, a distortion of stress response can be observed with the increase in strain amplitude beyond the linear regime. For the soy protein isolate dispersions the stress signal deformed not as strongly as in the case of SPI–FG mixed dispersions. This observation suggests that the addition of flaxseed gum increases the instantaneous shear dependence of in SPI–FG dispersions.

Subsequently, we applied the FT rheology to analyze the stress signal. The amplitudes of the third and fifth harmonics are plotted in Fig. 7a and b for soy protein isolate dispersion and SPI–FG mixed dispersion, respectively. The magnitude of second harmonic which represents the wall slip was found to be negligible in these dispersions.

For soy protein isolate dispersions, the variation in the amplitude of third harmonic with strain was quite monotonous (Fig. 7a), which increased from almost negligible value (near linear regime) to much higher values in the flow regime. This observation suggests that the soy protein dispersion behaves like soft sphere (Grand & Petekidis, 2008). The magnitude of fifth harmonic of soy protein isolate dispersion also exhibited increasing trend after a slow start

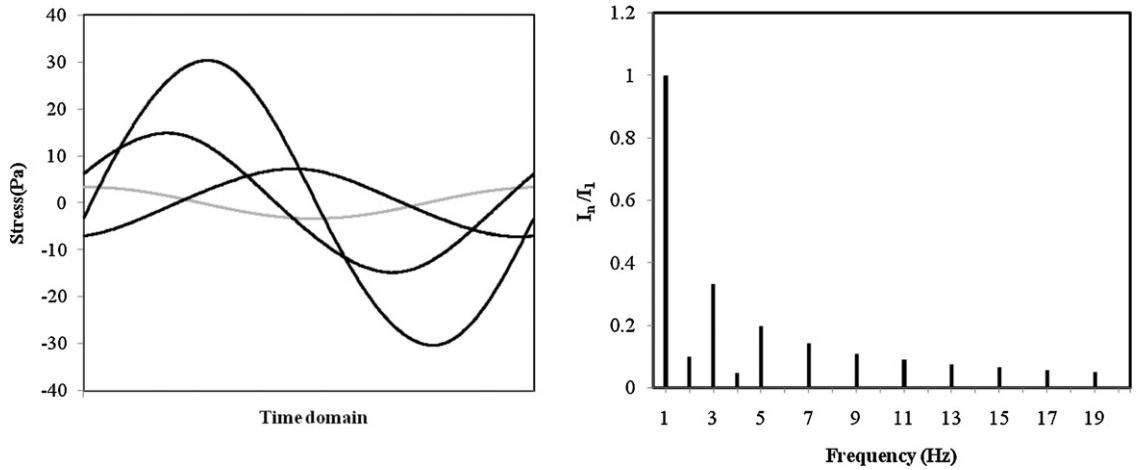

Fig. 6. Stress response data in time domain and the corresponding magnitude of FT rheology spectra for SPI–FG mixed dispersions at 1 Hz and strain amplitude of 250% (schematic).

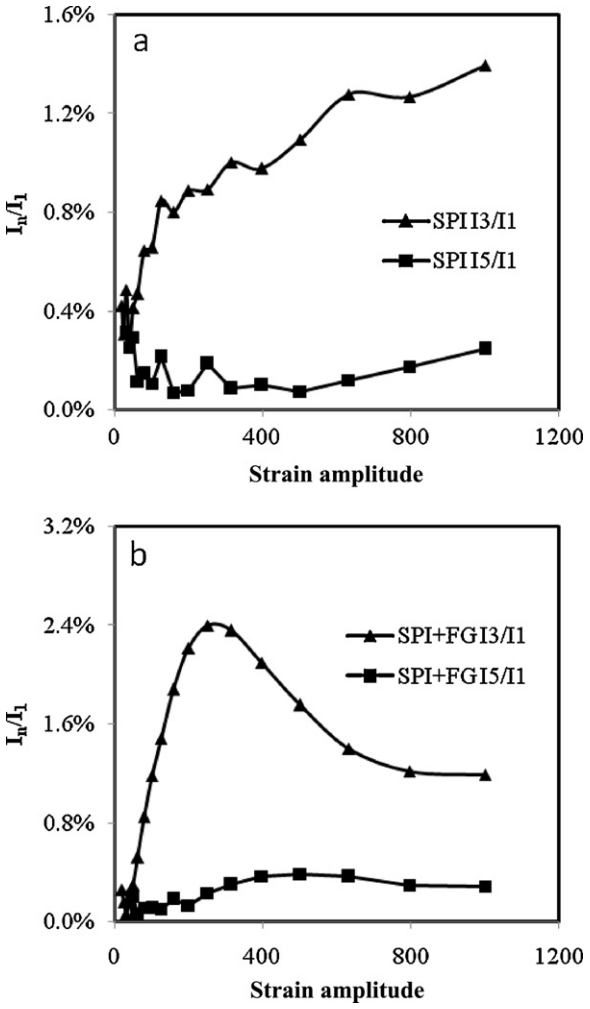

Fig. 7. Normalized amplitude, I_n/I_1, for the 3rd and 5th harmonic as a function of strain amplitude for SPI and SPI–FG mixed dispersions.

(lag phase) at low strain region. With the addition of flaxseed gum (Fig. 7b), the amplitude of the third harmonics increased sharply until a critical strain value of 250% was reached. At this critical strain, the magnitude of third harmonic was the highest (2.4%). The variation of fifth harmonic with shear strain was similar albeit the magnitude of the variation was much lower compared to that of the third harmonic. The peak value in the magnitude of the fifth harmonic was found to be around a strain value of 500%. These observations suggest that the SPI–FG mixed dispersions behave more like hard spheres (Grand & Petekidis, 2008) as opposed to the soft sphere behavior of soy protein isolate dispersions.

However, there is a noteworthy difference in the hard sphere behavior in the SPI–FG mixed dispersion compared to the hard sphere behavior of glassy poly-methylmetacrylate dispersion studied by Grand and Petekidis (2008). In the hard sphere model studied by these authors, once the magnitude of the third harmonic attains its maximum value it plateaus there and does not decrease when the amplitude of the strain is increased. In our SPI–FG mixed system, the magnitude of this third harmonic starts to decrease when the applied strain increases beyond the critical value (at which the amplitude of the third harmonic is the highest). The increase in the magnitude of third and fifth harmonics suggests to an increasing influence of instantaneous shear-thinning. The soy protein isolate dispersions exhibit greater strain softening when the strain amplitude increases. In the case of SPI–FG mixed dispersion, the strain softening reaches a peak at about shear strain of 250% beyond which this effect starts to decrease. At the strain value of 250%, the amplitude of the third harmonic reaches 1.40% for soy protein isolate dispersions and 2.40% for SPI–FG mixed dispersions. This implies that the addition of flaxseed gum increases the instantaneous strain softening effect on the SPI–FG mixed dispersions. The above observations suggest that the LAOS tests provide valuable information regarding the strain dependent non-linear deformation behavior in the microstructure of SPI–FG mixed dispersions.

4. Conclusions

The frequency sweep, steady shear measurements and LAOS tests were carried out to study the rheological behavior of SPI–FG mixed dispersions. The addition of even very small amount (0.3–0.7 (w/w), initial bulk concentration) of flaxseed gum significantly ($p < 0.05$) increase the apparent viscosity of the SPI–FG mixed dispersions compared to the viscosity of soy protein isolate dispersion. This finding suggests that the flaxseed gum can be used in soy protein isolate industry as a thicker. The shear rate and shear stress data of SPI–FG mixed dispersions can be predicted reasonably well ($R^2 > 0.95$) using the Power law model. It was also found that both the storage (G') and loss (G'') moduli of the SPI–FG mixed dispersions increased considerably with the increase in the flaxseed gum concentration. The FT rheology described the nonlinear stress versus strain data of SPI–FG gum mixed dispersions outside the linear viscoelastic region. The addition of flaxseed gum was found to increase the instantaneous stain softening response in the SPI–FG mixed dispersions systems.

Acknowledgment

This research was supported by National Natural Science Foundation of China (31000813).

References

Baeza, R. I., Carp, D. J., Pérez, O. E., & Pilosof, A. M. R. (2002). *LWT – Food Science and Technology*, *35*(8), 741–747.
Cain, F. W., Jones, M. G., & Norton, I. T. (1987). Spread. European Patent No. 872003942.
Chen, H. H., Xu, S. Y., & Wang, Z. (2004). Separation and purification of acidic polysaccharides and neutral polysaccharides in flaxseed gum. *Journal of Food and Fermentation Industry*, *1*, 96–100 [in Chinese].
Chen, H. H., Xu, S., & Wang, Z. (2006). Gelation properties of flaxseed gum. *Journal of Food Engineering*, *77*, 295–303.
Craciun, L., Carreau, J. P., Heuzy, M. C., Moan, M., & Ven, T. G. M. (2003). Rheological properties of concentrated latex suspensions of poly (styrene butadiene). *Rheologica Acta*, *42*, 410–420.
Cui, S. W. (2001). *Polysaccharide gums from agricultural products: Processing, structures and functionality*. Lancaster, PA, USA: Technomic Pub. Co., pp. 59–66.
Cui, W., Mazza, G., & Biliaderis, C. G. (1994). Chemical structure molecular size distribution and rheological properties of flaxseed gum. *Journal of Agriculture and Food Chemistry*, *42*, 1891–1895.
Erskine, A. J., & Jones, J. K. N. (1957). The structure of linseed mucilage (Part I). *Canadian Journal of Chemistry*, *35*, 1174–1182.
Galazka, V. B., Dickinson, E., & Ledward, D. A. (2000). Emulsifying properties of ovoalbumin in mixtures with sulphated polysaccharides: Effects of pH, ionic strength, heat and high-pressure treatment. *Journal of the Science of Food and Agriculture*, *80*, 1219–1229.
Grand, A., & Petekidis, G. (2008). Effects of particle softness on the rheology and yielding of colloidal glasses. *Rheologica Acta*, *47*(5–6), 579–590.
Hua, Y., Cui, S. W., & Wang, Q. (2003). Gelling property of soy protein–gum mixtures. *Food Hydrocolloids*, *17*(6), 889–894.
Hunt, K., & Jones, J. K. N. (1962). The structure of linseed mucilage. *Canadian Journal of Chemistry*, *40*, 1266–1279.
Hyun, K., Kim, S. H., Ahn, K. H., & Lee, S. J. (2002). Large amplitude oscillatory shear as a way to classify the complex fluids. *Journal of Non-Newtonian Fluid Mechanics*, *107*, 51–65.
Ikeda, S., & Nishinari, K. (2001). On solid-like rheological behaviors of globular protein solutions. *Food Hydrocolloids*, *15*, 401–406.
Ipsen, R. (1995). Mixed gels made from protein and kappa-carrageenan. *Carbohydrate Polymers*, *28*, 337–339.
Kallus, S., Willenbacher, N., Kirsch, S., Distler, D., Neidhoefer, T., Wilhelm, M., et al. (2001). Characterization of polymer dispersions by Fourier-transform rheology. *Rheologica Acta*, *40*, 552–559.

Klein, C. O., Spiess, H. W., Calin, A., Balan, C., & Wilhelm, M. (2007). Separation of the nonlinear oscillatory response into a superposition of linear, strain hardening, strain softening, and wall slip response. *Macromolecules*, *40*(12), 4250–4259.

Klein, C., Venema, P., Sagis, L., & Van Der Linden, E. (2008). Textural properties of agarose gels described by FT-rheology. In *AIP Conference Proceedings, 1027* (pp. 588–590).

Larson, R. G. (1999). *The structure and rheology of complex fluids*. Oxford University Press: Oxford.

Lu, L., Liu, X., & Tong, X. Z. (2006). Critical exponents for sol–gel transition in aqueous alginate solutions induced by cupric cations. *Carbohydrate Polymers*, *65*, 544–551.

Macosko, C. W. (1994). *Rheology: Principles, measurements, and applications*. VCH Publishers: New York.

Maltais, A., Remondetto, G. E., Gonzalez, R., & Subirade, M. (2005). Formation of soy protein isolate cold-set gels: Protein and salt effects. *Journal of Food Science*, *70*(1), C67–C73.

Molina, E., Papadopoulou, A., & Ledward, D. A. (2001). Emulsifying properties of high pressure treated soy protein isolate and 7S and 11S globulins. *Food Hydrocolloids*, *15*(3), 263–269.

Muralikrishna, G., Salimath, P. V., & Tharanathan, R. N. (1987). Structural features of an arabinoxylan and a rhamnogalacturonan derived from linseed mucilage. *Carbohydrate Research*, *161*, 265–271.

Özkan, N., Xin, H., & Chen, X. D. (2002). Application of a depth sensing indentation hardness test to evaluate the mechanical properties of food materials. *Journal of Food Science*, *65*(5), 1814–1820.

Petruccelli, S., & Añón, M. C. (1994a). Relationship between the method of obtention obtaining and the structural and functional properties of soy protein isolates. 1. Structural and functional properties. *Journal of Agricultural and Food Chemistry*, *42*, 2161–2169.

Petruccelli, S., & Añón, M. C. (1994b). Relationship between the method of obtention obtaining and the structural and functional properties of soy protein isolates. 2. Surface properties. *Journal of Agricultural and Food Chemistry*, *42*, 2170–2176.

Puppo, M. C., & Añón, M. C. (1999). Soybean protein dispersions at acidic pH. Thermal and rheological behavior. *Journal of Food Science*, *64*, 50–56.

Puppo, M. C., Lupano, C. E., & Añón, M. C. (1995). Gelation of soybean protein isolates in acidic conditions: Effect of pH and protein concentration. *Journal of Agricultural and Food Chemistry*, *43*, 2353–2361.

Renkema, J. M. S., Knabben, J. H. M., & van Vliet, T. (2001). Gel formation by b-conglycinin and glycinin and their mixtures. *Food Hydrocolloids*, *15*(4), 407–414.

Samat, S. K., Singhal, R. S., Kulkarni, P. R., & Rege, D. V. (1993). Protein–polysaccharide interactions: A new approach in food formulation. *International Journal of Food Science and Technology*, *28*, 547–562.

Sim, H. G., Ahn, K. H., & Lee, S. J. (2003). Three-dimensional dynamics simulation of electrorheological fluids under large amplitude oscillatory shear flow. *Journal of Rheology*, *47*, 879–895.

Steffe, J. F. (1996). *Rheological methods in food process engineering*. Freeman Press: East Lansing.

Tolstoguzov, V. B. (1997). Protein–polysaccharide interaction. In S. Damodaran, & A. Paraf (Eds.), *Food proteins and their applications* (pp. 171–198). NY, USA: Marcel Dekker Inc.

Tolstoguzov, V. B. (2003). Some thermodynamic considerations in food formulation. *Food Hydrocolloids*, *17*, 1–23.

Tschoegl, N. W. (1989). *The phenomenological theory of linear viscoelastic behavior. An introduction*. Berlin: Springer.

Wang, Y., Li, D., Wang, L. J., & Adhikari, B. (2011). The effect of addition of flaxseed gum on the emulsion properties of soybean protein isolate (SPI). *Journal of Food Engineering*, *104*(1), 56–62.

Wang, Y., Li, D., Wang, L. J., Wu, M., & Özkan, N. (2011). Rheological study and fractal analysis of flaxseed gum gels. *Carbohydrate Polymers*, *86*(2), 594–599.

Wang, Y., Wang, L. J., Li, D., Özkan, N., Chen, X. D., & Mao, Z. H. (2008). Effect of flaxseed gum addition on rheological properties of native maize starch. *Journal of Food Engineering*, *89*, 87–92.

Wang, Y., Wang, L. J., Li, D., Xue, J., & Mao, Z. H. (2009). Effects of drying methods on rheological properties of flaxseed gum. *Carbohydrate Polymers*, *78*(2), 213–219.

Wilhelm, M. (2002). Fourier-transform rheology. *Macromolecular Materials and Engineering*, *287*, 83–105.

Wilhelm, M., Maring, D., & Spiess, H. W. (1998). Fourier-transform rheology. *Rheologica Acta*, *37*, 399–405.