Rheological properties of soy protein isolate solution for fibers and films

Pengchao Liu ^a, Helan Xu ^a, Yi Zhao ^a, and Yiqi Yang ^{a,b,c,*}

Abstract:

For the first time, rheological behavior of soy protein isolate (SPI) solution with high concentration for fibers and films was studied. The results showed that SPI could be readily dissolved in urea/sodium sulfite aqueous system, and the SPI solution is suitable for wet spinning and film casting. The effects of concentration, temperature, and shear rates on the rheological properties of SPI solution were studied. Viscosity of SPI solution decreases with increasing temperature, which is good for the preparation of solution with high concentration and regenerated SPI fibers/films with good properties. All solution samples exhibited thixotropic behavior, which were different from traditional polymer solution for wet spinning and film casting process. Both in forward and backward measurements were carried out by the Power Law model. Under constant shear rates (80-160 s^{-1}), 18 wt% SPI solution was chosen to study the dependence of viscosity on time. Second order structural kinetic model, Weltman model, first-order stress decay models with zero and none-zero equilibrium stress values were used to fit the rheological data. Among the four models, Weltman model is more appropriate to fit the thixotropic data.

Key words: rheology; soy protein; wet spinning; film casting; regenerated protein fiber

1. Introduction

Regenerated protein fibers are prepared via purification, dissolution, and spinning processes from animal proteins or plant proteins (Xu, Liu, Mi, Xu, & Yang, 2015). Different from synthetic polymer fibers, regenerated protein fibers possess good biocompatibility, biodegradability, good hygroscopicity and soft hand, and thus are sustainable and environmentally friendly material (Poole, Church, & Huson, 2009). Study on the regenerated protein fibers began from 1930-50s, such as casein milk fibers, peanut fibers, zein fibers, and soy protein fibers (Hearle, 2007). Among all the plant protein resource, soy has the most protein amount (37-42%) and big production (282 million tons in 2014).

Pure soy protein fibers were studied from 1940. And the first patent about soy protein fibers was authorized to Toshiji Kajita and Ryohei Inoue (Inoue & Kajita, 1940). In 1945, Boyer from Ford Motor Company also applied a patent (William, Robert, & Crupi, 1945). However, the production of mid-twentieth soybean protein fibers was ceased at the end of the World War II (Rijavec & Zupin, 2011). Huang et al. prepared regenerated soy protein fibers again via wet spinning in 1995 (Huang, Hammond, Reitmeier, & Myers, 1995). Since 2000, researchers began to study composite soy protein fibers (Li, Zeng, Wang, Yang, & Wang, 2008; Zhang, Li, & Yu, 2011). However, the content of soy protein is less than 30 % in the composite fibers.

Soy protein can also be prepared to edible film or coatings. These biopolymer films have great potential application in the field of edible packaging. They act as barriers to control transferring of gas and volatile flavors (Gennadios, Brandenburg, Weller, & Testin, 1993; Park, Rhee, Bae, & Hettiarachchy, 2001). There are two main approaches to make

packing materials from proteins: wet processing and dry processing. The type of bonds stabilizing the protein film matrix is mainly hydrophobic, electrostatic, hydrogen and/or covalent, the relative importance of them being mainly dependent on the biochemical properties of each protein and the production method/processing conditions (Gómez-Estaca, Catalá, & Hernández-Muñoz, 2016). Researches usually differentiate two kinds of dry processing: thermo-pressing and extrusion. SPI films can be prepared by the use of extrusion (Chan, Lim, Barbut, & Marcone, 2014) and thermo-pressing (Garrido, Etxabide, Peñalba, de la Caba, & Guerrero, 2013) independently, sometimes they are combined, using extrusion for the mixing and partial modification of the components, and then obtaining the materials by thermo-pressing (Gómez-Estaca, Catalá, & Hernández-Muñoz, 2016).

To prepare fibers or films with good properties, the key step is dissolution of soy protein. Due to disulfide bond, hydrogen bond, hydrophobic effect and other secondary bond, soy protein is globular (Zhao, Zhao, Xu, & Yang, 2015). During the dissolving process, globular conformation should be modified to form molecules coil-denaturation. Denaturation is beneficial to modify the entanglement among proteins, leading to improvement of fiber strength after drawing. Hydrogen bond and disulfide bond were usually dissociated for dissolving. Urea was found to be an effective swollen agent for soy protein, because O and H atom in urea molecule can react with –OH in soy protein to break hydrogen bond (Kinsella, 1979). Disulfide bonds can be ruptured by oxidation, reduction, and exchanging effect (Wall, 1971). Among the above approaches, reduction is preferred. Most common reductants include sodium cyanide (Krull & Friedman, 1967), sodium sulfite (Reddy & Yang, 2007), cysteine (Xu & Yang, 2014; Xu, Cai, Xu, & Yang,

2014) and so on.

To date, wet spinning and electrospinning are two main methods to fabricate protein fibers. Steady spinning solution is the precondition no matter whichever method above will be used. Rheological properties of spinning solution play an important role in spinning process, structural formation, and fibers' properties, respectively, and thus are usually studied as an important parameter for wet spinning. Puppo et al. studied the effect of pH, concentration, and ionic strength on the rheological properties (Puppo & Añón, 1999). Varzakas et al. studied the gel strength from soy protein isolate and soy protein concentration (Varzakas, Labropoulos, & Anestis, 2011). Kim et al. studied the effect of volume fraction of oil droplet on the rheological properties (Kim, Renkema, & van Vliet, 2001). Murekatete et al. studied the gelation and rheological properties induced by salts and acid (Murekatete, Hua, Chamba, Djakpo, & Zhang, 2014). Wagner et al. studied the influence of concentration, water-imbibing capacity (WIC), salt addition, and thermal treatment on viscosity and rheological behavior of commercial soy isolates (Wagner, Sorgentini, & Añón, 1992). They also found that the apparent viscosity of dispersions of SPI depends on the WIC, the morphology and size of the particles, and the interaction of the hydrated particles (Añón, Sorgentini, & Wagner, 2001). However, these researches were always carried out for the applications of soy protein as food ingredients. In addition, viscosity also plays an important role in film casting. Until now, rheological study on the high concentration SPI solution for fibers and films has not been reported yet.

In this study, soy protein aqueous solutions for wet spinning and film casting were prepared with urea as swollen agents and sodium sulfite as reductants. Effects of

concentration, temperature, and shear rates on rheological properties were studied by rotational rheometer. Soy protein solution with 18 wt% concentration was chosen to study the thixotropic behavior by fitting the data with four theoretical models.

2. Experimental

2.1 Materials

Soy protein isolate (SPI, partially denatured) was a gift from Archer Daniels Midlands Company. It contains moisture (< 6%), protein (> 90 %), fat (< 4%), and ash (< 5%). Urea, sodium sulfite, and paraffin oil were purchased from VWR International, Bristol. All reagents were analytical grade and used as received.

2.2 Preparation of SPI solutions

In a typical experiment, SPI powder (100 g) was mixed with 8 M urea solution (399 g) with 1 % (w/w) sodium sulfite on weight of SPI used. The mixtures were swelling for 24 hours and then stirred at 80 °C for 2 hours to ensure the complete dissolution. The resultant solutions (20 wt%) came out tan and then were centrifuged to degas them at 9792 ×g for 10 min at ambient temperature (Allegra 25R Centrifuge, Beckman Coulter). The SPI solution was hermetically stored at ambient temperature and protected against moisture evaporation. Under the same conditions, SPI solutions with other concentrations (16 wt%, 18 wt%, and 22 wt %) were also prepared. During fiber extrusion/film casting, unreacted sodium sulfite will be washed away at high liquor-to-fiber/film ratio and subsequent 2 to 3 cycles of washing. Therefore, re-formation of disulfide bonds during solidification of fiber/film will not be avoided or reduced by extra sodium sulfite in the spinning dopes.

2.3. Rheological measurement

Rheological analysis was carried out on a rotational rheometer, R/S plus (Brookfield, U.S.A.). A coaxial spindle/chamber geometry (CC 25) was used. Shear viscosity η ($\dot{\gamma}$) was measured as a function of shear rate $\dot{\gamma}$ in the range of 0 to 240 s^{-1} . For each measurement, a fresh SPI solution was prepared, and then degassed SPI solution was poured into the geometry instrument, which had been kept at each measurement temperature without pre-shearing or oscillating. To prevent dehydration during rheological measurements, a thin layer of low-viscosity paraffin oil was spread on the exposed surface of the measured solution. For the 22 wt% sample, high viscosity cannot be detected by this rheometer due to out of upper limit at the temperatures lower than 40 °C. So 16 wt%, 18 wt%, and 20 wt% samples were chosen to study the influence of concentrations on the rheological behavior.

Flow behavior was described by the fitting of experimental data with the Power Law model:

$$\sigma = k\dot{\gamma}^n \quad (1)$$

Where σ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), k is the consistency coefficient (Pa s^n) and n is the flow behavior index.

The area of hysteresis loop was obtained by the difference between integrating the area for forward and backward measurements from $\dot{\gamma}_1$ (initial shear rate) to $\dot{\gamma}_2$ (final shear rate):

$$\text{Hysteresis loop area} = \int_{\dot{\gamma}_1}^{\dot{\gamma}_2} k\dot{\gamma}^n - \int_{\dot{\gamma}_2}^{\dot{\gamma}_1} k'\dot{\gamma}^{n'} \quad (2)$$

Where k , k' and n , n' are the consistency coefficients and flow index behavior for forward and backward measurements, respectively.

3. Results and Discussion

Rheological properties of SPI solution substantially influence the spinning process and mechanical properties of fibers, as well as casting and film properties. In particular, the rheology of the polymer solution, depending on the concentration and the polymer-solvent interaction, is considered as one of the key factors of the fiber spinning process (Um et al., 2004). We investigated the rheological behavior of SPI solutions to determine the optimum spinning conditions for the wet spinning of SPI filament.

In the urea/sodium sulfite system, SPI solution can flow in the concentration range of 16-20 wt% at ambient temperature. However, SPI solution usually becomes into gel at 22 wt% concentration (Figure 1). Puppo et al. found that the minimum protein concentration required for heat-induced gelation from the isolate was 7 wt% (Puppo & Añón, 1998). The urea/sodium sulfite system denatured the SPI effectively, which inhibited the formation of protein-protein interaction. Therefore, gel could not be formed even at higher concentrations in our system.

There are no covalent bonds forming or breaking in the formation of physical gel, and polymer form a cross-linked network through ionic bonding, hydrogen bonding, or chain entanglements of polymer-to-polymer interactions (Cai & Zhang, 2006). For the SPI solution, its gel belongs to physical gel. The hydrocolloids can be changed reversibly between a solution state and a gel state by lowering or raising the temperatures (Figure 1). The thermo-reversible indicates that disulfide bond formation and rearrangements do not occur upon heating. During the wet spinning and film casting processes, we can decrease the viscosity by increasing the temperature, which is important for wet spinning and film casting of solutions with high concentration.

Figure 1

3.1 Concentrations (16wt%, 18wt%, 20wt%)

As shown in Figure 2(a), at the same shear rates, apparent viscosity increases with increasing concentration. This is easy to understand by molecules chain entanglement theory. Higher concentration causes more entanglement among protein molecules. It is hard to move for the protein molecules due to more intermolecular friction. Another reason is that protein-protein interactions become dominant and more molecular water is immobilized with increased concentration, resulting in progressive increase in apparent viscosity of SPI solutions (Wagner, Sorgentini, & Añón, 1992). Moreover, with increasing shear rates, all the samples present shear thinning behavior, which is a typical pseudo-plastic of polymer solution. And the effect of shear thinning was reduced with a decrease of concentration. Shear thinning behavior of a polymer solution is attributed to the molecular entanglement, and the decreasing slope of shear viscosity against the shear rate (Kopperud & Hansen, 1998).

From Figure 2(b), hysteresis loop can be seen in the flow curves of shear stress versus shear rates. In addition, the hysteresis loop is clockwise, which is to say that shear stress in the shear rate increasing process (forward) is bigger than one in decreasing process (backward). It can be concluded that soy protein solution is thixotropic fluid, whose shear thinning behavior is time-dependent. According to the research of Zhang, clockwise hysteresis loop was considered as structural breakage by shearing or formation of new structure (Liang, Zhang, Xu, Dou, & Zhang, 2014). Some researchers evaluate the thixotropic magnitude using breakdown coefficient, K_d , which is defined as the ratio of the hysteresis area to the area beneath the forward curve in the following equation (Dokić, Dapčević, Krstonošić, Dokić, & Hadnađev, 2010).

$$K_d = \frac{A_{up} - A_{down}}{A_{up}}(3)$$

Where, A_{up} and A_{down} are the areas under forward and backward flow curves, respectively.

Figure 2

As shown in Table 2, increasing concentrations increased K_d . It is because K_d is an index of the energy required to break down the thixotropic structure. That is to say more energy is needed to destroy the structure at higher concentration.

Table 1

3.2 Temperatures

18 wt% was chosen to study the temperatures influence on the rheological behavior of soy protein solution. Its viscosity flow curves versus shear rate are shown in Figure 3(a), where the rheological data of other concentrations samples (16 wt%, 20 wt%, and 22 wt%) can be found in the Figure S1. Wagner et al. found that heating produced a viscosity increase in all his SPI dispersions. They thought that this increase could be ascribed to the formation of new structures and to the importance of hydrophobic interactions and disulfide bridges on those interactions (Wagner, Sorgentini, & Añón, 1992). However, Viscosity decreases with increasing temperatures in our system (Figure 3(a)). This is in agreement with synthetic polymer solution, which means urea/sodium system is a good solvent for SPI.

Similar with Figure 2(a), it shows shear thinning behavior, and the viscosity decreases faster in the low shear rate range ($< 100 \text{ s}^{-1}$). In addition, with increasing temperature, apparent viscosity decreases. This is due to more intensely molecules chain motion at higher temperature for getting more energy. From Figure 2(a) and Figure 3(a), we can see that SPI solution shows shear thinning behavior similar to common synthetic polymer solution. So it is concluded that globular soy protein can be dissolved in

urea/sodium sulfite aqueous system to form steady SPI solution.

SPI solution shows thixotropic behavior at different temperatures (Figure 3(b)). As shown in Table 1, K_d decreases with increasing temperatures. Since K_d is an index of the energy needed to break down the thixotropic structure, the energy needed to destroy structure decreases with increasing temperatures. This is different from oviductusranae hydrogel (Liang, Zhang, Xu, Dou, & Zhang, 2014) and corn starch (Dokić, Dapčević, Krstonošić, Dokić, & Hadnađev, 2010), which shows increased K_d . This is because they can form gel in their dissolved systems, which need more energy to break down the structure. In other words, SPI solution in the urea/sodium sulfite is steady in the range of 25 °C-70 °C, instead of forming gel.

Figure 3

In the shear rate range of this study, the Power Law model describes flow behavior of each sample. Non-Newtonian index n represents degree of deviation of solution from Newtonian fluid. At constant concentration, non-Newtonian index n increases with increasing temperatures at concentration of 16wt%-22wt% (Table 1). For the Newtonian fluid, viscosity maintains constant with increasing shear rate. The n equals 1. The less n value, the more degree of deviation from Newtonian fluid. It means that the viscosity is more dependent on shear rate (Lin & Ku, 2008).

At constant concentration, n increases with increasing temperatures. This is because improvement of moving ability of protein molecules and decrease in resistance between SPI solution layers. It will cause the dependence of viscosity to shear rate decreases (Matuana & Diaz, 2010). Moreover, at higher temperatures, there is more energy available for the destruction of entanglements.

At constant temperature, n decreases with increasing concentrations, illustrating that SPI solution are greatly influenced by the shear rate at higher concentrations. This is easy to understand for more chains entanglement at higher concentration. For all the samples, R^2 is greater than 0.99, which proves that the Power Law model is very suitable to describe the rheological property of SPI solutions.

Wagner et al. studied the rheological behavior of commercial soy protein isolates under different experimental conditions (Temperature, protein concentration, water imbibing capacity) (Wagner, Sorgentini, & Añón, 1992; Añón, Sorgentini, & Wagner, 2001). However, their research just focused on the rheological behavior itself of the SPI dispersion. In our research, we aimed to build connection between rheological behavior of SPI solution and wet spinning/film casting process. Rheological study is only the research method by which we can find the optimum condition of the SPI solutions for wet spinning and film casting.

In addition, in their research, SPI was dispersed in distilled water. However, we chose urea/sodium sulfite aqueous solution as dissolving system. Urea is a good breaker for hydrogen bond, while sodium sulfite is a dissociation agent for disulfide bond. Under the synergistic effect of them, SPI solution was prepared, not dispersion.

In the references, concentrations of SPI dispersion are 1.6-14 wt% and 1.6-16%, respectively. However, they are 16-22% in our system. High concentration is preferred for preparation of regeneration protein fibers with good strength. So we chose SPI solutions with higher concentrations as research objective.

From our rheological results above, we can discuss the correlation between rheological behavior of SPI solutions and wet spinning and film casting process. The

decrease in the drop rate of shear viscosity (n much closer to 1) implies a less entangled solution state and a less deteriorated viscosity by shear force encountered in the fiber spinning process (Um et al., 2004). As to SPI spinning solution, a lower drop rate of shear viscosity is observed at a higher heating temperature, a lower SPI concentration and a higher shear rate. Therefore, they are expected to result in better fiber spinnability theoretically. However, a higher SPI concentration is required for protein fibers with higher strength. So considered comprehensively from solutions' spinnability and fibers' strength, SPI solution are chosen for wet spinning with a higher concentration, a higher heating temperature, and a higher shear rate.

As to the casting process of protein films, it follows similar principles like wet spinning. A higher concentration is preferred for the films with better strength. At a higher heating temperature and a higher shear rate, the casting solutions show a lower viscosity and a less deteriorated viscosity. A lower viscosity makes the solution flow easily and casting smoothly. And a less deteriorated viscosity means the solution has better stability for casting. In summary, we can obtain SPI solutions which is suitable for fibers and films at higher concentrations, heating temperatures, and shear rates.

3.3 Viscosity activation energy

The effect of temperature on the rheological properties is illustrated in Figure 3 and Table 1. Viscosities of SPI solution at higher temperature were lower than those values obtained at lower temperatures. The temperature effect on the apparent viscosity of SPI solution at a constant shear rate will be probably modeled by an Arrhenius-type equation, which could be expressed by

$$\ln \eta = \ln A + \frac{E_{\eta}}{RT} \quad (4)$$

Where T is the Kelvin temperature, A is material constant, E_η is the viscous flow activation energy, and R is the universal gas constant. The parameters of the Arrhenius equation describing the viscosity-temperature relationship were determined by linear regression.

Figure 4

As shown in Figure 4 and Figure 5, Arrhenius model described a good correlation between temperature and apparent viscosity at different constant shear rates. From Figure 4, it was observed that there was a linear relationship of $\ln(\eta)$ versus $(1/T)$. The experimental data showed that the apparent viscosities of SPI solutions at different temperatures obey Arrhenius equation.

Figure 5

Figure 5 shows the viscous flow activation energies of SPI solution obtained from linear regression on semi-logarithmic plots of apparent viscosity versus temperature. From Figure 5, it was found that the E_η value of the SPI solution decrease with increasing temperature, implying that the effect of test temperature on the solution viscosity became less pronounced at higher shear rate. An increase in temperature led to an increase in the flowability of protein segments. Accordingly, the viscosity of protein solution decreased. For most polymers, the resistance becomes lower at higher shear rate, because the disentanglement of the molecular chains is stronger than the entanglement, leading to a reduced E_η (Li et al., 2009).

Usually, the viscous flow activation energy (E_η) represents the temperature sensitivity of the apparent viscosity. Larger E_η means a higher dependence of temperature on viscosity. Higher E_η values indicate a more rapid change in viscosity with temperature.

For the SPI solution, it is observed that the viscosity is more dependent on temperature with higher concentration and lower shear rates, which is consistent with discussion before. Thus, wet spinning and film casting of SPI solution should be at a higher shear rate and a relative higher concentration.

3.4 Time-dependent rheological modeling (18wt%, 25 °C)

From the above discussion, SPI solution show thixotropic property. The viscosity of solution is dependent on time. To study the time-dependent rheological behavior, 18 wt% sample at 25 °C was chosen to study at constant shear rate. Four theoretical models, including second order structural kinetic model, Weltman model, first-order stress decay models with zero and none-zero equilibrium stress values, were used to fit the rheological data.

3.4.1 structural kinetic model

$$\left[\frac{(\eta - \eta_{\infty})}{(\eta_0 - \eta_{\infty})} \right]^{1-n} = (n - 1)kt + 1 \quad (5)$$

Where η_0 is the initial apparent viscosity at $t = 0$ (structured state), and η_{∞} is the steady state apparent viscosity at $t \rightarrow \infty$ (non-structured state). n is the order of the structure breakdown reaction and k is the breakdown rate constant (Figure S2).

Structural kinetics model postulates that the change in time-dependent flow properties is associated with the shear-induced breakdown of the internal fluid structure and that the rate of this breakdown during shear depends on the kinetics of the structured state and non-structured state process (Abu-Jdayil, 2003). According to this model, irreversible structural breakdown will happen under the action of shear.

Table 2

For all samples investigated, it was found that their apparent viscosity data at a

constant shear rate could be correlated with Eq. (5) using $n=2$. Table 2 shows the parameters of the structural kinetic model (Eq. (5)) obtained for selected hydrocolloids. The rate constant, k , is a measure of the rate of the thixotropic breakdown. As shown in Table 2, k increased with increasing shear rate in the range of 40-160 s^{-1} .

The ratio of initial to steady state viscosity, η_0/η_∞ can be considered as a relative measure of the amount of structure breakdown, or in other words as a relative measure of the extent of thixotropy. In this study, the extent of thixotropy decreased with shear rate.

3.4.2 Weltman model

$$\tau = A + B \ln t \quad (6)$$

Where t is the shearing time (s), A and B are constant parameters, which characterize the time-dependent behavior.

Figure 6

Weltman model was used to describe the relationship between experimental shear stress and shearing time. This model postulates that the shear stress value decays in the logarithm form, where no balance exist (Weltmann, 1943). As shown in Table 3, the model fit well to the experimental data (R^2 value more than 0.98). The B value indicates the extent of thixotropy and it increased with shear rate for SPI solution. This was in agreement with that reported by Abu-Jdayil and Razavi (Abu-Jdayil, Al-Malah, & Asoud, 2002; Razavi, Najafi, & Alaei, 2008). Some researchers showed that the extent of thixotropy (B value) decreased with shear rate for waxy maize starch and starch-milk-sugar pastes (Abu-Jdayil & Mohameed, 2003; Dzuy Nguyen, Jensen, & Kristensen, 1998).

Table 3

3.4.3 First-order stress decay model with a zero stress value

$$\tau = \tau_0 e^{-kt} \quad (7)$$

Where τ_0 is the initial shear stress value and k is the breakdown rate constant.

The first-order stress decay model was determined by fitting the shear stress-time data, presenting in Figure S3 and Table 4. The lower R^2 (<0.85) values show that this model was not suitable for describing the time-dependent behavior of SPI solution.

Table 4

3.4.4 First-order stress decay model with a none-zero steady state stress value

$$\tau - \tau_{eq} = (\tau_0 - \tau_{eq}) e^{-kt} \quad (8)$$

Where τ_0 is the initial shear stress value, τ_{eq} is the equilibrium stress value and k is the breakdown rate constant.

The first-order stress decay model with a non-zero steady state stress value was used to fit shear stress-time data. The results of modeling are given in Figure S4 and Table 5. In this study, k increased with increasing shear rate.

Table 5

According to fitting curves and R^2 of four models above, we think the Weltman model is the best model to describe the time-dependent rheological behavior in the shear rate and time range of this study. As to why the Weltman model could be used to fit the experimental data, further discussion is needed.

4. Conclusions

Steady soy protein isolate solution was prepared in urea/sodium sulfite aqueous system for wet spinning and film casting. The results showed that SPI solution exhibited rheological behavior similar to synthetic polymer spinning solution using urea/sodium sulfite aqueous solution as dissolving system. Power Law model can give a good description to the experimental data, indicating that globular conformation of soy protein

can be changed to coil chain under the synergistic action of urea (hydrogen breaker) and sodium sulfite (disulfide bond breaker). It is prerequisite for wet spinning and film casting of globular protein. Viscosity of SPI solution can be adjusted by controlling the concentration, temperature and shear rate. So solution with higher concentration and lower viscosity, which is suitable for preparation of good regenerated soy protein fibers or films, can be obtained. However, different from synthetic polymer spinning solution, soy protein solution shows thixotropic behavior. Four theoretical models, including second order structural kinetic model, Weltman model, first-order stress decay models with zero and none-zero equilibrium stress values were used to fit the rheological data. Weltman model is more appropriate to fit the thixotropic.

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535

	T (°C)	k	n	R^2	k'	n'	R'^2	K_d
16%	25	5.28	0.64	0.9998	3.50	0.715	0.9999	0.051
	30	3.43	0.67	0.9999	2.55	0.722	0.9999	0.047
	35	2.29	0.70	0.9999	1.63	0.756	0.9999	0.043
	40	1.56	0.72	0.9999	1.13	0.775	0.9999	0.040
	45	0.96	0.75	0.9998	0.74	0.800	0.9999	0.033
	50	0.72	0.76	0.9993	0.50	0.829	0.9999	0.033
	60	0.27	0.85	0.9995	0.24	0.870	0.9995	0.025
	70	0.13	0.89	0.9983	0.11	0.927	0.9988	0.023
18%	25	54.47	0.43	0.9978	21.97	0.591	0.9999	0.110
	30	28.06	0.50	0.9990	13.02	0.634	0.9999	0.092
	35	15.41	0.55	0.9995	8.27	0.662	0.9999	0.075
	40	8.11	0.60	0.9997	4.88	0.689	0.9998	0.061
	45	5.28	0.62	0.9997	3.24	0.709	0.9998	0.059
	50	3.52	0.64	0.9998	2.21	0.727	0.9999	0.055
	60	1.56	0.68	0.9996	0.88	0.786	0.9997	0.058
	70	0.59	0.76	0.9989	0.44	0.817	0.9993	0.027
20%	25	197.77	0.33	0.9978	102.37	0.439	0.9970	0.120
	30	145.01	0.35	0.9967	53.61	0.535	0.9998	0.118
	35	73.82	0.42	0.9979	28.98	0.587	0.9999	0.114
	40	45.54	0.46	0.9974	19.14	0.615	0.9999	0.103
	45	23.32	0.50	0.9980	10.83	0.642	0.9996	0.089
	50	15.57	0.52	0.9982	7.21	0.656	0.9995	0.089
	60	7.36	0.54	0.9992	3.35	0.681	0.9993	0.091
	70	3.44	0.57	0.9988	1.52	0.718	0.9992	0.091
22%	40	221.11	0.30	0.9910	103.87	0.440	0.9977	0.088
	45	100.39	0.41	0.9975	56.56	0.508	0.9997	0.079
	50	50.38	0.48	0.9980	31.63	0.560	0.9997	0.064
	60	19.10	0.53	0.9983	13.14	0.599	0.9992	0.052
	70	9.00	0.55	0.9975	6.04	0.622	0.9983	0.053

538 Table 1. Power law parameters obtained for continuous forward and backward
539 measurements

541

$\dot{\gamma} \text{ (s}^{-1}\text{)}$	$k \text{ (*}10^{-4}\text{)}$	η_0/η_∞	R^2
40	2.18	1.252	0.96
80	3.11	1.233	0.98
160	3.84	1.212	0.98

542

543 Table 2. Degree and extent of thixotropy of selected hydrocolloids evaluated at different
 544 shear rates by the second-order structural kinetic model (Eq. (5))

545

546

$\dot{\gamma} \text{ (s}^{-1}\text{)}$	$A \text{ (Pa)}$	$B \text{ (Pa)}$	R^2
40	166.12	5.39	0.980
80	249.09	7.69	0.986
160	365.30	10.57	0.995

547

548 Table 3. The parameters of the Weltman model (Eq. (6))

549

550

551

$\dot{\gamma}$ (s ⁻¹)	τ_0 (Pa)	k (*10 ⁻⁶ s ⁻¹)	R^2
40	127.58	8.12	0.85
80	193.67	7.34	0.80
160	288.94	6.65	0.79

552

553 Table 4. The parameters of the First-order stress decay model with a zero-equilibrium
554 stress value (Eq. (7))

555

556

557

$\dot{\gamma} \text{ (s}^{-1}\text{)}$	$\tau_0 \text{ (Pa)}$	$\tau_{eq} \text{ (Pa)}$	$k \text{ (*}10^{-4} \text{ s}^{-1}\text{)}$	R^2
40	132.84	112.41	1.73	0.95
80	204.32	174.35	2.32	0.98
160	304.39	263.28	2.50	0.98

558

559 Table 5. The parameters of the First-order stress decay model with a none-zero steady
560 state stress value (Eq. (8))

Figure captions:

Figure 1. Reversible solution-gel transition depended on temperature (22%).

Figure 2. Viscosity (a) and hysteresis loop (b) of the flow curves of SPI solution as a function of shearing rates with different concentrations at 25°C.

Figure 3. Viscosity (a) and hysteresis loop (b) of the flow curves of SPI solution as a function of shearing rates at different temperatures.

Figure 4. Relationships between apparent viscosity and temperature for SPI solution with different concentrations at 16% (a), 18% (b), and 20 % (c), respectively.

Figure 5. Relationships between viscous flow activation energy and shear rate for SPI solution with different concentrations.

Figure 6. Test of the Weltman model with 18 % SPI solution at different shear rate

Figure 1

Heating →
← **Cooling**

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6