Thermal and Rheological Properties of *Lupinus albus* Flour

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ABSTRACT: The thermal and rheological properties of lupin flour were investigated by DSC and rheometry. DSC study showed that whole and defatted lupin meal had identical thermal properties, and lupin had the same glass transition as the wheat protein gluten. By measuring the linear rheological properties of a series of concentrations of defatted lupin suspensions, we found that defatted lupin suspensions exhibited strong viscoelastic solid properties, which were to some extent similar to those of gluten. Both storage (G') and loss (G'') moduli increased dramatically over a narrow range of lupin concentrations. The linear range of the rheological properties of lupin was very small. The stress relaxation studies showed that the lupin suspensions did not relax a decade within a thousand seconds, indicating that the molecules of lupin have strong physical interactions. This research offered new insight into physical properties of lupin and will be useful for further studies on applications for lupin.

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KEY WORDS: DSC, lupin proteins, rheology, thermodynamics, viscoelastic properties.

Lupin is an important legume plant (1). Its seeds contain high concentrations of proteins (more than 50%) and oil (up to 11%), which are comparable to those of soybeans. The possession of nutritional substances and a high concentration of proteins make lupin a promising dietary element (2). Like other plant proteins, lupin proteins are accompanied by various fibers. The fiber intake could improve glucose tolerance and consequently modify blood insulin and glucagon (2). In addition, lupin proteins lower serum cholesterol level, as do some other plant proteins (2). Lupin already has many human consumption applications, such as breadmaking (3), pasta products (3), meat substitutes (4), and egg and milk replacers (5).

In this paper, the thermal and rheological properties of lupin meal are investigated. The rheological properties of lupin indicate that it behaves as a strong viscoelastic solid material. The thermal behavior of lupin shows that it has the same glass transition as wheat protein gluten.

MATERIALS AND METHODS

Materials. Lupinus albus was provided by the Agricultural Research Station, Virginia State University (Petersburg, VA). The vital wheat gluten samples used in this study were donated by Dr. Ody Maningat of Midwest Grain Products, Inc. (Atchison, Kansas). The gluten contained a minimum of 75% protein (N × 5.7), 1.0–2.0% ash, 5.0–8.0% moisture, and 1.0–2.0% fat, as well as a maximum of 1.0% fiber. The gluten was used as received.

Sample preparation. Lupinus albus was hand-dissected and dehulled. The endosperm was milled into whole meal. Two kinds of lupin flour meals were prepared from the whole meal. (i) The nondefatted meal was prepared by passing the whole meal through a 40-mesh sieve. Then a 20% suspension was prepared in phosphate buffers at a pH of 6.8. The suspension was centrifuged at $1300 \times g$, and the precipitated material was then freeze-dried. (ii) The defatted lupin meal was made by mixing the whole meal with hexane in a ratio of 3:1 (hexane/meal). The material was centrifuged at $3000 \times g$ for 25 min; the pellet was air-dried and then passed through a 40-mesh sieve. The remaining steps for preparing defatted lupin meal were the same for the nondefatted lupin meal. The defatted lupin flour meal was suspended in a 0.05 M sodium phosphate buffer (pH 7.0 at 25°C) by mixing with a stirrer for the rheological measurements. The powder was well dispersed in the buffer, and no sedimentation was observed for 3 wk after preparation. At least two suspension samples were made for each concentration for the measurements.

Measurements. (i) DSC. DSC measurements were performed using a TA Modulated DSC™ 2920 (TA Instruments, New Castle, DE). A 50-mg sample was loaded in a stainless steel pan and then the pan was sealed. The gluten sample underwent a heating and cooling cycle in the range of 4 to 192°C. The lupin sample was heated from 25 to 250°C. The rate of heating or cooling was 3°C/min.

(ii) Rheology. A strain-controlled Rheometric ARES rheometer (Rheometric Scientific, Inc., Piscataway, NJ) was used to perform the rheology studies. A 50-mm diameter parallel-plate geometry was used. The temperature was controlled at 25 ± 0.1°C by a water circulation system. Linear viscoelastic measurements were conducted for the various lupin suspensions. To ensure that all the measurements were made within the linear viscoelastic range, a strain-sweep experiment was conducted initially. An applied shear strain in the linear range was adopted (0.1%) for the other viscoelastic property measurements for the same material; fresh samples were used for each experiment. Linear viscoelasticity indicates that the measured parameters are independent of applied shear strain. Small-amplitude oscillatory shear experiments were conducted over a frequency (ω) range of 0.01–100 rad/s,

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yielding the oscillatory shear storage (G') and loss (G'') moduli. The storage modulus represents the nondissipative component of mechanical properties. The elastic or "rubber-like" behavior is suggested if the G' spectrum is independent of frequency and greater than the loss modulus over a certain range of frequency. The loss modulus represents the dissipative component of the mechanical properties and is characteristic of viscous flow. The phase shift or phase angle (δ) is defined by $\delta = \tan^{-1}(G''/G')$ and indicates whether a material is solid with perfect elasticity ($\delta = 0$), or liquid with pure viscosity ($\delta = 90°$), or something in between. Stress relaxation experiments were conducted. These experiments measure the decrease in the modulus, $G(t)$, with t representing the time after the material is subject to a step increase in shear strain. The plateau modulus was obtained using the method of Xu *et al.* (6). The plateau modulus indicates that the stress relaxation modulus is nearly constant over a measured range of time.

RESULTS AND DISCUSSION

Figure 1 shows the DSC analysis of defatted lupin meal. The profile exhibited a glass transition and an exothermic transition indicating aggregations. The glass transition of defatted lupin was 0.26 J/g·°C, calculated from Figure 1. The middle point of the glass transition temperature was 63°C. This result indicates that lupin forms a rubbery or a pre-gel phase around this temperature. The onset and peak temperatures of the exothermic transition of lupin were 146 and 153°C, respectively (Fig. 1), which suggests that lupin was aggregated around this temperature. The behavior of whole lupin meal, which was nondefatted, was almost the same as the defatted lupin meal (data not shown). The glass transition of the whole lupin meal was 0.25 J/g·°C, the middle point of the glass transition temperature was 80°C, and the onset and peak temperatures of the exothermic transition were 147 and 163°C, respectively. Thus, the small amount of fat that the lupin meal contained had no effect on the behavior of the lupin meal. It also implied that the procedure of defatting lupin meal did not damage the lupin protein and other ingredients. The thermogram of vital wheat gluten also exhibited a glass transition change, although it was not so clear as that of lupin (Fig. 2). The heating and cooling cycle doubly confirmed that the glass transition was real and not an artifact (Fig. 2). The glass transition for gluten was 0.4 J/g·°C, and the middle point of the glass transition temperature was 63°C; these were very close to those of defatted lupin. However, gluten had no exothermic transition within the temperature range of the heating and cooling cycle. Around 150°C, some of the lupin proteins were denatured or partially denatured. The molecules then unfolded and aggregated. However, gluten molecules are very long and flexible, and they are not denatured at this temperature range. So gluten does not aggregate at this temperature range.

Rheological studies showed that lupin suspensions had strong viscoelastic properties. The linear dynamic frequency sweep results for three concentrations of defatted lupin suspensions are shown in Figure 3. The shapes of the G' and G'' curves were parallel, and G' were much greater than G''. The values of G' were slightly dependent on the frequency and that dependency was greater at the higher and lower frequency range studied (terminal zone behavior). The values of G'' were more dependent on the frequency than those of G', especially at higher frequencies. This implied that the lupin suspensions exhibited strong viscoelastic solid properties. At 300 mg/mL, the modulus (G') at the frequency of 0.1 rad/s for lupin suspension was 21 Pa. The phase shift was from 12° at this frequency. At 500 mg/mL, the storage modulus of 0.1 rad/s for lupin reached 1036 Pa, and the phase shift became 8°. Within this small concentration range, the storage modulus increased 50 times. The moduli for lupin suspensions increased dramatically with increased concentrations. The phase shifts were not changed much with the different concentrations, but became smaller at higher concentrations of lupin suspensions. This indicated that the lupin suspensions were more solid-like at higher concentrations. The measurements for the whole nondefatted lupin meal suspensions were identical to those of the defatted lupin suspensions. And the G' and G'' of the whole lupin suspensions were almost the

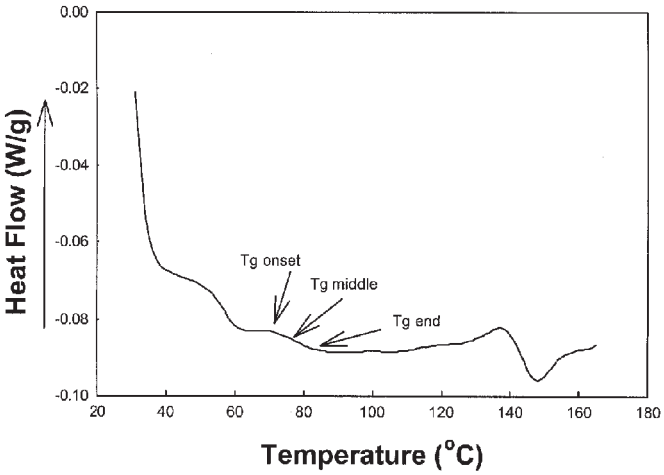

FIG. 1. DSC profile of defatted lupin meal during heating at 3°C/min.

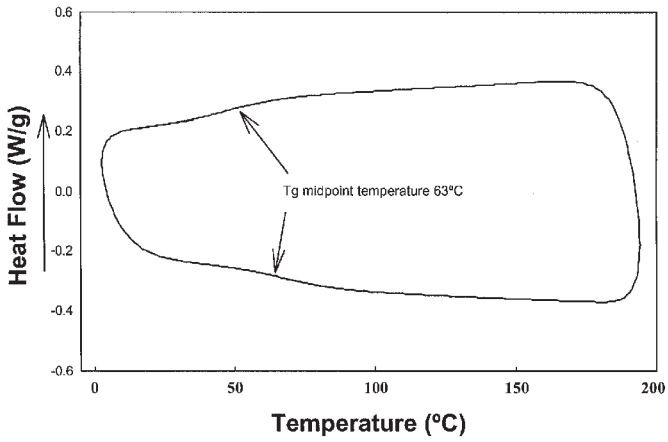

FIG. 2. DSC profile of the heating and cooling cycle of vital wheat gluten at a rate of 3°C/min.

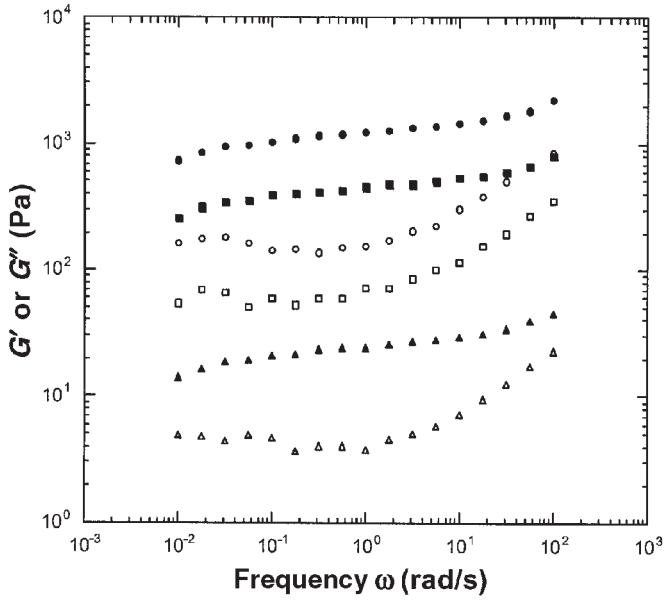

FIG. 3. The linear viscoelastic properties of the defatted lupin meal suspensions at a shear strain of 0.1% and 25°C. (△,▲) 300 mg/mL, (□,■) 400 mg/mL, (○,●) 500 mg/mL; (▲,■,●) G', (△,□,○) G''.

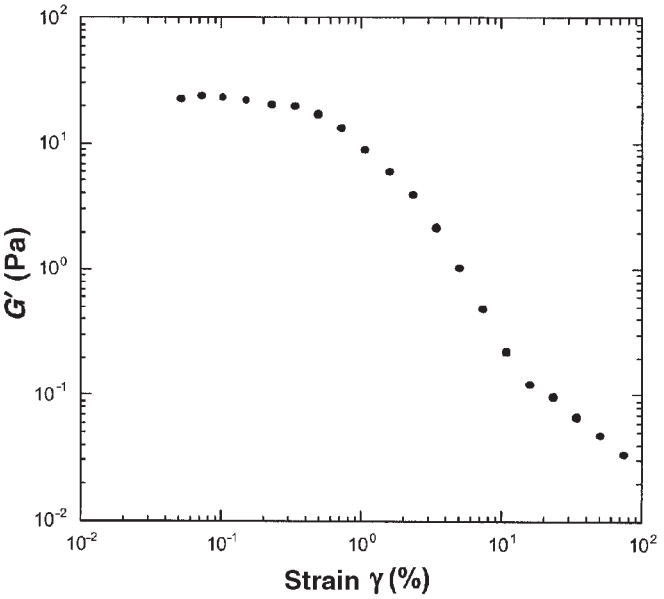

FIG. 4. Strain sweep experiment of the 300 mg/mL defatted lupin suspension at 25°C.

same as those of the defatted lupin suspensions (data not shown). This result, which is consistent with the thermal behaviors just discussed, suggested that the small amount of fat affects the properties of the lupin meal very little.

Our previous studies of gluten found behavior similar to that of lupin (6). The G' and G'' of gluten suspensions were strongly dependent on concentration. Within a very small concentration range, the frequency-independent storage modulus (G') of gluten suspensions increased several orders of magnitude (6). The linear range of the rheological properties of lupin suspensions was less than 0.3%, which was very small (Fig. 4). Stress relaxation measurements indicated that lupin suspensions exhibited slow relaxation behavior. After 2000 s, the lupin suspensions at all three measured concentrations relaxed less than one decade (Fig. 5). This long relaxation time implies that the material exists as a more entangled network that cannot quickly relax. This network structure may be due to physical intermolecular interactions or entanglement. If a network is tightly cross-linked chemically, there should not be any relaxation, and relaxation time should be infinite. In addition, the terminal zone behavior, shown in Figure 3, indicated that the network was not cross-linked. So there must be more physical intermolecular interactions than chemical ones in the network. Some networks that were tightly cross-linked chemically had a very wide linear range of viscoelasticity (7), which was not the case for lupin. Therefore, the more reasonable explanation for the structure is that much stronger molecule–molecule physical interactions occur in the lupin suspensions. The plateau moduli of $G(t)$ for 300, 400, and 500 mg/mL defatted lupin suspensions were 7, 150, and 530 Pa, respectively. Because the plateau moduli were proportional to the storage moduli (8), it was not surprising that the plateau moduli also depended very strongly on the concentration of the lupin suspensions. Results of this relaxation study also showed that lupin properties were somewhat similar to those of gluten (6).

Lupin contains more than 50% protein. This unique property indicates lupin may potentially be useful in many food and nonfood applications. However, in the literature, reports on the physical properties and structure–function relationships for lupin are infrequent. This work has shown that lupin exhibits strong viscoelastic properties like many other biological polymers such as gluten. It also has the identical glass

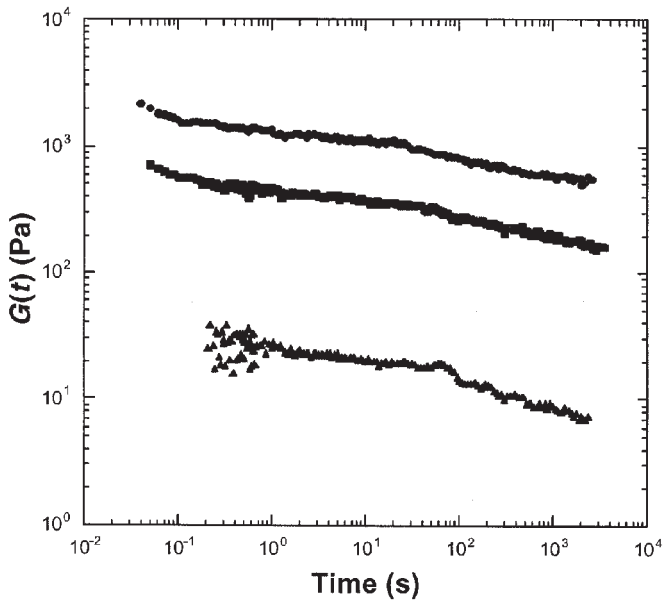

FIG. 5. Stress relaxation measurement of the defatted lupin meal suspensions at 25°C. The initial step strain was 0.1%. (▲)300 mg/mL, (■) 400 mg/mL, (●) 500 mg/mL.

transition temperature as gluten. Most lupin proteins are globular, whereas the protein molecules of gluten are long chains, indicating that direct comparison of the two may not be appropriate. However, they are both biopolymers and display somewhat similar properties, as evidenced by the use of lupin in breadmaking (3). Therefore, in many food and nonfood applications, there is a potential to replace part of the gluten or other biopolymers with lupin or vice versa.

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