

# Isostrength Comparison of Large-Strain (Fracture) Rheological Properties of Egg White and Whey Protein Gels

H. Li, A.D. Errington, and E.A. Foegeding

## ABSTRACT

The effects of protein concentration and heating conditions on the physical properties of whey protein isolate (WPI) (in 50 mM NaCl, pH 7) and egg white (pH 9) gels were examined. Egg white and WPI gels had similar values for shear stress at fracture (i.e., isostrength), while trends for shear strain at fracture were protein-type specific. The rigidity ratio ( $R_{0.3}$ ), ratio of the rigidity at fracture ( $G_f$ ) to the rigidity at 30% of fracture strain, measured departure from the stress-strain relationship of an ideal Hookean solid. All gels fit master curves of  $G_f$  vs  $R_{0.3}$ , which were described by a power law model of  $R_{0.3} = A(G_f)^{-0.19}$ , where "A" showed protein type-specific characteristics.

**Key Words:** gels, rheology, texture, egg white, whey proteins

## INTRODUCTION

THE ABILITY OF FOOD PROTEINS TO form heat-induced gels is one of their main functional properties. Protein gelation can be considered as the formation of a continuous and well-defined network, assembled from protein molecules or aggregates, surrounded by water. Gel networks are usually analyzed in terms of rheological, microstructural, and water-holding properties. Such properties are greatly affected by protein origin, dispersion conditions (protein concentration, pH, and salt) and gelling procedures (heating temperature, time, and rate) (Clark and Lee-Tuffnell, 1986).

The techniques used to characterize rheological properties of protein gels are classified as small- and large-strain (fracture) rheological measurements. Small-strain techniques are designed to nondestructively measure rheological properties of solids. In contrast, large-strain methods may destroy or fracture the sample into two or more pieces. Stress, strain, and rigidity or elasticity modulus are common parameters derived from large-strain measurements and may be determined either with or without fracture. The perception of texture, in part, is an evaluation of fracture properties when a gel-type food is consumed. In general, stress reflects the firmness or hardness of gels whereas strain is an indicator of deformability.

Heat-induced globular protein gels form

two general types of networks, stranded and particulate, based on overall appearance and microstructure (Clark and Lee-Tuffnell, 1986). In general, stranded gels are more translucent, hold more water, and are more elastic, while particulate gels are opaque and have lower water-holding ability (Clark et al., 1981; Hermansson, 1982; Bowland and Foegeding, 1995). Stranded gels have protein strand diameters in the order of nanometers, whereas particulate gels may have strand diameters in the order of micrometers (Clark et al., 1981; Stading et al., 1993). An intermediate structure between stranded and particulate networks is a mixed network.

Gel network structure and interactions within the network strands influence the rheological properties of protein gels. Stading and Hermansson (1990) reported that it was possible to differentiate between stranded and particulate  $\beta$ -lactoglobulin gels using viscoelastic measurements. However, fine-stranded whey protein isolate (WPI) and  $\beta$ -lactoglobulin gels formed at pH < 4 or > 7 had similar microstructures and small-strain rheological properties but differed greatly in large-strain (fracture) rheological properties (Standing and Hermansson, 1991; Foegeding, 1993; Errington, 1995; Errington and Foegeding, 1998). Thus, factors determining gel texture, i.e., large-strain (fracture) rheological properties, were not completely determined by network structure and small-strain rheological properties.

Differences in heat-induced gelation properties of egg white and whey proteins have been reported (Beveridge et al., 1984; Hsieh et al., 1993). Using small-strain rheological methods, Tang et al. (1994)

found that, at a given protein concentration, egg white (EW) protein solution had a lower gelation temperature than whey protein concentrate (WPC) protein solution, a higher initial gelation rate, and higher  $G'$  values (elastic rigidity) during heating and cooling. Furthermore, EW had a much lower minimum protein concentration ( $C_0$ ) for gelation. It is clear that EW and WP solutions differed in gelation properties when compared under similar gelling conditions (i.e., pH, heating temperature, and time). However, it is not clear whether large-strain rheological properties of gels were protein type-specific, or whether similar gels were formed but required different gelation conditions. The objective of this investigation was to determine whether EW and WPI form heat-induced gels with protein type-specific large-strain (fracture) rheological properties.

## MATERIALS & METHODS

### Egg white and whey protein isolate

Dehydrated egg white (EW) powder was obtained from Henningsen Food Inc. (Pt-39) (Moaha, Nebr., U.S.A.). The powder had a protein content of 82% to 85%, depending on lot, and initial pH close to 10. WPI (Bipro™) was obtained from Davisco Foods International Inc. (LeSueur, Minn., U.S.A.) and had a protein content of 91% to 93%, depending on lot, and initial pH close to 7. The protein concentrations in the EW and WPI solids were determined by the macro-Kjeldahl method (AOAC, 1984), using N factors of 6.38 and 6.25 for WPI and EW, respectively.

### Preparation of heat-induced protein gels

Protein suspensions were prepared by hydrating WPI in 50 mM NaCl or EW in deionized H<sub>2</sub>O at room temperature. Protein powders were hydrated by first mixing a small amount of solvent with solids to form a smooth paste, followed by more solvent, and stirring for 1 h. WPI dissolved readily to give thin, clear liquids, whereas EW required clarification by centrifugation (Sorvall RC-5B Refrigerated Superspeed Centrifuge and SS-34 Rotor) at 3000 × g at room temperature for 20 min.

Protein concentration (w/v) of WPI sus-

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pensions was based on Kjeldahl nitrogen. Protein concentration of EW suspensions after clarification was determined at 280 nm (UV160U UV-Visible Recording Spectrophotometer, Shimadzu) based on a standard curve, which related known concentrations to  $A_{280}$  values.

The pH of EW and WPI suspensions were adjusted to 9 and 7, respectively, using 2 N HCl or 1 N NaOH. Suspensions were brought to volume, vacuum-degassed for 30 min, then poured into stoppered glass tubes (i.d. 19 mm), which were pre-coated with Sigmacoate (Sigma Chemical Co., St. Louis, Mo., U.S.A.) for WPI or PAM® nonstick cooking spray (American Home Foods, Milton, Penn., U.S.A.) for EW suspensions. The material used to coat the glass tubes was matched with each protein suspension to minimize adhesion between gel and tube. Glass tubes filled with protein suspensions were covered with aluminum foil and placed in a water bath (65, 70, or 80 °C) for 5 to 30 min. Gels were cooled at room temperature ( $22 \pm 1$  °C) for 1 h and stored overnight at 4 °C. Torsional deformation to fracture was carried out the following day.

**Torsional deformation test**

Gels were equilibrated to room temperature and removed from the tubes. Cylindrical shaped gel samples were cut to 28.7 mm length. Plastic discs of approximately 27 mm diameter and 1 mm thick (Gel Consultants, Inc., Raleigh, N.C., U.S.A.) were attached to each end of the gel cylinder using cyanoacrylate ester glue ("Quicktite" Super Glue, Loctite Corp., Cleveland, Ohio, U.S.A.). The gel cylinders were ground on a precision milling machine (Model GC-PM92 US, Gel Consultants, Inc., Raleigh, N.C., U.S.A.) to a capstan shape with minimum diameter 1 cm at the center, mounted in a Hamann Torsion Gelometer (Model GC-TG92 US, Gel Consultants, Inc., Raleigh, N.C., U.S.A.), and twisted to fracture at a strain rate of 0.05

s<sup>-1</sup>. True shear stress at fracture (shear stress) and true shear strain at fracture (shear strain) were determined according to Diehl et al.(1979). Fracture rigidity ( $G_f$ ) was calculated as shear stress/shear strain. The rigidity ratio at 30% fracture strain ( $R_{0.3}$ ) was calculated as the ratio of fracture rigidity to the rigidity (stress/strain) at 30% fracture strain (Fig. 1). The value of 30% fracture strain was selected as a point that was well beyond the minimum sensitive of the Hamann Torsion Gelometer, yet well below the strain at fracture. Nine gel cylinder samples of each treatment were analyzed and each treatment was replicated at least twice. Data from all replications were pooled ( $n \geq 18$  per data point), and the means and standard deviations of the various parameters were recorded.

**RESULTS**

**EW and WPI gels prepared at 80 °C for 30 min**

A pH 9 aqueous dispersion was used for EW because this was the pH of fresh egg white and because the strength of heat-induced EW gels has been reported to be maximum around that pH (Hickson et al., 1980; Dunkerley and Zadow, 1981; Holt et al., 1984; Power and Nakai, 1985). Likewise, a pH 7 and 50 mM NaCl solvent was

used for WPI because of near maximum shear stress (Kuhn and Foegeding, 1991) and low enough salt concentration to maintain a stranded network in protein concentrations range of 6% to 19% w/v (Errington, 1995). Gelling conditions of 80 °C and 30 min were used as "standard" heating conditions to relate to previous investigations (Kuhn and Foegeding, 1991; Kocher and Foegeding, 1993; Bowland and Foegeding, 1995; Errington, 1995).

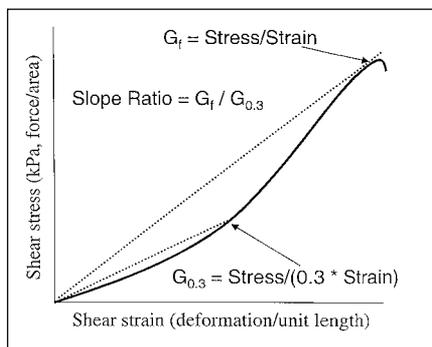
Shear stress (Fig. 2a) of EW and WPI gels increased with increasing protein concentration; shear stress values ranged from  $11.8 \pm 1.7$  kPa for a 7% EW gel to  $131.8 \pm 8.9$  kPa for a 19% WPI gel. EW gels and WPI gels followed the same stress-protein concentration relationship in the 6% to 19% protein concentration range, which could be described by a power law relationship of:

$$\text{shear stress} = 0.048 (\% \text{ protein})^{2.7},$$

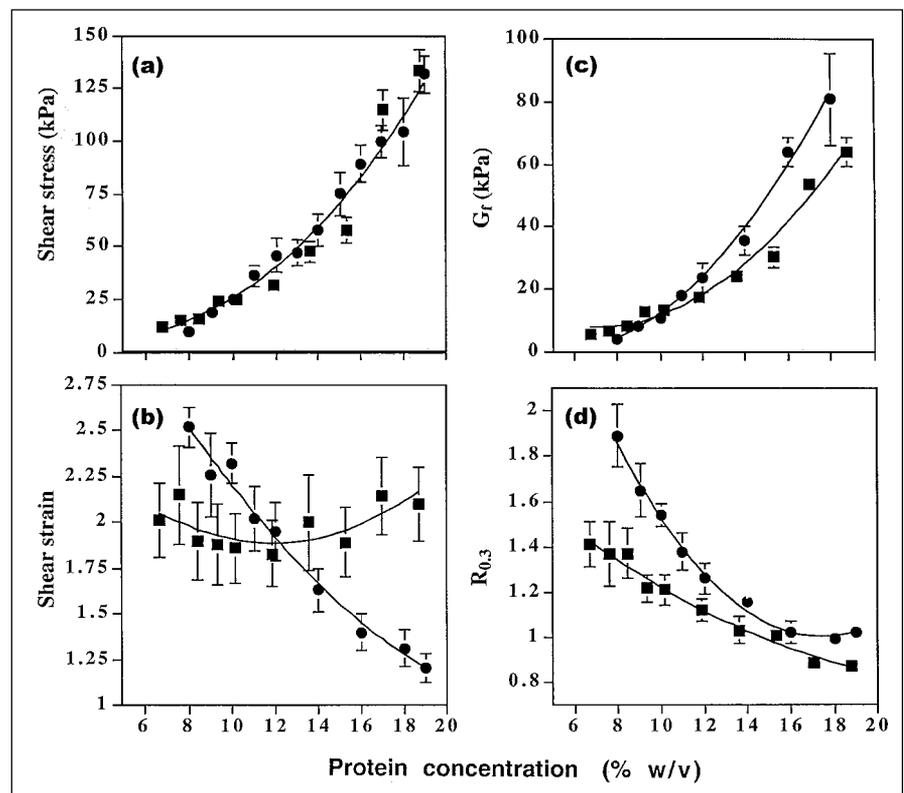
$$\text{with } r^2 = 0.97$$

That is, EW and WPI gels had similar strengths and required similar force/area to cause fracture at the same protein concentration.

While shear stress of EW and WPI gels increased with protein concentration in a similar fashion (Fig. 2a), changes in shear



**Fig. 1—Generalized stress-strain curve for protein gels. The slope of dotted lines corresponds to  $G_f$  and  $G_{0.3}$  values, with  $G_{0.3}$  representing the rigidity at 30% of the strain at fracture.**



**Fig. 2—Protein concentration dependence of shear stress (a), shear strain (b), fracture rigidity,  $G_f$  (c) and rigidity ratio,  $R_{0.3}$  (d) of EW and WPI gels made at 80 °C for 30 min. EW (■) and WPI (●) were dispersed in H<sub>2</sub>O, pH 9 and in 50 mM NaCl, pH 7, respectively. Error bars are standard deviations.**

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strain with protein concentration differed (Fig. 2b). Shear strains of WPI gels decreased with increasing protein concentration; shear strain was  $2.5 \pm 0.1$  at 8% protein (minimum protein concentration to form a gel firm enough for torsional deformation testing) and a value of  $1.2 \pm 0.1$  at 19% protein (Fig. 2b). In contrast, shear strains of EW gels were not sensitive to changes in protein concentration with a value of  $2.0 \pm 0.2$  in the 6% to 19% protein concentration range.

Fracture rigidity ( $G_f$ ) values increased with protein concentration, and there was a crossover between EW and WPI gels at  $\approx 10\%$  protein (Fig. 2c). At protein concentrations  $< 9\%$ , the  $G_f$  values were slightly greater for EW due to the lower shear strain. This was somewhat obscured due to the wide range of  $G_f$  values and the linear

scale. At protein concentrations  $> 10\%$ , WPI gels had greater  $G_f$  values and thus were more rigid than EW gels. Similar  $G_f$  values for EW and WPI gels were found at 9% to 10% protein. This indicated that, at 9% to 10% protein, the gel structure was probably similar; however, as shown below, this was not the case.

Rigidity ratios ( $R_{0.3}$ ) of EW and WPI gels decreased with increasing protein concentrations (Fig. 1d);  $R_{0.3}$  decreased from 1.4 for a 7% EW gel or 1.9 for an 8% WPI gel to between 0.9 and 1.0 for 19% EW or WPI gels. The difference of rigidity ratios between EW gels and WPI gels decreased as protein concentration increased; however, at 9% to 10% protein, the gels had different  $R_{0.3}$  values. At no protein concentration did shear stress, shear strain, and rigidity ratio match between gels.

### EW and WPI gels prepared at $< 80^\circ\text{C}$

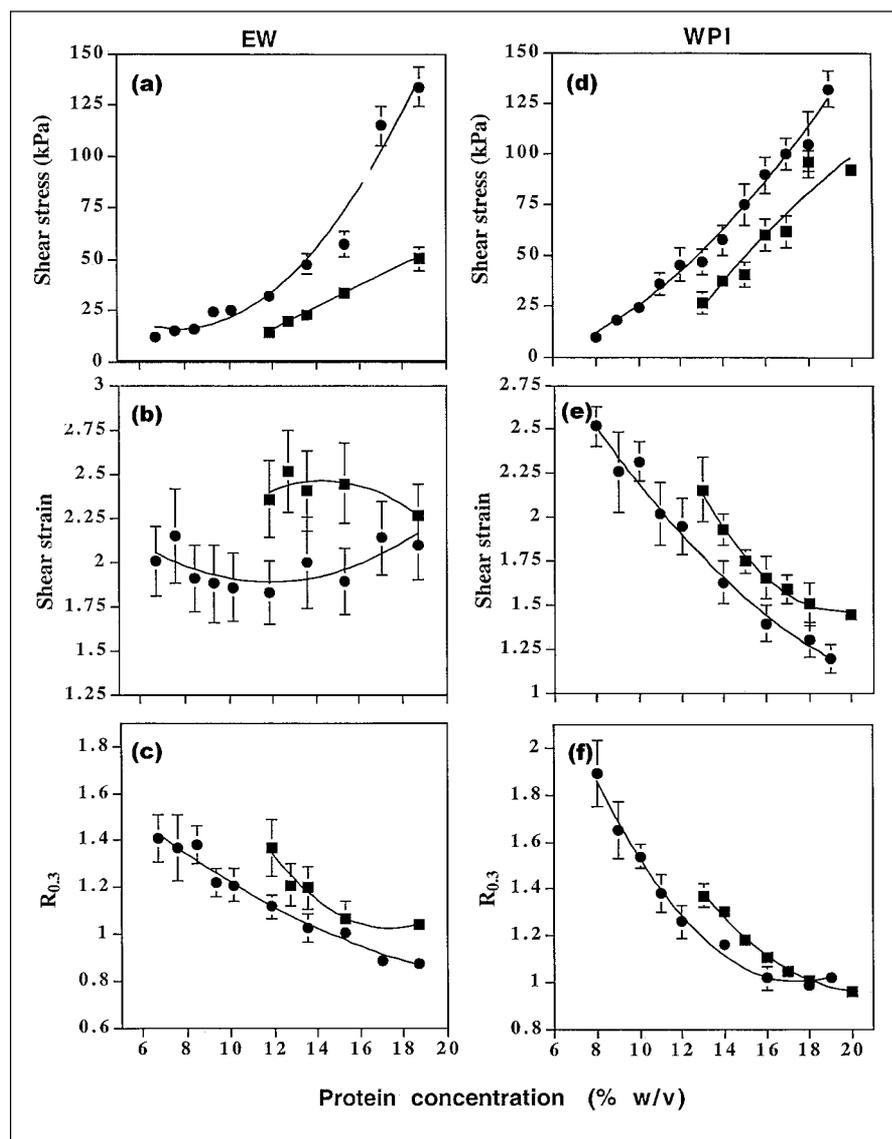
Changing gelling temperature can alter fracture properties of protein gels. EW gels and WPI gels were formed by heating at  $65^\circ\text{C}$  (EW) or  $70^\circ\text{C}$  (WPI) for 30 min (lowest temperatures for 12% protein EW or WPI dispersions to form a self-supporting gel). Changes in shear stress, shear strain, and rigidity ratio of EW and WPI gels formed at lower temperatures showed the same protein concentration-dependent patterns as those formed at a higher temperature ( $80^\circ\text{C}$ ) (Fig. 3). Specifically, for EW gels formed at  $65^\circ\text{C}$ , shear stress increased (Fig. 3a), and rigidity ratio decreased (Fig. 3c) with increasing protein concentrations and shear strains were not sensitive to protein concentration (Fig. 3b). For WPI gels formed at  $70^\circ\text{C}$ , shear stress increased (Fig. 3d) and shear strain and rigidity ratio decreased (Fig. 3e and 3f) as protein concentration increased.

The EW and WPI gels formed at  $< 80^\circ\text{C}$  had smaller shear stress, greater shear strain, and greater rigidity ratio values than gels formed at  $80^\circ\text{C}$  under the same protein concentrations (Fig. 3). Thus, at a given protein concentration, increasing heating temperature increased gel strength, decreased gel deformability, and decreased rigidity ratio. Since these trends were common between protein types, they appeared to be a general effect of increasing protein denaturation and/or changing the kinetics of gelation. The changes in shear stress and shear strain of WPI gels formed at  $70^\circ\text{C}$  with protein concentration paralleled changes in gels formed at  $80^\circ\text{C}$  (Fig. 3). Thus, the extent of shear stress decrease (Fig. 3d) and shear strain increase (Fig. 3e) due to a  $10^\circ\text{C}$  temperature decrease was similar at different WPI protein concentrations and could be explained by a shifted constant value. Changes in  $R_{0.3}$  values were somewhat parallel but at high protein concentration (e.g.,  $> 17\%$ ), WPI gels prepared at 70 and  $80^\circ\text{C}$  converged to similar rigidity ratios of approximately 1 (Fig. 3f).

The extent of shear stress change in EW gels with temperature decrease varied with protein concentration (Fig. 3a). At  $> 16\%$  protein, there was a greater decrease in shear stress due to the decrease in temperature from 80 to  $65^\circ\text{C}$ , compared to the lower protein concentration range.

### EW gels and WPI gels prepared at shorter heating times ( $< 30$ min)

Fracture rheological properties of protein gels can also be altered by changing heating time (Beveridge et al., 1980; Foegeding, 1992; Errington, 1995). Fracture rheological properties of 18% WPI gels formed at various heating times at  $80^\circ\text{C}$  were compared (Fig. 4). The shear stress and shear strain values were plotted by standardizing the parameters to the final



**Fig. 3—Protein concentration dependence of shear stress (a and d), shear strain (b and e) and  $R_{0.3}$  (c and f) of EW or WPI gels made at  $65^\circ\text{C}$  (EW) or  $70^\circ\text{C}$  (WPI) (■) and  $80^\circ\text{C}$  (●). EW and WPI were dispersed in  $\text{H}_2\text{O}$ , pH 9 and in 50 mM NaCl, pH 7, respectively, and heated at given temperatures for 30 min. Error bars are standard deviations.**

plateau values (gels heated for 25 to 30 min). In general, shear stress increased (Fig. 4a), and shear strain and rigidity ratio (Fig. 4b and 4c) decreased with increasing heating time. The major change occurred within the first 10 min. The WPI gels heated at 80 °C for 5 min had approximately 50% less strength and were about 50% more deformable than the final gels (heated for 30 min).

A similar heating time-dependent experiment was conducted with 10% protein EW gels. As was observed for 18% WPI gels, shear stress (Fig. 4d) increased. The rigidity ratio showed a slight decrease or no change (Fig. 4f) as heating time increased. There was a sharp change in shear stress and rigidity ratios from 5 to 15 min, followed by a plateau after 20 min. Shear

strain of EW gels did not change with heating time (Fig. 5e). Thus, EW gels heated at 80 °C for 5 min had about 45% less strength and similar deformability compared to gels heated 30 min.

## DISCUSSION

### Rigidity ratio

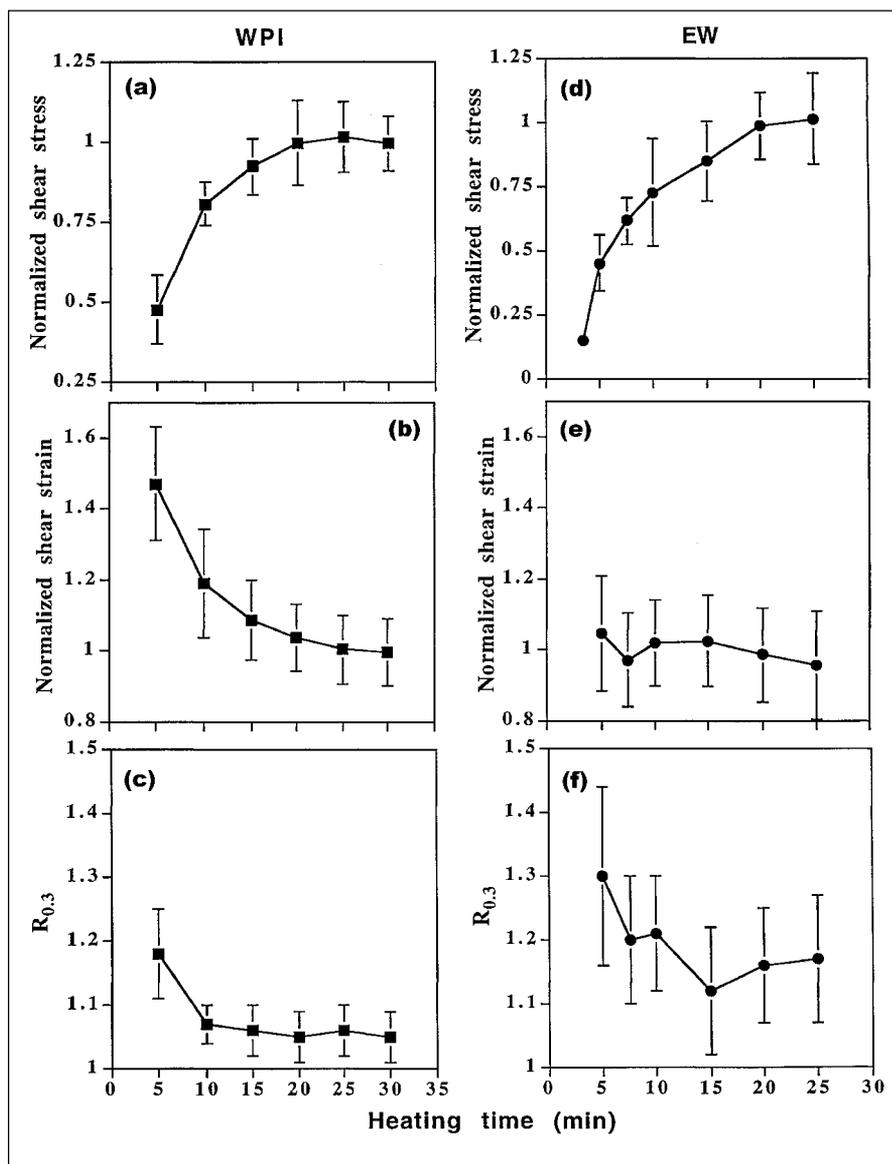
Torsional deformation testing measures two general rheological properties: (1) stress and strain responses under constant shear rate before fracture (stress-strain profile) and (2) stress and strain values at fracture. Changes before fracture are dynamic, and the values at fracture are a single static point measurement. Previous investigations on fundamental fracture rheological properties have focused on shear stress, shear

strain, and/or fracture rigidity (Beveridge et al., 1980; Bottcher and Foegeding, 1994; Bowland and Foegeding, 1995). We considered a new parameter, rigidity ratio or  $R_{0.3}$ , to describe the stress-strain profile. This was defined as the ratio of the rigidity at fracture to the rigidity at 30% of the fracture shear strain. The shape of stress-strain curves is quite specific for different types of materials (Atkins and Mai, 1985; Bot et al., 1996) and can be described by the values of  $R_{0.3}$ . A material behaving as an ideal Hookean solid (perfect elastic) would have  $R_{0.3} = 1$ . When the stress increase with deformation is greater than that of a perfect elastic gel,  $R_{0.3}$  is  $> 1$ , and this behavior is called "strain hardening." When the stress increase with deformation is less than that for a perfect elastic gel,  $R_{0.3}$  is  $< 1$ , and this is called "strain weakening." Note that only one reference point (i.e., at 30% fracture strain) and one strain rate (i.e.,  $0.05 \text{ s}^{-1}$ ) were investigated in our study, and the rigidity ratio may have different values if other reference points or shear rates were used for any specific stress-strain curve. However, a perfectly elastic material would always produce a rigidity ratio of unity and be independent to the reference point and strain rate used. This elastic behavior was observed in acrylamide gels (Foegeding et al., 1994).

### Fracture rheological properties of EW and WPI gels

Fracture shear stress of EW and WPI gels (Fig. 2) increased with protein concentration, and they had similar stress-protein concentration relationships in the protein concentration range of 6% to 19%. These results showed that a general scaling relationship between shear stress and protein concentration existed, regardless of protein origin (EW or WPI), under certain solution conditions. Changes in pH and salt concentration could be viewed as altering electrostatic properties so that the balance of proton dissociation/association (i.e., pH) and surface charge shielding (i.e., salt concentration) were similar between protein types. Alternatively, the pH and NaCl ions could alter the solvent quality so that gelation conditions were under equal chemical potential, producing similar polymer network properties (Nicholson, 1991).

The increase in shear stress could be due to several factors. An increase in protein concentration would cause an increase in density of protein strands that would require a greater force for rupture. This hypothesis is supported by a linear relationship between fracture strength and the area density of backbone bonds crossing the fracture plane (i.e., the number of backbone bonds per unit area) (Vincent, 1992). Also, as protein concentration increases, proteins have an enhanced tendency toward aggregation, resulting in thicker protein strands



**Fig. 4—Heating time-dependencies of shear stress (a and d), shear strain (b and e) and  $R_{0.3}$  (c and f) of 18% WPI and 10% EW gels prepared at 80 °C. EW and WPI were dispersed in  $\text{H}_2\text{O}$ , pH 9 and in 50 mM NaCl, pH 7, respectively, and heated at various times. Error bars are standard deviations.**

(Woodward and Cotterill, 1986). Arntfield et al. (1990) reported that ovalbumin concentration had no notable effect on denaturation temperature and enthalpy values in the protein concentration range of 5% to 15% (150 mM NaCl, pH 8.5). They concluded that variations in the networks formed at different ovalbumin concentrations were related to aggregation rather than denaturation.

Shear strain of WPI gels decreased greatly with increasing protein concentration, while shear strain of EW gels was not sensitive to changes in protein concentration (Fig. 2b). While EW and WPI gels had similar strength (shear stress) at the same protein concentration, WPI gels were more deformable (as measured by shear strain) than EW gels at protein concentrations < 12%, and less deformable than EW gels at > 12%. Rigidity ratios of EW and WPI gels decreased as protein concentration increased (Fig. 1d), while EW gels had lower rigidity ratios than those of WPI gels at the same protein concentration. EW and WPI gels became more rigid (as measured by  $G_f$ ) with increasing protein concentration. The observed changes in patterns of shear stress and shear strain with protein concentration for EW and WPI gels confirm previous reports (Beveridge et al., 1980; Woodward and Cotterill, 1986; van Kleef, 1986; Hsieh and Regenstein, 1989; Foegeding, 1992; Boye et al., 1997). Due to the different responses of individual fracture rheological properties to protein concentration change, EW and WPI gels cannot have the same values of all rheological properties at the same protein concentrations. Thus, at 9% to 10% protein, EW and WPI gels had similar shear stress, shear strain, and fracture rigidity values while their rigidity ra-

tios differed (Fig. 2). However, since a wide range of solution conditions were not investigated, there could possibly be a match of solvent conditions where stress, strain, and rigidity ratio converged at a common protein concentration.

Fracture rheological properties of protein gels can be altered by changing heating temperature and time. Increasing both increased the shear stress and decreased shear strain of WPI gels (Fig. 3 and 4). Increasing heating temperature decreased shear strain of EW gels, while shear strain did not change with heating time. Increases in shear stress of whey protein gel with heating temperature and time confirmed published reports (Mulvihill and Kinsella, 1987; Shimada and Cheftel, 1988; Foegeding, 1992; Aguilera and Rojas, 1996; Matsudomi et al., 1997). Boye et al. (1997) showed that water-holding ability as well as gel strength increased with protein concentration and heating temperature for WPI gels. The temperature-dependence of fracture rheological properties (Fig. 3) also indicated that EW could form stronger gels at lower temperatures (12% EW at 65 °C) than WPI (required heating at 70 °C to start to form a strong enough gel for the torsion test) at the same protein concentration. These results suggested that gelling conditions (temperature and time) could be used to match some of the fracture rheological parameters among different protein gels.

Note that shear strain of EW and WPI gels had different responses to protein concentration and heating time, but their shear stresses had a similar response. The differences in shear strain could be due to dissimilar gel network structures and/or molecular interactions within networks. Dispersion and heating conditions can alter denaturation and/or aggregation. The extent of protein unfolding, formation of inter-protein interactions (in particular, disulfide bonds), and extent of aggregation increases with heating temperature and time. In addition, different proteins have different sensitivities to changes in protein dispersion and heating conditions. Thus, different protein conformations in the pre-gel state lead to different molecular interactions in the final gel network and thus affect rheological properties. Any one or a combination of such factors could cause the differences in shear strain. However, since shear stress of EW and WPI gels had similar responses to protein concentration and heating conditions, it must be controlled by a different mechanism and seemed to be related to the mass of protein regardless of protein origin and conformational status.

Fractal analysis has been applied to relate the elastic properties of a gel to its network structure (Bremer et al., 1989; 1990; 1993; Shih et al., 1990; Hagiwara et al., 1997). In scaling theory (Shih et al., 1990), the structure of a gel network is considered

as a collection of closely packed fractal flocs. The elastic properties of the gel are a reflection of the fractal structure and interactions (Shih et al., 1990). Depending on the strength of the links between flocs in comparison to that within flocs, there could be two types of gel behavior: strong-link and weak-link. The strong-linked has higher elasticity in the links between neighboring flocs (interfloc) than those within the flocs. In the weak-linked type, the links within the flocs have a higher elasticity than those between flocs. A protein can form both strong- and weak-link types of gels due to varying dispersion conditions (protein concentration and salt) (Hagiwara et al., 1997).

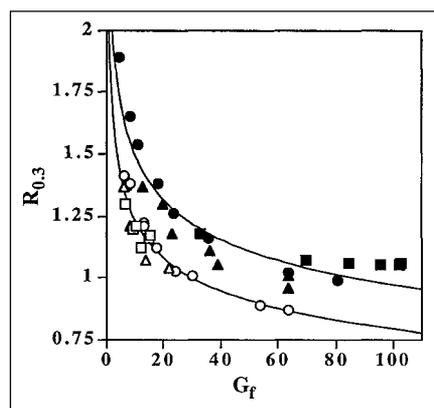
Another fractal analysis was proposed by Bremer et al. (1989; 1990; 1993). In the theory of fractal geometry, gels are classified into Type 1 and Type 2. The two types have different fracture mechanisms; the protein strands making up the gel network are stretched or shrunk under applied stress in the Type 1 gel, and the strands of Type 2 gels are bent under applied stress. Type 1 and 2 gels proposed by Bremer et al. (1989; 1990; 1993) correspond with strong-link gels in the Shih et al. (1990) model.

Both fractal models predict how strain would vary with network phase volume (i.e., protein concentration); however, the strain level that causes deviation from the linear elastic region is considered, rather than fracture strain. Nonetheless, such fractal models could be used as a first approximation for fracture strain scaling behavior. The models suggest that EW and WPI gels are strong-linked (Shih et al., 1990). EW gels are Type 1 gels (Bremer's theory) because fracture strain did not change with protein concentration, while WPI gels are Type 2 because shear strain decreased as protein concentration increased (Fig. 2) (Bremer et al., 1989; 1990; 1993).

### Correlation between fracture rigidity and rigidity ratio

Rigidity ratio ( $R_{0.3}$ ) can be viewed as a measure of fracture shear stress of a gel departing from that of a perfect elastic material. Thus, a higher  $R_{0.3}$  (> 1) indicates a greater shear stress at fracture relative to perfect elastic materials (i.e., strain hardening). A lower  $R_{0.3}$  (< 1) indicates a smaller shear stress at fracture relative to perfect elastic materials (i.e., strain weakening). Rigidity ratio values were in the range of 0.8 to 2 for WPI and EW gels. Based on deviation from a perfect elastic gel (i.e.,  $R_{0.3}$  is > or < 1), the strain hardening effect was greater (the difference was  $\Delta R_{0.3}=1$ ) than the strain weakening effect (the difference was  $\Delta R_{0.3}=0.2$ ).

Fracture rigidity measures stiffness of gel networks at fracture, and  $R_{0.3}$  is an indicator of the overall force-deformation



**Fig. 5— $R_{0.3}$  and  $G_f$  relationship of EW (open) and WPI gels (solid). Various concentrations of EW and WPI were dispersed in  $H_2O$ , pH 9, and in 50 mM NaCl, pH 7, respectively, and heated at various temperatures and times: ■ and □ = time-dependence (data from Fig. 4); ▲ and △ = lower heating temperature (data from Fig. 3); and ● and ○ = 80 °C heating temperature (data from Fig. 2)**

properties of a gel network. Thus, we examined the general relationships between  $R_{0.3}$  and  $G_f$  by combining data from different protein concentrations, heating temperatures, and times. A general relationship between  $R_{0.3}$  and  $G_f$  was found where less rigid gels had a relatively high strain hardening, which decreased as the gels became more rigid (Fig. 5). The  $R_{0.3}$  vs  $G_f$  curves of EW and WPI gels could be described by power law models as follows:  $R_{0.3} = 2.32 (G_f)^{-0.19}$  for WPI and  $R_{0.3} = 1.91 (G_f)^{-0.19}$  for egg white. A similar exponent of  $-0.19$  suggested a similar relationship between these properties for EW and WPI gels, whereas different front (multiplication) factors indicated protein-specific shifts in the relationship. At a similar  $G_f$  value, WPI gels had greater  $R_{0.3}$  values. Thus, at a similar stiffness, WPI gels showed more strain hardening behavior than EW gels. The  $R_{0.3}$  vs  $G_f$  curve described a master relationship between force-deformation and fracture properties regardless of dispersion condition (protein concentration) and gelling condition (heating temperature and time).

## CONCLUSION

EGG WHITE AND WPI GELS HAD SIMILAR strength (shear stress) at the same protein concentrations when gels were prepared at 80 °C for 30 min, and gel strength increased as temperature increased. These gels, while similar in strength, had different trends in gel deformability as protein concentration was increased. Shear strain of WPI gels decreased with protein concentration, and heating temperature and time, while shear strain of EW gels did not change with protein concentration and heating times. Rigidity ratio ( $R_{0.3}$ ) represented an additional rheological parameter (besides shear stress and shear strain) for network characterization.  $R_{0.3}$  is an indicator of stress-strain relationship departure from that of perfect elastic gels. Gels made at different protein concentrations, heating temperatures, and heating times formed master curves relating  $R_{0.3}$  to  $G_f$  values which could be described by a power law model. Similar exponents for EW and WPI gels suggest similar mechanisms for this relationship. Further study is needed to establish what physical and chemical factors are responsible for rheological properties that are common between EW and WPI

gels and to establish what causes the gels to have protein-specific rheological properties.

## REFERENCES

- Aguilera, J.M. and Rojas, E. 1996. Rheological, thermal and microstructural properties of whey protein-cassava starch gels. *J. Food Sci.* 61: 962-966.
- AOAC. 1984. *Official Methods of Analysis*, 14th ed. Association of Official Analytical Chemists. Arlington, VA.
- Arntfield, S.D., Murray, E.D., and Ismond, M.A.H. 1990. Dependence of thermal properties as well as network microstructure and rheology on protein concentration for ovalbumin and vicilin. *J. Texture Stud.* 21: 191-212.
- Atkins, A.G. and Mai, Y.W. 1985. *Elastic and Plastic Fracture: Metals, Polymers, Ceramics, Composites, Biological Materials*. Halsted Press, New York.
- Beveridge, T., Arntfield, K.S., Ko, S., and Chung, J.K.L. 1980. Firmness of heat-induced albumin coagulum. *Poult. Sci.* 59: 1229-1236.
- Beveridge, T., Jones, L., and Tung, M.A. 1984. Progel and gel formation and reversibility of gelation of whey, soybean, and albumen protein gels. *J. Agric. Food Chem.* 32: 307-313.
- Bot, A., van Amerongen, I.A., Groot, R.D., Hoekstra, N.L., and Agterof, W.G.M. 1996. Large deformation rheology of gelatin gels. *Polymer Gels and Networks* 4: 189-227.
- Bottcher, S.R. and Foegeding, E.A. 1994. Whey protein gels: fracture stress and strain and related microstructural properties. *Food Hydrocoll.* 8: 113-123.
- Bowland, E.L. and Foegeding, E.A. 1995. Effects of anions on thermally induced whey protein isolate gels. *Food Hydrocoll.* 9: 47-56.
- Boye, J.I., Alli, I., Ramaswamy, H., and Raghavan, V.G.S. 1997. Interactive effects of factors affecting gelation of whey proteins. *J. Food Sci.* 62: 57-65.
- Bremer, L.G.B., van Vliet, T., and Walstra, P. 1989. Theoretical and experimental study of the fractal nature of the structure of casein gels. *J. Chem. Soc. Faraday Trans. 1* 85: 3359-3372.
- Bremer, L.G.B., Bijsterbosch, B.H., Schrijvers, R., van Vliet, T., and Walstra, P. 1990. On the fractal nature of the structure of acid casein gels. *Colloids Surf.* 51: 159-170.
- Bremer, L.G.B., Bijsterbosch, B.H., Walstra, P., and van Vliet, T. 1993. Formation, properties and fractal structure of particle gels. *Adv. Colloid Interface Sci.* 46: 117-128.
- Clark, A.H., Judge, F.J., Richards, J.B., Stubbs, J.M., and Suggett, A. 1981. Electron microscopy of network structures in thermally-induced globular protein gels. *Int. J. Peptide Protein Res.* 17: 380-392.
- Clark, A.H. and Lee-Tuffnell, C.D. 1986. Gelation of globular proteins. In *Functional Properties of Food Macromolecules*. J.R. Mitchell and D.A. Ledward (Ed.), p. 203-272. Elsevier Applied Science Publishers, London.
- Diehl, K.C., Hamann, D.D., and Whitfield, J.L. 1979. Structural failure in selected raw fruits and vegetables. *J. Texture Stud.* 10: 371-400.
- Dunkerley, J.A. and Zadow, J.G. 1981. Rheological studies on heat-induced coagula from whey protein concentrates. *N.Z. J. Dairy Sci. Tech.* 16: 243-250.
- Errington, A.D. 1995. Rheological and microstructural analysis of whey protein isolate gels: the effect of concentration and pH. M.S. thesis, North Carolina State Univ., Raleigh.
- Errington, A.D. and Foegeding, E.A. 1998. Factors determining fracture stress and strain of fine-stranded whey protein gels. *J. Agric. Food Chem.* 46: 2963-2967.
- Foegeding, E.A. 1992. Rheological properties of whey protein isolate gels determined by torsional fracture and stress relaxation. *J. Text. Stud.* 23: 337-348.
- Foegeding, E.A. 1993. The effect of cations on rheological properties of whey protein gels. In *Food Proteins: Structure and Functionality*. D.D. Schwenke and R. Mothes (Ed.), p. 341-343. VCH, Weinheim, Germany.
- Foegeding, E.A., Gonzalez, C., Hamann, D.D., and Case, S. 1994. Polyacrylamide gels as elastic models for food gels. *Food Hydrocoll.* 8: 125-134.
- Hagiwara, T., Kumagai, H., and Matsunaga, T. 1997. Fractal analysis of the elasticity of BSA and  $\beta$ -lactoglobulin gels. *J. Agric. Food Chem.* 45: 3807-3812.
- Hermansson, A.-M. 1982. Gel characteristics—structure as related to texture and waterbinding of blood plasma gels. *J. Food Sci.* 47: 1965-1972.
- Hickson, D.W., Dill, C.W., Morgan, R.G., Suter, D.A., and Carpenter, Z.L. 1980. A comparison of heat-induced gel strengths of bovine plasma and egg albumen proteins. *J. Anim. Sci.* 5: 69-73.
- Holt, D.L., Watson, M.A., Dill, C.W., Alford, E.S., Edwards, R.L., Diehl, K.C., and Gardner, F.A. 1984. Correlation of the rheological behavior of egg albumen to temperature, pH, and NaCl concentration. *J. Food Sci.* 49: 137-141.
- Hsieh, Y.-L. and Regenstein, J.M. 1989. Texture changes on heating spray-dried egg white. *J. Food Sci.* 54: 1206-1208.
- Hsieh, Y.-L., Regenstein, J.M., and Rao, M.A. 1993. Gel point of whey and egg proteins using dynamic rheological data. *J. Food Sci.* 58: 116-119.
- Kocher, P.N. and Foegeding, E.A. 1993. Microcentrifuge-based method for measuring water-holding of protein gels. *J. Food Sci.* 58: 1040-1046.
- Kuhn, P. and Foegeding, E.A. 1991. Mineral salt effects on whey protein gelation. *J. Agric. Food Chem.* 39: 1013-1016.
- Matsudomi, N., Tomonobu, K., Moriyoshi, E., and Hasegawa, C. 1997. Characteristics of heat-induced transparent gels from egg white by the addition of dextran sulfate. *J. Agric. Food Chem.* 45: 546-550.
- Mulvihill, D.M. and Kinsella, J.E. 1987. Gelation characteristics of whey protein and  $\beta$ -lactoglobulin. *Food Technol.* 41(9): 102-111.
- Nicholson, J.W. 1991. *The Chemistry of Polymers*. Royal Society of Chemistry, Cambridge, UK.
- Power, W.D. and Nakai, S. 1985. Characteristics of edible fluids of animal origin: eggs. In *Food Chemistry*, O.R. Fenema (Ed.), p. 829-855. Marcel Dekker, Inc., New York.
- Shih, W.-H., Shih, W.Y., Kim, S.-I., Liu, J., and Aksay, I.A. 1990. Scaling behavior of the elastic properties of colloidal gels. *Phys. Rev. A* 42: 4772-4779.
- Shimada, K. and Cheftel, C. 1988. Texture characteristics, protein solubility, and sulfhydryl group/disulfide bond contents of heat-induced gels of whey protein isolate. *J. Agric. Food Chem.* 36: 1018-1025.
- Stading, M. and Hermansson, A.-M. 1990. Viscoelastic behavior of  $\beta$ -lactoglobulin gel structures. *Food Hydrocoll.* 4: 121-135.
- Stading, M. and Hermansson, A.-M. 1991. Large deformation properties of  $\beta$ -lactoglobulin gel structures. *Food Hydrocoll.* 5: 339-352.
- Stading, M., Langton, M., and Hermansson, A.-M. 1993. Microstructure and rheological behaviour of particulate  $\beta$ -lactoglobulin gels. *Food Hydrocoll.* 7: 195-212.
- Tang, Q.-N., McCarthy, O.J., and Munro, P.A. 1994. Oscillatory rheological comparison of the gelling characteristics of egg white, whey protein concentrates, whey protein isolate and  $\beta$ -lactoglobulin. *J. Agric. Food Chem.* 42: 2126-2130.
- van Kleef, F.S.M. 1986. Thermally induced protein gelation: gelation and rheological characterization of highly concentrated ovalbumin and soybean protein gels. *Biopolymers* 25: 31-59.
- Vincent, P.I. 1992. A correlation between critical tensile strength and polymer cross-sectional area. *Polymer* 13: 558-560.
- Woodward, S.A. and Cotterill, O.J. 1986. Texture and microstructure of heat-induced egg white gels. *J. Food Sci.* 51: 333-339.
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