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M. Reeve

P. Sherman

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RHEOLOGICAL AND PARTICLE SIZE CHANGES IN CORN OIL-IN-WATER EMULSIONS STABILIZED BY 7S SOYBEAN PROTEINS

M. Reeve and P. Sherman

Department of Food Science, King's College
(University of London)
Kensington Campus, Campden Hill Road, London W8 7AH
England

Abstract

The viscoelastic properties and mean drop size (D_m) of corn oil-in-water emulsions stabilized by 0.5-1.5% (wt/wt) 7S soybean proteins have been examined at various pH's. Changes in these parameters when the emulsions were stored at 4-5°C were measured also. Viscoelasticity parameters were derived from time-dependent strain behaviour at a constant low shear stress of 41.7 dyne cm-2. Although each emulsion showed a continuous increase in D_m during storage, due to drop coalescence, its instantaneous elastic modulus (G_o) rose initially over several days to an optimum value and then subsequently decreased. The trends in D_m and G_o, which indicated that the dominant process during early storage was drop flocculation and drop coalescence at longer times, were used to deduce the structure of the flocculated drop networks.

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Direct inquiries to P. Sherman
Telephone number: 44 1 937 5411

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Introduction

Rheological methods have been used for a long time to evaluate the flow properties of fluid and semi-solid foods. This involves the measurement of viscosity over a wide range of shear conditions. Foods exhibiting non-Newtonian flow, and this includes the majority of fluid and semi-solid foods, are usually shear thinning, thus, the viscosity decreases as the shear rate is increased, because there is a progressive breakdown of the internal two, or more, phase structure. More recently rheometers have been developed which permit these foods to be studied at very low shear stress which minimize the degree of structural breakdown in the test situation. Under these conditions, the internal structure is not broken down to any significant extent and the procedure offers an alternative, and sensitive, method for its study. This approach has distinct advantages when studying foods which have an emulsion based structure. It can help to identify structural changes long before there is any visible oil or water separation, or obvious changes in consistency.

The procedure has been applied recently to the study of oil-in-water (o/w) emulsions stabilised by the polyelectrolyte polysaccharide mesquite gum (Vernon Carter and Sherman, 1980), mayonnaise (Kiosseoglou and Sherman, 1983), corn oil-in-water emulsions stabilised with milk proteins and mono- and di-glycerides (Doxastakis and Sherman, 1983).

Because of the interest in using soybean proteins to manufacture simulated dairy-type food products a study is in progress to establish the influence of soybean proteins, when used in conjunction with mono- and di-glycerides, on the internal structure, rheological properties and long term stability of corn oil-in-water emulsions. This paper reports on part of this study which relates to the effect exerted by increasing concentration (0.5-1.5% wt/wt) of the 7S soybean protein fraction.

Materials and Methods

Materials

Water used to prepare the emulsions was distilled from an all Pyrex apparatus. Pure corn oil (Mazola, CPC U.K. Ltd., Esher, Surrey England) was used as the oil phase. It had a relative density

of 0.919 gm/ml at 20°C. All the chemicals used were of Analytical Reagent grade.

Isolation of 7S Soybean Protein

Cypressa soybeans (Katsouris Bros. Ltd., Drayton Park, London, England) were used. The variety was Hilum, Canadian White, 1983 harvest. The beans were stored at 4°C until they were required.

Soybeans were cracked, dehulled, the flour isolated and defatted as described elsewhere (Rivas and Sherman, 1983). The coarsely ground material was reground in a Gruphon grinder (Brook Motors, England) fitted with a 60 mesh screen. The resultant flour was defatted three times with hexane, air dried and stored in glass jars at 5°C until required. Fractionation of the flour into 7S and 11S protein fractions utilized the procedure of Saio et al. (1973).

Emulsion preparation

O/W emulsions were prepared using a 60/40 weight ratio of corn oil and aqueous phase. The aqueous phase contained the appropriate concentration of 7S protein.

The aqueous solution of protein was prepared by dissolving the 7S protein in water heated to 45°C and stirring continuously with a magnetic stirrer for 1 h. The vessel was covered with a foil lid during this time. At the end of 1 h, the aqueous solution had a pH of 4.5, and this was adjusted to pH 7.0 with 0.5 M NaOH. Vigorous stirring was then applied for 2 h, while maintaining a temperature of 45°C, and this produced a "milky" solution. The solution was filtered through fine muslin, cooled to room temperature, 0.01% (wt/wt) Penicillin G, or potassium sorbate, was introduced as a preservative and the solution was maintained at 4°C until it was required.

Corn oil was added slowly to the aqueous phase and dispersed therein with the aid of a magnetic stirrer. The coarse emulsion produced in this way was then homogenized, thereby reducing the mean drop size and narrowing the drop size distribution, by two passes through a Rannie homogenizer at a homogenizing pressure of 3400 kPa. Each homogenized emulsion was divided into four parts and the pH of each part was adjusted with 3M HCl or 3M NaOH. The pH values selected were 7.5, 5.5, 3.5, and 2.5, thus providing pH values on either side of the isoelectric point (pH 4.5) of the 7S protein. The emulsions were stored at 4°-5°C in a refrigerator.

Rheological evaluation of the o/w emulsions

The viscoelastic properties of each emulsion were examined, at 21.0° ± 0.1°C, at regular intervals during storage by means of its creep compliance-time behaviour at a constant low shear stress of 41.7 dyne cm^{-2}.

Preliminary tests made over a range of shear stresses indicated that the shear stress selected was within the shear stress range where the emulsions exhibited linear viscoelasticity, i.e., there was a linear relationship between the applied shear stress and the resulting shear strain, so that the creep compliance (strain/stress ratio) was independent of the magnitude of the stress applied. The measurements were carried out with a Deer rheometer (Deer Rheometer Marketing Co., Leeds, England) using cone-and-plate attachments. The cone angle was 2.0° and its diameter was 6.5cm. The plate diameter was 8.0cm. The rheometer was connected to a control console which provided digitial readout of the applied torsional force and angular velocity. The console was, in turn, coupled to a chart recorder (Servogor Z10, Labdata Instruments, Croydon Airport, Surrey, England). Creep compliance-time data were analysed in accordance with Inokuch'is (1955) procedure. Each emulsion was allowed to rest for 15-20 min before measurements were made so as to permit the reformation of any structure broken down when it was introduced into the rheometer.

Drop size distribution in emulsions

The distribution of drop sizes in each emulsion was evaluated each time that it was subjected to rheological examination using a disc centrifuge photosedimentometer MKIII (Joyce-Loebl, Newcastle, England) as described previously (Sherman and Benton, 1980). The mean volume diameter was calculated from each set of data. All emulsions were prepared and tested in duplicate. Values quoted are the mean values derived from the duplicate tests.

Results

All the emulsions, irrespective of their pH, the time for which they had been stored and 7S protein content, exhibited the creep compliance-time response characteristic of viscoelastic behaviour. The creep compliance response with time, J(t), of each emulsion could be represented by

$$J(t)=J_0 +J_1(1-\exp(-t/\tau_1))+J_2(1-\exp(-t/\tau_2)) + \frac{t}{\eta}N \quad (1)$$

where J_0 is the instantaneous elastic compliance, J_1 and J_2 are the first and second retarded elastic compliances, τ_1 and τ_2 are the first and second retardation times and τ_N is a Newtonian compliance.

From Eq. (1) six parameters are derived using the following relationships.

$$G_0 = {}^1/J_0 \quad (2)$$

where, G_0 is the instantaneous elastic modulus

$$G_1 = {}^1/J_1 \text{ and } G_2 = {}^1/J_2 \quad (3)$$

where, G_1 and G_2 are the first and second retarded elastic moduli, and

$$\tau_1 = J_1\eta_1 \quad \text{and} \quad \tau_2 = J_2\eta_2 \quad (4)$$

where, η_1 and η_2 are viscosities associated with J_1 and J_2

when $t \to 0$, Eq. (1) reduces to

$$J(t) = J_0 \quad (5)$$

so that at very short times after the small, constant, shear stress has been applied to each emulsion it behaves like a solid in that its response to the stress applied is characterised by

TABLE 1

Influence of pH and storage time on the instantaneous elastic modulus and mean drop volume of corn-oil in-water emulsions incorporating 0.5% 7S soybean proteins.

pH	Aging time (days)	Instantaneous elastic modulus (G_0) (dyne cm^{-2} x 10^{-3})	Drop mean volume diameter (μm)
7.5	0	2.3	0.221
	1	2.5	0.236
	3	2.7	0.289
	5	2.8	0.301
	10	1.3	0.330
	15	-	0.350
	20	-	0.374
5.5	0	2.4	0.219
	1	3.3	0.228
	3	3.4	0.239
	5	4.9	0.288
	10	1.8	0.308
	15	1.6	0.330
	20	1.4	0.336
3.5	0	2.1	0.215
	1	2.3	0.224
	3	5.0	0.237
	5	5.5	0.303
	10	3.7	0.336
	15	2.3	0.350
	20	1.8	0.362
2.5	0	2.3	0.226
	1	2.5	0.236
	3	2.7	0.287
	5	3.1	0.307
	10	2.2	0.334
	15	1.9	0.356
	20	-	0.367

TABLE 2

Influence of pH and storage time on the instantaneous elastic modulus and mean drop volume of corn oil-in-water emulsions incorporating 1.0% 7S soybean proteins.

pH	Aging time (days)	Instantaneous elastic modulus (G_0) (dyne cm^{-2} x 10^{-3})	Drop mean volume diameter (μm)
7.5	0	2.5	0.276
	1	2.7	0.287
	3	3.0	0.303
	5	3.6	0.355
	10	-	0.375
	15	-	0.401
	20	-	0.406
5.5	0	6.0	0.265
	1	8.2	0.277
	3	13.1	0.288
	5	16.4	0.301
	10	8.0	0.316
	15	4.1	0.322
	20	4.0	0.330
3.5	0	4.4	0.236
	1	4.7	0.256
	3	6.0	0.274
	5	7.3	0.289
	10	3.7	0.301
	15	3.4	0.311
	20	3.4	0.323
2.5	0	3.4	0.252
	1	3.6	0.270
	3	3.9	0.289
	5	4.0	0.298
	10	3.3	0.310
	15	3.1	0.319
	20	-	0.329

an elastic modulus. At longer times after the stress has been applied the response is more complex and appears to be a mixture of solid and liquid behaviour in that it is characterised, according to Eq. (1), by both elastic moduli and viscosities. This is due to some breakdown within the internal structure, so that there are present together both intact and ruptured structural components.

The G_0 values calculated for emulsions incorporating 0.5, 1.0 and 1.5% 7S protein are quoted in Tables 1, 2 and 3, respectively along with their mean volume diameters. Only the G_0 data are presented because they reflect the properties of the intact emulsion structure prior to any breakdown, and it is, therefore, the most useful parameter from which to draw conclusions relating to the internal structure.

The data in Tables 1-3 indicate that, irrespective of pH and 7S protein concentration, the internal structure of each emulsion underwent a distinctive pattern of change when it was stored. There was an initial increase in G_0, which generally continued through the first 5 days of storage, to a maximum value and then it decreased. At pH 7.5 or 2.5, the initial value of G_0 was lower than at pH 5.5 or 3.5, for a given 7S protein concentration, the only exception being the emulsion containing 0.5% protein at pH 3.5. In addition, G_0 changes in stored emulsions were less marked at pH 7.5 and 2.5 than at pH 5.5 and 3.5. At pH 5.5 and 3.5 the optimum value of G_0 was higher than at pH 7.5 or 2.5 the difference becoming more pronounced as the 7S protein concentration increased. For emulsions containing 1.0% or 1.5% 7S protein higher optimum values of G_0 were achieved at pH 5.5 than at pH 3.5 when stored. However, for emulsions containing 0.5% 7S protein the reverse applied, but the difference was relatively small, and it was probably not significant. At any pH and aging time selected G_0 increased with increasing concentration of 7S protein.

TABLE 3

Influence of pH and storage time on the instantaneous elastic modulus and mean drop volume of corn oil-in-water emulsions incorporating 1.5% 7S soybean proteins.

pH	Aging time (days)	Instantaneous elastic modulus (dyne $cm^{-2} \times 10^{-3}$)	Drop mean volume diameter (μm)
7.5	0	1.6	0.224
	1	2.0	0.236
	3	3.0	0.295
	5	3.3	0.304
	10	-	0.394
	15	-	0.408
	20	-	0.423
5.5	0	19.8	0.215
	1	20.5	0.231
	3	21.8	0.277
	5	27.3	0.295
	10	5.0	0.314
	15	2.6	0.321
	20	2.2	0.330
3.5	0	12.6	0.221
	1	13.1	0.227
	3	15.6	0.261
	5	18.7	0.315
	10	6.5	0.330
	15	3.9	0.350
	20	3.6	0.362
2.5	0	6.0	0.219
	1	8.7	0.226
	3	10.1	0.307
	5	10.9	0.338
	10	2.8	0.375
	15	2.3	0.383
	20	-	0.395

All the emulsions showed a progressive increase in their mean drop size when stored. This indicates that drop coalescence was initiated from the time that the emulsions were prepared. Rates of drop coalescence were derived from the rate of change in mean drop size (Vernon Carter and Sherman, 1980) during the slow phase of drop coalescence (Sherman, 1967). Coalescence rates at the four pH values selected for emulsions incorporating 0.5, 1.0 or 1.5% soybean protein are quoted in Table 4.

TABLE 4

Influence of pH on the slow rate of drop coalescence in corn oil-in-water emulsions incorporating 7S soybean proteins.

pH	Slow rate of drop coalescence in emulsions containing the following 7S soybean protein concentrations (wt/wt). (sec $\times 10^{-7}$)		
	0.5%	1.0%	1.5%
7.5	5.44	3.91	3.26
5.5	4.24	2.36	1.64
3.5	4.38	2.41	1.78
2.5	5.25	3.52	2.71

Discussion

An emulsion is not a thermodynamically stable system. Following its preparation the drops move closer together by the process of flocculation and they form aggregates. These aggregates grow larger during storage due to the amalgamation of smallish aggregates, or due to individual drops combining with the aggregates. The surfaces of the drops within the aggregates are not in direct contact. They are separated by a thin film of continuous (external) phase fluid, and the precise thickness of this film of immobilised fluid depends on the configuration of the film of emulsifier adsorbed around the surface of each drop and on its electrical charge. These two factors also determine the nature of the interaction between the drops and, consequently, the degree of viscoelasticity exhibited by the emulsions. Drop flocculation, and the resulting interaction between drops, increases G_o.

With regard to the structure of the flocculated drop aggregates, especially in the vicinity of their interacting surfaces, certain deductions can be made from the rheological data, the influence of pH thereon, and from the way in which proteins adsorb at an oil-in-water interface. Current theories relating to the adsorption of polymer molecules at interfaces are used for this purpose. The 7S protein fraction has a molecular weight of about 193,000 with 7S globulin, which has a molecular weight range 180,000-210,000 constituting more than 50% of the fraction. Lower molecular weight constituents are hemaglutenins, lipoxygenase and β-amylase (Sosulki, 1977). Following adsorption the behaviour of globular proteins, such as 7S soybean fraction, at an oil-in-water interface is not very different from that of adsorbed flexible proteins, (Graham and Phillips, 1979). Oil molecules reduce the van der Waal's cohesion between apolar side chains in the protein molecules so that they can unfold to a greater extent and develop a configuration resembling the loop and train structure of flexible proteins (Graham and Phillips, 1979). Provided the concentration of protein adsorbed on to the drop surfaces is not very low only portions of the protein molecules are actually adsorbed on to the drop surfaces (trains), while other segments (loops) project outwards from the surfaces.

The number of loops per unit area of surface increases with increasing adsorption of protein, which, in turn, depends on the concentration of protein incorporated in the emulsion. The pH also exerts an effect. At the isoelectric point of the protein the adsorbed

molecules are in their most compact configuration and there are more loops per unit area of drop surface than at higher or lower pH values, when the more expanded configuration is adopted. The longest loops projecting from drops in close proximity link up to form a network (Van Vliet et al. 1978 Sonntag et al. 1982). It is this network which makes the major contribution to G_o and it confers a weak gel-like structure on the thin film of continuous phase between adjacent drops. G_o increases as the number of interlinked loops increases.

During storage of the emulsions the adsorbed protein loops on the oil drops are either compressed and flattened, or they overlap Napper, (1977). At present it is not known which of these two processes occurs, but either would increase the degree of contact between loops. G_o would then increase provided that no other changes which had a more profound opposite effect were proceeding at the same time. The rheological data indicate that one of these two processes exerts the major effect during the first few days of storage. Since G_o increases most at pH values close to the isoelectric point, i.e. when it would be more difficult for loops to overlap than at higher or lower pH values due to the more compact protein configuration, it would appear that the protein loops are more likely to be flattened and compressed.

Concurrent with flocculation drops are coalescing, a process which reduces G_o, since G_o is inversely proportional to the third power of mean drop size (Sherman, 1970). Therefore drop flocculation and aggregation is the dominant process only during the early days of storage and then drop coalescence becomes the major factor. Protein concentration and pH influence the physical properties of the protein film around each drop through their effect on molecular concentration and configuration, as discussed previously. The more compact the configuration, and the slower the drainage rate of liquid from between drops, the more resistant will the protein film be to rupture. Both of these processes must precede drop coalescence.

Conclusions

Oil-in-water emulsions stabilised by 7S soybean protein fraction have a complex internal structure. When stored the oil drops develop a randomly close-packed configuration and they are linked together by long loops of protein which project from the surfaces of adjacent oil drops. Collectively, they form a weak gel structure within the thin films of aqueous phase between adjacent oil drops. The number of linkages, and their number per unit area of drop surfaces, is influenced by pH and the protein concentration incorporated in the emulsion. The flocculated emulsions exhibit viscoelasticity, and an elastic modulus, indicative of solid-like behaviour, can be derived for the flocculated drop structure from their strain response at very short times after the imposition of a constant low shear stress. This structure is not static. When the emulsions are stored loops are compressed and flattened and, simultaneously, drops coalesce.. During the initial days of storage the first process is dominant whereas later the second process is dominant.

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Discussion with Reviewers

M. Tung: The aqueous dispersions of protein were prepared with the pH adjusted to 7.0 and these were combined with oil and homogenized to form emulsions. Portions of these emulsions were then treated to adjust pH to 7.5, 5.5, 3.5 and 2.5. Would you expect the nature and disposition of proteins in these emulsions to be similar to emulsions prepared by first adjusting the pH of the protein dispersion prior to emulsion formation?

Authors: Adjusting the pH of the protein dispersion prior to emulsion formation would alter the configuration of the protein and, consequently, its rate of diffusion to, and rate of adsorption at, the oil-water interface. The ultimate configuration of the adsorbed protein could also be affected. All of these effects could produce differences in the viscoelasticity parameters, and the influence of aging time thereon, as compared with emulsions prepared as described in the paper.