Rheology of Lecithin Dispersions

Suvendu Bhattacharya*, M.H. Shylaja, M.S. Manjunath, and Udaya Sankar

Food Engineering Department, Central Food Technological Research Institute, Mysore 570 013, India

ABSTRACT: Dispersions of lecithin (1–25% solids, dry basis) in soybean oil or water were subjected to rheological measurement in a coaxial-cylinder viscometer. The different rheological characteristics determined included yield stress, flow behavior index, consistency index, and apparent viscosity. Pseudoplastic behavior was observed for all lecithin emulsions in oil and for dispersions in water. The flow behavior indices for lecithin–oil emulsions (0.855–0.875) were higher than for lecithin–water dispersions (0.472–0.584). Yield stresses were observed only for lecithin–water dispersions. An increase in the concentration of lecithin in oil or water increased yield stress, consistency index, and apparent viscosity. The apparent viscosities of the lecithin–oil emulsions were higher than those for corresponding lecithin–water dispersions. The power law model can adequately fit ($r \geq 0.988$, $P \leq 0.01$) the shear-rate vs. shear-stress data for lecithin–oil emulsions, whereas the Herschel–Bulkley model was suitable ($r \geq 0.988$, $P \leq 0.01$) for lecithin–water dispersions.
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KEY WORDS: Apparent viscosity, concentration, consistency index, flow behavior index, lecithin in oil or water, rheological model, yield stress.

Processing of emulsions is a complex operation with many variables that influence final product quality. To understand and improve the processing performance of food emulsions, a good knowledge of their flow behavior is necessary (1). Rheology has importance for processing equipment design, product development, and storage and transportation of the suspensions (2,3). For non-Newtonian materials, single-point measurements are inadequate for flow characterization. For lecithin samples, appropriate plots of shear rate vs. shear stress over the shear rate range of processing interest are needed for adequate rheological representation and application, including scale-up and design of flow systems (3).

Lecithin is a surfactant that can be used to create emulsions of two or more incompatible substances. Lecithin has many applications; it is used as an emulsifier in food preparations, bakery products, candies, chewing gums, chocolates, dehydrated foods, dyes, ice creams, instant foods, and pasta products as well as in animal feeds (4). With lecithin, emulsions can be made with high or low HLB (hydrophilic/lipophilic balance) of oil-loving and water-loving phases or substances

(5). Lecithin is also used in medicine, especially as a dietary source for polyene phosphatidylcholine, in the treatment of cardiovascular diseases, as an emulsifier and wetting agent in penicillin dispersions, and in emulsions of intravenous alimentation. Highly purified phosphatidylcholine is used as excipient and drug carrier, and it serves as the active ingredient of various pharmaceutical products that are administered orally, topically, and parenterally (6). Thus, lecithin emulsions or suspensions in oil or water are commercially important, and rheological data of such suspensions are needed for its wide use.

Preliminary studies on viscosity of egg lecithin in water showed that dispersions with less than 1.8% solids are Newtonian in nature, but above that concentration they behave as non-Newtonian liquids and exhibit time-dependent (thixotropic) characteristics (7). Detailed rheological studies on lecithin emulsions or dispersions are scarce.

The purpose of this work is to obtain rheological data on lecithin emulsions/dispersions at different concentrations when the continuous phase is either oil or water. The suitability of common rheological models to explain the shear rate/shear stress data is also examined.

MATERIALS AND METHODS

Materials. Topcithin 50 lecithin, a liquid vegetable lecithin that consists of a natural mixture of polar and nonpolar lipids, was obtained from Lucas Meyer (Hamburg, Germany). Soybean oil (unrefined) was obtained from the local market. The compositions and characteristics of the lecithin and soybean oil, as determined by AOCS methods (8), are shown in Table 1.

Preparation of lecithin emulsions/dispersions. Lecithin-in-oil emulsions were made by stirring the required amounts (dry basis) of lecithin in oil with a glass rod for 5 min. However, because making uniform dispersions of lecithin in water by this method was extremely difficult, the lecithin-in-water dispersions were prepared in a cone-type homogenizer (Model # 5394; Remi, Bombay, India). The samples were homogenized with a speed of 8000 rpm for 5 min. Lecithin-in-oil emulsions, prepared by stirring with a glass rod, did not show any difference in their rheological behavior when compared to samples that were prepared in a homogenizer (results not presented).

Rheological measurements. A controlled-stress rheometer (Model #RT10; Haake GmbH, Karlsruhe, Germany) with a coaxial cylinder attachment [ratio of the external diameter of

*To whom correspondence should be addressed.
E-mail: suvendu@nicfos.ernet.in

TABLE 1
Composition and Characteristics of Lecithin and Soybean Oil

	Method used[a]	Lecithin	Soybean oil
Moisture (%)	Ja 2a-46	0.9	0.0
Acetone-insolubles (%)	JA 4-46	64.6	0.1
Oil content[b]		35.4	99.9
Peroxide value (meq of peroxide/1000 g of sample)	Ja 8-87	5.4	36.0
Acid value (mg KOH/g of sample)	Ja 6-55	23.9	261.2

[a]Keyed to methods in Reference 8.
[b]Calculated as the difference of 100 and content of acetone insolubles.

the rotating bob (41.42 mm in diameter and 50.03 mm in height) to the internal diameter of the stationary cylinder was 0.954] was used to determine the rheological behavior of lecithin dispersions in water or in soybean oil. A constant temperature of $20 \pm 0.1°C$ was maintained during the measurement. Forty shear-rate/shear-stress data points were obtained for each sample at an increasing shear rate up to 500 s^{-1} within a period of 300 s. All rheological measurements were conducted on triplicate samples, and the whole process, including sample preparation, was repeated once.

The shear-rate and shear-stress data were fitted to some of the common rheological models, such as the power law (Eq. 1) and the Herschel–Bulkley (HB) equations (Eq. 2):

$$\sigma = k_P (\dot{\gamma})^{n_P} \qquad [1]$$

$$\sigma = \sigma_{0HB} + k_{HB} (\gamma)^{n_{HB}} \qquad [2]$$

In these equations σ represents shear stress (in units of mPa); σ_o, yield stress (mPa); k, consistency index (mPas^n); γ, shear rate (s^{-1}); n, flow behavior index (dimensionless); subscript P, power law model; and subscript HB, Herschel-Bulkley model. The suitability of a model was judged by finding the correlation coefficient (r) and checking its statistical significance at a probability (P) level of 0.01. The flow behavior index and consistency index (for the power law and HB models) were estimated by the regression of shear rate vs. shear stress data (9). For the Herschel–Bulkley model, the experimental yield stress values were used.

The yield stress of the samples was determined experimentally by using the stress relaxation technique (10–13) at a shear rate of 3 s^{-1}. The apparent viscosity (at a shear rate of 103 s^{-1}) of the samples was determined from the experimental values of shear rate and shear stress.

RESULTS AND DISCUSSION

Soybean oil is a Newtonian liquid and showed a viscosity of 89.5 ± 0.2 mPas at 20°C. The rheogram (plot of shear rate vs. shear stress) of lecithin dispersions (in oil or in water) shows that they are non-Newtonian in nature and exhibit pseudoplastic behavior; a sample plot is provided for 3% suspensions in oil and in water (Fig. 1).
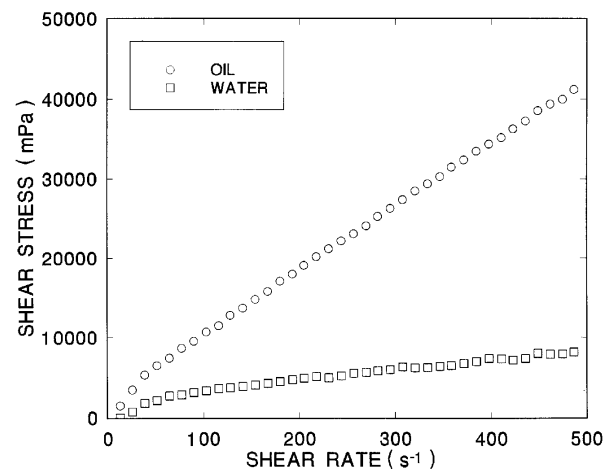

FIG. 1. Sample rheogram for 3% lecithin dispersions in water and in oil.

Yield stress. Yield stress was not observed for the lecithin emulsions in soybean oil. The yield stress of the lecithin dispersions in water, determined by stress relaxation technique, was between 5 and 1000 mPa. It increases markedly with concentration (Fig. 2) and is particularly prominent when the concentration is high ($\geq 15\%$). The high yield stress for concentrated samples occurs as a result of crowding the noncontinuous phase. An increase of the yield stress of the samples due to elevation in solids concentration has also been observed for suspensions that contain pulp in applesauce (14), tamarind seed gum (15), chickpea flour (16), and cooked corn flour (12,13).

The yield stress and concentration C [expressed as concentration of lecithin in emulsion/dispersion (% dry basis)] can be expressed by a power law ($r = 0.989$, $P \leq 0.001$) relation (Eq. 3):

$$\sigma_0 = 6.430 \, C^{1.549} \qquad [3]$$

Suitability of rheological model. The power law model (Eq. 1) was suitable ($r \geq 0.998$, $P \leq 0.01$) for the emulsions
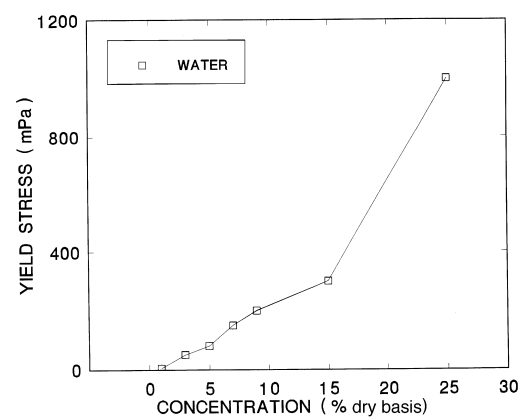

FIG. 2. Yield stress of lecithin dispersions at different concentrations in water.

that contained lecithin in oil, whereas the HB model (Eq. 2) fitted ($r \geq 0.988$, $P \leq 0.01$) the shear rate/shear stress data well for lecithin-in-water dispersions. Hence, the power law and the HB model were used to calculate the different rheological parameters (n and k) of the lecithin dispersions in oil and in water, respectively.

Flow behavior and consistency index. The lecithin dispersions, in oil and in water, behaved like pseudoplastic liquids. The flow behavior index (n) was between 0.855 and 0.875 for lecithin emulsions in oil, whereas it was between 0.472 and 0.584 for lecithin–water dispersions. The slightly lower n values for the lecithin–water dispersions indicate that they are more pseudoplastic than corresponding lecithin–oil emulsions. The n values remained fairly constant for lecithin–oil emulsions when the concentration of solids was enhanced (Fig. 3). The linear relationship (Eq. 4) between concentration and flow behavior index was poor ($r = 0.476$) for lecithin–oil emulsions, but moderate r values (-0.753) were obtained for lecithin–water dispersions (Eq. 5):

$$n = 0.858 + 5.543 \times 10^{-4} \, C \qquad [4]$$

$$n = 0.570 - 3.145 \times 10^{-3} \, C \qquad [5]$$

The consistency index (k) was distinctly higher for lecithin–water dispersions (247–1208 mPa^n) than for lecithin–oil (162–233 mPa^n) emulsions (Fig. 4). The k values are more sensitive to the concentration of lecithin in water when compared to the corresponding oil samples, and an increase in the level of lecithin increases the consistency values.

The consistency index can be related to the solid concentration by a power law relationship for lecithin–oil ($r = 0.890$), and by an exponential relation for lecithin–water ($r = 0.932$) samples, as represented by Equations 6 and 7, respectively.
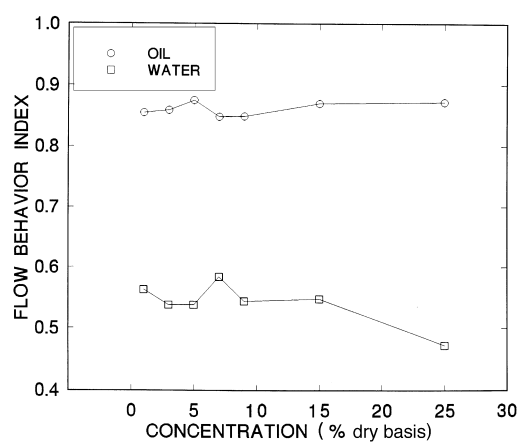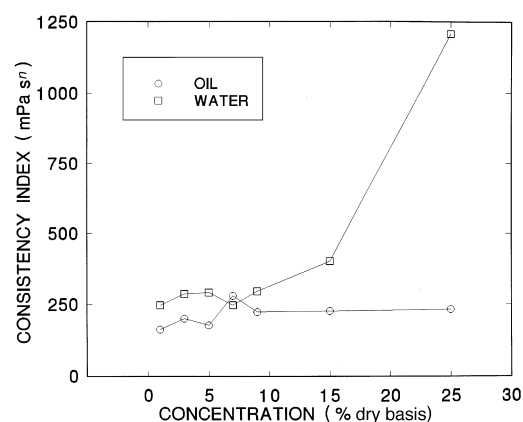

FIG. 4. Dependence of consistency index on concentration of lecithin in water and in oil.

$$k = 165.140 \, C^{0.116} \qquad [6]$$

$$k = 198.310 \, e^{0.063 \, C} \qquad [7]$$

A power law relation, similar to Equation 6, yields a poor r value (0.716) for lecithin–water dispersions, possibly because of the presence of a yield stress term. These latter dispersions fit well to a rheological model (the Herschel–Bulkley model) that has a yield stress term.

The relationship between n and solids concentration has been reported to be linear, and for k it is exponential (12). Launay and co-workers (17) have mentioned that the logarithm of the solids concentration (log C) shows a linear relationship with n (or log k), but these empirical relationships are valid only in a limited concentration range.

Apparent viscosity (η). An increase in lecithin concentration in oil or in water markedly increases the apparent viscosity of the samples. The apparent viscosity (determined at a shear rate of 103 s^{-1}) of lecithin–oil emulsions (82.7–128.7 mPas) was distinctly higher than that for lecithin–water (32.6–114.3 mPas) dispersions (Fig. 5). This is due to higher n values for the former, compared to the latter.

The effect of solids concentration on the apparent viscosity η can be described either by an exponential (11,18,19) or a power law relationship (16,20). In the present study, a power law relationship ($r = 0.958$, $P \leq 0.001$) fitted better (Eq. 8) than the exponential ($r = 0.880$) equation for lecithin–oil emulsions. On the contrary, the exponential equation (Eq. 9) suits better ($r = 0.968$) for lecithin–water dispersions than a power law equation ($r = 0.775$).

$$\eta = 83.502 \, C^{0.133} \qquad [8]$$

$$\eta = 27.680 \, e^{0.052C} \qquad [9]$$

The rheology of emulsions is influenced by several factors, including interparticle forces. In a dilute emulsion, such as milk, the particles are far apart, interparticle interactions are
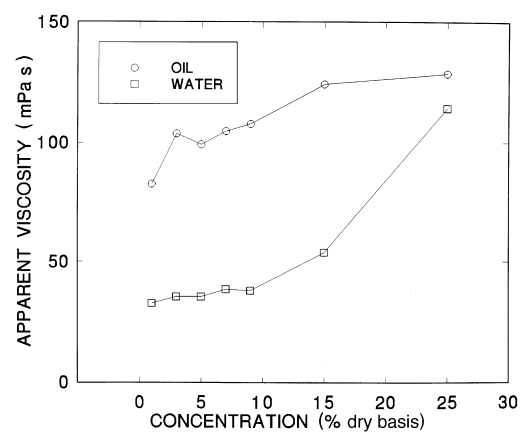

FIG. 3. Flow behavior index (n) of lecithin samples (in oil and in water) at different concentrations.

FIG. 5. Apparent viscosity (at a shear rate of 103 s^{-1}) of lecithin samples (in oil and in water) at different concentrations.

weak, and hence the liquid has low viscosity and is Newtonian in behavior. In concentrated emulsions, such as mayonnaise, the particles are close, resulting in strong interparticle interactions, which make such systems highly viscous with viscoelastic behavior (1).

In conclusion, lecithin dispersions (1–25% concentration, dry basis) in oil or in water behave like pseudoplastic liquids. Pseudoplasticity is pronounced for lecithin–water dispersions; they exhibit only yield stress. The power law model was suitable ($r \geq 0.998$, $P \leq 0.01$) for lecithin–oil emulsions, whereas the HB model adequately ($r \geq 0.988$, $P \leq 0.01$) fits the lecithin–water dispersions. The relationship between concentration and rheological characteristics (consistency index and apparent viscosity) followed power equations for lecithin–oil emulsions, but exponential models were suitable for lecithin–water dispersions.

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