Rheology and Stability of Phospholipid-Stabilized Emulsions

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ABSTRACT: Lecithin in cosmetic emulsions produces a unique "skin feel," which can be related to its rheological properties. In this study, water-in-oil (w/o) and oil-in-water (o/w) emulsions were made from a cosmetic-grade caprylic/capric triglyceride with deoiled lecithin and hydroxylated lecithin. Synthetic surfactants commonly used in commercial cosmetic products were used as controls. Optical light microscope investigation showed significant differences in the structures of the w/o and o/w emulsions made with the lecithins. Freeze/thaw tests were conducted to evaluate emulsion stability. The o/w emulsion (oil/water = 20:80) was stable with 3% hydroxylated lecithin at room temperature. However, 4% hydroxylated lecithin was needed for stabilizing the emulsion with an oil-to-water ratio of 20:80 or 30:70 through the freeze/thaw treatments. With 4% deoiled lecithin, the w/o emulsion showed a water-holding capacity up to 80%, which was also stable through two freeze/thaw cycles. All emulsions in this study exhibited pseudoplastic flow, in which a minimum shearing stress, a yield value, was required before flow became linear. In general, the emulsion viscosity increased as lecithin content increased. Changing the oil-to-water ratio also affected the emulsion viscosity. The deoiled lecithin-based w/o emulsions had higher yield values than hydroxylated lecithin-based o/w emulsions. Therefore, more force was needed to spread the w/o emulsions. In addition, because w/o emulsions had more viscous continuous phases and a greater volume of internal phases, the w/o emulsions were more viscous than the o/w emulsions.

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KEY WORDS: Cosmetic emulsions, emulsifier, lecithin, viscosity, yield value.

Phospholipids occur naturally in the cell membrane structures of plants and animals (1). Phospholipid extracts are called lecithin and may contain many different types of phospholipids. Because of the polarity of phospholipids, lecithin behaves as a surfactant. Commercial lecithin is a mixture of phospholipids obtained from soybeans during oil processing and is used as an emulsifier in many foods. With emulsifying, wetting, dispersing, and viscosity-modifying properties, lecithin has also been widely applied in other industries. The consumer demand for natural products gives lecithin an advantage in today's cosmetic surfactant market.

Early uses of lecithin in cosmetics included the addition of egg yolks to skin and hair preparations, but soybean lecithin can now be found in a variety of products. The primary reason lecithin is used in cosmetics is to impart good "skin feel" (2). It has been reported that lecithin in cosmetics enhances spreading and absorption as well as moisturizing efficiency (2). Many cosmetic products are oil-in-water (o/w) or water-in-oil (w/o) emulsions, which are usually stabilized by petrochemical emulsifiers. However, some synthetic surfactants cause eye or skin irritations (3). Lecithin has not been found irritating and is an effective emulsifier that is generally recognized as safe (GRAS). Therefore, it has the potential to replace synthetic emulsifiers in stabilizing cosmetic emulsions. Lecithin studies have focused on the emulsification properties in o/w and w/o emulsions (4–6) and on the effects of phospholipid composition and the fatty acid composition on those properties (7,8). Cosmetic emulsion stability is usually measured by a freeze/thaw stability test (9). However, a detailed study of the rheology of lecithin-stabilized cosmetic emulsions has not been done and would be a valuable tool in understanding the texture and flow properties for commercial cosmetic formulations.

The objective of this study was to examine the properties of novel cosmetic emulsions stabilized solely by commercial lecithins. The effects of lecithin type and concentration on the rheological properties, microstructure, and stability of cosmetic emulsions were also investigated.

MATERIALS AND METHODS

Materials. All emulsions were prepared with deionized water and a cosmetic-grade caprylic/capric triglyceride, Captex 300 (Abitec Corporation, Columbus, OH). The lecithins used were Lecigran 5750 (Riceland Foods, Inc., Stuttgart, AR), which is deoiled lecithin that contains 97% acetone-insoluble material, and Biophilic H (Lucas Meyer, Decatur, IL), a hydroxylated lecithin. Two synthetic emulsifiers, polyglyceryl-3-monooleate, Caprol 3GO, and polyglyceryl-6 distearate, Caprol 6G2S (Abitec Corporation) were used as controls for the w/o and o/w emulsions, respectively.

Emulsion preparation. For the o/w emulsion, the hydroxylated lecithin (Biophilic H) (5 g) and caprylic/capric triglyceride (Captex 300) (20 g) were heated together to 70°C in a beaker with gentle stirring until the lecithin was completely dissolved in the oil. A Bowl Rest mixer (Hamilton Beach,

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Inc., Washington, NC) was set at low speed to gradually mix 80 mL water (70°C) into the oil phase. This mixture was slowly stirred for 8 min, then for an additional 2 min at the maximum speed setting. The emulsion was then allowed to come to room temperature with slow stirring.

For the w/o emulsion, the deoiled lecithin (Lecigran 5750) (4 g) was first dissolved in 20 g caprylic/capric triglyceride (Captex 300) in a beaker at 60°C. Water (80 mL, 60°C) was gradually added to the oil phase with slow mixing. The low-speed mixing was continued for 5 min, followed by high speed for 2 min. The emulsion was then allowed to equilibrate to room temperature while stirring at low speed for 2 min.

Microscopic examination. An Optiphot light microscope (Nikon Co., Tokyo, Japan) was used to observe the structure of the emulsions. The emulsion samples were smeared on Superfrost microscope slides (Fisher Scientific, Pittsburgh, PA) and observed at 40× magnification.

Freeze/thaw stability. The w/o emulsions were made with 2–4% w/w deoiled lecithin (Lecigran 5750) and 20:80, 30:70 oil-to-water ratios. In the o/w emulsions, hydroxylated lecithin (Biophilic H) was varied from 3 to 4% with different oil/water ratios between 20:80 and 30:70. The emulsion samples were held at a temperature of −5°C for 24 h by using a Neslab RTE100 Circulator (Neslab Instruments, Inc., Newington, NH). The samples were then allowed to equilibrate to room temperature. Two freeze/thaw cycles were conducted for each emulsion (9).

Rheology. The w/o emulsions were prepared with 3, 4, and 5% w/w deoiled lecithin (Lecigran 5750) and oil/water ratios of 20:80, 25:75, and 30:70 (w/w). The o/w emulsions were prepared with 4, 5, and 6% w/w hydroxylated lecithin (Biophilic H) and oil/water ratios of 10:90, 15:85, 20:80, 25:75, and 30:70. The control for the w/o emulsions was 40:60 oil/water stabilized by 5% w/w polyglyceryl-3-monooleate. The control o/w emulsion was 20:80 oil/water with 5% polyglyceryl-6-distearate. Flow behavior of the emulsions was determined with a Haake VT 550 Rheometer (Haake Mess Technik GmbH Co., Karlsruhe, Germany) with a SV-DIN sensor. All rheological tests were conducted at room temperature 24 h after the emulsions were made. The shear rate of the measurements started at 0.15 s^{-1} and finished at 50 s^{-1}. Rheology curves were generated by using shear rate vs. shear stress. Any change in viscosity was observed as change in the slope of the curve, and the yield value was the shear stress where the emulsion viscosity started to decrease (10).

RESULTS AND DISCUSSION

Microscopic examination. Structures of the emulsions observed with a light microscope are shown in Figure 1. The structures of lecithin-stabilized w/o and o/w emulsions (Fig. 1A, 1B) are quite different. The o/w emulsion shows round droplets uniformly dispersed in the system, and the w/o emulsion appears to have a dense dispersed internal phase. According to Rydhag and Wilton (11), phospholipids in o/w emulsions are adsorbed at the oil droplet surface and form a

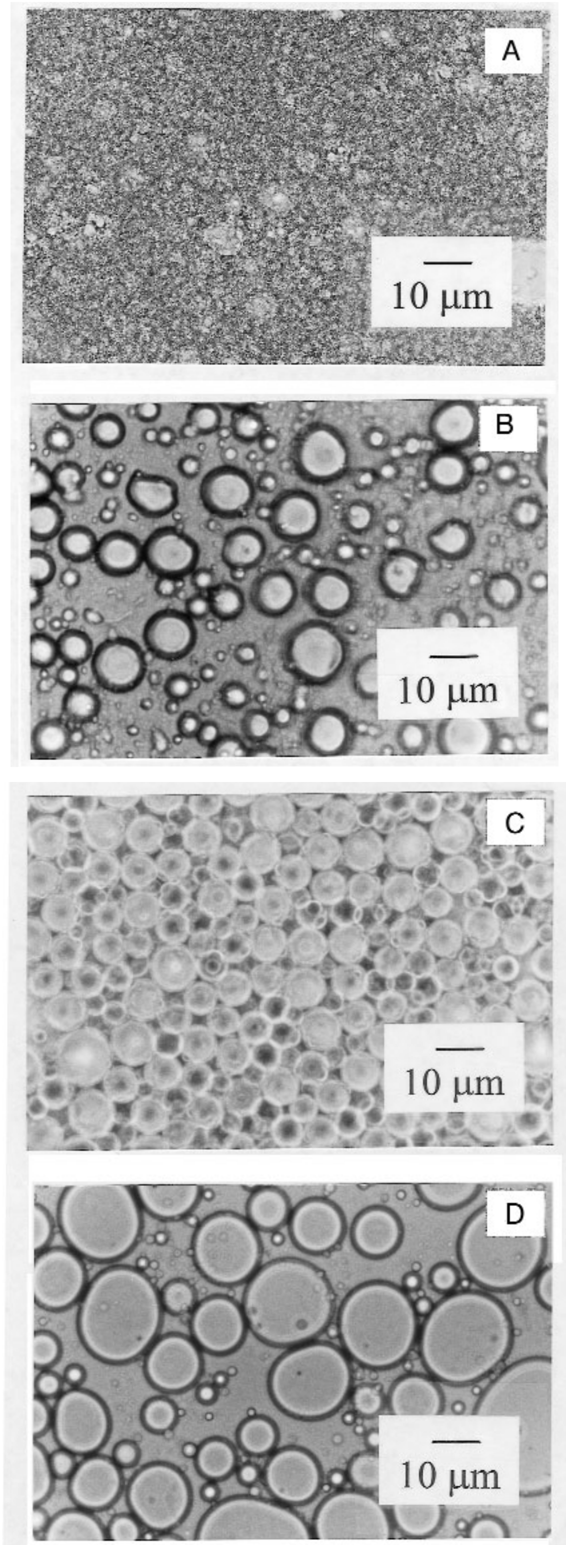

FIG. 1. Structures of the emulsions observed under a light microscope (40×). A: w/o (water-in-oil) emulsion, 20:80 oil/water, 3% deoiled lecithin (Lecigran 5750; Riceland Foods Inc., Stuttgart, AR); B: o/w (oil-in-water) emulsion, 20:80 oil/water, 4% hydroxylated lecithin (Biophilic H; Lucas Meyer, Decatur, IL); C: w/o emulsion, 50:50 oil/water, 5% polyglyceryl-3-monooleate (Caprol 3GO; Abitec Corporation, Columbus, OH); D: o/w emulsion, 20:80 oil/water, 5% polyglyceryl-6-distearate (Caprol 6G2S; Abitec).

TABLE 1
Freeze/Thaw Stability of Deoiled and Hydroxylated Lecithins (Lecigran 5750 and Biophilic H)-Stabilized Emulsions[a]

Emulsifier	Emulsifier content (%)	Emulsion type	Water/oil ratio	First cycle	Second cycle
Lecigran 5750	4	w/o	20:80	Uniform	Uniform
Lecigran 5750	3	w/o	20:80	Separated	—
Lecigran 5750	3	w/o	30:70	Uniform	Uniform
Lecigran 5750	2	w/o	30:70	Separated	—
Caprol 3GO	5	w/o	40:60	Separated	—
Biophilic H	4	o/w	20:80	Uniform	Uniform
Biophilic H	4	o/w	30:70	Uniform	Uniform
Biophilic H	3	o/w	20:80	Uniform	Separated
Biophilic H	3	o/w	30:70	Separated	—
Caprol 6G2S	5	o/w	20:80	Uniform	Uniform

[a]Synthetic surfactants polyglyceryl-3-monooleate and polyglyceryl-6-distearate (Caprol 3GO and Caprol 6G2S) were used as controls. Suppliers: Lecigran 5750, Riceland Foods Inc., Stuttgart, AR; Biophilic H, Lucas Meyer, Decatur, IL; Caprol 3GO and Caprol 6G2S, Abitec Corporation, Columbus, OH. Abbreviations: w/o, water-in-oil; o/w, oil-in-water.

multilayer lamellar structure, whereas in the w/o emulsion, phospholipids stabilize the emulsion by forming reverse miscellar structures. In this study, the internal phase of the w/o emulsion, water, was four times the external phase in weight (oil/water, 20:80), the particles were closely packed, and the particle shapes were distorted. The polyglyceryl-3-monooleate-stabilized w/o emulsion had larger droplet sizes than that with the deoiled lecithin (Fig. 1D). This suggests that an emulsion with deoiled lecithin may be more stable than an emulsion with polyglyceryl-3-monooleate. The polyglyceryl-6-distearate-based emulsion (Fig. 1C) incorporated more air in the emulsion than the hydroxylated lecithin-based emulsion (Fig. 1A) of the same type (o/w) under the emulsion preparation conditions. The film walls of the dispersed droplets in the hydroxylated lecithin-based emulsion appear smoother and thicker than those in the polyglyceryl-6-distearate-based emulsion, which may account for the unique skin feel obtained from the former.

Emulsion stability. The freeze/thaw stability of each emulsion is shown in Table 1, and a stable emulsion was judged to have no phase separation after the two cycles. A w/o emulsion with an oil/water ratio of 30:70 was stable with 2% w/w deoiled lecithin at room temperature but did not tolerate the freeze/thaw cycles unless the deoiled lecithin was increased to 3% w/w. Increasing the proportion of water (oil/water = 20:80) also increased the need for deoiled lecithin (from 3 to 4%) so as to maintain uniformity through the two freeze/thaw cycles. The additional deoiled lecithin content can enhance the network of the emulsion system so that the emulsion can be more tolerant to freeze/thaw abuse. In comparing deoiled lecithin to polyglyceryl-3-monooleate (5%) for stabilizing w/o emulsions, the former made a stable emulsion and had a high water-holding capacity (80%). The w/o emulsion (oil/water = 30:70) made with 4% polyglyceryl-3-monooleate was not uniform for 24 h at room temperature. Commercial cosmetic emulsions that use petrochemicals as an emulsifier usually include clay or other thickeners to optimize the viscosity of the emulsion and to enhance its stability (9). But the deoiled lecithin-based w/o emulsions were already very viscous without thickener, and high viscosity is an important factor in emulsion stability. The polyglyceryl-6-distearate (5% w/w) produced o/w emulsions (oil/water = 20:80) that were stable through two freeze/thaw cycles.

Rheological characteristics. Shear stress and viscosity values of an emulsion change as shear rate is increased. Figure 2 illustrates shear stress vs. viscosity of an emulsion (3% deoiled lecithin, 20:80 = oil/water) under increasing shear rate. Shear stress is inversely proportional to viscosity. Figure 3 shows the rheology curves of w/o emulsions (oil/water = 20:80) made with 1–4% deoiled lecithin and polyglyceryl-6-distearate. The emulsions had increased shear stress and increased viscosity with increased levels of lecithin. Formation of lecithin aggregates resulted in increased emulsion yield values (12). Table 2 shows the yield values of the emulsions tested in this study. The yield values of the emulsions with 1, 2, and 4% deoiled lecithin were 34, 106, and 205 Pa, respectively. These indicate that emulsions with different deoiled lecithin contents started to flow at different levels of shear stress. The emulsifier polyglyceryl-3-monooleate-stabilized

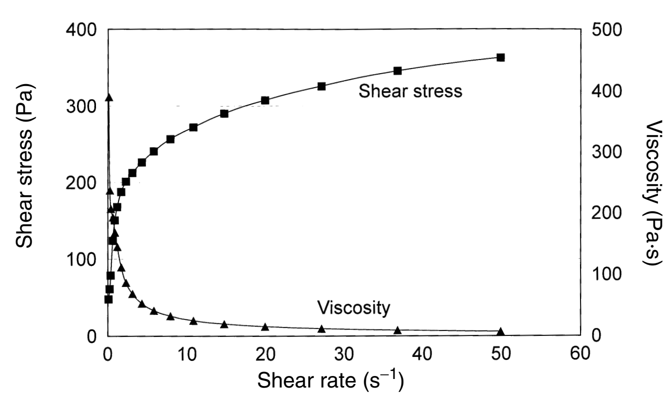

FIG. 2. Changes of shear stress and viscosity at increasing shear rate. The water-in-oil emulsion consisted of a 20:80 oil/water (w/w) ratio with 3% deoiled lecithin (Lecigran 5750). See Figure 1 for company source.

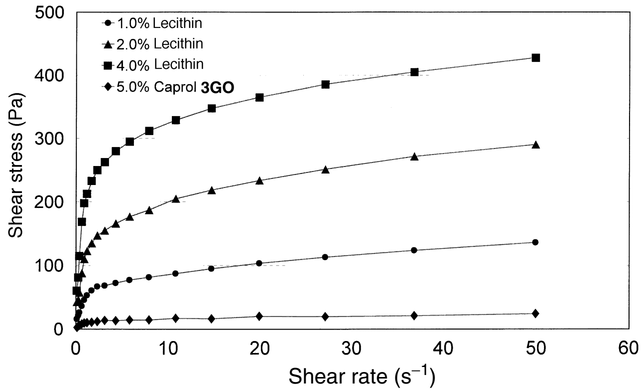

FIG. 3. Rheology curves of water-in-oil emulsions prepared with 20:80 oil/water (w/w) and 1–4% deoiled lecithin (Lecigran 5750). Control was 40:60 oil/water and 5% polyglyceryl-3-monooleate (Caprol 3GO). See Figure 1 for company sources.

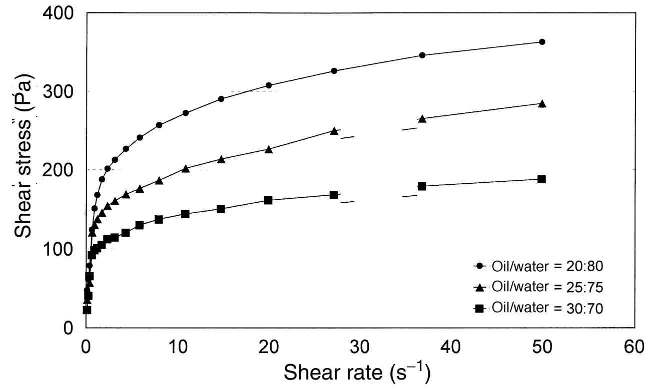

FIG. 4. Rheology curves of water-in-oil emulsion prepared with various oil/water ratios and 3% deoiled lecithin (Lecigran 5750). See Figure 1 for company source.

w/o emulsion had the lowest viscosity and had a yield value of 6 Pa. The rheological parameters are a reflection of interactions and of particle structure. The presence of lecithin changes the attractive forces between the particles; therefore, the rheological characteristics of the emulsion are affected by the type and amount of the emulsifier (13).

Figure 4 compares the flow characteristics of the w/o emulsions with 3% deoiled lecithin and variable oil/water ratios. It is common that increasing the internal phase proportion of an emulsion results in increased viscosity. The viscosity of the emulsions increased considerably as the water content was increased. The increased water content also resulted in a higher yield value of the emulsions. When the oil/water ratios of the emulsions were 20:80, 25:75, and 30:70, the yield values were 160, 126, and 95 Pa, respectively. At low shear rates, the emulsions exhibited a steep curve in reaching their yield values. Figure 5 shows the rheological changes of emulsions of 20:80 oil/water ratio with 4% deoiled lecithin after the freeze/thaw cycle. The viscosities of the emulsions before and after freezing were similar when the emulsions attained linear flow.

The o/w emulsions were made with 4, 5, and 6% hydroxylated lecithin and an oil/water ratio of 20:80 (Fig. 6). The increase in shear stress with shear rate was relatively small compared to the w/o emulsions (Fig. 3). The yield values were increased (7, 9, and 17 Pa) with an increased level of hydroxylated lecithin (4, 5, and 6%). The emulsions with greater levels of lecithin exhibited greater shear stress and viscosity for a given shear rate. The polyglyceryl-6-distearate-stabilized o/w emulsion had a yield value of only 1 Pa. It was lower than that of the emulsion with 4% hydroxylated lecithin, and when linear flow was established, the

TABLE 2
Yield Values of Deoiled and Hydroxylated Lecithin (Lecigran 5750 and Biophilic H)-Stabilized Emulsions[a]

Emulsifier	Emulsifier content (%)	Emulsion type	Water/oil ratio	Yield value (Pa)
Lecigran 5750	1	w/o	20:80	34.4 ± 5.3
Lecigran 5750	2	w/o	20:80	105.5 ± 14.8
Lecigran 5750	3	w/o	20:80	160.7 ± 13.3
Lecigran 5750	3	w/o	25:75	126.4 ± 10.5
Lecigran 5750	3	w/o	30:70	94.7 ± 6.5
Lecigran 5750	4	w/o	20:80	204.8 ± 14.6
Caprol 3GO	4	w/o	30:70	9.4 ± 0.8
Biophilic H	4	o/w	10:90	2.2 ± 0.8
Biophilic H	4	o/w	15:85	5.7 ± 1.1
Biophilic H	4	o/w	20:80	7.3 ± 1.5
Biophilic H	4	o/w	25:75	3.9 ± 0.6
Biophilic H	4	o/w	30:70	5.1 ± 1.1
Biophilic H	5	o/w	20:80	9.3 ± 3.2
Biophilic H	6	o/w	20:80	16.5 ± 3.2
Caprol 6G2S	4	o/w	20:80	1.2 ± 0.3

[a]Synthetic surfactants polyglyceryl-3-monooleate and polyglyceryl-6-distearate (Caprol 3G0 and Caprol 6G2S) were used as controls. For suppliers and abbreviations, see Table 1.

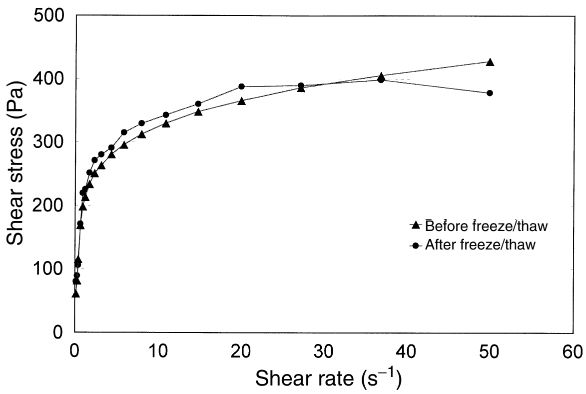

FIG. 5. Rheology curves of water-in-oil emulsion (20:80 oil/water, 4% deoiled lecithin) before and after two freeze/thaw cycles.

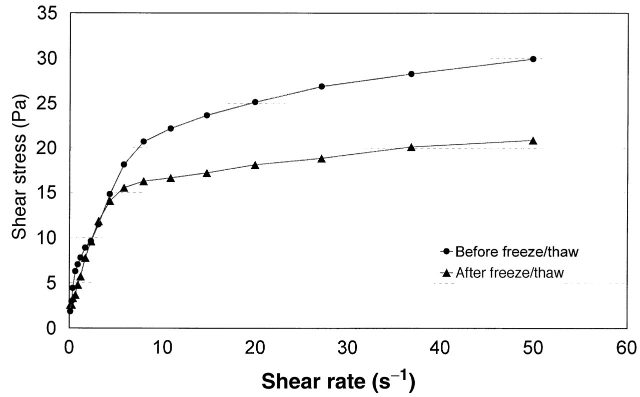

FIG. 8. Rheology curves of oil-in-water emulsions (20:80 oil/water, 4% hydroxylated lecithin) before and after two freeze/thaw cycles.

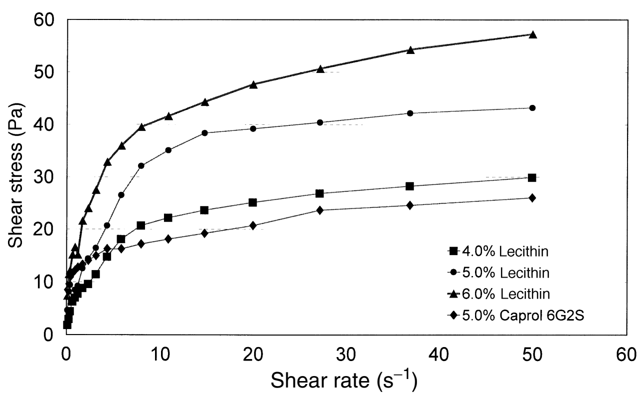

FIG. 6. Rheology curves of oil-in-water emulsions prepared with 20:80 oil/water (w/w) and 4–6% hydroxylated lecithin (Biophilic H). Control was made with 20:80 oil/water (w/w) and 5% polyglyceryl-6-distearate (Caprol 6G2S). See Figure 1 for company sources.

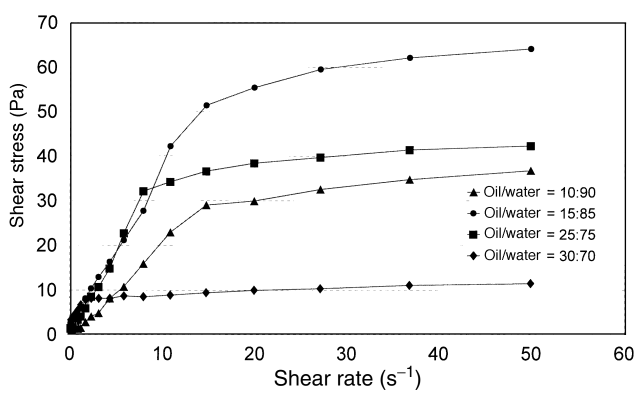

FIG. 7. Rheology curves of oil-in-water emulsions prepared with various oil/water ratios and 5% hydroxylated lecithin (Biophilic H). See Figure 1 for company source.

polyglyceryl-6-distearate-based emulsion had a lower viscosity than the hydroxylated lecithin-based emulsions. When the o/w emulsions were stabilized with the same level of hydroxylated lecithin (5%) and had various oil-to-water ratios (Fig. 7), the shear stress was increased with increased oil/water ratio in the range of 10:90 to 15:80 but was reduced when the oil/water ratio was 20:80 or more. The yield values were 2, 6, 4, and 5 Pa for the emulsions prepared with oil/water ratios of 10:90, 15:85, 25:75, and 30:70, respectively. The o/w emulsions with oil/water ratios higher than 20:80 became less stable with only 4% hydroxylated lecithin. Figure 8 shows the rheology of an o/w emulsion after the two-cycle freeze/thaw. The emulsion that had 80 parts water and 20 parts oil showed a decrease in viscosity after freezing.

Soy lecithin is valuable in controlling the rheology of MCT emulsions which could be exploited in food and cosmetic systems.

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