A Comparative Study of Mayonnaise and Italian Dressing Prepared with Lipase-Catalyzed Transesterified Olive Oil and Caprylic Acid

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ABSTRACT: Viscoelastic properties of mayonnaise and Italian salad dressing prepared with olive oil and enzymatically synthesized structured lipid (SL) from caprylic acid and olive oil were studied using an SR5000 dynamic stress rheometer. Storage modulus (G') and loss modulus (G'') were determined as functions of frequency, temperature, and stress. Frequency sweeps did not show significant differences between dressings prepared with olive oil or SL. For all mechanical spectra, G' values were consistently higher than G'' values. Both Italian dressing and mayonnaise samples displayed similar gel-like characteristics. Mayonnaise and Italian dressings made with olive oil separated when they were brought to room temperature from refrigeration temperatures. SL-based mayonnaise did not separate. Only minor separation was observed in SL-based Italian dressing. A change in the crystallization properties of the two oils was probably responsible for the differences observed after refrigeration. Both SL-based and unmodified olive oil-based mayonnaise and Italian dressing samples had similar viscoelastic character.

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KEY WORDS: Caprylic acid, Italian dressing, mayonnaise, olive oil, rheology, structured lipid, viscoelasticity.

Growing consumer interest in "foods that heal" has stimulated a great deal of research on the production and food applications of nutraceuticals. Lipid scientists must demonstrate that healthy oils can be successfully substituted for existing oils. Structured lipids (SL) are defined as triacylglycerols (TAG) that have been modified by incorporation of new fatty acids, restructured to change the positions of fatty acids or the fatty acid profile from the natural state, or synthesized to yield novel TAG (1). SL may be synthesized to provide medical and/or health benefits or to produce reduced-calorie lipids.

It has been demonstrated that an SL containing octanoic acid at the 1- and 3-positions and a long-chain fatty acid in the 2-position is more rapidly hydrolyzed and efficiently absorbed than typical long-chain triacylglycerols (LCT) (2). The ease of hydrolysis and absorption of medium-chain triacylglycerols (MCT) makes them useful as a dense source of energy in patients with pancreatic insufficiency and fat malabsorption problems. MCT also lowers both serum cholesterol and tissue cholesterol in animals and man, and even more significantly so than conventional polyunsaturated oils (3). Because of their reduced caloric value (8.3 kcal for MCT and 9 kcal for LCT) and lower tendency to deposit as depot fat (4), SL from medium- or short-chain fatty acids and long-chain fatty acids (LCFA) can be used to produce reduced-calorie foods. Salad dressings, sauces, and dips are attractive media for the delivery of SL because of their traditionally high fat content. McNeil Consumer Health Co. (Ft. Washington, PA) recently launched Benecol® margarine spreads and salad dressings as media for delivering cholesterol-reducing stanol esters.

Rheological properties of foods have an important role on the perception of taste or flavor. Smoothness, graininess, and viscosity can all influence perception. Extensive rheological studies have been carried out on mayonnaise, more so than on other salad dressings, because it is a more stable emulsion and it exhibits more complex viscoelastic rheological behavior (5). Studies have shown that TAG exhibit a consistent trend in viscosity based on fatty acid composition (6). As the equivalent carbon number (ECN) of the oil increases, so does the viscosity of the TAG (6). Our previous study (7) of the viscosity of this SL and olive oil showed that olive oil has a higher viscosity than the SL at three different temperatures (Table 1). The objective of the current study was to examine the rheological properties of mayonnaise and Italian salad dressings made with SL prepared from caprylic acid and olive oil and compare them with those made with unmodified olive oil.

TABLE 1
Physical Characteristics of Olive Oil and Structured Lipid[a]

			Olive oil	Structured lipid
Viscosity (Pa·s)	@ −4°C		0.28	0.17
	@ 4°C		0.17	0.11
	@ 25°C		0.06	0.04
Melting point (°C)			−5.6	−17.5
Fatty acid profile (mol%)				
		C8:0	0.00	43.49
		C16:0	8.57	7.17
		C16:1	1.32	2.25
		C18:0	2.42	0.43
		C18:1	70.37	36.89
		C18:2	16.60	9.41
		C18:3	0.71	0.35

[a]From Reference 7.

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MATERIALS AND METHODS

Materials. Two liters of SL were prepared by enzymatically transesterifying caprylic acid and olive oil in a packed bed bioreactor as described previously (7). The fatty acid composition of olive oil and SL are shown in Table 1. *Rhizomucor miehei* lipase, Lipozyme IM60 from Novo Nordisk Biochem North America Inc. (Franklinton, NC), was used to catalyze the reaction. Caprylic acid was obtained from Aldrich Chemical Company (Milwaukee, WI). A 100% mild olive oil (Bertolli, imported from Italy) was obtained from a local grocery store.

Sample preparation. Mayonnaise consisted of the following ingredients (wt%): whole egg, 21%; oil, 71%; vinegar, 6%; and salt, 2%. Mayonnaise was prepared in a KitchenAid heavy-duty mixer (St. Joseph, MI). The egg, vinegar, and salt mixture was vigorously blended while oil was gradually mixed in, to create an emulsion. The Italian salad dressing was a dry mix, which required addition of water, vinegar, and oil. The proportions of the ingredients were as follows: spice mix, 9.5%; water, 14.3%; vinegar, 32.0%; and oil, 44.2%. The mix was blended together for several minutes in a KitchenAid heavy-duty mixer until the dressing appeared emulsified by visual inspection.

Rheological analysis. Viscoelastic properties of salad dressings were analyzed using a Dynamic Stress Rheometer SR5000 (Rheometrics Scientific, Piscataway, NJ). Parallel plate geometry was used, with a diameter of 40 mm and a gap of 1.2 mm. Temperature control was carried out with a Peltier element. Small-amplitude oscillatory experiments were carried out within the linear viscoelastic region of each sample. The linear range at which viscoelastic properties were independent of strain rates for mayonnaise was at a strain of <4% and <1.5% for Italian dressing. Storage modulus (G'), loss modulus (G''), and loss tangent (tan δ) vs. frequency were measured for all samples. Frequency sweep tests were carried out in a frequency range varying from 0.5 to 10 Hz with the test temperature held at 4°C and a constant strain of 1%. Temperature sweeps were also performed to determine the effect of temperature changes on the rheological properties of the samples. Temperature ranged from 0 to 30°C, frequency was kept constant at 1.0 Hz, and strain was at 1%. A dynamic stress sweep was conducted on all samples. Frequency was maintained at 1.0 Hz, temperature was at 4°C, and stress varied from 0.1 to 500 Pa.

Emulsion stability. Emulsion stability was determined in terms of amount of oil separated from an emulsion during centrifugation (8,9). Samples of mayonnaise and Italian dressing were centrifuged in 13-mL polypropylene tubes in a Dynac II Centrifuge (Parsippany, NJ) at 1500 rpm for 25 min at room temperature. Amounts of released oil were visually determined immediately after the tubes were removed from the centrifuge.

Statistical analysis. The Statistical Analysis System (Cary, NC) was used to analyze data (10). Significance was determined at $P < 0.05$.

RESULTS AND DISCUSSION

Storage modulus (G') and loss modulus (G'') were determined for all samples in their linear viscoelastic region. A test temperature of 4°C was chosen to simulate recommended storage temperature for preservative-free dressings. All samples exhibited little frequency dependence in their G' and G'' values. In all samples tested, G' values gradually increased and then leveled off as short-range dynamics were tested (Fig. 1). Average G'' values were about 22% of average G' values in both mayonnaise samples. Average G' and G'' values for olive oil-based mayonnaise (OOM) were not significantly ($P < 0.05$) different from those of SL-based mayonnaise (SLM). In strain-dependent networks, there is a higher dependence on frequency for the dynamic moduli and smaller differences between moduli values (11). Strain-dependent networks appear different from true gels in that they flow under relatively small stresses and are therefore more solutionlike (11). Xanthan gum is an example of a strain-dependent network. The Italian dressing dry mix contained less than 2% xanthan gum. In Italian dressing samples, average G'' values were about 50% of the average G' values. Average G' and G'' values were not significantly different ($P > 0.05$) for Italian dressing samples. Olive oil Italian dressing (OOI) showed a higher elastic modulus when the short-range conformational dynamics were tested. As frequency increased, OOI appeared more elastic than SL-based Italian (SLI) dressing (Fig. 2). The difference between G' and G'' values was virtually unchanged for Italian dressings made from olive oil and SL. This indicates that the type of oil used did not change the strain dependence of the dressings under the above-stated conditions. Loss tangent (tan $\delta = G''/G'$) gives a direct indication of whether different samples behave

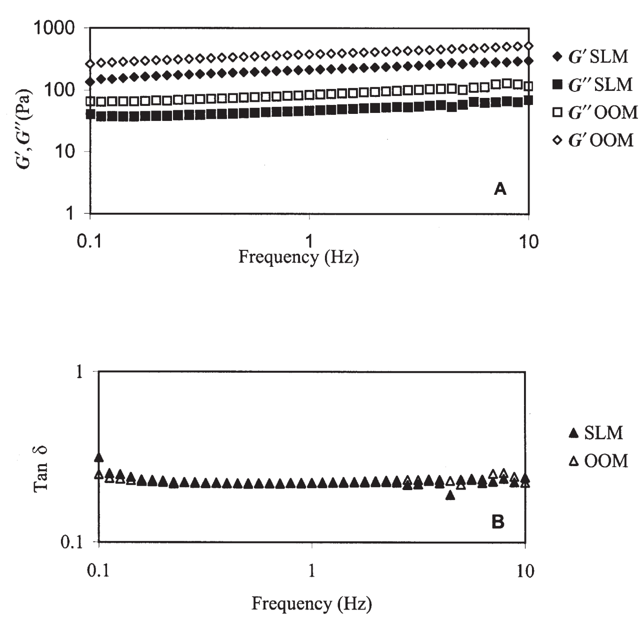

FIG. 1. (A) Storage modulus (G') and loss modulus (G'') vs. frequency for structured lipid mayonnaise (SLM) and olive oil mayonnaise (OOM). (B) Loss tangent (tan δ) vs. frequency sweep data.

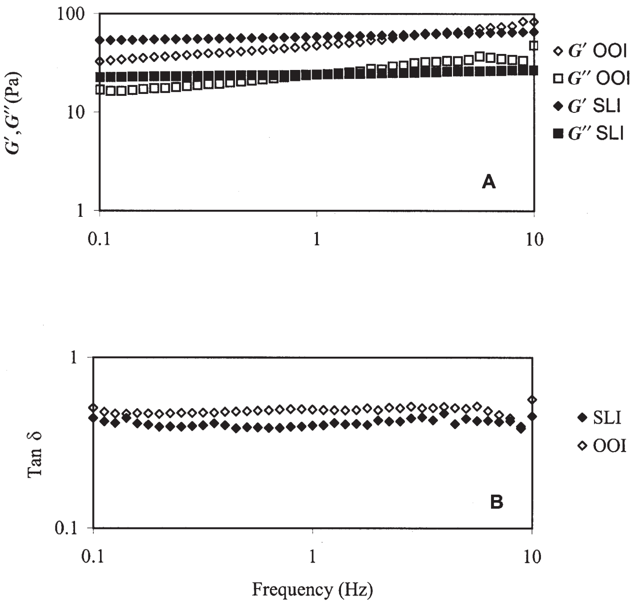

FIG. 2. (A) Storage modulus (G') and loss modulus (G'') versus frequency for structured lipid Italian (SLI) and olive oil Italian (OOI) dressings. (B) Loss tangent (tan δ) vs. frequency sweep data.

as liquids or as solids, i.e., show viscous or elastic behavior. The more elastic the sample, the lower the tan δ value (12). Figures 1B and 2B show that tan δ values follow the same trends for mayonnaise and Italian dressing made with SL and olive oil. In mayonnaise as well as in Italian dressing samples, there was an initial decrease in tan δ values with an increase in frequency. Within most of the frequency range covered, tan δ did not appear to be influenced by frequency, a

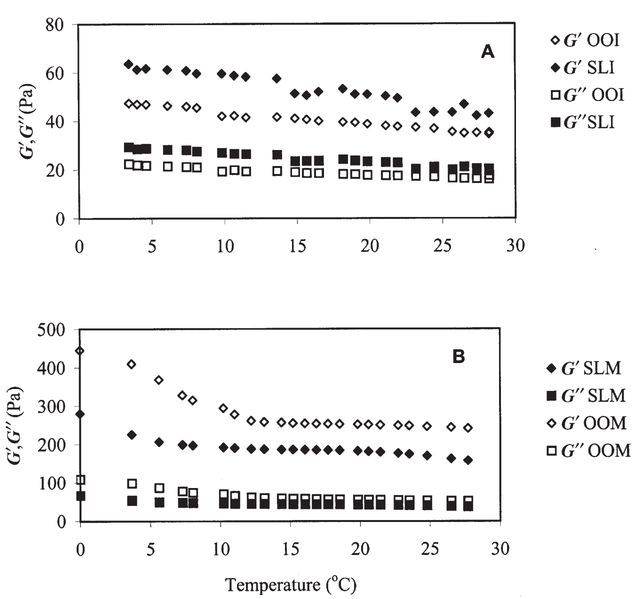

FIG. 3. Temperature dependence of (A) storage modulus (G') and loss modulus (G'') for OOI and SLI and (B) storage modulus (G') and loss modulus (G'') for OOM and SLM. See Figures 1 and 2 for abbreviations.

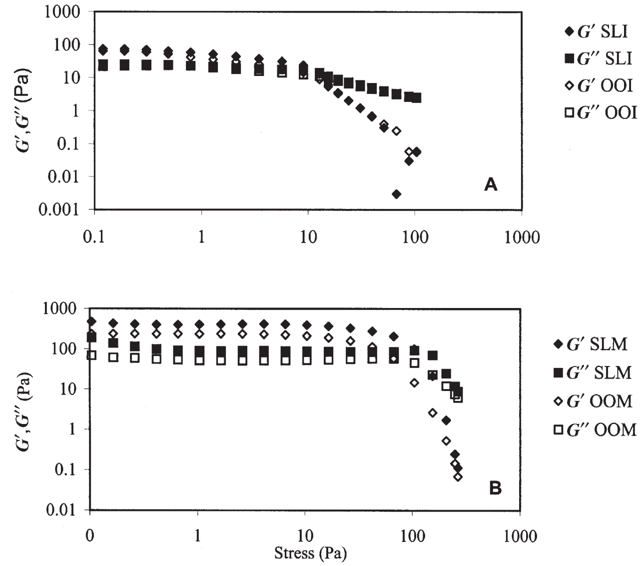

FIG. 4. Storage modulus and loss modulus vs. stress for (A) OOI and SLI and (B) OOM and SLM. See Figures 1 and 2 for abbreviations.

characteristic that is indicative of gel-like behavior. There was no significant difference in average tan δ values between dressings made with olive oil and SL.

Temperature sweeps demonstrate the temperature dependence of a sample's rheological parameters. G' and G'' were determined as functions of temperature at a fixed frequency. In this study the temperature was increased from zero to 30°C. These temperatures were chosen to simulate storage temperatures and temperature fluctuations that may occur during transportation. Because SL and olive oil displayed different melting profiles, a temperature sweep may bring out differences in physical properties that may not otherwise be obvious. In general, at lower temperatures, viscoelastic systems tend to be more elastic, therefore G' values tend to be higher. Figure 3 shows the results obtained with the temperature sweep. With increasing temperatures, a gradual decrease in G' and G'' was observed in Italian dressing samples, whereas the decrease was sharper in mayonnaise samples. This may be due to the higher viscosity of mayonnaise compared to the Italian dressing samples. At about 10°C, there were no further changes in G' and G'' in both mayonnaise and Italian dressing samples. There was, however, a significant drop in G' values for OOM, (33%) and for SLM (31%) at 10°C. From Figure 3B it may be proposed that the emulsions broke down at about 10°C, with flocculation of fat gradually occurring as the temperature was increased, culminating in coalescence at about 10°C.

A dynamic stress sweep applies a range of stresses, each at a constant frequency, with successive measurements taken at each of the commanded stresses. The point at which G' and G'' curves cross each other during a stress sweep can be used as an indication of how long mayonnaise structures endure in the mouth (13). From Figure 4 we can see that with Italian dressing samples, G' and G'' curves crossed at about 10 Pa

(Fig. 4A). In the mayonnaise samples, G' and G'' curves also crossed at similar stress levels, about 75 Pa (Fig. 4B). This difference in stress levels accurately represents the greater strength of the gel structure in mayonnaise. SLM and OOM behaved differently under different stress levels. The G' values for mayonnaise were significantly ($P < 0.05$) lower for OOM than for the SLM counterpart. The sharp drop in G' and G'' values represents a complete breakdown of the structures at higher stress levels.

The amount of oil separated during centrifugation is related to the degree of creaming or destabilization of oil droplets in the emulsion. In the SL dressings, no oil droplets coalesced at the top layer of the samples, whereas with the olive oil dressings there was significant separation of oil from the emulsion. After centrifugation, up to 50% of the OOM separated, and up to 44.5% of the OOI separated out as oil. No separation was observed in the SLM samples, and about 5% of the SLI separated out as oil. This observation could be attributed to the fact that olive oil crystallizes at refrigeration temperatures. The presence of crystals may destabilize an emulsion when the fat is in the dispersed phase by piercing the aqueous film that remains between closely approaching globules, thereby allowing oil to flow from one globule to the other (14,15). This induces complete coalescence when the crystals are liquid or partial coalescence if the droplets still contain crystalline matter. Because of the incorporation of caprylic acid (43.5 mol%) into olive oil, the crystallization temperature of the SL was different from that of unmodified olive oil. Differential scanning calorimetric analysis (7) of the oils showed the melting point of olive oil to be –5.6°C, and that of SL –15.5°C. Because of its lower crystallization temperature, SL may have the advantage of greater emulsion stability over olive oil under a range of temperature conditions. Evidence of separation was not observed with the temperature sweep, even though a softening effect was observed. The G' and G'' values for OOM and SLM, dropped by similar percentage values.

OOM, SLM, and Italian salad dressings displayed similar viscoelastic properties, which indicates similar structural and textural properties. The SLM and Italian dressings were significantly more stable than their olive oil-based counterparts. They may also have health advantages associated with caprylic acid and olive oil. Structured lipids made from olive oil and caprylic acid were successfully substituted for olive oil in Italian salad dressings and mayonnaise and could be used in mainstream foods.

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