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Properties of Low-Moisture Viscoplastic Materials Consisting of Oil Droplets Dispersed in a Protein–Carbohydrate–Glycerol Matrix: Effect of Oil Concentration

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The influence of oil concentration and baking on the properties of low-moisture composites consisting of oil droplets dispersed in a protein–carbohydrate–glycerol matrix was investigated. These composites were produced by blending canola oil, whey protein concentrate (WPC), corn syrup, and glycerol together using a high-speed mixer. The resulting system consisted of oil droplets dispersed in a polar matrix. Some composites were analyzed directly after preparation, while others were analyzed after being heated at 176 °C for 10 min to simulate baking. The "lightness" of the composites was greater before baking (higher L value), but the color was more intense after baking (higher a and b values). The lightness and color intensity of the composites decreased as the oil concentration increased, with the effects being more pronounced in the baked samples. The ζ potential of the oil droplets (measured after dilution at pH 6) was highly negative (approximately -40 mV), indicating that whey protein was adsorbed to the droplet surfaces. The mean particle diameter (measured after dilution at pH 6) increased appreciably after baking, which was attributed to droplet flocculation. The rheological properties of the unbaked and baked materials were characterized by squeezing flow viscometry, which showed that the measurements associated with consistency and yield stress increased with increasing oil concentration and with baking.

KEYWORDS: Emulsion; whey protein concentrate; flocculation; squeezing flow; rheology

INTRODUCTION

In the majority of oil-in-water (O/W) emulsions produced by the food industry, the oil droplets are dispersed within an aqueous phase that consists predominantly of water but may also contain other polar components, such as sugars, proteins, carbohydrates, and minerals (*1, 2*). The oil droplets are usually surrounded by a thin layer of surface-active material that facilitates emulsion formation and prevents droplet aggregation, e.g., amphiphilic surfactants, phospholipids, proteins, or polysaccharides (*1, 2*). Recently, we have shown that low-moisture (<5 wt %) viscoplastic composites (VPC) that consist of oil droplets (~62 wt %) dispersed within a protein–carbohydrate–glycerol matrix can be produced (*3*). These composites were produced by blending the oil phase with whey protein, glycerol, and corn syrup solids and were then analyzed before and after a simulated baking process. Our data suggested that the oil droplets were stabilized by globular protein molecules

adsorbed to their surfaces during the blending process. The stability, rheology, and appearance of these composite materials depended on the type and amount of sugars and polyols present in the polar phase, as well as on whether they were subjected to the baking process. In particular, squeezing flow viscometry measurements indicated that the consistency and yield stress of the composites increased with baking, which was attributed to whey protein unfolding and aggregation. These composite materials are fairly unusual within the food industry because they have a microstructure similar to that of traditional oil-in-water emulsions (i.e., fat droplets dispersed within an aqueous medium), but they contain very little water. This type of composite material may therefore have useful applications within the food industry as a carrier of polar and nonpolar flavors, or in providing desirable textural and mouthfeel attributes, e.g., as low-moisture fillings for cookies, crackers, or baked goods.

At present, the major factors that determine the overall physicochemical properties of the low-moisture composites described above are poorly understood. One of the most distinctive characteristics of the composite materials developed in our previous study was the high level of small neutral polar molecules in the continuous phase, i.e., glycerol, and oligosac-

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charides from the corn syrup. Previous studies have shown that these types of small neutral polar molecules (often termed "cosolvents") can influence the functionality of adsorbed and nonadsorbed globular proteins through a variety of physicochemical mechanisms (*4–8*). First, the thermal stability of proteins is influenced by differences in the preferential interactions between the protein surface and cosolvent–solvent molecules in the surrounding solution (*9–12*). Second, the strength of protein–protein interactions is influenced by the ability of cosolvents to modulate the attractive and repulsive forces between proteins (*4, 5, 8*). Third, the frequency of protein–protein encounters is reduced by the presence of cosolvents due to their ability to increase the viscosity of the cosolvent/solvent mixture surrounding the proteins (*13, 14*). We therefore postulate that the high levels of neutral polar molecules present in the composites would influence the functionality of the whey proteins and, therefore, the bulk physicochemical properties of the composites. The main purpose of our previous study was to examine the impact of the polar phase composition on the properties of the VPC materials (*3*).

Another distinctive characteristic of the low-moisture composites developed in our previous study was the relatively high oil droplet concentration (>60%). The rheological properties of oil-in-water emulsions are dominated by droplet–droplet interactions at high droplet concentrations because the droplets are in such proximity (*2*). Consequently, we anticipate that droplet concentration would have a strong impact on the bulk rheological characteristics of the composites. A major objective of this study was therefore to determine whether the rheological properties of the viscoplastic composites are determined mainly by the presence of the oil droplets or by the presence of the sugars, polyols, and polymers dispersed in the continuous phase. The results of this study should also be of considerable practical importance for the development of reduced fat versions of composites with potential application in reduced calorie foods.

EXPERIMENTAL PROCEDURES

Materials. Corn syrup 200D was kindly donated by Tate & Lyle Food Ingredients (Decatur, IL). The manufacturer reported that the dextrose equivalent (DE) of this sample was 26 and the moisture content was 22.5% with a small amount of contamination from other materials (<0.05%). Powdered whey protein concentrate (WPC) (lot JE 001-3-922) was obtained from Davisco Foods International (Le Sueur, MN). As stated by the supplier, the composition of the WPC powder was $81.5 \pm 1.0\%$ proteins, $7.0 \pm 1.5\%$ lipids, $4.8 \pm 0.2\%$ moisture, $3.0 \pm 0.5\%$ ash, and $7.0 \pm 1.0\%$ lactose. Glycerol was purchased from Fisher Scientific (Pittsburgh, PA). Canola oil was purchased from a local supermarket.

Preparation of Viscoplastic Composites. Glycerol, corn syrup, and oil were weighed into a beaker and heated to 74 °C for 1 min using a microwave oven. WPC powder was weighed and placed into the bowl of a high-speed mixer (N-50, Hobart Corp., Troy, OH). The preheated liquids (glycerol, corn syrup, and oil) were added to the bowl and mixed well with WPC for 1 min at speed 1 and then mixed continuously for 10 min at speed 2 using a whisk attachment. The composition of the polar phase used to prepare the viscoplastic composites consisted of 31.8 wt % corn syrup, 63.7 wt % glycerol, and 4.5 wt % WPC. This polar phase was mixed with canola oil to form viscoplastic composites (VPC) with oil concentrations ranging from 20 to 60%, but with the same polar phase composition.

Baking of Viscoplastic Composites. The viscoplastic composites (VPC) were placed into a cylinder hole (2.6 cm radius; 1.5 cm height) within a metal baking tray (35 cm × 26.5 cm), baked in an oven at 176 °C for 10 min (internal temperature reached 126 °C), and then cooled at room temperature.

ζ Potential Measurements. The electrical charge of the oil droplets in VPC was measured by particle electrophoresis. Viscoplastic com-

posites (1 g) were dispersed in 10 mL of distilled water and mixed using a magnetic stir plate for 15 min prior to analysis, which gave a final pH ranging from 6.0 to 6.3. The resulting oil-in-water emulsions were then injected into the measurement chamber of a particle electrophoresis instrument (ZEM 5003, Zetamaster, Malvern Instruments, Worcester, U.K.), and the ξ potential was determined by measuring the direction and velocity that the droplets moved in the applied electric field. The ξ potential measurements are reported as the average and standard deviation of measurements made on two freshly prepared samples, with five readings made per sample.

Particle Size Measurements. The size of the particles in the VPC after dilution was measured by laser diffraction. Samples of the VPC (1 g) were dispersed in 10 mL of distilled water and mixed using a magnetic stir plate for 15 min prior to analysis, which gave a final pH ranging from 6.0 to 6.3. The particle size distribution of the resulting emulsions was then measured by laser light scattering (Mastersizer X, Malvern Instruments Ltd., Malvern, U.K.). This instrument finds the particle size distribution that gives the best fit between the experimental measurements and predictions made using light scattering theory (i.e., Mie theory). A refractive index ratio of 1.08 was used by the instrument to calculate the particle size distributions. Measurements are reported as the volume-weighted mean diameter: $d_{43} = \sum n_i d_i^4 / \sum n_i d_i^3$, where n_i is the number of droplets of diameter d_i. The particle size measurements are reported as the average and standard deviation of measurements made on two freshly prepared VPC samples, with two readings made per sample. These measurements should provide an indication of the tendency for droplets in the VPC to aggregate with each other. Nevertheless, it should be noted that the dilution process used to prepare the samples for particle size analysis would cause considerable disruption of the microstructure of the droplets in the original composites.

Oiling Off. The amount of free oil present in the composites after storage was determined using a dye dilution technique (*15*). A solution of dyed oil was prepared by dispersing Oil Red O (0.001 wt %) in canola oil and stirring the mixture overnight using a magnetic stirrer. A known mass of VPC material (3 g) was placed into a test tube, and a known amount of dyed oil was poured onto its surface. The dyed oil on the surface was then gently mixed to incorporate any free oil arising form the VPC, and the tube was then centrifuged at 20000 rpm for 20 min to allow the dyed oil to move to the top. A fraction of the dyed oil was transferred from the surface of the VPC, and its absorbance was measured at 520 nm using a UV–visible spectrophotometer (Ultrospec 3000 pro, Biochrom Ltd., Cambridge, U.K.) with canola oil as a blank. Any decrease in the absorbance of the dyed oil after it had been in contact with a VPC sample was due to its dilution with free oil. The percentage of free oil in a VPC was then calculated as the mass of free oil divided by the total mass of oil in the original VPC × 100 (*15*).

Squeezing Flow Viscometry Measurements. Viscoplastic composite samples were prepared using the procedure described above. The VPC were tested either before or after baking, with the samples being stored at ambient temperature for 24 h before being tested. The VPC samples were compressed between Teflon plates (64 mm diameter) mounted on a Texture Analyzer TA-XT2 (Texture Technologies Inc., Scarsdale, NY) equipped with a 25 kg load cell and interfaced with a computer. The compression rate was 0.3 mm/s, and the final specimen height was set to 1 mm in all experiments. After the final height had been reached, the decaying force was monitored for at least 2 min prior to the crosshead withdrawal. The force, height, and time were recorded and saved. The results are expressed as the apparent compressive stress at 1.0 mm height and the apparent residual stress after relaxation for 120 s at the final height of 1 mm. The apparent stress was defined as the measured force divided by the plates' surface area (*16*).

Water Activity. The a_w value of the VPC samples was measured using a water activity instrument (AquaLab, Decagon).

Color (tristimulus) Measurements. Reflectance spectra of VPC samples were measured using a UV–visible spectrophotometer (UV-2101PC, Shimadzu Scientific Instruments, Columbia, MD). VPC were contained within specially designed measurement cells that were covered with a thin plastic film. Spectra were obtained over the wavelength range of 380–780 nm. Spectral reflectance measurements
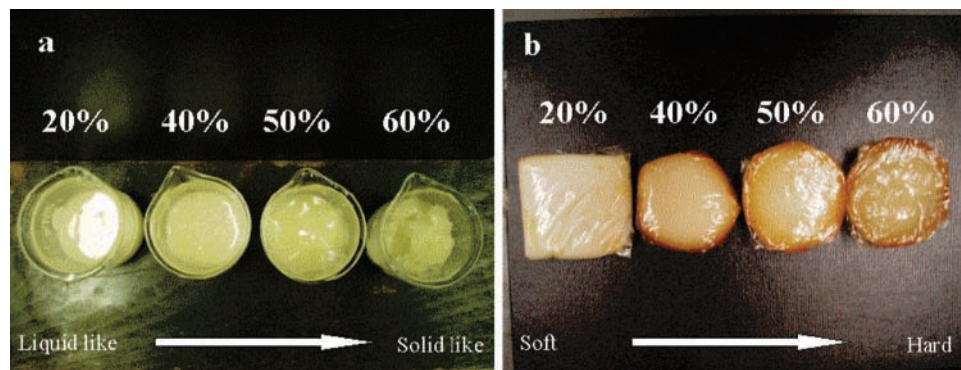
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Figure 1. Photographs of viscoplastic composites stabilized with WPC containing different oil concentrations before (**a**) and after (**b**) baking (176 °C for 10 min, internal temperature reached 126 °C).

were obtained relative to a barium sulfate ($BaSO_4$) standard white plate. The tristimulus coordinates (L, a, and b values) of the sample were calculated from their spectral reflectance ([17]).

Optical Microscopy. The microstructure of selected VPC was determined using optical microscopy (Nikon microscope Eclipse E400, Nikon Corp.). A smear of VPC sample was placed on a microscope slide, covered by a coverslip, and observed at a magnification of $400\times$. An image of the emulsion was acquired using digital image processing software (Micro Video Instruments Inc., Avon, MA) and stored on a personal computer.

Statistical Analysis. Experiments were performed at least twice using freshly prepared samples. Averages and standard deviations were calculated from these duplicate measurements.

RESULTS AND DISCUSSION

Effect of Oil Concentration on General Properties. Initially, we recorded the general appearance and properties of the composites (**Figure 1**). The composites were prepared using the method described above and then some were analyzed directly, whereas others were baked at 176 °C for 10 min (internal temperature reached 126 °C) and then analyzed. Before being baked, composites with low oil content (20 and 40%) had fluid-like or weak gel-like characteristics, whereas those with high oil contents (50 and 60%) had more rigid and plastic-like characteristics. In addition, the surfaces of the composites appeared glossy at low oil levels, but matt at high oil levels. After being baked, all of the composites gelled and were more rigid than the corresponding unbaked composites. These general observations indicated that the droplets made an important contribution to the overall rheology and appearance of the composites; i.e., the overall properties were not just dominated by the properties of the continuous phase (glycerol–corn syrup–protein). This observation is consistent with the fact that oil droplet concentration has a major impact on the rheology of oil-in-water emulsions and filled gels ([2, 18, 19]).

Effect of Droplet Concentration on Composite Tristimulus Values. The tristimulus values (L, a, and b) of composites containing different droplet concentrations (20–60%) were measured using the instrumental method described earlier (**Table 1**). In the absence of oil, both the lightness (L value from 87 to 91%) and color intensity (a value from −1 to 2%; b value from 2 to 8%) of the composites increased slightly after baking, which indicated that baking promoted some change in the light scattering and/or absorption of light by the samples. The increase in color intensity after baking may be attributed to the formation of a brown color, which was probably due to a Maillard reaction between sugars and proteins during heating ([20]). The increase in the lightness after baking may have been due to a change in the size or concentration of any particles that scattered light, such as protein aggregates or sugar crystals ([21]). The lightness

Table 1. Effect of Oil Concentration on Tristimulus Values (L, a, and b) of Viscoplastic Composites Stabilized with WPC before and after Baking

	oil content (%)	L	a	b
before baking	0	86.8 ± 1.0	−1.0 ± 0.01	1.8 ± 0.1
	20	75.8 ± 3.3	−1.0 ± 0.01	5.0 ± 0.6
	40	65.6 ± 1.7	−1.1 ± 0.07	3.8 ± 0.3
	50	62.3 ± 2.3	−1.1 ± 0.02	3.5 ± 0.5
	62.3	58.8 ± 2.8	−0.9 ± 0.01	2.9 ± 0.7
after baking	0	91.2 ± 1.4	1.9 ± 0.01	7.8 ± 0.1
	20	68.4 ± 3.5	6.9 ± 0.01	5.0 ± 0.1
	40	58.8 ± 1.9	2.7 ± 0.07	3.8 ± 0.1
	50	56.5 ± 2.1	1.5 ± 0.02	3.5 ± 0.1
	62.3	41.4 ± 2.6	0.3 ± 0.1	2.9 ± 0.1

and color intensity of the composites decreased as the oil concentration increased, with the effects being more pronounced in the baked samples (**Table 1**). The observed decrease in lightness with an increase in oil concentration in this study is different from the findings of earlier theoretical and experimental studies with oil-in-water emulsions, which showed that emulsion lightness tends to increase with increasing oil concentration due to greater light scattering ([21–24]). This difference can mainly be attributed to the fact that the polar phase used in this study strongly scattered light (which we attribute to the presence of sugar crystals and/or protein aggregates), whereas the polar phase (water) used in conventional oil-in-water emulsions does not scatter light strongly itself. In addition, the intensity of light scattering by fat droplets in composite materials is likely to be much lower than in conventional emulsions because the contrast in refractive indices between the oil and polar phases is considerably smaller ([24, 25]). Consequently, increasing the oil droplet concentration reduces the total amount of polar phase in the composite materials, thereby decreasing the overall degree of light scattering. Similarly, the baked polar phase contributes a brownish color to the composite materials, which accounts for the observed decrease in color intensity as the polar phase concentration is decreased in the baked composites (**Table 1**).

Effect of Droplet Concentration on Water Activity. Water activity is an important parameter influencing the quality of many low-moisture food products ([26]), so it was important to examine the influence of droplet concentration on it. The water activity of composites with different oil droplet concentrations was measured before and after baking (**Figure 2**). The water activity decreased when the composite was baked, which can be attributed to the fact that some of the water molecules would have evaporated at the elevated temperatures that were used. The water activity also decreased appreciably as the oil
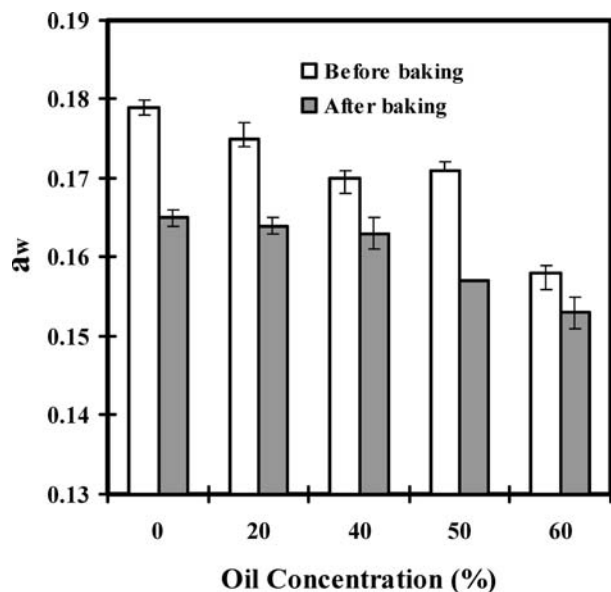
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Figure 2. Dependence of water activity on oil concentration for viscoplastic composites stabilized with WPC before and after baking (176 °C for 10 min, internal temperature reached 126 °C).

concentration increased. The overall water content of the composites decreased with increasing oil concentration, but the composition of the polar phase was the same for all samples regardless of oil content. Previous studies have shown that the water activity of the aqueous phase of oil-in-water emulsions is the same as the water activity of the overall emulsion (*27*). This phenomenon can be attributed to the fact that oil is immiscible with water and does not act as a solute that contributes to the colligative properties of water and therefore to its activity. Hence, the decrease in water activity with an increase in oil concentration cannot be attributed to the decrease in the overall moisture content in the composites. The observed effect may have existed because some of the water molecules diffused into the oil phase, or because the oil droplets slowed the movement of water molecules through the composites, thereby preventing them from reaching thermodynamic equilibrium within the water activity meter.

Effect of Oil Concentration on Droplet Characteristics. Information about the presence of whey protein molecules at the oil droplet surfaces was obtained by particle electrophoresis measurements. The ζ potential of the oil droplets was negative (−37 to −45 mV) and relatively insensitive to droplet concentration and baking (data not shown). This negative value is similar to that previously reported for whey protein-stabilized oil droplets under similar pH conditions (*28, 29*), which suggests that the oil droplets in the composites were stabilized by whey protein.

The mean diameter of the particles present in the composites after dilution was relatively small ($d_{43} \approx 3-5 \ \mu$m) and independent of oil concentration before baking but increased appreciably after baking (**Figure 3**). These results suggested that there was some aggregation of the oil droplets during the baking step, e.g., flocculation and/or coalescence. We postulated that the observed increase in particle size after baking was partly due to droplet flocculation induced by thermal denaturation and aggregation of free and adsorbed proteins (*14, 30, 31*). Optical microscopy showed that there was no big difference in the overall microstructure of the composites before and after baking except for the composite containing 60% oil, which showed some evidence of large droplets indicative of coalescence and oiling off (**Figures 4** and **5**).
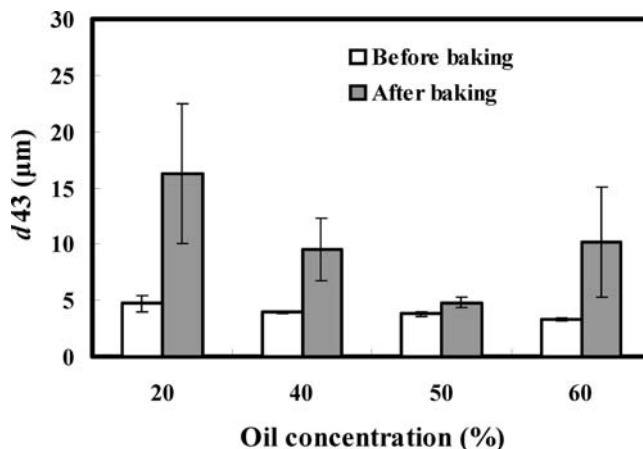

Figure 3. Dependence of mean particle diameter (d_{43}) on oil concentration for viscoplastic composites stabilized with WPC before and after baking (176 °C for 10 min, internal temperature reached 126 °C).
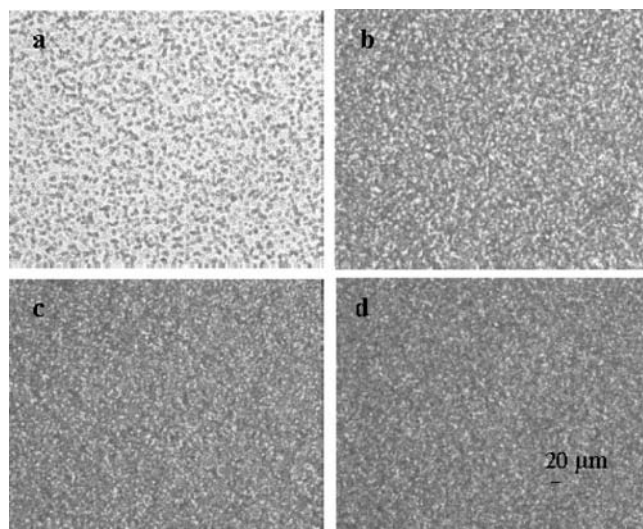

Figure 4. Photomicrographs of viscoplastic composites stabilized with WPC containing 20 (**a**), 40 (**b**), 50 (**c**), and 60% oil (**d**) before baking.

To obtain additional information about the relative stability of the composites to baking, we measured the percentage of total oil that was released by the samples when they were centrifuged. The percentage of oil released from the composites before baking clearly decreased with an increase in droplet concentration (**Figure 6**). On the other hand, the percentage of oil released from the composites after baking appeared to be fairly insensitive to oil concentration from 20 to 50 wt % oil but increased appreciably at the highest value of 60 wt % oil (**Figure 6**). The major difference between the unbaked and baked samples was the state of the whey proteins. In the baked samples, the proteins would have been thermally denatured and highly aggregated, whereas in the unbaked samples, they would have been largely native and nonaggregated. The decrease in the amount of oil released with an increase in oil concentration observed in the unbaked composites may have occurred for a number of reasons. First, the increase in the consistency of the composites with an increase in oil concentration (see below) may have made it more difficult for the oil to be released. Second, the fact that there was less protein present per unit amount of oil at high oil concentrations may have meant that the droplet surfaces were less protected against coalescence. The relatively large amount of oil released from the baked composites containing high oil concentrations may have been caused
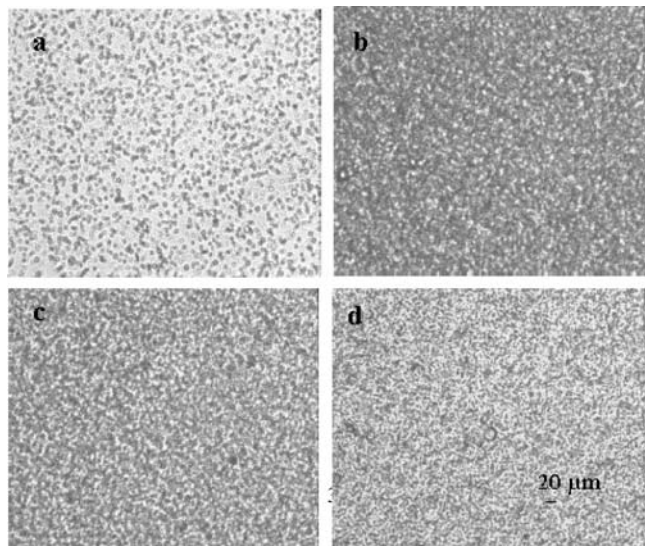
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Figure 5. Photomicrographs of viscoplastic composites stabilized with WPC containing 20 (**a**), 40 (**b**), 50 (**c**), and 60% oil (**d**) after baking (176 °C for 10 min, internal temperature reached 126 °C).
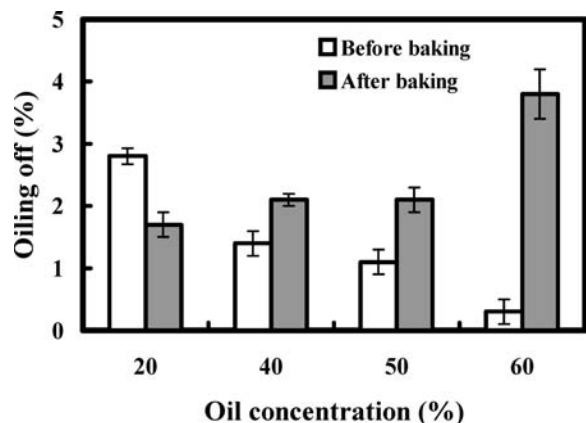

Figure 6. Dependence of oiling off on oil concentration for viscoplastic composites stabilized with WPC before and after baking (176 °C for 10 min, internal temperature reached 126 °C).

Figure 7. Typical stress–relaxation curve (**a**) and force vs height relationship [plotted in linear (**b**) and logarithmic (**c**) coordinates] of viscoplastic composites stabilized with WPC containing 60% oil before and after baking (176 °C for 10 min, internal temperature reached 126 °C).

by the droplets being close together, and therefore, it was easier for the more rigid interfacial membranes to be torn during the centrifugation process (*32, 33*).

Effect of Droplet Concentration on Rheological Parameters. Composite rheology was characterized by lubricated squeezing flow viscometry, which involved compressing composites uniaxially between parallel Teflon plates at a controlled displacement rate to cause a biaxial extensional flow (*34*). Typical force versus time and force versus height relationships of composites containing 60% oil are shown in **Figure 7**. The force increased steeply as the upper plate moved downward. Once the plate reached the final height, which was set to 1 mm, the movement of the upper plate was halted and the decreasing force was recorded as the sample relaxed. The linear part of the logarithmic force–height relationship (**Figure 7c**) represents the region of dominant squeezing flow (*34*). The data points obtained at specimen heights above this range correspond to a transient flow regime and hence were discarded.

The rheological parameters obtained from the curves in **Figure 7** for composites containing different oil concentrations are shown in **Figure 8**. The apparent compressive stress at 1 mm height was used as a measure of the sample's *consistency*. The residual apparent stress after relaxation for 120 s was used as a measure of
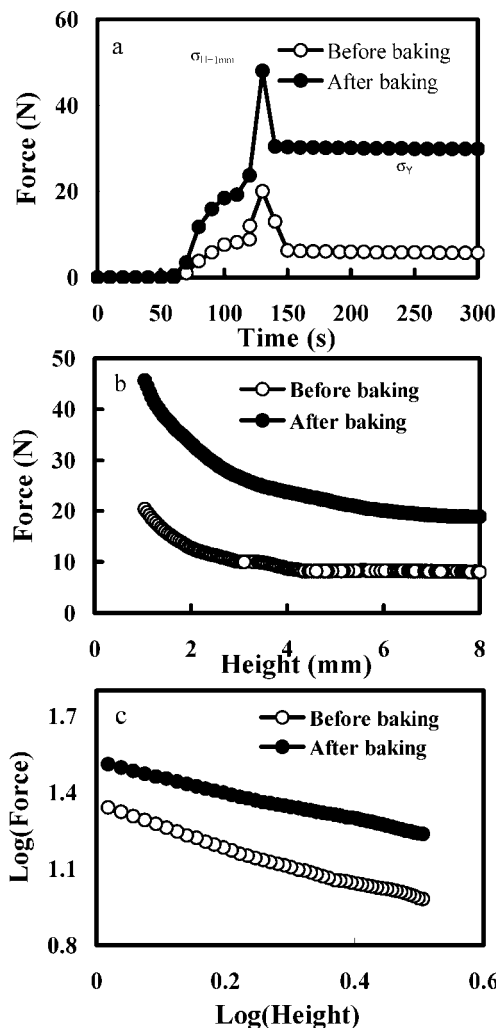
the sample's *plasticity*. This residual apparent stress has been correlated to the samples' apparent yield stress (*34*). For all compositions, the measures of consistency and plasticity of the composites were appreciably higher after baking than before baking. This strengthening of the composites after baking can be attributed to thermal denaturation and aggregation of the protein molecules in the continuous phase and at the oil–water interface (*35–37*). Protein aggregation led to the formation of a network throughout the system that gave it mechanical strength. The consistency and plasticity were appreciably higher for composites containing relatively high droplet concentrations ($\geq$40 wt %) than the values of those containing lower droplet concentrations (**Figure 8**). It is well known that the consistency and yield stress of oil-in-water emulsions increase steeply when the droplet concentration exceeds a particular value (30–40 wt %), which is attributed to strong droplet–droplet interactions (*2, 18*). Our results therefore indicate that the composites prepared in this study act like conventional oil-in-water emulsions in terms of their rheological behavior. From a practical standpoint, the rheological data indicate that the removal of fat droplets from the composites may have an appreciable effect on their overall textural characteristics.

Conclusions. The aim of this study was to examine the influence of oil concentration on the physicochemical properties of low-moisture viscoplastic composites produced by blending
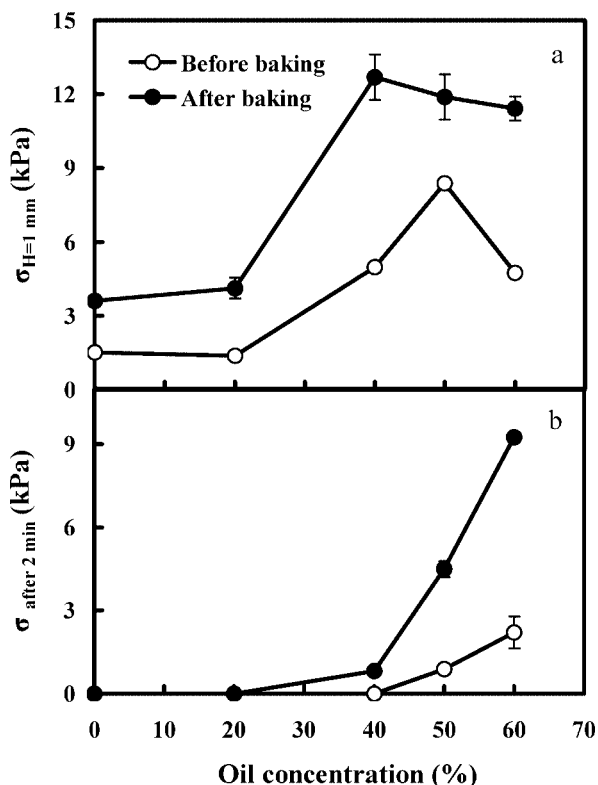
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Figure 8. Dependence of apparent compressive (**a**) and residual (**b**) stresses on oil concentration for viscoplastic composites stabilized with WPC before and after baking (176 °C for 10 min, internal temperature reached 126 °C).

together oil, glycerol, whey protein, and corn syrup. These composite materials consisted of oil droplets stabilized by whey proteins adsorbed to the droplet surfaces. Baking increased the consistency and yield stress of the composites, which was attributed to whey protein denaturation and aggregation. The overall appearance, stability, and rheology of the composites (baked and unbaked) depended strongly on the amount of oil present. The consistency and yield stress increased as the droplet concentration increased. If oil is removed from the composites, then the product formulation must be changed to provide rheological and optical characteristics similar to those of the original product.

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