

Properties of Low Moisture Composite Materials Consisting of Oil Droplets Dispersed in a Protein–Carbohydrate–Glycerol Matrix: Effect of Continuous Phase Composition

YEUN SUK GU,[†] MARIA G. CORRADINI,[†] D. JULIAN MCCLEMENTS,[†] AND
 JULIA DESROCHERS^{*,‡}

Biopolymer and Colloids Research Laboratory, Department of Food Science, University of Massachusetts, Amherst, Massachusetts 01003, and Kraft Foods Global, Inc., Glenview, Illinois 60025

The influence of continuous phase composition on the properties of low moisture (<3% water) composite materials consisting of oil droplets dispersed in a protein–carbohydrate–glycerol matrix was investigated. These composites were produced by blending canola oil (62.3%), whey protein concentrate (1.7%, WPC), and corn syrup and glycerol together (36.0% combined) using a high speed mixer equipped with a whisk. The polyol composition was varied by changing the ratio of corn syrup to glycerol in the system while keeping the total concentration of these two polyol components constant. Some composites were analyzed directly after preparation (“unbaked”), while others were analyzed after heating at 176 °C for 10 min to simulate baking of a food product (“baked”). The “lightness” of the composites was greater before baking (higher *L* value), but the color intensity of the composites was greater after baking (higher *b* value), which was attributed to Maillard browning reactions. The brownness of the baked composites increased with increasing corn syrup concentration, which was attributed to Maillard browning reactions. Squeezing flow viscometry indicated that the consistency and yield stress of the composites increased with baking, which was attributed to whey protein unfolding and aggregation. These rheological parameters also increased with increasing corn syrup concentration, which was attributed to its influence on the continuous phase rheology and on the interactions between the whey proteins. This study shows that the continuous phase composition and thermal history of low moisture composite materials have a large impact on their final physicochemical properties.

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

INTRODUCTION

Normally, the oil-in-water emulsions used in the food industry consist of oil droplets dispersed in a continuous phase that is predominantly water (1, 2). These microphase separated systems form because of the thermodynamic incompatibility of the polar water molecules and the nonpolar oil molecules. The physicochemical properties of oil-in-water emulsions depend on their composition, microstructure, processing, and history (2). Recent studies have shown that low moisture (<5% water; $a_w < 0.2$) composite materials can be produced by blending oil, protein, corn syrup, and glycerol together (3, 4). These composite materials consist of nonpolar oil droplets dispersed in a polar continuous phase consisting of whey protein, corn syrup, and glycerol (4) and are therefore analogous to traditional oil-in-water emulsions that also consist of nonpolar oil droplets dispersed in a polar continuous phase (water). The oil droplets

are stabilized by whey protein molecules adsorbed to their surfaces during the blending procedure. These composite materials are optically opaque, have good water holding capacity, and exhibit viscoplastic rheological behavior. In addition, they can be baked in an oven, which increases their apparent yield stress, consistency, and opacity. This type of composite material could be used in food applications where low moisture content is needed, for example, as a filling in dried food products that provides a desirable texture and flavor.

At present, there is a poor understanding of the major factors that determine the overall physicochemical properties of the low moisture composite materials described above. The purpose of the present study was therefore to examine the influence of continuous phase composition on the properties of unbaked and baked composite materials produced by blending canola oil, whey protein, corn syrup, and glycerol together. This information is practically important because it will indicate how composite materials with different physicochemical properties can be produced by systematically manipulating product composition.

* To whom correspondence should be addressed. E-mail: julia.desrochers@kraft.com.

[†] University of Massachusetts.

[‡] Kraft Foods Global, Inc..

The continuous phase of the low moisture composite materials is essentially a gel consisting of a whey protein network embedded in a corn syrup and glycerol matrix, with a small amount of water present from the corn syrup (4). In aqueous solutions, whey protein gels are produced when "reactive" protein molecules interact with each other and form a three-dimensional network. These reactive molecules are formed when the temperature exceeds the thermal denaturation temperature of the whey protein molecules, causing them to unfold and expose nonpolar and sulfhydryl groups normally buried in their interior (5). Network formation then occurs due to hydrophobic attraction and thiol–disulfide interchange reactions between exposed nonpolar and sulfhydryl groups on the surfaces of different whey protein molecules. We postulate that a similar mechanism occurs in the low moisture composite materials but that the water molecules are replaced by polyol molecules (corn syrup and glycerol). The type and number of polyol molecules that surround the globular proteins could affect gel network formation in a number of ways (6). First, the polyol composition determines the thermal denaturation temperature of the globular proteins due to a preferential interaction mechanism (i.e., preferential exclusion or accumulation of solvent molecules around the protein surface), thereby determining the fraction of reactive protein molecules available for participation in gel formation at a specific temperature (7). Second, the polyol composition influences the frequency of collisions between globular protein molecules by altering the aqueous phase viscosity. Third, polyols modulate the strength of the interactions between globular protein molecules through a preferential interaction mechanism, thereby altering the rigidity of the final gel formed (6, 7). Different types of polyol molecules have different effects on these three mechanisms depending on their dimensions and their interaction with the protein molecules. For example, sucrose is more effective than glycerol at increasing the thermal denaturation temperature of globular proteins and at increasing the attractive forces between unfolded proteins, which has mainly been attributed to a steric exclusion effect (7, 8). We would therefore expect that changing the ratio of glycerol to corn syrup in the composite materials would influence their bulk physicochemical properties indirectly by altering the unfolding and aggregation of the proteins and directly by altering the bulk physicochemical properties of the continuous phase (e.g., rheology and appearance). The objective of this paper is therefore to determine how the aqueous phase composition (ratio of sugar to glycerol) and thermal history of low moisture composite materials influence their overall physicochemical properties.

MATERIALS AND METHODS

Materials. Corn syrup 200D, which is a highly viscous clear liquid, was kindly donated by Tate & Lyle Food Ingredients (Decatur, IL). The manufacturers reported that the dextrose equivalent of this sample was 26 and the moisture content was 22.5% with a low amount of contamination from other materials (<0.05%). Powdered whey protein concentrate (WPC) was obtained from Davisco Foods International (Lot no. JE 001-3-922, Le Sueur, MN). As stated by the supplier, the composition of the WPC powder was 81.5 ± 1.0% proteins, 7.0 ± 1.5% lipids, 4.8 ± 0.2% moisture, 3.0 ± 0.5% ash, and 7.0 ± 1.0% lactose. Glycerol (glycerin) was purchased from Fisher Scientific (Pittsburgh, PA). Canola oil was purchased from a local supermarket.

Methods. Preparation of Composite Material. Glycerol, corn syrup, and oil were weighed into a beaker and heated using a microwave oven for 1 min to an internal temperature of 74 °C (measured after the contents of the beaker were mixed). This temperature and time combination were used because a previous study indicated that it produced stable composite materials (3). WPC powder was weighed

and placed into the bowl of a high speed mixer (N-50, Hobart Corporation, 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 final composition of the composite materials was prepared by mixing 1.7 wt % WPC, 62.3 wt % oil, and 36.0 wt % polyol (glycerol + corn syrup). The ratio of glycerol to corn syrup in the polyol fraction was varied as follows: 1, 24 wt % glycerol + 12 wt % corn syrup (2:1); 2, 26 wt % glycerol + 10 wt % corn syrup (2.6:1); 3, 28 wt % glycerol + 8 wt % corn syrup (3.5:1); 4, 30 wt % glycerol + 6 wt % corn syrup (5:1); and 5, 32 wt % glycerol + 4 wt % corn syrup (8:1). It should be noted that if the same preparation procedure was used as described above with the exception of omitting the microwave preheating step, then a composite material could not be prepared. Instead, the system separated into a layer of oil on top of a layer of protein–glycerol–corn syrup.

Baking of Composite Materials. Some of the composite materials were placed into cylindrical holes (2.6 cm radius; 1.5 cm height) within a metal baking tray (35 cm × 26.5 cm), heated in an oven at 176 °C for 10 min (final internal temperature = 126 °C), and then cooled at room temperature. This procedure was carried out to simulate the baking process that a food material might experience during preparation.

ζ-Potential Measurements. The electrical charge on the emulsion droplets was measured by particle electrophoresis. A small sample of the composite material (1 g) was dispersed in 10 mL of distilled water and mixed using a magnetic stir plate for 15 min prior to analysis. The oil-in-water emulsion formed was then diluted with distilled water and injected into the measurement chamber of a particle electrophoresis instrument (ZEM 5003, Zetamaster, Malvern Instruments, Worcs., United Kingdom), and the ζ-potential was determined by measuring the direction and velocity that the droplets moved in the applied electric field. The pH of the diluted samples placed into the measurement cell was determined to be 6.5 ± 0.2. The ζ-potential measurements are reported as the average and standard deviation of measurements made on two freshly prepared samples, with five readings made per sample. It should be noted that dilution of the low moisture composites with water may have caused some changes in the interfacial characteristics of the droplets.

Particle Size Measurements. The size of the particles in the composite material was measured by laser diffraction. A small sample of the composite material (1 g) was dispersed in 10 mL of distilled water and mixed using a magnetic stir plate for 15 min prior to analysis. The oil-in-water emulsion formed was then diluted with distilled water, and the particle size distribution was measured by laser light scattering (Mastersizer X, Malvern Instruments Ltd., Malvern, United Kingdom). This instrument finds the particle size distribution that gives the best fit between the experimental measurements and the 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 pH of the diluted samples placed into the measurement cell was determined to be 6.5 ± 0.2. The particle size measurements are reported as the average and standard deviation of measurements made on two freshly prepared samples, with two readings made per sample.

Squeezing Flow Viscometry Measurements. Composite materials were prepared and placed into cylindrical holes inside a metal baking tray using the procedure described above. Some of the composites were baked as described earlier and then held at room temperature for 24 h. The composites were then gently removed from the baking tray using a spatula and placed on the bottom plate of the rheology equipment. The 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 interfaced to a personal computer. The compression rate was 0.3 mm s⁻¹, and the final specimen height was set to 1 mm in all experiments. After the final height had been reached, any stress relaxation in the composite material was monitored by measuring the change in force for at least 2 min prior to crosshead withdrawal. The force, height, and time were recorded and saved on the computer for analysis. The results are expressed as the maximum apparent compressive stress at the final height of 1.0 mm

(σ_c) and the apparent residual stress after relaxation for 120 s after the final height of 1 mm (σ_Y). The apparent stress was defined as the measured force divided by the cross-sectional area of the plate (9).

Color Measurements. Reflectance spectra of baked and unbaked composite materials were measured using a UV–visible spectrophotometer (UV-2101PC, Shimadzu Scientific Instruments, Columbia, MD). Composite materials 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 were performed relative to a barium sulfate (BaSO_4) standard white plate. The tristimulus coordinates (L , a , and b values) of the composite materials were calculated from their spectral reflectance (10).

Oiling Off Measurements. The amount of free oil present in the emulsion after storage was determined by using a dye dilution technique (14). Oil Red O in canola oil (0.001 wt %) was stirred overnight using a magnetic stirrer. An emulsion (3 g) was placed into a tube, followed by pouring dye solution on the surface of the sample. The mixture was gently mixed and centrifuged at 20000 for 20 min to allow colored oil to float. A fraction of the diluted dye was transferred from the surface of samples, and its absorbance was measured at 520 nm with UV–visible Spectrophotometer (Ultraspec 3000 pro, Biochrom Ltd., Cambridge, United Kingdom) using canola oil as a blank. The change in absorbance was due to the dilution of the pigment by free oil in an emulsion and expressed as amount of free oil. The percentage of free oil in an emulsion was then calculated as the mass of free oil divided by the mass of oil in the original emulsion (3 g).

Water Activity Measurements. The a_w value of the samples was measured by placing the samples into a water activity instrument (Aqualab, Decagon) at room temperature.

Optical Microscopy. The microstructure of selected composite materials was determined using optical microscopy (Nikon microscope Eclipse E400, Nikon Corporation, Japan). A small amount of composite material 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

Influence of Preheating on Preparation of Unbaked Composites. When the composites were prepared using the method described above, they formed viscoplastic materials that looked fairly homogeneous. On the other hand, if the glycerol–corn syrup–oil mixture used to prepare the composite materials was not heated in a microwave oven (to an internal temperature of 74°C) prior to mixing with the whey protein, then a viscoplastic composite could not be formed. Instead, the final system consisted of a thick layer of oil on top of a whitish optically opaque material, which presumably contained the corn syrup, glycerol, and protein. There are a number of possible reasons that preheating the glycerol–corn syrup–oil mixture may have been necessary for the formation of the composite materials. For example, (i) it may have changed the viscosity of the oil and polar phases thereby making them easier to blend and disrupt, (ii) it may have increased the solubility of the protein or corn syrup in the polar continuous phase, or (iii) it may have promoted partial denaturation of the whey proteins thereby increasing their surface activity and ability to stabilize the oil droplets. At present, we do not know the precise reason that the preheating step is necessary, but our experiments clearly show that this step must be carried out to make stable viscoplastic composite materials. Preliminary experiments carried out in our laboratory recently suggest that partial denaturation of the whey proteins is necessary to promote their functionality in the preparation of composite materials.

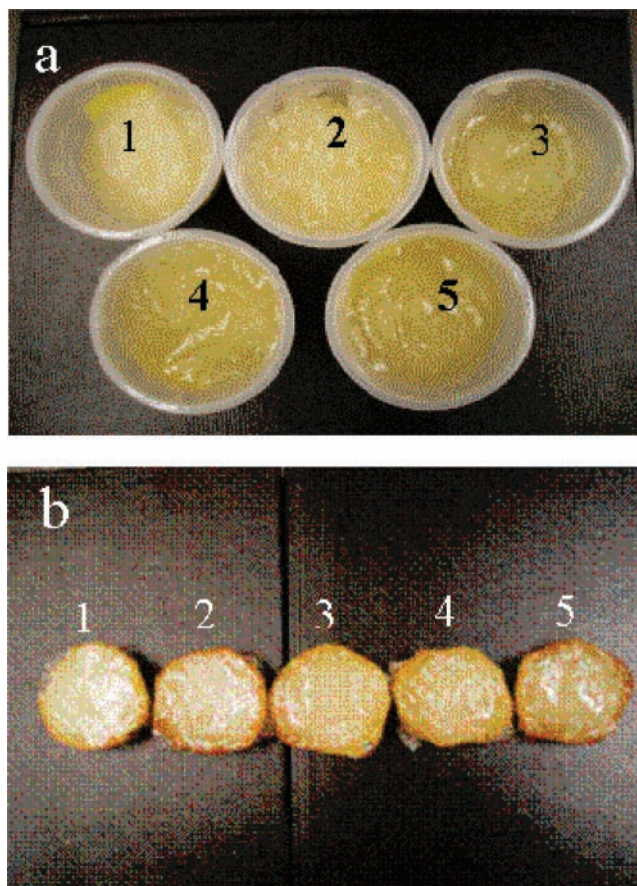


Figure 1. Photograph of composite material stabilized with WPC containing different polyol compositions (1, 24% glycerol + 12% corn syrup; 2, 26% glycerol + 10% corn syrup; 3, 28% glycerol + 8% corn syrup; 4, 30% glycerol + 6% corn syrup; and 5, 32% glycerol + 4% corn syrup) before and after baking (176°C for 10 min, internal temperature reached at 126°C).

General Textural Characteristics of Composites. Composite materials were prepared using the method described in the Materials and Methods section, and then, some were analyzed directly (“unbaked” samples), whereas others were baked at 176°C for 10 min and then analyzed (“baked” samples). Initially, we recorded the general appearance and properties of the unbaked and baked composite materials by manual inspection (Figure 1). The photographs show that all of the composite materials had a yellowish opaque appearance with a shiny surface before heating and that they were all brownish-yellow opaque gels after heating. Before baking, the composite materials containing relatively low glycerol contents ($\leq 26\%$) were more resistant to compression than those containing higher glycerol contents when pressed with a spatula. After baking, all of the composite materials formed gels that were more rigid than the corresponding unbaked samples. In addition, the resistance to compression of the baked samples increased with decreasing glycerol content. These qualitative visual observations indicated that the polyol composition (glycerol to corn syrup ratio) did have an appreciable effect on the general texture of the composite materials both before and after baking. We therefore carried out a series of more quantitative experiments to systematically examine the influence of polyol composition on their properties.

Effect of Polyol Composition on the Appearance of Composite Materials. The tristimulus coordinates (L , a , and b values) of baked and unbaked composite materials with different polyol compositions were measured (Table 1). Here, L repre-

Table 1. Influence of Polyol Composition (Glycerol-to-Corn Syrup Ratio) on the Color Coordinates (*L*, *a*, and *b* Values) of Unbaked and Baked Composite Materials Containing 1.7 wt % WPC, 62.3 wt % Oil, and 36.0 wt % Polyol (Glycerol + Corn Syrup)^a

% glycerin: % corn syrup	<i>L</i>	<i>a</i>	<i>b</i>
before baking			
24:12	57.7 ± 1.4	-1 ± 0.1	2.9 ± 0.1
26:10	49.0 ± 2.3	-0.7 ± 0.05	1.2 ± 0.6
28:8	42.2 ± 1.3	-0.4 ± 0.08	-1.4 ± 0.1
30:6	41.2 ± 2.1	-0.3 ± 0.1	-1.5 ± 0.2
32:4	43 ± 1.2	-0.3 ± 0.1	-1.3 ± 0.3
after baking			
24:12	46.3 ± 0.4	-0.1 ± 0.08	7.1 ± 0
26:10	41.1 ± 0.5	-0.2 ± 0.1	5 ± 0
28:8	39.3 ± 1.9	-0.5 ± 0.04	2.7 ± 1
30:6	36.4 ± 1.1	-0.6 ± 0.08	-0.6 ± 0.5
32:4	36.3 ± 0.6	-0.4 ± 0	-0.7 ± 0.2

^a The baked samples were heated at 176 °C for 10 min.

sents the “lightness”, and *a* and *b* are color intensity coordinates where $+a$ is the red direction, $-a$ is the green direction, $+b$ is the yellow direction, and $-b$ is the blue direction (2). Before baking, the *L* and *b* values of the composite materials increased as the corn syrup concentration increased, but the *a* value only changed slightly. The increase in lightness with corn syrup concentration was attributed to an increased amount of light scattering by undissolved particles present in the polar continuous phase. Pure corn syrup was a highly viscous transparent solution, but the addition of protein caused it to become cloudy, presumably because of the formation of sugar crystals or insoluble protein aggregates that scattered light. These particulates may have been formed because both the sugar and the protein molecules competed for the available water in the system, which may have caused one or both of them to become partially insoluble. The increase in yellowness (positive *b* value) with increasing corn syrup concentration was attributed to the fact that pure corn syrup had a light brown color, whereas pure glycerol was optically transparent. After baking, the *L* and *b* values increased appreciably as the corn syrup concentration increased, but the *a* value changed only slightly, which can be attributed to the same factors that determined the appearance of the unbaked samples. The lightness of the composites was greater before baking, but the yellowness (positive *b* value) of the composites was greater after baking. The decrease in lightness after baking may have been due to the fact that a fraction of the sugar crystals or protein particles dissolved at the elevated temperatures experienced during baking, thereby causing less light scattering. The increase in color intensity after baking can be attributed to the formation of a brownish-yellow color (observed visually), which was probably due to a Maillard reaction that occurred during baking between reducing sugars in the corn syrup solids and amino groups on the whey proteins (11, 12).

Effect of Polyol Composition on the Water Activity of the Composite Materials. The water activity of the composites is practically important because it may influence their suitability for applications in low moisture materials where redistribution of water molecules may adversely affect product quality, e.g., cookies, crackers, and snacks. The water activity of composite materials containing different polyol compositions was therefore measured before and after baking (Figure 2). The water activity of the unbaked and baked composite materials decreased as the glycerol concentration increased, which can be attributed to the fact that the corn syrup solids were the major source of water

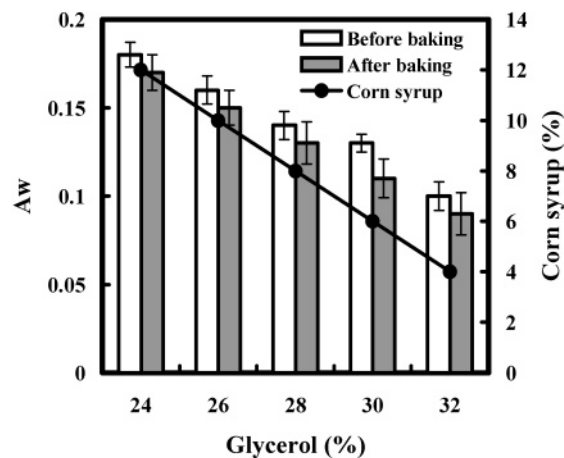


Figure 2. Dependence of water activity on polyol compositions for composite material stabilized with WPC before and after baking (176 °C for 10 min, internal temperature reached at 126 °C).

in the system (~22.5% of corn syrup solids was water). The baked composites had a lower water activity than the unbaked composites, which can be attributed to some water evaporation during the baking process. These results show that the water activity of the composites can be manipulated by altering the ratio of glycerol to corn syrup, which may be important for practical applications where a specific water activity is required.

Effect of Polyol Composition on Droplet Characteristics.

The ζ -potential of the oil droplets in the composites was measured before and after baking. The ζ -potential of the droplets was independent of polyol concentration, being -47 ± 4 mV before baking and -38 ± 1 mV after baking (data not shown). The negative charge on the droplets can be attributed to the presence of a layer of adsorbed whey protein molecules, since previous studies have shown that whey protein-stabilized droplets have a similar ζ -potential under comparable pH conditions ($\text{pH} = 6.5 \pm 0.2$) (13, 14). The fact that the droplet charge did not change appreciably with polyol composition suggests that the droplets were always stabilized by whey protein even though the solvent composition was changed. The decrease in negative charge after baking suggests that there may have been some chemical change in the proteins during the heating step that reduced the number of anionic carboxyl groups ($-\text{COO}^-$) or increased the number of cationic amino groups ($-\text{NH}_3^+$). The most likely chemical reaction that occurs during baking is the Maillard reaction between amino groups on the whey proteins and carbonyl groups on the corn syrup solids (11). Nevertheless, the Maillard reaction causes a loss of amino groups on proteins (11), thereby causing an increase in the negative charge of the droplets, which is the opposite of what we observed. An alternative explanation for the observed decrease in negative charge after baking may be physical changes in the system, such as an alteration in the surface load or in the thickness of the interfacial layer (15).

Before baking, the mean particle diameter of the composites increased as the glycerol concentration increased, with d_{43} increasing from ~ 3 μm for 24% glycerol to ~ 12 μm for 32% glycerol (Figure 3). The fact that the size of the oil droplets in the unbaked composites increased with increasing glycerol concentration was confirmed by optical microscopy, since many more large individual oil droplets were observed in the sample containing 32% glycerol than in the one containing 24% glycerol (Figure 4). It therefore seems that droplet disruption within the high speed mixer was more effective at lower glycerol and higher corn syrup concentrations. The efficiency of droplet

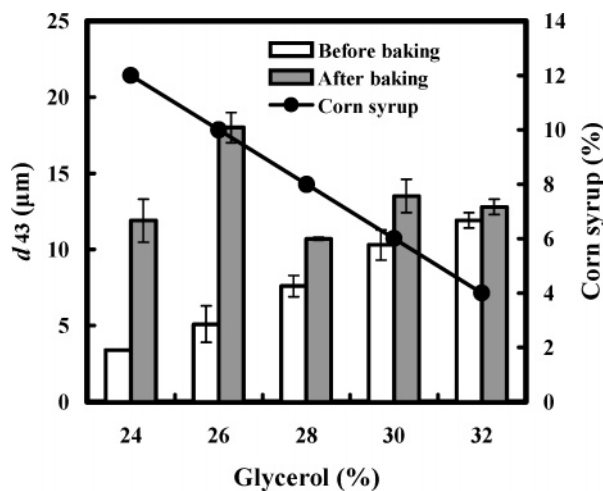


Figure 3. Dependence of mean particle diameter (d_{43}) on polyol compositions for composite material stabilized with WPC before and after baking (176 °C for 10 min, internal temperature reached at 126 °C).

disruption within a mixer is strongly influenced by the viscosity ratio of the dispersed to the continuous phases (2). Hence, the higher continuous phase viscosity of the composites with high corn syrup contents (see below) may have improved the efficiency of droplet disruption during the mixing process.

After baking, the mean particle diameter ($d_{43} \approx 10\text{--}20 \mu\text{m}$) of the composites was higher than before baking (Figure 3). This might be attributed to either droplet flocculation or droplet coalescence. We believe that this increase in particle size was mainly due to droplet flocculation since optical microscopy measurements indicated that the size of the individual droplets in the composite materials was fairly similar before and after heating (Figures 4 and 5). It is known that heating whey proteins above their thermal denaturation temperature (around 70 °C) causes them to unfold and interact with other protein molecules, often promoting droplet flocculation (5). There was no obvious trend in the mean particle size with glycerol concentration after baking.

Additional information about the tendency of the oil droplets to aggregate was obtained by measuring the degree of oiling-off when the composites were centrifuged (Figure 6). The baked composites exhibited a greater degree of oiling-off than the unbaked composites, and the amount of oiling-off increased with increasing glycerol content both before and after baking. These results suggest that corn syrup decreased the susceptibility of the composites to oiling-off induced by centrifugation, whereas baking promoted their susceptibility to oiling-off. The fact that the baked composites exhibited more oiling-off than the unbaked composites may be attributed to the fact that baking increased the covalent cross-linking of whey proteins adsorbed to the oil droplet surfaces (5). If a sufficiently large stress is applied parallel to an interface that is comprised of a highly cohesive layer of emulsifier molecules, then it may cause the interfacial membrane to tear, leaving exposed emulsifier-depleted patches that promote coalescence and oiling-off (16). It has been reported that this mechanism is important in protein-stabilized emulsions where the adsorbed protein membranes have been extensively cross-linked (as in the baked samples), particularly under highly applied mechanical stresses such as the centrifugal forces generated during the oiling-off test. The increase in the amount of oiling off with increasing glycerol might be due to the fact that glycerol is less effective at increasing the thermal denaturation temperature than sugars (7, 17). Hence, there may have been more extensive protein unfolding and aggregation at

lower glycerol concentrations, leading to a more cross-linked interfacial membrane that was more susceptible to tearing during centrifugation (16). It should be noted that the oiling-off test used in this study subjects composite materials to mechanical forces that could induce membrane tearing and oil release, whereas there may be no oiling-off in the undisturbed composite materials.

Effect of Polyol Composition on Rheological Parameters.

The rheology of unbaked and baked composite materials was characterized by squeezing flow viscometry. The overall rheological properties of a particulate material are known to depend on the characteristics of the disperse phase (e.g., particle concentration, interactions, and viscosity) and on the characteristics of the continuous phase (e.g., rheology) (18). We therefore measured the rheology of the composites in the absence and presence of the dispersed phase (i.e., the oil droplets) so as to identify the relative importance of dispersed and continuous phase properties on the overall rheology.

Derivation of Rheology Parameters. Typical force vs time relationships of unbaked and baked composite materials (1.7% WPC, 62.3% oil, 24% glycerol, and 12% corn syrup) squeezed between an upper and a lower Teflon plate are shown in Figure 7. The force increased steeply as the upper plate moved downward through the sample, compressing it and squeezing it between the plates. Once the plate reached the final height, which was set to a 1 mm gap between the upper and the lower plates, the movement of the upper plate was halted and the decreasing force was recorded as the sample relaxed. The following rheological parameters were derived from the force vs time profiles (19, 20).

Apparent Compressive Stress. The apparent compressive stress (σ_c) was determined by measuring the force ($F_{1\text{mm}}$) at the final sample heights (1 mm), which was within the region where squeezing flow was dominant. $\sigma_{H1} = F_{H1}/(\pi r^2)$, where r is the radius of the plates. This parameter gives a measure of the consistency of the material; the higher σ_c is, the greater the resistance to compression is.

Apparent Residual Stress (σ_Y). The apparent residual stress (σ_Y) was determined by measuring the force ($F_{120\text{s}}$) at a given time (120 s) after the final sample height (1 mm) had been reached: $\sigma_Y = F_Y/(\pi r^2)$. This parameter provides a measure of the plasticity of the material; the higher σ_Y is, the greater the stress required to initiate flow is.

Rheological Properties of Composites Containing Oil Droplets. The rheological parameters of unbaked and baked composite materials with different polyol compositions are summarized in Table 2. The apparent compressive and residual stress of both the unbaked and the baked composite materials decreased with increasing glycerol content, indicating that glycerol decreased the consistency and plasticity of the composites. At a particular polyol composition, the apparent compressive and residual stresses were greater after baking than before baking, indicating that the baked samples had a higher consistency and plasticity than the unbaked samples. Possible reasons for the influence of sample composition and heating on the properties of the composite materials are discussed below.

Rheological Properties of Continuous Phase of Composites. As mentioned above, the overall rheology of particulate materials depends on the characteristics of the dispersed phase as well as on the rheological properties of the continuous phase (18). To obtain some information about the relative contribution of the dispersed and continuous phases to the overall rheology of the composites, we also measured the rheological properties of the continuous phase. In this case, the composite materials

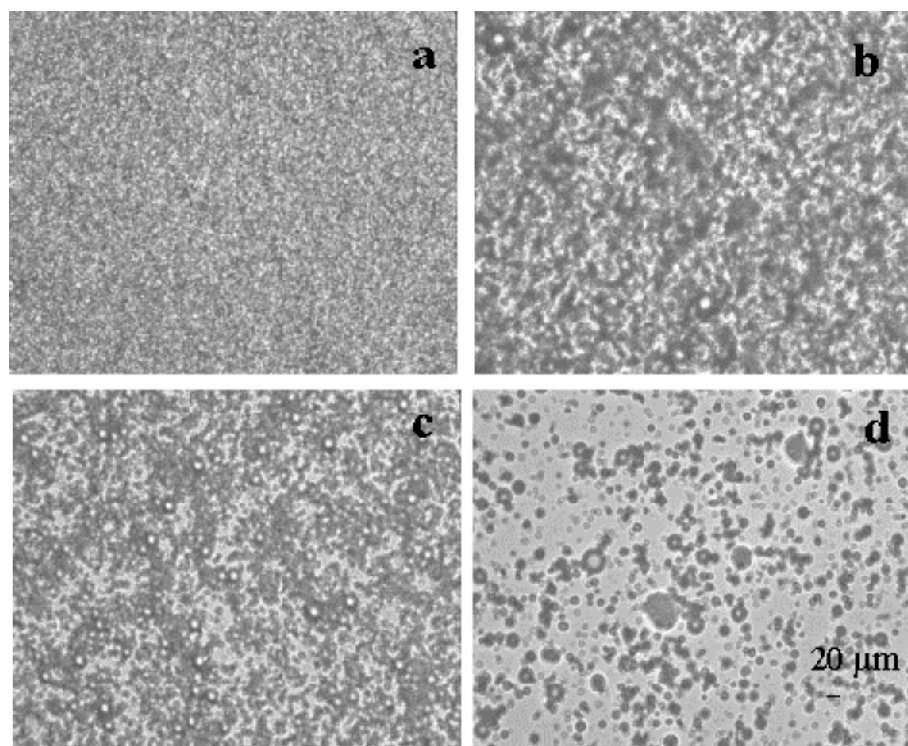


Figure 4. Photomicrographs of composite material stabilized with WPC containing different polyol compositions before baking. (a) 24% Glycerol + 12% corn syrup; (b) 28% glycerol + 8% corn syrup; (c) 30% glycerol + 6% corn syrup; and (d) 32% glycerol + 4% corn syrup.

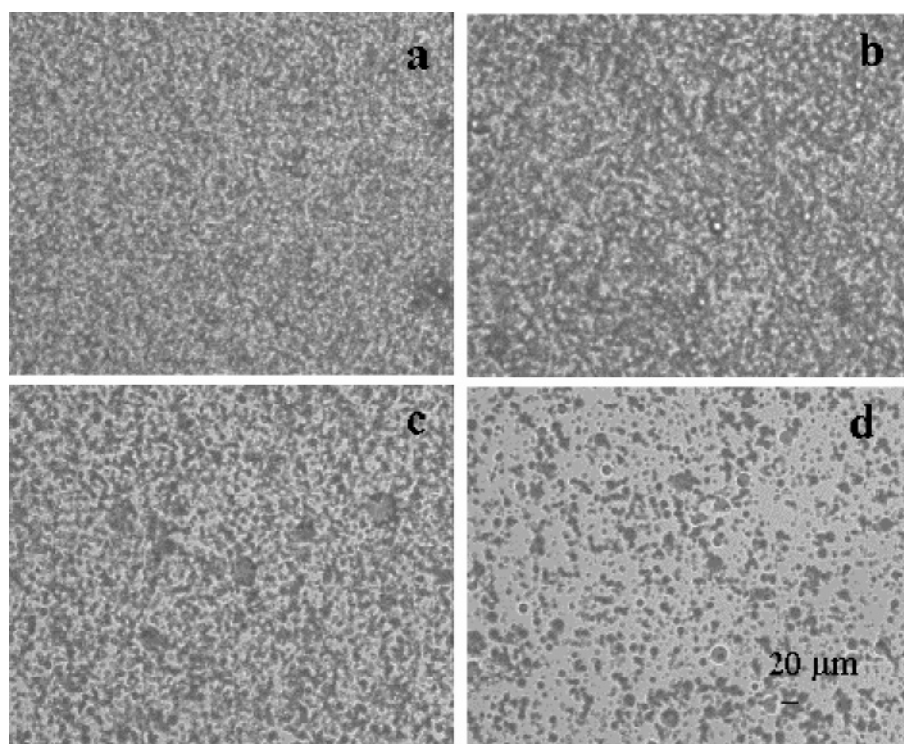


Figure 5. Photomicrographs of composite material stabilized with WPC containing different polyol compositions after baking (176 °C for 10 min, internal temperature reached at 126 °C). (a) 24% Glycerol + 12% corn syrup; (b) 28% glycerol + 8% corn syrup; (c) 30% glycerol + 6% corn syrup; and (d) 32% glycerol + 4% corn syrup.

were prepared using the same procedure as described in the Materials and Methods section, except that the oil phase was omitted. The rheological parameters of the continuous phase of composite materials with different polyol compositions are shown in **Table 3**.

The apparent compressive stress of both the unbaked and the baked continuous phases decreased with increasing glycerol

content, indicating that glycerol decreased the consistency (as it did in the composites). At a particular polyol composition, the maximum apparent stress was greater after baking than before baking, suggesting that the baked samples had a higher consistency than the unbaked samples. The apparent residual stress of the continuous phases of the unbaked and baked samples was zero for all polyol compositions. At a particular

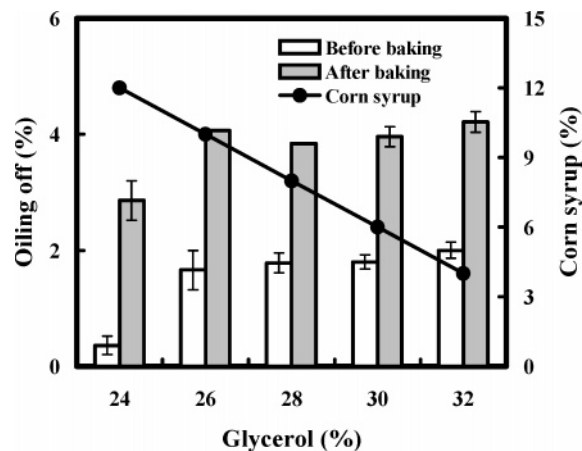


Figure 6. Dependence of oiling off on polyol compositions for composite material stabilized with WPC before and after baking (176 °C for 10 min, internal temperature reached at 126 °C).

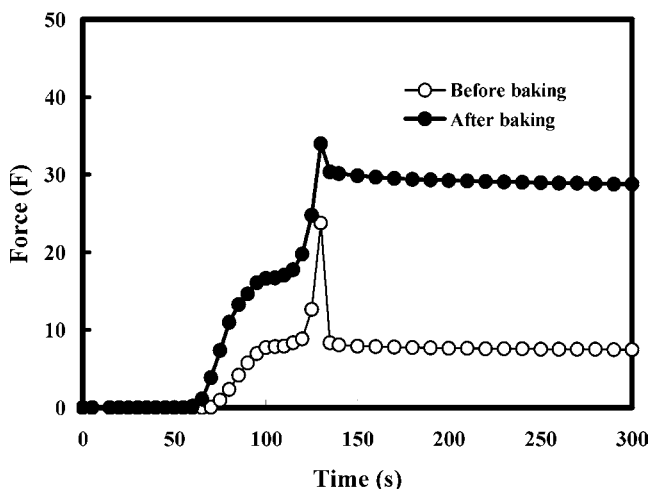


Figure 7. Typical force vs height relationships and stress relaxation curves of composite material stabilized with WPC containing 24% glycerol and 12% corn syrup in the aqueous phase in the presence of oil before and after baking (176 °C for 10 min, internal temperature reached at 126 °C).

Table 2. Influence of Polyol Composition (Glycerol-to-Corn Syrup Ratio) on Rheology of Unbaked and Baked Composite Materials Containing 1.7 wt % WPC, 62.3 wt % Oil, and 36.0 wt % Polyol (Glycerol + Corn Syrup)^a

% glycerol: % corn syrup	σ_c (kPa)	σ_y (kPa)
unbaked		
24:12	7.1 ± 0.09	2.2 ± 0.14
26:10	5.3 ± 1.2	1.3 ± 0.57
28:8	4.9 ± 0.26	0.8 ± 0.03
30:6	3.5 ± 0.20	0.3 ± 0.13
32:4	3.1 ± 0.58	0.2 ± 0.04
baked		
24:12	13.1 ± 0.57	9.1 ± 0.11
26:10	8.7 ± 0.41	4.9 ± 0.32
28:8	7.0 ± 0.59	3.7 ± 0.54
30:6	5.5 ± 0.08	2.6 ± 0.08
32:4	4.7 ± 0.37	2.1 ± 0.28

^a The baked samples were heated at 176 °C for 10 min.

polyol composition, the apparent compressive and residual stresses of the composite materials containing oil droplets were appreciably higher than for the continuous phase containing no

Table 3. Influence of Polyol Composition (Glycerol-to-Corn Syrup Ratio) on Rheology of Unbaked and Baked Composite Materials Containing 4.5 wt % WPC and 95.5 wt % Polyol (Glycerol + Corn Syrup)^a

% glycerol: % corn syrup	σ_c (kPa)	σ_y (kPa)
unbaked		
24:12	6.0 ± 0.15	0
26:10	4.6 ± 0.06	0
28:8	3.5 ± 0.02	0
30:6	2.4 ± 0.02	0
32:4	1.8 ± 0.04	0
baked		
24:12	8.4 ± 0.06	0
26:10	7.0 ± 0.15	0
28:8	5.9 ± 0.06	0
30:6	4.9 ± 0.39	0
32:4	3.5 ± 0.02	0

^a The baked samples were heated at 176 °C for 10 min.

oil droplets (Tables 2 and 3). This highlights the important role that the oil droplets play in determining the overall rheology of the composite materials. This is to be expected since it is well-known that the rheology of conventional oil-in-water emulsions changes from liquidlike to viscoplastic-like as the oil concentration exceeds a critical level and the oil droplets interact strongly with each other (2, 18). The composite materials have relatively high oil concentrations (62.3 wt %); therefore, the droplets will be in close contact. The increase in apparent consistency and yield stress of the composite materials after baking can be attributed to thermal denaturation and aggregation of proteins adsorbed onto different oil droplets, since this would lead to the strengthening of the attractive interactions between the droplets.

The consistency and yield stress of the composites decreased as the glycerol concentration increased (Table 2), which may be partly attributed to the influence of glycerol on the continuous phase rheology since its consistency also decreased with increasing glycerol concentration (Table 3). In addition, the ratio of glycerol to corn syrup may also have influenced the thermal denaturation and aggregation of the protein molecules, since different polyols are known to impact the thermal stability and interactions of proteins differently (6).

In conclusion, the aim of this study was to examine the influence of polyol composition (glycerol to corn syrup ratio) and thermal history on the preparation, structure, and properties of composite materials formed by blending oil, whey protein, glycerol, and corn syrup together. Optical microscopy showed that the composite materials consisted of nonpolar oil droplets dispersed in a polar continuous phase. The concentration of these oil droplets was relatively high (62.3 wt %) so that that they were closely packed together, which gave both the baked and the unbaked composite materials their characteristic viscoplastic rheology. ζ -Potential measurements suggested that the oil droplets were surrounded by a layer of adsorbed whey protein molecules. The increase in consistency and yield stress of the composite materials after baking was therefore attributed to thermal denaturation and aggregation of proteins adsorbed onto different oil droplets, since this would lead to the strengthening of the attractive interactions between the droplets. On the other hand, thermal denaturation and aggregation of the adsorbed proteins made the droplets more susceptible to droplet coalescence and oiling off when a mechanical force (centrifugation) was applied to the system. This was attributed to tearing of the highly cross-linked interfaces leading to exposure of oil.

The rheology of the composites was also found to depend on the polyol composition of the continuous phase. The consistency and yield stress of the composites decreased as the glycerol concentration increased, which may be partly attributed to the influence of glycerol on the continuous phase rheology since the consistency also decreased with increasing glycerol concentration in the continuous phase without oil droplets. This study has provided some useful insights into the factors that influence the appearance, rheology, and stability of low-moisture composite materials that may be useful for utilization in the food and other industries.

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