J Am Oil Chem Soc (2011) 88:33–38
DOI 10.1007/s11746-010-1647-1

ORIGINAL PAPER

Ultrasonic Attenuation Measurements of the Mixing, Agglomeration, and Sedimentation of Sucrose Crystals Suspended in Oil

Umut Yucel · John N. Coupland

Received: 11 May 2010 / Revised: 1 July 2010 / Accepted: 7 July 2010 / Published online: 28 July 2010

Abstract The structure and properties of solid-in-oil dispersions are important in many industrial products, notably chocolate, yet are difficult to characterize by existing methodologies. Sensors based on ultrasonic attenuation measurements offer potential to characterize changes in these systems. Sucrose crystals ($d \sim 29.8$ μm) were dispersed into corn oil (8–16 wt%) in a stirred tank. The dispersed crystals were agglomerated by the addition of small volumes of water (<1%) and finally allowed to sediment quiescently. The processes were monitored continuously by ultrasonic attenuation measurements (2.25 MHz). Ultrasonic attenuation increased with increasing sucrose crystal concentration and with the degree of agglomeration. Adding water also decreased the equilibrium sediment density and decreased the time taken for the sucrose to sediment out quiescently. Water-induced agglomeration led to the formation of a few very large particles as inferred from sedimentation kinetics and confirmed by micrometer measurements of crystal agglomerates. In conclusion, ultrasonic attenuation measurements provide a variety of novel approaches that can be used to characterize suspensions of particles in oil.

Keywords Ultrasound · Sensor · Sucrose · Vegetable oil · Aggregation · Dispersion · Sedimentation · Conching

Introduction

Several food processing operations involve dispersing powders in liquids. During the mixing process, powder agglomerates are broken up and the viscosity of the suspension decreases. For example in chocolate conching, a long mixing process at elevated temperatures is necessary to disperse sucrose, cocoa solids, and milk powder in liquid cocoa butter and convert the product from a paste to a smooth liquid [1].

Particle dispersion involves three steps: wetting the surface with liquid and displacing air, deagglomerating the wetted clumps, and finally maintaining particle separation and preventing sedimentation. Clearly, the strength and nature of the inter-particle forces will determine the efficiency and effectiveness of the process. When hydrophilic particles are dispersed in a non-polar liquid any small amount of water present will adsorb at the particle surfaces and hold the powder in clumps by forming water bridges, i.e., strong capillary forces [2]. This is particularly important in chocolate conching when a small amount for water can rapidly agglomerate the sucrose particles and increase the suspension viscosity. For example, Chevalley [3] showed that the presence of 3–4% water increases the viscosity of molten chocolate markedly as compared to the typical moisture concentrations of 0.5–1.5%. Emulsifiers can assist the dispersion of fine particles by adsorbing at the surface and providing some steric repulsion [4].

The degree of agglomeration can be followed by measuring the particle size of the particles directly or inferred from apparent viscosity measurements [1, 5] or from sedimentation measurements [4]. For studies of agglomerates formed by weak adhesion, sedimentation experiments are more suitable than rheological measurements as the forces

---

Electronic supplementary material The online version of this article (doi:10.1007/s11746-010-1647-1) contains supplementary material, which is available to authorized users.

U. Yucel · J. N. Coupland (✉)
Department of Food Science, The Pennsylvania State University,
337 Food Science Building, University Park, PA 16801, USA
e-mail: coupland@psu.edu

applied to the aggregate during measurement are less [6]. Sediments formed from non-agglomerated particles tend to be more dense than sediments formed from agglomerated particles [7]. For example, the sediment volumes formed from dispersions of sucrose in oil increased 50% with an increase in water concentration from 0 to 1% [8].

Dispersions of crystals at concentrations and sizes commonly used in industry are often opaque, and so optical methods are unsuitable to study aggregation directly. However, ultrasound propagates well through most fluids and can be used to characterize dispersions. Acoustic waves move as a series of compressions and rarefactions in the material they are passing through. Wave propagation depends on the thermal and physical properties, such as density and elasticity, of the media so measurement of acoustic properties is related to material properties. Ultrasound is high frequency (i.e., >18 kHz) sound that at low power levels is non destructive and useful for sensing applications. Ultrasonic velocity and attenuation (i.e., the logarithmic loss of the wave energy with distance) can both be measured [9]. However, attenuation measurements are often preferred for dispersion characterization, as attenuation is less affected by small changes in temperature [10].

Ultrasonic attenuation measurements have been used to measure the concentration [11], size [12], and degree of agglomeration [13] of fine particle suspensions. Previously, we demonstrated the use of ultrasonic attenuation measurements to follow the mixing kinetics of lactose crystals into a saturated aqueous lactose solution [14]. There was a large increase in attenuation of the sample immediately upon addition of the powdered lactose, which decreased during mixing to a steady state value dependent on the solids loading. Particle sedimentation kinetics can also be followed by measuring ultrasonic properties as a function of height and time during gravitational separation. This method has been applied to creaming measurements in emulsions [15, 16] including the effects of flocculation [17].

In summary, the processes of dispersing sucrose particles in oil are important in chocolate conching but are difficult to characterize. The presence of water is known to induce sucrose crystal aggregation and affect the rheology of the suspension. While ultrasonic attenuation measurements have been widely applied to dispersion characterization, they have not been used to study dispersions of sucrose crystals in oil. In this work we integrate an ultrasonic sensor into a stirred tank to measure the processes of (i) mixing, (ii) agglomeration in the presence of water, and (iii) quiescent sedimentation of sucrose crystals in vegetable oil. We show that ultrasonic attenuation measurements give a good indication of the kinetics and extent of these processes and provide a novel sensor for use in dispersion characterization.

Materials and Methods

Materials

Corn oil and confectioner's sugar (finely ground sucrose) were bought from a local market. Sucrose was stored in a desiccator with Drierite until used. The crystals were characterized at room temperature by optical microscopy (Olympus BX-41, Hitech Instruments, Edgemont, PA; 20X) equipped with a SPOT Insight QE camera (SPOT Diagnostic Instruments, Sterling Heights, MI), static light scattering after dispersing in isopropanol (Horiba LA-920, Irvine, CA assuming a relative refractive index of 1.12. There was a wide distribution of crystal sizes and shapes with a volume-weighted average diameter ($d_{4,3}$) of 29.8 ± 1.6 μm (see Electronic Supplementary Material). X-ray diffraction measurements (Rigaku MiniFlex II, Rigaku Americas Corp., The Woodlands, TX) showed the crystals were crystalline sucrose [18], with negligible diffuse background (data not reported). The moisture content of the corn oil and desiccated sucrose were measured by Karl-Fisher titration as <0.1 wt% and 0.43 wt% respectively.

Mixing

The previously described stirred tank system fitted with ultrasonic sensors was used for mixing and sedimentation experiments [14]. A known amount of corn oil was introduced into the tank (a cylinder with an internal diameter of 10.4 cm and a height of 15.0 cm) and agitated with a blade impeller (5 cm length. 1.3 cm width with an 0.6 cm diameter shaft) located in the center of the tank 7.5 cm from the bottom of the tank and driven at 600–650 rpm by a laboratory scale stirrer (STIR PAK laboratory stirrer, Model 4554, Cole Parmer, Chicago, IL). Desiccated sucrose crystals (8–16 wt%) were quickly added (i.e., in less than 30 s), and after the crystals were uniformly dispersed within the oil (i.e., no change in the mean sensor response with time), water was added to induce crystal agglomeration. Water was added rapidly as a single aliquot from a pipette. In some experiments, the stirrer was stopped after mixing and subsequent quiescent sedimentation kinetics were followed ultrasonically.

All experiments were conducted at room temperature. Sample temperature, as monitored with a k-type thermocouple (0.1 °C sensitivity), fluctuated around 22.8 °C with a maximum deviation of 0.4 °C. All experiments were performed at least in triplicate.

Ultrasound

The course of mixing process was followed on-line by ultrasonic attenuation measurements as described in detail by Yucel and Coupland [14], and summarized as follows. An electrical square wave pulser/receiver (Panametrics 5077 PR, Waltham, MA) was used to excite an ultrasonic transducer (2.25 MHz center frequency, Panametrics V606, Waltham, MA). The resultant ultrasonic pulse passed down a Plexiglas delay line (0.8 cm) coupled into the wall of the tank containing the sample, through the sample (10.4 cm) and was detected by a second identical transducer-delay line mounted at the opposite side of the container. The received signal was digitized by the same pulser/receiver and captured using a digital storage oscilloscope (LeCroy 9310c, Chestnut Ridge, NY). The overall acoustic beam path was 12 cm (i.e., the total sample thickness was 10.4 cm plus the thickness of the two delay-lines, 1.6 cm) and the transducers were located 5 cm from the bottom of the tank. Attenuation data was collected automatically by a Lab View (version 7.1, National Instruments, Austin, TX) virtual instrument. The pulse gain was increased 03 dB for each 2 wt% increase in sucrose concentration to ensure an acquirable acoustic signal was transmitted between the transducers. The energy of the incident pulse at each gain was calibrated with respect to the water. The energy loss within the sample was evaluated as a normalized power transmission loss (NPTL) [14]:

$$\mathrm{NPTL} = 10\log(I_{\mathrm{water}}/I_{\mathrm{measured}}) \tag{1}$$

where I_{water} and I_{measured} are the signal intensities measured in water and the sample, respectively.

Solid Bed Density and Solid Bed Height

The packing properties of the dispersed particles can be used as an indication of the degree of the agglomeration. After mixing was attained, dispersions were characterized by means of solid bed density (SBD) and solid bed height measurements. Aliquots (~7 mL) of the dispersion was sampled into a 10-mL glass tube (1 cm diameter), and allowed to sediment over 48 h. The sediment was characterized as the ratio of sediment volume to total volume, i.e., normalized solid bed height (NSBH). The SBD was also calculated as described by Mongia and Ziegler [7], i.e., the ratio of the total mass of the solids to the volume of the sediment.

Results and Discussion

Dispersing the Sucrose Crystals into Oil

The changes in ultrasonic signal on adding sucrose to oil are illustrated in Fig. 1. The initial NPTL is not zero because pure oil dissipates more ultrasonic energy than water; however, as soon as the desiccated sucrose powder was added into oil (1 min) there is a sudden increase. The NPTL then decays back to a steady state value over approximately 2,000 s. Although only data from a single experiment is shown, the process is highly reproducible and all mixing profiles for the same composition effectively overlaid one another.

When solid powder is added to a liquid, it first distributes itself as clusters of particles with air pockets between and around them. As the mixing continues, the surfaces of individual particles are wetted with oil, the particle clusters are broken down and air is released. Entrained air bubbles can attenuate sound very strongly [14]. It was expected that changes in air content is mainly responsible for the changes seen in Fig. 1, although changes in the effective particle size due to deagglomeration may play some role.

In this case, the plateau in the NPTL (i.e., steady state mixing) was reached after approximately 2,000 s. However, in our earlier work when lactose crystals were added to saturated aqueous lactose solution the steady state plateau was reached in only 120 s [14]. This difference may be because sucrose crystals are hydrophilic in nature, and thus surface wetting by water is expected to be faster than by oil. Another possible mechanism for the elongated mixing time may be related to the presence of small amounts of residual water in sugar (i.e., 0.43%), which can support the agglomerates by strong capillary forces.

Equilibrium NPTL (i.e., the steady state value from Fig. 1) increased approximately linearly with sucrose concentration (Fig. 2a), as is typical for dispersions provided their microstructure remains reasonably constant with changing concentration [19]. In this case, NSBH also increased approximately linearly with sucrose concentration (Fig. 2b) suggesting that the SBD, i.e., the way the particles pack together is unchanged (~0.47 kg sucrose/m^3 oil). Note that in both NPTL and NSBH the linear relationship with sucrose concentration began to break down at the highest concentration selected (16 wt%) perhaps because of the increased importance of particle–particle interactions.

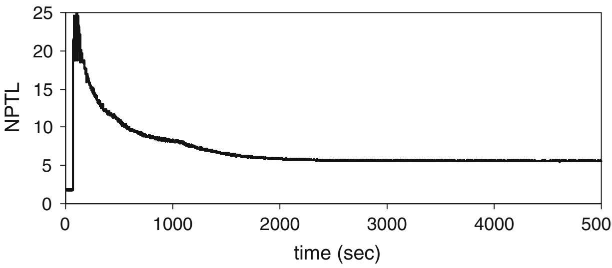

Fig. 1 Kinetic changes in NPTL upon addition of 80 g sucrose crystals into 920 g corn oil (i.e., 8 wt% dispersion). The sucrose was added at 60 s and the total addition time was less than 30 s. Measurements were made every 0.5 s and the line shown is a moving average over three points

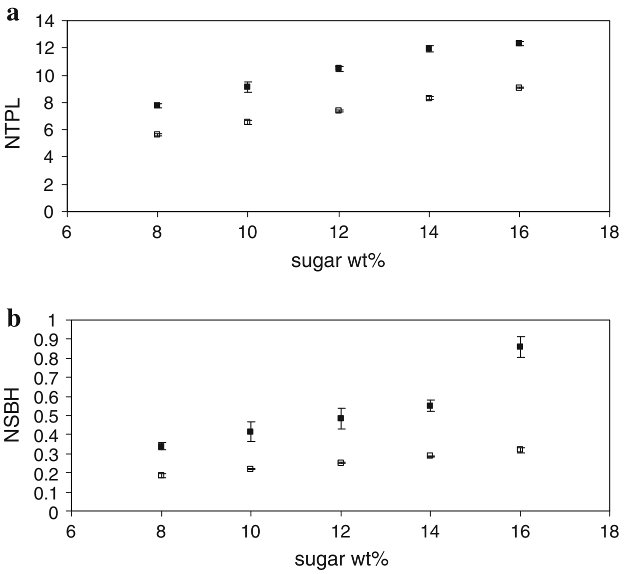

Fig. 2 **a** Steady state and quasi steady state (i.e., 3,000 s after water addition) NPTL and **b** NSBH for sucrose dispersions in corn oil dispersions containing (*open squares*) 0 and (*closed squares*) 1 wt% water (relative to the mass of sucrose). In each experimental run the plateau value was calculated as the average of 300 measurements made over 150 s. *Points* and *error bars* are the mean and standard deviation of six experimental replications

Addition of Water

After the sucrose was fully dispersed into corn oil (i.e., steady state NPTL response in Fig. 1), 1 wt% (with respect to the mass of sucrose) was added into the dispersion (Fig. 3). After a small lag time (30 s) following the instantaneous water addition, NPTL increased rapidly over approximately 300 s to a new plateau value. In fact, the plateau continued slowly but significantly to increase with time (slope 2.1×10^{-4} s^{-1}, $p < 0.05$). However, this slope was not considered important to the present work and the data were truncated at 3,000 s which was defined as a quasi steady state after the addition of water. The noise in the ultrasonic signal was much greater in the presence of added water. There was no change in signal when water was added to oil in the absence of sucrose (data not reported).

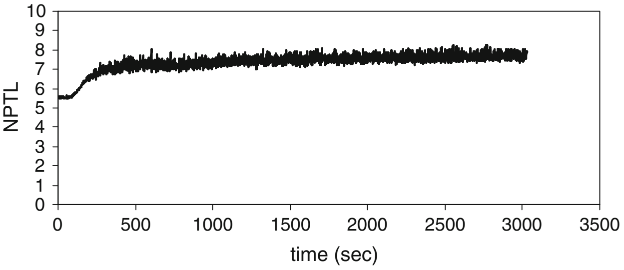

Fig. 3 Kinetic changes in NPTL upon addition of 1 wt% water (relative to the mass of sucrose) into 8 wt% sucrose dispersions in corn oil (i.e., 0.8 mL into the dispersion of 80 g sucrose in 920 g corn oil). Water was added after 50 s. Measurements were made every 0.5 s and the line shown is a moving average over three points

When water is present, it partitions onto the surface of the hydrophilic sucrose crystals and holds them together as aggregates via strong capillary forces [8]. The change in particle microstructures leads to the change in NPTL observed.

Addition of water also led to an increase in the sediment volume because aggregated particles pack together less efficiently (Fig. 2b, see also photograph of the sedimented particles in the electronic supplementary material). The SBD was approximately 0.25 (kg sucrose/m^3 oil) for all samples containing added water (except 16%). To test for differences between slope of SBD with sucrose concentration in the linear region (i.e., excluding 16 wt% dispersions) for dry and water-added systems, stepwise regression (for $\alpha = 0.1$) and ANOVA ($p < 0.05$) analysis were performed in Minitab 15. No significant interaction was found between two factors (i.e., sugar and water concentration), and any small difference in the slopes is statistically insignificant. Thus, the structures of agglomerated particles (i.e., determined by water concentration) were not affected by sucrose concentrations in the selected range. Moreover, changing the amount of water added while holding the sucrose concentration constant led to a progressive increase in bed height suggesting the aggregates were larger in the presence of water (Table 1).Our findings are similar to those of Johansson and Bergenstahl [8] who showed that the volume of a sucrose crystal (largest particle dimension of 30 μm) sediment in refined soybean oil increased 50% when the moisture content increased from 0 to 1%.

Sedimentation

After the dispersions had reached steady state (i.e., samples without added water) or quasi steady state (i.e., samples with added water), the mixing was stopped and the particles were allowed to sediment out under gravity. During sedimentation, changes in NPTL at a fixed cross-section

Table 1 Normalized solid bed height (NSBH) for 8 wt% sucrose in oil dispersion (i.e., 80 g sucrose, 920 g oil) as a function of amount of water added relative to the mass of sucrose

% Water	NSBH
0	0.184 ± 0.022^a
0.5	0.273 ± 0.018^b
1	0.340 ± 0.019^c

Data are shown as means ± standard deviation ($n = 6$) and values marked with different letters were significantly different from one another ($p < 0.05$)

through the sample (i.e., acoustic beam path) were measured (Fig. 4).

In the water-free samples (Fig. 4a), there was no change in NPTL for approximately 18,000 s after mixing stopped, and then the signal briefly increased followed by a decrease to a NPTL value equal to that of sucrose-free oil. Presumably, during the lag period, the sedimenting particles entering to the top of the ultrasonic beam path volume from above matched by those leaving from the bottom and the signal was unchanged. That is to say that because the rate of sedimentation at the bottom of the beam path is less than the rate of sedimentation at the top of the beam path, the increase in NPTL after the lag must be due to an accumulation of particles in the beam path. The rate of sedimentation tends to decrease as volume fraction increases [20] so the accumulation of particles near the bottom of the tank may serve to slow the movement of particles lower down more than the ones higher up. Alternatively the difference in the settling rates of differently sized particles may contribute to the change in signal seen. The final decrease in NPTL to a steady state value corresponding to sucrose-free oil is obviously due to the sedimentation of all of the sucrose particles to below the beam path.

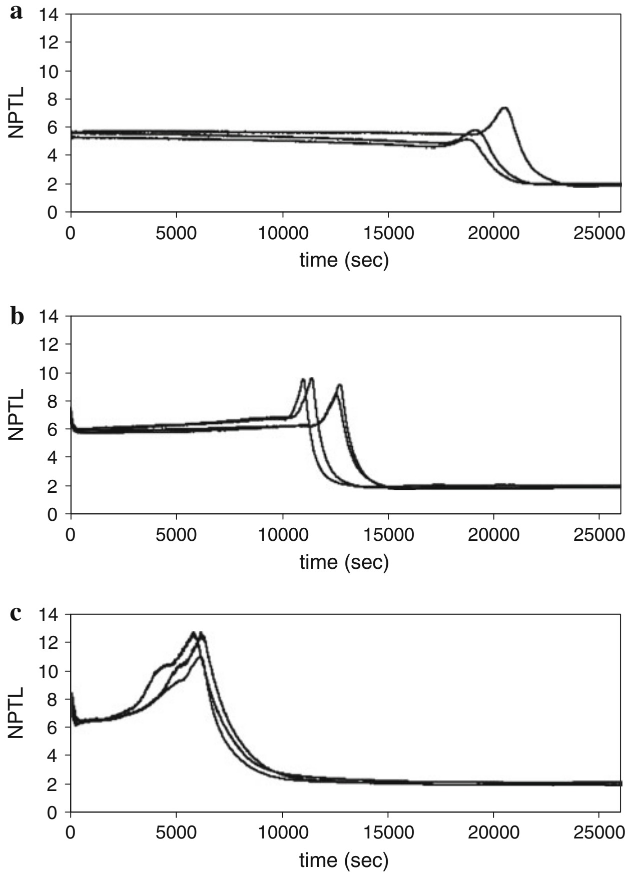

Fig. 4 NPTL change due to sedimentation of sucrose particles in corn oil (8 wt%) with different water additions of **a** 0, **b** 0.5, and **c** 1 wt%. Measurements were made every 0.5 s and the line shown is a moving average over three points. The *different lines* on each plot represent data from three or four replicate experiments

The sedimentation profiles of samples containing water (Fig. 4b, c) were similar to those of the water-free samples with two important differences. First, the time lag before changes were seen decreased with increasing water content; and second, there was an immediate drop in NPTL in the first few minutes after the mixing was stopped. Adding water led to particle aggregation (see NSBH data for these samples in Table 1) and large particles sediment more quickly. Increasing the added water content from 0 to 1% (with respect to the mass of sugar) decreases the sedimentation time (taken as the time to reach the steady state plateau) from approximately 23,000–10,000 s. Assuming the particles movement is governed by Stokes law this would correspond to a $\sqrt{2}$ increase in effective particle size on water addition assuming the agglomerates were uniform. However, the very rapid initial decrease in NPTL was probably due to the formation of a few very large aggregates which sedimented much more quickly. When the samples were analyzed with a micrometer (i.e., sensitive to the largest particles present), particles in the water-free samples were too small to be detected (i.e., <0.1 mm) while the some of the particles at the bottom of the sediment bed in the water-added samples were in the order of 1.5 mm. The fact that the water-added samples were much more heterogeneous than the water-free samples may contribute to the increased noise in the NPTL signal after adding water (Fig. 3).

Conclusions

The aim of this study was to demonstrate the application of ultrasonic attenuation measurements to monitor the (i) mixing, (ii) agglomeration in the presence of water, and (iii) quiescent sedimentation of sucrose crystals in vegetable oil. Ultrasonic attenuation increased rapidly on addition of sucrose then decayed during mixing to a steady state value proportional to the amount of sucrose added. Ultrasonic attenuation increased after sugar crystals aggregated in the presence of added water. Quiescently the sugar particles sediment from the suspension and the characteristic time for sedimentation could be measured by the ultrasonic attenuation sensor and increased with the amount of water.

These findings are the first to demonstrate the effect of dispersion concentration on ultrasonic attenuation in the sucrose oil system and the first to show that attenuation depends on the state of aggregation in this system. Together these measurements provide a good insight into the state of oil-continuous dispersions and may be practically useful in controlling chocolate conching, flavor slurry development, and other oleochemical processes. The ultrasonic sensor demonstrated here is both non-invasive and non-destructive and can measure suspension properties directly and without dilution. One potential disadvantage of ultrasonic measurements in a real system is that small air bubbles attenuate sound strongly and could overwhelm the changes due to the crystal dispersion. Care should be taken to rigorously exclude all bubbles from the measurement system.

This study is also the first use of a simple fixed-position ultrasonic sensor to characterize sedimentation kinetics. The fixed-transducer arrangement allows a simpler measurement of sedimentation behavior than existing technologies where the transducers are mounted on a moving robot arm. However caution should be taken that the position of the transducer is such that the sedimentation can be measured over a reasonable time period. Transducers placed too low in the device would quickly be covered by the sediment and give no further indication of changes while transducers mounted too high would quickly have no particles remaining in the beam path to be quantified. Analysis of the sedimentation patterns would allow calculation of the effective size of the particles present.

Acknowledgement This work was supported by a grant from the Center for Food Manufacturing (Penn State).

References

1. Beckett ST (2009) Conching. In: Beckett ST (ed) Industrial chocolate manufacture and use, 4th edn. Wiley, Chichester, pp 192–223
2. Johansson D, Bergenstahl B (1992) The influence of food emulsifiers on fat and sugar dispersions in oils. II. Rheology, colloidal forces. J Am Oil Chem Soc 69(8):718–727
3. Chevalley J (1999) Chocolate flow properties. In: Beckett ST (ed) Industrial chocolate manufacture and use, 3rd edn. Blackwell Science, Oxford, pp 182–200
4. Johansson D, Bergenstahl B (1992) The influence of food emulsifiers on fat and sugar dispersions in oils. I. Adsorption, sedimentation. J Am Oil Chem Soc 69(8):705–717
5. Beckett ST (2001) Milling, mixing and tempering–an engineering view of chocolate. Proc Inst Mech Eng 215(E):1–8
6. Johansson D, Bergenstahl B (1995) Sintering of fat crystal networks in oil during post crystallization processes. J Am Oil Chem Soc 72:911–920
7. Mongia G, Ziegler GR (2000) The role of particle size distribution of suspended solids in defining the flow properties of milk chocolate. Int J Food Prop 3(1):137–147
8. Johansson D, Bergenstahl B (1992) The influence of food emulsifiers on fat and sugar dispersions in oils. III. Water content, purity of oils. J Am Oil Chem Soc 69(8):728–733
9. Chanamai R, Coupland JN, McClements DJ (1998) Effect of temperature on the ultrasonic properties of oil-in-water emulsions. Colloids Surf A Physicochem Eng Aspects 139:241–250
10. Povey MJW (1997) Ultrasonic techniques for fluid characterization. Academic Press, San Diego
11. Bamberger JA, Greenwood MS (2004) Using ultrasonic attenuation to monitor slurry mixing in real time. Ultrasonics 42:145–148
12. Holmes AK, Challis RE, Wedlock DJ (1993) A wide bandwidth study of ultrasound velocity and attenuation in suspensions: comparison of theory with experimental measurements. J Coll Int Sci 156:261–268
13. Bryant CM, McClements DJ (1999) Ultrasonic spectrometry study of the influence of temperature on whey protein aggregation. Food Hydrocoll 13:439–444
14. Yucel U, Coupland JN (2010) Ultrasonic characterization of lactose dissolution. J Food Eng 98:28–33
15. Pinfield VJ, Dickinson E, Povey MJW (1994) Modeling of concentration profiles and ultrasonic velocity profiles in a creaming emulsion: importance of scattering effects. J Coll Int Sci 166:363–374
16. Basaran TK, Demetriades K, McClements DJ (1998) Ultrasonic imaging of gravitational separation in emulsions. Colloids Surf A Physicochem Eng Aspects 136:169–181
17. Chanamai R, Herrmann N, McClements DJ (2000) Probing floc structure by ultrasonic spectroscopy, viscometry, and creaming measurements. Langmuir 16:5884–5891
18. Labuza TP, Labuza PS (2004) Influence of temperature and relative humidity on the physical states of cotton candy. J Food Proc Preserv 28:274–287
19. Challis RE, Povey MJW, Mather ML, Holmes AK (2005) Ultrasound techniques for characterizing colloidal dispersions. Rep Prog Phys 68:1541–1637
20. Darby R (2001) Chemical engineering fluid mechanics, 2nd edn. Marcel Dekker, New York