Ultrasonic Determination of the Effect of Shear on Lipid Crystallization

Chiara Garbolino, Gregory R. Ziegler, and John N. Coupland*
Department of Food Science, The Pennsylvania State University, University Park, Pennsylvania 16802

ABSTRACT: The design and calibration of a novel rheometer incorporating ultrasonic sensors are described. The instrument is capable of the simultaneous measurements of torque, rate of temperature change, and ultrasonic properties of a liquid as a function of time, temperature, and shear rate. The effect of shear rate on the crystallization onset temperature of a sample of confectionery coating fat is studied using this device. The instrument detected the phase transition in the sheared sample as abrupt changes in all of the measured parameters. The onset temperature increased significantly with shear rate, implying lipid crystallization can be accelerated by mixing. There were also significant differences between sensing modalities.

Paper no. J9163 in *JAOCS 77*, 157–162 (February 2000).

KEY WORDS: Crystallization, shear, tempering, ultrasonics.

Food oils are a mixture of compounds (1) which show extensive mutual solubility and freezing point depression, and so melt over a range of temperatures (1). In oils as in other materials, the initial formation of a solid region in a liquid continuum is hindered by the energy cost of generating an interface, and frequently there is considerable supercooling below the thermodynamic melting point before a phase transition is observed. The situation is further complicated in many food lipids, importantly cocoa butter, which can form a number of kinetically stable crystalline forms (polymorphs).

Completely liquid oils behave as Newtonian fluids whose viscosity depends on temperature *via* the Arrhenius equation. At the onset of the range of temperatures over which crystallization occurs, the higher-melting portions begin to freeze, and the liquid oil becomes a solid-in-liquid dispersed system with needle-shaped fat crystals in a liquid continuous phase (2). Dispersed systems typically have a non-Newtonian viscosity higher than that of the continuous phase (3). As the temperature is further decreased, lower-melting fractions solidify on the surface of the primary crystals which become larger and begin to interact. Eventually the solid fraction forms a continuous network filling the container, and the sample begins to show elastic properties and behaves as a plastic solid. Further crystallization reinforces the network, and the solid becomes harder and more brittle. The strength of the solid and hence the texture of the food depend on the number and size of the crystals and their interactions, which are a function of the chemical composition and thermal history of the sample. The semicrystalline structure of fats is important for the texture, stability, and quality of a variety of food products including butter, chocolate, and ice cream.

Sophisticated food processing operations have been developed to control crystallization in food lipids, particularly in the fields of chocolate, margarine, and shortening manufacture. To produce good solid chocolate, it is necessary to crystallize it in a stable polymorphic form (4). This is achieved by a process of tempering where the melt is exposed to a controlled-temperature profile under shear, the aim being to create 1–3% of the desired crystals in an otherwise liquid continuum. When the semisolid fat is then cooled in a mold, the desirable crystals will spread throughout the bulk. The effect of time and temperature on the tempering process is well understood (5), and although the importance of shear is well appreciated (6), its precise effects are less studied. One investigation of cocoa butter crystallization showed that shearing leads to a more narrow crystal size distribution and a faster conversion of less to more stable crystal habits (6).

In order to study the effect of known shear on a fluid, it is necessary to define the geometry through which deformation occurs and ensure laminar flow. This is commonly achieved in rheometer design, but in order to study the effects of an applied shear field on a phase transition it is necessary to incorporate some other solids-sensing principle. The solids content of fat is commonly determined by nuclear magnetic resonance or differential scanning calorimetry (DSC) methods (7). However, the specific instrumental requirements of both of these methods make them difficult to incorporate into a controlled shear device. Ultrasonic measurements have been applied successfully to the determination of the solids content of bulk fats, emulsions (8), dairy products, and muscle foods (9). They are ideal for sensing operations in a process environment, as they are noninvasive, nondestructive, and can be made in opaque media or through container walls (10). An ultrasonic device can therefore be readily incorporated into a rheometer without disrupting the defined flow conditions.

Ultrasound is high-frequency (>20 kHz) mechanical waves that are transmitted as a series of deformations in a material (10,11). In a sensing application, the power of the sound and hence the magnitude of the oscillations are small and nonde-

---

*To whom correspondence should be addressed at Department of Food Science, 103 Borland Lab., The Pennsylvania State University, University Park, PA 16802. E-mail: coupland@psu.edu structive to the structures through which it passes (11). In this case we are concerned with longitudinal ultrasound where the oscillations occur in the direction of transmission of the sound. The material transmitting sound is alternately compressed and rarefied by the passing wave, and the efficiency of the transmission is a measure of the capacity of the sample to store and release the mechanical energy. Ultrasonic measurements are therefore directly related to important mechanical and thermodynamic parameters of a material with the important advantage of being relatively easy to measure.

In this paper we describe the design of a device capable of using ultrasonic measurements to measure the crystallization of fats under controlled shear conditions. We then describe some experiments on the effect of shear on the crystallization of a confectionery coating fat.

Instrument design. The instrument was conceived as a controlled-strain, coaxial cylinder rheometer. The inner (moving) cylinder (diameter 20.2 mm), controlled rate motor, and torque sensor (Sensor System SVII; Haake Buchler Instruments, Saddle Brook, NJ) were taken from a commercial instrument (RotoVisco RV12; Haake). The outer cylinder (diameter 41.2 mm) was specially designed and built for this experiment. The sample holder was constructed from thin-walled (3 mm) aluminum to ensure good heat transfer. It was fitted with a support for an ultrasonic transducer arranged so the sound it produced would travel through the outer cylinder wall into the sample, reflect from the rotating inner cylinder, and be detected by the same transducer. The outer wall of the rheometer was flattened to allow good contact with the transducer without the need for a couplant but the inner surfaces remained curved with no apparent loss of signal quality. A schematic diagram of the equipment design is shown as Figure 1A. The ultrasound was transmitted from the transducer to the sample through a Plexiglas delay line. Plexiglas was selected not for its optical clarity but rather because its acoustic properties are more closely matched to fat and hence more energy would transmit into the sample.

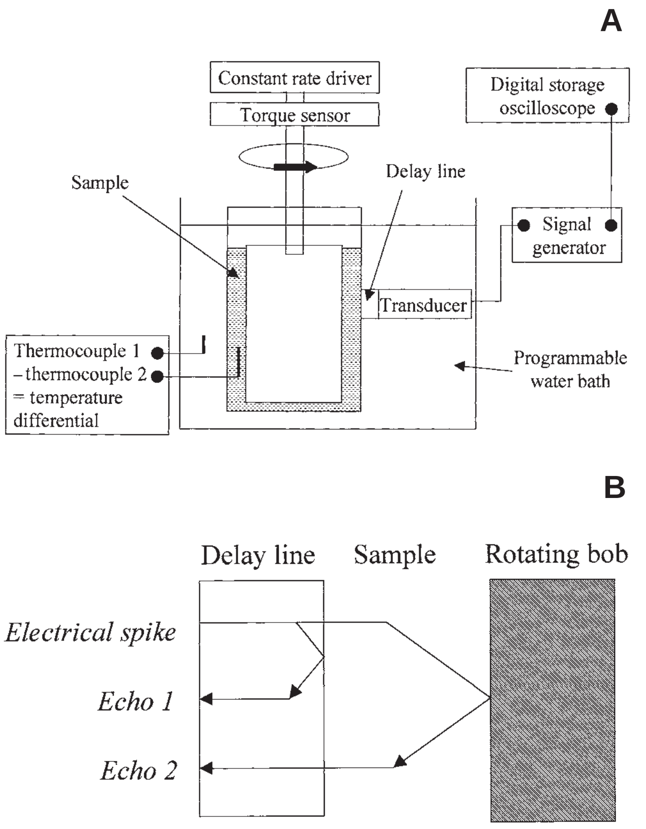

FIG. 1. (A) Schematic diagram showing the instrument design. (B) Illustration showing the acoustic path through the instrument and the source of the echoes.

The acoustic path and source of the reflections are illustrated diagrammatically in Figure 1B. An electrical spike signal (Panametrics 500 PR; Waltham, MA) is passed to a 2.25 MHz broadband ultrasonic transducer (Panametrics V323-SU), which converts the energy to ultrasound. The transducer is pressed against the Plexiglas delay line so the sound pulse travels directly into the plastic and is partially reflected at the sample interface. The reflected part returns to the transducer and is reconverted to an electrical signal (echo 1). The transmitted part travels through the sample, reflects from the rotating inner cylinder, and returns through the delay line to the transducer (echo 2). A digital storage oscilloscope (LeCroy 9310c; Chestnut Ridge, NY) was used to capture the data; the signals were averaged over 200 pulses to reduce signal noise. A typical oscilloscope trace is shown as Figure 2.

The ultrasonic part of the instrument was effectively a modified ultrasonic pulse-echo reflectometer (12). The time between the selected echoes (Fig. 2) was that required for two passes through the oil and was therefore inversely proportional to the speed of sound. In the context of this work, it was considered unnecessary to convert the echo times into velocity measurements as this would require a calibration which would introduce more uncertainty into the data without adding any new in-

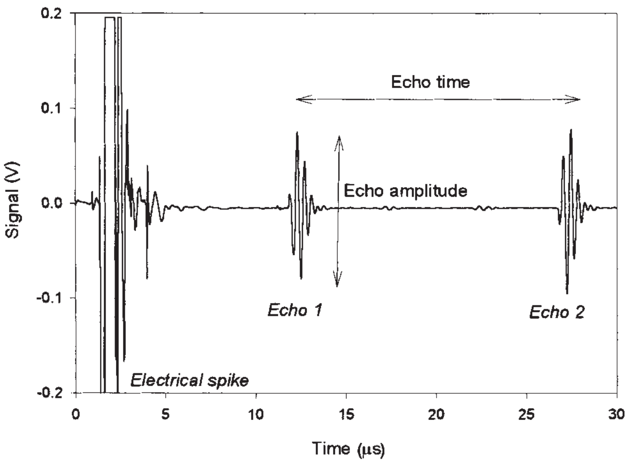

FIG. 2. Sample oscilloscope trace showing the signal features measured. Echo time is the time between the echoes returning from the outer cylinder-sample and sample-inner cylinder interfaces. Echo amplitude is the magnitude of the signal reflected from the outer cylinder-sample interface.

sights. We appreciate that ultrasonic velocity is a fundamental parameter of a material and may therefore be valuable to some workers. Ultrasonic velocity may be calculated by dividing the times reported into the distance traveled by the wave (21 mm). The magnitude of the echo from the wall-sample interface was also recorded (Fig. 2). This signal could be converted to a reflection coefficient and hence fundamental physical and acoustic data by appropriate calibration but again was considered unnecessary in this case, as we are concerned with relative changes in signal. The measured ultrasonic properties were independent of shear rate (0–512 rpm) for water.

The sample container was immersed in a computer-controlled water bath (Fig. 1A). The water bath was capable of precise temperature control (±0.01°C) and programmed ramping. The rate of controlled temperature change attainable was investigated by filling the rheometer with corn oil and cooling the bath at a programmed rate from 50 to 10°C. Corn oil was chosen for this purpose as it has similar thermal properties to the liquid confectionery coating fat to be investigated in this study, but does not show a phase transition over this temperature range. During cooling, the temperatures in the bath and in the oil were measured using thermocouples (type T, Cu-CuNi; Omega Instruments, Stamford, CT) connected to a microprocessor thermometer (HH21, Omega Instruments). A linear cooling rate of –0.5°C min^{-1} could be obtained with no difference between the measured temperatures. (As noted below, a temperature lag was measured in the event of a phase transition.)

The Haake rheometer modified in this work is fitted with a torque sensor (sensitive over the range 10^2–10^4 Pa). Preliminary measurements with a series of Newtonian calibration oils (Cannon Instrument Company, State College, PA) showed the response of the torque sensor increased linearly with rotation rate, and the slope was proportional to the stated viscosity of the calibrant (0.4–40 Pa·s) (data not reported).

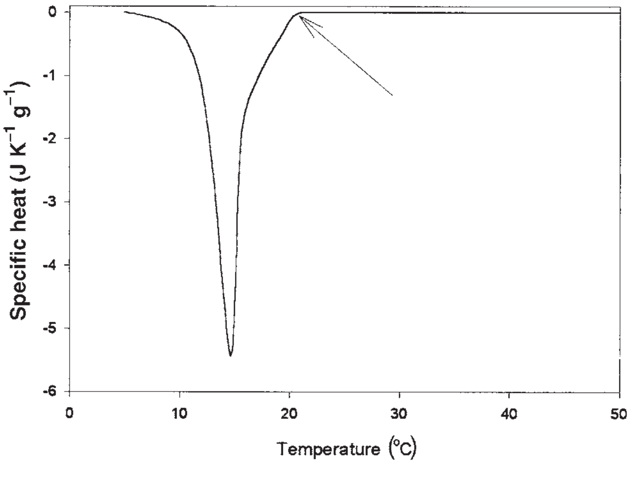

FIG. 3. Sample differential scanning calorimetry trace for confectionery coating fat cooled from 50°C at 0.5°C min^{-1}. The onset of crystallization is marked with an arrow.

MATERIALS AND METHODS

A sample of confectionery coating fat (hydrogenated and fractionated mixture of soybean and cottonseed oils) was used in the crystallization studies (CLSP870; Loders Croklaan cocoa butter substitute "high *trans*," Glen Ellyn, IL). The crystallization behavior of this fat was measured using DSC (Perkin-Elmer DSC-7, Norwalk, CT). A sample of the fat was loaded into an aluminum DSC pan, heated to 50°C, held for 30 min, and cooled at –0.5°C min^{-1} to 5°C. (The thermal pretreatment was assumed to melt out any residual solid structure in the fat.) A typical specific heat curve is shown as Figure 3. There was a single crystallization exotherm with an onset of 20.7 ± 0.5°C and a maximum of 14.9 ± 0.2°C (data are reported as the means and SD of three replicate measurements). The enthalpy of melting was 96.5 ± 4.5 J g^{-1}. Confectionery coating fat was selected for use in this work as it has similar physical and thermal properties to cocoa butter but only has a single stable polymorphic form.

The inner cylinder of the rheometer was programmed to rotate at constant rate (0–512 rpm). A sample of the molten fat was poured into the rheometer at 50°C, held for 30 min, then cooled at –0.5°C min^{-1} until crystallization had occurred and no further measurements could be made. At intervals during the cooling, the ultrasonic echo time, echo amplitude, temperature differential, and torque reading were recorded.

RESULTS AND DISCUSSION

The results of a typical crystallization experiment for the confectionery coating fat are shown as Figure 4. The torque readings (Fig. 4A) of the liquid oil are low, and any changes due to temperature are too small to be recorded by the relatively insensitive instrument used. However, at the crystallization point, the torque increased suddenly, corresponding to the formation of a solid-in-liquid fat dispersion. To express the rheological properties of an increasingly non-Newtonian fluid such as a partially crystalline fat as a single, characteristic viscosity is unjustified, and so we report the data as torque measured.

The temperature differential (Fig. 4B) between the water bath and the oil was ~0 throughout most of the experiment, but at the crystallization point lagged the water bath by several degrees because of the phase change. The temperature differential recorded is in essence a cruder version of the DSC experiments reported above. Temperature differential measurements showed more random fluctuations than the other data recorded and are believed to be the least reliable sensor used.

The echo time (Fig. 4C) in the liquid fat decreased approximately linearly with decreasing temperature at ~0.033 μs °C^{-1}. This is consistent with previously reported measurements of the temperature dependency of the speed of sound in liquid vegetable oils (13). At the crystallization point, there was a rapid decrease in echo time due to the higher speed of sound in the solid fat compared to the liquid oil (14). The speed of sound increases approximately linearly with the solids content of a solid fat/liquid oil mixture at a given temperature (14), and given suf-

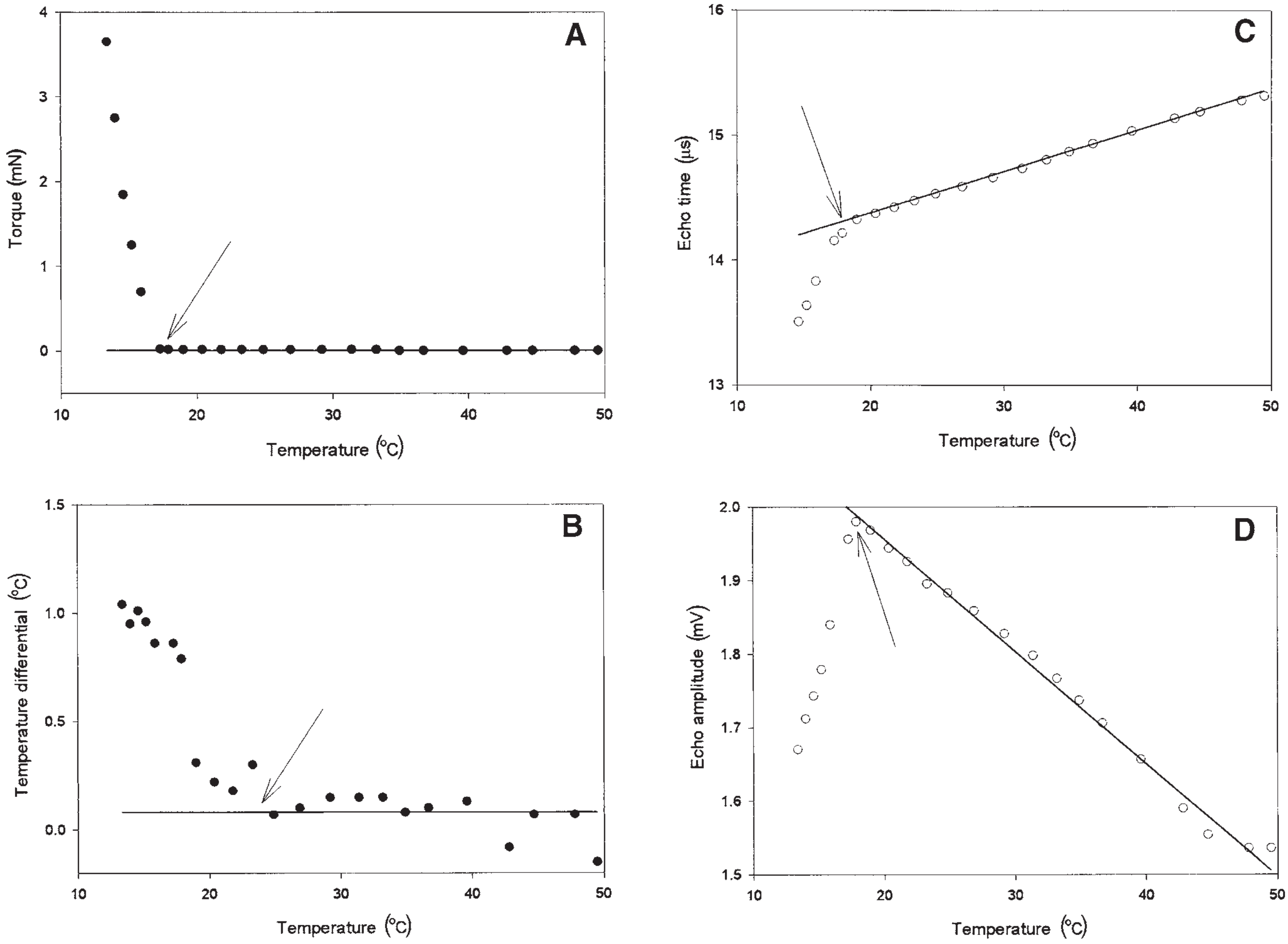

FIG. 4. Sample data for the shear crystallization of a confectionery coating fat sample cooled from 50°C at 0.5°C min^{-1} with an inner cylinder rotation rate of 64 rpm. Lines shown are linear regressions fitted to the readings made on liquid fat (25–45°C) and extrapolated, arrows mark the onset of crystallization. (A) Torque readings, (B) temperature difference, (C) echo time, and (D) echo amplitude.

ficient data on the acoustic properties of the materials, it would be possible to replot these data as solids content as a function of temperature. However the solid fat sample used was too highly attenuating to be adequately characterized by this technique and no such conversion could be made.

The echo amplitude (Fig. 4D) increased with decreasing temperature and then rapidly decreased on crystallization. The proportion of radiation reflected at an interface is an indication of the dissimilarity between the two phases. In the present work, the rapid decrease in signal on crystallization is due to the oil becoming solid and hence more similar to Plexiglas.

In all cases there was an approximately linear change in the measured parameter with temperature in the liquid oil followed by a rapid change at the onset of solidification. A linear regression was fitted to the liquid portion of the curve (25–45°C) and extrapolated across the entire temperature range. The onset of crystallization was taken as the temperature at which the measured value deviated from the regression as shown with arrows in Figure 4.

The experiment was repeated at a range of rates of rotation (0, 64, 256, and 512 rpm). The temperature dependencies of the readings were in all cases similar to those reported in Figure 4, but the temperature of the onset of crystallization varied with measurement principle and with shear rate. The measured onset temperatures are summarized in Table 1 as the means and SD from three replicate experiments. The onset of crystallization measured by DSC was assumed to correspond to the zero shear readings in the rheometer. No torque readings could be made at zero shear.

The data were compared by analysis of variance using a general linear model procedure for unbalanced samples (15); significance is reported at the 5% confidence level ($P < 0.05$). Means were compared by pre-established contrasts. There were no interactions between variation due to shear rate and measurement method so the data could be validly combined for different speeds to compare methods (and vice versa). There were significant differences between all the measurement methods at each speed. Comparing different shear rates for the echo amplitude, the temperature differential and torque measurements, 0 and 512 rpm, 64 and 256 rpm, and 64 and 512 rpm were signif-

TABLE 1
Effect of Shear Rate and Measurement Method on the Crystallization Onset Temperature (°C) of a Confectionery Coating Fat Sample^{a}

	Rotation rate /rpm				
	$n = 0$	$n = 64$	$n = 256$	$n = 512$	$\bar{x}$
DSC	20.7 ± 0.5	ND^{b}	ND^{b}	ND^{b}	20.7^{a}
Echo time	20.1 ± 0.2	19.0 ± 0.1	22.1 ± 0.4	22.7 ± 0.8	21.0^{b}
Echo amplitude	18.6 ± 0.8	18.5 ± 0.7	21.8 ± 0.8	21.3 ± 0.1	20.1^{c}
Temperature difference	19.3 ± 3.6	19.5 ± 0.6	24.2 ± 1.2	23.5 ± 0.2	21.6^{d}
Torque	ND*	17.7 ± 0.6	21.5 ± 0.4	22.3 ± 0.3	20.5^{e}
$\bar{y}$	19.7^{a}	18.7^{a}	22.4^{b}	22.5^{b}	

[a] Data are shown as mean ± SD ($n = 3$). As there is no interaction between shear rates and measurement method, column and row mean temperatures are presented. Means data which are not significantly different ($P < 0.05$) to others in the row (column) are shown with similar roman superscripts.
[b] Not determinable; DSC, differential scanning calorimetry.

icantly different. The echo time measurements showed 0 and 64 rpm were statistically different both from each other and all other speeds. In summary, comparing the rotation rates within every method, faster rotation produced a higher crystallization temperature.

The onset of crystallization in confectionery coating fat increases with shear consistent with the observations of Windhab and Zeng on cocoa butter (6). While a full explanation of this observation is unjustified based on these limited data, we can provide the following hypothesis. Fat crystallization occurs in two stages—nucleation and growth (4). The crystal nuclei probably form in a heterogeneous manner around existing imperfections (dust particles or other suspended insoluble solids or imperfections in the container walls); more solid material is then deposited on the primary nucleation sites. It seems unlikely that primary nucleation is affected by shear, but the growth of the crystals and their interactions are likely to be faster in a stirred vessel where interparticle collisions occur more frequently. [An analogy to this may be the observation by Dickinson and Williams (16) that the rate of emulsion droplet coalescence increases with stirring rate.]

The variation observed between the analytical methods is to be expected as the techniques are sensitive to different physical changes associated with the same liquid–solid transition. The echo time is, in effect, an average across the whole sample, echo amplitude is more sensitive to the properties of the fat at the surface from which it reflects, and torque only detects changes in bulk properties as they interact with the moving cylinder. (Temperature differential is neglected in this discussion because of the large amount of noise in the signal.)

Conventionally, crystallization would be expected to initiate at the coolest part of the sample, the outer cylinder wall. The primary crystals would then grow into the bulk as a result of diffusionally or orthokinetically limited accumulation at the crystal surface. Echo amplitude (largely a surface property) would therefore be expected to detect the phase transition first. In fact, crystallization was detected first by the echo time followed by torque then echo amplitude—the reverse of the sequence suggested above. It seems more probable, particularly in the light of the shear rate observations, that despite the inevitable temperature gradient, crystallization is initiated at the highest shear rate part of the sample, the moving inner cylinder, and the solids move out from there. (This is supported by the observation that when the apparatus was disassembled at the end of an experiment the fat was removed as a plug attached to the inner cylinder, the density increase of crystallization having pulled it away from the outer wall.) In conclusion, shearing catalyzes crystallization in fats and possibly many other processes, and the instrument described here is a unique tool to study this phenomenon.

This configuration of acoustic sensors has many applications in fats and oils processing and beyond. Conventional ultrasonic through-transmission or pulse-echo techniques place some geometrical constraints on the sample size and shape whereas the reflectance method can be applied on any container. In chocolate manufacture, acoustic reflectance could noninvasively measure the degree of temper in a closed machine or (indirectly) the viscosity of melt flowing through an enrober. As a bench-top instrument, the rheometer could be used to calculate the shear-rate dependency of many physical and chemical transformations, provided the ultrasonic properties of the reagents and product were sufficiently different.

ACKNOWLEDGMENTS

The authors are grateful to the Center for Food Manufacturing for support of this work, to Ken Henderson of the Cannon Instrument Company for donation of the calibration oils and many helpful discussions, and to Maria Labreveux for assistance with the statistical analysis of data.

REFERENCES

1. Nawar, W.W., Lipids, in *Food Chemistry*, 3rd edn., edited by O. Fennema, Marcel Dekker Inc., New York, 1979, pp. 225–319.
2. Johansson, D., Colloids in Fats, Ph.D. Thesis, Department of Food Science, University of Lund, Lund, Sweden, 1994.
3. Dickinson, E., *An Introduction to Food Colloids*, Oxford University Press, Oxford, 1992.
4. Lawler, P.J., and P.S. Dimick, Crystallization and Polymor-

phism of Fats, in *Food Lipids: Chemistry, Nutrition, and Biotechnology*, edited by C.C. Akoh and D.B. Min, Marcel Dekker, Inc., New York, 1998, pp. 229–250.
5. Malssen, K.F., A.J. Langervelde, and H. Shkenk, Cocoa Butter Crystallization—New Details of the Static Phase Transition Scheme, in *ZDT Chocolate Technology '98*, Koln, Germany, 1998.
6. Windhab, E.J., and Y. Zeng. High Shear and Seed Crystallization of Chocolates, in *Ibid*.
7. Pare, J.R.J., and J.M.R. Belanger (eds.), Instrumental Methods in Food Analysis, in *Techniques and Instrumentation in Analytical Chemistry*, Vol. 18, Elsevier, New York, 1997.
8. McClements, D.J., and M.J.W. Povey, Comparison of Pulsed NMR and Ultrasonic Velocity Measurements for Determining Solid Fat Contents, *Int. J. Food Sci. Tech. 23*:159–170 (1988).
9. Miles, C.A., G.A.J. Fursey, and R.C.D. Jones, Ultrasonic Estimation of Solid/Liquid Ratios in Fats, Oils, and Adipose Tissue, *J. Sci. Food Agric. 36*:218–228 (1985).
10. McClements, D.J., Ultrasonic Characterization of Foods and Drinks: Principles, Methods, and Application, *Crit. Rev. Food Sci. Nutr. 37*:1–46 (1997).
11. Coupland, J.N., and D.J. McClements, Ultrasonics, in *Non-Destructive Evaluation of Food Materials*, edited by S. Gunasekaran, Marcel Dekker, New York, in press 2000.
12. McClements, D.J., and P. Fairley, Ultrasonic Pulse Echo Reflectometer, *Ultrasonics 29*:58–62 (1991).
13. McClements, D.J., and M.J.W. Povey, Ultrasonic Velocity Measurements in Some Liquid Triglycerides and Vegetable Oils, *J. Am. Oil Chem. Soc. 65*:1791–1796 (1998).
14. McClements, D.J., and M.J.W. Povey, Solid Fat Content Determination Using Ultrasonic Velocity Measurements, *Int. J. Food Sci. Technol. 22*:419–428 (1987).
15. Anonymous, *SAS/STAT User's Guide, Version 6*, SAS Institute, Cary, NC, 1990.
16. Dickinson, E., and A. Williams, Orthokinetic Coalescence of Protein-Stabilized Emulsions, *Colloids Surf. A 88*:317–326 (1994).

[Received March 5, 1999; accepted October 28, 1999]