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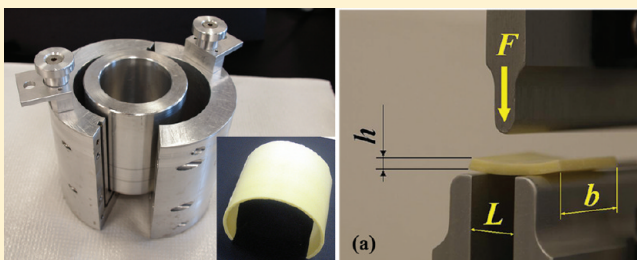
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# Thermal and Mechanical Properties of Cocoa Butter Crystallized under an External Laminar Shear Field

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**ABSTRACT:** In this work, the effects of laminar shear on nanoscale structure and physical properties of triglyceride crystal networks were quantified. Cocoa butter (CB) was crystallized in the presence and absence of an external shear field. Samples were crystallized under a shear rate of approximately  $340 \text{ s}^{-1}$  in two different ways, by using a continuous Couette-type laminar shear crystallizer and by using a standard paddle mixer. Using different analytical methods and physical models, the mechanical strength and thermal properties of the crystallized CB were characterized. Cocoa butter crystallized under an external shear field had a stronger network with higher breaking force, Young's, and storage modulus than statically crystallized samples. The sheared samples also had a smaller crystallite size (300 nm length, 130 nm width). Here we also show that the arrangement of the crystalline component influences the material's strength. The Young's modulus was increased by about 30% in samples that exhibited crystalline alignment. Moreover, higher average peak melting temperature ( $\sim 0.8^\circ\text{C}$ ) and full width at half maximum of the thermogram curves, fwhm, ( $\sim 0.9^\circ\text{C}$ ) were observed for the statically crystallized samples. In the presence of crystalline alignment, the melting point of cocoa butter was decreased slightly, about  $0.5^\circ\text{C}$ . This work demonstrates the substantial effects of laminar shear applied during crystallization of cocoa butter on its functional properties including melting, hardness, and rigidity.



## INTRODUCTION

Most of the functional and sensory attributes of fat-structured food products depend on the thermal and mechanical properties of their fat crystal networks. Factors at the nano- and microstructural levels influence the macroscopic rheological properties of the fat, including hardness and texture.<sup>1–6</sup> Studies have demonstrated the relationship between different structural levels of a fat crystal network and its physical properties.<sup>7–14</sup> These levels of structure are defined during the formation of the network and include the polymorphism of the solid state, the size of the individual nanocrystalline units formed, the size and morphology of clusters of these unit nanocrystals, the strength of intercrystalline forces in the network, the spatial distribution of network mass, and obviously the total amount of solid material present.<sup>5,6,15–18</sup>

A significant amount of research has shown that crystal habit (polymorphism, crystal size, and shape) of fat crystals and ultimately their functionality is greatly affected by heat, mass, and momentum transfer conditions established during the crystallization process.<sup>17,19–23</sup> Therefore, by modifying processing conditions (i.e., crystallization temperature, cooling rate, and agitation rate), the crystal habit and the subsequent properties of the crystal network can be tailored. Several research groups have investigated the effects of agitation and cooling rate on crystallization kinetics, crystal structure, and consistency of fat systems.<sup>24–27</sup> Bolliger et al. (1999)<sup>11</sup> proposed that the variations in the physical properties of CB crystallized under different shear rates are related to shape/size influence of the crystals

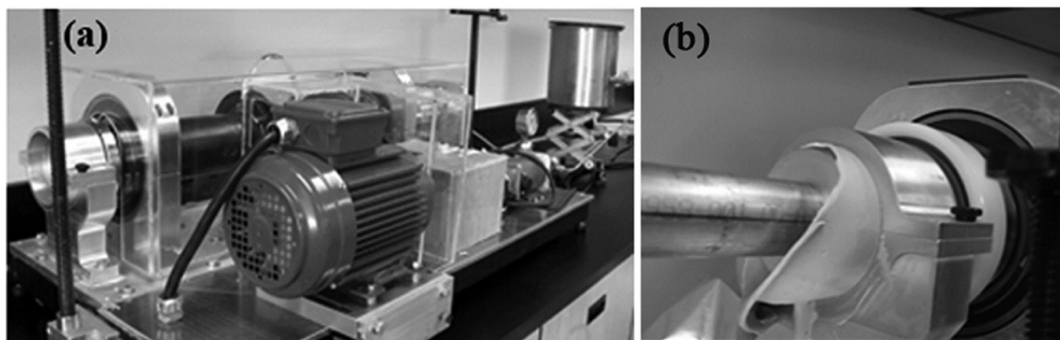
rather than the type of modification. Padar et al. (2009)<sup>28</sup> observed fraction formation and compositional changes during growth of cocoa butter crystallites crystallized under shear. They suggested that the variation in the melting profile in sheared CB is related to the accumulation of higher melting TAGs when an external field is applied. Campos et al. (2010)<sup>14</sup> found that blending cocoa butter with tristearin affects its domain size and consequently the bending elastic modulus. However, detailed information on crystal size and geometry under shear was not reported in these studies. Some other studies have shown the effect of fat microstructure on its melting profile and reported different melting temperatures for different particle sizes.<sup>11,29</sup> Guthrie (2008) reported a lower melting temperature for cocoa butter crystallized under shear and suggested that the lower melting point at high shear rates was caused by crystallization of either a different polymorph or of lower melting temperature TAGs solidifying into the  $\beta_V$  structure.<sup>30</sup> While most of these studies have concentrated mainly on the microstructural properties of the materials, the influence of nanoscale characteristics on the physical properties of a polycrystalline network have been yet to be fully investigated.

It is the purpose of this work to determine the effects of laminar shear crystallization and nanoparticle's properties such as

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**Figure 1.** (a) The continuous laminar shear crystallizer; (b) a cocoa butter sheet was obtained continuously upon crystallization in the laminar shear crystallizer.

domain structure, crystal size, and crystalline alignment within the network on the physical properties of cocoa butter, the structuring material in chocolate and confections. The rheological properties of crystallized cocoa butter were characterized using small and large deformation rheology and ultrasonic techniques. The fracture force of cocoa butter, as well as the Young's and storage moduli, were used to assess material functionality such as hardness and network strength. Particular emphasis is placed on finding a correlation between material physical properties and nanoscale structure in the network.

## MATERIALS AND METHODS

**A. Materials.** Cocoa butter was used as the lipid of choice for the study of laminar shear on the crystallization of triglyceride molecules. The cocoa butter used in this study was donated by Mars Chocolate North America (New Jersey, USA). The cocoa butter was heated in an oven at 70 °C to ensure complete melting. The fat was held at this temperature for at least 30 min before use to ensure destruction of the crystal memory.

**B. Sample Preparation.** *Crystallization Procedure Used To Induce Crystalline Orientation.* The molten sample was pumped through a continuous laminar shear crystallizer in the Couette-type configuration (two concentric cylinders, an inner bob with an outer rotating cup) (Figure 1)<sup>31</sup> at a flow rate of 30 mL/min. A shear rate of approximately 340 s<sup>-1</sup> was applied and the cocoa butter was crystallized from the melt (60 °C) to 20 °C for 13 min. Cooling was achieved by three water jackets connected to a cooling water bath. The resulting solid sheet of CB was stored for 7 days in an incubator set at 20 °C. This sample will be referred to as the "oriented sample" (OR) throughout the rest of this study.

*Crystallization Procedure for Sheared and Statically Crystallized Samples.* Sheared and non-sheared (statically crystallized) samples with the same dimensions and shape as the oriented sample were crystallized in a different shear cell (Figure 2). This shear cell was in the Searle configuration (the inner bob rotates while the outer cup remains stationary). The shear cell consisted of two concentric aluminum cylinders with a 2.5 mm gap in between. The outer cylinder was designed such that it could be disassembled readily to aid in the extraction of the sample. To this end, the outer cylinder was halved lengthwise. A groove, to allow the fitting of an O-ring, was cut into the contact points between the two halves. The O-ring provided a tight seal between the two halves, preventing the leakage of sample. A groove was also cut into the bottom of the cup. A matching groove was also machined on the bottom of the bob. This groove allowed a bearing to be installed. This bearing would affect the rotation of the bob. The bob was connected to a variable-speed motor. The applied shear rate was



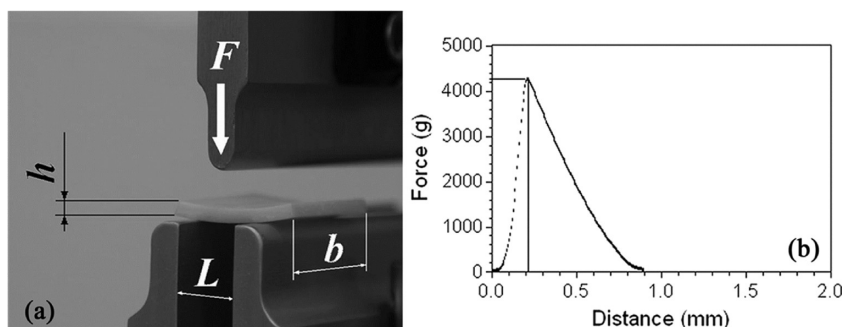
**Figure 2.** The disassembled Shear cell used for the preparation of the static and sheared samples, with a piece of crystallized sample obtained from the shear cell.

controlled by varying the angular velocity of the bob. A cooling jacket was also included in the design so that the sample may be cooled using an appropriate cooling regime.

The sheared specimen (SH) was created by isothermally crystallizing molten cocoa butter (in a flask) inside a temperature-controlled water bath (Neslab RTE-111, Fisher Scientific, St. Louis, MO) from 60 to 20 °C at a rate of 3 °C/min. The crystallization process was carried out for 30 min. During cooling, a Lightnin mixer (Lightnin Labmaster LIU10F, Wytheville, VA, USA) was used to agitate the melt at a shear rate of approximately 340 s<sup>-1</sup>. The partially crystallized cocoa butter was then transferred into the above-described shear cell kept at 20 °C to allow the material to set.

The statically crystallized sample (ST) was made by transferring the molten cocoa butter into the heated (60 °C) shear cell. By adjusting the temperature of the water bath attached to the shear cell, the cocoa butter was cooled to 20 °C at a rate of 3 °C/min. The shear cell was then transferred to an incubator set at 20 °C to complete the crystallization process. The sheared and statically crystallized samples were stored for 7 days in an incubator set to 20 °C before further study.

**C. Powder X-ray Diffraction.** The polymorphism of the crystallized samples was determined through powder X-ray diffraction (XRD) techniques using a Rigaku Multiplex Powder X-ray diffractometer (Rigaku, Tokyo, Japan). The apparatus had a 1/2° divergence slit, a 1/2° scatter slit, and a 0.3 mm receiving slit. The accelerating voltage and current of the X-ray copper tube was set at 40 kV and 44 mA, respectively. Approximately 1 g of the crystallized sample was placed onto a prechilled glass X-ray slide. The glass slide was chilled by holding it in an incubator set to the crystallization temperature (20 °C).



**Figure 3.** (a) The three-point bending stage with the dimensions used in eq 1. (b) A plot of force as a function of displacement obtained from the three-point bending test.

The filled slide was placed on the X-ray sample holder, which was also set to 20 °C. Scans were performed from 0 to 30 deg at a scanning rate of 2°/min. The results were analyzed using MDI's Jade 9 powder X-ray analysis software package (Materials Data Incorporated, Livermore, California). Two determinations of three replicates were performed.

**D. Solid Fat Content Measurements.** Solid fat content (SFC) was measured by means of pulsed nuclear magnetic resonance (p-NMR) using a Bruker Minispec spectrometer, (Bruker Optics Ltd., Milton, ON, Canada). Glass NMR tubes (10 mm diameter, 1 mm thickness, and 180 mm height) were filled with approximately 3 g of the crystallized samples (samples were cut in small pieces and placed in the tube). Crystallized samples were kept at the crystallization temperature, 20 °C, for 7 days to monitor the SFC variation during storage. Two determinations of three replicates were performed.

**E. Differential Scanning Calorimetry (DSC).** The thermal behavior of the crystallized samples was monitored (every 7 days for the first month and after 120 days) using a Dupont 2910 differential scanning calorimeter (TA Instruments, Mississauga, ON, Canada). After the crystallized cocoa butter samples were created, small pieces of each sample were cut and placed in prechilled aluminum DSC pans. The size of the pieces was judged so that they just fill the bottom of the DSC pan; a sample weight of approximately 10 mg was weighed using Electronic analytical balance (Sartorius GMBH, model 1702, Gottingen, Germany). The pans were sealed with an encapsulation press (TA Instruments, Mississauga, ON, Canada) and were transferred into the DSC cell, present at the sample temperature. The cell was allowed to stabilize for 5 min at this temperature before the sample was heated to 50 °C at a rate of 1 °C/min. The peak melting temperatures were obtained from the thermograms using TA Instruments Universal Analysis 2000 (TA Instruments, Mississauga, ON, Canada). The apex of the melting profile was considered to be the melting point of the sample. A horizontally set baseline was chosen to calculate the specific melting enthalpy. The full width at half-maximum of the peaks (fwhm) was determined by PeakFitv4.12 software (SeaSolve software Inc., Framingham, MA, USA). Samples were run in triplicate.

**F. Mechanical Properties Testing.** *Small Deformation Rheology (Shear Storage Modulus Measurements).* A TA Instruments AR2000 controlled stress dynamic rheometer was used to perform the rheological measurements. The linear viscoelastic range (LVR) was determined using oscillatory stress sweep tests at a frequency of 1 Hz, within the range of 5–104 Pa stress and a maximum applied normal force of 5 N. The experiments were carried out using an 8-mm stainless steel parallel plate (standard steel parallel plate-S/N511080). To prevent slippage, sandpaper (grade 100) was glued to the lower surface of the geometry and the upper surface of the peltier base of the rheometer with crazy glue. The peltier plate base was set at 20 °C to maintain the desired experimental temperature.

*Large Deformation Rheology.* Crystallized samples were cut into equal size pieces (~20 mm length and ~8 mm width) and were placed on a three-point bending geometry. A Stable Micro Systems material tester (model SMS TA XT Plus, Texture analyzer), with a 5 kg load cell was used to measure the breaking points of the samples. As illustrated in Figure 3, once the trigger force was attained, the applied force was increased until the sample fractured into two pieces. This was recorded as the maximum force and referred to as the "hardness" of the sample. The distance to the breaking point was the resistance of the sample to bending and was related to the "fracturability" of the sample.

The force ( $F$ ) necessary to break the crystallized cocoa butter at a speed of 3 mm/s, as well as the deformation of the sample pieces to the point of fracture ( $d$ ), was calculated with Texture Exponent software (Stable Micro Systems Ltd., Godalming, Surrey, UK). The force-displacement graph was fit and its slope (usually referred to as the bending stiffness coefficient) was used to extract the Young's modulus ( $E$ ) of the sample using the following equation:<sup>7,32</sup>

$$E = \text{slope} \times \frac{L^3}{4bh^3} \quad (1)$$

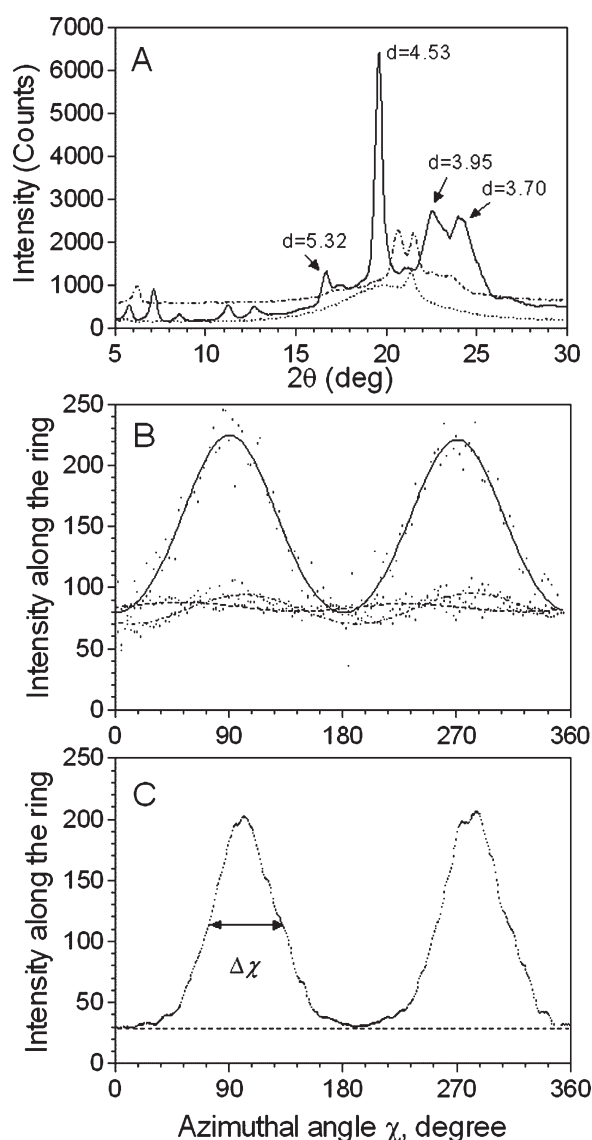
where  $L$  is the separation between the two supporting points,  $b$  and  $h$  are the sample length and thickness, respectively (Figure 3a).

## EXPERIMENTAL RESULTS

Triglycerides are known to crystallize in a number of different polymorphic forms, depending on their chemical compositions and processing conditions;<sup>33–38</sup> therefore, X-ray diffraction (XRD) patterns were used to characterize the phase behavior of all the samples in this study. Figure 4A shows a typical two-dimensional (2-D) XRD pattern with the corresponding diffraction plots in both small angle (SAXS) and wide angle (WAXS) regions. In the statically crystallized sample after 15 min of crystallization, the XRD profile displays one small diffraction peak in the WAXS region at 21.4° 2 $\theta$  (4.15 Å), characteristic of form II, or  $\alpha$  polymorph. After 1 h of crystallization, this peak faded away and two new peaks appeared at 20.6° 2 $\theta$  (4.3 Å) and 21.5° 2 $\theta$  (4.1 Å), characteristic of form IV ( $\beta'$ 1). This modification of diffraction patterns indicates that the polymorphic structure of the statically crystallized sample was in the process of transforming from form II to IV during the experiment. In this sample, the sharp peak of form V was not observed until 48 h, which is evidence of the slow transformation of cocoa butter to form V under static conditions.

However, the rapid transformation of the less stable form to the most stable form,  $\beta_v$ , was observed in this time frame when cocoa butter was crystallized under shear. In shear-crystallized samples only after 15 min, two new diffraction peaks appeared in the SAXS region at 1.5° 2 $\theta$  (61 Å)





**Figure 4.** (A) 4X-ray diffraction patterns in small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) of CB after 15 min crystallization under the static (···) and dynamic conditions (—), and after 55 min statically crystallization (---). (B) Azimuthal plot from XRD pattern of cocoa butter  $\beta$  phase obtained from the static (----), sheared (···), and oriented (—) samples. (C) Azimuthal plot showing the orientation fraction of cocoa butter above the dotted line, and  $\Delta\chi$  is the azimuthal width of the oriented portion.

and  $2.7^\circ 2\theta$  ( $33.05 \text{ \AA}$ ), and one very sharp peak emerged in the WAXS region at  $19.9^\circ 2\theta$  ( $4.53 \text{ \AA}$ ) accompanied by at least two smaller peaks on the larger  $2\theta$  side, one at  $22.5^\circ 2\theta$  ( $3.95 \text{ \AA}$ ) and the other at  $24.1^\circ 2\theta$  ( $3.70 \text{ \AA}$ ), corresponding to the stable form,  $\beta_V$ .

Detailed inspection of the effects of laminar shear on crystalline orientation during the crystallization of cocoa butter has already been reported by Maleky and Marangoni (2008),<sup>31</sup> and the presence of crystalline orientation in the sample crystallized in a continuous laminar shear crystallizer was documented there. In this study, the extent of alignment of the crystalline material was investigated using small-angle X-ray diffraction to obtain the characteristic small angle 002 diffraction ring of the  $\beta$  polymorph. To evaluate crystalline orientation, azimuthal plots from the 2D diffraction patterns were obtained by plotting the intensity around the diffraction rings, as shown in Figure 4B.

**Table 1.** Degree of Orientation ( $\Delta\chi$ ) and the Orientation Ratio  $X_r$  of the Crystallized Cocoa Butter Samples

sample (CB)	static (ST)	sheared (SH)	oriented (OR)
degree of orientation ( $\Delta\chi$ )	ND <sup>a</sup>	157.45	85.69
orientation ratio ( $\chi_r$ , %)	ND	23.42	64.72

<sup>a</sup> ND = not determined.

The azimuthal profile of the oriented sample shows peaks that are separated by  $180^\circ$  and reflect a greater proportion of crystallographically oriented material compared to the sheared and the statically crystallized samples. In order to estimate the degree of orientation in the samples, the full width at half-maximum ( $\Delta\chi$ ) of the azimuthal plot was obtained by fitting a Gaussian distribution to the peaks obtained. As well, the proportion of oriented/nonoriented materials in each crystallized sample ( $X$ ) was determined by comparing the ratio of the area above the dotted line over the total area under the plot (Figure 4C).<sup>31</sup> The calculated values of degree of orientation ( $\Delta\chi$ ) and proportion of oriented material ( $X_r$ ) are reported in Table 1. The oriented sample displayed a large orientation ratio and small azimuthal width corresponding to a high degree of orientation in this sample. The actual full width at half-maximum value of the statically crystallized sample could not be calculated because the noise in the azimuthal plots did not allow the determination of a meaningful value of the azimuthal width.

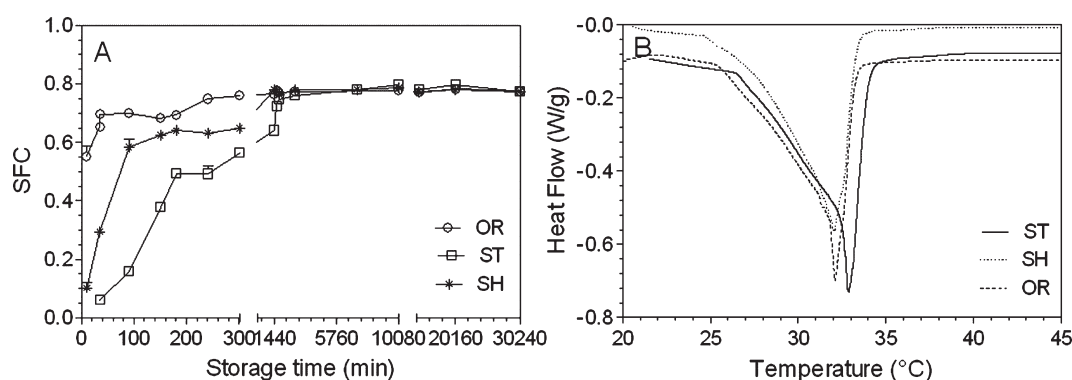
Because of the major effect of the volume fraction of crystalline solids in fats on rheological properties the amounts of solid fat in the crystallized samples were measured and monitored during the experimental period. It is evident that under dynamic crystallization conditions, the laminar shear applied to the samples accelerates the crystallization process relative to static condition. Statistical analysis confirmed that all samples had a similar solid fat content, 78%, after one day storage as shown in Figure 5A.

## ■ THERMAL PROPERTIES

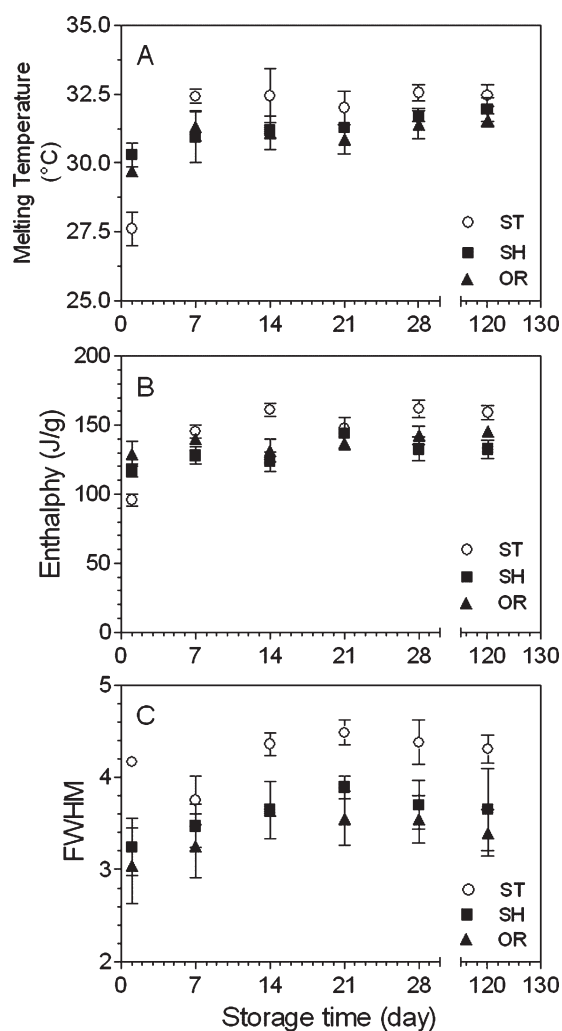
The thermal behavior of the cocoa butter samples during a postcrystallization storage period was monitored to determine if crystallization of cocoa butter under laminar shear had an effect on melting behavior. A typical DSC melting profile (heat flow versus temperature) of a sample stored for 28 days after crystallization is shown in Figure 5B.

The melting temperature, enthalpy of melting, and the full width at half-maximum of the melting peaks as a function of storage time are shown in Figure 6A–C. Values in these figures are the means values  $\pm$  standard deviations of three experiments with multiple measurements each.

Figure 6A shows that after one day of crystallization, statically crystallized cocoa butter samples had an average peak melting temperature of  $27.6^\circ\text{C}$  (which corresponds to the  $\beta'$  form).<sup>17,21</sup> At the same time, sheared-crystallized samples displayed a higher melting point, an average of  $30.3$  and  $29.7^\circ\text{C}$  for the sheared and oriented samples, respectively (corresponding to the stable  $\beta_V$  form). This can be attributed to the shear induced acceleration of the polymorphic transformation of cocoa butter crystals to their more stable beta form. This figure also illustrates an increase in the melting temperature of the statically crystallized sample after 7 days of storage. This gradual increase could be interpreted as a consequence of transition from  $\beta'$  crystallites to the stable  $\beta$  form over time, in agreement with the powder XRD analysis. A closer look at Figure 6A reveals that after the first week of crystallization, the melting point of the statically crystallized sample exceed those of shear-crystallized samples. This figure also shows that



**Figure 5.** (A) Crystallization curves of the samples during the period of study. (B) A typical graph of the DSC melting profile of the samples after 28 days of crystallization, static (ST), sheared (SH), oriented (OR).



**Figure 6.** Melting temperature (A), enthalpy of melting (B), and the full width at half-maximum (fwhm) of the DSC peaks (C), of the crystallized samples, static (ST), sheared (SH), oriented (OR) as a function of time. Symbols represent the average  $\pm$  standard error of replications.

the melting point of the oriented sample was slightly ( $0.5^{\circ}\text{C}$ ) lower than that of the sheared sample.

Similar trends were found in the plots of enthalpy of melting over time. At the end of day 1, the melting enthalpy for the

statically crystallized sample was smaller than those of the sheared and oriented samples. At the end of the first week, the melting enthalpies of the three samples were comparable, and after the second week, a higher average enthalpy of melting was observed for the statically crystallized sample, as shown in Figure 6B.

To further investigate the relationship between the structural factors and the thermal properties of the samples, the widths of the DSC curves were compared, and we noticed that the peaks of the shear-crystallized samples were sharper than the statically crystallized ones. This has been quantitatively compared by plotting the full width at half-maximum (fwhm) of the DSC curves versus storage time, as presented in Figure 6C. Higher values of fwhm are observed in the statically crystallized sample where the oriented sample shows the lowest fwhm among the samples.

## MECHANICAL PROPERTIES

To quantify the effects of laminar shear on the mechanical strength of cocoa butter, the shear storage modulus of the samples was measured using small deformation rheology. The trends for changes in the storage modulus for all samples as a function of storage time are shown in Figure 7A.

As expected, a clear trend was found: a higher elastic modulus was observed for the samples crystallized under dynamic conditions compared to the statically crystallized one. These results might suggest that cocoa butter in the  $\beta'$  form has a lower  $G'$  than cocoa butter in the  $\beta$  form, thus attributing the mechanical strength of the material to the structure of the solid state, or polymorphism. The storage modulus of the statically crystallized sample increases gradually from day 1 and a plateau region is established at day 14. The observed increase in the static sample's  $G'$  during the first 2 weeks cannot be attributed to the solid fat content variation as SFC remained constant after day 1.

Previously, Brunello et al. (2003)<sup>12</sup> reported the presence of large crystallite of cocoa butter at  $20^{\circ}\text{C}$  under static conditions and growth of the crystal cluster over time. These microstructural changes, induced by changes in polymorphism, can be responsible for the changes in mechanical properties of the static sample. This figure also shows a slight difference, about  $\sim 10\%$ , between the shear modulus of the sheared and oriented samples.

The effects of shear crystallization on the samples' hardness were investigated by performing a three-point bending test. The force required to break the samples (the fracture force) was recorded and plotted against time, results shown in Figure 7B.

Similar to the storage modulus results, we see a clear increase in breaking stress of the shear-crystallized samples relative to the statically crystallized samples. For the statically crystallized sample, the breaking force increases in time until a plateau region is reached. Comparing the dynamic and statically crystallized samples, the latter shows a lower hardness during the experimental period. The observed breaking force is relatively comparable for the sheared and oriented samples.

As outlined in the Materials and Methods section, the Young's modulus of the samples was determined from the slope of the breaking curve using eq 1 and is presented in Figure 7C. One can see that shear crystallization of the samples affected their elastic moduli, where after 28 days of storage, the oriented

sample exhibited the highest Young's modulus and sheared and statically crystallized samples had 15% and 50% smaller moduli, respectively.

## DISCUSSION

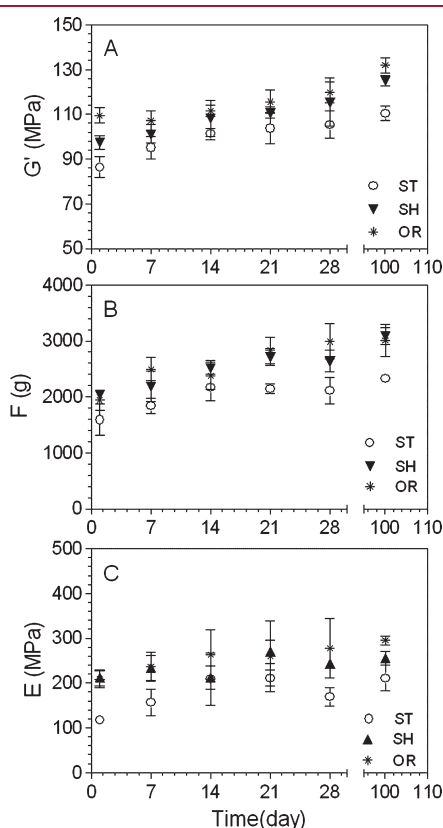
The presence or absence of shear, as well as the type of shear, during crystallization strongly affected final materials properties in cocoa butter. This difference could not be explained using solid fat content or polymorphism arguments — all samples had similar SFCs and polymorphic forms. Therefore, the differences observed in mechanical and thermal properties could be due to crystal size, intercrystalline forces and/or the spatial distribution of solid mass in the networks. As previously mentioned, several studies have related the physical properties variation of CB to its particle size and shape.<sup>11,18,39–41</sup> Thus, a detailed structural analysis of the cocoa butter samples may explain the relationship between their functionality behavior and crystalline size and morphology.

Previous studies have shown the influence of processing conditions on the microstructure of a fat crystal network,<sup>26,27,42,43</sup> and we have recently documented the effect of laminar shear on the crystal size and morphology of cocoa butter.<sup>41,44</sup> We have investigated the nanostructure of statically and shear-crystallized cocoa butter and shown that the samples studied in this work are anisotropic in terms of their micro/nanostructure. Shear induced a reduction in the nanoparticles dimensions where smaller nanoplatelets are observed in the sheared and oriented samples compared to the statically crystallized samples (Figure 8), in agreement with previously published effects on tristearin.<sup>45</sup> The length was reduced from an average of 2000 nm in the statically crystallized sample to 300 nm in sheared/oriented samples, while the width was reduced from 165 nm to 130 nm. This finding may explain the differences in the hardness and stiffness observed between the static and shear-crystallized samples where particle size is one of the major factors affecting the rheological properties of a plastic fat.<sup>15,46–48</sup>

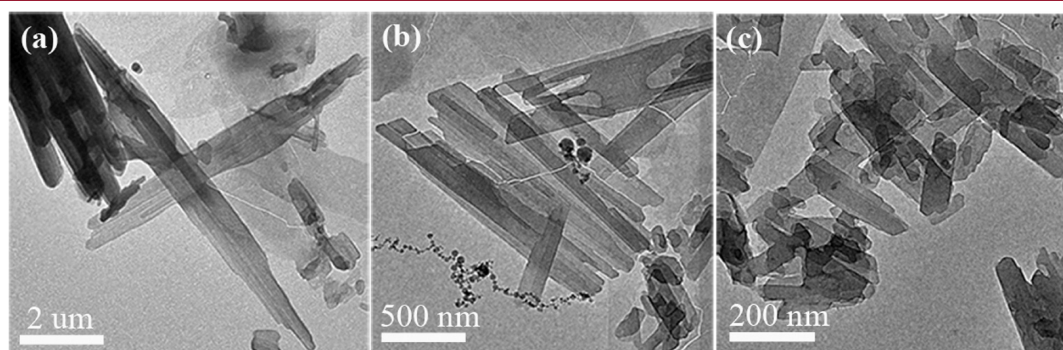
Our group has shown that the Young's modulus of fats is a function of the fractal arrangements of the microstructural elements within the network (D) and the volume fraction of the solid fat ( $\Phi$ ):<sup>48,49</sup>

$$E \sim \Phi^{1/(d-D)} \quad (2)$$

Narine and Marangoni (1999),<sup>39</sup> Marangoni (2000),<sup>48</sup> and Marangoni and Rogers (2003)<sup>50</sup> proposed a general model for the relationship between the Young's modulus and the microstructure of a high volume fraction aggregate network. Depending on the morphology of the flocs, a constant,  $\lambda$ , is



**Figure 7.** Shear modulus (A), breaking force (B), and Young's modulus (C) of the crystallized samples, static (ST), sheared (SH), oriented (OR) as a function of time. Symbols represent the average  $\pm$  standard error of replications.



**Figure 8.** Cryo-TEM micrographs of the samples static (a), sheared (b), oriented (c), displaying different nanoplatelet morphology and size.



defined in the model which is independent of the volume fraction of solids and dependent on the strength of van der Waals' interactions between crystals as well as their size:

$$E \approx \lambda \Phi^{1/(3-D)} = \frac{A}{2\pi a \varepsilon d_0^2} \Phi^{1/(3-D)} \quad (3)$$

where  $A$  is the effective Hamaker's constant,  $a$  is primary crystal size,  $\varepsilon$  is the yield strain, and  $d_0$  corresponds to the average equilibrium distance between flocs.

Using the fractal dimensions of the samples obtained from polarized light microscopy,<sup>44,51</sup> ( $D_{OR} = 1.64$  and  $D_{ST} = 1.41$ ) and the measured volume fraction of the solid  $\Phi = 0.78$ , a higher  $\lambda$  parameter is obtained in the shear-crystallized samples relative to the statically crystallized samples ( $\lambda_{ST} = 143.7$  MPa and  $\lambda_{OR} = 237.2$  MPa). This result confirms that the differences between the rheological properties of the samples are related to the particles characteristics and their interactions within the network, as stated in eq 3.

Assuming equal van der Waals' interparticle distances ( $d_0$ ) and similar strains at the limit of linearity ( $\varepsilon_{ST} = \varepsilon_{OR} = 0.01\%$ ) for the static and oriented samples we obtain:

$$\frac{\lambda_{OR}}{\lambda_{ST}} = \left( \frac{A_{OR}}{A_{ST}} \right) / \left( \frac{a_{OR}}{a_{ST}} \right) = 1.65 \quad (4)$$

Replacing the ratio of equivalent diameter of the samples ( $a_{OR}/a_{ST} = 2.05$ ) in eq 4, the ratio of Hamaker constant is determined,  $A_{OR}/A_{ST} = 0.80$ .

This demonstrates that the increase in modulus of elasticity upon shearing is mainly due to a reduction in nanocrystal size. Shearing induces the formation of a more molecularly mixed solid state,<sup>27</sup> and thus the crystal melt interfacial tension between the sheared cocoa butter crystals and the melt should be lower than in the static case. The Hamaker constant is a direct function of the crystal melt interfacial tension. It is rather ironic that a decrease in the crystal-melt interfacial tension is responsible for a greater nucleation rate, and thus a smaller final crystal size, while at the same time this decrease causes a reduction in the magnitude intercrystalline van der Waals' forces — effects that have opposite effects on mechanical strength. In this light, these authors wonder whether one should always be discussing changes in the ratio of  $A/a$  (Hamaker constant over particle size) rather than separate effects on Hamaker constant and particle size where these parameters are highly correlated to each other.

The reported values of the nanoparticles size may also be used to compare the thermal properties of the cocoa butter samples crystallized under the presence and absence of external shear field. Care must be taken, however, in drawing such conclusions on the basis of crystalline size alone as changes in the TAGs composition may happen when cocoa butter is crystallized under shear. A detailed quantitative XRD analysis in SAXS region is required to investigate the alteration of cocoa butter lamellar compositions under the applied laminar shear. This is not in the scope of the present work and is a worthwhile future study.

Studies have shown that the thermal properties of materials are affected by the size and distributions of the melting crystals.<sup>29,52–55</sup> Using Gibbs free energy for constructing the crystalline state from melt, several research groups<sup>56–58</sup> derived the phase transition relationship for lamellar crystals in polymer systems (generalized Gibbs–Thomson equation) when crystallization and melting occurs on the lateral crystal phase by removal

of a complete sequence:

$$T_i = T_i^0 \left( 1 - \frac{2\sigma_{ei}}{l_i \Delta H_{ui}} \right) \quad (5)$$

where  $T_i$  is the melting temperature of a finite sized polymer crystal of thickness  $l_i$ ,  $T_i^0$  is the equilibrium melting temperature (melting point) of an infinitely large crystal ( $l_i \rightarrow \infty$ ), and  $\sigma$  is the surface energy at the lamellar interface, and,  $\Delta H_{ui}$  is melting enthalpy.

According to this equation, the melting point ( $T_m$ ) of crystalline phases depends on the thickness of their crystalline domains, with thicker lamellae exhibiting a higher  $T_m$ . This is in good agreement with our finding as we have shown that the crystallization under laminar shear conditions reduces the thickness of the lamella by an amount that is roughly one lamellar layer.<sup>44</sup> The nanoplatelets' thickness, obtained from Scherrer analysis of the 001 SAXS reflection, yielded a domain size of 54.8 nm for the specimens crystallized under laminar shear and 58.2 nm for the statically crystallized samples. This finding may also explain the observed deviation between the fwhm of the statically crystallized and shear-crystallized samples. Studies have shown that the fwhm of the DSC curve can be influenced by the thickness of lamellae in addition to the particle morphology.<sup>52–55</sup>

As shown in Figure 6C, the statically crystallized cocoa butter displayed a broader DSC melting curve compared to the sheared and oriented samples. This can be related to the presence of larger crystals with a more heterogeneous distribution of sizes in this sample. The thermal event occurs faster in the sheared-crystallized sample since shear induces a more generalized nucleation which leads to a homogeneous distribution of the small crystals of a similar size.

Crystallizing cocoa butter under laminar shear yields a fat with a sharper DSC peak with a 0.5 °C lower peak melting temperature than the sample crystallized under a conventional turbulent shear field. A higher mechanical strength (~15% higher) is also observed in the oriented sample relative to the sheared sample.

While the average sizes of the nanocrystals in these samples are comparable, there must be other factors besides nanocrystal dimensions that influence these functional properties. Narine and Marangoni (2002)<sup>1</sup> reported the presence of a sharp crystallization peak in fats with more ordering in the spatial distribution of their microstructural elements. They suggest that the rapid release of heat can be attributed to the ordered array of crystals surrounded by liquid leading to a better heat transfer. In general, the effective heat transfer in a two-phase medium with phase change depends on the thermal conductivity of each phase, the latent heat and the particle (crystal) size of the solid phase as well as the arrangement of the solid particles in the liquid phase. In many materials, the thermal conductivity of the solid phase is higher than that of the liquid phase; however, Debaste et al. (2008)<sup>59</sup> reported that the thermal conductivity of the liquid cocoa butter at 41 °C is higher than that of solid cocoa butter at 23 °C ( $K_{41} \text{ °C} = 0.12 \text{ W m}^{-1} \text{ °C}^{-1}$  and  $K_{23} \text{ °C} = 0.09 \text{ W m}^{-1} \text{ °C}^{-1}$ ). The higher thermal conductivity of the liquid may explain the more efficient heat transfer in the ordered array of crystals as follows: the solid nanoparticles (crystalline) in the samples absorb energy to melt and also have lower thermal conductivity which both reduces the rate of heat transfer through the particles. Since in the samples with ordered array of crystals, each individual particle is surrounded with liquid, its entire surface is in contact with the oil and therefore the overall



**Table 2. Shear Storage Modulus of Samples Obtained by Ultrasonics and Corresponding Young's Moduli Obtained from eq 3<sup>a</sup>**

sample (CB)	storage modulus ( $G'$ , Pa)	Young's modulus ( $E$ , Pa)
static	$124.2 \pm 3.74^A$	$255.5 \pm 7.68^A$
sheared	$167.4 \pm 2.4^B$	$357.27 \pm 5.22^B$
oriented	$197.2 \pm 9.1^C$	$447.76 \pm 20.49^C$

<sup>a</sup>Superscript Letters Correspond to Statistically Significant Differences Between the Values ( $P < 0.05$ ).

solid–liquid interface area is increased leading to higher heat transfer from liquid to solid particles and therefore the melting process is accelerated. As melting happens faster, its contribution in the reduction of the overall heat transfer is less noticeable compared to the nonoriented crystals, (this results in a higher heat transfer rate for the oriented sample). It is worth noting that due to the nature of the system, a quantitative heat transfer analysis requires a finite element simulation that takes all above-mentioned parameters into account and is not in the scope of this research.

A number of publications have shown the influence of particle alignment on the mechanical strength of polycrystalline materials.<sup>60–64</sup> Nielsen (1967)<sup>65</sup> suggested that with nonspherical particles the type and degree of particle orientation can greatly affect the mechanical properties. Stafco (1962)<sup>64</sup> has shown that the bending strength of particleboards with randomly dispersed flakes may be increased up to 70% by aligning the flakes. This suggests that in this study, crystalline orientation can be the cause of the observed increase in mechanical strength of the oriented CB samples. For the set of measurements reported here, a higher modulus of elasticity ( $\sim 15\%$  higher) was obtained in the oriented sample compared to the sheared one. The shear modulus of the oriented sample was also greater than that of the sheared sample. However, the increase in  $G'$  with orientation is relatively smaller than the increase in  $E$ . This finding shows the effect of the crystalline alignment on the strength and hardness of the crystallized cocoa butter samples in the direction perpendicular to the orientation direction. In the following, the measurement of these parameters in the direction parallel to the orientation direction is described. Since the samples used in this study are curved and only 2.5 mm thick, we could not find any conventional rheological method suitable for these measurements. Therefore, the storage modulus of the samples in the direction parallel to the alignment direction was determined using an ultrasonic technique developed by the authors.<sup>41</sup> As reported in Table 2, the obtained shear modulus of the curved samples exhibit a similar trend obtained for the perpendicular direction, where  $G'$  in the oriented sample is higher than the other two samples.

The Young's modulus is then calculated using the theory of continuum mechanics and the relation among the elasticity constants:

$$E = 2G(1 + \nu) \quad (6)$$

where  $\nu$  is the Poisson ratio. The Poisson ratio for different samples is calculated by substituting the measured  $E$  and  $G'$  of the rheology measurement (Figure 7A,C) into eq 6. Then, knowing  $G'$  and  $\nu$ , the Young's modulus for the direction parallel to the orientation direction is obtained. Table 2 lists the values of  $E$  and

$G'$  for different samples, where the Young's modulus of the oriented sample is  $\sim 30\%$  higher than sheared sample. One can also notice that in the direction parallel to the orientation direction Young's modulus is higher than that of the perpendicular direction. This is in agreement with the results from oriented block copolymers<sup>61</sup> which displayed a different yield force and Young's modulus depending on the loading direction relative to lamellar orientation. Nielosen and Landel (1994) attribute the smaller elastic modulus in the perpendicular direction to the van der Waals' forces acting between molecules in that direction. They deduce that in the parallel direction the applied force acts on strong covalent bonds.<sup>7</sup> However, understanding the intermolecular behavior and the cause of different Young's moduli in two perpendicular directions require a more thorough investigation.

## CONCLUSION

In this study, we have shown the significant effects of laminar shear applied during crystallization of polycrystalline materials on their physical properties. It was shown that mechanical strength of the samples is not only dependent on the concentration of the particles and polymorphic behavior but also those factors such as the geometry of dispersed phase, particle shape, size, and distribution. A higher modulus of elasticity was observed in the samples with aligned and smaller nanocrystals.

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