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Development of an ultrasonic shear reflection technique to monitor the crystallization of cocoa butter

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ABSTRACT

The quasi-isothermal crystallization process of cocoa butter was monitored by an ultrasonic shear reflection technique utilizing a custom-built experimental set-up in a temperature controlled environment. To facilitate the interpretation of the measurement results, the propagation of shear waves was first theoretically studied in different configurations of gas, liquid or solid layers with varying thickness for the case of normal incidence, yielding theoretical equations of the shear wave reflection coefficient (swRC) for different layering conditions. The typical experimentally observed pattern of the swRC during quasi-isothermal cocoa butter crystallization was subsequently linked to the theoretical equations. The remarkable oscillatory damped response in the swRC as function of the crystallization time could be explained by constructive and destructive interference of a first reflection at the boundary between a plexiglass delay line and the crystallized cocoa butter and a second reflection occurring at the interface between crystallized and liquid substance. This hypothesis was supported by the excitation frequency dependence of the oscillations. The quality of the fit of the theoretical model to the experimental results was very good and also the reproducibility between different independent measurements was acceptable. Finally, measurements at different temperatures (18 °C and 20 °C) suggested that the technique was able to detect differences in crystallization behavior, as measurements at 18 °C displayed faster oscillations compared to measurements at 20 °C. Moreover, this was also confirmed by the theoretical model, as a higher value of the crystallization rate parameter *K*, exhibited more rapid oscillations.

1. Introduction

In the production of fat containing food products, insight in the crystallization behavior of fats is of utmost importance to obtain the desired product functionality and product quality. The crystallization process consists of triglycerides crystallizing in a particular polymorphic form and the aggregation of these crystals into clusters and larger microstructures until a continuous three-dimensional network is formed (Narine & Marangoni, 1999). Several methodologies exist to monitor the crystallization process, with the major contemporary techniques being differential scanning calorimetry (DSC), pulsed nuclear magnetic resonance (pNMR), X-ray diffraction (XRD), rheology and polarized light microscopy (PLM) (Foubert, Dewettinck & Vanrolleghem, 2003). Even though the microstructure development most likely affects the macroscopic properties to a great extent (Narine & Marangoni, 1999), rheology and PLM are the only techniques of the abovementioned that can actually monitor microstructural characteristics. Furthermore, all these techniques are applied off-line in the assumption that the tested batch is representative of the entire production line, while in reality variation exists in most process streams. So, there is a need for in-line monitoring, which — apart from providing more accurate information — can also yield considerable financial benefits. Expensive rework or disposal of out-of-specification products can be avoided as the process variables can be adjusted by monitoring crystallization during the production process (Kress-Rogers, 2001). Moreover, primary trends in the food industry nowadays are reduced-fat products and *trans* fat replacement because of human health concerns (Acevedo & Marangoni, 2014; Ma & Boye, 2013). However, as fat determines to a large extent the product quality, it is a challenge to produce healthy products while retaining many of the quality characteristics (Marangoni et al., 2012). An in-line method could provide important information on the structural development during processing and thus stimulate product innovation.

In the last decade, several feasible techniques for in-line monitoring of fat crystallization have been suggested: NMR-MOUSE (nuclear magnetic resonance-mobile universal surface explorer) (Martini, Herrera & Marangoni, 2005b), laser backscattering (Hishamuddin, Stapley &

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Nagy, 2011), near-infrared (NIR) spectroscopy (Bolliger, Zeng & Windhab, 1999) and ultrasonic techniques (Coupland, 2004; Häupler et al., 2014; Martini, Herrera & Marangoni, 2005b; Saggin & Coupland, 2004). Because the topic of this paper is the development of an ultrasonic shear reflectance technique to monitor fat crystallization, the focus in the following brief literature review will be on the application of ultrasonic techniques in fat crystallization monitoring.

Ultrasonic waves are mechanical or elastic waves with a frequency higher than the upper limit of human hearing (16 kHz) for which two important types of waves can be distinguished (Povey & McClements, 1988). In compressional waves (or longitudinal waves) the particles move in the same direction as the propagating wave (McClements, 1997). This type of propagation is supported by solid as well as fluid media (Létang et al., 2001). On the contrary, in shear waves (or transversal waves) the movement of the particles is perpendicular to the direction of the propagating wave (McClements, 1997). Therefore, shear waves only propagate in materials having shear elasticity (Létang et al., 2001).

Ultrasonic inspection is capable of performing rapid and precise measurements which are non-destructive, relatively inexpensive, non-hazardous and can be fully automated, which make it highly suitable for in-line monitoring (Martini, Bertoli, Herrera, Neeson & Marangoni, 2005a; McClements & Povey, 1992). However, this technique also has some drawbacks and limitations for particular applications, which explain why ultrasonic monitoring, although very promising, is not widely used in the food industry to date. Especially the application of ultrasonics to monitor fat crystallization is hampered by the high attenuation of the ultrasonic signal in lipids with high solid fat content (SFC) (Coupland, 2004). Furthermore, pure solid triglycerides tend to form voids during cooling, and at the same time, systems with high SFC tend to detach from the container wall, causing an air gap (McClements & Povey, 1992; Saggin & Coupland, 2002). Air bubbles and layers of air scatter and reflect ultrasound very strongly because of the large difference in acoustic impedance between gas bubbles and fat, which leads to substantial amplitude reduction of the transmitted signals (Coupland, 2004). So, the main problem of performing ultrasonic measurements on fat samples is to get the ultrasonic pulse through the material (Martini, Bertoli, Herrera, Neeson & Marangoni, 2005a).

The research reported in literature about this topic, varies in the type of ultrasonic waves used, the applied waveforms for excitation, and the chosen ultrasonic measurement set-up. As compressional waves are the easiest to generate and detect, a lot of research has been published on their use for fat monitoring applications (Povey & McClements, 1988). The pulse-echo technique is the simplest and therefore most widely used ultrasonic measurement technique (McClements, 1997). In this technique, a transducer which is directly connected to a sample sends out a short pulse which travels across the sample until it reaches the opposite cell wall, where it is reflected back to the transducer. The same transducer acts as receiver and records the reflected signal. By analyzing the resulting echoes, several ultrasonic parameters can be determined: the ultrasonic velocity (v), the attenuation coefficient (α) and the acoustic impedance (Z), the latter being the product of density (ρ) and v (McClements, 1995, 1997). The ultrasonic velocity measurements can be used to calculate the SFC, because of the substantial difference in the speed of sound in the solid phase (approximately 2000 m/s) as compared to the liquid phase (approximately 1400 m/s) (Bijnen et al., 2002). However, Singh, McClements, and Marangoni (2004) showed that the correlation between the ultrasonic velocity measurements and the SFC was only applicable for samples with an SFC lower than 20% at a thickness of 1.6 cm. By upgrading the excitation waveform to a chirp, Martini, Bertoli, Herrera, Neeson, and Marangoni (2005a) reported measurements through an 8.11 cm thick sample with an SFC of ~20% in a through transmission mode. The attenuation coefficient also depends on the SFC, but is found to be more sensitive to the microstructure than velocity measurements (McClements & Povey, 1992). Moreover, Häupler et al. (2014), using a chirp wave excitation, demonstrated that the attenuation of tempered cocoa butter is higher than the attenuation of untempered cocoa butter at the same SFC level at frequencies of 1.7 and 3 MHz, suggesting that the attenuation is also polymorph dependent. Saggin and Coupland (2002) used a modified pulse echo technique to measure the compressional wave reflection coefficient (cwRC) of a series of confectionery coating fats and cocoa butter dispersions in corn oil. The main advantage of this reflection approach was that it could be used with highly attenuating materials, since the waves do not have to travel across the material. However, a disadvantage is that reflectance only depends on the surface properties of the sample and can be misleading if this region is not representative of the bulk (Coupland, 2004).

Contrary to compressional waves, shear waves have much less frequently been investigated in a fat crystallization context. To our knowledge, only Saggin and Coupland (2004) have proposed a shear reflectance technique to calculate the shear modulus and dynamic viscosity of different solid fat dispersions with varying SFC, but these properties were not measured during the crystallization process itself. Interestingly, they observed that the shear ultrasonic properties revealed a sensitivity to the sample microstructure. In other reports, a similar shear reflectance technique has also been suggested to study the crystallization of forming biopolymer films (Peura et al., 2008) and polychloroprene films (Alig & Tadjbakhsch, 1998).

Most of the recent studies concerning ultrasonic measurements of crystallizing fats deal with emulsions or dispersions of fat crystals in a liquid oil, rather than with bulk fats, presumably because of the very high attenuation of the latter. However, because of the difference in physical state between bulk fats and dispersions, and therefore also in the interaction with the propagating wave, the results of dispersions cannot be readily transferred to bulk fats.

Based on this literature review, it was decided to study the potential of an ultrasonic shear reflectivity technique to continuously monitor the crystallization process of pure cocoa butter. Because the wave-matter interaction in semi-crystalline fats is less well known than in emulsions (Saggin & Coupland, 2002), this work started with the construction of a theoretical model of the propagation of shear waves in a layer of crystallizing cocoa butter. Subsequently, ultrasonic shear reflectivity experiments were performed at different crystallization temperatures (18 °C and 20 °C) and the evolution of the observed shear wave reflection coefficient (swRC) was linked to the theoretical model.

2. Materials and methods

The cocoa butter used in this study was a standard factory product of West-African origin which was kindly provided to us by Barry Callebaut (Wieze, Belgium).

2.1. Sample preparation

The cocoa butter was melted in a furnace at 85 °C for 30 min to erase all crystal memory. Subsequently, 20 g of the sample was air-cooled statically until 30 °C was reached. This temperature was chosen as a compromise between avoiding the presence of air bubbles and preventing a high temperature increase of the plexiglass delay line (see Experimental set-up). Both features would have a negative effect on the ultrasonic measurements as air bubbles attenuate the signal whereas temperature gradients influence the ultrasonic properties. Furthermore, completely melted cocoa butter does not crystallize statically above 30 °C.

2.2. Experimental set-up

Fig. 1 presents a schematic overview of the custom-built experimental set-up. A shear wave transducer is attached with a shear wave couplant to the bottom side of a plexiglass delay line, above which the