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Development of a single droplet freezing apparatus for studying crystallisation in cocoa butter droplets

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ABSTRACT

The single droplet freezing apparatus described by Pore et al. (2009), which allows crystallisation to be monitored *in situ* by X-ray diffraction, was modified to allow rapid switching of coolant gas and monitoring by video microscopy. The apparatus was used to study drops of cocoa butter undergoing simulated spray freezing at high cooling rates, *e.g.* 130 K/min. The transformation of an Ivory Coast cocoa butter to the Form V polymorph was significantly faster in drops (~40 h) than in static bulk samples (10 days) crystallised under isothermal conditions. Phase transformation was observed from Forms I/II → III → IV → melt → V, with Form V crystallising directly from the melt at 28.6 °C. Numerical simulations of the temperature evolution within the droplet established that the drops are not isothermal, explaining why nucleation was initially observed in the lower (upstream) part of the droplet.

1. Introduction

Cocoa butter is a naturally occurring, edible fat produced from the cacao bean, and is one of the major ingredients of chocolate. It consists of a mixture of triacylglycerides (TAGs) and exhibits polymorphic phase behaviour, existing in six distinct crystalline forms. These are labelled Forms I to VI following the Wille & Lutton nomenclature (Wille and Lutton, 1966) or γ, α, β' and β using the Larsson nomenclature (Larsson, 1966). Form I is the least thermodynamically stable polymorph and Form VI is the most stable. The different polymorphs can be identified via their sub-cell structure using X-ray diffraction (XRD) Clarkson et al., 1934. They can also be distinguished using differential scanning calorimetry (DSC). XRD offers unambiguous identification of the crystals present and is thus the preferred method of characterisation. Much of the chocolate literature employs the Roman classification, originally based on melting point data, and for this reason it is used here.

Real time XRD studies using laboratory X-ray diffractometers have been carried out to observe the evolving crystalline structure in cocoa butter in both static (Van Malssen et al., 1996, 1999, 1996a,b) and sheared crystallisation (Sonwai, 2002). Synchrotron XRD offers improved resolution, rapid data collection and simultaneous small (SAXS) and wide (WAXS) angle measurements, corresponding to the long and short range spacing in the crystal lattice (Macmillan et al., 2002; Macmillan and Roberts, 2002; Van Langevelde et al., 2001). In most of these studies, the cocoa butter sample is held in temperature controlled sample holder (Van Malssen et al., 1996b), a thin capillary tube (Lopez and Ollivon, 2009), or a bespoke cell (Ueno et al., 1999). The cocoa butter samples are usually heated to 50–70 °C for 15–30 min to avoid memory effects (Van Langevelde et al., 2001), and then cooled, at a rate similar to that used in DSC (*e.g.* 0.5–20 K/min), or crash cooled at 50 K/min, to the required temperature. Droplet samples of cocoa butter have not previously been studied by XRD until the development of the single droplet freezing apparatus reported by Pore et al. (2009).

The use of a droplet suspended in a flowing medium is common in heat and mass transfer studies (Fuchs, 1959). The single droplet freezing apparatus (SDFA) was developed by (Hindmarsh et al., 2007) to study temperature transitions in freezing droplets of aqueous food solutions. The SDFA allows the thermal history of a droplet to be monitored by suspending it on a fine thermocouple and subjecting it to a cold, dry air stream. This apparatus was originally used with video imaging to study the freezing behaviour of dairy solutions. SDFA devices have also been constructed for use in MRI machines for mapping emulsion creaming and solidification within droplets (Hindmarsh et al., 2004).

Gwie et al. (2006) used an SDFA to study spray-freezing of tripalmitin and cocoa butter. Their SDFA was later modified to fit into a laboratory X-ray system by Pore et al. (2009), allowing *in-situ* real time monitoring of the freezing process. It was possible to observe the transformation from Form I to the higher melting polymorphs,

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Nomenclature

Bi	Biot number (hL/k)
c_x	percentage of phase x present (%)
C_D	drag coefficient
C_p	specific heat capacity (J/kg K)
d	droplet diameter (m)
D	duct diameter (m)
g	specific heat capacity (m/s^2)
h	average surface film heat transfer coefficient used in simulation (W/m^2 K)
h_o	surface averaged heat transfer coefficient (W/m^2 K)
H	enthalpy (J)
ΔH	enthalpy change of crystallisation, DSC testing (J/g)
I	intensity (a.u.)
k	thermal conductivity (W/m K)
K	shape factor used in Scherrer analysis (~0.9)
L	characteristic length (m)
m	mass (kg)
n	normal to boundary
Nu	Nusselt number
Pr	Prandtl number
q_{conv}	convective heat flux of droplet (W)
Q_L	latent heat released per unit gram of cocoa butter (J/g)
r	radial coordinate (m)
R	duct radius (m)
Re_{ch}	chamber Reynolds number, $Re_{ch} = \frac{Du^*}{\nu}$
Re_d	particle Reynolds number, $Re_d = \frac{Vd}{\nu}$
Re_{st}	Reynolds number, flow straightener, $Re_{st} = \frac{D_{st}u^*_{st}}{\nu}$
s	volume-weighted particle size (m)
t	time (s)
T	temperature (°C)
T_a	inlet air temperature (°C)
T_c	local temperature of the cocoa butter at the liquid/air interface (°C)
T_d	droplet temperature (°C)
T_f	mean freezing temperature measured by droplet thermocouple (°C)
T_0	initial temperature (°C)
T_s	temperature of solder in simulation (°C)
u	velocity within droplet, simulation (m/s)
u	local air velocity (m/s)
u^*	superficial air velocity (m/s)
u_d	air velocity upstream of droplet (m/s)
U	overall heat transfer coefficient (W/m^2 K)
V	terminal velocity of droplet in free fall (m/s)
w	corrected full width at half maximum (radians)
w_{obs}	observed full width at half maximum (radians)
w_s	instrumental broadening estimated using silver behenate standard (radians)

Greek symbols

θ	Bragg diffraction angle (°)
φ	polar angle (radians)
λ	wavelength (Å)
ρ	density (kg/m^3)
ν	dynamic viscosity (m^2/s)
μ	kinematic viscosity (Pa s)

Subscripts

a	air
c	cocoa butter
s	solder

Acronyms

DSC	differential scanning calorimetry
HWA	hot wire anemometer
POP	1,3-dipalmitoyl-2-oleoyl-glycerol
POS	1-palmitoyl-2-oleoyl-3-stearoyl-glycerol
SOS	1,3-distearoyl-glycerol

which were consistent with the temperature-phase transitions reported for static bulk samples crystallised under isothermal conditions by Van Malssen et al. (1999). Form V was first observed after 2 h at 24 °C, with complete transformation into Form V after 4 h; this is considerably shorter than the 1 week reported by van Malssen et al. The droplets were 2 mm in diameter, small enough to be suspended on a thermocouple junction, but large enough to interact with the X-ray beam (collimator 0.8 mm diameter).

This paper reports a substantial redesign of the X-ray SDFA to improve the consistency and accuracy of *in situ* observation of crystallisation with well-controlled temperature steps. The apparatus is able to maintain the droplet temperature at 70 °C, followed by cooling at 2–5 K/s to a temperatures as low as −10 °C. A short study of the crystallisation of a Côte d'Ivoire cocoa butter demonstrates the versatility of the device and further explores the low Biot number hypothesis proposed by Pore et al. (2009) for the rapid phase transformation in droplets. The experiments are accompanied by numerical evaluations of heat transfer with the drop to determine whether the temperature distribution within the droplets is uniform.

2. Material and methods

2.1. Apparatus

Fig. 1 shows a schematic and photograph of the SDFA. The chamber is a cylindrical Perspex duct of length 130 mm and diameter 33 mm, with air entering at the base and discharging to atmosphere at the top via 6 equally spaced 5 mm diameter holes. Chilled, dry air enters the bottom of the chamber, marked **e**, via 8 mm i.d. reinforced PVC tubing and passes through a flow straightener, marked **d**, consisting of a cylindrical duct of diameter 16.5 mm containing a honeycomb network of 3 mm diameter plastic straws.

The inlet air temperature, T_a, was measured at the entrance to the main chamber by a K-type thermocouple (marked **c**). The cocoa butter droplet was suspended from the junction of a thin K-type thermocouple, 50 μm in diameter (labelled **b**), located on the central axis 35 mm from the air inlet. The thermocouple junction has a drop of solder attached (50/50 Sn/Pb, diameter 0.9 mm), coated with nail varnish, to help droplets adhere without promoting nucleation. The thermocouple wires upstream of the droplet are encased in insulating reinforced PVC tubing of outer diameter 2 mm. The vertical position of the droplet can be adjusted. Both the inlet air temperature, T_a, and the droplet temperature, T_d, were monitored and recorded on a PC using a PicoLog data logger (Pico Technology, St. Neots, UK) at 0.25 s intervals.

The X-ray beam enters through an opening in the side wall of diameter 3 mm (**f**) and exits through an opening of diameter 10 mm (**g**) opposite; both openings are taped over with 1 mm thick Kapton© film. The chamber is mounted between the collimator and detector of the X-ray diffractometer. The spatial configuration of the X-ray system prevented the use of long entry ducts required to obtain fully developed flow patterns.