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Characterization of melting properties in dark chocolates from varying particle size distribution and composition using differential scanning calorimetry

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ABSTRACT

Melting properties in dark chocolates processed from varying particle size distribution (PSD), fat and lecithin content were studied using differential scanning calorimetry (DSC). Compositional parameters were PSD (D_{90} (90% finer than this size) of 18, 25, 35 and 50 μm), fat (25%, 30% and 35%) and lecithin (0.3% and 0.5%) contents. Variations in PSD had no influence on crystallinity of products. Fat and lecithin content influenced the degree of crystallinity and melting properties (T_{end}, T_{index} and ΔH_{melt}) of the products. Increasing fat content caused consistent increases in degree of crystallinity and crystal size distribution, thus effecting significant changes in T_{end}, T_{index} and ΔH_{melt} of their derived products. Increasing lecithin content however reduced the crystal sizes in products. Particle size (PS) increases had limited effects on T_{onset}, T_{peak}, and ΔH_{melt} independent of fat and lecithin content. Significant decreases in T_{end} and T_{index} were noted with PS increases at all fat and lecithin contents. Similar increases in T_{end} and T_{index} were noted with increases in fat content at all PS and lecithin levels. Contrary, increasing lecithin content in products resulted in significant decreases in T_{end}, T_{index} and ΔH_{melt}. Thus, variations in fat and lecithin contents during dark chocolate manufacture influence the crystallinity of products, and with PSD, they all influence the melting index (duration) of their derived products.

1. Introduction

Dark chocolates are suspensions of sucrose and cocoa particles, coated in phospholipids in a continuous fat phase, generally cocoa butter, with total solid content of 65% to 75%. The outcome is production of a smooth suspension of particulate solids in cocoa butter (Beckett, 1999; Whitefield, 2005), solid at ambient temperature (20–25 °C) but forms a smooth dense suspension at oral temperatures (37 °C). This oral liquefaction is defined by the fat melting characteristics and influences the perception of flavour and mouthfeel attributes. The intensity of perceived taste and flavour changes over time as the chocolate is melted, manipulated and mixed with saliva (Afoakwa, Paterson, & Fowler, 2007; Ziegler & Hogg, 1999).

Central to chocolate sensory character is a continuous-phase lipid composition (primarily cocoa butter), which influences melting properties and mouthfeel character. Continuous-phase lipids are primarily triacylglycerides (TAGs) dominated by 1,3-disaturated-2-oleoylglycerol type: 1,3-dipalmitoyl-2-oleoylglycerol (POP), 1-palmitoyl-2-oleoyl-3-stearoylglycerol (POS) and 1,3-distearoyl-2-oleoylglycerol (SOS) and smaller quantities of mono- and di-acylglycerides, polar lipids, free fatty acids and fat-soluble compounds (Chaiseri & Dimick, 1987). Cocoa butter can crystallize as a function of triglyceride composition (fatty acids; Talbot, 1999) into six polymorphic forms (I–VI), where Form I is the least stable and V, the most desirable form, which can transform to VI, the most stable, in storage. Polymorphic triglyceride forms differ in distance between fatty acid chains, angle of tilt relative to plane of chain end methyl group and manner in which triglycerides pack in crystallization (Ali, Selamat, CheMan, & Suria, 2001; Talbot, 1999). In manufacture, a thermal process known as tempering is used to obtain the desirable form V (or $ß_2$) in cocoa butter with a melting temperature of 32–34 °C, and conferring the desired glossy appearance, good snap, contraction and enhanced shelf life (Beckett, 2000; Seguine, 1991; Talbot, 1999; Timms, 2003). Poorly tempered chocolate develops in storage a white or grey surface layer, fat bloom, subsequently converting from form V into the more stable form VI.

Particle size distribution influences rheology and texture with specific surface area and mean particle size influencing yield stress, plastic viscosity, product spread and hardness (Afoakwa, Paterson, & Fowler, 2008a; Beckett, 2000; Chevalley, 1999). Smaller particles improve sensory properties (Ziegler, Mongia, & Hollender, 2001) but plastic viscosity and yield stress increase due to changes in surface area of particles in contact with fat phase. Particle size optimisations can reduce requirement for viscosity modifiers and improve process control (Afoakwa et al., 2008a). Although PSD and composition in chocolate influences on rheology and sensory

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characters have been described (Afoakwa, Paterson, Fowler, & Vieira, 2008b; Afoakwa et al., 2008a; Mongia & Ziegler, 2000; Ziegler et al., 2001), their influence on melting behaviour still remains unknown.

During chocolate manufacture, the crystalline state and the proportion of solid fat present are important in determining the melting character in finished products. Differential scanning calorimetry (DSC) has been used to characterize changes in chocolate melting profiles and measures the relative amounts of each crystalline state (Tabouret, 1987; Walter & Cornillon, 2001, 2002; Ziegleder & Schwingshandl, 1998); and peaks corresponding to latent heat, are observed in temperature ranges related to melting of specific polymorphs (McFarlane, 1999). Such information is relevant to sensory character and impacts on mechanical and rheological properties of chocolate and confectionery shelf life (Hartel, 2001). In this study DSC was used to characterize the effects of particle size distribution, fat and lecithin content on the crystallinity, crystal size distribution and melting profiles of finished dark chocolates.

2. Materials and methods

2.1. Materials

Cocoa liquor of Central West African Origin was obtained from Cargill Cocoa Processing Company (York, UK); sucrose (pure beet extra fine granulated) from British Sugar Company (Peterborough, UK); pure prime pressed cocoa butter and soy lecithin from ADM Cocoa Limited (Koog aan de Zaan, Netherlands) and Unitechem Company Ltd. (Tianjin, China), respectively.

The recipe (Table 1) and formulations used for the production of samples have been described previously (Afoakwa et al., 2008a). Chocolates were formulated with total fat of 25–35% (w/w) from cocoa liquor and cocoa butter with >34% total cocoa: composition as specified for dark chocolate by relevant directives (Codex Revised Standard, 2003; European Commission Directive, 2000). Experimental samples (5 kg batch for each formulation) were produced by mixing sucrose and cocoa liquor in a Crypto Peerless Mixer (Model K175, Crypto Peerless Ltd., Birmingham, UK) at low speed for 2 min and then at high for 3 min, then using a 3-roll refiner (Model SDX 600, Buhler Ltd., CH-9240 Uzwil, Switzerland) to a specified particle size (D_{90}:18 ± 1 μm, 25 ± 1μm, 35 ± 1 μm & 50 ± 1 μm) conducting particle size analysis, during refining, to ensure D_{90} values. Refined chocolates were placed in plastic containers and conditioned at 50–55 °C for 24 h to ensure melting of fat within chocolate mass prior to conching in a Lipp Conche (Model IMC-E10, Boveristr 40-42, D-68309, Mannhein, Germany) at low speed for 3.5 h at 60 °C. Lecithin and cocoa butter were added and mixtures then conched at high speed for 30 min to effect adequate mixing and liquefaction. Samples were kept in sealed plastic containers at ambient (20–22 °C) and moisture and fat contents determined using Karl Fischer and Soxhlet methods (ICA, 1988) and (ICA, 1990).

2.1.1. Tempering procedure

Samples were incubated at 50 °C for 4 h for melting and tempered using an Aasted Mikrovert laboratory continuous three-stage tempering unit (Model AMK 10, Aasted Mikroverk A/S, Farum, Denmark). Chocolate was pumped through the multi-stage units and a worm screw drove the product through the heat exchangers. Sensors located at specific points in the equipment measured the temperature of both the chocolate and the coolant fluid at each stage. The temperatures of each of the three stages were thus set and controlled independently of each other to obtain a final chocolate temperature of ~27 °C to promote crystal growth of the desired triacylglyceride fractions. Pre-crystallization was measured using a computerized tempermeter (Exotherm 7400, Systech Analytics, SA, Switzerland). A built-in algorithm was used to ensure an optimal temper regime of Slope 0 ± 0.3 (5.0 ± 1 CTU). The principle of this method has been described by Nelson (1999). The tempered chocolate was moulded using plastic moulds: 80 mm length; 20 mm breadth; and 8 mm height, allowed to cool in a refrigerator (5 °C) for 2 h before de-moulding onto plastic trays and conditioned at 20 ± 2 °C for 14 days before analysis.

Table 1
Recipes used for the formulation of the dark chocolate

Ingredient	25% Fat (w/w)		30% Fat (w/w)		35% Fat (w/w)	
Sucrose (%)	58.80	59.00	49.70	49.90	40.70	40.80
Cocoa liquor (%)	35.90	35.50	45.00	44.60	54.00	53.70
Cocoa butter (%)	5.0	5.0	5.0	5.0	5.0	5.0
Lecithin (%)	0.3	0.5	0.3	0.5	0.3	0.5

2.2. Determination of particle size distribution

A MasterSizer® Laser Diffraction Particle Size Analyzer equipped with MS 15 Sample Presentation Unit (Refractive index 1.590) (Malvern Instrument Ltd., Malvern, England) was used. About 0.2 g of refined dark chocolate was dispersed in vegetable oil (Refractive index 1.450) at ambient temperature (20 ± 2 °C) until an obscuration of 0.2 was obtained. The sample was placed under ultrasonic dispersion for 2 min to ensure particles were independently dispersed and thereafter maintained by stirring during the measurement. Size distribution was quantified as the relative volume of particles in size bands presented as size distribution curves (Malvern MasterSizer® Micro Software v 2.19). PSD parameters obtained included specific surface area, largest particle size (D_{90}), mean particle volume (D_{50}), smallest particle size (D_{10}) and Sauter mean diameter (D[3,2]). The four PSD used for the study are as shown (Table 2).

2.3. Determination of melting properties of dark chocolates

Differential scanning calorimeter (DSC Series 7, Perkin Elmer Pyris, Norwalk, CT, USA) equipped with a thermal analysis data station was calibrated using indium and octadecane at a scan rate of 5 °C/min using an aluminium pan as reference. Samples (~5 mg) were loaded into 40 μl capacity pans with holes and sealed with lids using a sample press. Pans were heated at 5 °C/min from 15–55 °C in a N_2 stream. Onset temperature (T_{onset}), peak temperature (T_{peak}), end temperature (T_{end}) and enthalpy of melting (ΔH_{melt}) were calculated automatically by the software. Melting index (T_{index}) was computed as ($T_{\text{end}} - T_{\text{onset}}$), as described by Vasanthan and Bhatty (1996). Each sample was analyzed in triplicate and mean values and standard deviations reported.

2.4. Experimental design and statistical analysis

Three experimental variables comprising PSD, fat and lecithin contents were used. Other variables including refiner temperature and pressure, conching time and temperature were held constant. A 4 × 3 × 2 factorial experimental design was used with: PSD (D_{90}): 18, 25, 35 and 50 μm; fat: 25%, 30% and 35% (w/w); lecithin: 0.3% and 0.5% (w/w). Statgraphics Plus 4.1 (Graphics Software System, STCC, Inc, Rockville, USA) examined melting properties (T_{onset}, T_{end}, T_{index}, T_{peak} and ΔH_{melt}) using two-way analysis of variance (ANOVA) and multiple range tests to determine the effects of factors and their interactions. Tukey multiple comparisons (95% significance level) was employed to determine the differences between levels. All process treatments and analysis were conducted in three replicates and the mean values reported.

Table 2
Particle size distribution of the dark chocolates

Particle size (PS) $d(0.9)$[a] (µm)	Fat content (%)	Lecithin (%)	Particle size distribution				
			Specific surface area (m^2/g)	D(v,0.1)[a] (µm)	D(v,0.5)[a] (µm)	D[3,2][a] (µm)	D(v,0.9)[a] (µm)
18 ± 1.0	25	0.3	1.98 ± 0.02	1.12 ± 0.02	4.81 ± 0.05	2.66 ± 0.04	18.53 ± 0.19
		0.5	1.95 ± 0.05	1.06 ± 0.04	4.62 ± 0.09	2.56 ± 0.02	18.88 ± 0.70
	30	0.3	1.84 ± 0.03	1.07 ± 0.03	4.93 ± 0.05	2.70 ± 0.04	18.76 ± 0.46
		0.5	1.93 ± 0.01	1.01 ± 0.03	4.85 ± 0.04	2.56 ± 0.02	18.67 ± 0.50
	35	0.3	1.53 ± 0.03	1.40 ± 0.05	6.04 ± 0.06	3.12 ± 0.05	18.70 ± 0.24
		0.5	1.55 ± 0.05	1.37 ± 0.03	6.01 ± 0.05	3.22 ± 0.03	18.50 ± 0.25
25 ± 1.0	25	0.3	1.68 ± 0.08	1.19 ± 0.04	5.45 ± 0.04	2.83 ± 0.04	25.47 ± 0.04
		0.5	1.61 ± 0.02	1.25 ± 0.02	5.79 ± 0.07	3.01 ± 0.04	25.73 ± 0.57
	30	0.3	1.57 ± 0.02	1.31 ± 0.02	5.92 ± 0.06	3.06 ± 0.03	25.30 ± 0.65
		0.5	1.58 ± 0.02	1.17 ± 0.03	5.65 ± 0.04	2.98 ± 0.02	25.76 ± 0.40
	35	0.3	1.46 ± 0.02	1.44 ± 0.05	6.60 ± 0.06	3.40 ± 0.06	25.10 ± 0.32
		0.5	1.44 ± 0.03	1.46 ± 0.03	6.65 ± 0.03	3.46 ± 0.04	25.01 ± 0.13
35 ± 1.0	25	0.3	1.43 ± 0.04	1.43 ± 0.04	6.73 ± 0.07	3.31 ± 0.03	35.98 ± 0.14
		0.5	1.48 ± 0.09	1.37 ± 0.03	6.44 ± 0.06	3.41 ± 0.04	35.06 ± 0.26
	30	0.3	1.39 ± 0.02	1.51 ± 0.03	6.72 ± 0.02	3.50 ± 0.02	35.73 ± 0.27
		0.5	1.46 ± 0.04	1.41 ± 0.04	6.66 ± 0.05	3.47 ± 0.06	35.45 ± 0.58
	35	0.3	1.28 ± 0.05	1.67 ± 0.06	7.49 ± 0.06	3.84 ± 0.05	35.55 ± 1.14
		0.5	1.28 ± 0.01	1.68 ± 0.04	7.59 ± 0.05	3.86 ± 0.03	35.23 ± 0.75
50 ± 1.0	25	0.3	1.29 ± 0.01	1.62 ± 0.03	7.70 ± 0.03	3.76 ± 0.05	50.29 ± 0.65
		0.5	1.31 ± 0.02	1.56 ± 0.05	7.67 ± 0.06	3.73 ± 0.04	50.12 ± 0.48
	30	0.3	1.34 ± 0.04	1.56 ± 0.03	7.69 ± 0.05	3.70 ± 0.06	50.40 ± 0.79
		0.5	1.18 ± 0.05	1.79 ± 0.05	8.25 ± 0.05	3.92 ± 0.04	50.41 ± 0.90
	35	0.3	1.12 ± 0.04	2.02 ± 0.04	8.95 ± 0.09	4.42 ± 0.06	50.01 ± 0.48
		0.5	1.07 ± 0.03	2.05 ± 0.04	9.21 ± 0.03	4.54 ± 0.04	50.15 ± 0.46

Mean values ± standard deviations from triplicate analysis.

[a] D(v,0.1), D(v,0.5), D[3,2] and D(v,0.9) respectively represent 10%, 50%, Sauter mean diameter and 90% of all particles finer than this size.

3. Results and discussion

3.1. Particle size distribution of dark chocolates

Wide variations in PSD (Table 2) were observed for 18, 25, 35 and 50 µm (Fig. 1) using D_{90} values (>90% finer) that correlate with chocolate character and micrometer measurements of largest particles (Beckett, 2000). The volume histograms showed narrow (18 µm PS) and wide (25 µm PS) bimodal and narrow (35 µm PS), and wide (50 µm PS) multimodal size distributions (Fig. 1). These PSD range 18–50 µm covers the optimum minimum and maximum sizes with direct effects on texture and sensory character in finished chocolate (Beckett, 2000; Ziegler & Hogg, 1999).

Data on PSD (Table 2) gave specific surface area, mean particle volume D(v,50) and Sauter mean (D[3,2]) with increasing D_{90} particle sizes. An inverse relationship in D_{90} from 18–50 µm and specific surface area was significant with direct relationships with Sauter mean and mean particle diameters (Table 2). Largest PS (D_{90}) was directly proportional to D_{10}, D_{50} and Sauter mean (D[3,2]), and inversely proportional to specific surface area of particles. Increasing fat from 25% to 35% of samples gave significant reductions in specific surface area with increases in all other PSD parameters (Table 3), explaining that the fat content of samples during refining had a direct influence on PSD. Beckett (1999) concluded largest particle size and solids specific surface area were the two key parameters for chocolate manufacture. The former determines chocolate coarseness and textural character, the latter is associated with requirement of fat for desirable flow properties. Specific surface area has been inversely correlated with component PSD previously (Beckett, 1999; Sokmen & Gunes, 2006; Ziegler &

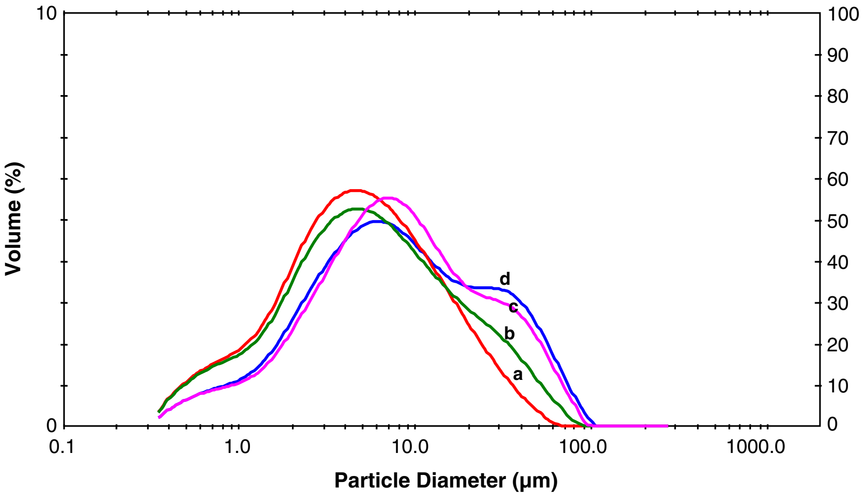

Fig. 1. Particle size distribution of dark chocolate with D_{90} of (a) 18 µm (b) 25 µm (c) 35 µm (d) 50 µm.

Table 3
ANOVA Summary of *F*-ratios from particle size distribution

Process variables	Specific surface area	D(v,0.1)	D(v,0.5)	D[3,2]
A: Particle size (D_{90})	302.77*	455.54*	1007.84*	546.01*
B: Fat	115.88*	312.87*	311.17*	228.10*
$A \times B$	4.37*	6.63*	2.59*	3.52*

* Significant *F*-ratios at $P \leqslant 0.05$.

Hogg, 1999). Fat content analyses showed values of 25 ± 1, 30 ± 1 and 35 ± 1 respectively. Moisture contents were also within the range 0.80–0.98%.

3.2. Melting properties of dark chocolate

Peak onset corresponds to the temperature at which a specific crystal form starts to melt; peak maximum, that at which melting rate is greatest; and end of melting, completion of liquefaction – all these information are related to the crystal type. Peak height, position and resolution are dependent on sample composition and crystalline state distribution (McFarlane, 1999). All the samples exhibited similar distinct single endothermic transitions between 15 and 55 °C, the range expected for chocolate melting profiles. Fig. 2 shows a typical DSC thermogram used for evaluating the melting properties of dark chocolates manufactured from varying PSD, fat and lecithin content. It recorded that heat capacity c_p gradually and consistently increased to onset temperature (T_{onset}), and then progressively increased more rapidly until peak temperature (T_{peak}), after which it decreased to the end temperature (T_{end}) indicating the chocolate was completely melted.

3.3. Effects of particle size distribution

PSD influences chocolate rheological and microstructural properties as well as texture in derived molten and tempered products (Afoakwa, Paterson, Fowler, & Vieira, in press; Afoakwa et al., 2008a). The thermogram (Fig. 3) showed similar peak shapes and sizes for dark chocolates manufactured with varying PSD, suggesting no characteristics differences in crystallinity and degree of crystallization between the products. Table 4 shows values for key DSC parameters (T_{onset}, T_{end}, T_{peak}, ΔH_{melt} and T_{index}). Increasing PS from 18 μm to 50 μm caused no significant ($P = 0.675$) changes in T_{onset}, at all fat and lecithin levels (Table 5). Values for T_{onset} were in the range of 26.5–26.6 °C in products containing 25% fat and 0.3% lecithin at 18 μm and 50 μm PS respectively. Similar insignificant differences ($P > 0.05$) in T_{onset} were noted with varying PS at all fat and lecithin levels (Table 5). Likewise, T_{peak} in products with varying PSD, fat and lecithin contents showed only marginal differences. The results (Table 4) showed that T_{peak} of products with increasing PS from 18 μm to 50 μm ranged between 32.3 °C and 32.5 °C respectively in products containing 25% fat and 0.3% lecithin, and this trend was similar at all fat and lecithin concentrations. These showed that the initiation and maximum temperatures in dark chocolate melting are independent of PSD, with mean values for T_{onset} and T_{peak} of ~26.5 °C and ~32.4 °C, respectively (Table 4). Similar non-significant differences ($P > 0.05$) in ΔH_{melt} were found between products with varying PS at all fat and lecithin contents (Table 5). Values of ΔH_{melt} in products with increasing PS from 18 μm to 50 μm ranged from 30.07 J/g to 30.62 J/g in products containing 25% fat and 0.3% lecithin, and this marginal and insignificant differences ($P > 0.05$) in trends were similar at all fat and lecithin levels. The non-significant relationship between PSD and ΔH_{melt}, implies that enthalpy of melting was similar for chocolates at all PS at specified fat and lecithin levels. This indicates that irrespective of the ingredient (fat or lecithin content) used for the formulation, dark chocolates produced with varying PS would require similar energy to complete melting.

In contrast, varying PSD had significant effects on T_{end} and T_{index} of products. Generally, there were inverse relationships between particle size and T_{end} and T_{index}, at all fat and lecithin contents (Table 4). Products with smaller PS (18 μm) at 25% fat and 0.3% leci-

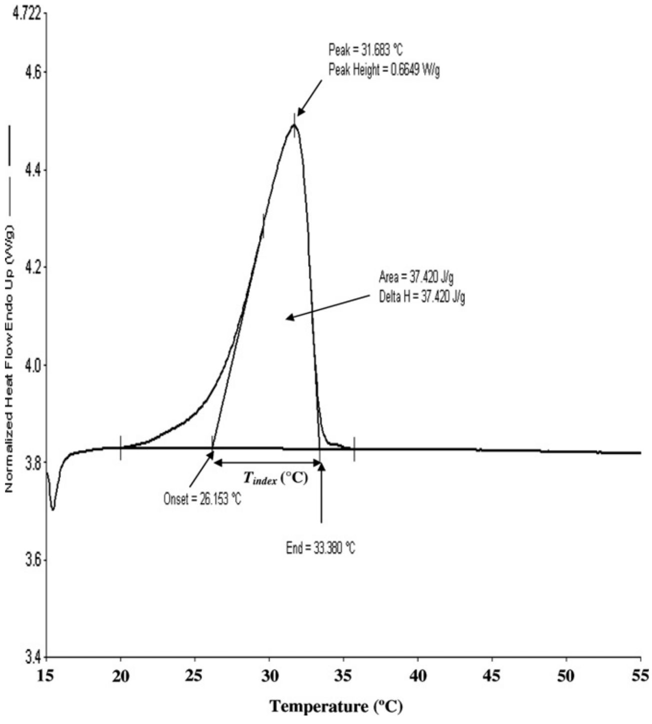

Fig. 2. Illustration of DSC thermogram used to characterize the melting properties.

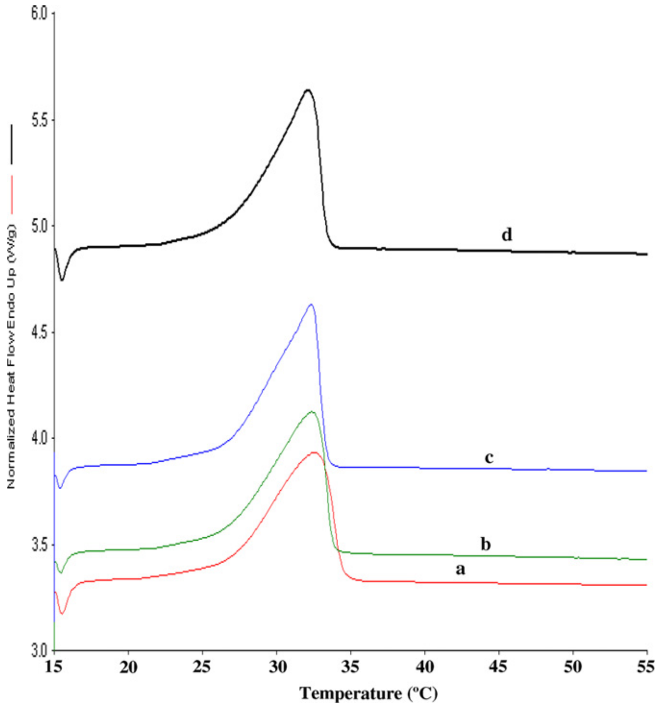

Fig. 3. Typical DSC thermograms for dark chocolate at 30% fat and 0.5% lecithin content varying PSD: (a) 18 μm, (b) 25 μm, (c) 35 μm and (d) 50 μm.

Table 4
Melting properties of dark chocolate from varying PSD, fat and lecithin content

Particle size (D_v,0.9) (μm)	Fat (%)	Lecithin (%)	Melting properties				
			T_{onset} (°C)	T_{end} (°C)	T_{index} (°C)	T_{peak} (°C)	ΔH_{melt} (J/g)
18 ± 1.0	25	0.3	26.2 ± 0.2	34.6 ± 0.3	8.4 ± 0.2	32.5 ± 0.2	30.07 ± 0.38
		0.5	26.0 ± 0.1	34.2 ± 0.4	8.2 ± 0.4	32.0 ± 0.3	28.20 ± 0.12
	30	0.3	26.5 ± 0.3	34.4 ± 0.4	7.9 ± 0.2	32.5 ± 0.4	36.52 ± 1.05
		0.5	26.3 ± 0.2	33.9 ± 0.2	7.5 ± 0.3	32.4 ± 0.3	30.02 ± 0.42
	35	0.3	26.4 ± 0.1	33.8 ± 0.2	7.4 ± 0.1	32.4 ± 0.2	44.59 ± 0.62
		0.5	26.5 ± 0.2	33.7 ± 0.3	7.2 ± 0.3	32.5 ± 0.2	43.10 ± 1.23
25 ± 1.0	25	0.3	26.3 ± 0.1	34.4 ± 0.2	8.1 ± 0.2	32.4 ± 0.3	30.52 ± 0.73
		0.5	26.3 ± 0.2	34.1 ± 0.2	7.8 ± 0.3	32.4 ± 0.3	29.08 ± 0.46
	30	0.3	26.6 ± 0.2	33.9 ± 0.3	7.3 ± 0.4	32.2 ± 0.1	37.09 ± 1.24
		0.5	26.5 ± 0.1	33.5 ± 0.2	7.0 ± 0.3	32.5 ± 0.3	32.46 ± 0.66
	35	0.3	26.6 ± 0.3	33.7 ± 0.2	7.1 ± 0.3	32.2 ± 0.1	45.01 ± 1.42
		0.5	26.5 ± 0.2	33.5 ± 0.3	7.0 ± 0.1	32.2 ± 0.1	43.41 ± 1.28
35 ± 1.0	25	0.3	26.3 ± 0.1	34.2 ± 0.5	7.9 ± 0.2	32.6 ± 0.3	30.68 ± 0.28
		0.5	26.4 ± 0.1	34.0 ± 0.4	7.6 ± 0.3	32.4 ± 0.3	28.60 ± 0.34
	30	0.3	26.6 ± 0.3	33.8 ± 0.2	7.2 ± 0.2	32.4 ± 0.2	37.19 ± 0.94
		0.5	26.7 ± 0.3	33.7 ± 0.1	7.0 ± 0.1	32.6 ± 0.2	34.01 ± 0.63
	35	0.3	26.8 ± 0.4	33.6 ± 0.3	6.8 ± 0.3	32.8 ± 0.3	45.15 ± 1.05
		0.5	26.9 ± 0.4	33.4 ± 0.2	6.5 ± 0.1	32.2 ± 0.3	42.79 ± 0.84
50 ± 1.0	25	0.3	26.6 ± 0.2	34.0 ± 0.4	7.4 ± 0.5	32.3 ± 0.2	30.62 ± 0.53
		0.5	26.7 ± 0.1	33.9 ± 0.2	7.2 ± 0.3	32.4 ± 0.2	28.62 ± 0.23
	30	0.3	26.8 ± 0.3	33.5 ± 0.3	6.7 ± 0.3	32.9 ± 0.4	37.29 ± 0.15
		0.5	26.7 ± 0.3	33.3 ± 0.3	6.6 ± 0.2	32.2 ± 0.2	33.25 ± 1.05
	35	0.3	26.8 ± 0.4	33.2 ± 0.1	6.4 ± 0.1	32.7 ± 0.3	45.40 ± 0.87
		0.5	26.8 ± 0.3	33.0 ± 0.4	6.2 ± 0.4	32.4 ± 0.1	43.43 ± 0.46

Mean values from triplicate analysis ± standard deviation.

Table 5
ANOVA Summary of *F*-values of the melting properties

Process variables	T_{onset} (°C)	T_{end} (°C)	T_{index} (°C)	T_{peak} (°C)	ΔH_{melt} (J/g)
A: Particle size	1.53	11.00*	199.84*	0.84	121.52
B: Fat	12.54	32.32*	2330.26*	0.23	3535.29*
C: Lecithin	2.43	18.18*	148.84*	3.13	376.74*
$A \times B$	0.89	2.89*	99.22*	0.49	4.22
$A \times C$	2.16	2.39	31.69*	0.91	1.46
$B \times C$	2.45	0.53	198.58*	0.66	401.87*
$A \times B \times C$	1.73	1.01	19.76*	2.17	3.73

* Significant *F*-ratios at $P \leqslant 0.05$.

thin content had T_{end} value of 34.6 °C, whilst those with 50 μm had 34.0 °C, representing a difference of 0.6 °C. Similar marginal but significant ($P < 0.05$) decreasing trends in T_{end} were observed at all fat and lecithin levels (Table 5), suggesting that dark chocolates with larger PS (50 μm) require slightly lower temperatures to complete melting than their corresponding smaller PS (18 μm) products. However, T_{end} values in all the products were in the range 33.0 to 34.6 °C indicating all samples had similar Form V (ß$_2$) polymorphic stability. A similar inverse relationship was observed between T_{index} and PSD. The data (Table 4) showed that increasing PS for 18 μm to 50 μm in chocolates containing 25% fat and 0.3% lecithin caused significant ($P < 0.05$) reductions in T_{index} from 8.4 °C to 7.4 °C, respectively. ANOVA showed significant ($P < 0.05$) influence of PSD on T_{end} and T_{index} with significant interactions for fat and lecithin contents (Table 5). Multiple range test revealed significant differences ($P = 0.001$) between T_{end} of products containing 18 μm, 35 μm and 50 μm, indicating that chocolates with finer particles would take relatively longer time to melt than their corresponding products with larger particles, suggesting their possible relationships with the relative strengths of the inter-particle aggregations and flocculation in the different products. Chocolates with smaller PSD (D$_{90}$, 18μm) have been found to contain higher particle-to-particle strengths with resultant increases in hardness (texture) than their corresponding larger PSD (D$_{90}$, 50 μm) (Afoakwa et al., in press; Do, Hargreaves, Wolf, Hort, & Mitchell, 2007; Afoakwa, Paterson, Fowler, & Vieira, 2008d). Do et al. (2007) also noted that decreases in the amount of particle aggregation and structure build up in flow affect chocolate melt down, suggesting that in its crystallized state, the particle skeleton of chocolates with larger PS is less interconnected, providing less resistance to breakage and melt down. This knowledge is important as it provides information on likely oral melting behaviour with an impact on temporal components of flavour release and also oral epithelial sensation. Beckett (1999) and Ziegler et al. (2001) noted that variations in PS might influence melt, flavour, colour and gloss of chocolates.

3.4. Effects of fat content

Data from the DSC (Fig. 4) indicated that varying fat content produced changes in crystallinity and melting properties observed in the differences in their peak widths. This suggests that the fat content in dark chocolates during manufacture influences the degree of crystallinity and crystal size distribution (CSD) of their corresponding tempered products. Lonchampt and Hartel (2004) also noted that amount and composition of fat in chocolate production had unpredictable effects on crystal size, and polymorphism and crystallization rate in products. Hartel (2001) concluded distribution of crystal sizes in foods play key roles in final product quality, defined by total and specific characteristics of the crystalline material. Number of crystals and range of sizes, shapes, and polymorphic stability, as well as arrangements in network structures dictates mechanical and rheological properties. Knowledge and control of CSD can be important for optimising processing conditions.

Results from the DSC data on T_{onset}, T_{end}, T_{peak}, ΔH_{melt} and T_{index} with varying fat content are as shown on Table 4. ANOVA and multiple mean comparisons showed no significant difference ($P > 0.05$) for T_{onset} and T_{peak} in chocolates with different fat contents (Table 5), implying limited influence on temperatures for onset and peak melting. There were significant differences ($P < 0.05$) among T_{end}, T_{index} and ΔH_{melt} (Table 5). Increasing fat content from 25% to 35% caused consistent reductions in T_{end} from 34.6 °C to 33.8 °C

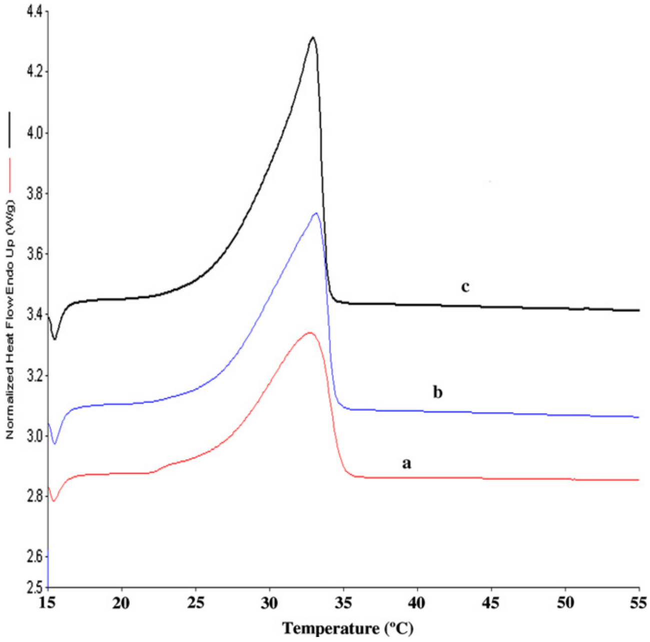

Fig. 4. Typical DSC thermograms for dark chocolate at 18 μm PS and 0.5% lecithin content with varying fat content: (a) 25%, (b) 30%, (c) 35%.

in products containing 18μm PS and 0.3% lecithin level. Similar marginal but significant ($P < 0.05$) decreasing trends in T_{end} with increasing fat content were noted at all PS and lecithin concentrations (Table 5). These suggest that low fat (25%) chocolates completed melting at higher temperatures than those with more fat (30–35%). Likewise, increasing fat content caused consistent decreases in T_{index} of products, suggesting an inverse relationship of T_{index} with fat content (Table 4). Products with lower (25%) fat content, 18 μm PS and 0.3% lecithin had T_{index} of 8.4 °C and this reduced consistently with from 7.9 °C and 7.4 °C, respectively with increasing fat content to 30% and 35%. Similar reducing trends in T_{index} were noted at all PS and lecithin levels. These explain that lower fat chocolates required longer time to melt than similar products with higher fat contents, again with a likely impact on behaviour during consumption. Lower melting duration in high fat chocolates can be attributed to reductions in inter-particle interactions and increased free-moving plastic flow, possibly related to yield value of products (Afoakwa et al., in press; Beckett, 2000; Do et al., 2007). Fat fills voids between particles in molten chocolate and reduces resistance to flow, with a direct relationship between fat content and ΔH_{melt}, independent of particle size. This implies that enthalpy is reduced in products of lower fat contents. From ANOVA and multiple comparison tests, fat content had the greatest influence on melting characteristics in these chocolates (Table 5).

3.5. Effects of lecithin

The amphiphilic nature of lecithin promotes deagglomeration with effects on physical properties (Beckett, 2000; Dhonsi & Stapley, 2006; Lonchampt & Hartel, 2004; Talbot, 1999). Fig. 5 shows typical DSC thermograms for dark chocolate manufactured from varying lecithin content (0.3% and 0.5%) at 18 μm PS and 30% fat content. The thermograms (Fig. 5) revealed the effect of lecithin concentration on crystallinity of products. The differences observed in peak widths suggest a moderate reducing effect of lecithin addition on degree of crystallinity, with consequential effect on some melting properties of products. Earlier studies reported that lecithin content had significant ($P < 0.001$) effect on the rheological and textural properties of dark chocolates with significance among the interactions with PS and fat content (Afoakwa et al., 2008a, 2008b). Table 4 shows the results from the DSC data on T_{onset}. T_{end}, T_{peak}, ΔH_{melt} and T_{index} with varying lecithin. Analysis of the values deduced from ANOVA and multiple mean comparisons showed no significant difference ($P > 0.05$) between T_{onset} and T_{peak} for the different lecithin concentrations, but significant differences ($P < 0.05$) among T_{end}, T_{index} and ΔH_{melt} (Table 5). Both Johansson and Bergenstahl (1992), and Lonchampt and Hartel (2004) reported lecithin influences sugar coating, fat crystallization, crystal growth, polymorphism and oil migration, but has limited effect on solid fat content.

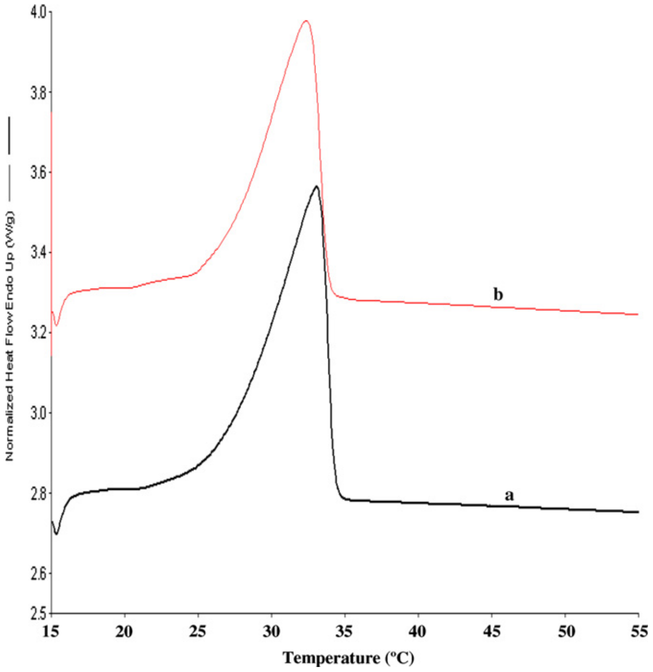

Fig. 5. Typical DSC thermograms for dark chocolate with varying lecithin content showing (a) 0.3%, (b) 0.5% at 18 μm PS and 30% fat content.

Generally, there were inverse relationships between T_{end} and T_{index}, independent of particle size and fat content (Table 4). Thermograms (Fig. 5) showed increasing lecithin content influenced crystal dimensions and melting character in products. Increasing lecithin content of products from 0.3% to 0.5% caused marginal but significant differences in T_{end} of products, noticeable at all PS and fat concentrations (Table 4). The T_{end} values were between 33 and 34 °C, an indication that the crystallizations were in ßV polymorph, imply limited influence under normal tempering conditions. On the other hand, T_{index} decreased consistently with increasing lecithin content, suggesting that products containing lower lecithin levels (0.3%) might require relatively longer residence time to melt than those of their corresponding products with higher lecithin levels (0.5%), with likely impact on the melting residence time of products during consumption. The lower melting index (duration) observed with products containing higher lecithin levels might be attributed to sugar coating ability of lecithin during processing, and thus reducing their inter-particle interaction to induce chocolate melting properties. Dhonsi and Stapley (2006) reported lecithin migrates to sugar/fat interfaces and coats sugar crystals, influencing rheology and aiding dispersion of sugar crystals in the continuous phases. Chevalley (1999) suggested lecithin forms a monolayer on sugar particle surfaces allowing greater mobility in suspensions while increasing fat spreadability. Increasing lecithin content caused significant and consistent decreases in ΔH_{melt}, trends noted at all PS and fat content (Table 4). This implies that products with relatively higher lecithin content would require lower enthalpies to melt than those of their corresponding products with lower lecithin levels. Significant ($P < 0.05$) interactions were observed among all the processing parameters. Multiple comparison test revealed that fat content had the greatest effect on T_{index} and ΔH_{melt} of dark chocolates followed by lecithin content and then PSD (Table 5).

4. Conclusion

Variations in PSD, fat and lecithin content during dark chocolate manufacture influence to varying levels, the degree of crystallinity and melting properties (T_{end}, T_{index} and ΔH_{melt}) of their derived products. Changes in PSD had no effect on the crystallinity of products. Increasing fat content resulted in consistent increases in crystallinity of products formed during tempering. Products containing 25% fat had the smallest crystal size, followed by those with 30%, with the 35% fat having the largest crystal size, causing significant changes in T_{end}, T_{index} and ΔH_{melt} of products. Similarly, increasing lecithin content from 0.3% to 0.5% moderately reduced the crystallinity of products with significant variations in T_{end}, T_{index} and ΔH_{melt} of products. Neither PSD, fat nor lecithin content influenced initiation (T_{onset}) or maximum (T_{peak}) melting temperatures. Chocolates with finer particles, higher fat and lower lecithin contents, took longer and higher temperatures to complete melting than their corresponding products with larger PS, lower fat and higher lecithin content. This suggest that for chocolate of the same composition, processed under identical conditions, the PSD of the suspended non-fat solid, fat and lecithin contents play important roles in determining their melting behaviour. These findings would have application in defining chocolate quality as the nature of crystalline material, dimensions of crystals and polymorphic stability dictate the mechanical and rheological properties of chocolate products.

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