Original article

Microstructure and mechanical properties related to particle size distribution and composition in dark chocolate

Emmanuel Ohene Afoakwa,[1,2]* Alistair Paterson,[1] Mark Fowler[2] & Joselio Vieira[2]

1 Centre for Food Quality, SIPBS, University of Strathclyde, Royal College Building, 204 George Street, Glasgow G1 1XW, UK
2 Nestle Product Technology Centre York, P.O. Box 204, Haxby Road, York YO91 1XY, UK

(Received 22 June 2007; Accepted in revised form 5 September 2007)

Summary Composition in dark chocolate was varied and the effects determined on microstructure, using light microscopy, and mechanical properties of molten and tempered chocolates, using a TA.HD Plus Texture Analyser. Compositional parameters were particle size distribution (PSD) (D_{90} of 18, 25, 35 and 50 μm), fat (25%, 30% and 35%) and lecithin (0.3% and 0.5%) contents. Micrographs revealed wide variations in sugar crystalline network structure and inter-particle interaction strengths related to PSD and fat level. Samples containing 25% fat had more crystal agglomerates, well flocculated with greater particle-to-particle interaction strengths than those with higher (30% and 35%) fat contents. Increasing the D_{90} to 35–50 μm caused broadening of the PSD, with particles becoming coarser, which were similar at all fat levels. Mechanical analysis showed that PSD, fat and lecithin content significantly influenced firmness of molten chocolate and hardness of solid (tempered) chocolate with significant interactions among factors. Particle size was inversely correlated with firmness (1235–173 g) and hardness (7062–5546 g). Greatest effect of PSD was with 25% fat and 0.3% lecithin. With higher fat and lecithin contents, the PSD influence was reduced. It was concluded that PSD, fat and lecithin contents and their interactions were central to mechanical properties of dark chocolates.

Keywords Chocolate, fat content, lecithin, mechanical properties, microstructure, particle size distribution, texture.

Introduction

Dark chocolate has high concentrations (65–75% by vol.) of suspended solid particles comprising of sugar crystals and cocoa solids, dispersed in a continuous matrix of cocoa butter. The materials used have physical characteristics that can vary significantly within a relatively small temperature range. During processing, mixtures of sugar and cocoa liquor of overall fat content of 25–35% are refined to particle size (PS) < 30 μm typically by combination of two- and five-roll refiners (Beckett, 2000) that not only effect PS reduction but also break agglomerates and distribute lipid-coated particles through the continuous phase.

Final PS critically influences chocolate rheological and sensory properties. Particle size distribution (PSD) and composition of other ingredients, notably cocoa butter in continuous phases, determines the character in finished dark chocolate (Afoakwa *et al*., 2007a).

Chocolate texture appears improved by a bimodal distribution of particles with a small proportion of up to 65 μm but most lower at < 35 μm although these values are influenced by product type and composition (Beckett, 1999; Awua, 2002). Textural properties constitute one of the three main acceptability factors used by consumers to evaluate quality, the others being appearance and flavour. Texture is important because the human brain has evolved critical evaluation of mechanical properties and chocolate, like most food products (Lillford, 1991; Bourne, 2002), can therefore be accepted or rejected on the basis of this quality factor.

Microstructure is a fundamental variable influencing transport phenomenon and physical properties of foods determining perceived quality in terms of mechanical and sensorial attributes (Kulozik *et al*., 2003). Consequently, microstructure is important for manipulation or regulation of texture and related to composition and physical forces influencing mechanical properties (van Marle *et al*., 1997; Afoakwa & Sefa-Dedeh, 2002). Varela *et al*. (2007) noted that successful delivery in new product development requires understanding of factors that influence texture. Improvement on the quality of existing foods and new product formulations require interventions at microscopic level. Most

*Correspondent: E-mail: e.afoakwa@strath.ac.uk

doi:10.1111/j.1365-2621.2007.01677.x

elements that critically participate in transport properties, physical and rheological behaviours, textural and sensorial characters are < 100 μm in diameter (Aguilera, 2005). Bourne (2002) concluded texture is derived from food structure, and relationship between microstructure and rheological and textural properties has been studied (Kulozik *et al*., 2003; Pereira *et al*., 2003; Remeuf *et al*., 2003; Braipson-Danthine & Deroanne, 2004; Sandoval-Castilla *et al*., 2004; Christiansen *et al*., 2006; Baixauli *et al*., 2007). However, there is limited information on relationship between microstructure and mechanical properties of finished dark chocolates, specifically on how PSD and composition affect the microstructure and mechanical properties. Such information may lead to improvements in quality assurance, as well as process and product design during chocolate manufacture. The objective of this work was to study the influence of PSD and composition on dark chocolate microstructure and how it relates to the mechanical properties of finished chocolates.

Materials and methods

Materials

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

Experimental design

Three experimental variables used in this study were PSD, fat and lecithin contents. Refiner temperature and pressure, and conching time and temperature, and added cocoa butter (5%) were held constant. A $4 \times 3 \times 2$ factorial experimental design was used:

1 PSD (D_{90}): 18, 25, 35 and 50 μm
2 Fat content: 25%, 30% and 35%
3 Lecithin content: 0.3% and 0.5%

Preparation of chocolate samples

A typical dark chocolate recipe was used, which contained cocoa liquor, sugar, cocoa butter and emulsifier (lecithin) (Table 1). Chocolates were formulated to contain total fat contents of 25–35% (w/w) and a minimum of 35% total cocoa: composition specified in standards of identity for dark chocolate of Codex Revised Standard (2003) on Chocolate and Chocolate Products, and Directive 2000/36/EC on Cocoa Products and Chocolate (European Commission Directive, 2000).

Table 1 Recipes used for the formulation of the dark chocolate

Ingredient (%)	25% Fat (% by wt)		30% Fat (% by wt)		35% Fat (% by wt)	
Sucrose	58.8	59.0	49.7	49.9	40.7	40.8
Cocoa liquor	35.9	35.5	45.0	44.6	54.0	53.7
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

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 speed for 3 min, then using a three-roll refiner (Model SDX 600, Buhler Ltd., CH-9240 Uzwil, Germany) to a specified PS (D_{90}: 18 ± 1, 25 ± 1, 35 ± 1 and 50 ± 1 μm) by conducting PS analysis, during refining, to ensure D_{90} values. Refined chocolates were placed in plastic containers and conditioned under high temperature environment (50–55 °C) for 24 h to ensure total fat melting within the chocolate mass prior to conching in a Lipp Conche (Model IMC-E10, Boveristr 40–42, D-68309, Mannheim, Germany) at low speed for 3.5 h at 60 °C. All the lecithin and cocoa butter (5%) were then added and conching continued at high speed for further 30 min to ensure adequate mixing and liquefaction. Samples were stored in sealed plastic containers at ambient temperature (20–22 °C) and moisture and fat contents determined using Karl Fischer (ICA, 1988) and Soxhlet methods (ICA, 1990).

Samples for hardness measurements were incubated at 50 °C for 4 h for melting prior to tempering. The molten chocolate was tempered using a laboratory scale mini-temperer (Model AMK 10, Aasted Mikroverk ApS, Farum, Denmark) and precrystallisation was measured using an Exotherm 7400 tempermeter (Systech Analytics SA, Neuchâtel, Switzerland) to ensure the chocolate has temper value (slope) of 0 ± 0.2 TU. The tempered chocolate was then moulded using plastic moulds of dimension 80 mm length, 20 mm breadth, and 8 mm height, and allowed to cool in a refrigerator (5 °C) for 2 h before de-moulding. The moulded finished chocolates were packed onto plastic trays and conditioned at ambient temperature (20 ± 2 °C) for 2 weeks before analysed.

Determination of particle size distribution

Measurement of PSD was made using the Malvern MasterSizer® Micro Laser Diffraction Particle Size Analyzer equipped with small sample dispersion unit (RI 1.590) (Malvern Instrument Ltd., Malvern, UK). About 0.2 g refined chocolate was dispersed in vegetable

oil (RI 1.450) at ambient temperature (20–22 °C) until an obscuration of 0.2 was obtained and ultrasonic dispersion (2 min) ensured particles were independently dispersed and stirring kept particles dispersed during measurement. Size distribution was determined as relative volume of particles in size bands and presented as size distribution curve and statistics (Malvern Master-Sizer® Micro Software version 2.19).

Microstructure analysis

Microstructures were observed using a high resolution polarised light microscope (Olympus Optical U-PMTVC, Tokyo, Japan). One drop (10 μL) of molten chocolate (previously heated at 55 °C to destroy crystal memory) was placed on a preheated (55 °C) glass slide. A cover slip was carefully placed over the sample, parallel to the plane of the slide and centred to ensure sample thickness was uniform. Specimens were observed immediately at 20× magnification and micrographs (black and white images) were captured using a digital camera (Model 2.1 Rev 1; Polaroid Corporation, NY, USA) and observed using Adobe Photoshop (version CS2; Adobe Systems Inc., NJ, USA).

Mechanical properties

Firmness of the molten chocolates were determined using a TA.HD Plus Texture Analyser (Stable Micro Systems, Haslemere, Surrey, UK), equipped with a back extrusion rig and a compression disc of 35 mm diameter attached to an extension bar using 50-kg load cell (Fig. 1a). Samples were incubated at 50 °C for 75 min for melting and transferred to a standard back extrusion container (50 mm diameter) immediately. Work done in back extruding 100 mL chocolate was determined by measuring force in compression. The test was replicated eight times at a pretest speed of 1.0 mm s^{-1}, test speed of 5.0 m s^{-1} at a distance of 50 mm above the top of the sample, penetrated to a depth of 30 mm, and returned to starting position. The plunger was cleaned after each measurement. Temperature of the chocolate samples was controlled during the experiment using Haake K20 Thermo-regulator (Thermo Electron Corp., Karlsruhe, Germany). Mean values were recorded and a force–time curve obtained using XT.RA Dimension, Exponent 32 software (Stable Micro Systems). Maximum compression force during the extrusion thrust was denoted as firmness of the sample.

Hardness of the solid tempered chocolate was measured using a TA.HD Plus Texture Analyser with a penetration probe (needle P/2) on an extension bar, a 50-kg load cell and a sample platform (Fig. 1b). A puncture test determined maximum penetration force through a standard sample: length, 80 mm; breadth, 20 mm; height, 8 mm. Tests were replicated eight times at a pretest speed of 1.0 mm s^{-1}, test of 2.0 mm s^{-1}, through penetration depth of 5 mm at 20 °C, and mean values recorded. Maximum compression force in penetration was denoted as sample hardness.

Statistical analysis

Statgraphics Plus 4.1 (Graphics Software System, STCC Inc., Rockville, USA) was employed. Firmness and hardness values were analysed using analysis of variance (ANOVA) and multiple comparison tests to determine the effects of PSD, fat and lecithin contents on the studied parameters and their interactions. Fisher's l.s.d. multiple comparison procedure was applied to compare the

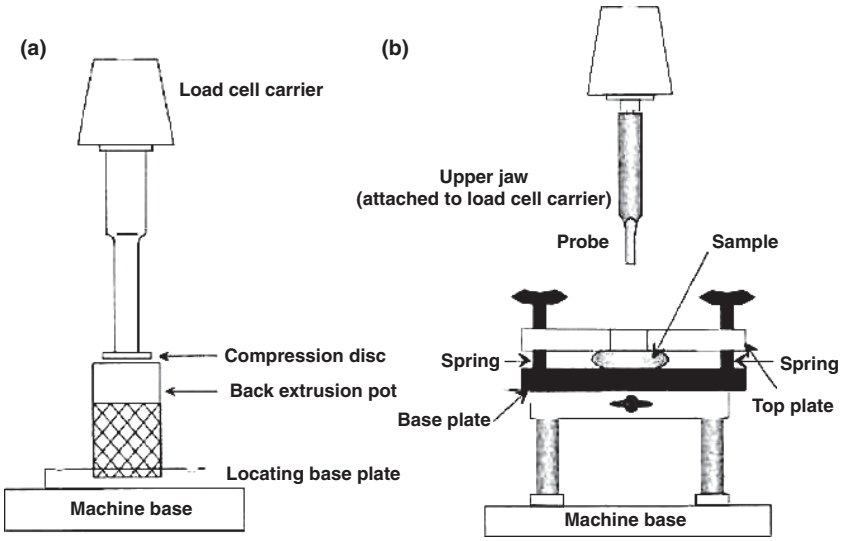

Figure 1 Back extrusion rig (a) and puncture test rig (b) used for texture measurements of molten and solid chocolates, respectively.

treatment means. Significance was at 5% probability level ($P \leq 0.05$).

Results and discussion

Particle size distribution of the dark chocolates

Wide variations in PSD (Table 2) were observed for 18, 25, 35 and 50 μm (Fig. 2) using D_{90} values (>90% finer), which correlate with chocolate sensory character and with micrometer measurements of largest particles (Beckett, 2000). The volume histograms showed size distributions ranging from narrow (18 μm PS, Fig. 2) and wide (25 μm PS, Fig. 2) bimodal to narrow (35 μm PS, Fig. 2) and wide (50 μm PS, Fig. 2) multimodal. These PSD ranging from fine (18 μm) to coarse particles (50 μm) cover optimum, minimum and maximum sizes with direct effects on rheological, textural and sensory qualities in chocolate (Ziegler & Hogg, 1999; Beckett, 2003; Afoakwa *et al.*, 2007b).

Data from the PSD (Table 2) showed variations in specific surface area, D(v,10 or 10% of all particles finer than this size), mean particle volume D(v,50 or 50% of all particles finer than this size), Sauter mean (D[3,2]) and mean particle (D[4,3]) diameters with increasing D_{90} PS. There was a significant inverse relationship in D_{90} from 18 to 50 μm led and specific surface area, with direct relationships with Sauter mean and mean particle diameters (Table 2). Thus, largest PS (D_{90}) is directly

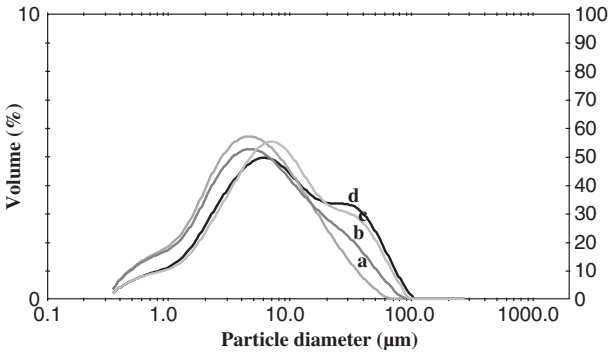

Figure 2 Particle size distribution of dark chocolate with D_{90} of (a) 18 μm (b) 25 μm (c) 35 μm (d) 50 μm.

Table 2 Particle size distribution of the dark chocolates

PS *d*(0.9)[a] (μm)	Fat content (%)	Lecithin (%)	PSD					
			Specific surface area ($m^2\ g^{-1}$)	D(v,0.1)[a] (μm)	D(v,0.5)[a] (μm)	D[3,2][a] (μm)	D[4,3][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	7.84 ± 0.08	18.53 ± 0.19
		0.5	1.95 ± 0.05	1.06 ± 0.04	4.62 ± 0.09	2.56 ± 0.02	7.76 ± 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	7.91 ± 0.05	18.76 ± 0.46
		0.5	1.93 ± 0.01	1.01 ± 0.03	4.85 ± 0.04	2.56 ± 0.02	8.13 ± 0.06	18.67 ± 0.50
	35	0.3	1.53 ± 0.03	1.40 ± 0.05	6.04 ± 0.06	3.12 ± 0.05	8.47 ± 0.03	18.70 ± 0.24
		0.5	1.55 ± 0.05	1.37 ± 0.03	6.01 ± 0.05	3.22 ± 0.03	8.40 ± 0.05	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	10.27 ± 0.07	25.47 ± 0.04
		0.5	1.61 ± 0.02	1.25 ± 0.02	5.79 ± 0.07	3.01 ± 0.04	10.28 ± 0.03	25.73 ± 0.57
	30	0.3	1.57 ± 0.02	1.31 ± 0.02	5.92 ± 0.06	3.06 ± 0.03	10.28 ± 0.14	25.30 ± 0.65
		0.5	1.58 ± 0.02	1.17 ± 0.03	5.65 ± 0.04	2.98 ± 0.02	10.35 ± 0.05	25.76 ± 0.40
	35	0.3	1.46 ± 0.02	1.44 ± 0.05	6.60 ± 0.06	3.40 ± 0.06	10.39 ± 0.08	25.10 ± 0.32
		0.5	1.44 ± 0.03	1.46 ± 0.03	6.65 ± 0.03	3.46 ± 0.04	10.38 ± 0.06	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	13.31 ± 0.08	35.98 ± 0.14
		0.5	1.48 ± 0.09	1.37 ± 0.03	6.44 ± 0.06	3.41 ± 0.04	13.19 ± 0.12	35.06 ± 0.26
	30	0.3	1.39 ± 0.02	1.51 ± 0.03	6.72 ± 0.02	3.50 ± 0.02	13.24 ± 0.07	35.73 ± 0.27
		0.5	1.46 ± 0.04	1.41 ± 0.04	6.66 ± 0.05	3.47 ± 0.06	13.47 ± 0.05	35.45 ± 0.58
	35	0.3	1.28 ± 0.05	1.67 ± 0.06	7.49 ± 0.06	3.84 ± 0.05	13.56 ± 0.09	35.55 ± 1.14
		0.5	1.28 ± 0.01	1.68 ± 0.04	7.59 ± 0.05	3.86 ± 0.03	13.53 ± 0.08	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	17.58 ± 0.05	50.29 ± 0.65
		0.5	1.31 ± 0.02	1.56 ± 0.05	7.67 ± 0.06	3.73 ± 0.04	17.33 ± 0.16	50.12 ± 0.48
	30	0.3	1.34 ± 0.04	1.56 ± 0.03	7.69 ± 0.05	3.70 ± 0.06	17.52 ± 0.06	50.40 ± 0.79
		0.5	1.18 ± 0.05	1.79 ± 0.05	8.25 ± 0.05	3.92 ± 0.04	17.63 ± 0.09	50.41 ± 0.90
	35	0.3	1.12 ± 0.04	2.02 ± 0.04	8.95 ± 0.09	4.42 ± 0.06	17.72 ± 0.05	50.01 ± 0.48
		0.5	1.07 ± 0.03	2.05 ± 0.04	9.21 ± 0.03	4.54 ± 0.04	18.08 ± 0.28	50.15 ± 0.46

Mean values ± SD from triplicate analysis.
[a]D(v,0.1), D(v,0.5), D[3,2], D[4,3] and D(v,0.9) represent 10%, 50%, Sauter mean diameter, mean particle diameter and 90% of all particles finer than this size, respectively.

Table 3 ANOVA summary of *F*-ratios from PSD

Process variables	Specific surface area	D(v,0.1)	D(v,0.5)[a]	D[3,2][a]	D[4,3][a]
PS (D_{90})	302.77*	455.54*	1007.84*	546.01*	8388.61*
Fat	115.88*	312.87*	311.17*	228.10*	23.21*
Interactions					
PS × fat	4.37*	6.63*	2.59*	3.52*	2.08

Mean values ± SD from triplicate analysis.
*Significant *F*-ratios at $P \leq 0.05$.
[a]D(v,0.1), D(v,0.5), D[3,2] and D[4,3] represent 10%, 50%, Sauter mean diameter and mean particle diameter of all particles finer than this size, respectively.

proportional to the D_{10}, D_{50}, Sauter mean (D[3,2]) and mean particle diameters (D[4,3]), and inversely proportional to the specific surface area of particles. Similarly, increasing fat content from 25% to 35% led to significant reductions in specific surface area with consequential increase in all the other PSD parameters (Table 3), suggesting fat content during refining has a direct influence on PSD.

Beckett (1999) concluded largest PS and solids specific surface area are the two key parameters for chocolate manufacture. Largest particle diameter determines chocolate coarseness and textural character and specific surface area is associated with requirement of fat to obtain desirable flow properties. Specific surface area has been inversely correlated with component PSD in chocolate (Beckett, 1999; Sokmen & Gunes, 2006). Fat content analyses showed that the levels were within ranges of 25 ± 1, 30 ± 1 and 35 ± 1, respectively. Moisture contents were also within the range 0.80–0.98%.

Microstructural properties of molten dark chocolate

Light microscopy was used to characterise the variations in sugar crystalline network, particle-particle interaction strengths and particle-fat phase behaviour from molten dark chocolate with varying PSD and fat concentration. Micrographs (Figs 3–5) showed clear variations in microstructure among samples from different PSD (Table 2) and fat contents.

Samples containing 25% fat showed high solids packing intensity with extensive particle-particle interaction strengths at all PS (Fig. 3a–d) so that the crystalline network was disperse with large specific surface area (Table 2), and with smaller particles filling the spaces between the larger; the result was a high bed density. At lower PS (18 μm), particle number increased in parallel with points of contact, particle-particle interactions and greater packing ability. The increased particle-particle interactions, amount of and specific surface area, and mean particle diameter resulted in

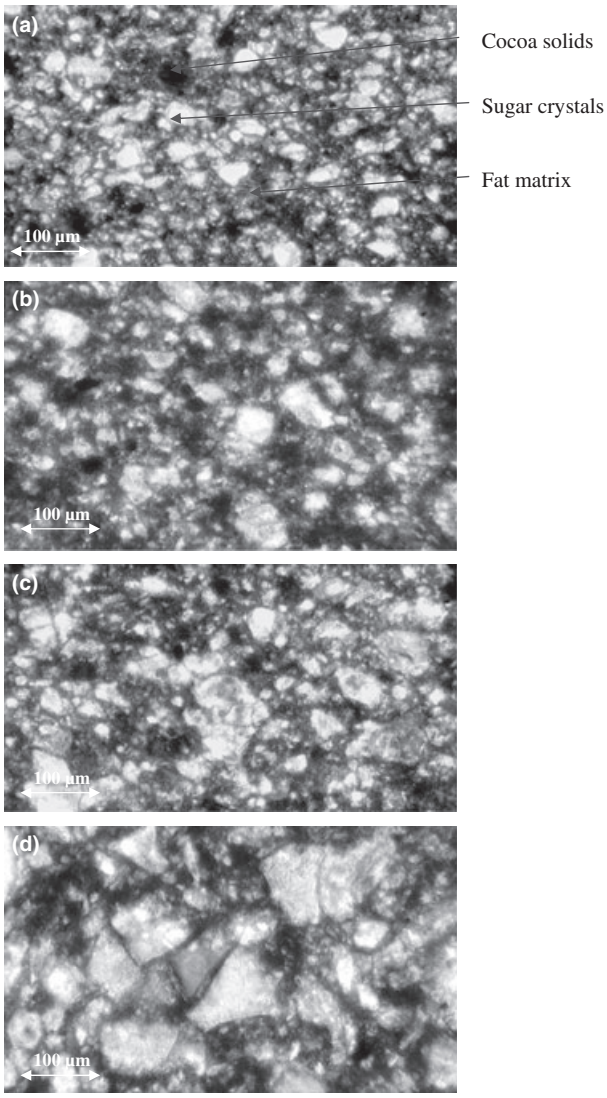

Figure 3 Microstructure of dark chocolate containing 25% fat with PS (D_{90}) of (a) 18 μm (b) 25 μm (c) 35 μm (d) 50 μm.

flocculation and agglomeration, forming spanning stress bearing paths, restricting mobility and compartmentalisation of the matrix (Fig. 3a and b).

With PS ranging between 35 and 50 μm, particles were coarser, leading to PSD broadening into multimodal distributions (Fig. 2), that reduced solid loading, and specific surface area (Table 2). As PS were increased, the packing ability of solids became restricted, leading to fewer particle-particle interactions (Fig. 3c and d). Prasad *et al.* (2003) also noted rates of formation and disruption of aggregates were functions of flow induced shear stresses, particle volume fraction and interaction energy. The observed greater flocculation and agglomeration of sugar crystals network and

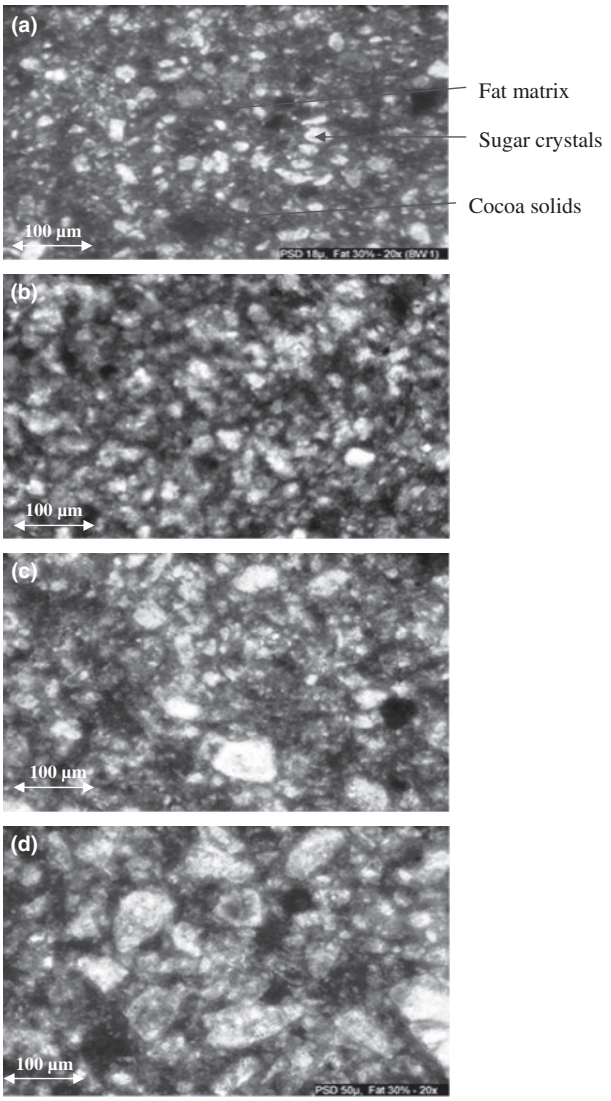

Figure 4 Microstructure of dark chocolate containing 30% fat with PS (D_{90}) of (a) 18 µm (b) 25 µm (c) 35 µm (d) 50 µm.

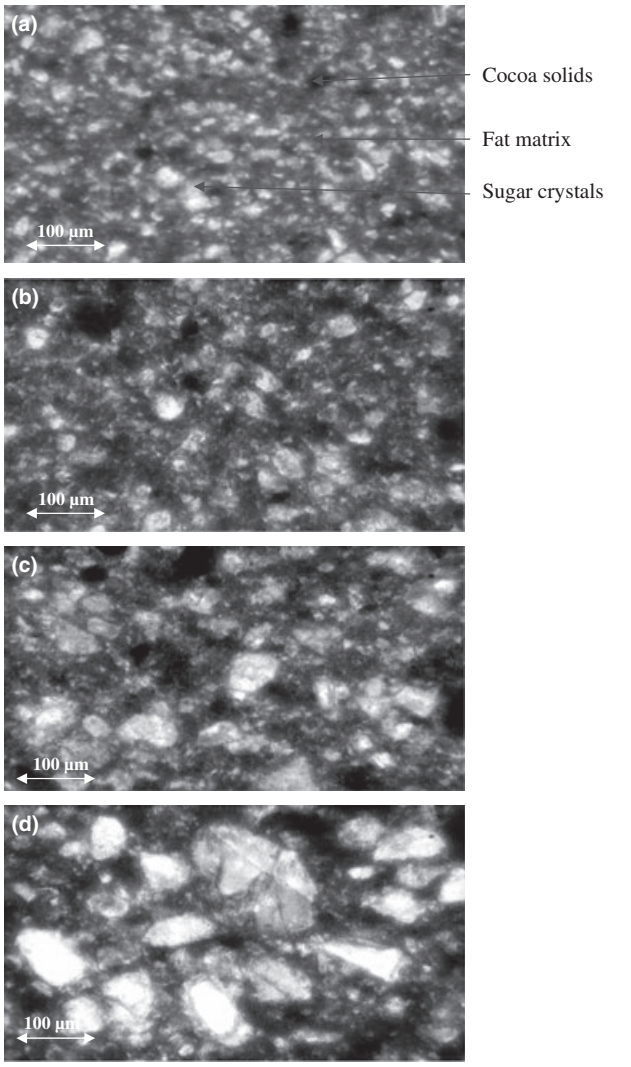

Figure 5 Microstructure of dark chocolate containing 35% fat with PS (D_{90}) of (a) 18 µm (b) 25 µm (c) 35 µm (d) 50 µm.

high inter-particle interaction with 25% fat, explained higher rheological (Beckett, 1999; Chevalley, 1999) and mechanical properties (firmness and hardness) observed with low fat chocolates. Servais *et al*. (2004) noted that yield stress depended on amount of small particles (specific surface area) and interactions, and originated in mechanical (friction) and chemical interactions between particles. Prasad *et al*. (2003) concluded yield value was determined by inter-particle contacts, with a consequent linear dependence on mean PS or, more accurately, on specific surface area.

With higher fat (Figs 4 and 5), there were less dense sugar crystalline networks and reduced particle–particle interactions, with more open structures and void spaces between the crystals. This could be related to the higher fat content in the suspension, which tends to wet the matrix with fat thereby opening up the fat phase, as fat filled the voids within the crystal network. Beckett (1999) attributed this to the free-moving lubricating plastic flow, more connected with forces between solid particles. Fat fills spaces between solid particles in molten chocolate and reduces resistance to flow, with greatest effect at lower PS. However, the microstructure of D_{90} PS >35 µm shows very large spherical and dispersed crystalline grains within the suspension (Figs 3c and d, 4c and d, 5c and d), that is suggested to be the cause of grittiness associated with chocolates processed with $D_{90} > 35$ µm (Beckett, 2000).

The qualitative structural information illustrated by the micrographs thus provides a mechanistic explanation for quantitative differences in rheological, textural and sensory character in dark chocolates with varying PSD and fat content. This knowledge can improve the quality of models developed to optimise PSD in influencing flow, textural and sensory character in chocolate. Release of structural mobility and compartmentalisation can be achieved by controlling microstructure during processing. Aguilera (2005) explained that structure has the largest effect on sound and food behaviour in biting. Structuring of particles within the multiphase chocolate systems during processing could be optimised to enhance resistance to flow, reduce grittiness perceived in chocolate with particle $D_{90} > 35$ μ, with consequential effects on the quality characteristics of finished chocolates.

Mechanical properties

Firmness of molten chocolate

In molten chocolate, firmness is a discrete property, determining spreadability. An inverse relationship between PS and firmness was observed at all lecithin levels (Fig. 6), with a minimum at 25% fat. An eightfold reduction was recorded in firmness from 1235 g with 18 μm to 173 g at 50 μm PS at 25% fat and 0.3% lecithin, and trends were similar with 0.5% lecithin at 25% fat. With 30% fat, changes in PS and lecithin content had significant effect on firmness, whereas with 35% fat changes were not significant. The higher

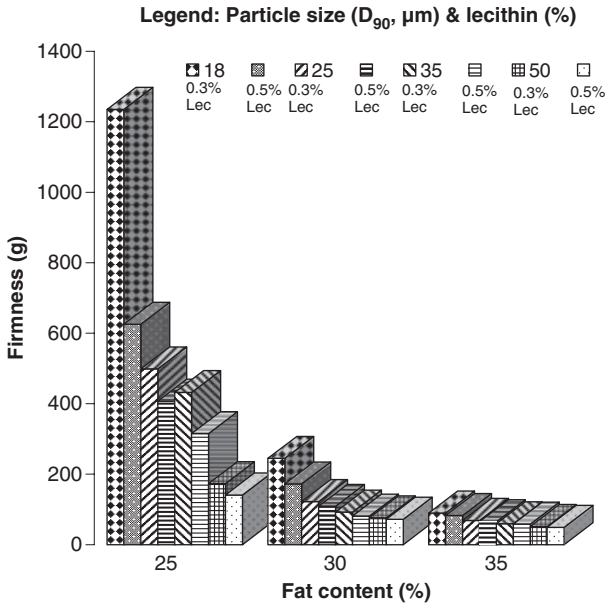

Figure 6 Effects of PSD, fat and lecithin content on firmness of molten dark chocolate.

firmness noted in the low fat chocolate denoting an inverse relationship with PS could be explained by the fact that as distribution of PS becomes wider with a large specific surface area, smaller particles fill the spaces between larger, reducing firmness for that solid concentration. Increasing fat content to 35% reduced specific surface area (Table 2), restricting solids packing ability. At lower PS, number of particles increases in parallel with points of contact between particles, resulting in higher firmness and restricted spreadability.

Increasing fat from 25% to 30% led to reduced firmness at all PS and lecithin concentrations. At low PS (18 μm), a 5% increase in fat was correlated with an up to sixfold reduction, with a greater effect at lower PS (18–25 μm) and lecithin levels. At 35% fat, firmness values were similar at all PS and lecithin levels, suggesting fat promoted free-moving flow by lubricating solid particles and reducing resistance to flow mostly at lower PS. Increasing lecithin from 0.3% to 0.5% resulted in significant decreases in firmness notably at lower fat content and PS with up to twofold reductions. Lecithin migrates to sugar/fat interfaces and coats sugar crystals, influencing flow behaviour and dispersing crystals in the fat phase (Beckett, 2000; Dhonsi & Stapley, 2006). Chevalley (1999) noted lecithin monolayers on crystal surfaces enhance suspension mobility increasing fat spread ability. The observed variations in firmness or spreadability of molten dark chocolate resulting from the combined effects of PSD, fat and lecithin could have significant application during chocolate manufacture. With exception of 18 μm PS samples, the level of firmness in all the dark chocolates formulated with 30% and 35% fat were similar, and such lack of discrimination in spreadability of 30% and 35% fat in molten chocolates could have significant implications for production cost in chocolate confectionery industry. Afoakwa *et al*. (2007b) noted that PSD could be manipulated with the combined action of fat and lecithin to control the rheological properties of dark chocolates, with enormous significance on quality control and reduction on production cost.

Statistical analysis on the data indicated that PSD, fat and lecithin contents and their interactions significantly affected firmness (Table 4). Multiple range tests revealed that at low fat content, PSD had significant ($P < 0.001$) effects on spreadability, but at 30% and 35% fat effects were reduced. Combined effects of PSD, fat and lecithin content can be manipulated to control firmness or spreadability with the potential for reduced costs.

Hardness of tempered dark chocolates

Hardness also showed inverse relationships with PS, fat and lecithin with significant reductions at all fat contents, greatest in low fat (25%) chocolates containing 0.3% lecithin (Fig. 7). At 25% fat, hardness decreased from 7062 g with 18 μm PS to 5546 g at

Table 4 ANOVA summary of *F*-values of the mechanical properties

Process variables	Firmness	Hardness
A: PS (D_{90})	1595*	979*
B: fat	5971*	6921*
C: lecithin	578*	167*
Interaction		
PS × fat	842*	161*
PS × lecithin	225*	7.48*
Fat × lecithin	393*	17.7*
PS × fat × lecithin	157*	32.5*

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

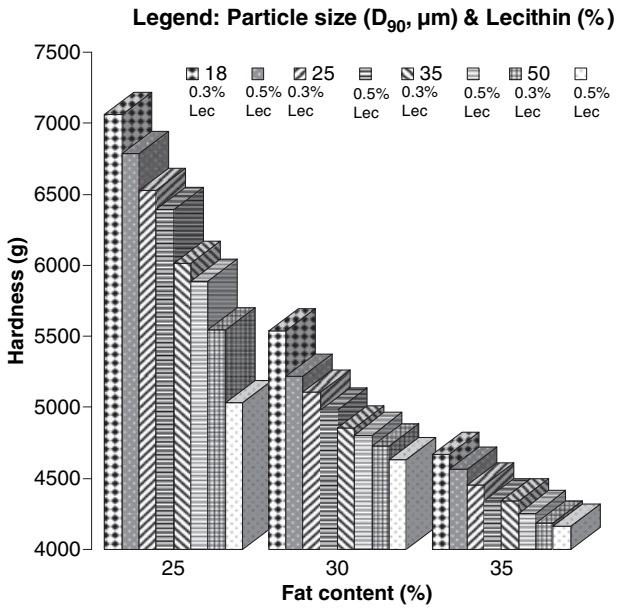

Figure 7 Effects of PSD, fat and lecithin content on hardness of tempered dark chocolate.

50 µm. Similar trends in hardness were noted at 30% and 35% fat with 0.3% lecithin at all PS but less pronounced at higher PS (Fig. 7). The higher hardness with low (25%) fat chocolates and lower (18–25 µm) PS can be attributed to more particle-particle interactions, and amount, specific surface area and mean diameter of particles with spanning of stress bearing paths increasing hardness. Hardness of dark chocolate, from inter-particle contacts, shows dependency on mean PS and particle diameters and specific surface area. Fat content was inversely related ($P < 0.001$) to hardness at all PS and lecithin levels (Fig. 7). Combined effects of fat content and PSD thus have greatest influence on hardness of dark chocolates, but effects are less pronounced at higher fat and lecithin contents (Fig. 7) where fat coats particle surfaces and reduces inter-particle interaction to induce softening observed in microstructural analyses of the products.

Significant reductions were also noted with increasing lecithin from 0.3% to 0.5% as amphiphilic properties promote de-agglomeration of clumps and wetting, inducing softening. Significant interactions were observed between all parameters (Table 3) indicating combined effects could be manipulated to reduce hardening of dark chocolates.

Conclusion

Particle size distribution and ingredient content were significant factors determining microstructural and mechanical properties of dark chocolates. Microstructural analysis revealed that the smaller particles (D_{10}, D_{50}), largest particles (D_{90}) and specific surface area had direct influence on packing ability and inter-particle interactions. At low (25%) fat concentrations, inter-particle interaction of crystals led to flocculation, with an impact on microstructure and behaviour of molten and tempered products. Increasing fat reduced the crystalline network density, created more open and void spaces which fill with fat, reducing resistance to flow, and enhancing spreadability and softening. Mechanical analyses showed PS were inversely correlated with firmness and hardness, which were more pronounced at lower fat and lecithin levels. Higher fat and lecithin levels showed reduced effects on mechanical properties. Fat had the greatest influence on mechanical properties, followed by PSD and then lecithin content. Microstructural examination showed that PSD with fat and lecithin could be manipulated to control mechanical properties of both molten and tempered (solid) dark chocolates, with importance for new product development and production cost during chocolate manufacture.

Acknowledgment

The present study was co-funded by the Government of Ghana and Nestlé Product Technology Centre (York, UK). The sponsors are gratefully acknowledged for the research support. We thank Steve Beckett, Angela Ryan, Jeremy Hargreaves Angel Manez and Hugh Powell (Nestlé PTC, York) for useful technical discussion.

References

Afoakwa, E.O. & Sefa-Dedeh, S. (2002). Textural and microstructural changes associated with post-harvest hardening of trifoliate yam (*Dioscorea dumetorum*) pax tubers. *Food Chemistry*, **77**, 279–284.

Afoakwa, E.O., Paterson, A. & Fowler, M. (2007a). Factor influencing rheological and textural qualities in chocolate – a review. *Trends in Food Science and Technology*, **18**, 290–298.

Afoakwa, E.O., Paterson, A. & Fowler, M. (2007b). Effects of particle size distribution and composition on rheological properties of dark

chocolate. *European Food Research and Technology* (Published online) doi: 10.1007/s00217-007-0652-6.
Aguilera, J.M. (2005). Why food microstructure? *Journal of Food Engineering*, **67**, 3–11.
Awua, P.K. (2002). *Cocoa Processing and Chocolate Manufacture in Ghana*. Pp. 102–118. Essex: David Jamieson and Associates Press Inc.
Baixauli, R., Sanz, T., Salvador, A. & Fiszman, S.M. (2007). Influence of the dosing process on the rheological and microstructural properties of a bakery product. *Food Hydrocolloids*, **21**, 230–236.
Beckett, S.T. (1999). *Industrial Chocolate Manufacture and Use*. 3rd edn, Pp. 153–181, 201–230, 405–428. 460–465. Oxford: Blackwell Science.
Beckett, S.T. (2000). *The Science of Chocolate*. Royal Society of Chemistry.
Beckett, S.T. (2003). Is the taste of British milk chocolate different? *International Journal of Dairy Technology*, **56**, 139–142.
Bourne, M. (2002). *Food Texture and Viscosity: Concepts and Measurements*. Pp. 124–148. San Diego: Academic Press.
Braipson-Danthine, S. & Deroanne, C. (2004). Influence of SFC, microstructure and polymorphism on texture (hardness) of binary blends of fats involved in the preparation of industrial shortenings. *Food Research International*, **37**, 941–948.
Chevalley, J. (1999). Chocolate flow properties. In: *Industrial Chocolate Manufacture and Use* (edited by S.T. Beckett). Pp. 182–199. New York, NY: Chapman & Hall.
Christiansen, K.F., Krekling, T., Kohler, A., Vegarud, G., Langsrud, T. & Egelandsdal, B. (2006). Microstructure and sensory properties of high pressure processed dressings stabilized by different whey proteins. *Food Hydrocolloids*, **20**, 650–662.
Codex Revised Standard (2003). Codex Alimentarius Commission Revised Standard on cocoa products and chocolate. Report of the Nineteenth Session of the Codex Committee on cocoa products and chocolate. Alinorm 03/14, 1–37.
Dhonsi, D. & Stapley, A.G.F. (2006). The effect of shear rate, temperature, sugar and emulsifier on the tempering of cocoa butter. *Journal of Food Engineering*, **77**, 936–942.
European Commission Directive (2000). European Commission Directive 2000/36/EC on cocoa and cocoa products. *Official Journal of the European Communities*, **L 197**, 19–25.
ICA (International Confectionery Association) (1988). *Determination of Moisture Content of Cocoa and Chocolate products, Analytical Method 26*. CAOBISCO, rue Defacqz 1, B-1000 Bruxelles: Belgium.
ICA (International Confectionery Association) (1990). *Determination of fat content of cocoa and Chocolate Products*. Analytical Method 37. CAOBISCO, rue Defacqz 1, B-1000. Brusells.
Kulozik, U., Tolkach, A., Bulca, S. & Hinrichs, J. (2003). The role of processing and matrix design in development and control of microstructures in dairy food production – a survey. *International Dairy Journal*, **13**, 621–630.
Lillford, P.J. (1991). Texture and acceptability of human foods. In: *Feeding and the Texture of Foods* (edited by J.F.V. Vincent & P.J. Lillford). Pp. 231–243. Cambridge: Cambridge University Press.
van Marle, J.T., Stolle-Smitts, T., Donkers, J., van Dijk, C., Voragen, A.G.J. & Recourt, K. (1997). Chemical and microscopic characterization of potato cell wall during cooking. *Journal of Agriculture and Food Chemistry*, **45**, 50–58.
Pereira, R.B., Singh, H., Munro, P.A. & Luckman, M.S. (2003). Sensory and instrumental textural characteristics of acid milk gels. *International Dairy Journal*, **13**, 655–667.
Prasad, V., Trappe, V., Dinsmore, A.D., Segre, P.N., Cipelletti, L. & Weitz, D.A. (2003). Universal features of the fluid to solid transition for attractive colloidal particles. *Rideal Lecture, Faraday Discuss*, **123**, 1–12.
Remeuf, F., Mohammed, S., Sodini, I. & Tissier, J.P. (2003). Preliminary observations on the effects of milk fortification and heating on microstructure and physical properties of stirred yoghurt. *International Dairy Journal*, **13**, 773–782.
Sandoval-Castilla, O., Lobato-Calleros, C., Aguirre-Mandujano, E. & Vernon-Carter, E.J. (2004). Microstructure and texture of yoghurt as influenced by fat replacers. *International Dairy Journal*, **14**, 151–159.
Servais, C., Ranc, H. & Roberts, I.D. (2004). Determination of chocolate viscosity. *Journal of Texture Studies*, **34**, 467–497.
Sokmen, A. & Gunes, G. (2006). Influence of some bulk sweeteners on rheological properties of chocolate. *LWT- Food Science & Technology*, **39**, 1053–1058.
Varela, P., Salvador, A. & Fiszman, S. (2007). Changes in apple tissue with storage time: rheological, textural and microstructural analyses. *Journal of Food Engineering*, **78**, 622–629.
Ziegler, G. & Hogg, R. (1999). Particle size reduction. In: *Industrial Chocolate Manufacture and Use* (edited by S.T. Beckett). Pp. 182–199. New York, NY: Chapman & Hall.