Effects of tempering and fat crystallisation behaviour on microstructure, mechanical properties and appearance in dark chocolate systems

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ABSTRACT

Fat crystallisation behaviours in dark chocolates from varying particle size distribution (PSD) (D50 of 18, 25, 35 and 50 μm) was studied, yielding products from different temper regimes (optimal temper, over-temper and under-temper), and their effects on mechanical properties and appearance evaluated. Microstructures of derived products were determined using stereoscopic binocular microscopy. Wide variations in mechanical properties and appearance were noted in products from different particle size and temper regimes. Particle size (PS) was inversely related with texture and colour, with the greatest effects noted in hardness, stickiness and lightness at all temper regimes. Over-tempering caused significant increases in product hardness, stickiness with reduced gloss and darkening of product surfaces. Under-tempering induced fat bloom in products with consequential quality defects on texture, colour and surface gloss. Micrographs revealed variations in surface and internal crystal network structure and inter-particle interactions among tempered, over-tempered and under-tempered (bloomed) samples. Under-tempering caused whitening of both surface and internal periphery of products with effects on texture and appearance. Thus, attainment of optimal temper regime during pre-crystallisation of dark chocolate was central to the desired texture and appearance as both over-tempering and under-tempering resulted in quality defects affecting mechanical properties and appearance of products.

1. Introduction

Tempering is a technique of controlled pre-crystallisation employed to induce the most stable solid form of cocoa butter, a polymorphic fat in finished chocolates. The process consists of shearing chocolate mass at controlled temperatures to promote crystallisation of triacylglycerols (TAGs) in cocoa butter to effect good setting characteristics, foam stability, demoulding properties, product snap, contraction, gloss and shelf-life characteristics. Time-temperature protocols and shearing are employed to induce nucleation of stable polymorphs with the formation of three-dimensional crystal network structure influencing the microstructure, mechanical properties and appearance of products. The crystal network organisation and the polymorphic state of the TAGs crystals as affected by the crystallisation conditions are major factors determining rheological and textural properties of crystallised TAGS systems (Herrera and Hartel, 2000; Narine and Marangoni, 1999; Toro-Vazquez et al., 2004; Pérez-Martínez et al., 2007; Altimiras et al., 2007).

Cocoa butter, the only continuous fat phase in dark chocolates, consist of a mixture of ~40–50 different TAGs dominated by 2-oleyl glycerides of palmitic and stearic acids, mainly, 1-palmitoyl-2-oleoyl-3-stearoylglycerol (POS) 35%, 1,3-distearoyl-2-oleoylglycerol (SOS) 23% and 1,3-disaturated-2-oleoylglycerol type: 1,3-dipalmitoyl-2-oleoylglycerol (POP) 15% (Lipp and Anklam, 1998; Segall et al., 2005; Afoakwa et al., 2007a). These occur as symmetric triacylglycerols that contain a central monounsaturated fatty acid, with saturated fatty acids in the 1 and 3 positions, which dominate the crystallisation, polymorphism and phase transformations, thus provide chocolate with its unusual textural and other sensory properties.

Particle size distribution influences rheological and textural properties of both molten and tempered dark chocolates, with effects on microstructure, product spread, tempering and pre-crystallisation behaviour, hardness and sensorial qualities (Chevalley, 1999; Beckett, 2000; Afoakwa et al., 2007b; Do et al., 2007; Afoakwa et al., 2008a). Smaller particles improve sensory properties (Ziegler et al., 2001) but plastic viscosity and yield stress increase due to changes in surface area of particles in contact with fat phase. Chocolate production processes, such as refining, conching, tempering and crystallisation mechanisms result in physical and compositional attributes, influencing product quality and stability through the supply chain occurring during production, storage,
distribution and ultimately sensory character in consumption and product identification.

Instrumental measurements can act as complements for sensory evaluations (Lawless and Heymann, 1998) with statistically significant correlations (Mohamed et al., 1982; Meullenet et al., 1997; Rosenthal, 1999; Ali et al., 2001; Bourne, 2002). Appropriate strategies can objectively assess features of texture and appearance such as gloss, colour, shape, roughness, surface texture, shininess, and translucency (Leemans et al., 1998; Jahn et al., 2001; Hatcher et al., 2004; Briones and Aguilera, 2005; Briones et al., 2006; Altimiras et al., 2007; Afoakwa et al., 2008a). Knowledge of tempering effects on product texture and appearance attributes can have significant commercial implications.

With recent innovations and growth in chocolate confectionery industry, understanding the factors influencing chocolate microstructure, texture and appearance would be of value in predicting changes in quality. This study was therefore aimed at investigating effects of tempering and fat crystallisation behaviours on microstructure, mechanical properties and appearance in dark chocolates varying in particle size distribution.

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 cane 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, formation and production of samples have been described previously (Afoakwa et al., 2007b). Chocolates were formulated with total fat of 35% (w/w) from sucrose, cocoa liquor, cocoa butter and lecithin. Experimental samples (5 kg batch for each formulation) were produced by mixing sucrose (40.8%) and cocoa butter and lecithin. Experimental samples (5 kg batch for each formulation) were produced by mixing sucrose (40.8%) and cocoa butter and lecithin. The recipe, formation and production of samples have been described previously (Afoakwa et al., 2007b). Chocolates were formulated with total fat of 35% (w/w) from sucrose, cocoa liquor, cocoa butter and lecithin. Experimental samples (5 kg batch for each formulation) were produced by mixing sucrose (40.8%) and cocoa butter and lecithin. The recipe, formation and production of samples have been described previously (Afoakwa et al., 2007b). Chocolates were formulated with total fat of 35% (w/w) from sucrose, cocoa liquor, cocoa butter and lecithin. Experimental samples (5 kg batch for each formulation) were produced by mixing sucrose (40.8%) and cocoa butter and lecithin. The recipe, formation and production of samples have been described previously (Afoakwa et al., 2007b). Chocolates were formulated with total fat of 35% (w/w) from sucrose, cocoa liquor, cocoa butter and lecithin. Experimental samples (5 kg batch for each formulation) were produced by mixing sucrose (40.8%) and cocoa butter and lecithin. The recipe, formation and production of samples have been described previously (Afoakwa et al., 2007b). Chocolates were formulated with total fat of 35% (w/w) from sucrose, cocoa liquor, cocoa butter and lecithin. Experimental samples (5 kg batch for each formulation) were produced by mixing sucrose (40.8%) and cocoa butter and lecithin.

2.2. Determination of particle size distribution

A MasterSizer® Laser Diffraction Particle Size Analyzer equipped with M5 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 ($D_{32}$).

2.3. Tempering experiment

Samples were incubated at 50 °C for 4 h for melting and tempered using 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. Based on our earlier work modelling temperature controls to study tempering behaviour (Afoakwa et al., 2008b), the temperature of each of the coolant fluids (Zones 1:2:3) was thus set as 26:24:32 °C, 21:19:32 °C and 18:16:32 °C, respectively for attaining the under-tempered, optimally-tempered and over-tempered regimes. The degree of pre-crystallisation was measured using a computerized tempermeter (Exotherm 7400, Systech Analytics, Neuchâtel, Switzerland) and a built-in algorithm provided the tempering curves and temper readings in chocolate temper index (slope), corresponding to optimal temper (slope 0), under-temper (slope 1.0) and over-temper regimes (slope -1.0). The principle of this method has been described by Nelson (1999). Chocolate from the three regimes were moulded using plastic moulds: 80 mm length; 20 mm breadth; and 8 mm height. The final products were 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. Triplicate measurements were taken for each product composition and the mean values recorded.

2.4. Texture measurements

Mechanical properties of chocolates (hardness and stickiness) were measured using TA-HD Plus Texture Analyzer with a penetration probe (needle P/2) attached to an extension bar and a 50 kg load cell and a platform reported by Afoakwa et al. (2008a). Maximum penetration and withdrawal forces through a sample (80 × 20 mm, depth 8 mm) were determined with 8 replications at a pre-speed of 1.0 mm/s, test of 2.0 mm/s, post speed of 10.0 mm/s, penetrating 5 mm at 20 °C, converting mean values of the penetration force exerted by the 50 kg load cell into hardness (g force) and the withdrawal force with time into stickiness (g force s) data, respectively using XT:RA Dimension, Exponent 32 software (Stable Micro Systems, Godalming, Surrey, UK).

2.5. Colour and gloss measurements

HunterLab Miniscan™ XE Colorimeter Model 45/0 LAV (Hunter Associates Inc., Reston, VA) calibrated with white ceramic reference standard was used. Colour images of chocolate surfaces were converted into XYZ tristimulus values, which were further converted to CIELAB system: $L^*$ (lightness), $a^*$ (green to red) and $b^*$ (blue to yellow) with values from −120 to +120. Information was obtained using a software algorithm (Matlab v. 6.5; The Math-Works, Inc., Natick, MA); hue angle ($h^*$) = arctan ($b^*/a^*$ ); chroma ($C^*$) = [($a^*$)² + ($b^*$)²]¹/². Mean values from five replicate measurements and standard deviations were calculated.

Gloss of chocolate surface was measured using the multiple angle Tricor Gloss meter (805A/806H Gloss System, Elgin, IL). Reflectance was measured at an incidence light angle of 85° from the normal to the chocolate surface, in accordance with ASTM method.
D523. A polished black glass plate with a refractive index of 1.567 was used as standard surface (ASTM, 1995) and given a gloss value of 200. Gloss was reported as gloss units (GU) based on determinations (in triplicate) at six positions along a chocolate sample. As a reference, a surface with a gloss value less than 10 GU is considered a low gloss surface (BYK, 1997; Briones et al., 2006).

2.6. Image acquisition and capture

A colour digital camera (Canon Powershot, Model A70, MA, USA) was mounted on a stand inside a large box with internal black surface impervious to light. Images of the optimally tempered, under-tempered and over-tempered samples were captured before storage and after 14 days in storage. The iris was operated in manual mode, with the lens aperture at f=8 and speed 1/20 (no zoom, no flash) to achieve high uniformity and repeatability. The camera was gray balanced before each imaging session. Uniform diffuse lighting was used to illuminate the samples. The lighting system consisted of four CIE source D65 lamps (60 cm length and 18 W; Model TLD/965, Philips, Singapore) placed above the sample at a 45° angle to maximize diffuse reflection responsible for colour. The angle between the camera lens axis and the sample was around 90° to reduce gloss. A Kodak gray card with 18% reflectance was used as a white reference to standardize the illumination level. The gray-level image (1600 x 1200 pixels) of this card was divided into 192 blocks, each one of 100 x 100 pixels. After calibration, samples were placed in the field of view of the camera and an image of 1600 x 1200 pixels (approximately covering the whole area of the tablet) was acquired and stored in JPEG (joint photographic experts group, a standard for compressing digital photographic images) format of high resolution and superfine quality.

2.7. Microstructural determinations

Chocolate samples were characterised using stereoscopic binocular microscope (Nikon, SMZ-2T, Tokyo, Japan) equipped with a variable removable lens. Micrographs (coloured 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). Triplicate experiments were conducted capturing 6 images per sample, and micrographs representing the surface of each temper regime captured and presented. Samples were then sectioned (cut) into two pieces using a knife and the internal microstructures observed.

2.8. Experimental design and statistical analysis

Two experimental variables comprising temper regime and PSD were used. Other variables including refiner temperature and pressure, conching time and temperature were held constant. A 3 x 4 factorial experimental design was used comprising:

(i) Temper regime: optimal temper, under-temper and over-temper.
(ii) PSD ($D_{90}$): 18, 25, 35 and 50 µm.

Statgraphics Plus 4.1 (Graphics Software System, STCC, Inc, Rockville, USA) examined mechanical properties (hardness and stiffness) and appearance (colour [L, C*, h*] and gloss) using two-way analysis of variance (ANOVA) and multiple comparison tests to determine effects of factors and their interactions. Tukey multiple comparisons (95% significance level) determined differences between levels. All experiments were conducted in triplicates and the mean values reported.

3. Results and discussion

3.1. Particle size distribution of dark chocolates

These findings (Fig. 1), previously reported (Afoakwa et al., 2008a), show volume histograms consisting of narrow (18 µm PS) and wide (25 µm PS) bimodal and narrow (35 µm PS), and wide (50 µm PS) multimodal size distributions. This PSD range 18–50 µm using $D_{90}$ values (>90% finer) covers optimum minimum and maximum sizes with direct effects on texture and sensory character in manufacture (Ziegler and Hogg, 1999; Beckett, 2000). Data from the PSD as previously described (Afoakwa et al., 2008a) showed variations in specific surface area, mean particle volume $D_{v,50}$, Sauter mean ($D_{3,2}$) and mean particle diameter ($D_{4,3}$) with increasing $D_{90}$ particle sizes. Specific surface area (SSA) was inversely correlated with the different component of PSD. Similar inverse relationships of SSA with all the other components of PSD have been reported (Beckett, 1999; Ziegler and Hogg, 1999; Sokmen and Gunes, 2006). Beckett (1999) concluded largest particle size and solids specific surface area are the two key parameters for chocolate manufacture. The former determines chocolate coarseness and textural character, the latter with desirable flow properties. Fat contents of the products were 35 ± 1% and moisture within the range of 0.90–0.98%.

![Fig. 1. Particle size distribution of dark chocolate with $D_{90}$ of (a) 18 µm (b) 25 µm (c) 35 µm (d) 50 µm.](image-url)
3.2. Fat crystallisation behaviours during tempering of dark chocolate

Four different temper regimes (untempering, under-tempering, over-tempering and optimal tempering) were characterised (Fig. 2) each with its unique characteristic crystallisation behaviour. In optimal tempering, the temperature of the chocolate remained constant for sometime during cooling, to initiate formation of stable fat crystals. The crystallisation heat released was then balanced by an equal amount of cooling energy causing the growth of stable crystal nuclei in adequate amounts, which during post-tempering conditioning mature to effect shelf stability of the product. The temperature of the chocolate dropped further when the liquid cocoa butter was transformed into solid crystals resulting in solidification of the products (Fig. 2). Beckett (2000) reported that properly tempered chocolate shows formation of Form V, the most desirable polymorphic form which confers appropriate product snap, contraction, gloss and shelf-life characteristics.

Under-tempering (insufficient tempering) was caused by the relatively higher temperatures released between the multi-stage heat exchangers during tempering. The process caused development of more crystallisation heat within the product during solidification, effecting quick cooling, as more liquid fat was transformed quickly into solid form, resulting in the formation of very few stable fat crystal nuclei (Fig. 2). Distinct increase in temperature was observed at the beginning of the crystallisation, which declined again after reaching a maximum point where most of the stable crystals formed were re-melted prior to cooling. Un tempered chocolate, produced no stable fat crystals as the heat exchange system generated higher crystallization heat during cooling, resulting in quick cooling of the completely melted product with no inflexion point for stable fat crystal formation (Fig. 2). Beckett (2000) explained that the crystallisation processes in both untempered and under-tempered chocolates lead to the formation of unstable Form IV polymorph, which later transforms into more stable Form VI polymorph during storage. Preliminary studies showed that untempering and under-tempering regimes exhibits different crystallisation behaviours but results in similar unstable fat crystal nucleation and growth, with similar associated storage polymorphic transformations and defects in products. Storage of the under-tempered products under ambient temperature (20–22 ºC) for 14 days of conditioning induced blooming in samples, effecting various quality changes in the products as reported in this study. Products from under-tempering regime were used in this study.

Over-tempering occurred when relatively lower temperatures were exchanged between the multi-stage heat exchangers of the tempering equipment, causing significant part of the liquid fat to withdraw from the continuous phase of the chocolate, and transformed into solid form when less liquid fat was available for pumping the product. The process released little crystallization heat during cooling, rendering a rather flat and slow cooling curve (Fig. 2). This crystallisation process results in too many small stable seed crystal formation leading to reduced strengths in the polymorphic stabilities of the fat crystals formed during the process (Talbot, 1999). As a substantial part of the phase transition (from liquid to solid) took place before the chocolate reached the mould, less contraction occurred in the mould, leading to demoulding problems with defects in final product quality and storage characters (Hartel, 2001; Lonchampt and Hartel, 2004).

3.3. Effect of temper regime and PSD on mechanical properties

Hardness showed an inverse relationship with particle sizes, with significant reductions at all temper regimes, and greatest in the under-tempered (bloomed) products (Fig. 3). Hardness of the optimally-tempered products decreased from 5318 g with 18 μm PS to 4259 g at 50 μm. Similar trends in hardness were noted with the over-tempered samples, decreasing from 6064 g with 18 μm PS to 4651 g at 50 μm, and from 6533 g with 18 μm PS to 5459 g at 50 μm in the bloomed products (Fig. 3), suggesting differences in hardness with varying PS at all temper regimes. Particle sizes have been noted as an important parameter in the hardness of fat crystal networks in many confectionery products (Narine and Marangoni, 2002; Campos et al., 2002; Marangoni and Narine 2002; Pérez-Martínez et al., 2007). Earlier studies showed inverse relationships of hardness in tempered dark chocolates with particle sizes at varying fat and lecithin levels (Afoakwa et al., 2008a), attributed to the relative strengths of their particle-to-particle interactions.
Do et al. (2007) also reported consistent reductions in hardness (texture) of milk chocolates with increasing particle sizes. The results showed that the under-tempered products had the greatest hardness (texture), attributable to the re-crystallisation process undergone by the fat in the under-tempered chocolates resulting in intense hardening of products. This trend in hardness was followed by the over-tempered samples with the optimal tempered products possessing relatively lesser hardness levels, suggesting over-tempering of dark chocolates leads to increased hardness of samples at all PS as compared to their respective optimally-tempered products.

Chocolate stickiness showed an inverse relationship with particle sizes at all temper regimes, and the greatest trends were noted in the over-tempered products (Fig. 4). Stickiness of the optimally-tempered products decreased consistently from 380.67 g with 18 µm PS to 325.25 g at 50 µm. Likewise, the levels of stickiness in the over-tempered samples decreased from 447.92 g with 18 µm PS to 365.10 g at 50 µm, and from 336.86 g with 18 µm PS to 309.20 g at 50 µm in the bloomed products (Fig. 4), explaining that the over-tempered products had the greatest stickiness levels, followed by the optimally tempered products with the bloomed samples having the least. 

Narine and Marangoni (2001) noted that stickiness of confectionery gives information about deformability related to oral sensory characters. Analysis of variance (ANOVA) suggested significant differences ($P < 0.05$) in both hardness and stickiness levels with particle sizes and temper regimes. Significant interactions were observed between all parameters (Table 1) suggesting the combined effects of PSD and tempering could be manipulated to reduce hardening and stickiness in dark chocolates. Multiple comparison tests showed over-tempered products were significantly harder and stickier than the optimally-tempered – important for quality control and in new product development.

### Table 1

ANOVA Summary of F-values of texture measurements

<table>
<thead>
<tr>
<th>Process variables</th>
<th>Hardness</th>
<th>Stickiness</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Particle size ($D_{90}$)</td>
<td>577.47***</td>
<td>5191.25***</td>
</tr>
<tr>
<td>B: Temper regime</td>
<td>419.16***</td>
<td>21562.10***</td>
</tr>
<tr>
<td>A x B</td>
<td>7.21**</td>
<td>22.51**</td>
</tr>
</tbody>
</table>

Significant F-ratios at $^* P < 0.05, ^{**} P < 0.01, ^{***} P < 0.001$.

### Table 2

Effects of temper regime and PS on gloss and colour measurements

<table>
<thead>
<tr>
<th>Temper regime</th>
<th>Particle size ($D_{90}$) (µm)</th>
<th>Gloss (GU)</th>
<th>Colour measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$L^*$</td>
</tr>
<tr>
<td>Optimally-tempered</td>
<td>18</td>
<td>158.6 ± 1.43</td>
<td>45.49 ± 0.42</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>150.3 ± 1.78</td>
<td>44.79 ± 1.16</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>146.6 ± 0.84</td>
<td>43.86 ± 0.40</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>144.6 ± 1.27</td>
<td>42.19 ± 0.56</td>
</tr>
<tr>
<td>Over-tempered</td>
<td>18</td>
<td>142.0 ± 0.64</td>
<td>44.05 ± 0.40</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>140.7 ± 2.07</td>
<td>43.43 ± 1.02</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>129.0 ± 1.28</td>
<td>42.26 ± 0.21</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>121.3 ± 1.36</td>
<td>41.87 ± 0.48</td>
</tr>
<tr>
<td>Under-tempered</td>
<td>18</td>
<td>7.3 ± 0.24</td>
<td>81.47 ± 1.44</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>5.3 ± 0.32</td>
<td>80.60 ± 1.26</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>5.0 ± 0.15</td>
<td>80.09 ± 0.83</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>4.3 ± 0.28</td>
<td>78.76 ± 0.96</td>
</tr>
</tbody>
</table>

Means ± standard deviation from triplicate analysis.

Lightness ($L^*$), chroma ($C^*$) and hue ($h^*$) followed similar trends with varying PS at all temper regimes (Table 2). Significant ($P < 0.001$) and linear effects on $L^*$ were recorded with increasing particles from 18 to 50 µm, with consequential decreases in $L^*$ noticeable but dependent on temper regime (Table 3). Similar decreases in $C^*$ and $h^*$ with increasing PS were also noted. Thus, dark chocolate became lighter as $D_{90}$ decreased from 50–18 µm and as PS increased (18–50 µm) $C^*$ and $h^*$ were significantly decreased, with levels pronounced in the under-tempered samples. Similarly, temper regime affected to varying levels all the colour measurements. The under-tempered samples attained relatively higher $L^*$-values than both the optimally-tempered and over-tempered samples. The blooming process resulted from under-tempering of samples caused increases in $L^*$ from 81.47, 80.60, 80.09 and 78.76, respectively for the products with 18 µm, 25 µm, 25 µm and 50 µm, an indication that all the under-tempered samples had become whiter in colour within the 14 days conditioning period. As well, the blooming caused great reductions in $C^*$ and $h^*$ in the under-tempered products at all PS (Table 2). Hutchings (1994) stated that $L^*$, $C^*$ and $h^*$, respectively represent food diffuse reflectance of light, degree of saturation and hue luminance, which are dependent on particulate distribution, absorptivity and scatter-
ing factors or coefficients. In a densely packed medium, scattering factor is inversely related to particle diameter (Saguy and Graf, 1991). Chocolates with varying particle sizes differ in structural and particulate arrangements influencing light scattering coefficients and thus appearance (Afoakwa et al., 2008a).

Similar decreasing trends in $L^*$ were noted in both tempered and over-tempered samples with increasing PS. However, the over-tempered samples had relatively lower $L^*$ values at all PS as compared to their corresponding optimally tempered products (Table 2). These suggest that over-tempering reduces the degree of lightness in dark chocolates, effecting product darkening and thus affecting quality. However, no noticeable effect on $C^*$ and $h^*$ were observed among the tempered and over-tempered products (Table 2). Thus, changes in colour in dark chocolates were primarily dependent on PS and temper regime. Bloomed dark chocolates tend to scatter more light, appear lighter and less saturated than over-tempered and optimally tempered products. The blooming process resulted in higher scattering coefficients, with subsequent paleness (whitening) - higher $L^*$ values. Hartel (1999) reported that the whitish haze in bloomed chocolate is caused by the dispersion of light of fat crystals. Similar effects of PS on the degree of whitening during blooming have been reported (Altimiras et al., 2007). Colour of foods may be affected by various optical phenomena among them scattering and surface morphology, therefore an accurate understanding of the influence of appearance on measured colour is essential.

Table 3
ANOVA Summary of F-values of colour and gloss measurements

<table>
<thead>
<tr>
<th>Process variables</th>
<th>$L^*$</th>
<th>$C^*$</th>
<th>$h^*$</th>
<th>Gloss</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Particle size ($D_{90}$)</td>
<td>516.04***</td>
<td>80.99***</td>
<td>15.08***</td>
<td>111.46***</td>
</tr>
<tr>
<td>B: Temper regime</td>
<td>2960.75***</td>
<td>17482.54***</td>
<td>2302.96***</td>
<td>10183.49***</td>
</tr>
<tr>
<td>A x B</td>
<td>29.95**</td>
<td>43.86**</td>
<td>12.15*</td>
<td>23.01***</td>
</tr>
</tbody>
</table>

Significant F-ratios at* $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$.

Fig. 5. Photographic images of (a) fresh and (b) matured (conditioned) optimally-tempered, under-tempered and over-tempered dark chocolates (18 µm PS).
Gloss relates to capacity of a surface to reflect directed light at the specular reflectance angle with respect to the normal surface plane (ASTM, 1995). Significant \( P < 0.001 \) and linear effects on gloss were observed with increasing PS from 18 to 50 \( \mu \text{m} \), with consequential decreases in gloss, greatly dependent on the temper regime (Table 3). Gloss of dark chocolates was reduced as \( D_{90} \) increased from 18–50 \( \mu \text{m} \) at all temper regimes. As well, differences in temper regime influenced the gloss measurements to varying levels. Blooming of the under-tempered samples caused drastic reduction in gloss of the products than their respective tempered and over-tempered samples. The bloomed samples containing 18 \( \mu \text{m} \) PS had gloss value of 7.3 GU, while the corresponding tempered and over-tempered products had 158.6 GU and 142.0 GU, respectively. Similar trends were noticed at all PS (Table 2). Beckett (2000) noted tempering was important for gloss, a key quality attribute in chocolate. In under-tempered chocolates light scattering is caused by reductions in surface regularity. Gloss stability of edible coating formulations of chocolates have been studied (Trezza and Krochta, 2000; Lee et al., 2002; Briones et al., 2006).

ANOVA showed that PS and temper regime both significantly \( P < 0.001 \) influenced \( L^{*}, C^{*}, h^{*} \) and gloss, with significant \( P < 0.05 \) interactions (Table 3), all influencing appearance. Multiple comparison tests showed under-tempering had the greatest influence on appearance and gloss of products but differences between optimally and over-tempered products were significant. Attention to tempering is important for consistency in dark chocolate appearance and quality control.

3.5. Effect of temper regime on product image

Digital images of dark chocolates (18 \( \mu \text{m} \) PS) were assembled to show surface appearances of optimal, under- and over-tem-
pered products before and after the 14 days conditioning (Fig. 5). Initially surface appearances were similar and smooth but after 14 days, clear differences were apparent. Optimally and over-
tempered chocolates maintained their characteristic glossy appearance and dark brown colour but the under-tempered sam-
ple had bloomed, with appearance of surface whitish spots, ren-
dering them dull and hazy in colour (Fig. 5). Similar increases in
whiteness in under-tempered (bloomed) chocolates have been re-
ported (Lonchamp and Hartel, 2004, 2006; Altimiras et al., 2007).
Hartel (1999) explained this phenomenon as re-crystallisation of
fats from a less stable Form IV to a more stable Form VI poly-
morph, with changes in light dispersion on small surface fat crys-
tals (>5 μm), consequently impacting on both appearance and
textural attributes. Fat bloom development, mechanisms and ef-
facts on chocolate appearance, quality and marketability has been
extensively studied (Bricknell and Hartel, 1998; Ali et al., 2001;
Hartel, 2001; Timms, 2003; Walter and Cornillon, 2001, 2002;
Lonchamp and Hartel, 2004, 2006; Altimiras et al., 2007; Smith
et al., 2007).

3.6. Effect of temper regime on microstructure

Microstructural examination using stereoscopic binocular
microscopy after the 14 days conditioning showed clear variations in
both surface and internal peripheries of products from varying
temper regimes (Fig. 6). Over-tempered products had relatively
darker surfaces and internal peripheries than optimally tempered
confirming the reported relative differences in L* (Table 2). Under-
tempered products showed both bloomed surface and internal
periphery with large whitish, and distinct smaller brown spots
(Fig. 6). The observed whitish appearance on surfaces and internal
peripheries appear to be mixtures of re-crystallised fat and sugar
crystals, and the small brown spots, cocoa solids. Lonchamp and
Hartel (2004, 2006) suggested these whitish spots were primarily
sugar crystals and cocoa powder and nearly devoid of fat. This
difference in interpretation is the subject of further studies.

4. Conclusion

Fat crystallisation behaviour during tempering of dark choco-
late play vital roles in defining the structure, mechanical properties
and appearance of products. Wide variations in mechanical proper-
ties and appearance occurred in products from different PS and
temper regimes. Particle size was inversely related with texture
and colour, with the greatest effects noted with hardness, sticki-
ness and lightness at all temper regimes. Over-tempering caused
increases in product hardness, stickiness with reduced gloss and
darkening of product surfaces. Under-tempering induced fat bloom
in products with consequential quality defects in texture, colour
and surface gloss. Micrographs revealed clear variations in surface
and internal crystal network structure and inter-particle interac-
tions among tempered, over-tempered and under-tempered
(bloomed) samples. Blooming caused whitening of both surface
and internal periphery of products with consequential effects
on texture and appearance. Hence, attainment of optimal temper
during tempering (pre-crystallisation) of dark chocolate is vital to
the desired texture and appearance of products, as both over-temper-
ning and under-tempering result in quality defects affecting
mechanical properties and appearance of products.

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