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Texture and microstructure of cocoa butter replacers: Influence of composition and cooling rate

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ABSTRACT

In this study, the effect of cooling rate on cocoa butter replacers with similar content of saturated fat but different types of saturated fatty acids was evaluated. Two fats with a high content of monounsaturated asymmetric triacylglycerol were studied (62.1% and 70.9%, respectively); one with a high content of palmitic acid (P-rich) and one with a high content of stearic acid (S-rich). Different cooling rates (0.1, 0.5 and 2 °C/min) were applied during crystallization and samples were stored at different times (0 h, 1 day and 7 days) prior to analysis by pNMR, texture analysis, oscillatory rheometry and microscopy. For the S-rich fat, cooling rate influenced brittleness to a higher extent compared with storage modulus and hardness whereas for the P-rich fat cooling rate influenced hardness and storage modulus to a higher extent compared with brittleness. For the S-rich fat, an increase in brittleness around 75% and an increase in storage modulus around 25% were observed for faster cooling whereas no significant effect of cooling rate on hardness was observed after 1 week of storage. An increase in hardness and storage modulus around 30% and 50%, respective, and no significant increase in brittleness was observed for faster cooling of the P-rich fat.

The different behaviour depended on the relative inter- and intraparticle links in the fat crystal network. For the S-rich fat, faster cooling provided stronger interparticle links, most likely as a result of formation of solid bridges, which lead to a more brittle texture. For the P-rich fat, faster cooling provided stronger intraparticle links and an increase in the sum of weak interparticle links resulting in a harder but not brittle texture. The results contribute to clarify the mechanisms behind effects of cooling rate on different textural characteristics of fat and show the importance of understanding effects on the relative strength of inter- and intraparticle links in the fat crystal network to be able to tailor the textural properties of fats.

1. Introduction

In chocolate and confectionery production, vegetable oils are used to reduce cost, simplify production and improve

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functionality and stability of products. Many sensory attributes of chocolate and confectionery products depend on the underlying fat crystal network. Therefore, cocoa butter alternatives must contribute with an optimized melting profile and provide a desirable texture (Shukla, 2005). Due to

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functional differences such vegetable oils can be distinguished as equivalent, substitute or replacers. Cocoa butter replacers contain the same main fatty acids as cocoa butter but have a high content of asymmetric triglycerides (TAGs) and are thus only partly comparable with cocoa butter (Shukla, 2005). Although, cocoa butter replacers do not require the strict tempering procedure required for cocoa butter, the processing conditions applied during crystallization are important.

It is generally accepted that the textural properties of fat is determined by the amount of crystallized fat present and some microstructural factors such as crystal size and morphology, polymorphic behaviour, and the degree of crystal aggregation. Control of crystallization is thus important for control of the final texture of fat.

One of the key factors which determines the crystallization behaviour of fat is the TAG-composition. Even small changes in the TAG-composition can have an impact on the crystallization and thus final properties of fat. Natural oils and fats consist of a broad range of TAGs making it difficult to understand and model the crystallization behaviour. Each TAG has its own polymorphic and melting behaviour and this together with specific interaction within a mixture of TAGs makes the phase behaviour of TAG mixtures complex (Sato, 2001; Timms, 1984).

Previously, most studies have focused on the effect of TAGcomposition on crystallization behaviour in simple mixtures of pure TAGs. However, some newer studies have considered the effect of TAG-composition on the crystallization and microstructural development in systems with natural oils and fats (De Graef, Vereecken, Smith, Bhaggan, & Dewettinck, 2012; Vereecken, Foubert, Smith, & Dewettinck, 2009; Vereecken, De Graef, Smith, Wouters, & Dewettinck, 2010; Vereecken, Foubert, Smith, Sassano, & Dewettinck, 2010).

Beside the chemical composition, the crystallization behaviour of fat is influenced by different dynamic factors such as cooling rate, agitation and crystallization temperature (Metin & Hartel, 2005). Such dynamic process factors can thus influence both the microstructural development as well as the final textural characteristic of fat.

Fast cooling leads to a high degree of supercooling at any point in time during the crystallization process compared with slower cooling. Therefore, increasing the cooling rate may affect the microstructural characteristic and thus the texture by increasing the supersaturation, which will affect nucleation and crystal growth rate (Sato, Bayés-García, Calvet, Cuevas-Diarte, & Ueno, 2013). Several authors have investigated the effect of cooling rate on crystallization behaviour, microstructure and texture of fat (Campos, Narine, & Marangoni, 2002; Herrera & Hartel, 2000a, 2000b; Humphrey & Narine, 2007; Maleky, Acevedo, & Marangoni, 2012; Perez-Martinez, Alvarez-Salas, Charo-Alonso, Dibildox-Alvarado, & Toro-Vazquez, 2007; Wiking, De Graef, Rasmussen, & Dewettinck 2009). In general, faster cooling provides smaller crystals and a harder fat.

Different crystallization processes might proceed during storage of fat such as polymorphic transformation, Ostwald ripening (dissolution of small crystals and growth of larger crystals), aggregation of crystals and possible formation of solid bridges between crystal aggregates (Himawan, Starov, & Stapley, 2006; Johansson & Bergenstahl, 1995). Such process can influence the microstructure and thus the textural characteristic of fat. Therefore, studying post-crystallization effects is important for getting the entire picture of changes introduced during the nucleation and crystal growth phase.

The objective of this study was to elucidate the relation between triacylglycerol composition, microstructure and texture of fats used for cocoa butter replacers. The texture of crystallized fats was characterized using oscillatory rheometry and penetration test with needle and cone geometries. The microstructure was studied using polarized light microscopy (PLM) and confocal laser scanning microscopy (CLSM). The crystallization kinetic and thermal behaviour was studied using pulsed nuclear magnetic resonance (pNMR) and differential scanning calorimetry (DSC) to reveal the relationship between crystallization behaviour, microstructure and texture.

2. Material and methods

2.1. Materials

Fats used as cocoa butter replacers were studied. Two fats with either a high content of palmitic acid (P-rich fat, palmitic acid content of 54.0 weight/weight %) or stearic acid (S-rich fat, stearic acid content of 32.8 weight/weight %) were evaluated. The relative triacylglycerol (TAG) and fatty acid composition of the two fats are provided in Table 1. A high oleic sunflower oil

Table 1 – Fatty acid and triglyceride composition.

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	P-rich fat	S-rich fat
Fatty acids		
Mysteric acid (M): 14:0	1.2	0.5
Palmitic acid (P): 16:0	54.0	29.7
Stearic acid (S): 18:0	9.8	32.8
Oleic acid (O): 18:1	27.6	29.2
Linoleic acid (Li): 18:2	5.3	5.4
Arachidic acid (A): 20:0	-	1.3
TAG		
SSO	1.5	13.5
SOS	-	6.0
SOO	1.5	4.3
SOA	-	1.6
SLiS	-	3.8
SLiO	-	1.4
PSS	-	1.3
PSO	9.1	23.9
PPS	2.6	1.9
PPP	6.1	1.3
PPO	30.4	10.0
POS	6.2	9.8
POP	14	4.3
POO	7.3	2.8
PLiS	3	6.4
PLiP	8	2.8
PLiO	2.4	-
000	1.9	-
MOP	1.7	-

Relative fatty acid and triacylglycerol compositions (weight/weight %) of studied fats. Only fatty acids and triacylglycerols present at above 1% are included in the table.

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