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Visualization of oil migration in chocolate using scanning electron microscopy–energy dispersive X-ray spectroscopy

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ABSTRACT

We have developed a novel method to observe oil migration in chocolate using scanning electron microscopy and energy dispersive X-ray spectroscopy (EDX). If silicone oil is used as the mobile phase in migration, the amount of migrated silicone oil can be evaluated using the EDX signal. Compound chocolate placed on the silicone-oiled cotton resulted in the appearance of liquid oil droplets on the surface of the chocolate within 10 days at 24 °C. Fat blooming was also induced by these oil droplets at 2.5 months. The amount of silicone oil that migrated into the chocolate was evaluated based on the weight change of the chocolate and the EDX signal
from the silicone oil. Quantitative analysis indicated that two independent migration mechanisms, diffusion and capillary force, induced migration. In addition, the EDX signal indicated superfast migration from a spot that was distinct from the area of diffusion or capillary force migration. The EDX signals from phosphorus or magnesium atoms were helpful in identifying cacao particles in chocolate since these elements were specific to the particles in chocolate. Homogeneous distribution of silicone oil was observed around the particles in chocolate, thus, these particles might not help to produce a specific migration pathway in chocolate.

1. Introduction

Fat bloom, caused by the formation of needle-shaped fat crystals, is a significant problem in the confectionery industry. It is a greyish haze which forms on the surface of chocolate during storage and is promoted by storage near the melting point, temperature fluctuation, and oil migration (Lonchampt & Hartel, 2004; Rousseau, 2006). Customers dislike the visual appearance and textural attributes of bloomed chocolate, and this deterioration results in decreased consumer confidence. When chocolate is stored at a temperature above the melting point of form V crystals, melt-mediated transformation leads to the development of form VI crystals which grow to cause fat blooming. Temperature fluctuation causes liquid oil to pump out from the inside of the chocolate to the surface, even at a low temperature (Sonwai & Rousseau, 2010). The pumped liquid oil dissolves the surface of the chocolate and promotes recrystallization for blooming. These two issues are promoted by temperature change, however, fat bloom induced by oil migration occurs independently of temperature. If chocolate comes into contact with other ingredients containing liquid oil, the liquid oils in chocolate and the other ingredients migrate and mix together. Thus, migration promotes the softening of filled chocolate, the hardening of fillings, and fat bloom. Therefore, oil migration is a serious problem in praline chocolates, chocolate-covered cookies and chocolates with nuts.

Oil migration is thought to occur by diffusion or capillary flow in chocolate to the surface (Ziegler, 2009). The driving force for diffusion is assumed to be the difference in chemical components: the triacylglycerol (TAG) concentration gradient in domains of confectionery chocolate products. If the liquid fraction of oil in a filling has a different TAG composition than cocoa butter, oil migration occurs. This diffusion has been the preferred explanation for oil migration in chocolate products (Aguilera, Michel, & Mayer, 2004; Altimiras, Pyle, & Bouchon, 2006; Ghosh, Ziegler, & Anantheswaran, 2002; Miquel, Carli, Couzens, Wille, & Hall, 2001). The possibility of capillary flow has also been studied: pores exist inside chocolate because of volume shrinkage during crystallization and the volume of this vacancy has been calculated to be 1% of chocolate (Loisel, Lecq, Ponchel, Keller, & Ollivon, 1997). Mass transportation occurs through these pores via capillary force. The contribution from these two mechanisms is difficult to distinguish because they exhibit similar time dependence (Aguilera et al., 2004). In addition, another migration mechanism,

Abbreviations: TAG, triacylglycerol; EDX, energy dispersive X-ray spectroscopy; SEM, scanning electron microscopy.

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pressure-driven convection flow, has been proposed (Altimiras et al., 2006; Dahlenborg, Millqvist-Fureby, Bergenståhl, & Kalnin, 2011; Dahlenborg, Millqvist-Fureby, Brandner, & Bergenståhl, 2012; Dahlenborg, Millqvist-Fureby, & Bergenståhl, 2015a).

Numerous approaches have been utilized in the quantitative investigation of oil migration. Quantification of fat composition using chromatography is a common technique in the analysis of oil migration (Talbot, 1996; Ziegleder, Moser, & Geiwe-Greguska, 1996a; Ziegleder, Moser & Geiwe-Greguska, 1996b), however, spatial resolution is low because the samples must be divided for this analysis. Magnetic resonance imaging has been used to observe the inner structure of chocolate and to monitor oil migration in chocolate (Duce, Carpenter, & Hall, 1990; Guiheneuf, Couzens, Wille, & Hall, 1997). Magnetic resonance imaging is a nondestructive quantitative analytical method and thus is advantageous for oil migration investigation. Using this method, kinetic analysis of oil migration has made much progress, and has been used to determine the diffusion coefficient in model confectionery products (Guiheneuf et al., 1997; Lee, McCarthy, & McCarthy, 2010; McCarthy and McCarthy, 2008; Miquel et al., 2001; Rumsey & McCarthy, 2012). A flat-bed scanner combined with dye stain is a convenient technique for observing oil migration (Marty, Baker, Dibildox-Alvarado, Rodrigues, & Marangoni, 2005; Marty, Baker, & Marangoni, 2009). These techniques provide quantitative information on oil migration kinetics. A combination of scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) is a novel approach in the investigation of migration and blooming in chocolate. EDX is an analytical technique to identify elemental composition of a sample by measuring energy of characteristic X-ray from a specimen. Kinta and Hatta (2005, 2007) were the first to report on SEM–EDX in chocolate analysis (Kinta & Hatta, 2005, 2007). Using brominated vegetable oil as a die in SEM–EDX, Dahlenborg, Millqvist-Fureby, and Bergenståhl (2015b) found that the size of particles in chocolate affects migration velocity, and significantly increased the developing rate of fat bloom. They found that smaller particles of cocoa powder and sugar resulted in increased migration. A theoretical approach calculated that the velocity of capillary force migration was considerably faster than the migration rate obtained in the experimental results (Altimiras et al., 2006). In addition, Reinke et al. (2015) used small angle X-ray scattering to report that oil migration through pores occurred within seconds. These findings may support the significance of capillary force in oil migration. However, the oil migration pathway has not been observed directly, and details of oil migration remain obscure.

The aim of this study was to demonstrate a novel approach to quantitative analysis of oil migration using SEM–EDX. Silicone oil was used as the mobile phase in this study and its distribution was visualized using EDX. Silicone oils have advantageous physical properties, such as high thermal and oxidation stability, and low viscosity and surface tension. The surface tension of silicone oils is lower than that of other natural oils, so that they spread easily over an interface, and are widely used as deformers and release agents in the industrial field. In the present study, the significant property of silicone oils was low solubility in cocoa butter: silicone oil and cocoa butter are immiscible therefore the diffusion of silicone oil into chocolate is negligible. Using silicone oil as the mobile phase of oil migration in chocolate, we investigated the significance of capillary force and diffusion in oil migration.

2. Materials and methods

2.1. Materials

Commercial compound milk chocolate bars (Meiji Co., Ltd., Japan) and canola oil (The Nisshin Oillio Group, Ltd., Japan) were purchased at a local market. The chocolate contained sugar, cocoa powder, vegetable oil, whole milk powder, cocoa butter, and soy lecithin, in descending order of content. Silicone oil, Element14* PDMS 10-JC was obtained from Momentive Performance Materials Inc. (Japan). The physical properties of the silicone and canola oils are presented in Table 1.

2.2. Sample preparation

For the migration experiments, a chocolate bar was broken into pieces ($32 \times 26\,\mathrm{mm}^2$) using a sharp knife. A piece of chocolate was placed on a cotton pad (also $32 \times 26\,\mathrm{mm}^2$) impregnated with silicone oil or canola oil in a polystyrene case. The volume of the oils was 600 μl, the weight of the canola oil was 552 mg, and that of the silicone oil was 562 mg. The samples were incubated at 24 °C in an air incubator. To confirm the migration ability of silicone oil in the relatively high liquid oil environment of chocolate, the chocolate samples were stored at 24 °C. Stored chocolates were used for further experiments.

2.3. Weight change and hardness measurements

Weight change during storage was measured. The cotton pad was removed from the chocolate, and the weight of the chocolate was measured without wiping oil from the contact face. The measured samples were returned to the cotton pad in an incubator and used for further weight measurements. Hardness was measured using a penetrometer (EX-210E, Elex Science Co., Ltd., Japan) with a penetration rod that had a base diameter of 64.91 mm, a cone height of 29.08 mm, and a cone weight of 102.51 g. A penetration test was performed on the oil contacting face of the chocolate samples. These measurements were repeated at least five times.

2.4. SEM and EDX observations

The central part of the stored chocolate was cut out in a block shape ($3 \times 3 \times 4\,\mathrm{mm}^3$) using a sharp knife. When the tip of the knife was inserted into the chocolate, the chocolate was loosened and a piece of chocolate was released. The fragment was carefully trimmed to become a block shape. The surface of the chocolate block was coated with Au using a sputter coater (E-1010, Hitachi Instruments, Japan), and the cross-section was observed using SEM (S-2380, Hitachi Instruments, Japan). The acceleration voltage was 15 kV. To avoid artifacts in the SEM image, the area of chocolate where the knife had made contactwas not observed. Element

Table 1
Physical properties of silicone and canola oils.

	Dynamic viscosity (mm^2/s)	Density ($\mathrm{g/cm}^3$)	Surface tension (mN/m)	Pour point (°C)
Element14 PDMS 10-JC	10 (25 °C)	0.935 (25 °C)	20.1 (25 °C)	Below −60
Canola oil	50.91 (37.8 °C)	0.906 ~ 0.920 (25 °C)	31.7 (20 °C)	Below −18