Journal of Food Engineering 92 (2009) 261–268

Contents lists available at ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

Oil migration in chocolate: A case of non-Fickian diffusion

J. Román Galdámez [a], Kristin Szlachetka [c], J. Larry Duda [d,†], Gregory R. Ziegler [b,*]

[a] Sabic Innovative Plastics Mt. Vernon, Inc., Mt. Vernon, IN 47602, United States
[b] Department of Food Science, Pennsylvania State University, 341 Food Science Building, University Park, PA 16802, United States
[c] The Solae Company, St. Louis, MO 63188, United States
[d] Department of Chemical Engineering, United States

ARTICLE INFO

Article history:
Received 28 April 2006
Received in revised form 9 October 2008
Accepted 2 November 2008
Available online 28 November 2008

Keywords:
Chocolate
Oil migration
Phase behavior
Tortuosity
Model

ABSTRACT

Oil migration through filled chocolate products during storage periods is inevitable and is responsible for the loss of the original quality of the product. A model that predicts the extent of oil migration can help food engineers optimize the post-production period, thereby delivering an acceptable quality product to consumers.

In this work, a predictive model is proposed based on an explicit formulation of the diffusion problem in terms of the molecular diffusivity and the internal microstructure of chocolate. This work overcomes the limitations of the previous models by including a moving boundary, which allows for swelling of the chocolate slab and replacing the effective diffusion coefficient with a more physically meaningful one, which includes a tortuosity term that varies with oil concentration. The model has been validated against experimental mass uptake curves.

1. Introduction

The chocolate confectionery market is dominated by composite products such as pralines, filled chocolates or snack bars, where a chocolate or confectionery coating layer is in direct contact with a fat-based cream, biscuit, nut or nut paste. The marketable lifetime of these products is often limited by fat or oil migration, e.g. the fillings may contain large amounts of highly mobile oils, such as peanut or hazelnut oil that migrates into the chocolate coating causing quality loss (see Fig. 1). Quality defects arising from oil migration include softening of the coating, hardening of the filling, deterioration in sensory quality and a greater tendency to fat bloom. For this reason, oil migration has been extensively studied (Aguilera et al., 2004; Khan and Rousseau, 2006; Ziegleder et al., 1996a,b; Choi et al., 2007).

1.1. Mechanism of oil migration

Dark chocolate is a mixture of cocoa butter, chocolate liquor, and sugar. Milk chocolate contains milk solids as well. Commercial dark chocolate typically contains between 25% and 40% cocoa butter with the rest being variable amounts of sugar and solid cocoa powder. Chocolate is a dispersion of solid cocoa particles, sugar crystals, and milk powder (in the case of milk chocolate) in a continuous phase of solid and liquid fat, whose proportions depend on temperature (Ziegler et al., 2004).

Cocoa butter comprises a mixture of saturated and unsaturated fats; oleic acid (O), stearic acid (S), and palmitic acid (P) account for more than 95% of the fatty acids in cocoa butter. Cocoa butter contains high levels of the triacylglycerols (TAGs) POS, POP, and SOS that are crystalline at normal storage temperatures; some of the unsaturated TAGs in cocoa butter have low melting points making it partly liquid at room temperature.

The triacylglycerols in nut-based fillings, which often contain hazelnut or almond oils, such as triolein (OOO), LOO, LLO, POO, and SOO, where L stands for lauric acid, are predominately liquid at room temperature. Originally, the driving force for diffusion was assumed to be a difference in liquid fat content, but recently diffusion has been attributed to a gradient in triacylglycerol concentration within some domains of the product (Ghosh et al., 2002). In a series of experiments where a bar of chocolate was brought into contact with a nougat filling, Ziegleder et al. (1996a,b) showed that after sufficient time the main triacylglycerols of hazelnut oil had almost evenly distributed between chocolate and filling. On the other hand, little of the triacylglycerols of the cocoa butter had migrated into the filling.

Molecular or Fickian diffusion is widely used by food engineers as a general model for mass transfer. In the literature, there are several attempts to model fat migration using simplified solutions to Fick's Second Law of diffusion (Ziegleder et al., 1996a; Choi et al., 2007). As the first approximation, Ziegleder et al. (1996a) employed the short-time solution with a constant diffusion

* Corresponding author. Tel.: +1 814 863 2960; fax: +1 814 863 6132.
E-mail address: grz1@psu.edu (G.R. Ziegler).
† Deceased.

0260-8774/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jfoodeng.2008.11.003

Nomenclature

$C_{FP}(t)$	hazelnut concentration in filter paper [kg/m^3]
D_{eff}	effective diffusion coefficient [m^2/s]
D_0	diffusion coefficient in the liquid phase of the cocoa butter [m^2/s]
j^v_{HZ}	diffusivity flux of hazelnut oil with respect to the volume average velocity [kg/m^2 s]
K	partition distribution constant
$L(t)$	slab thickness expressed as a function of time [m]
$\bar{L}$	dimensionless slab thickness
t	Time [s]
$\bar{t}$	dimensionless time
$r_{SF\to LF}$	rate of crystal dissolution [kg/m^3 s]
$\bar{V}_i$	specific volume of species i [m^3/g]
w^{FAT}_{HZ}	weight fraction of hazelnut oil in the cocoa butter phase
x	position [m]

Greek letters

α	aspect ratio
λ	time lag [hours]
ξ	immobilization variable
ρ^T_{HZ}	mass concentration of hazelnut oil in the total chocolate [kg/m^3]
ρ^T_{SF}	mass concentration of solid crystals in the total chocolate [kg/m^3]
ρ^{LF}_{HZ}	mass concentration of hazelnut oil in the liquid cocoa butter [kg/m^3]
ρ_{s0}	mass concentration established instantaneously at the surface at time zero [kg/m^3]
$\bar{\rho}$	dimensionless mass concentration
τ	global tortuosity factor
ϕ^{Fat}_{SF}	volume fraction of solid fat in the cocoa butter phase
ϕ^T_{NF}	volume fraction of non-fat solid in chocolate
ϕ^T_{LF}	volume fraction of liquid fat in chocolate
v^v	volume average velocity

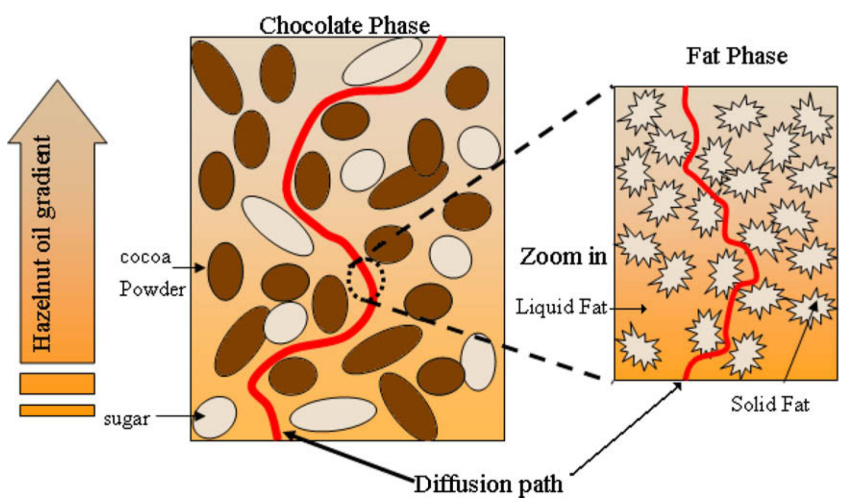

Fig. 1. Schematic representation of hazelnut oil migration into chocolate.

coefficient. Effective diffusion coefficients were extracted from the experimental data of the mass of the migrated oil plotted against the square root of time. Ziegleder et al. (1996b) observed a linear correlation between the logarithm of the effective diffusion coefficients so obtained and the liquid fat content in the chocolate.

Models based on the so-called Fickian diffusion with a constant diffusivity fail to accurately describe the migration of oil into chocolate (Choi et al., 2007), and because of this some have suggested that a mechanism other than diffusion, e.g. capillary pressure, is responsible for oil migration. However, it is equally likely that simplified models fail to accurately reproduce experimental data because simplifying assumptions are not fulfilled. In addition to constant diffusivity, these simplified solutions neglect swelling and interaction between the oil and the cocoa butter. Recent observations of oil migration through chocolate using magnetic resonance imaging have shown that the dominant mechanism is diffusion, and that if capillary pressure is involved it is a minor contributor (Deka et al., 2006).

Shetty (2004) proposed a new model that modified the effective diffusivity depending on the fat phase behavior. The idea behind this model is simple: the migrating oil disturbs the equilibrium between the liquid and solid phase present in the fat phase of chocolate. Oil migration decreases the solid fat content and thereby increases diffusion. Shetty's (2004) model used the same expression for the relationship between the effective diffusion coefficient and the liquid fat content obtained by Ziegleder et al. (1996b). The difference in the Shetty (2004) model was that the liquid fat content was calculated independently through an experimental phase diagram.

On the basis that the exact mechanism of oil migration in chocolate remains poorly understood, the present paper proposes a new model, based on molecular diffusion, to try to help elucidate the mechanism underlying fat migration. The model will account for structural parameters such as fat crystal microstructure and tortuosity and allows for chocolate swelling in order to overcome some of the drawbacks present in the previous models.

1.2. Phase behavior

Most chocolate confectionery products contain between 18% and 40% cocoa butter. Cocoa butter, as with most natural fats, contains at least two phases, i.e. liquid and solid, whose proportions vary with temperature. Cocoa butter can crystallize in six different polymorphic forms, referred to as I–VI, with β forms V and VI being