Surface energy investigation of chocolate adhesion to solid mould materials

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A B S T R A C T

Chocolate residues staying behind on the mould surface during chocolate bar manufacture are responsible for production losses, and increased processing costs due to equipment cleaning. This study investigates the determining role of surface energy in chocolate adhesion to the mould substrate and the ease of its demoulding. Four materials (quartz glass, stainless steel, polycarbonate, and Teflon) were investigated as mould substrates. A classical contact angle approach was used for the surface energy determination of mould materials. Chocolate-mould adhesion was measured by a simple separation test between the solidified chocolate and a mould probe using a Texture Analyser. The results demonstrated that surface energy of the mould material is a key determining factor of chocolate-mould interaction and has a significant influence on the adhesion of cocoa butter and dark chocolate to the mould. Further analysis has shown that the electron donor component of the surface energy is the main differentiating factor determining the extent of chocolate adhesion. It is concluded that a high surface energy material is generally not favourable for fabrication of the mould. For clean demoulding, the mould material should have a surface energy below $30 \, \mathrm{mN \, m^{-1}}$ and an electron donor component of the surface energy of approximately $15 \, \mathrm{mN \, m^{-1}}$.

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1. Introduction

1.1. General background

Adhesion is an important physical phenomenon commonly observed in many food-related situations. With respect to the sensory evaluation of food products, the terms stickiness and adhesion are often used interchangeably (Adhikari et al., 2001). Even though both these terms describe well understood phenomena, their meanings can vary somewhat depending on the context. For example, in relation to oral sensory perception, the term stickiness was defined by Jowitt (1974) as "possessing the textural property manifested by a tendency to adhere to contacting surfaces, especially the palate, teeth, and tongue during mastication." This definition therefore does not refer to stickiness of non-oral surfaces, which is commonly encountered in the manufacturing and transportation of foods. A more general description has been given by Hoseney and Smewing (1999), who described stickiness as "the force of adhesion that results when two surfaces are contacted with each other." The general consensus is that the term adhesion refers to the attractive interaction between two surfaces upon close contact, and in particular the energy that is required to separate these surfaces.

Adhesion or stickiness can be a desirable attribute in some food applications. For example, the adhesion between two food structural components is beneficial and desirable in food coating applications, as demonstrated by Brake and Fennema (1993) in studying the adhesion of an edible coating with chocolate or peanut butter. Adhesion of the food material to the equipment surface could be beneficial for some specific processing operations, e.g. for effective mixing of food ingredients during extrusion cooking. However, in most cases food adhesion is undesirable and a cause for concern. For example, the adhesion of food components to food packaging is generally undesirable as it may cause visual defects of surface texture and lead to consumer rejection of the food (Chen, 2007). The adhesion of food components to processing equipment is of considerable concern to food manufacturers because it leads to fouling of production lines, lower product yields, and increased economic costs (Adhikari et al., 2001; Michalski et al., 1997). In this manuscript we are concerned with the application of chocolate manufacturing, where adhesion and sticking of chocolate to the mould surface is a substantial ongoing problem, leading to poor product appearance, production losses (normally those products are considered out of quality standards and rejected), and increased processing costs in equipment cleaning.

1.2. Chocolate demoulding

The main ingredients of chocolate are cocoa butter, cocoa solids, and sugar, together with milk solids in the case of milk chocolate

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Nomenclature

$\gamma_s, \gamma_l, \gamma_i$	surface tension of a solid, a liquid, or material i ($mN\,m^{-1}$)
$\gamma_{sl}, \gamma_{sv}, \gamma_{lv}$	interfacial tension of the solid/liquid, solid/vapour and liquid/vapour interphase, respectively, ($mN\,m^{-1}$)
γ^+, γ^-	electron-acceptor and electron-donor parameters of the surface tension ($mN\,m^{-1}$)
γ^{LW}, γ^{AB}	Lifshitz-van der Waals and acid–base components of the surface tension ($mN\,m^{-1}$)
θ	Contact angle (°)

θ_a, θ_r	advancing and receding contact angle (°)
H	(contact angle) Hysteresis (°)
ΔG_a	free energy of adhesion ($mN\,m^{-1}$)
W_a	work of adhesion ($mN\,m^{-1}$)
$W_{a\ water}^p$	surface hydrophilicity ($mN\,m^{-1}$)
β_1	empirical constant (0.0001057) (($m\,mN^{-1}$)²)
E_a	experimental adhesion ($N\,m^{-2}$)

(Fryer and Pinschower, 2000). During processing these ingredients are mixed to form a dispersion of cocoa solids (particles) and sugar crystals in a continuous fat phase, consisting of fat crystals and liquid fat (Aguilera et al., 2004). One of the final stages of chocolate processing is the moulding stage, where tempered chocolate is deposited in moulds and subsequently cooled. During cooling the polymorphic cocoa butter crystallises and the chocolate solidifies. In the demoulding stage, the solidified chocolate bars are removed from the moulds.

The process of demoulding is opposed by the adhesive force between chocolate and the mould surface, which tends to hold the chocolate bars in the mould. In order to overcome the adhesive force, application of a mechanical force is needed to facilitate the separation, using a blow from a hammer, or a mechanism that twists the mould (Cruickshank, 2005). Furthermore, the ease of demoulding depends on the state of crystallization of the fat phase of the chocolate. Chocolate tempering is aimed at the generation of Form V crystals, which leads to a volumetric contraction of the tempered chocolate during solidification, and consequently an easy demoulding (Tewkesbury et al., 2000). However, for untempered chocolate, not contraction but expansion has been observed during cooling (Nelson, 1999). In addition, some other specific steps during chocolate processing may result in increased adhesion between chocolate and mould, causing intermittent problems in demoulding and consequently leading to surface defects, poor product appearance, and low consumer acceptability.

The extent of formation of chocolate deposits on a mould surface during demoulding will depend on the balance between the adhesion force (between the chocolate and the mould surface) and the cohesion force within the chocolate itself. Therefore, a greater ease of chocolate demoulding could be achieved in two ways: by decreasing the surface adhesion or by increasing the cohesion force of chocolate. The latter solution is, of course, not the manufacturers' desired choice, because it implies modifying the desirable texture and sensory properties of chocolate. Focus here is therefore on how to minimize the adhesion force between chocolate and mould surface. To address this issue, an understanding of the interaction between the deposited chocolate and the mould surface is required.

Various theories and mechanisms have been proposed to explain surface adhesion, e.g. mechanical interlocking, wetting, and thermodynamical adsorption, electrostatic adhesion, diffusion, chemical adhesion, and weak boundary layers (Michalski et al., 1997; Comyn, 1997). Of these theories, the concept of thermodynamically driven surface adhesion is probably the most relevant for food applications. Many researchers have considered that the extent of adhesion is predominantly determined by the surface energy of the substrate, especially in the case of bio- and crystalline fouling (Michalski et al., 1998, 1999; Zhao et al., 2005; Pereni et al., 2006; Rosmaninho and Melo, 2006). Bhandari and Howes (2005) reviewed the stickiness properties of foods during drying, and concluded that surface energy of the materials with which

the food is in contact is a critical factor in relation to the adhesion. According to them, many authors, however, do not take the solid surface energy into account when investigating the adhesion of food to processing equipment surfaces.

The present study applies the principles of thermodynamic adhesion and surface energy to the case of chocolate adhesion, with the aim of establishing relationships between the thermodynamic work of adhesion and the observed extent of adhesion of chocolate to mould materials.

1.3. Thermodynamics of adhesion

The interactions between a liquid and a solid–vapour interface can be characterised by the contact angle. This is the angle θ that a liquid drop makes when placed on a solid surface, as shown in Fig. 1. Kwok and Neumann (1999) described the measured contact angle as the result of three interfacial tensions in mechanical equilibrium. The relationship between the balanced forces in three-phase contact is conveniently described by Young's equation,

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos\theta \qquad (1)$$

where γ_{sv}, γ_{sl}, and γ_{lv} are the surface tensions of the solid–vapour, solid–liquid, and liquid–vapour interfaces, respectively. The different interfaces aim to reduce their interfacial area and consequently minimize the overall interfacial energy of the system. A practical disadvantage of Young's equation is that it contains only two readily measurable quantities: the contact angle, θ, and the liquid–vapour surface tension, γ_{lv}.

The thermodynamic work of adhesion (W_a), or the negative of the free energy of adhesion ($-\Delta G_a$), can be interpreted as the work required to separate a unit area of solid–liquid interface between two different materials to leave a "clean" solid surface and a liquid surface, both in equilibrium with the vapour phase. It can be described by the equation of Dupré (Karbowiak et al., 2006):

$$W_a = \gamma_{sv} + \gamma_{lv} - \gamma_{sl}. \qquad (2)$$

The equation of Dupré is based on the assumption that there is negligible liquid surface area change upon adhesion to a solid surface (Lyklema, 2000). Combining Eqs. (1) and (2) yields the Young-Dupré adhesion model:
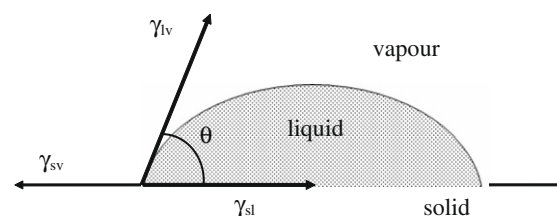

Fig. 1. A schematic representation of a liquid drop placed on a solid surface. The subscripts s, l, and v stand for solid, liquid, and vapour, respectively.