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Surface energy investigation of chocolate adhesion to solid mould materials

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ABSTRACT

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 mN m $^{-1}$ and an electron donor component of the surface energy of approximately 15 mN m^{-1}.

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

γ_s, γ_l, γ_i	surface tension of a solid, a liquid, or material i ($\mathrm{mN\,m^{-1}}$)
γ_{sl}, γ_{sv}, γ_{lv}	interfacial tension of the solid/liquid, solid/vapour and liquid/vapour interphase, respectively, ($\mathrm{mN\,m^{-1}}$)
γ^+, γ^-	electron-acceptor and electron-donor parameters of the surface tension ($\mathrm{mN\,m^{-1}}$)
γ^{LW}, γ^{AB}	Lifshitz-van der Waals and acid–base components of the surface tension ($\mathrm{mN\,m^{-1}}$)
θ	Contact angle (°)
θ_a, θ_r	advancing and receding contact angle (°)
H	(contact angle) Hysteresis (°)
ΔG_a	free energy of adhesion ($\mathrm{mN\,m^{-1}}$)
W_a	work of adhesion ($\mathrm{mN\,m^{-1}}$)
$W_{a\ water}^{p}$	surface hydrophilicity ($\mathrm{mN\,m^{-1}}$)
β_1	empirical constant (0.0001057) ($(\mathrm{m\,mN^{-1}})^2$)
E_a	experimental adhesion ($\mathrm{N\,m^{-2}}$)

(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,

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos\theta \tag{1}$$

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):

$$W_a = \gamma_{sv} + \gamma_{lv} - \gamma_{sl}. \tag{2}$$

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:

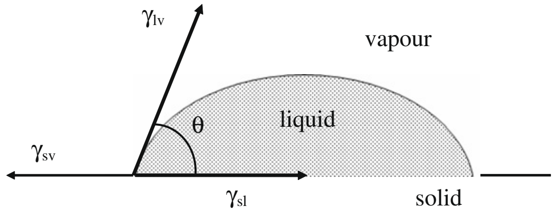

Fig. 1. A schematic representation of a liquid drop placed on a solid surface. The subscripts s, l, and v stand for solid, liquid, and vapour, respectively.

$$W_a = \gamma_{lv}(\cos\theta + 1). \tag{3}$$

In this equation the only unknowns are the liquid–vapour surface tension, γ_{lv}, and the contact angle, θ, two quantities which are relatively easy to determine experimentally. With respect to the present study, the contact angle (θ) refers to the angle that chocolate makes with the solid surface, the mould, and the liquid–vapour surface tension, γ_{lv}, refers to the chocolate-vapour surface tension.

2. Materials and methods

2.1. Materials

Polycarbonate, poly(tetrafluoroethylene) (PTFE) (Teflon) (Barkston Plastics Ltd., Leeds) and stainless steel 316 (Richard Austin Alloys, Leeds) were chosen as solid substrates because of their commercial application in confectionery productions. Industrial chocolate moulds are now commonly made from polished polycarbonate, although they were traditionally made from stainless steel. Flexible PTFE and/or silicon rubber moulds have also shown practical advantages, due to their flexibility and low surface energy. The appropriate surface finish of polycarbonate and stainless steel was obtained by abrasion, using a P600 (3M™, MarineWare, Southampton) wet or dry abrasive paper and an abraded surface plate. For the PTFE surface finish, a fine turn was used. Quartz glass (Scientific Optics, Hastings) with an optical finish was chosen as the reference material, because of its well-known high surface energy. The solid surfaces were cleaned with detergent (Springdawn High Active) containing 5% ionic surfactant and 5–15% non-ionic surfactant, followed by distilled water (MilliPore) and acetone (AR grade) prior to their use in surface energy or adhesion force determination. Probe or test liquids used for surface energy calculations were deionized, distilled water (MilliPore), formamide (Sigma-Aldrich, $\geqslant$99% purity) and diiodomethane (Sigma-Aldrich, ~99% purity). Samples used for surface adhesion determination were dark chocolate (52% cocoa solids, Nestlé commercial recipe) and deodorized cocoa butter (100% cocoa solids, ADM Cocoa, Koog aan de Zaan), obtained from Nestlé PTC, York.

2.2. Contact angle measurements

Contact angles were determined using the sessile drop method in an apparatus specifically designed for this purpose. The apparatus consisted of a Perspex chamber fitted with a Peltier fan (Stable Micro Systems) for temperature control. Inside the chamber a stand carrying a CCD video camera (Optivision) was used as a base to hold the solid surfaces. Prior to the measurement, the liquids were placed inside the chamber in order to reach thermal equilibrium and also equilibrium between the vapour and liquid phases. Sessile drops (2–10 μl) were deposited on the solid surface using a micro-syringe (Hamilton). Advancing (θ_a) and receding (θ_r) contact angles were obtained by increasing and decreasing the volume of the drop, respectively. Contact angles were determined from digital images using the DropSnake program, which is based on a cubic B-spline snake (active contours), similar to the polynomial-fitting approach (Stalder et al., 2006). The averages of the left and right contact angle of five different drops placed on two different clean surfaces were used to determine the reported surface energy values.

The surface tension of each of the probe liquids was measured using a Krüss K10 ST digital tensiometer (Krüss), with a platinum Wilhelmy plate. The surface tensions measured agreed within ±1.2 mN m^{-1} of those found in the literature, and therefore surface tension components of the probe liquids are taken as the literature values, as shown in Table 1. The surface tensions and contact angles of the probe liquids on the different solid surfaces were measured in the temperature range 20–40 °C, as this is the temperature range over which the chocolate comes into contact with the mould.

2.3. Surface free energy

To interpret the surface free energy in terms of the intermolecular interaction forces at the interface, and to calculate the solid surface tension, γ_{sv}, several semi-empirical approaches have been developed in the literature. These approaches mainly correlate liquid surface tension with the contact angle for the determination of the surface energy. Here we consider five of the most widely used approaches for the determination of γ_{sv}.

2.3.1. Zisman critical surface tension approach

Fox and Zisman (1950) introduced the concept of the critical surface tension, γ_c, as a measure of the 'wettability' of solid surfaces. Their approach is based on a plot of the cosine of the contact angle versus the surface tension of the test liquids. Linear regression of the data determines γ_{lv} at the value of cos $\theta = 1$ (i.e. $\theta = 0$), which is defined as the critical surface tension of wetting. Liquids with a surface tension below γ_c are expected to spread easily on the respective solid surface.

2.3.2. Fowkes surface tension component approach

Fowkes (1964) was the first to postulate the solid surface free energy to be composed of a sum of different surface tension components. These components are the result of the attractive forces existing between the solid surface layer and the liquid phase due to different intermolecular forces at the surface

$$\gamma = \gamma^d + \gamma^n, \tag{4}$$

here γ^d is the dispersive part and γ^n is the non-dispersive (or polar) part of the surface tension. The dispersive component results from molecular interactions due to London (van der Waals) forces, whereas the non-dispersive component results from non-London (e.g. Keesom and Debye) forces (Kwok and Neumann, 1999). Fowkes assumed a geometric mean of the dispersion force components of the surface tension to represent the balance of intermolecular forces at the interface. Combining this geometric mean with the Young's equation yields

$$\gamma_l(1 + \cos\theta) = 2\sqrt{\gamma_s^d \gamma_l^d}. \tag{5}$$

Consequently, the contact angle of only one liquid is required for the calculation of the dispersion force component of the solid surface energy (Sharma and Rao, 2002).

Table 1
Surface tension components of probe liquids (from Good, 1992; Van Oss, 2006).

Liquid	Total surface tension, γ_l^{tot} (mN m^{-1})	Dispersive component, γ_l^{lw} (mN m^{-1})	Polar component, γ_l^{ab} (mN m^{-1})	Electron acceptor, γ_l^{+} (mN $m^{-1)}$]	Electron donor, γ_l^{-} (mN m–^{1})
Deionised water	72.8	21.8	51.0	25.5	25.5
Formamide	58.0	39.0	19.0	2.28	39.6
Diiodomethane	50.8	50.8	0	0	0

2.3.3. Owens and Wendt geometric mean approach

Owens and Wendt (1969) further extended Fowkes' concept of surface tension components, by dividing the total surface energy into two components, a dispersion force component and a hydrogen bonding component, the latter consists of both hydrogen bonding and dipole–dipole interactions

$$\gamma_l(1+\cos\theta) = 2\sqrt{\gamma_s^d\gamma_l^d} + 2\sqrt{\gamma_s^p\gamma_l^p}. \tag{6}$$

In this approach, the contact angles of at least two liquids with known surface tension components (e.g. water and diiodomethane) are required in order to calculate the surface tension of the solid surface and its components.

2.3.4. Van Oss, Chaudhury and Good approach

This is also known as the Lifshitz–van der Waal/acid–base approach. The basis of this approach is again the Fowkes methodology, except that the interactions taking place at the interface are separated into long range Lifshitz–van der Waals (LW) interactions and short range hydrogen bonding (SR) interactions. The Lifshitz–van der Waals (LW) interactions include all the electrodynamic contributions: the dispersion (London) force, the orientation (Keesom) force, and the induction (Debye) force. The short range polar or hydrogen bonding (SR) interactions can be classified as Lewis acid–base interactions, including the electron acceptor, γ^+, and the electron donor, γ^-, interactions (Van Oss et al., 1988a; 1988b), i.e.,

$$\gamma_l(\cos\theta+1) = 2\left(\sqrt{\gamma_s^{lw}\gamma_l^{lw}} + \sqrt{\gamma_s^+\gamma_l^-} + \sqrt{\gamma_s^-\gamma_l^+}\right). \tag{7}$$

The contact angles of at least three liquids (two polar and one apolar) with known surface tension components are required to calculate the surface tension of the solid material and its components (Kwok and Neumann, 1999; Sharma and Rao, 2002).

2.3.5. Equation of state (EQS) approach

Neumann and co-workers (Neumann et al., 1974; Li and Neumann, 1992) proposed an equation of state for the solid surface energy, based on a modified Berthelot's combining rule. They used an empirical constant, β, which was obtained by fitting their equation of state to a set of contact angle data from polymeric solids. Kwok and Neumann (1999) further modified the equation of state specifically for applications to solid–liquid free energy determination. Combining the modified equation of state with Young's equation leads to

$$\gamma_l(1+\cos\theta) = 2\sqrt{\gamma_s\gamma_l\left(1-\beta_1(\gamma_s\gamma_l)^2\right)}, \tag{8}$$

where $\beta_1 = 0.0001057\ (\mathrm{m/mN})^2$. The advantage of this method is that only one liquid is required in order to calculate the surface free energy. However, this approach determines only the total surface free energy with no consideration of the components.

2.4. Determination of chocolate-mould adhesion

Experimental determination of chocolate adhesion to the mould surface was performed on the TA-XTplus Texture Analyser (Stable Micro Systems), using a fixture specifically developed for this work. The surface adhesion force (or stickiness) was measured by pulling the flat probe off a solid chocolate sample, as shown schematically in Fig. 2, imitating the forces involved in the demoulding process of chocolate bars. The principle of the method is the same as that used by Adhikari et al. (2007) and Werner et al. (2007) in measuring the tensile strength (surface stickiness) of carbohydrate and protein solutions using a probe tack test, mimicking the stickiness feeling that is observed when a surface is touched. This probe separation method has also been recently used in our laboratory for the stickiness quantification of fluid food materials (Chen et al., 2008).

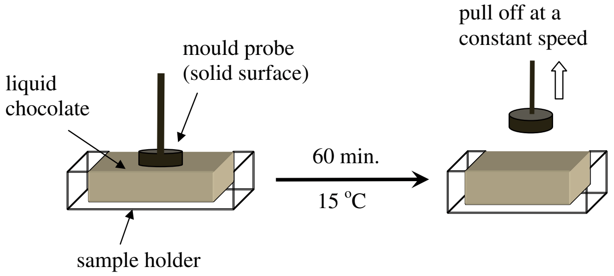

Fig. 2. A schematic diagram of the procedure and conditions of the surface adhesion measurements.

All adhesion tests were carried out in a modified Peltier chamber (Stable Micro Systems) under a controlled environment of temperature and relative humidity. A flat probe (18.9 mm in diameter, 5 mm in thickness) was brought into contact with the non-tempered, liquid chocolate sample. The contact or chocolate-mould interface is created at a temperature of around 30 °C, depending on the type of chocolate used. Prior to contact, both chocolate and mould probe were thermally equilibrated in the controlled environment for 30 min. Once the interface had been created, the temperature was adjusted to 15 °C and the sample was left without disturbance for 60 min, ensuring complete solidification. The temperature of the air (environment) during the cooling stage was measured, and no significant difference between experiments was observed, indicating that the cooling rate of the air was similar between experiments. The cooling rate of the solid materials was not determined, and no adjustments in cooling rate were made with changing mould material. During chocolate manufacturing, processing conditions are not adjusted to the type of mould used, and consequently the thermal diffusivity and variations in cooling rate of the solid material are not taken into consideration. The flat probe, attached to the Texture Analyser, was then pulled off the sample at a constant speed of $0.001\ \mathrm{m\,sec^{-1}}$ over a distance of 5 mm. The chocolate container was held firmly in its original position with the help of a titanium covering plate screwed to the base of the Texture Analyser. In the centre of the covering plate is an opening to allow free movement of the probe.

The experimental adhesion force, E_a, is defined as the force per surface area,

$$E_a = \frac{\textit{adhesion force}}{\textit{surface area}}, \tag{9}$$

where the adhesion force is the peak separation force measured by the probe pulling test and the surface area is the contacting area between the probe and the chocolate.

The measurement of the adhesion force of two different polycarbonate mould probes was repeated four times. As the results obtained for these measurements showed low standard deviations (<10%), the procedure was accepted as generally valid. Subsequent measurements were repeated four times for each surface.

3. Results and discussion

3.1. Characterization of mould surfaces

The empirical approaches described in Section 2.3 have been applied for the determination of the surface energy of the polycarbonate surface. Results given in Fig. 3 show that the calculated surface energy values based on these various approaches lie in the range 31–39 mN m^{-1}. Statistical analysis (independent samples, Student *t*-test, $P < 0.05$) showed that the results obtained via the Fowkes and Van Oss methods were indistinguishable. Results from the other approaches, however, were statistically different. The Van Oss result conveniently lies in the mid-range of the calculated values. The Van Oss method has also been commonly used previously for food-related studies (Michalski et al., 1998; Zhao et al., 2005; Liu et al., 2006; Pereni et al., 2006; Rosmaninho and Melo, 2006), and its acid–base approach is therefore adopted here as a convenient tool for the comparison of surface energy of the different mould materials and for relating the surface energy to the work of adhesion.

Table 2 shows the total surface energy and the individual surface energy components using the Van Oss acid–base approach for the different mould materials. The values of the total surface energy can be ranked as follows: Teflon < polycarbonate < stainless steel < quartz glass. Statistical analysis (independent samples, Student *t*-test, $P < 0.05$) showed that all the mould surfaces had significantly different values of the surface energy, as expected. The trend seen for the total surface energy, with the lowest value for Teflon and the highest for quartz glass, correlates well with trends of literature values (Lewin et al., 2005; Güleç et al., 2006). However, the actual numerical values do deviate, as a result of different empirical approaches used in the surface energy calculation and different experimental conditions. On average, the surface energy of Teflon reported in this study, 8.9 mN m^{-1}, is fairly low compared to values reported in literature, which range from 18.6 to 23.9 mN m^{-1} (Lewin et al., 2005). It was noticed that the experimental contact angles obtained in this work were moderately higher than those observed by Lyklema (2000). It is suspected that this deviation may be caused by the relative inaccuracy of the DropSnake method at high contact angles, leading as a result to a lower total surface energy. Statistical analysis further indicated that the surface energy components are significantly different for the four mould materials, except for the electron acceptor component which is small and similar for all the mould materials. The electron donor component, γ_s^-, of the solid surface energy seems to be the main differentiating factor amongst the different mould materials.

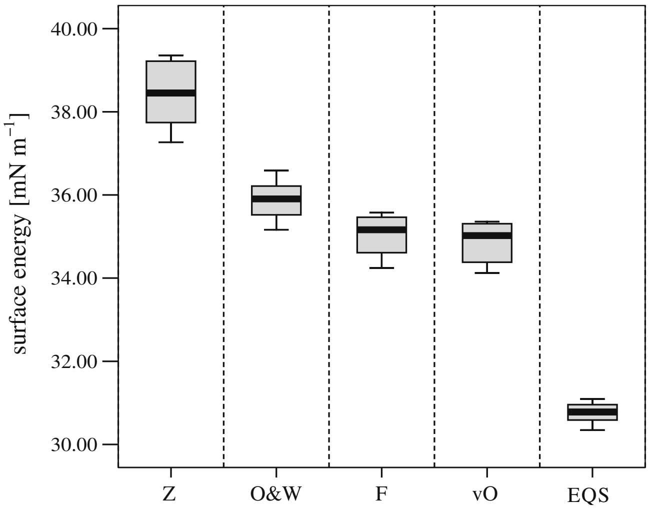

Fig. 3. Surface energy of polycarbonate calculated using different empirical approaches: Zisman (Z), Owens and Wendt (O&W), Fowkes (F), Van Oss (vO), and Equation of State (EQS).

Table 2 also gives the estimated surface hydrophilicity of the various solid materials. This is an important parameter for surface characterization, and it was determined here using the method described by Krisdhasima et al. (1992). In this method the quantity $W^{p}_{a\ water}$ as the index of surface hydrophilicity, based upon the interaction between a solid surface and water, using the polar component of the work of adhesion

$$W^{\mathrm{p}}_{\mathrm{a\,water}} = \gamma_{water}(cos\theta + 1) - 2\sqrt{\gamma^{\mathrm{LW}}_{\mathrm{water}}\gamma^{\mathrm{LW}}_{\mathrm{s}}}. \qquad (10)$$

The $W^{p}_{a\ water}$ values estimated for the mould materials used in this study compare well to those reported for similar materials by Michalski et al. (1999). More importantly, the surface hydrophilicity appears to differ distinctively between the mould materials, indicating its potential use as another discriminating factor with regards to the measured adhesion force. Quartz glass, one of the most hydrophilic of surfaces, has the highest value (71.42 mN m^{-1}), whereas Teflon, a well-known hydrophobic surface, has even a negative surface hydrophilicity (−2.78 mN m^{-1}).

Surface contact angles can be determined in two different ways: advancing and receding. The former mode gives the so-called advancing contact angle, θ_a, and the latter gives the receding contact angle, θ_r. An ideal surface would have almost identical advancing and receding contact angles. However, in reality, most materials have significantly different advancing and receding contact angles, and the difference between the two is called the contact angle hysteresis, H (=$\theta_a - \theta_r$). The effect is believed to be caused by factors such as surface roughness, surface heterogeneity, and/or surface chemistry (Lyklema, 2000). Table 3 gives the value of the surface contact angle hysteresis for each of the four different mould materials. It appears that all four materials have relatively high values of contact angle hysteresis, due to probably heterogeneous surface chemistry or surface roughness. The polycarbonate and stainless steel surfaces, which have both been treated with abrasive paper, show similar values for *H*. Therefore it is reasonable to believe that their surface roughness is the main cause of contact angle hysteresis. In general, contact angle hysteresis was found to be significantly different for the four mould materials, but there was no obvious trend of correlation with the set of surface adhesion measurements. As a result, it is not expected that this factor can make a significant contribution to understanding the variation of the surface adhesion of chocolate with the solid surface energy.

Table 2

Total surface energy, surface energy components and surface hydrophilicity of mould materials as determined by the Van Oss acid–base approach.

	Surface energy (mN m^{-1})					Surface hydrophilicity (mN m^{-1})
	γ_s^{tot}	γ_s^{lw}	γ_s^{ab}	γ_s^{+}	γ_s^{-}	$W^{p}_{a\ water}$
Polycarbonate	34.86	33.17	1.69	0.51	1.44	19.24
Stainless steel	40.57	37.0	3.49	0.21	16.96	45.88
Teflon (PTFE)	8.89	9.20	0.31	0.083	0.31	−2.78
Quartz glass	54.36	38.88	15.48	1.84	32.70	71.42
Dark chocolate	22.57	22.23	0.35	0.077	0.59	9.38

Table 3
Contact angle hysteresis (H) of water, diiodomethane and formamide on the four different mould materials.

	H_{water}	$H_{formamide}$	$H_{diiodomethane}$
Polycarbonate	57.4	43.5	41.2
Stainless steel	52.7	42.5	30.3
Teflon (PTFE)	39.9	37.1	37.7
Quartz glass	30.5	–	10.3

3.2. Chocolatemould adhesion

Surface adhesion of dark chocolate and cocoa butter has been investigated for the different mould materials. As shown in Fig. 4, two parameters were measured: the adhesion force, expressed as the separation force per unit surface area ($N m^{-2}$), and the left-over residue at the probe surface, expressed as the amount of chocolate per unit surface area ($mg m^{-2}$). It was found that the adhesion force for dark chocolate was consistently higher than the force required to pull the same mould material off the solidified (non-tempered) cocoa butter surface. The quartz glass surface stands out for its highest separation force for both dark chocolate and cocoa butter. It was also noticed that the amount of residue left-over at the probe surface was rather different amongst the various mould surfaces and between dark chocolate and cocoa butter, suggesting the involvement of different failure mechanisms in the surface adhesion. According to Werner et al. (2007) and Adhikari et al. (2003), the failure of surface bonding is via one of three different mechanisms: cohesive failure, cohesive–adhesive failure, and adhesive failure. The relative magnitude of the sample-probe adhesion force and the cohesion strength of the sample determine which mechanism dominates surface bonding failure. By examining the probe surfaces after separation, two main types of separation were identified in this study: adhesive failure and cohesive–adhesive failure. This can be seen from the two inserted pictures in Fig. 4, one with a clean surface separation and one with chocolate residue left-over at the probe surface, representing the two cases, respectively.

The transition from adhesive failure to cohesive failure for probes of high surface energy is clearly reflected by the amount of residue left on these probes (see Fig. 4). For the dark chocolate samples a clean separation was observed for the polycarbonate, Teflon and stainless steel surfaces, indicating an adhesive failure at the chocolate-mould interface, due to the cohesive strength of the chocolate sample exceeding the interfacial adhesive bonding strength between mould material and chocolate. However, the quartz glass surface showed cohesive–adhesive failure, indicating a combination of both cohesive and adhesive failure, resulting in chocolate residues left on the mould probe surface. This suggests that dark chocolate has a much stronger surface adhesion force with the quartz glass surface than the other mould materials. For the case of cocoa butter, it was found that only the Teflon surface gave a clean surface separation with minor cocoa butter residues. All other mould materials showed cohesive–adhesive failure with cocoa butter. This suggests a significant difference in cohesive strength between dark chocolate and cocoa butter. It is likely that the presence of the sugar and cocoa particles in the chocolate greatly enhances the cohesiveness (internal strength) of the fat crystal network. Differences in crystallinity (polymorphism) between dark chocolate and cocoa butter further contribute to the observed differences in cohesive strength.

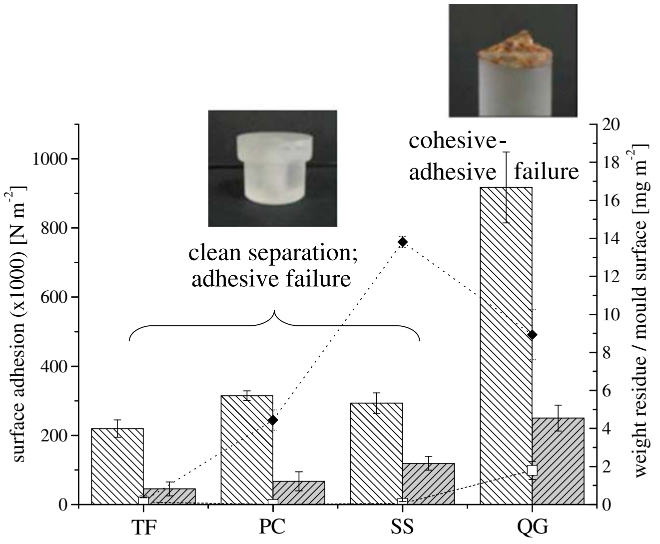

Fig. 4. Surface adhesion of chocolate and cocoa butter on different mould materials (Teflon (TF), polycarbonate (PC), stainless steel (SS), and quartz glass (QG)) and the amount of residues after probe separation. The column bars represent the surface adhesion: ▨ dark chocolate, and ▨ cocoa butter. The lines represent the residue weight per mould surface area: □ dark chocolate, and, ◆ cocoa butter.

In order to evaluate the change in the surface of the mould probe after its contact with chocolate, the surface contact angle of water and the glossiness of the probes have also been monitored. Fig. 5A shows the change of surface glossiness, whilst Fig. 5B shows the change of water contact angle of the four probes after their contact with chocolate. The contact angle of water on the mould surface showed a significant increase for most mould materials, indicating an enhanced hydrophobicity of the probe material. The increase in surface hydrophobicity was lowest for the Teflon surface, which had the lowest hydrophilicity (last column in Table 2) prior to contacting the chocolate.

The glossiness is a measure of the extent of light reflection by the surface. Its magnitude is affected by parameters like surface roughness and composition. A decrease in glossiness of the mould surface indicates a change of its surface layer, either an increased roughness or the adsorption of components from the sample which consequently changes the composition of the surface layer. Results from surface contact angle and glossiness measurements seem to suggest an important fact that, even though these probes have a clean separation with little surface residue (as seen in Fig. 4 for stainless steel, polycarbonate, and Teflon), the surface after contact appears to be rather different. It is therefore highly likely that a very thin layer of chocolate (fat) deposits onto the probe surface during its contact with chocolate, making the surface more hydrophobic and less glossy, as shown in Fig. 5C.

3.3. Work of adhesion

The Young-Dupré adhesion model (Eq. (3)) uses the contact angle of the adhesive on a solid surface for the determination of the work of adhesion. Unfortunately, however, due to the viscoelastic nature and relatively high melting point of chocolate, it is not practicable to measure the contact angle of chocolate on different mould surfaces under ambient conditions. Therefore, in order to obtain some indication of the interactions involved and the degree of wetting, cocoa butter was used as a model replacement system to represent chocolate in the application of the Young-Dupré equation. The contact angles of cocoa butter on the respective mould materials, and the corresponding values of the work of adhesion, W_a, are shown in Table 4. It can be seen that Teflon gives the largest contact angle but the smallest work of adhesion. In contrast, quartz glass has the smallest contact angle but the largest work of adhesion. The four mould materials can be ranked in the following order of increasing work of adhesion: Teflon < polycarbonate < stainless steel < quartz glass. This is exactly the same order as for the total surface energy, as discussed previously (see Table 2). Of course, it should be noted that chocolate and cocoa butter are two different materials, which would be expected to have different values for the work of adhesion. Therefore, the results in Table 4 can only be treated as a useful approximation to the behaviour expected for chocolate.

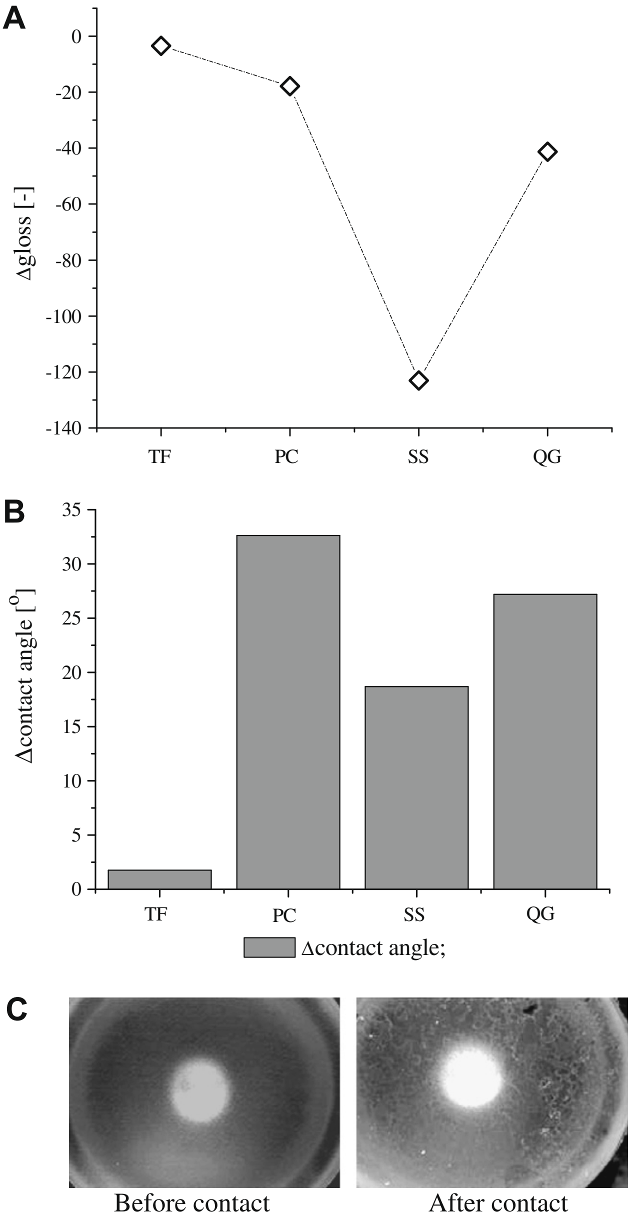

Fig. 5. Differences of contact angle (A) and surface glossiness (B) of mould surfaces (Teflon (TF), polycarbonate (PC), stainless steel (SS), and quartz glass (QG)) before and after chocolate contact. C shows images (scale 1:0.34) of polycarbonate surfaces before and after contact with chocolate, respectively.

Table 4
Contact angles (θ) and work of adhesion (W_a) of cocoa butter on different mould materials.

	θ [degrees]	std.dev	W_a [mN m^{-1}]
Polycarbonate	35.6	2.4	56.9
Stainless steel	27.9	1.5	59.1
Teflon (PTFE)	47.5	1.5	52.6
Quartz glass	23.2	2.9	60.2

3.4. Relating surface energy to surface adhesion

Plotting the thermodynamic work of adhesion, W_a, against the total surface energy, γ_s^{tot}, gives a linear relationship ($R^2 = 0.97$) (see Fig. 6A). This implies that the total surface energy and the thermodynamic work of adhesion are strongly correlated, and in principle could be used interchangeably. Fig. 6B plots surface adhesion force against the surface energy and a direct (but non-linear) correlation is also evident between these two parameters.

The curves fitted to the data in Fig. 6B indicate the possible existence of a critical surface energy, below which the chocolate has minimal surface adhesion with the mould substrate. For both cocoa butter and chocolate the apparent critical surface energy of the mould substrate is ~30 mN m^{-1}. A significant increase in surface energy beyond this value leads to a pronounced increase in surface adhesion. The existence of a minimum surface energy has been observed previously by Michalski et al. (1999), who proposed a critical surface tension (~38 mN m^{-1}) for the adherence of emulsion residues. Recently, Boulangé-Petermann et al. (2006) have also indicated the presence of a critical polarity, when defining the relationship between the polar component of the surface energy and oil removal. And Liu et al. (2006), in investigating the

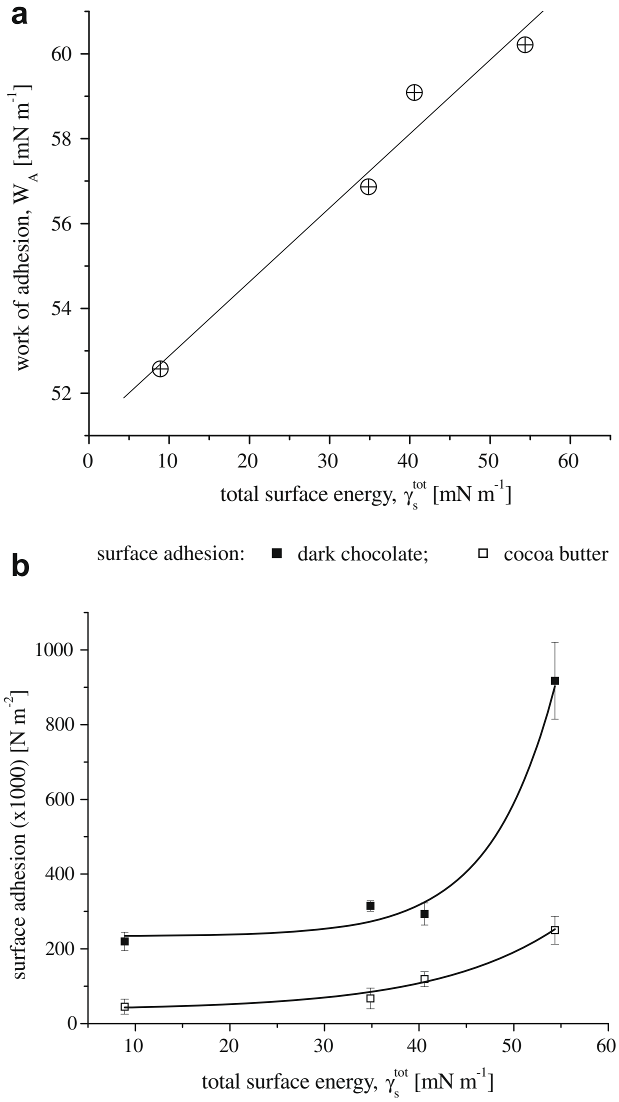

Fig. 6. Work of adhesion (A), and surface adhesion of dark chocolate (■) and cocoa butter (□) (B) as a function of total surface energy.

force required to remove a food deposit from solid substrates, have found a minimum adhesive strength at a surface energy of 22–26 mN m^{-1}. Similar conclusion has also been made by Mars in a patent claim that moulds with surface energy below 30 mN m^{-1} as having optimum demoulding properties (Mars, 1999).

Relating surface energy components to mould–chocolate adhesion indicates a linear relationship between the polar or Lewis acid-base component and the experimental adhesion of both dark chocolate ($R^2 = 0.97$) and cocoa butter ($R^2 = 0.97$). As the electron donor component, γ_s^-, can be used as an effective differentiating factor, Fig. 7 plots this component against the surface adhesion. The positive relationship between the electron donor component and the probe separation force is obvious. In fact, the trend line fitted to the data in Fig. 7 indicates a similar functional dependence for the electron donor component as previously obtained for the total surface energy. A critical value of the electron donor component (~15 mN m^{-1}) can be inferred. Below this critical value, the value of mould-chocolate adhesion remains minimal. It is noteworthy, however, that the cocoa butter adhesion tends to zero at low γ_s^- whereas that for the chocolate remains finite.

Chocolate adhesion to mould materials therefore shows a strong correlation with the surface energy of these respective mould substrates. The hardness and gloss of the chocolate samples, combined with the surface adhesion data, indicate that the crystallization of the cocoa butter (or the continuous fat phase) is affected by the surface energy of the mould substrates. According to Mullin (2001), heterogeneous nucleation can be induced by the presence of foreign bodies or surfaces. It is possible that the varying surface energies of the mould substrates used in this study are responsible for differences in degrees of nucleation, consequently resulting in different crystal structures. Crystal growth results in structures with a minimum surface area and consequently minimum surface energy, according to the traditional surface energy theories, and so the surface energy of the chocolate-mould interface is likely to play a role in determining the final crystal structure.

Cho et al. (2003) and Rosmaninho and Melo (2006) independently investigated the effect of substrate surface energy on the crystallization behaviour of isotactic polypropylene and calcium phosphate, respectively. They both found that the microstructure of the final crystallized sample depended on the surface energy of the substrate. Rosmaninho and Melo (2006) found that solid substrates with a high electron donor component of the surface energy showed a higher number of nucleation sites, enabling the formation of a more compact structure. Cho et al. (2003) observed different crystalline morphologies, dependent on the substrate surface energy. It was believed that the formation of a purely transcrystalline region (transcrystallites) on high energy substrates was responsible for an increase in interfacial adhesion strength. On low energy substrates, however, both spherulites and a minority of transcrystallites were present, resulting in fracturing at the boundary of these two morphologies. A similar effect of substrate surface energy was also observed by Zhao et al. (2005) when investigating the microstructure of calcium phosphate deposits. These observations seem to have some parallel in the chocolate solidification on mould surfaces observed in this work. One may expect that different surfaces (or surfaces of different energy) will lead to different crystal structures, which consequently will affect the microstructure of the chocolate in the surface region. Based on the above results and discussion, it is clear that a material with a high surface energy (i.e., a high electron donor component) should not be used as a mould material. Such a material would be expected to produce a more compact structure of chocolate with strong crystal–crystal interactions in the interface region, which will tend to make demoulding more difficult.

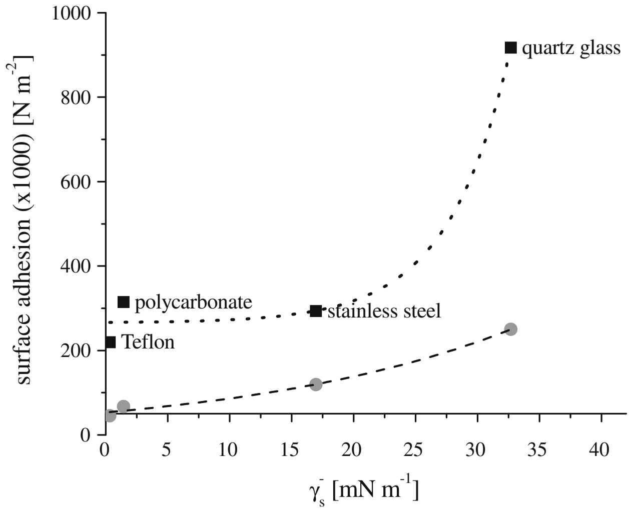

Fig. 7. Surface adhesion of dark chocolate (■) and cocoa butter (◎) as a function of the electron donor component of surface energy.

4. Conclusions

The properties of the mould surface have been shown to have significant influences on how chocolate adheres and solidifies during the moulding process. The separation of solidified chocolate from the mould was found to be dominated by two different failure mechanisms, adhesion failure or cohesive failure, depending on the nature of mould surface. Teflon, polycarbonate, and stainless steel showed clean surface separation of the chocolate, and a mechanism of adhesive failure; but quartz glass, a material of much higher surface energy, showed predominantly cohesive failure with substantial amounts of chocolate residue left on the probe surface. The measured separation forces showed a direct correlation with the surface energy of the mould and the work of adhesion. A high surface energy material is generally unfavourable for easy separation of the mould from the chocolate. A solid material with a surface energy below 30 mN m^{-1} (and an electron donor component of ~15 mN m^{-1}) is recommended as a suitable mould material for chocolate production.

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