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Effect of nut oil migration on polymorphic transformation in a model system

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Abstract

Fat migration in confectionery products can lead to significant deterioration in quality. This occurs not only through loss in texture contrast between chocolate and filling but also through the appearance of fat bloom on the surface of the chocolate. This latter aspect is often, although not exclusively, linked to the transformation of the cocoa butter β_V phase into β_{VI}. In this study, the influence of hazelnut oil on the polymorphic transformation of cocoa butter has been determined, showing that even small additions (1%) of nut oil can have a significant impact on the rate of transformation. Additionally, use of a model system has shown that polymorphic transformation in cocoa butter is linked to the degree of migration of nut oil from a filling. Portions of the cocoa butter close to the filling experience both greater degrees of migration and faster transformation.

Keywords: Fat migration; Cocoa butter; Bloom; Chocolate

1. Introduction

In many multi-component chocolate products in which two fat phases are in contact, fat migration occurs to a greater or lesser degree, depending on storage conditions (Choi, McCarthy, & McCarthy, 2005; Jana & Thakar, 1993; Wootton, Weedon, & Munk, 1970). Such migration usually leads to a significant loss of quality (Talbot, 1990; Wootton et al., 1970) and, consequently, oil migration is an important issue. Products commonly affected by fat migration are chocolate articles with nut-based centres, coated biscuits or wafers and cream-filled chocolates. More often than not, fat migration involves the movement of softer fats into harder ones (Talbot, 1990; Timms, 2003), praline filled chocolate shells being typical products exhibiting such a process (Fig. 1a).

Quality reduction in products can be exhibited in several ways. Softening of the chocolate is immediately apparent when handling the product but the centre often becomes harder at the same time. These two effects together can lead to a loss of sensory distinction between the components of the product. If the migration from the filling occurs at a faster rate than in the reverse direction, there is a consequent swelling of the chocolate. Frequently the chocolate becomes discoloured. Finally, the increase in the liquid fat content of the chocolate can increase the rate of fat bloom formation on the chocolate surface. However, if the triacylglycerols (TAG) that migrate into the chocolate are 'incompatible' with cocoa butter, additional softening occurs (over and above that expected by dilution) due to a eutectic effect (Herzing, 1989; Paulicka, 1986; Rossell,

Abbreviations: TAG, triacylglycerol; CB, cocoa butter; HZ, hazelnut oil; HS, hardstock fat; GLC, gas–liquid chromatography; XRD, X-ray diffraction; DSC, differential scanning calorimetry; pNMR, Pulsed nuclear magnetic resonance.

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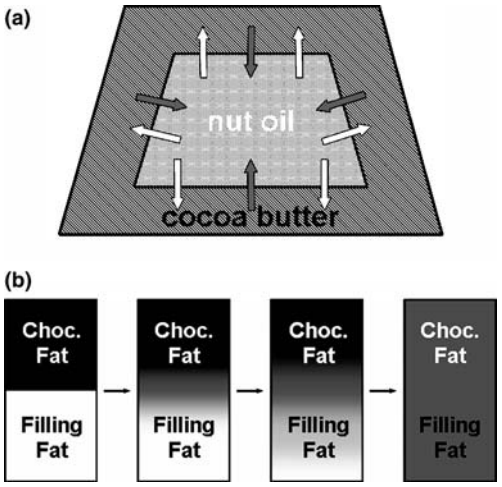

Fig. 1. (a) Migration occurs both from centre to shell and vice versa. (b) Given sufficient time, the composition of the fat phase in the centre and the shell will become identical.

1973; Timms, 2002). This further increase in the liquid fat content of the chocolate can also increase the rate of, or trigger, fat bloom formation.

Many approaches have been adopted in the study of fat or oil migration. These encompass measurement of both the physical and the chemical changes occurring. Changes in the melting profile have been determined by pulsed nuclear magnetic resonance (pNMR) and DSC (Tabouret, 1987; Walter & Cornillon, 2001; Walter & Cornillon, 2002; Ziegleder & Schwingshandl, 1998) and hardness measurements have been used to quantify the degree of softening (Ali, Selamat, Man, & Suria, 2001; Talbot, 1989). Chromatographic methods have enabled the tracking of individual TAG types into chocolate (Timms, 2003; Wootton et al., 1970; Ziegleder, Moser, & Geier-Greguska, 1996a; Ziegleder, Moser, & Geier-Greguska, 1996b) and, more recently, magnetic resonance imaging has been employed as a non-invasive means to follow liquid oil movement in composite products (Guiheneuf, Couzens, Wille, & Hall, 1997; Miquel, Carli, Couzens, Wille, & Hall, 2001; Miquel & Hall, 2002; Miquel, Evans, & Hall, 1998; Simoneau, McCarthy, & German, 1993; Walter & Cornillon, 2001; Walter & Cornillon, 2002).

Fat migration is driven by a concentration gradient between the differing TAG compositions of the adjacent fat phases and will ultimately lead to a completely identical composition of the two fat phases (Fig. 1b). Ziegleder's group have applied, to filled chocolate products, equations developed for describing the diffusion of non-polar molecules into plastic (Ziegleder et al., 1996a; Ziegleder et al., 1996b; Ziegleder & Schwingshandl, 1998). Along with previous empirical studies (e.g. Chaveron, Ollivon, & Adenier, 1976), this work enables us to identify the significant factors affecting migration and its effects, which are:

- Contact area.
- Ratio of the two fat phases.
- Solid fat contents.
- Fat level and non-fat solid particles.
- Particle size.
- Viscosity.
- Storage temperature.
- Fat type.

In most confectionery fats, solid and liquid phases exist in equilibrium. If two different fats are placed in contact with one another there will be a mixing of their liquid phases. Migration thus takes place via the liquid phases of the adjacent fats and involves the movement of TAG that are liquid at the storage temperature or are dissolved in other (liquid) TAG. As this mixing takes place, the equilibrium between solid and liquid phases in each fat is disturbed and some of the previously solid material may dissolve in the new liquid phase (Ziegler & Szlachetka, 2005). Thus TAG that are generally considered to be solid at the relevant temperature are able to migrate by dissolution in the liquid phase, movement to the adjacent layer and, on occasion, subsequent re-crystallisation. For example, if cocoa butter is in contact with hazelnut oil, the liquid TAG of the oil migrate into the cocoa butter while, perhaps to a lesser extent, the principal, solid cocoa butter TAG migrate in the opposite direction. Theoretically, given sufficient time, the composition of the two juxtaposed fats will become identical (Fig. 1b) and will be an average of the two original compositions, taking into account the relative amounts of the two fats initially. However, the time required may be too long for this kind of equilibrium to be observed in practice.

Another migration mechanism, capillary rise, has been put forward (Aguilera, Michel, & Mayor, 2004; Marty, Baker, Dibildox-Alvarado, Neves Rodrigues, & Marangoni, 2005), which postulates that the liquid oil is drawn into pores or holes in the solid fat, or chocolate, matrix. However, the true mechanism of fat migration has yet to be established (Aguilera et al., 2004), but it is likely that a combination of diffusion and capillary rise mechanisms operate (Guiheneuf et al., 1997).

In many products, fat migration leads to bloom. In this study we attempt to relate the migration of liquid oil to an increased rate of polymorphic transformation, which is often linked to bloom formation.

In the first part of the present study, the effect of hazelnut oil on the polymorphic transformation of cocoa butter was determined by addition of hazelnut oil (HZ) to cocoa butter (CB), followed by tempering and storage. The second part of the study examined the migration of HZ into CB, and its effect on polymorphic transformation.

2. Materials and methods

2.1. Fats used

The three fats used in this investigation were hardstock (HS), hazelnut oil (HZ) and cocoa butter (CB). The cocoa

butter was supplied by Barry Callebaut (Banbury, UK). The hardstock was a fractionated trans-hardened fat, CLSP194, obtained from Loders Croklaan B.V. (Wormerveer, The Netherlands). Hazelnut oil was obtained by chopping fresh, raw hazelnuts in a food processor and crushing them using a mortar and pestle. The resulting oily paste was wrapped in filter paper and cloth and pressed in a hydraulic plate press at 50 °C and 300 bar for 24 h to remove the oil. Oil was recovered from the filter cloth by soxhlet extraction. The hydraulic press was built in our laboratory and had parallel plates (20×20 cm) that were heated by circulating water through channels within the plates.

2.2. Solid fat content

Solid fat contents were determined by pNMR by placing samples into glass test-tubes of 10 mm diameter and measuring using a Bruker PC20 Minispec pulsed NMR spectrometer. No stabilization or tempering procedure was applied to the samples so that previous sample history could be retained.

2.3. Fat composition

Fats were analyzed using gas–liquid chromatography (GLC), separating TAG according to their molecular weights. Fats were dissolved (1.0 mg/ml) in iso-octane and analyzed by GLC on 10×0.53 mm 0.1 μm film Quadrex DB5. Oven temperature programming of 200–325 °C at 10 °C/min followed by 325–355 °C at 5 °C/min was used. Helium carrier gas was set at 40 kPa. Data were presented according to the total number of carbon atoms in the acyl chains of each TAG, i.e. the Carbon Number.

2.4. Polymorphism

X-ray diffraction (XRD) patterns were obtained at 20 °C using a Philips generator and Philips PW1050/25 powder diffractometer with X'Pert APD software. Samples were pressed into an aluminium sample holder approximately $10 \times 10 \times 1$ mm in size, to present a flat surface to the beam of CuK_α radiation of 1.54 Å wavelength. A diffraction pattern was collected between 18 and 26° 2θ over a period of 6 min.

2.5. Calculating β_V and β_{VI}

To generate standard CB β_V and β_{VI} diffractograms, a sample was tempered according to the following procedure:

1. Approximately 100–150 g of fat was melted at 50 °C in a 500 ml beaker and stirred whilst cooling in a water bath at 20 °C. Stirring was carried out using a metal spatula ensuring crystallisation on the walls and bottom of the beaker was homogeneously incorporated throughout the mass.
2. When the sample became too thick to stir effectively, the beaker and contents were transferred to a water bath at 30 °C and stirring continued until the sample was pourable.
3. When the pourable state was achieved, the mass was deposited into polycarbonate chocolate moulds of 50 g capacity, and subsequently cooled in a Blum cooling tunnel with a temperature profile of 15–10–15 °C at a wind speed of 3 ms^{-1} for a total of 20 min.

A diffractogram was obtained after storing the sample for 1 day at 20 °C. A bar of CB was stored in a cabinet cycling between 15 °C and 25 °C for 10 weeks and a further diffractogram obtained. The former matched published patterns for β_V and the latter matched those for β_{VI} CB (Sato & Koyano, 2001). These two diffractograms provided the basis of the standard β_V and β_{VI} patterns used in the calculations.

The method adopted here assumes that the diffraction pattern obtained for a sample of mixed polymorphs is the sum of the individual diffraction patterns of the components of the mixture (Fig. 2). Thus, if a mixture is composed of 40% β_V, 40% β_{VI} and 20% liquid, the measured X-ray diffractogram can be reproduced by adding pure β_V, pure β_{VI} and liquid patterns in the ratio 40:40:20.

In order to allow for differences in the background intensity (due to different sample surface, changes in incident beam etc.), all intensities were adjusted to give the same average background reading between 25.8° and 26° 2θ prior to calculations. This was achieved by normalizing according to the average measured values between 25.8° and 26° 2θ (a region in which no peaks are seen)

$$I_{A,2\theta} = I_{M,2\theta}/I_{ave}$$

where $I_{A,2\theta}$ is the adjusted intensity at angle 2θ, $I_{M,2\theta}$ is the measured sample intensity at angle 2θ and I_{ave} is the average intensity between 25.8° and 26° 2θ.

To form the necessary pure β_V and β_{VI} diffractograms, allowance must be made for the fact that at 20 °C (where the patterns have been measured), a portion of the CB remains liquid. The diffractogram of liquid oil is a very broad, rounded peak that must be subtracted from the measured data to yield the pure, 100% solid β_V or β_{VI} pattern. The liquid diffractogram was obtained by fully melting the CB prior to obtaining the diffractogram. This was subtracted from the patterns obtained from the tempered and stored CB according to the amount of liquid present as measured by pNMR

$$I_{P,2\theta} = (I_{A,2\theta} - X_L * I_{L,2\theta})/(1 - X_L)$$

where $I_{A,2\theta}$ = adjusted intensity at angle 2θ of CB sample, $I_{P,2\theta}$ = intensity of pure 100% β_V or β_{VI} at angle 2θ, $I_{L,2\theta}$ = adjusted intensity of 100% liquid CB at angle 2θ and X_L = proportion of liquid phase measured by pNMR. Thus, when this calculation applied to β_V CB, $I_{P,2\theta}$ represents the intensity of the pure β_V solid (i.e. I_V) and when

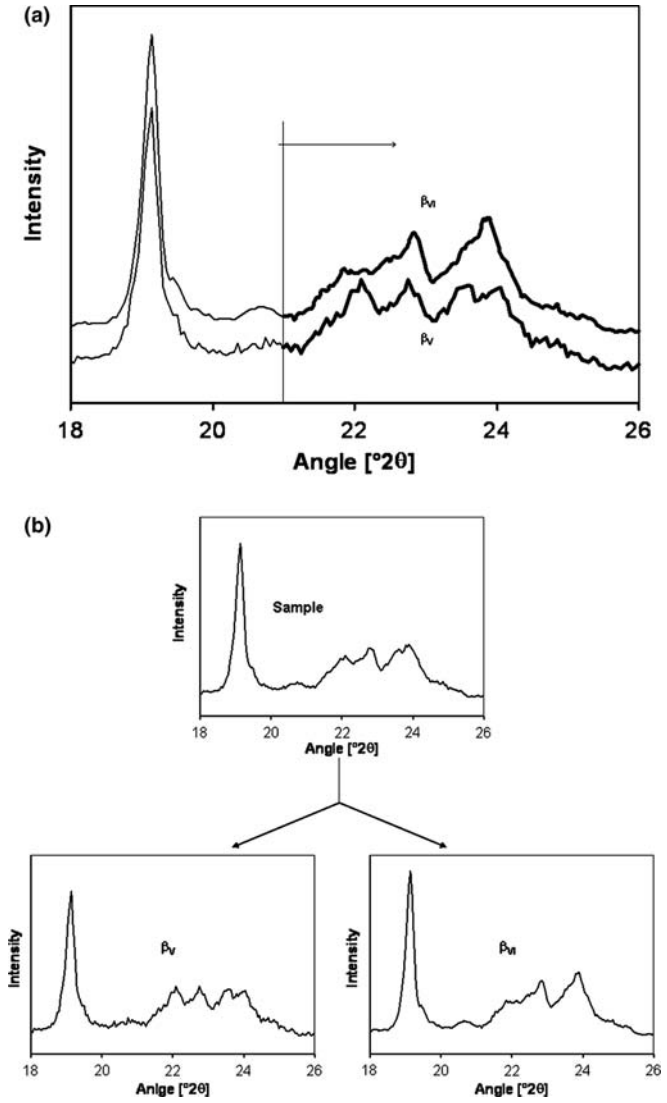

Fig. 2. (a) Highlighted areas of the β_V and β_{VI} polymorph diffractograms are used to calculate the sample composition. (b) The polymorphic composition of the sample is determined from a linear fit of the pure polymorphs to the sample diffractogram.

applied to β_{VI} CB, $I_{P,2\theta}$ represents the intensity of the pure β_{VI} solid (i.e. I_{VI}).

Finally, to determine the proportions of each polymorph in a sample, normalized diffractograms were fitted to the patterns determined for the liquid oil and for the pure β_V and β_{VI} forms using a multiple linear fit between 21° and 26° 2θ.

$$I_M = X_V * I_V + X_{VI} * I_{VI} + (1 - X_V - X_{VI}) * I_L$$

where I_M = adjusted measured intensity for the sample mixture, I_V = calculated intensity for pure β_V, I_{VI} = calculated intensity for pure β_{VI}, I_L = adjusted intensity for liquid oil, X_V = proportion of sample in β_V form and X_{VI} = proportion of sample in β_{VI} form.

Note that this method presupposes that the presence of liquid oil does not cause a shift in the spacings of either β polymorph. Final data is presented as a percentage of the solid phase that is in the specified polymorph, i.e. $100*X_{VI}/(X_V + X_{VI})$. Thus 40% β_{VI} indicates that 40% of the solid phase is in the β_{VI} form, while the remainder is still in the β_V form.

2.6. Effect of liquid oil

To examine the effect of liquid oil on polymorphic transformation, blends were produced by mixing CB and HZ at 60 °C to give levels of HZ of 0, 1 2, 5, 10 and 20%.

The HZ/CB blends were tempered according the procedure detailed above. After tempering, samples of HZ/CB were stored at 15 °C, 20 °C or 25 °C. The polymorphic form of the fats was determined at intervals during storage using X-ray diffraction. In addition, the solid fat content and polymorphic form were determined after 1 day storage at 20 °C and again after 6 months at 25 °C to establish the effect of HZ on each CB β polymorph.

2.7. Effect of migration

To examine the migration of HZ into CB, a model system was constructed (Fig. 3) based on the 'washer test' model of Talbot, 1996. The model filling comprised HZ with 15% HS that was mixed with icing sugar in the ratio 40:60 fat:sugar. The model was formed using a Perspex base onto which was glued a steel washer having a hole of internal diameter of 10 mm and depth of 2.5 mm. Into the resulting well was deposited the filling material, which was levelled off. The fillings were cooled in a cooling tunnel (as above). Five slim steel washers (shims), having the same external and internal diameter as the washer but being only 0.5 mm deep, were stuck in a stack on top of the first washer. CB, tempered using the procedure described above, was deposited on top of the filling in the resulting well and cooled in a cooling tunnel as described above. Samples were stored at 20 °C, 25 °C and 28 °C. At intervals during storage, one model sample was removed and the shims separated from the washer using a razor blade. The shims were separated from each other by use of the same blade and each layer of cocoa butter (0.5 mm thick circular slice of 10 mm diameter) was analyzed by XRD and GLC.

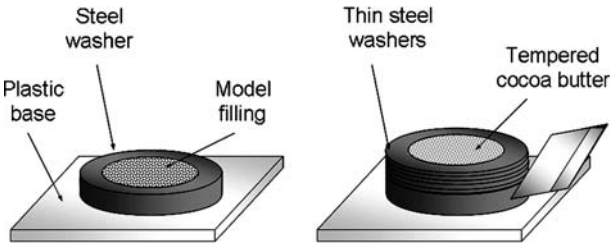

Fig. 3. Model filled chocolate. A steel washer (2.5 mm thick) is glued to a plastic base. Filling is deposited in the central hole (10 mm diameter), and cooled. Five thin washers (0.5 mm thick) are stuck in stack on top of the first washer. Tempered cocoa butter is deposited in the central hole. At intervals during storage, thin washers are removed using a razor blade.

2.8. Calculation of migration

The amount of filling fat that had migrated into the cocoa butter was calculated from the GLC analysis of the stored sample and the analyses of the CB, HZ and HS. In any mixture the Carbon Number values are a linear combination of those of the component fats. In this study, a simplifying assumption was made that the individual triacylglycerols of each fat migrate together. From the analyses of the CB, HZ and HS, a multiple linear regression analysis was performed on the sample composition fitted to the following equation:

$$CN_S = X_{CB} * CN_{CB} + X_{HZ} * CN_{HZ} + (1 - X_{CB} - X_{HZ}) * CN_{HS}$$

where CN = indicates the value of a specific Carbon Number, X indicates proportion of specific fat present and subscripts S, CB, HZ and HS indicate parameters relating to sample, cocoa butter, hazelnut oil and hardstock respectively. The amount of migration was equal to $(1 - X_{CB})$.

3. Results and discussion

3.1. General

The GLC Carbon Number composition of the three oils is given in Table 1. As is evident, there is sufficient difference between them (especially CB and HZ) to make determination of migration possible by Carbon Number GLC.

3.2. Effect of liquid oil content

Solid fat contents of CB/HZ blends are shown graphically in Fig. 4. The addition of HZ has a consistent effect on the solid fat content, reducing the solid fat in line with the added oil (i.e. 20% HZ led to a reduction of about 20% solid), particularly at 20 °C and 25 °C (Fig. 4b). This is in line with the observation by Lovegren, Gray, and Feuge (1976) that addition of liquid oil to CB or CB stearin decreased the final melting point. However, after 6 months storage at 25 °C (data not shown) – at which point all samples had transformed to β_{VI}–solid fat contents were reduced more than would be expected from the level of addition. That is, addition of 20% HZ decreases the solids content at 20–30 °C by around 26%. Ziegler, Shetty, and Anantheswaran (2004) similarly noted that oil migrating into a coating would dissolve some of the existing solid phase such that the solid fat content is reduced not only by the simple presence of the liquid oil but also by dissolution of the solid phase.

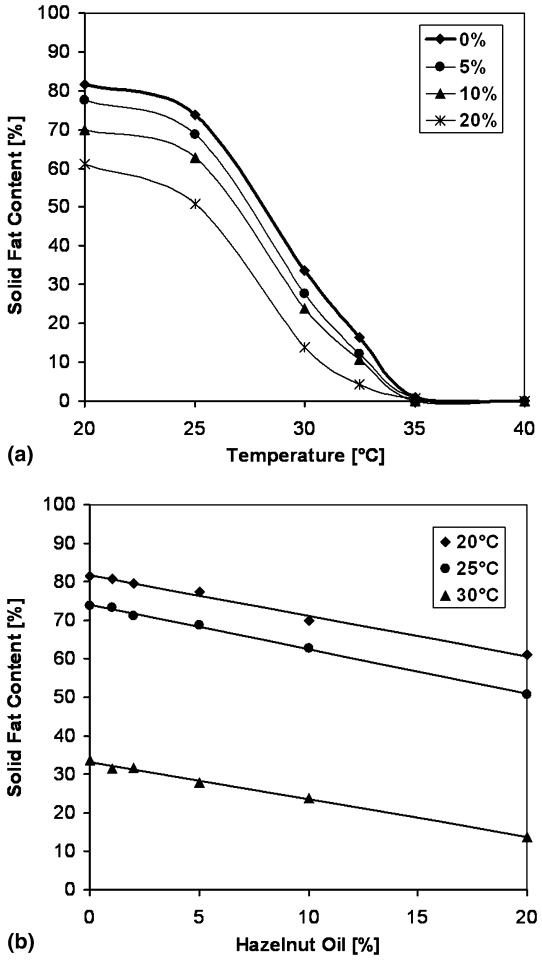

Fig. 4. Solid fat content of cocoa butter as a function of (a) temperature for different hazelnut oil levels. (b) Hazelnut oil level for different temperatures.

The difference between the effect of the HZ on β_V and β_{VI} may arise for two possible reasons. Firstly, in tempering and cooling the CB, crystallisation occurs relatively rapidly. In this situation, it is possible for some TAG to be incorporated into the solid phase that might otherwise remain in the liquid phase. The β_{VI} forms from a slow recrystallisation, where such TAG can be excluded from the growing crystal. Secondly, the β_{VI} structure is denser and more closely packed suggesting that, to be incorporated, TAG must have a greater similarity (or affinity) to the growing solid phase. Thus, as β_{VI} grows at the expense of β_V, some TAG will be rejected from the growing solid and be left in the liquid phase.

The blends had solid contents at 20 °C ranging from 61% (20% HZ) to 81.6% (0% HZ) and at 25 °C ranging from 50.8% (20% HZ) to 73.3% (0% HZ). Transformation of these fats from β_V to β_{VI}, as measured by XRD, is illustrated in Fig. 5 for storage at 20 °C and 25 °C. The increasing speed of transformation with addition of HZ was apparent at all temperatures. For example, after 5 weeks

Table 1
Triacylglycerol Carbon Number GLC of fats[a]

	C46	C48	C50	C52	C54	C56	Other
Cocoa butter	0.0	0.3	18.1	45.5	33.7	2.1	0.3
Hazelnut oil	0.0	0.0	0.7	15.4	82.7	1.2	0.0
Hardstock	0.2	1.9	16.2	54.0	25.9	1.4	0.4

[a] C*nn* indicates TAG having acyl groups whose carbons sum to *nn*.

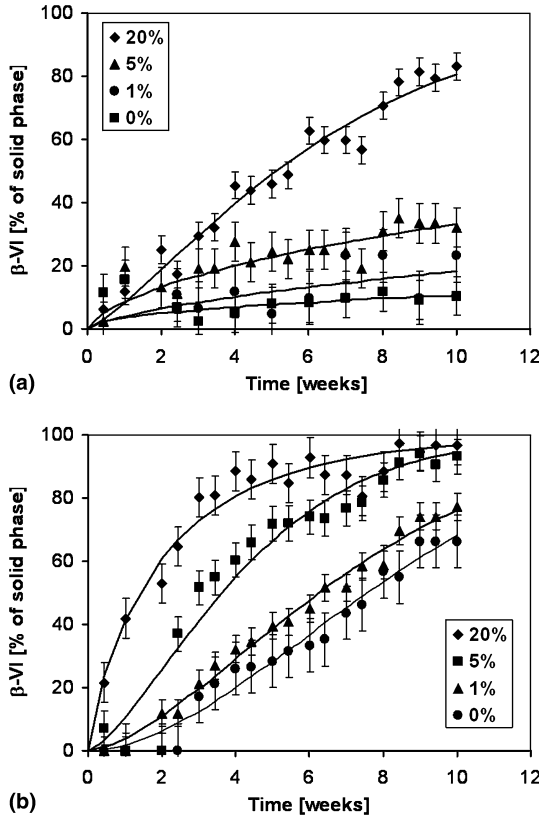

Fig. 5. Formation of β_{VI} in cocoa butter as a function time for various hazelnut oil contents (a) at 20 °C and (b) 25 °C.

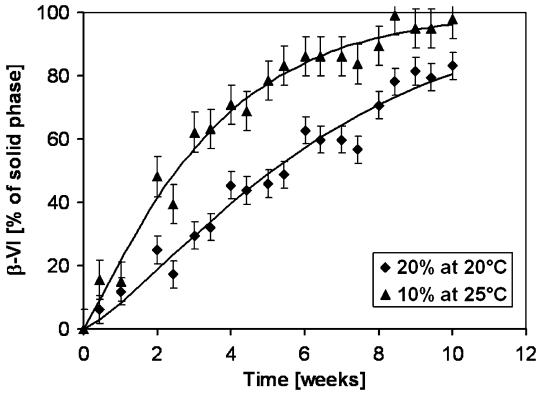

Fig. 6. Formation of β_{VI} in cocoa butter with added hazelnut oil as a function time for 20% oil at 20 °C (61% solid by pNMR) and 10% oil at 25 °C (63% solid by pNMR).

at 25 °C, CB was 28.3% β_{VI} while CB with 20% HZ was almost fully transformed from β_V to β_{VI}. Note that even 1% HZ was sufficient to raise the transformation rate compared to pure CB, and as little as 5% HZ led to almost complete transformation after 10 weeks at 25 °C. Lovegren et al. (1976) also noted a tendency to faster polymorphic transformation when liquid oil was added to CB or a CB fraction. As anticipated, increased temperature led to faster transformation (compare Fig. 5a and b) at all levels of HZ addition. Transformation at 25 °C was considerably faster than at 15 °C and 20 °C, with addition of 10% HZ having a greater effect at 25 °C than addition of 20% HZ at 20 °C (Fig. 6). Since the amount of solid fat in each of these cases is similar (60–63%, from the dilution experiments), it may indicate that the rise in temperature itself increases the transformation rate or, alternatively, that HZ provides an accelerating effect over and above that of increased liquid oil content. Note that there is less difference in transformation rate between different levels of HZ as the temperature increases, i.e. the lines in Fig. 5b are closer together than those in Fig. 5a. This emphasizes the fact that temperature is an important factor in polymorphic transformation. At 15 °C (data not shown) and 20 °C (Fig. 5b), pure CB undergoes very little transformation over the 10 week period. But at both of these temperatures, addition of 1% HZ is enough to start the transformation within the 10 weeks storage.

The reason for the accelerating effect of even small levels of HZ is not at all clear. The increase in the amount of liquid phase would seem to be insignificant, even taking into account some degree of dissolution. CB contains a total of around 80% trisaturated and mono-unsaturated TAG (Gunstone, Harwood, & Padley, 1984), and has around 80% solid at 20 °C. Considering the phase behaviour of such a system, it might be anticipated that at least some of these TAG remain in solution in the liquid phase while, in contrast, some of the lower melting TAG are incorporated into the solid, i.e. the 80% solid at 20 °C is not composed of solely trisaturated and mono-unsaturated TAG. Addition of HZ, i.e. mainly low melting TAG (Mottram, Woodbury, & Evershed, 1997), represents a significant increase in tri-unsaturated TAG. Without HZ, the principal low melting TAG are those containing two oleic acids or one linoleic. These TAG have one and two saturated acids, respectively. As such, they may be more easily incorporated into the mono-unsaturated TAG solid than would tri-unsaturated TAG. The presence of the HZ tri-unsaturated TAG may be sufficient to encourage recrystallisation of the β_V phase into β_{VI} following tempering and crystallisation. However, this doesn't address the accelerating effect found during migration (see below) and, to date, no evidence exists to support this or any other hypothesis.

3.3. Migration

Analysis of CB layers from the model system showed a degree of scatter in the data, although overall trends may still be seen. The overall trend (see Fig. 7a for 20 °C data, for example) is that which is expected, in that the concentration of filling fat in the CB is highest nearest the interface with the filling, dropping off with distance from the interface. In addition, although the level of migration is similar for all temperatures near the interface, at higher temperatures the gradient of the drop off is less so that migration is greater for higher temperatures (cf. lower temperatures) at the furthest point (2.0–2.5 mm). These observations are consistent with the findings of Adenier,

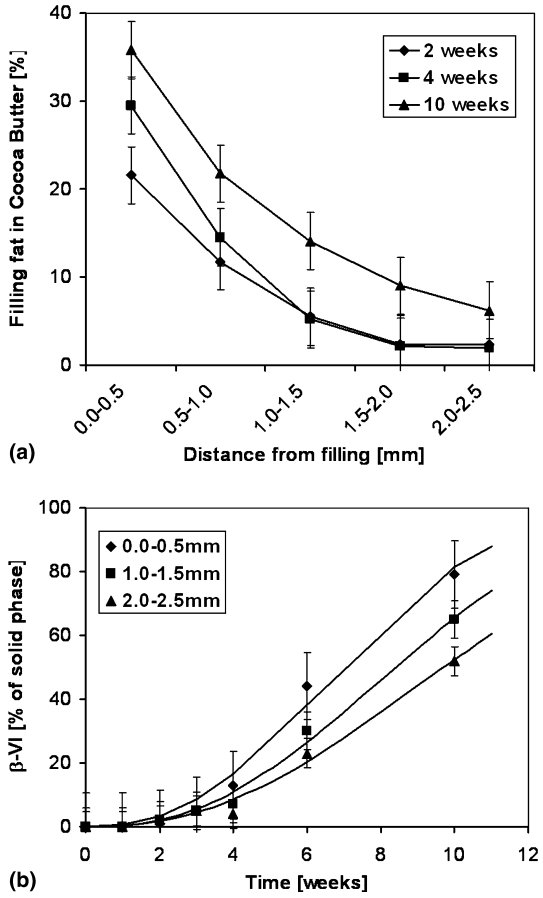

Fig. 7. (a) Proportion of filling fat in cocoa butter layer as a function of distance from filling layer for samples stored for various times at 20 °C. (b) Transformation of cocoa butter into form β_{VI} at 20 °C as a function of time for different distances from the filling.

Chaveron, and Ollivon, 1993 and Chaveron et al. (1976). As with the latter work, there was no great increase here in the amount of 'coating' or reduction in 'filling' accompanying the migration. This suggests that, in this system, while the TAG migrate from the HZ filling into the CB, there is a corresponding migration of CB TAG into the HZ (although the filling composition was not analyzed in this work). If the migration of TAG was mainly one way, a change in volume would be expected for both HZ (shrinking) and CB (expanding) phases. Alternatively, it may be postulated that channels or pores in the CB take up the liquid HZ without increasing the volume of the CB, whilst loss of HZ from the filling leaves behind holes. However, the degree of migration here is considerable, which would suggest that the latter mechanism, if applicable at all, cannot be the full explanation. The filling fat concentration in the cocoa butter showed an almost exponential decrease from the interface, as Marty et al. (Marty et al., 2005) have observed in a similar system where peanut oil structured by interesterified hydrogenated palm oil is placed adjacent to cocoa butter. Levels of migration were higher in their work, but this may be due to the fact that their cocoa butter was untempered and more prone to recrystallisation in to more stable polymorphs, leading to more gaps between crystals and greater potential for capillary draw. In our system, the cocoa butter, tempered as described, yielded a smooth solid phase without granularity, which was found to be in the β_V polymorph.

From the first part of the study, it was anticipated that the migration of oil would accelerate the polymorphic transformation from β_V to β_{VI}. In the samples stored at 20 °C, the CB closest to the filling transforms faster, although the difference is not large at the shorter times (Fig. 7b). There also is less variation with distance at 25 °C and much less at 28 °C, although the effect of temperature itself is significant. This may be due to the fact that the migration profile becomes shallower as the temperature increases, as noted earlier. Nevertheless, overall transformation rates are higher than seen for pure CB so the migrating oil has accelerated the transformation to a certain degree.

In examining the data at 20 °C (Fig. 7a), the CB furthest from the filling contains about 6% filling fat after 10 weeks. If this level had been present from the start, transformation would be expected to reach around 50% β_{VI} – which is indeed close to what is attained. Note that this is despite having lower levels of migration at earlier times. Nevertheless, even at 1 week, the amount of filling fat is 2% and a significant effect was seen with even 1% addition of HZ (Fig. 5a).

In the CB closest to the filling, the amount of filling fat is around 35% after 10 weeks (17% after 1 week). Since, from the addition 20% HZ, the transformation would be expected to be more than 80%, it is a little surprising that the degree of transformation to β_{VI} does not exceed this value. However, it should be noted from Fig. 5 that the effect of HZ per percentage addition reduces as more is added. That is, the effect of adding 5% HZ is less than five times that of 1% addition (in fact, around 2.5 times, in terms of time to 50% conversion), and the effect of adding 20% HZ is not four times that of 5% addition (in fact less than double). Thus it might be supposed that the effect of adding 35% oil is relatively close to that of adding 20% oil. Additionally, in determining the degree of migration by the amount of filling fat present, it should not be forgotten that the filling fat includes 15% HS, which also migrates. Thus, not only does 35% filling fat represent less than 30% HZ, but the HS itself may have some small inhibiting effect on transformation. Also note that where oil is added prior to tempering, it may already influence the way in which the solid phase crystallizes, which could affect the subsequent re-crystallisation into the β_{VI} form.

Thus, HZ increases the rate of formation of β_{VI} in CB, even at low levels of migration and this migration has the biggest effect on transformation rate at lower temperatures. Although increasing the understanding of migration and polymorphic transformation, this study also serves to illustrate how much is yet to be done to in this area. In

addition, it should be noted that bloom formation was not assessed in this work and that the formation of β_{VI} may not, of itself, lead to bloom.

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