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Effect of Antibloom Fat Migration from a Nut Oil Filling on the Polymorphic Transformation of Cocoa Butter

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In confectionery products, loss in texture contrast between chocolate and filling and the appearance of fat bloom on the surface of the chocolate can be caused by fat migration. Bloom is often linked to the transformation of the cocoa butter β_V polymorph into β_{VI}. A previous study showed that small additions (1%) of nut oil can have a significant impact on the rate of transformation and that migration of nut oil from a filling would increase polymorphic transformation of cocoa butter. In the present study, antibloom fat was added to the filling in a model system. The antibloom fat migrated with the nut oil and inhibited the transformation of cocoa butter from the β_V polymorph into β_{VI}. Despite experiencing migration of greater amounts of nut oil, cocoa butter closest to the filling transformed more slowly than that farther away (i.e., the reverse of the situation in the absence of antibloom fat).

KEYWORDS: Fat migration; bloom; chocolate

INTRODUCTION

Migration occurs, to a greater or lesser degree, in many chocolate confectionery products in which two fat phases are in contact. The extent and effect of migration depend on many factors, which have previously been described (*1*). Such migration usually leads to a significant loss of quality (*2, 3*) and, consequently, oil migration is an important issue. Products commonly affected by fat migration are chocolate articles with nut-based centers, coated biscuits or wafers, and cream-filled chocolates. A more detailed overview of fat migration is given in our previous paper (*1*).

Because fat migration usually involves the movement of softer fats into harder ones (*2, 4*), our previous study (*1*) examined the effect of nut oil migration on the polymorphic transformation of cocoa butter from the β_V phase into the β_{VI} phase using a model system. In brief, this work showed that, when added to cocoa butter prior to tempering, even small amounts (1%) of hazelnut oil had a significant accelerating effect on the polymorphic transformation, but that per percent, the effect decreased with higher levels of addition (e.g., the effect of 20% was not 4 times that of 5% oil but, rather, less than double). Following migration of the oil in the model system, the nut oil concentration in the cocoa butter showed an almost exponential decrease from the interface, as Marty et al. (*5*) have observed in a similar system in which peanut oil migrated into cocoa butter. Polymorphic transformation of cocoa butter in this system was shown to be linked to the degree of migration of nut oil from the filling. The cocoa butter closest to the filling experiences both greater degrees of migration and faster transformation.

Fat bloom in chocolate remains an important factor in consumer complaint and, although much work has been undertaken on the phenomenon, there is much still to be understood regarding its causes, mechanism, and remedy (*6*).

In an attempt to address the problem of bloom caused by polymorphic transformation in chocolate, several additives have been identified (see ref *7* for a brief review). Additives studied have been surface active agents (emulsifiers) (*8*) as well as triacylglycerols (TAG) themselves. One TAG route has been to produce crystal seeds of symmetric disaturated, monounsaturated triacylglycerol to cause cocoa butter to crystallize in, and remain in, the β_V polymorph. To this end powdered 1,3-dibehenyl-2-oleoylglycerol (BOB) can be used (*9–11*). This addresses the issues of poor tempering, incomplete crystallization in the cooling tunnel, or temperature abuse during storage by providing high melting point crystals to seed the crystallization of the cocoa butter triacylglycerols. Other TAGs are proposed as antibloom additives. Milk fat and its fractions are known to delay the occurrence of bloom, to a certain degree (*12*). Other solutions are based on molecules containing both long and medium acyl chains (*13–15*) and work by inhibiting the transformation from the β_V to β_{VI} polymorph (*16*). However, the precise mechanism of action of antibloom additives is still very much a matter for debate.

The work reported here examines the effect of incorporating an antibloom fat into the filling fat phase, follows its migration

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into the cocoa butter phase, and determines its influence on the polymorphic transformation of the cocoa butter. As such, it builds on our previous work, and it is recommended that our earlier paper (*1*) be read in conjunction with this paper.

MATERIALS AND METHODS

Fats Used. The four fats used in this investigation were hardstock (HS), antibloom fat (AB), hazelnut oil (HZ), and cocoa butter (CB). The cocoa butter was supplied by Barry Callebaut (Banbury, U.K.). The hardstock was a fractionated trans-hardened fat, CLSP194, obtained from Loders Croklaan B.V. (Wormerveer, The Netherlands). The antibloom fat from the PRESTINE range from Loders Croklaan was based on fractionated, interesterified hydrogenated palm oil/hydrogenated palm kernel oil. 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.

Fat Composition. Fats were analyzed using gas–liquid chromatography (GLC), separating TAGs according to their molecular weights. Fats were dissolved (1.0 mg/mL) in iso-octane and analyzed by GLC on 10 m × 0.53 mm, 0.1 μm film Quadrex DB5. Oven temperature programming of 200−325 at 10 °C/min followed by 325−355 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, that is, the carbon number.

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

Calculating β_V and β_{VI}. The relative proportions of β_V and β_{VI} polymorphs in the CB were determined as described in our previous paper (*1*). In brief, the standard β_V diffractogram was obtained from freshly tempered and cooled cocoa butter, whereas the standard β_{VI} diffractogram was obtained by cycling this cocoa butter between 15 and 25 °C each day for 10 weeks. These standard patterns were used to determine the proportion of the two β polymorphs in each sample. (Note that the method assumes that the diffraction pattern for a sample of mixed polymorphs is the sum of the diffraction patterns of the individual polymorphs in the mixture.) The data are presented as a percentage of the solid phase that is present in the specified polymorph; that is, 40% β_{VI} indicates that 40% of the solid phase is in the β_{VI} form, whereas the remainder is still in the β_V form.

Effect of Migration of Antibloom Fat. Three filling fat blends were made, with various amounts of AB. The total amount of AB + HS was always 15% with the remainder being HZ. Thus, blends containing 0, 5, and 15% AB were mixed with icing sugar in the ratio 40:60 fat/sugar to create the model fillings. A model system was constructed (as previously described in ref *1*) based on the "washer test" model of Talbot (*17*) (see **Figure 1**). The filling material was deposited in the center of the bottom washer and was leveled off. This was cooled in a cooling tunnel. Tempered CB (see ref *1* for method) was deposited on top of the filling in the center of the five thin steel washers (shims) on top and the whole assembly cooled in a cooling tunnel. The cocoa butter was checked by X-ray diffraction after cooling to ensure that it had been correctly tempered and had crystallized into the β_V polymorph. Samples were stored at 20, 25, and 28 °C. At intervals during storage, one sample was removed and the shims separated from the bottom 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.

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 individual fats: CB, HZ, HS, and AB. In any mixture the carbon number values are a linear combination of those of the component fats. In our previous paper (*1*) (which describes the method for calculating degree of migration), a simplifying assumption was made that the individual triacylglycerols of each fat migrate together. In this study, we initially separately determined the amounts of HZ, CB, HS, and AB but later determined the total of the filling fat components (HZ + HS + AB) present in the CB to quantify migration.

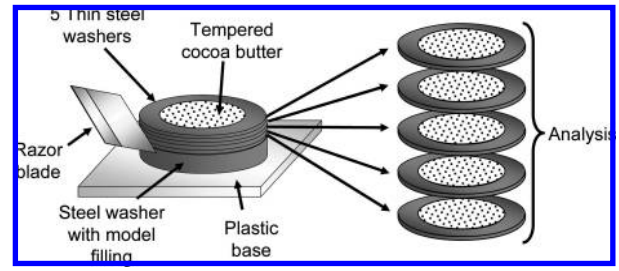

Figure 1. Diagram of the filled chocolate model. A steel washer (2.5 mm thick) is glued to a plastic base. Filling is deposited in the central hole (10 mm diameter) and cooled. Five thin washers (0.5 mm thick) are stacked on top of the first washer. Tempered cocoa butter is deposited in the central hole. Thin washers are removed using a razor blade for analysis.

RESULTS AND DISCUSSION

The GLC carbon number composition of the four oils was measured in quadruplicate, and the results are given in **Table 1**. As is evident, there is sufficient difference between them (especially between AB and the other fats, but also between the filling fat components and the CB) to make determination of migration possible by GLC carbon number.

Migration. Single measurements of composition were made on samples to determine migration. In the determination of the amount of migration that had taken place, initial calculations were made to determine the presence of each of the individual filling fats in the CB. However, there was a large degree of scatter in the data. Nevertheless, plotting the amount of AB present in all CB samples against the amount of the other two fats (HZ and HS) produced a straight line correlation with coefficients of 0.57 and 0.64 (for 90 points), respectively, for 5 and 15% AB in the filling, indicating significance at >99.9%. The calculated slopes were 0.051 and 0.155, respectively, for 5 and 15% AB systems, suggesting that the AB comigrated with the other fats. Thus, the quantification of migration was simplified by assuming that all of the fats present in the filling fat migrated together. By this method, the average standard error in calculation of migrated fat across all samples was 1.06% (migrated filling fat) and the maximum error was 7.85%. This compares with values of migrated filling fat of up to 50.81%.

As found in our previous study (*1*), the concentration of filling fat in the CB layer decreased from the interface toward the surface (see **Figure 2a**, which is typical of the profiles observed). Marty et al. (*5*) measured a similar concentration profile in a migration model using nut oil containing Nile red dye moving into cocoa butter, although the degree of migration was greater in their system (due, perhaps, to their use of untempered cocoa butter; in our system the cocoa butter was tempered and was found to be in the β_V polymorph at the start). Other studies, using magnetic resonance imaging (MRI), also show a migration profile similar, in some instances, to that observed here (*18*). In common with the latter study, **Figure 2a** shows that the filling fat concentration at any distance increased with storage time; that is, the whole concentration profile shifted upward. The degree of migration was similar for all filling compositions. **Figure 2b**, for example, shows the concentration profile after 10 weeks at 20 °C for all three filling compositions.

Table 1. Triacylglycerol GLC Carbon Number of Fats[a]

	C36	C38	C40	C42	C44	C46	C48	C50	C52	C54	C56	other
cocoa butter							0.3 (0.09)	18.1 (0.19)	45.5 (0.22)	33.7 (0.21)	2.1 (0.14)	0.3
hazelnut oil								0.7 (0.12)	15.4 (0.17)	82.7 (0.25)	1.2 (0.13)	
hardstock						0.2 (0.10)	1.9 (0.14)	16.2 (0.16)	54.0 (0.23)	25.9 (0.20)	1.4 (0.13)	0.4
antibloom fat	3.4(0.15)	4.7(0.14)	7.7(0.17)	16.8(0.18)	16.5(0.17)	21.9 (0.20)	20.3 (0.21)	5.2 (0.16)	2.5 (0.14)	1.0 (0.11)	0.1 (0.08)	

[a] C*nn* indicates TAG having acyl groups whose carbons sum to *nn*. Average of four measurements (standard deviation given in parentheses).

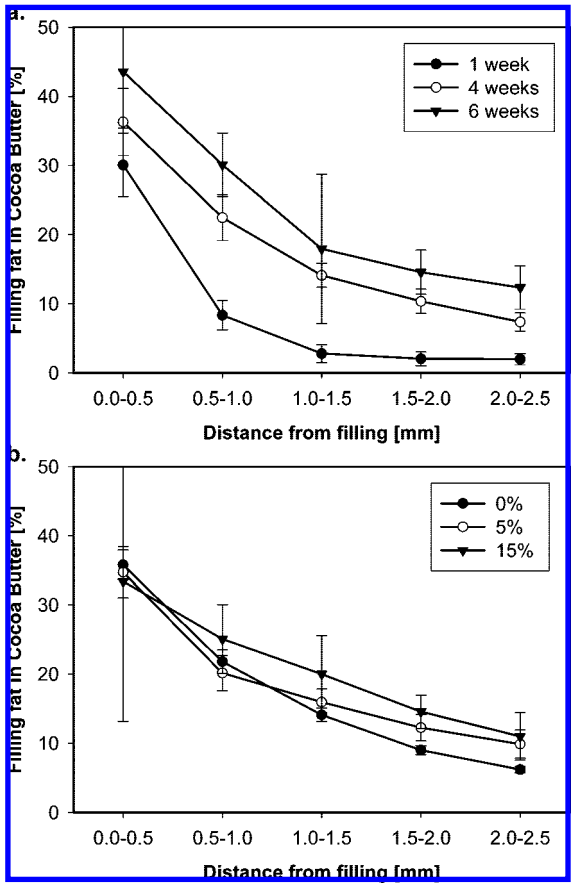

Figure 2. Migration profile as a function of distance from filling: (**a**) containing 15% antibloom fat during storage at 25 °C after 1, 4, and 6 weeks; (**b**) containing 0, 5, and 15% antibloom fat after 10 weeks of storage at 20 °C.

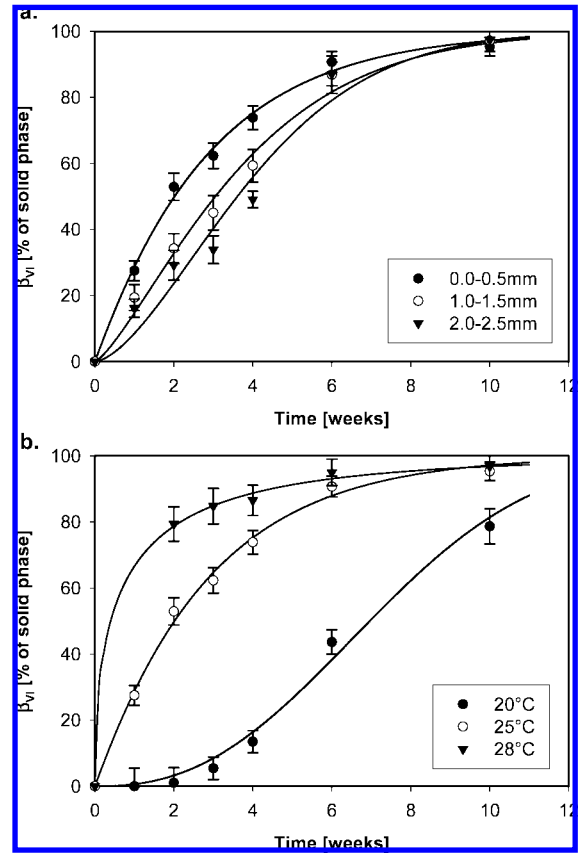

Figure 3. Formation of β_{VI} in cocoa butter as a function of time at 25 °C and distance from the filling of 0–0.5, 1–1.5, and 2–2.5 mm for (**a**) 0% antibloom fat in the filling and (**b**) 15% antibloom fat in the filling. Lines are fitted to the Johnson−Mehl−Avrami–Erofeyev−Kolmogorov (JMAEK) model: $f = 1 - \exp(-kt^n)$, where f = % solid that is β_{VI}, t is time, k is the rate constant, and n is the Avrami exponent. The JMAEK model was used here simply for convenience because it gives rise to a curve of similar form to that observed. However, in this study, no significance can be placed on the values of the calculated parameters because the composition of the system varies with time.

From our previous study (*1*) it was found that the migration of oil accelerated the polymorphic transformation from β_V to β_{VI}. This is confirmed in **Figure 3a**, where, without AB, it can be seen that the cocoa butter closest to the filling, which experienced the greatest degree of migration, also had a higher rate of transformation than the cocoa butter farthest away. As before, the polymorphic transformation rate increased with temperature (**Figure 3b**), being significantly faster at 25 °C compared to that at 20 °C. When HS was replaced (partly or wholly) by AB, migration of the filling fat occurred at a similar rate (data not shown). However, **Figure 4a** shows that the polymorphic transformation rate was affected in the opposite manner when AB was included in the filling, compared to filling with none. The cocoa butter closest (0.0–0.5 mm) to the filling transformed at less than half the rate when 15% AB was present compared to 0% AB. The AB migrated with the HZ and served to inhibit the transformation from β_V to β_{VI}. A similar, but smaller, effect was seen for 5% AB in the filling (**Figure 4b**).

Comparison of **Figures 3b** and **4b** (20 °C curve in the former figure and 5% curve in the latter) shows that, with the addition of just 5% AB to the filling, the transformation rate at 25 °C was reduced to around that expected at 20 °C without AB.

Thus, from our previous paper (*1*), 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. This leads to the cocoa butter closest to the filling transforming the most rapidly. However, the present study demonstrates that antibloom fat present in the filling phase can migrate into the cocoa butter and slow the rate of polymorphic transformation (or recrystallization). This results in the lowest transformation rate occurring in the cocoa butter

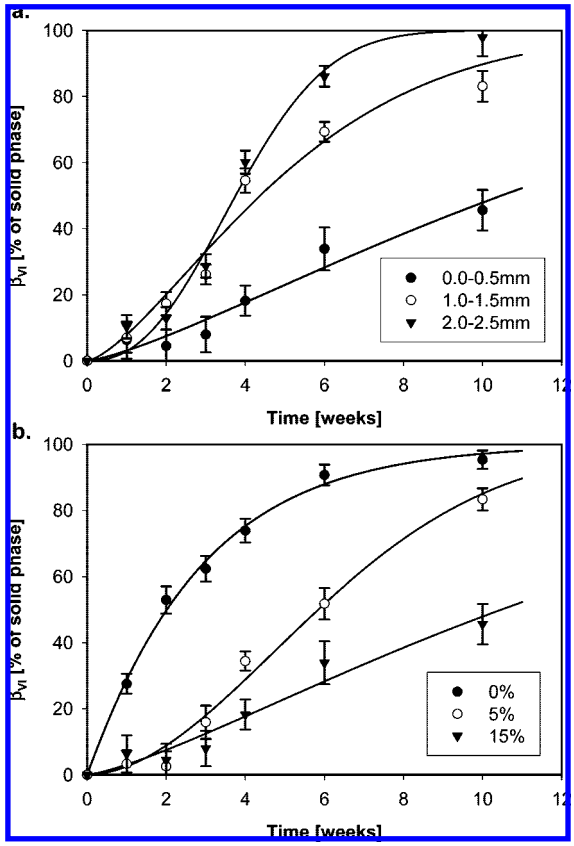

Figure 4. Formation of β_{VI} in cocoa butter closest to the filling as a function of time at 25 °C for levels of antibloom fat in the filling of 0, 5, and 15%. Lines are fitted to the JAMEK model (see **Figure 3** for details).

closest to the filling fat rather than in that farthest away. Thus, the accelerating effect of the nut oil is more than compensated for by the inhibiting effect of the antibloom fat. Finally, it should be noted that this work has quantified the appearance of the β_{VI} polymorph, not the occurrence of bloom, and that, although these two may be linked, the formation of β_{VI} may not, of itself, lead to bloom.

ABBREVIATIONS USED

TAG, triacylglycerol; CB, cocoa butter; HZ, hazelnut oil; HS, hardstock fat; AB, antibloom fat; GLC, gas–liquid chromatography; XRD, X-ray diffraction.

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