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MODIFICATIONS OF PHYSICAL PROPERTIES OF COCONUT OIL AND ANHYDROUS MILK FAT AS A RESULT OF BLENDING

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The role of fats in food technology is mainly to develop the desired consistency. The simplest way to reach this goal is the blending of different fats. The aim of our work was to study the solidification and melting properties of blends of coconut oil and anhydrous milk fat. Pure fats and their 25–75%, 50–50%, and 75–25% blends were investigated. Melting profile and isotherm crystallization were measured by pNMR. Non-isotherm melting and solidification were detected by differential scanning calorimetry (DSC). Possible applications of the blends were established. Results show that AMF and coconut oil has limited miscibility, which is dependent on the temperature. Below 22 °C AMF is the softening component, above 22 °C the effect is inverse. Coconut oil accelerates solidification of AMF, however, basic crystal forms of AMF remained.

Keywords: coconut oil, anhydrous milk fat, melting properties, solidification, fat blend

Coconut oil is one of the most widely used fats in the food industry. Due to its melting and crystallization characteristics, margarine and shortening production as well as confectionary industry consider coconut oil as a basic material in product formulation. Since these kinds of products consist of other fat materials, it is important to study the counter relationship of coconut oil and other fats when they are blended. In our study, coconut oil and anhydrous milk fat (AMF) were blended in different ratios, the modifications of the most important physical properties, melting profile and solidification, were studied. Our earlier studies (Somogyi et al., 2009) indicated that the modification of these parameters should be highly affected by the restricted miscibility of coconut oil and AMF.

1. Materials and methods

1.1. Materials

Anhydrous milk fat was gathered from local confectionary factory (Bonbonetti Choco Kft). The origin of the coconut oil was commercial wholesaler (Barco CO). Five hundred cm^3 of the materials were heated up to 80 °C in order to eliminate crystal structure. Pure fat samples and 25–75%, 50%–50%, and 75–25% blends of AMF and coconut oil were prepared in liquid state in volumetric flasks, and then cooled to 5 °C and kept in refrigerator until measurements were conducted.

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1.2. Methods

Fatty acid composition of pure fats was analysed by gas chromatograph (GC) according to the methods based on MSZ ISO 5508:1992. The type of the apparatus was HP 5890 GC system, with SGE BPX 70 column with parameters 50 m×0.22 mm×0.25 μm. Heating was from 150 °C to 210 °C (with 1.3 °C min^{-1} heating rate). Pressure: 14 psi, injector: 250 °C split, split ratio: 100:1. Detector: 250 °C, FID. The carrier gas was hydrogen, the flow rate was 0.6 cm^3 min^{-1}, injection pressure was 0.965 bars. Identification of fatty acids was based on the retention times using fatty acid methyl ester standards.

Solidification was detected by measuring solid fat content with pNMR (Bruker Minispec 120) apparatus. The measurement, based on the method reported by Campos and co-workers (2010) was modified as follows: samples were heated up to 80 °C and kept there for 15 min. The completely liquid samples were adjusted in NMR tubes and put into a 5 °C thermostat. Measurements were done every 5 min for 90 min. Three parallel measurements had been done and average values were reported.

Slip melting point (SMP) was measured to characterize the melting properties of the samples by the official standard method (MSZ EN ISO 6321:2002).

The melting profile of the fats was established by the solid fat content curves (SFC) by means of pNMR apparatus (Bruker Minispec 120, Bruker, Germany) following the AOCS (2005) method (AOCS Cd 16b-93). The samples were heated to 80 °C and held for 15 min in order to eliminate crystal memory. All samples were kept at 60 °C for 15 min, cooled down to 0 °C, and maintained at this temperature for 60 min. Finally, before measurements, samples were held at the temperature of the measurements for 30–35 min. Temperatures were: 10, 20, 30, 40, and 50 °C. Three parallel measurements were done and average values were reported.

Differential scanning calorimetry (DSC) measurements were done in order to follow the solidification and melting phenomena during cooling and heating. Of each sample 20–25 mg was put into 100 μl alumina sample holders. The temperature program was as follows: samples were cooled to 0 °C by 1 °C min^{-1} and kept at this temperature for 10 min. Heating was performed from 0 °C up to 80 °C at 1 °C min^{-1}. Samples were kept at this temperature for 30 min, and then the cooling program was applied at 1 °C min^{-1} to –20 °C and kept under this condition for 10 min. Finally, the samples were heated up to ambient temperature. Measurements were done during the constant speed heating and cooling processes. Results were elaborated by Callisto Processing 1.076 computer program using linear base line. Heat flow and enthalpy of exotherm and endotherm peaks were recorded and calculated.

2. Results and discussions

Fatty acid compositions of the samples are shown in Table 1. AMF contained a great variety of fatty acids. Our results are consistent with the literature data (e.g. Firestone, 1999; O'Brien, 2009). Saturated fatty acids covered more than 70% of the total. Palmitic acid, oleic acid, myristic acid, and stearic acid were the dominant compounds. C4:0–C12:0 fatty acids were found in 12%, as characteristic to the AMF. Coconut oil contained lauric acid (45.7%) and myristic acid (18.5%) as the dominant components. The total of the saturated fatty acids exceeded 90%. These findings are in accordance with the well-known literature data (e.g.: Marina et al., 2009).

Table 1. Fatty acid composition (%) of coconut oil and anhydrous milk fat

Fatty acid composition (%)		
Fatty acid	Coconut oil	AMF
C4:0	0.0	1.9
C6:0	1.3	1.5
C8:0	6.7	1.1
C10:0	5.6	2.8
C10:1	0.0	0.3
C12:0	45.9	4.2
C12:1	0.0	0.1
C13:0	0.0	0.1
C13:1	0.0	0.1
C14:0	18,5	12.5
C14:1	0.0	1.4
C15:0	0.0	1.2
C15:1	0.0	0.3
C16:0	9.5	34.8
C16:1 *tr*	0.0	0.00
C16:1 *cis*	0.0	1.7
C17:0	0.0	0.6
C17:1	0.0	0.2
C18:0	3.1	10.7
C18:1 *tr*	0.00	0.53
C18:1*cis*	7.0	19.0
C18:2 *tr*	0.00	0.82
C18:2*cis*	1.7	1.4
C18:3 *tr*	0.00	0.00
C18:3*cis*	0.0	0.4
C20:0	0.1	0.5
C20:1	0.0	0.1
C20:2	0.0	0.0
C22:0	0.1	0.0
C22:1	0.0	0.0
C24:0	0.0	0.1
C24:1	0.0	0.0
not id.	0.5	1.65
Sum	100.0	100.0
Summa *trans*	0.00	1.35

Results of isotherm crystallization of the samples are demonstrated in Figure 1A, where the solid fat content in percentages is shown as a function of time in min. Since relative standard deviations were less than 5% in each case, average values were presented. Crystallization curves show that approximately within 40 min fats solidified almost completely. It is also clear that AMF solidified in a two-step mechanism and the other samples show different phenomena. This two-step solidification of AMF has been reported by other authors (Herrera et al., 1999; Wiking et al., 2001) as well. The slope of the curves became higher for AMF if the amount of coconut oil in the blend exceeded 50%. Additionally, the equilibrium SFC decreased by the increasing amount of AMF in the blend. Equilibrium solid fat content of the blends was closer to the pure AMF, indicating that coconut oil does not raise the solid fat content strongly in the presence of AMF. This finding is attributed to the medium chain fatty acids of coconut oil that have relatively low melting temperature: 44.2 °C and 53.9 °C for lauric acid and myristic acid, respectively (Gunstone, 1986). This finding is a possible indicator of retarded miscibility (Braipson-Danthine, 2006).

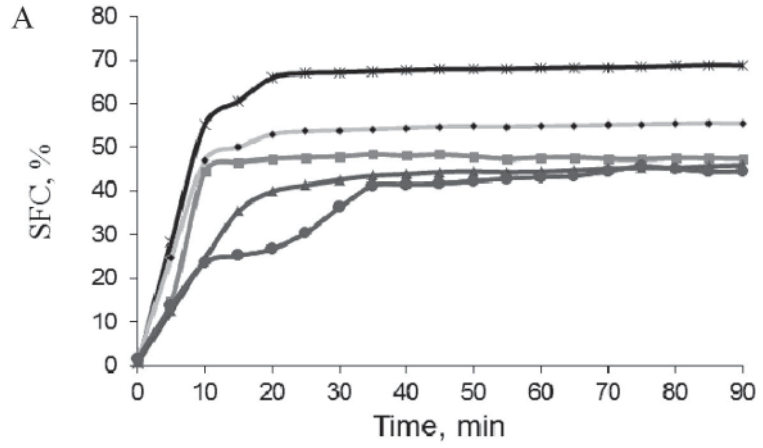

Fig. 1A. Isotherm crystallization of pure fats and blends.
:Coconut oil; :25–75% AMF–coconut oil; : 50–50% AMF–coconut oil;
: 75–25% AMF–coconut oil; : AMF

In Figure 1B cooling thermograms of the samples are shown. Coconut oil had a great exotherm peak at 9.5 °C (enthalpy: –90 J g^{-1}). Similar thermogram was detectable in case of 25–75% AMF–coconut oil blend. On the other hand, the 50–50% and 75–25% AMF–coconut oil blends showed analogous thermograms as AMF. Sample of 50–50% AMF-coconut oil had a wide exotherm peak with low heat content beside the bigger peak. While the latter is characteristic of the coconut oil, the other may contain the tryglicerides both of AMF and coconut oil. Low energy indicates less stability. This phenomenon is associated with the limited miscibility of AMF and coconut oil.

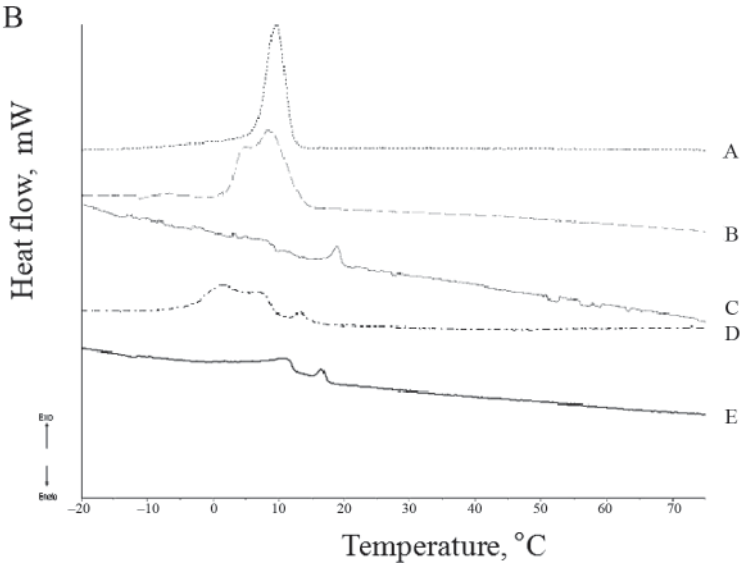

Fig. 1B. Differential scanning calorimetry cooling curves of pure fats and blends.
A: Coconut oil; B: 25–75% AMF–coconut oil; C: 50–50% AMF–coconut oil; D: 75–25% AMF–coconut oil; E: AMF

Melting properties of the investigated samples are summarized in Figure 2. In Figure 2A slip melting points of the samples are shown. Results proved that AMF had the highest and coconut oil the lowest SMP value. Blends presented decreasing SMP values according to the increasing amount of coconut oil (31.5, 27, 25.3, 24.7, and 23.7 °C, respectively). Solid fat content of the samples are shown in Figure 2B. From the figure it can be seen that coconut oil had the highest and AMF the lowest SFC value at low temperature. Coconut oil and the blends melted rather fast. Individual SFC values of the blends were close to each other and the shape of the SFC curve was similar. Similar results were reported by LIEW and co-workers (2001). SFC curve of the AMF performed a characteristic plateau between 20 °C and 25 °C. At higher temperatures, AMF and 50–50%, 75–25% (AMF–Co) contained more solids than pure coconut oil and 25–75% samples.

SFC curves crossed each other and this indicates the limited miscibility of AMF and coconut oil and the existence of eutectic phenomena. From the results we could state that in the temperature range below 20–22 °C AMF is the softening component, but above 25 °C it is the coconut oil.

The eutectic behaviour is highly important in food application. Producers must carefully apply these blends, since the texture of the final product could undergo undesirable changes. Melting thermograms measured by DSC are shown in Figure 2C. Coconut oil had a double peak at 22 °C (enthalpy: 90 J g^{-1}), AMF showed more complex crystal structure. Three smaller endotherm peaks were characteristic of melting. Total enthalpy of them was 57 J g^{-1}. These three peaks were detectable also for 75–25% and 50–50% blends, but the position and the enthalpy values were slightly different. Blend of 25% AMF and 75% coconut oil had only two peaks that were similar to the pure coconut oil, and the sum of the enthalpies was higher (67 J g^{-1}).

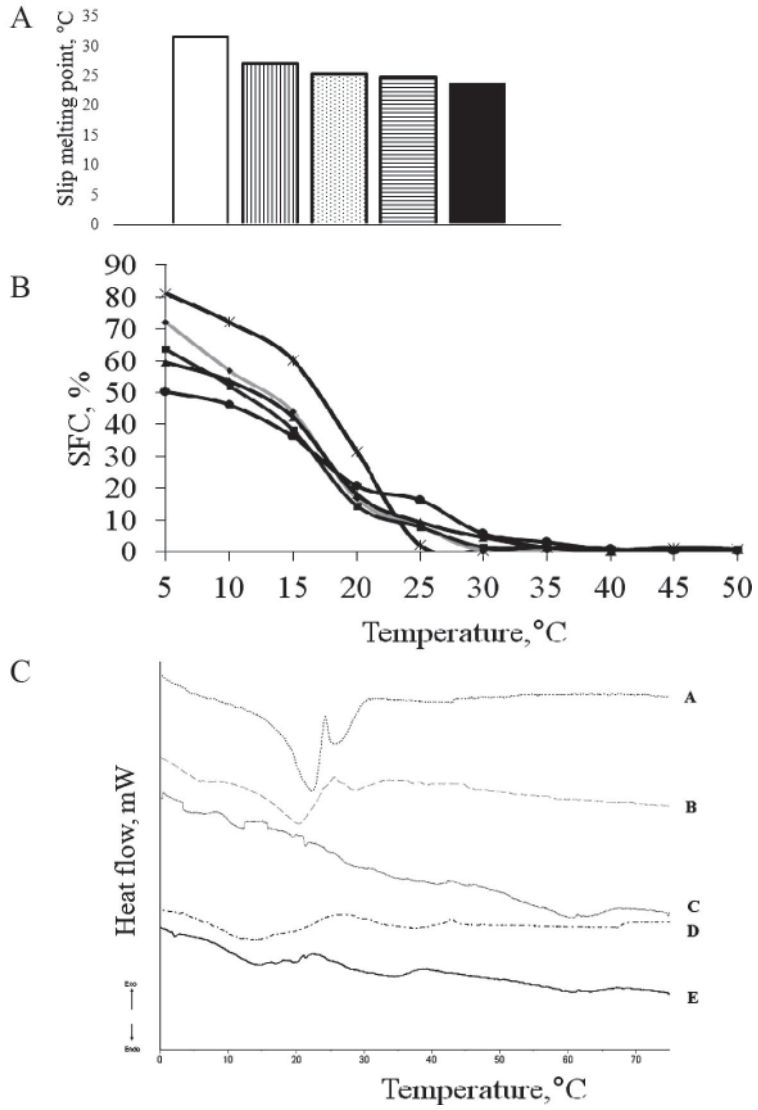

Fig. 2A. Slip melting points of pure fats and blends.
□: AMF; ▥:75–25% AMF–coconut oil; ⚃: 50–50% AMF-coconut oil;
▤:25–75% AMF–coconut oil; ■: coconut oil

Fig. 2B. SFC curves of pure fats and blends.
:Coconut oil; :25–75% AMF–coconut oil; : 50–50% AMF–coconut oil;
: 75–25% AMF–coconut oil; : AMF

Fig. 2C. Differential scanning calorimetry melting curves of pure fats and blends.
A: Coconut oil, B: 25–75% AMF–coconut oil, C: 50–50% AMF–coconut oil,
D: 75–25% AMF–coconut oil, E: AMF

3. Conclusions

Based on the results the following conclusions can be drawn:

Coconut oil accelerates the solidification of AMF due to the fast polymorph transition (β' to β). This is proved by the fact that in the presence of coconut oil the two-step crystallization is eliminated. Additionally, the velocity of solidification increases by the increasing amount of coconut oil. During crystallization the characteristic crystal forms of AMF remain. We could conclude that AMF served the pattern of crystallization.

Melting process is governed by AMF, because the melting profiles of the blends are similar to the pure AMF. This conclusion is supported by the fact that crystal forms of AMF are present during melting as it is detected by DSC.

The AMF–coconut oil blends show temperature-dependent eutectic phenomenon. Below 22 °C AMF is the softening component, above 22 °C coconut oil has the similar effect. Despite that AMF has higher SMP, AMF is considered as harder fat only above 22 °C. Individual values of solid fat content prove that below 22 °C coconut oil has more solids than AMF.

As practical conclusions it can be stated that beneficial characteristics of coconut oil can be utilized for products that need cooled handling until consumption, e.g. dairy desserts, because these fats are completely miscible at low temperature.

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