Effect of Vegetable Fats on the Physical Properties of Animal Fats

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Thesis Book

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1. INTRODUCTION

Blends of animal fats and vegetable fats are increasingly used in the food industry. There are several complex food systems in which fats of different origin are in a mixed form. Many scientific results are available about the properties of natural fats but there is limited information on the physical characteristics of fat mixtures. The already reported research work dealt with blending of fats with oils. There is a lack of systematic investigations of fat blends in Hungary in particular. The role of fat blends is mostly to develop the desired texture especially in the meat and industries, commercial bakeries, and manufactures of preservatives. This role is filled due to the characteristic thermal properties of the fats. Fats can be characterized by their chemical composition and physical properties like miscibility and crystallization. In food industry different purposes require different types of fats. Hard and quickly melting as well as plastic and slowly melting fats are typical. In confectionery, bakery, and spread-making technologies the temperature-rang in which the fats are melting or keep their semi-soft consistency is very important. Temperature-dependence may be remarkably different in many cases because individual fats melt differently. In my work I divided fats into six groups in this respect. These are: cocoa-butter type, palm oil type, cocos fat type, lard fat type, butterfat type and poultry-fat type fats. Cocoa butter type fats are those that have narrow melting-temperature intervals. The first group characterizes so-called CBE (cocoa butter equivalent) fats that have symmetrical triglyceride structure with a narrow melting range. In my work cocoa butter represents these materials. The second group covers all the palm-type fats. These materials consist of various fatty acids, their melting temperature range is wide and they are typically ß' stable materials. Palm mid fraction (PMF) represents the group. The third group of vegetable fats is the lauric type group. The group is represented by the coconut oil.

Of the animal fats the first group was that of the lard-type fats. Fats in this group have wide-range melting intervals and melt uniformly. A typical triglyceride of these is POO, but several fatty acids form its composition. The dominant polymorph form is the β crystal. Lard was choosen to represent this group. Next is the butterfat-type group: they have a wide melting range and the presence of short chain (C4–C14) fatty acids is typical. Anhydrous milk fat (AMF) represents this group. The third group of the animal fats is the group of poultry fat-type materials. These melt at low temperatures, but the melting range is wide. These are typically olein-type materials which are represented by goose fat.

The modification of the physical properties of fats may be performed by hydrogenation, interesterification, fractionation as well combination of these. Industry prefers the simplest way, consequently blending is commonly used. Several scientific results have been reported regarding lipid mixtures, but the majority dealt with fat/oil blending. It is necessary to understand the possible modifications caused by blending because food industry uses different fats in foodstuffs. The aim of the work is to find new information on the effect of blending on the physical properties as well as on the interaction of different fats. These new findings can be utilized in product development.

2. OBJECTIVES

Three vegetable fats and three animal fats were involved in my work that have significantly different characters. The aim of the work was to establish the effect of vegetable fats on the characteristics of animal fats if in addition to the simple mixing there was no previous and follow-up tempering applied. Technological feasibility was studied by investigating the physical characteristics of the blends.

Consequently interactions of the different characteristics were established as a result of simple blending (without chemical reactions).

It must be emphasized that my work focused on the effect of vegetable fats on the animal fats. In this way the binary systems were studied from the point of view of the properties of animal fats. Consequently previous tempering or stabilization of vegetable fats was not in the scope of the measurements.

The aims of my work can be summarized as follows.

1. To establish the miscibility of the animal and vegetable fats by means of detection of the eutectic phenomenon
2. To establish the interactive effect of the characteristics of pure animal and vegetable fats on the melting profile. Do characteristics interact extensively or intensively or in any other way?

3. To establish the feature of the solidification-crystallization process particularly in respect whether the fats form different or common crystals.
4. To establish how the texture characteristics of the fats modify as a result of blending. Texture characteristics are those that can be measured by penetrometry (hardness) as well as rotation and oscillation rheometry (storage modulus, yield value).

Based on the results of the above detailed measurements, the establishment that the blending of fats fulfil what sort of technological criteria for production and application.

3. MATERIALS AND METHODS

3.1. Materials

Materials involved in the investigations were collected from industrial producers and local markets.

- **lard**: METRO Wholesaler's own brand (Aro)
- **butterfat**: AMF (Anhydrous Milk Fat) from Bonbonetti Choco Ltd.
- **poultry fat**: METRO Wholesaler ("Valdor" goose fat)
- **cocoa butter**: from Bonbonetti Choco Ltd.
- **palm fat**: Palm mid fraction (PMF) from Puratos Hungary Ltd
- **coconut oil**: from Mayer's Ltd ("Barco" coconut oil)

According to the considerations detailed as aim of the work, samples were prepared similarly to the industrial practices used. In actual food systems fats interact without previous tempering. Sample preparation followed the so-called "static crystallization" mode. Samples were completely melted at 100°C, and kept there for 30 minutes in order to destroy crystal memory. The following blends were prepared by 25–75 m/m %, 50–50 m/m % and 75–25 m/m % ratios. Accuracy was two decimals in grams. Only animal/vegetable fat blends were prepared. After preparation, samples were poured into NMR tubes and 250 cm^3 beakers and stored at 5°C until measurements for at least three days. This method made possible the spontaneous stabilization and simulated industrial chilled storage.

3.2. Methods

3.2.1. Fatty acid composition

Fatty acid composition of pure fats was analysed by means of gas chromatograph HP 5890 GC System type following standard methods of ISO 5508:1990 and ISO 5509:1990).

3.2.2. Solid Fat Content by p NMR

Solid fat content of the samples was measured by nuclear magnetic resonance spectroscopy (NMR) in order to describe the melting and solidification process. Measurements were performed following the AOCS method (Cd 16b–93). For melting profile the temperatures of the measurements were as follows: 5°C, 10°C, 15°C, 20°C, 25°C, 30°C, 35°C, 40°C, 45°C and 50°C.

For the measurements of isotherm crystallization, samples were heated up to 80°C and kept at this temperature for 15 minutes in order to eliminate all the crystal forms and the fat became completely liquefied. Samples were put into 10°C thermostat thereafter and solid fat content was measured every five minutes for 90 minutes.

3.2.3. Slip melting point

Slip melting point (SMP) was measured under the regulation of the standard: MSZ EN ISO 6321:200 (Animal and Vegetable Fats and Oils to establish the melting point of the fats by open capillary method (slip melting point))

3.2.4. Calorimetric measurements by Differential Scanning Calorimeter

Calorimetric measurements were done by Setaram Differencial Scanning Calorimeter (DSC) microcalorimeter. In each case 20–25 mg sample was put into 100 μl aluminum pan. The melting and cooling program was previously established. During measurements heat flow and temperature was recorded and enthalpies were calculated.

3.2.5. Texture analysis

Penetrometry

Measurements were done by Stable Micro Systems TA. XT Plus (SMS) equipment. Samples (150 cm^3) were put into uniform beakers (250 cm^3) and measured after storage at 10°C for at least three days. Conditions of the measurements were:

- penetration head: cylindrical, diameter: 5 mm
- speed of penetration: 2 mm/s
- depth of penetration: 15 mm
- temperature of the sample: 10°C

Results of penetrometrical measurements were: F1 (force needed to penetrate into the material), Fmax (maximal force during penetration), W (total work during penetration) and parallel quantities obtained by extraction of the head. Since all quantities changed similarly only F1 was chosen to characterize the texture. According to other reported research findings F1 was called as hardness.

Rheological measurements

For rheological measurements Anton Paar Physica MCR 301 type equipment was applied both in rotation and oscillation mode. Measuring cell was H–PTD200, type of the cone: CP25-1; the measurements were performed with cone-plate arrangement.

3.2.6. Evaluation methods

Results of slip melting point, F1 (hardness), G' (storage modulus) and τ_0 (yield value) were elaborated by ANOVA. In the model, dependent variables were the slip melting point, F1, G' and τ_0; explanatory variables were the composition data. Normality was verified by analysis of skewness and kurtosis. Homogeneity of standard deviations was analysed by Levene–test. In case of homogeneity the Tukey test was applied, otherwise calculation was done by Games-Howell test.

4. NEW SCIENTIFIC RESULTS

1. Based on the results of my measurements the following statements can be made regarding the miscibility of animal and vegetable fats:
   1.1 I stated that of the materials involved in my work, (based on the eutectic phenomena) coconut oil and lard as well as coconut oil and AMF are limitedly miscible.
   1.2 I stated that the miscibility is temperature-dependent. In the lard-coconut blend the eutectic phenomenon appears above 20°C and at the AMF-coconut oil blend above 15°C.

2. Based on the calculated AVRAMI parameters that solidify the blends at 10°C, crystallization occurs with spontaneous nucleation and linear growth. Differences at individual fat types are as follows:
   2.1. Solidification of lard was retarded by cocoa butter. The equilibrium SFC values do not follow the blending ratios. Equilibrium SFC values develop according to the blending ratios in the case of fractionated palm fat (PMF) and coconut oil. Crystal structure specific to the lard is eliminated by coconut oil if it is present at least 75% in the blend. Cocoa butter and fractionated palm oil do not have such an effect.
   2.2. I verified that the two-step solidification of AMF is eliminated by 25% cocoa butter and coconut oil, or 50% fractionated palm fat. I stated that in the presence of cocoa butter and coconut oil the equilibrium SFC values are less compared to the blending ratios, but follow the blending ratio in the case of fractionated palm fat. Crystal forms characteristic to the AMF solidify at different temperatures even in the presence of vegetable fat at 50%.
   2.3. I stated that solidification of goose fat is carried out in two steps. This phenomena remains in the presence of coconut oil and remains up to 25% presence of cocoa butter and fractionated palm fat. I verified that equilibrium SFC values fit to the blending ratios in the case of cocoa butter and fractionated palm fat, but do not in the case of coconut oil.

   I verified that 25% cocoa butter, 50% coconut oil, and 75% fractionated palm fat can modify the crystal structure of animal fat.

3. Melting properties of the investigated samples are described in the following points.
    3.1. I stated that cocoa butter and fractionated palm fat (PMF) hardly modify the melting profile of lard if they are at least 50% in the blend. Coconut oil can impact similarly from a 75% ratio. Based on the calorimetric measurements I proved that vegetable fat makes the melting more complex if it is present in the blend max 50%. Vegetable fat in 75% in the blend likens the melting to the vegetable fat. Additionally I stated that the presence of coconut oil is detectable regardless of the blending ratio.
    3.2. I stated that the two-step melting of AMF remains in the presence of vegetable fats. I verified that the presence of vegetable fat up to the 50% melting occurs in three steps. I stated additionally that the slip melting point does not indicate the fact of blending.
    3.3. I stated that melting of goose fat is characterized by a sharp decrease in SFC (even. 80%) between 15–20°C. Cocoa butter at 25%, fractionated palm fat and coconut oil at 75% diminish this characteristic. I stated additionally that thermal characters of the blends are similar to the vegetable fats if the latter are present at least 75%.

4. For the texture measurements of the investigated fat blend I can state the following:
    4.1. I verified that at 10°C vegetable fats are harder than animal fats. Differences are even six times in favour of vegetable fats. Changes follow exponentially in each case.
    4.2. I verified that yield values measured at 50°C in rotation mode at 0.156 1/s shear rate varied in a narrow range but animal fats had higher values than vegetable fats.
    4.3. I verified that storage moduli measured in an oscillation mode at 50°C were higher at vegetable fats than at AMF and goose fat, but less than at lard.

5. PRIMARY PUBLICATIONS RELATED TO THE DISSERTATION

1. Original Research Papers (published in referred (IF) journals)

1.1. **A. Soós** – L. Somogyi – G. Jakab – B. Imre (2014): Modifications of physical properties of coconut oil and anhydrous milk fat as a result of blending, ACTA Alimentaria (43. kötet különszám, közlésre elfogadva)

1.2. **A. Soós** – Cs. Pecznyik – L. Somogyi – I. Zeke (2013): Effect of animal fats on the physical properties of palm fat, ACTA Alimentaria (43. kötet 4. szám közlésre elfogadva)

2. Papers published in other Journals:

2.1. Kovács Anna - **Soós Anita** - Dr. Somogyi László (2010) Egészségtudatos étrendbe illeszthető majonéz termék kifejlesztése, Élelmiszer tudomány technológia 2. (különszám), 20-21.

2.2. **Soós Anita** – Dr. Somogyi László (2010): Zsírblendek kristályosodási jelenségének tanulmányozása, Élelmiszer tudomány technológia 1. különszám, 15-16.

3. Conference Full Papers in Hungarian:

3.1. **Soós Anita** – Zeke Ildikó – Pecznyik Csilla – Dr. Somogyi László (2012): Egyes zsírkeverékek kristályosodási tulajdonságai. XXXV. Kémiai Előadói Napok, 2012. október 29-31., Szeged konferencia kiadvány oldalszáma: 109-113

3.2. Pecznyik Csilla – **Soós Anita** – Dr. Somogyi László (2012): Vajzsír hatása a növényi olajok olvadási tulajdonságaira. XXXV. Kémiai Előadói Napok, 2012. október 29-31., Szeged konferencia kiadvány oldalszáma: 101-104

3.3. Dr. Somogyi László – **Soós Anita** – (2009): Zsírblendek kristályosodási jelenségének tanulmányozása, LippayJános – Ormos Imre – Vas Károly Tudományos Ülésszak. 2009. október 28-30., Budapest

3.4. Dr. Somogyi László - Dr. Dalmadi István - **Soós Antia** (2007): Olivaolaj keverékek érzékszervi és műszeres elemzése. Lippay János-Ormos Imre-Vas Károly Tudományos Ülésszak. 2007. november 7-8., Budapest.

4. Conference Proceedings In Hungarian

4.1. **Soós Anita** - Dr. Somogyi László – Zeke Ildikó (2014): Módszerek kókuszzsír keverékek technológiai felhasználhatóságának elemzésére. Aktualitások a táplálkozástudományi kutatásokban IV. Budapesti Workshop, 2014.január 16. Budapest

Somogyi László - **Soós Anita** (2007): Olivaolaj keverékek aromavizsgálata In. Összefoglalók: Lippay-Ormos-Vas Tudományos Ülésszak

5. International Conference (full paper) (5 points)

5.1. **Soós Anita** – Dr. Somogyi László – Imre Balázs- Jakab Gábor – Modifications of physical properties of coconut oil and anyhidrous milk fat as a result of blending, Food Science Conference 2013. With research for the success of Darányi Program, Budapest, 2013. november 7-8. ISBN 978-963-503-550-2

5.2. **Soós Anita** - Horti Krisztina - Pecznyik Csilla - Dr. Somogyi László - Effects of animal fats on the texture and the melting profile of palm mid fraction (PMF) PhD hallgatók VIII. Nemzetközi Konferenciája, Miskolc, 2012. augusztus 6-10.

6. International Conferences (proceeding) (2 points)

6.1. 11th INTERNATIONAL CONFERENCE OF FOOD PHYSICS AND INNOVATIVE TECHNOLOGIE, 10 to 12 of June 2014, Plovdiv, Bulgaria

6.2. Műszaki Kémiai Napok, Veszprém, 2014.május 14-16.