Physical interactions between cupuassu and cocoa fats

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RESUMEN

Interacciones físicas entre grasas de cupuassu y cacao.

Cupuassu (*Theobroma grandiflorum*, Sterculiaceae) es una fruta nativa amazónica que hoy día sólo se cultiva en esta región. Las semillas con un 16%, aproximadamente, del peso seco, tienen, aproximadamente, el 60% de grasa y pueden usarse como sustituto de manteca de cacao. En general, estas grasas son similares a las del cacao, aunque muestran diferencias en algunas de sus propiedades físicas. El objetivo de este estudio fue analizar algunas propiedades físicas y de cristalización de la grasa de cupuassu, de la manteca de cacao y de mezclas de las dos grasas. Los análisis realizados fueron: punto de goteo, contenido en grasa sólida, índice de dureza y la curva de enfriamiento de Jensen. El tiempo de cristalización inferior y la mayor suavidad que muestra la grasa de cupuassu frente a la manteca de cacao, sugieren algunas ventajas del uso de la misma. Todas mezclas fueron compatibles. El contenido en grasa sólida, a temperatura ambiente, de la manteca de cacao fue superior a la de la grasa de cupuassu y las mezclas. La grasa de cupuassu mostró un punto de goteo inferior al de la manteca de cacao. Esta grasa y las mezclas estudiadas podrían usarse en los rellenos y productos del chocolate en temporada fría.

PALABRAS-CLAVE: Cupuassu - Chocolate – Grasa - Propiedades físicas.

SUMMARY

Physical interactions between cupuassu and cocoa fats.

Cupuassu (*Theobroma grandiflorum*, Sterculiaceae) is an Amazonian native fruit and nowadays is cultivated only in Amazonian region. The seeds that come to about 16% of the dry weight can be used to derive a cocoa butter like product and the content of fat in the seeds is about 60% dry weight. In general, these fats are similar to those of cocoa, although they show difference in some physical properties. The objective of this study was to analyse some physical and crystallization properties of the cupuassu fat, cocoa butter and some mixtures between the two fats. The analyses performed were: dropping point, solid fat content, hardness index and Jensen cooling curve. The results suggested some advantages of the use of cupuassu fat, as lower crystallization time and smoothness than cocoa butter. The mixtures showed compatibility, cocoa butter showed bigger solid fat content at room temperature than cupuassu fat and the mixtures. Cupuassu fat had a lower dropping point than cocoa butter. The possible use of cupuassu fat and the mixtures could be in fillings and cold weather chocolate products.

KEY-WORDS: Chocolate – Cupuassu - Fat - Physical properties.

1. INTRODUCTION

Cocoa butter is the only continuous fat phase in chocolate and is therefore responsible for the dispersion of the other constituents. Efforts have been made to find an alternative to cocoa butter and to replace parts of the cocoa butter in chocolate, for economic and technological reasons (Lipp & Anklam, 1998).

Cupuassu is one of Amazonian's most popular fruit species, commanding excellent prices during its harvest season. Its developing market outside Amazonia is supplied with frozen pulp, produced mainly in Pará, Rondônia, Amazonas and Acre. Cupuassu's seed is very rich in fats (± 57% dry weight), which is 91% digestible by humans. In general, these fats are similar to those of cocoa, although they have a different fatty acid profile (Vasconcelos et al., 1975; Venturieri, 1993).

The interactions between cocoa and cupuassu fat and the cupuassu fat alone could be of interest to confectionery and chocolate industry.

Physical properties of an oil or fat are of critical importance in determining its use. This is particularly true for the large quantity and variety of oils and fats used in various forms as food. A fat is a material that is composed of an intimate mixture of liquid and solid phases whose main constituents are triglycerides (triacylglycerols). Triglycerides are the main components of cocoa butter and other oils and fats. The physical state of a fat may vary from a liquid to a viscous fluid to a plastic solid to a brittle solid.

In general, a number of properties are to be considered in determining degree of compatibility. Among these are composition, thermal properties, rheological properties and crystallographic properties. A completely compatible extender should exhibit crystallographic properties equivalent to those of cocoa butter – alone and in mixture with cocoa butter. In thermodynamic terms, it should exhibit ideal solid solubility in admixture with cocoa butter. This requires that the molecules of the fat are capable of isomorphously replacing cocoa butter molecules in the lattice of the latter, and vice versa (Lannes & Medeiros, 2000).

The conditions to obtain complete or ideal solid solubility are: similar polymorphism, equivalent

thermal properties, similar molecular size, shape and packing (Timms, 1985).

Cocoa butter is a unique, naturally occurring fat containing mainly monounsaturated and diunsaturated glycerides in which palmitooleostearin constituents a single dominant glyceride.

Cocoa butter obtained from fruits grown at low temperature is soft and contains high diunsaturated triacylglycerols and high unsaturated fatty acids, i.e., oleic and linoleic acid. Twenty-four cocoa butters were characterized according to their triglyceride composition (Chaiseri & Dimick, 1989). All cocoa butters gave a relative homogeneous pattern, except the cocoa butter from Bahia-Brazil. This cocoa butter contains a significantly lower amount of monounsaturated triacylglycerols (POP, POS) and a higher amount in di-unsaturated triacylglycerols (SOO, POO), which might explain its unsatisfactory crystallization behaviour (Lipp & Anklam, 1998; Lannes & Gioielli, 1995).

Several workers have attempted to prepare cocoa-butter-like products from other fats which have some degree of resemblance to cocoa butter and which could be modified into cocoa-butter-like fats. The various methods tried include esterification (inter, trans and directed), hydrogenation, fractionation, mixture or combination of these in order to have a product with a melting point around 36°C and a sufficient degree of hardness and brittleness so that the finished product retains its shape at normal room temperature (Baliga & Shitole, 1981).

The physical properties of greatest interest are the crystallization and melting phenomena that encompass both solid fat content and polymorphic behaviour. While the solid fat content measured by dilatometry or nuclear magnetic resonance (NMR) evaluates the physical nature of the fat, it is necessary to obtain information about the crystallization rate or its polymorphic changes. Differential scanning calorimetry (DSC) measurements of the crystallization and melting phenomena of pure forms of the three principal triglycerides present in cocoa butter and related confectionery fats.

Cooling curves have been used to determine the comparative merits of various hard butters in relation to cocoa butter. These curves are obtained by observing the temperature of the sample at intervals during relatively rapid cooling. The crystallization finishes when the maximum temperature is reached, being due to the heat of crystallization. The necessary intervals to reach the minimum and maximum temperatures, supply information about the behaviour of the fat and of the chocolate mass. These intervals are also influenced, partly, by the polymorphic forms of the cocoa butter. The faster these points are reached, the best is the quality of the fat (Lannes & Gioielli, 1995).

Chocolate products are regarded the world over a special "treat". Their attraction lies in the unique flavour of the roasted cocoa bean, and in the characteristic brittle texture, the "snap" and the "crunch" experience in breaking and chewing. This texture is derived from the fat and must be accompanied by a rapid melt-in-mouth sensation and no residual greasy feeling.

Cocoa butter, which amounts to 25-36% in finished chocolate, is responsible for the smooth texture, contractibility, flavor release, and gloss of the product. The special position of chocolate among other food products is not only based on its taste and nutritional value. Moreover, physical parameters are important, such as brittleness (the "snap" when the chocolate breaks) and the fast and complete melting in the mouth. The fat phase is the only continuous phase in chocolate, thus responsible for melting behaviour and the dispersion of all other constituents. Cocoa butter itself exists in different crystal modifications. A careful tempering of the chocolate is necessary in order to obtain the fine crystals in the correct form (β-modification). Without this tempering, cocoa butter tends to crystallize in rather coarse crystals, with the tendency to blooming. Blooming describes the unfavorable occurrence of big white fat crystals on the surface of the chocolate (Bricknell & Hartel, 1998).

The intention of this work is to study interactions between cocoa butter and cupuassu fat using the cooling curves, melting point and solid fat content curves.

2. MATERIAL AND METHODS

2.1. Material

Mixtures between cocoa butter (deodorized) and cupuassu fat (not treated) were made as following proportions (Table I):

Table I
Mixtures

MIXTURES	PROPORTIONS (%)	
	Cocoa butter	Cupuassu fat
M1	10	90
M2	90	10
M3	70	30
M4	30	70
M5	50	50
M6	100	0
M7	0	100

2.2. Methods

2.2.1. *Cooling curve*

Jensen cooling curve was obtained according to the method of Standard British Institution, where 75g of sample was warmed approximately to (45-50°C) in a glass tube provided with ring stirrer and digital thermometer. For test repeatability purposes, the test system was kept in a water bath at 60°C during 15 min. The room temperature was stabilized at 23°C. The sample in the tube was placed in bath at 60°C during 15 min. Then, it was removed and constant and slow stirred until temperature reached 40°C, cooling without stirring continued up to 35°C. The tube with sample was then transferred to a jacket glass recipient and placed in refrigerated bath at 17°C. When the temperature of the sample reached 32°C, the temperature was recorded at the start of each minute, with slow stirring in defined intervals (after 5, 20, 35 and 50 s). The temperature was recorded until the first crystallization sign (British, 1976).

2.2.2. *Solid fat content*

SFC values of fat samples were analysed with a Bruker/NMS 120 Minispec/NMR analyser. A AOCS method 16b-93, of solid fat content by low-resolution nuclear magnetic resonance analyse, was used to measure the SFC of tempered samples (AOCS, 1997).

2.2.3. *Melting point*

Mettler dropping-point method was used. Samples were chilled in the freezer at -10°C for one hour. Heating rate was 2°C/min.

2.2.4. *Hardness (Texture)*

Hardness was measured using TA-XT2 instrument (Stable Micro Sistem), at 15, 20, 25, 30°C, the cone 20°C probe was set to penetrate 10.0 mm with speed of 2.0 mm/s, in triplicate. The results were used to create the iso-hardness diagram.

3. RESULTS AND DISCUSSION

Solid fat content (SFC) is an important indicator of hardness. Fats with the lowest SFC used in the chocolate manufacture result in the softest products, because chocolate made with a harder fat contains more fat crystals than with a soft fat. The trends in chocolate hardness relative to the SFC profiles of the pure fat systems are worth consideration.
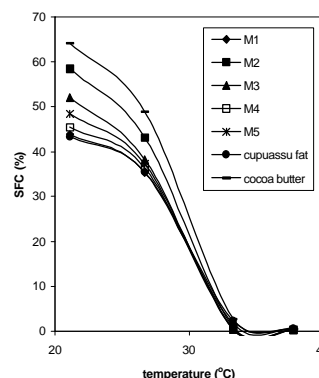

Figure 1
Solid fat content curves of cupuassu fat, cocoa butter, and their mixtures

The profiles of the solid curves of all samples were the same (Figure 1). However, cocoa butter had the higher solid percentage than the rest of samples while cupuassu fat has the lower. It is more smooth than mixtures and cocoa butter. Cupuassu fat would be useful in filled chocolate manufacture as a softer filling fat compatible with cocoa butter.

The melting point of a fat is thus an empirical property related to the experimental method of determination and not a basic physical property, like the melting point of a pure compound.

Fats are invariably mixtures of mixed triglycerides and each individual triglyceride has its own melting point. The fat has a melting range. What we understand by melting point of a fat is really the end of the melting range. The advantages of the Mettler dropping-point method include the automatic endpoint detection, availability of different heating rates from 0.2 to 10 $^{\circ}$C/min, and good precision. Dropping point is generally lower than the softening point of AOCS Cc 3-25 method.

The dropping point is proportional to the percentage of the each fat as can be seen in Table II. Cupuassu fat had a higher dropping point than the cocoa butter and the mixtures.

Table II

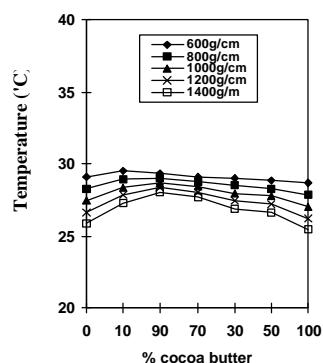| SAMPLE	DROPPING POINT ($^{\circ}$C)
Cocoa butter	25.1
Cupuassu fat	28.7
M1	27.9
M2	26.3
M3	24.7
M4	26.5
M5	25.4

Figure 2
Iso-hardness curves of mixtures between cocoa butter and
cupuassu fat

The mixture is affected according to the proportion of the different fat. The hardness and crystallinity of the fat phase is affected. The temperature plays an important role in the phase behaviour of these mixtures. The phase diagram of a mixture of two components, a binary mixture, can be considered.

The behaviour of mixtures of cocoa butter and cupuassu fat is described in Figure 2. It was observed that the fats are not completely miscible over the full range of composition. In defining the practical areas of formulation it is useful to examine this diagram.
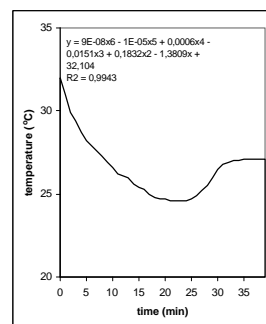
Figures 3 to 8 present the cooling curves by Jensen method for cocoa butter, cupuassu fat and the mixtures.

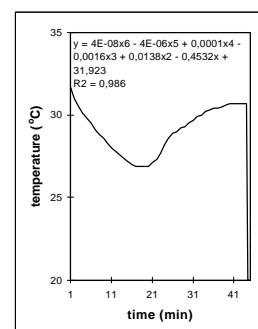The cooling curves are represented by a polynomial regression curve using Excell 5.0 program.
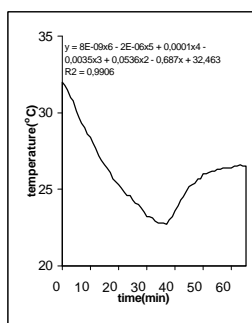
Tmin = 22.7° C   Tmax = 26.6° C
time = 37 min   time = 63 min
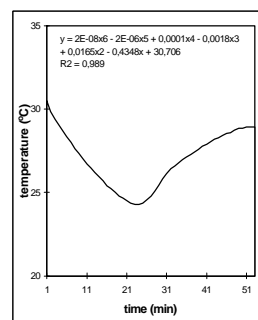
Figure 3
Cooling curve of cocoa butter

Tmin = 24.6° C   Tmax = 27.1° C
time = 21 min   time = 35 min
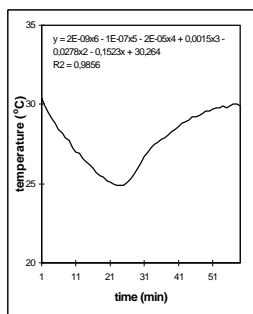
Figure 4
Cooling curve of cupuassu butter

Tmin = 26.9 °C   Tmax = 30.7 °C
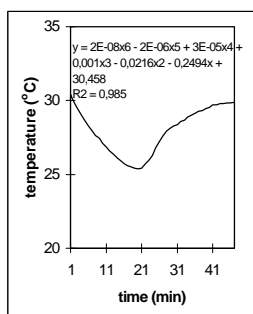**time = 17 min   time = 40 min**

Figure 5
Cooling curve of mixture 1

Tmin = 24.3 °C   Tmax = 29.0 °C
time = 24 min   time = 51 min

Figure 6
Cooling curve of mixture 2

$y = 2E-09x^6 - 1E-07x^5 - 2E-05x^4 + 0,0015x^3 - 0,0278x^2 - 0,1523x + 30,264$
$R^2 = 0,9856$

Tmin = 24.9 °C   **Tmax = 30.0 °C**
time = 23 min   **time = 57 min**

Figure 7
Cooling curve of mixture 3

$y = 2E-08x^6 - 2E-06x^5 + 3E-05x^4 + 0,001x^3 - 0,0216x^2 - 0,2494x + 30,458$
$R^2 = 0,985$

Tmin = 25.4 °C   **Tmax = 29.9 °C**
time = 20 min   **time = 45 min**

Figure 8
Cooling curve of mixture 4

The crystallization velocity of the fats may be obtained by cooling curve. Crystallization finishes when the maximum temperature is reached. The necessary time to reach the minimum and maximum temperature gives informations about the fat behaviour and quality. The profile of the Jensen cooling curves is similar to both cupuassu and cocoa fats, but differences exist on the time of crystallization and temperatures. Cocoa butter has lower minimum temperature (22.7°C/24.6°C) and higher minimum time (37min/21min), lower maximum temperature (26.6°C/27.1°C) and higher maximum time (63 min/35 min) than cupuassu.

While the profile of the cooling curves is similar for all samples the time of crystallization and temperatures are different.

Among the samples analysed, cocoa butter had the lowest minimum temperature and the highest

$y = 3E-08x^6 - 3E-06x^5 + 0,0001x^4 - 0,0009x^3 + 0,0043x^2 - 0,3998x + 30,905$
$R^2 = 0,9924$
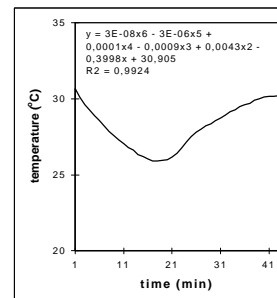
Tmin = 25.9 °C   **Tmax = 30.4 °C**
time = 17 min   **time = 44 min**

Figure 9
Cooling curve of mixture 5

minimum time, the lowest maximum temperature and the highest maximum time. Cupuassu fat had the lowest maximum time. Mixture M1 had the highest minimum temperature and the highest maximum temperature.

The time of crystallization vs. shape of crystal fraction can give important clues for the crystallization mechanism of a particular substance. The difference between the velocity of crystallization from pure sample and the mixtures might be due to the specific interactions of the acylglycerols.

In a chocolate production, the properties of the product are function of the fat phase. Proper crystallization of the fat on the enrobed piece is important to finished product quality. The main requirement is that the surface be glossy, with the desired shade of brown.

Using cooling curves it is possible to investigate the additives effects. The cooling curve is related with the viscosity of the tempered fats. If the cooling curve varies, so the viscosity, the color and the conservation of the product also vary.

Cupuassu fat shows lower crystallization time than cocoa butter, so cupuassu fat has better quality than cocoa butter. Mixture M1 shows lower crystallization time than the other ones. The rates of crystallization, as determined by Jensen cooling curve, were also different for all mixtures. Analysed softer fats with low solid fat contents crystallized more slowly, which would then lead to products as chocolate of inferior physical properties.

The rate of crystallization is a key parameter of the fat. The crystallization behaviour of fats and lipids has two major industrial implications as processing of the end products made of fat crystals, such as chocolate and separation of specific fats and lipids materials from natural resources. The physical properties of greatest interest are the crystallization

and melting phenomena that encompass both solid fat content and polymorphic behavior of fats.

4. CONCLUSIONS

- The profile of the Jensen cooling curves is similar to both cupuassu and cocoa fats, but differences exist on the time of crystallization and temperatures;
- Cocoa butter and cupuassu fat show compatibility;
- Cocoa butter has more solids percentage at room temperature than cupuassu fat;
- Cupuassu fat would be useful in filled chocolate manufacture as a softer filling fat compatible with cocoa butter .

ACKNOWLEDGMENTS

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