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Isothermal Crystallization Kinetics of Mango (*Mangifera indica*) Almond Seed Fat

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Abstract: In this study, the kinetics of isothermal crystallization of mango (*Mangifera indica*) almond seed fat var. Manila (MAF) was analyzed, within the theoretical context of the Sestak-Berggren model, the Avrami Equation and its modification by Khanna and Taylor. The results showed that the induction times for the formation of crystalline nuclei increased with the crystallization temperature (3.3 min at 8°C and 10.9 min at 12°C). The supercooling level notably influenced the MAF crystallization rate, since the global constant of crystallization rate, Z, grew 3.3 times from 12 to 8°C (for fractions of fat solids between 0.25 and 0.75, Z was 0.2904, 0.1584 and 0.0879 min^{-1} at 8, 10 and 12°C, respectively) and the Avrami parameter r was higher than 4; this demonstrates the effect of fat system complexity due to its multi-component nature and the heterogeneous character of this crystallization process, which includes additional participation of nucleation sites. The modified model by Khanna and Taylor provided better parametrial values than the other two studied for explaining MAF crystallization kinetic.

Key words: Crystallization kinetics, isothermal crystallization, mango almond fat, fat crystallization, Avrami equation, Khanna and Taylor equation

INTRODUCTION

It is known that the interchange of fats and oils in the industrial environment is a result of several factors, like the availability and cost of raw materials, market preferences, legislation, etc. In some production sectors there is increased interest for using oil and fat substitutes and equivalents there, where well known items have wide spread domestic and industrial use (Young, 1985).

The mango seed (*Mangifera indica*, L.), among many other wastes from industrialized fruits in the world, is a good example of the potentiality of agroindustrial residues that have become alternate sources of important fats from the point of view of their compositions and their physical and nutritious properties (Jiménez-Bermúdez *et al*., 1995; Lakshminarayana *et al*., 1983; Solís-Fuentes *et al*., 2001; Solís-Fuentes and Durán-de-Bazúa, 2005; Narashima-Char *et al*., 1977).

Mango Almond Fat (MAF) is one of the most important components of *Mangifera indica* seed because of some of its physicochemical characteristics that resembles those presented for cocoa butter (Solís-Fuentes and Durán-de-Bazúa, 2005).

Nevertheless concerning the potentiality of fats coming from non-traditional sources such as those extracted from the mango almond, it is evident that their commercial development and industrial application often require the generation of more knowledge in regard to some more specific characteristics like polymorphic properties and phase behavior. Biological fats and oils are meta-stable materials and they suffer state and phase transitions during processing and storage. The understanding of such transitions, molecular mobility and stability and their relationships is fundamental for achieving product quality control (Roos, 1995; Solís-Fuentes and Durán-de-Bazúa, 2004; Solís-Fuentes *et al*., 2005). The majority of lipid transitions in foodstuffs, some medicines and cosmetics, associated with processing and storage behavior, are between the solid and liquid states and several polymorphic solid phases (Roos, 1995; Sato, 1999).

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The target of the present investigation was to study the kinetics of MAF isothermal crystallization, within the frame work of the Sestak-Berggren, Avrami and Khanna and Taylor models, which have been used to study the isothermal crystallization process of plastic polymers and other fats and vegetable oils.

MATERIALS AND METHODS

MAF extraction and purification: The fat of the mango almond seed was obtained from physiologically mature fruits (Manila variety) using the methodology delineated by Solís-Fuentes and Durán-de-Bazúa (2004). The fruits were obtained from mango plantations of Central Veracruz region during crop of year 2005.

Isothermal crystallization: Kinetic studies of isothermal crystallization were realized in agreement with the Koyano *et al.* (1989) methodology. A DSC 2910 calorimeter (TA Instruments, New Castle, OF; USA) equipped with a station for the analysis of information was used. The fat samples were weighed in a 2950 thermo-balance (TA Instruments, New Castle, DE; USA), with weights between 5-10 mg and placed in aluminium capsules sealed hermetically. Isothermal conditions were reached after the MAF samples were melted at 90°C and cooled rapidly to the pre-established crystallization temperature; then, they were kept at this temperature sufficiently long for the fat to crystallize. Calorimetric data were collected and isothermal crystallization curves were obtained. Isothermal crystallization temperatures were selected in accordance with preliminary assays and those recommended by TA Instruments (1997). The chosen temperatures were 8, 10 and 12°C. The collected DSC data were used to calculate crystallization induction times and the solid-liquid fat relationships dependent on time and temperature.

MAF isothermal crystallization was studied in terms of the models of Sestak-Berggren (Sestak, 1984; Foreman and Blaine, 1998), Avrami (1940) and Khanna and Taylor (1988).

Isothermal crystallization models

Sestak-Berggren model: The adjustment of experimental data to the Sestak-Berggren model was tested with Thermal Solutions software (TA Instruments, 1997). The model, also known as auto-catalyzed, is defined by Eq. 1:

$$\frac{dC}{dt} = kC^{m}(1-C)^{n} \quad (1)$$

where C is the crystallized fat fraction, dC/dt is crystallization rate, k is the specific constant of crystallization rate and m and n are numbers that represent the reaction order, m being an independent reaction order. The adequacy of the model was judged according to the degree of closeness of experimental information to the regression line in a graph of Log (dC/dt) vs Log [(1-C) C (m/n)]. If the coincidence is strict, the model is pertinent; in the opposite case, it must be considered to be another model (TA Instruments, 1997).

The activation energy was estimated, in the context of this model, with the methodology described by Sichina (1998). The slope of the straight regression line from a graph of 1/T against ln t, provides the value of Ea/R, where t is the time of the exothermic maximum when isothermal crystallization occurred.

Avrami model: Solid fractions for each time during the isothermal crystallization of MAF, [F = f (t)], were used to adjust the experimental data to the original Avrami model (Eq. 2):

$$1 - F = \exp(-Zt^{r}) \quad (2)$$

One ln t vs ln [-ln (1-F)] graph, using F between 0.25 and 0.75 (Avrami, 1940), was used. The parameter *r* was estimated by the slope of the regression line and Z from the origin ordinate (ln Z).

Model modified by Khanna and Taylor: In the same way, F = f (t) data were adjusted, by regression, to the model modified by Khanna and Taylor (Eq. 3):

$$1 - F = \exp(-Zt)^{r} \quad (3)$$

ln t vs ln [-ln (1-F)] graphs were made using F between 0.25 and 0.75 for each crystallization temperature (Khanna and Taylor, 1988). Parameter *r* was calculated with the slope and Z with the origin ordinate (rlnZ).

The energy of activation (Ea) and the pre-exponential factor (A_0) were as estimated by means of Arrhenius' equation.

RESULTS AND DISCUSSION

Isothermal curves: Figure 1 shows the curves of MAF isothermal crystallization. The induction times (τ) and exothermic maximum times for each of the studied crystallization temperatures is showed.

Sestak-Berggren (auto-catalyzed) model: The shape analysis of the isothermal crystallization curves suggested an auto-catalyzed crystallization process, because the maximum peaks of heat production appeared after 30% of the area had crystallized (Sestak, 1984). A graph of Log (dC/dt) vs Log [(1-C) C (m/n)] (Fig. 2) allowed the calculation of kinetic parameters n, m and k. At 12°C the order of reaction n was 0.871±0.047 and

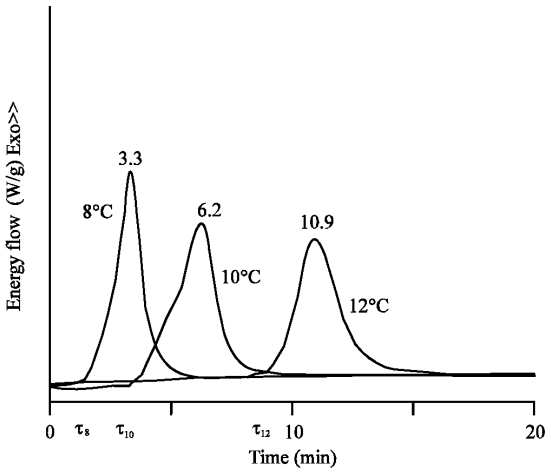

Fig. 1: Isothermal curves of MAF crystallization

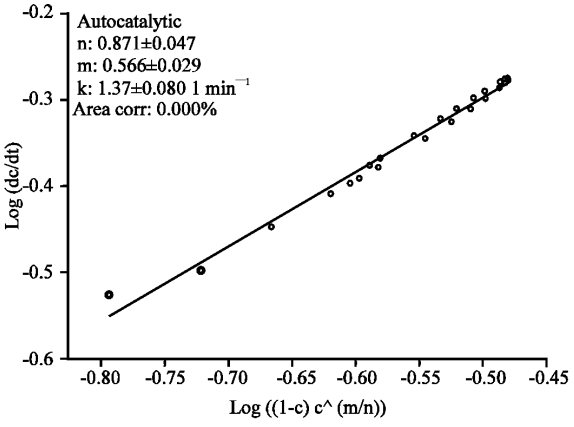

Fig. 2: Experimental data adjust for MAF isothermal crystallization at 12°C

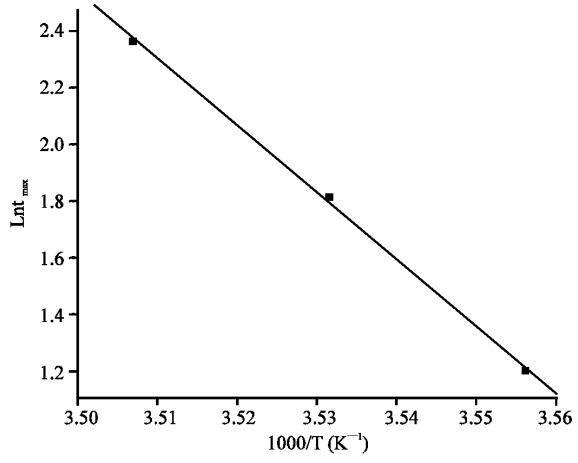

Fig. 3: 1/T vs ln t_{max} graph for Ea estimation in the Sestak-Berggren model

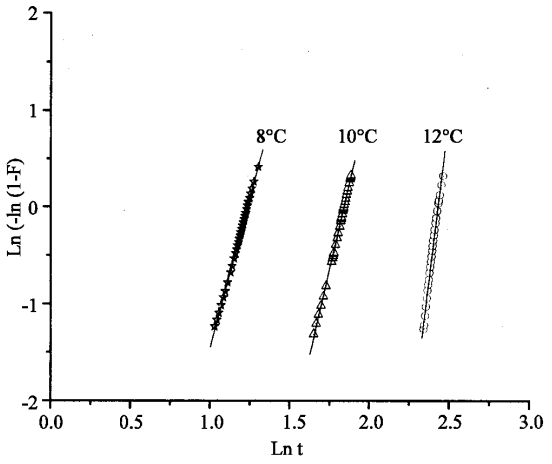

Fig. 4: ln t vs ln [-ln (1-F)] Graph with F between 0.25 and 0.75 for 8, 10 and 12°C

the independent reaction order, m was 0.566 ±0.029. The specific constant rate of crystallization, k, was 1.37±0.080 min^{-1}. Constant k was 2.27 min^{-1} at 10°C and 3.79 min^{-1} at 8°C. A graph of 1/T against ln t of the experimental data adjusted with R = 0.999 (Fig. 3). Ea was 201.6 kJ mol^{-1} and Arrhenius' pre-exponential factor was 2.068×10^{37}. This value is near to the Ea of triacylglycerid (TG) isothermal crystallization obtained in other investigations (Toro-Vázquez *et al.*, 1999).

The estimation of the r Avrami value from the n and m parameters was 2, which suggests a two-dimensional growth of MAF nuclei; nevertheless, this result should be taken with caution because, till now this estimation method has tried only with some materials simpler than and chemically different from, natural fats.

Avrami equation: One of the models mainly used to analyze the kinetics of crystallization, firstly, of polymers and, later, of many other materials, lipids among them, is that of Avrami. His estimations are important because, for some materials, they enclose a physical meaning. The value of r depends on the shape of the crystal nucleus and its rate and growth form. When nucleation sites are formed instantaneously, r is 1 with nuclei having needle form and growth in only one dimension; r is 2 when molecules integrate to nuclei in two dimensions and 3 for nuclei that can have three-dimensional growth. When additional nucleation sites with participation of different molecules from those of the original nuclei appear sporadically, the value of r turns out to be a larger whole number (Foreman and Blaine, 1998).

Figure 4 shows ln [-ln (1-F)] against ln t in a graph of the experimental data transformed to model with Avrami's equation at 8, 10 and 12°C, respectively, at F values between 0.25 and 0.75.

Table 1: Index r and global constant rate, Z, for MAF isothermal crystallization at 8, 10 and 12°C

	F (0.25 to 0.75)			
	Z min^{-1}			
Temperature (°C)	Original model[a]	Modified[b]	r	R
8	4.6×10^{-4}	0.2904	5.7	0.99
10	1.88×10^{-6}	0.1584	7.1	0.99
12	4×10^{-15}	0.0879	13.6	0.99
Ea		203.15[c]		0.99

[a]Avrami equation, [b]Equation modified by Khanna and Taylor, [c]In kJ mol^{-1}

The Avrami index, r values at studied temperatures are presented in Table 1. The correlation coefficient R> 0.99 shows that the experimental data described well with the regression model. It is evident that their values are higher than 3, which is the value assigned to spherical forms of nuclei with three-dimensional growth obtained with many other relatively simple materials.

At a given temperature parameter r changed when the solids fraction range was changed. It can be shown that this parameter in the material studied is highly sensitive to the extent of crystallization and is affected by the composition and level of complexity of the system. Some research reports show that some crystalline polymers present r values higher than 3 and more complex materials have presented Avrami indexes of 4 and more (Foreman and Blaine, 1998; Kawamura, 1979; Toro-Vazquez *et al*., 2000; Smith, 2001).

It is important to note that the Avrami model has been used mainly in the crystallization analysis of materials relatively simpler in composition, such as plastic polymers. The crystallization of fats and oils has been studied in theoretically ideal binary or ternary systems less complex than natural fats like pure triacylglycerol (TG) crystallization from a solution. In other paper (Solís-Fuentes and Durán-de-Bazúa, 2003), it was shown that MAF has a relevant content of saturated long-chain fatty acids that can determine high melting points and low solubility of TG. This TG interacts with many other TGs in minor quantities, with different properties and thermal behavior, which determines, as a whole, the forms and rapidity of the formation and growth of crystal nuclei. It is known that the crystallization of natural fats and oils is mainly heterogeneous due to the fact that, even in carefully purified fats there are lipid molecules different from TG (mono and di -glycerids, phospholipids, etc.) that can act as embryonic particles of crystalline nuclei. Sato and Koyano (2001) have analyzed the enhancing effect of some of these minor components in the crystallization of cocoa butter.

Khanna and Taylor´s modified model: Table 1 also presents the values of the MAF global constant of crystallization, Z, from original Avrami equation and the modified model proposed by Khanna and Taylor. In all cases it shows the tendency of the crystallization rate to decrease with an increase in the temperature. Nevertheless, the difference in Z magnitude order becomes evident. In the first case, Z values were notably lower in orders of magnitude and they were highly sensitive to F intervals. The Khanna and Taylor equation provided Z with magnitude orders higher than the values obtained from the original Avrami model. Thus Z, when the solids fraction was between 0.25 and 0.75, was 0.2904, 0.1584 and 0.0879 min^{-1} at 8, 10 and 12°C, respectively; these values did not change significantly, when the range of F was changed.

Avrami model results showed that the supercooling level reached notably influenced the fat crystallization rate; the Z value, when the Khanna and Taylor model was used, grew 3.3 times when the temperature went from 12 to 8°C; this situation implies an important sensitivity of the MAF crystallization rate when the cooling degree reached these temperature levels.

A more detailed explanation of temperature effect on the MAF isothermal crystallization rate would have to define which factor controls the global process of crystallization (integration or diffusion of molecules to the crystal nuclei) with a complementary analysis of the influence of temperature on MAF viscosity.

The Z values and temperature relationships were analyzed with Arrhenius´ equation. The Ea value for MAF isothermal crystallization obtained with the modified Khanna and Taylor equation was 203.15 kJ mol^{-1}, very similar to the one calculated with the auto-catalyzed model.

CONCLUSIONS

According to the calculated Z and Ea values, the MAF isothermal crystallization data adjusted better to the modified Avrami equation than the other ones studied. This was not so for parameter r (Avrami index), because the calculated r values depended on the extent of crystallization and they were higher than the theoretical ones. The auto-catalyzed model presented some results that were relatively coincidental with those obtained with the modified Avrami equation, so its usefulness for analyzing the isothermal crystallization of fats and oils (although more experimental evidence is needed) seems to be promising.

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