THE KINETICS OF CRYSTALLIZATION OF TRIPALMITIN IN OLIVE OIL: AN ARTIFICIAL NEURAL NETWORK APPROACH

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ABSTRACT

Experimental measurements of the variation in the solid fraction during crystallization of lipid mixtures are often correlated in terms of the so-called Avrami model. In this paper, the above model was employed to describe measurements taken during the crystallization of blends of tripalmitin in olive oil at high concentrations. Although the blends appeared to behave ideally, the Avrami model failed to describe the experimental results over the entire range of tripalmitin concentration investigated. This discrepancy appears to be correlated with the interfacial free energy. As an alternative to the description of lipid crystallization experiments, the use of continuous-time artificial neural network (ANN) approximators is proposed. For the system studied here, the ANN successfully reproduced the experimentally observed behavior for all temperatures and tripalmitin concentrations used.

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INTRODUCTION

The crystallization behavior of edible fats is important in many food formulations and products, including confectionery, bakery, margarines and spreads. The understanding of the crystallization behavior of fats is very important for many of these applications. Although a large number of studies exists on the polymorphism, phase behavior and kinetics, a complete understanding of the factors affecting the rate of crystallization of fats is yet to be reached (Gordon and Rahman 1991).

In this contribution the crystallization behavior of mixtures of olive oil and tripalmitin was studied. The olive oil which is the most widely used specialty oil and has also been used as a margarine substitute; however, its consistency is too "fluid" to gain further acceptance as substitute for margarine-like fats. One possible alternative to improve its consistency is its combination with another fat to form a plastic fat. A plastic fat contains at least 10% of crystallized material forming a tridimensional matrix that traps the noncrystallized components (Larsson 1994) or crystallizing the system. The formation of a plastic fat can be achieved by adding palm oil to olive oil. In this work, mixtures of olive oil and tripalmitin were used as a simple model system for this process.

The main experimental tool employed was the use of differential scanning calorimetry (DSC) thermo-analytical curves in isothermal and scanning mode. The DSC curves of fats afford valuable information. It is generally accepted that the partial area under the crystallization peak (exotherm) is equivalent to the percentage of liquid fat remaining at a selected temperature (MdAli and Dimick 1994). Thus, it is possible to obtain curves representing the overall crystallization of the blends.

The crystallization behavior is usually modeled as a combination of nucleation and crystal growth. The nucleation is the thermodynamic molecular process that initiates many phase transitions. There is a strong motivation to study nucleation because phase transitions are pervasive in many physical phenomena. The nucleation process is usually divided into homogeneous and heterogeneous classes. In homogeneous nucleation the substances and their environment are assumed to be in the pure state. On the other hand, for heterogeneous nucleation the presence of a foreign material or surface plays a central role. A majority of nucleation theories are limited to the description of homogeneous nucleation. Consequently, of all the nucleation theories, homogeneous nucleation is the simplest. Its simplicity does not undermine its significance, however, as its concepts are applied by many theoretical studies to explain more complicated processes (Olson and Hamill 1996). Nonetheless, there are still gaps between the nucleation theory and the kinetics of phase transition. In this approach, the Kolmogorov-Johnson-Mehl-Avrami theory offers a good starting point, because it is an exact solution for the expected fraction

transformed in a nucleation and growth reaction in an infinite specimen, when nucleation is random in the untransformed volume and the radial growth rate after nucleation is constant until impingement (Cahn 1996).

Kolmogorov proposed the first model for phase transitions in 1937 (K-model) in the form of an equation for the noncrystallized volume fraction, which is exact when the crystallization process is just dependent on the amount of crystals present at a given time. After the paper of Kolmogorov appeared, Mehl and Johnson (1939) applied an original statistical method for the calculation of the noncrystallized fraction. Their model is a particular case of the K-model. Avrami (Avrami 1939, 1940, 1941) applied the Johnson-Mehl method introducing the concept of the dimensionality of the crystal growth. Many authors, following the ideas proposed by Avrami, applied the Johnson-Mehl method to other models different from that of the K-model. These models are sometimes referred to as Avrami-like models. A particular, and common, choice is the so-called Avrami equation, which involves an exponential dependence of the crystal growth with respect to time, and includes a dimensionality index.

The use of Avrami-like equations in lipids has been reported in several studies (Toro-Vazquez and Dibildox-Alvarado 1997; Gallegos-Infante and Rico-Martinez 1999). However, the Avrami equation has shown some deficiencies in modeling the phase transitions. This implies that the kinetics of crystallization cannot be described within the framework of the existing theoretical models (Shepilov and Baik 1994). Furthermore, the use of other models, for instance diffusion-based models, is limited because their parameters must be fitted for every system and every set of data, a cumbersome and tedious process.

In this contribution the use of artificial neural networks (ANN's) as an alternative for modeling the kinetics of the crystallization of lipid systems is illustrated. The ANN's have widely been used over the last two decades as a general tool for black-box modeling of nonlinear processes with excellent results (Weigend and Gershenfeld 1993). Moreover, the ANN's have proven amenable to the inclusion of partial knowledge of the fundamental model of the systems. The model was selected in the form of a continuous model (an ordinary differential equation) (Rico-Martinez *et al.* 1992). The selection of this type of model is motivated by inherent potential to include knowledge from classical nucleation theories into the empirical ANN approximator. The large majority of ANN-tools for system identification are based on the construction of discrete-approximators (for an example in crystallization applications see) Ishida and Zhan 1995, which can easily be related to the measurements from an experiment, but often cannot be linked directly to the fundamental description of the physical-chemical phenomenon taking place in the system. In this contribution we demonstrate the applicability of such a continuous ANN identifier to the reproduction of the crystallization behavior of blends of olive oil and tripalmitin. These predictions with the one offered by the Avrami approach are compared.

MATERIALS AND METHODS

Tripalmitin (99% pure) from Sigma Chemicals (St. Louis, MO) was used without any further purification. Refined olive oil from Ibarra Co. (Ensenada, BC, México) was used. All samples of olive oil were taken from the same batch. The olive oil was filtered with a membrane filter (Nalgene, filter 0.2 μm) to eliminate dust and other foreign particles.

A Perkin-Elmer Model DSC-7 (Norwalk, CT) complete with data station and plotter was used to obtain the thermograms. A piece of indium (6.786 mg) sealed in an aluminum sample pan and cooled at 10C/min was used as the reference.

Solutions of tripalmitin in olive oil were made and mass percentages of tripalmitin in olive oil were 100, 72.5, 62.5 and 0. The solutions were prepared in Eppendorf tubes and heated in a water bath (80C) for 30 min. Samples of approximately 10 mg of each solution were introduced in a DSC pan for analysis. All experiments were replicated two times.

Before scanning, and in order to destroy crystal nuclei, each sample was kept in the DSC at 80C for 30 min and thermograms were subsequently obtained using a constant cooling rate of 10C/min rate until 20C. From these thermograms, we selected four temperatures below the crystallization temperature of the sample to perform further isothermal experiments. For isothermal experiments the selected temperature was reached at a cooling rate of 10C/min, heating the sample at 80C for 30 min and held there for 1 h.

The experiments were not performed on pure olive oil and 0.35-tripalmitin mass fraction because the crystallization temperature was outside the DSC interval used. No irregular peaks or other type of anomalous behavior were observed in the experiments.

The bulk crystallization rate was calculated from the DSC isothermal crystallization curves following the methodology suggested by Kawamura (1979). The induction time of crystallization was obtained according to the procedure proposed by Sato and Kuroda (1987), and the interfacial free energy following Olson and Hamill (1996).

The experimental data were used to "train" the ANN. For purposes of comparison, the results were also fitted to an Avrami-like equation. The fitting of the Avrami equation was performed with a statistical nonlinear regression module (StatSoft Inc., Tulsa, OK).

The ANN approximator has the form of a black-box model. The architecture of the ANN is schematically depicted in Fig. 1(a). The ANN identifier is a four-layer feed forward ANN that predicts the rate of crystallization as a function of the current fraction of solids, the temperature and the initial concentration of tripalmitin and olive oil. Both initial concentrations of tripalmitin and olive oil were used as inputs to the ANN because the total

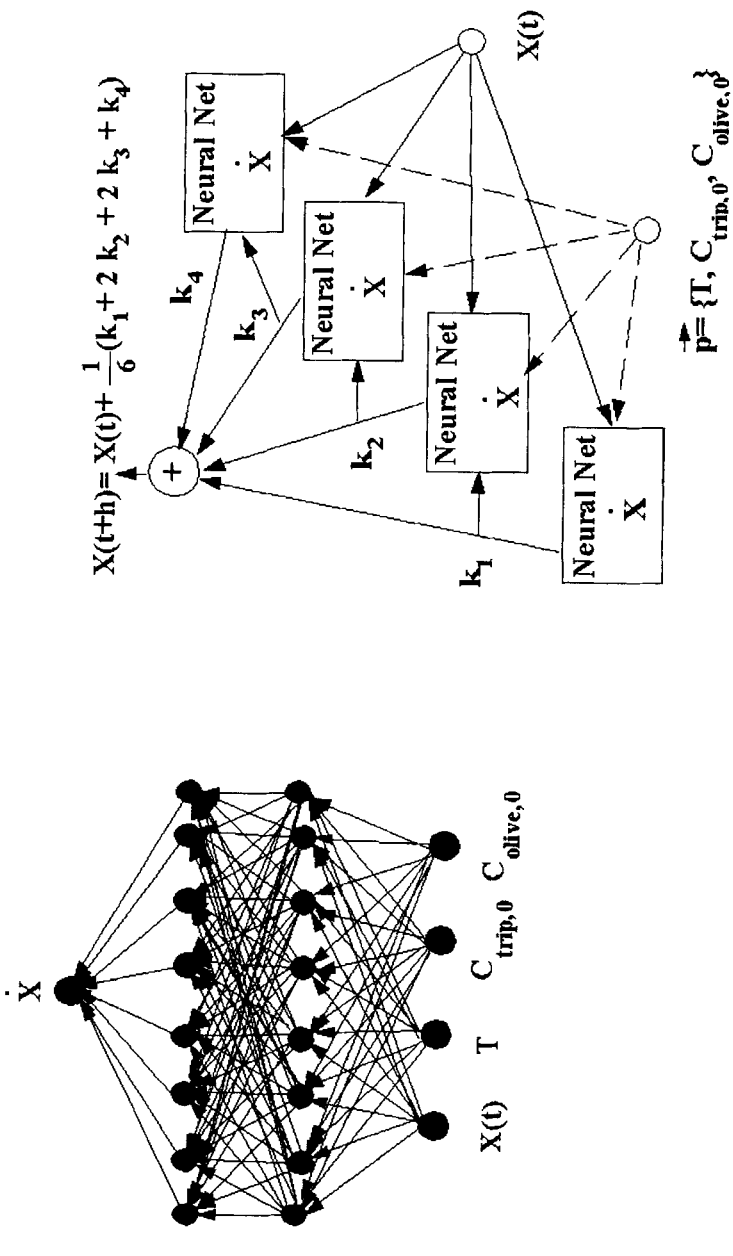

FIG. 1. (a) THE ARCHITECTURE OF A FOUR LAYER ANN (b) THE FRAMEWORK OF THE ANN USED IN THIS WORK

amount of material in each experiment was not constant. A posteriori analysis of the experimental data with the ANN approximator confirmed that the predictions were independent of the total amount of material used for the run. Thus, an equally appropriate, and simpler, set of inputs were the temperature and the initial fraction of tripalmitin in the crystallizing mixture. The "hidden" layers had 10 neurons each with nonlinear activation function of sigmoidal shape ($g(x) = 1/2\ (1+\tanh(x))$). The input layer consisted of four linear neurons (the inputs were the solid fraction at time t, the temperature, and the initial amounts of tripalmitin and olive oil). The output layer was formed with a single neuron (rate of crystallization) and training, to give a solid fraction. For the training, the ANN was embedded within a numerical integrator (4^{th} order Runge-Kutta) framework as depicted in Fig. 1(b). The "composite" network resulting from this procedure allowed us to formulate the training of the original ANN as least squares problem (Reed 1993). By using the predictions of the rate of crystallization coupled with the integrator, one might predict the amount of solid at the next time interval, which was in turn compared with the experimentally observed value. The resulting error and its derivatives were used to find a new set of network parameters with a smaller error (least squares fit). The problem was solved as a minimization problem using a standard conjugate gradient algorithm. It was precisely this minimization problem which is denominated "training" in the neural network literature.

The training set was formed using experimental data from 10 different initial conditions. In order to validate the training of the ANN, cross validation was used (Reed 1993). The probe set included data from 6 initial conditions different from the ones included in the training set. As mentioned earlier, the training was performed using a conjugate gradient (CG) minimization technique. Convergence was declared after 6 complete CG cycles. The ANN is trained to predict the crystallization rate at a given time, based on experimental data taken at different time intervals (for these experiments the tie between measurements was 1.5 s). In order to predict the complete crystallization curve one only needs to feed the solid fraction at an initial time (and the "fixed" parameter values: temperature of the isothermal experiment, and initial concentrations of olive oil and tripalmitin). The curve was thus calculated by "iterating" (numerically integration) the predicted crystallization rate until the required final time. The results discussed below were obtained using this procedure: they constitute "long-term" predictions.

The predictions given by the ANN approximator and the Avrami equation were statistically tested according to the procedures suggested by Bates and Watts (1988). This procedure involved comparisons between the experimentally observed and predicted values, as well as residual analysis. ANOVA analysis involving the experimental data not included in the training of the ANN was also performed.

RESULTS AND DISCUSSION

The behavior of the crystallization temperature as a function of tripalmitin mass fraction was linear. This behavior suggests that the blends behave ideally; however, the limited numbers of experimental points did not allow us to make a conclusive statement. In the temperature interval studied in our experiments, peaks other than the one assigned to tripalmitin or any other type of anomalous behavior in the thermograms were not observed. The olive oil, however, is a complex mixture of triacylglycerols and other lipids, but does not contain tripalmitin.

Figure 2 depicts the induction time as a function of temperature and tripalmitin mass fraction. One possible explanation for the smaller induction times observed for pure tripalmitin with respect to those in the blends is related to the presence of polymorphism: one type of polymorphic form for pure tripalmitin and a different one for the blends. However, in order to verify the validity of this argument one must determine the polymorphic forms. Such determination was beyond the scope of this contribution. Additionally the presence of olive oil decreased the temperature of crystallization of the blends with respect to that of pure tripalmitin; a similar behavior has been reported in blends of tripalmitin and triolein (Ng 1989). The fact that olive oil modifies the melting behavior of tripalmitin indicates unequivocally the existence of intermolecular interactions at the crystal-solution interface. Such interactions might also modify the interfacial free energy and hence affect the rate of formation of crystal nuclei (Cahn and Hilliard 1958). At room temperature the tripalmitin is a simple saturated solid whereas olive oil is complex liquid oil. Phase behavior in such systems is complicated by mutual interactions among the triacylglycerol components and may result in the formation of (1) solid solutions, (2) eutectic mixtures and/or (3) chemical compounds. Any of these interactions will produce deviations in the behavior of ideal blends; however, the behavior was found to be ideal. Thus, one can conclude that interactions at the interface crystal-solution are present, but these effects do not produce a deviation from the "ideal" situation at the macroscopic level. From the foregoing discussion, it may be concluded that tripalmitin is the only crystallized compound in the blends forming a plastic fat. Thus, the rate of crystallization measured should correspond to tripalmitin.

Figure 3 represents a comparison, with respect of the temperature grouping of our experiments, between the errors associated with the predictions obtained from the two models evaluated. From this figure we observe that the Avrami approach does not satisfactorily predict the crystallization kinetics in some cases. On the other hand, the ANN is successful in reproducing the observed behavior for the complete interval of temperatures studied. The failure of Avrami's model can be attributed to the large supercooling involved in the poorly predicted

cases. The kinetics of the bulk rate crystallization are often described with Avrami or Avrami-like equations. This approach is reliable within the interval of solid fraction (0.25 - 0.75). In Fig. 4, an example of comparison between the experimental data is presented; the "best" fit was achieved with an Avrami-like equation and an "average" prediction of the ANN constructed. The ANN predictions were superior even within the recommended interval of validity of the Avrami model. Table 1 summarizes the error and the standard deviations observed for both the Avrami and ANN models. The ANN exhibits smaller errors, as well as smaller standard deviation of the errors, for all experimental conditions studied here. Although the ANN was trained to perform short-term predictions (time-interval 1.5 s), the errors described in this table pertain to long-term predictions. That is, an initial state, which belongs to the nucleation stage of the experiment, was fed to the ANN and the whole crystallization curve was generated. A noninteger index of dimensionality (n) for all experimental conditions with the Avrami model (Table 1) was observed. Such noninteger indeces may signal the presence of heterogeneous growth of the crystals, thus indicating that the use of Avrami-like models may not be appropriate for modeling this system. Furthermore, when n is noninteger, the presence of clusters has been reported in lipids (Gallegos-Infante and Rico-Martinez 1999). Both the presence of clusters and the heterogeneous growth are not accounted for in the original formulation of the Avrami equation. In summary, our system may be one of those that according to Shepilov and Baik (1994) cannot be explained by Avrami-like formulations.

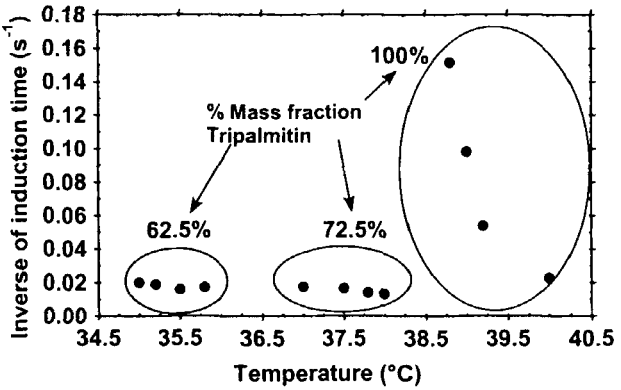

FIG. 2. EFFECT OF THE TEMPERATURE AND MASS FRACTION OF TRIPALMITIN ON THE INDUCTION TIME

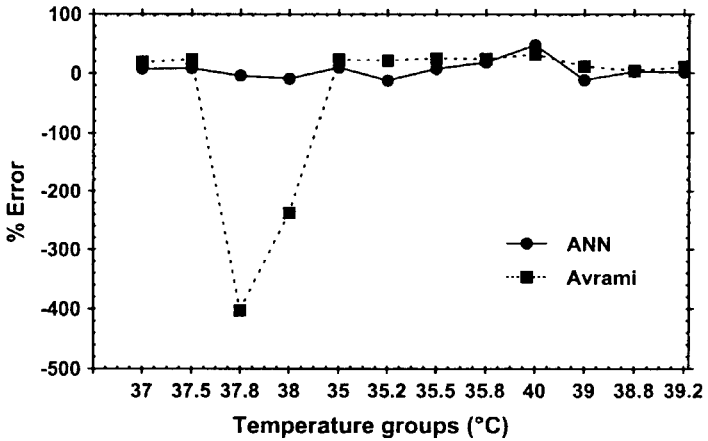

FIG. 3. COMPARISON OF ANN VERSUS AVRAMI MODEL IN FUNCTION OF THE ERROR IN EACH TEMPERATURE GROUP USED

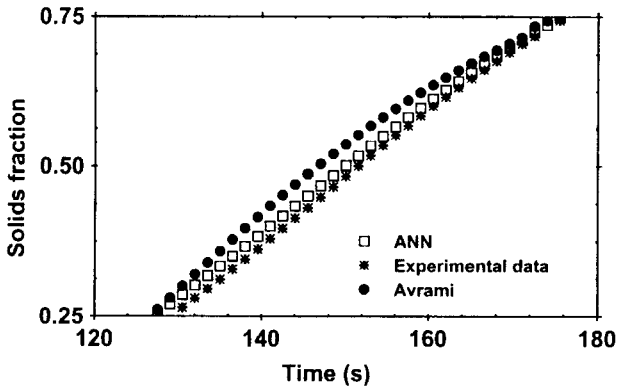

FIG. 4. AN EXAMPLE OF THE COMPARISON BETWEEN ANN VERSUS AVRAMI MODEL

TABLE 1.
ERROR ASSOCIATED TO AVRAMI AND ANN MODEL FOR EACH EXPERIMENTAL CONDITION

Mass Fraction of Tripalmitin (%)	Temperature (C)	% Error of Avrami model* (Mean±SD**)	% Error of ANN model (Mean±SD)
100	38.8	4.060± 34.5	2.32 ± 1.08
100	39	11.305± 28.17	-11.31± 20.46
100	39.2	10.211± 26.22	1.22 ± 5.46
100	40	31.321± 43.08	27.34± 28.79
72.5	37	18.986± 38.99	7.61± 8.18
72.5	37.5	22.906± 41.29	8.23± 3.45
72.5	37.8	-402.447± 1118.64	-4.18 ± 5.87
72.5	38	-237.388± 613.57	-9.02 ± 8.05
62.5	35	22.707± 38.74	9.13 ±7.19
62.5	35.2	21.208± 37.44	-12.22 ±1.566
62.5	35.5	24.688± 40.24	7.21 ± 6.92
62.5	35.8	23.893± 47.60	11.87 ± 5.91

* The % Error is respect to system Supose constant time, the SD is respect the time
** SD= Standard Desviation.

In the classical theory of nucleation the interfacial free energy plays a main role in the phase transformation. Changes in this property modify the rate of nucleation. Figure 5 shows the behavior of the interfacial free energy, as a function of the temperature and mass fraction of tripalmitin. From this figure it is clear that the blends do not behave differently in terms of the analysis of variance; however, for pure tripalmitin a difference of several orders of magnitude was observed. Ng (1989) reported that tripalmitin in triolein solutions undergoes a lowering of its interfacial free energy value but the magnitude of the change reported was only one order of magnitude. For comparative purposes the values reported for the interfacial free energy for pure tripalmitin were similar to the ones reported for Ng (1989), with minor differences due to the different temperatures used. A possible explanation involves tripalmitin crystals

forming a matrix that traps the noncrystallized components of the olive oil. The olive oil adsorbed at the crystal-solution interface interacts with the tripalmitin to bring about the reduction in the interfacial free energy. Because the reduction is very drastic, many molecules from the olive oil components should be adsorbed in this interface. However, the interface between the two coexisting phases is not well defined and its thickness appears to increase with increasing temperature. Note also that for each mole fraction group of tripalmitin, in blend with the olive oil, does not observe statistically significant differences: the interfacial free energy appears to be independent of the temperature in the blends. On the other hand, for pure tripalmitin there is a clear, but small, dependence of the interfacial free energy with temperature. Similar temperature dependence, as that of the blends, has been reported for isotropic systems of nonuniform composition or density (Cahn and Hilliard 1958).

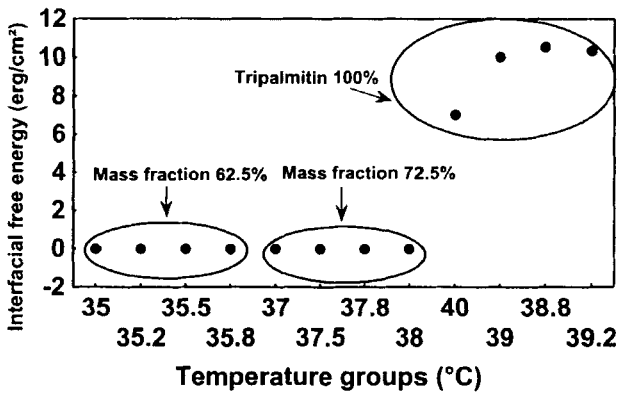

FIG. 5. EFFECT OF THE TEMPERATURE AND MASS FRACTION ON THE INTERFACIAL FREE ENERGY

Figure 6 compares the Avrami-like model and the ANN approximator as a function of tripalmitin mass fraction. The Avrami model failed to reproduce the behavior observed for a tripalmitin concentration of 72.5%; however, it gave reasonable predictions for the other two mass fraction groups. For the groups belonging to concentrations of 62.5 and 72.5% of tripalmitin no significant differences were observed in the interfacial free energy, free energy, temperature increase, induction time and nucleation rate; however the change in the bulk crystallization rate was not properly captured by the Avrami approach. We believe that the explanation lies in the fact that the blends form a plastic fat and

the interactions in the solid-solution interface cannot be described by such an approach. The ANN, on the other hand, was successful for all concentration groups.

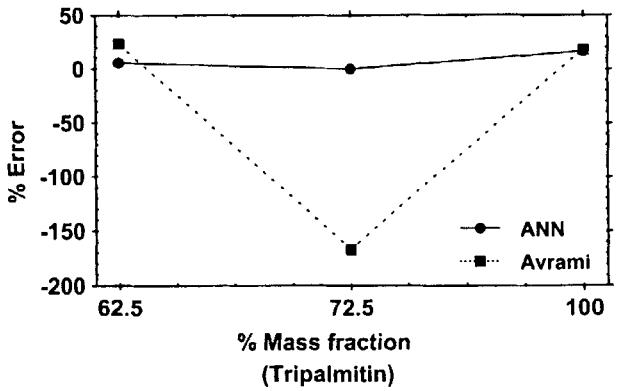

FIG. 6. COMPARISON BETWEEN ANN VERSUS AVRAMI MODEL IN FUNCTION OF THE MASS FRACTION OF TRIPALMITIN

The influence of the amount of tripalmitin on the crystallization temperature of the blends was found to be linear, thus indicating that the blends behave ideally. However, classical nucleation theories in the form of an Avrami-like equation fail to properly capture the behavior observed. In the blends, only tripalmitin crystallized forming a matrix that trapped the olive oil.

Two polymorphic tripalmitin forms were observed: one in the melt and a different one when the crystallization occurred in the blends. Thus, olive oil influenced the type of tripalmitin polymorphic form by producing instabilities in the triacylglycerol molecules.

CONCLUSIONS

The applicability of one type of artificial neural networks in the reproduction of crystallization curves of complex lipid systems was demonstrated. The continuous-time ANN was able to reproduce the dependence of the crystallization rate on the initial conditions and temperatures for all the experimental conditions explored.

The failure of the Avrami approach in describing the crystallization behavior appears to be associated with several events not taken into account in the formulation of such a model. Firstly, the formation of clusters during nucleation, and secondly, a very drastic lowering of the interfacial free energy in the blends which could be associated with diffusion limiting processes. In this later approach, it is clear that more comprehensive theories for nucleation and crystallization of lipids should be developed. Given the importance of the processes involved in these operations, such theories may have an important impact in many industries. The use of ANN approximators may play an important role in the development of applications in the absence of more refined theories as illustrated in this paper. Furthermore, the continuous-time ANN architecture used here can also assist in the formulation of new theories. Such a structure is amenable to the inclusion of partial knowledge of the fundamental model of a system, thus allowing the testing of "incremental" refinements of new theories. Using this approach, further studies on the crystallization of model systems without the added complexity introduced by the mixture involved in olive oil are in progress.

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