

Margarines: A Rheological Study

J.A. Segura^a, M.L. Herrera^{b,*} and M.C. Añón^b

^aMolinos Río de La Plata, Buenos Aires, Argentina and

^bCentro de investigación y Desarrollo en Criotecnología de Alimentos (CIDCA), Consejo Nacional de Investigaciones Científicas y Técnicas, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, Argentina

ABSTRACT: Time-dependent flow properties of both commercial and pilot plant-made margarines were characterized under steady shear. Flow curves were fitted to the kinetic expression $\tau = \tau_i + a e^{-k_1 t} + b e^{-k_2 t}$. A first-order kinetic model did not describe the observed destruction process of the margarine structure in an adequate manner. In the proposed model, two structures with different destruction rates are postulated. Each structure contributes to a part of the shear stress necessary to deform the margarine sample. The parameters τ_i , a and b are temperature-dependent. Decreasing temperatures produce an exponential increase of τ_i , a linear increase of b and an increase of a up to a point beyond which it remains constant. A physical interpretation of the model is proposed. The role of the aqueous phase was also studied. Greater hardness was detected at higher water content. Parameter τ_i increased, at any selected temperature, with increasing aqueous phase content of the sample. Parameter a increased with decreasing temperatures and higher water content. On the other hand, parameter b was not affected by the amount of aqueous phase. This kinetic model could be employed to perform studies on the influence of different parameters of margarine formulation on its rheologic behavior. *JAOCs* 72, 375–378 (1995).

KEY WORDS: Different water contents, margarine, mathematical model, physical interpretation, rheology, texture, thixotropic behavior.

Knowledge of the rheologic properties of a semisolid food, such as margarine, is important in process design, quality control, and development of new products (1,2).

It is known that in margarines the mechanical characteristic of firmness/softness at a given temperature reflects the proportions of liquid and crystalline fat (3). Firmness is increased by hydrogenation of the base stock due to the formation of saturated and *trans* fatty acids from unsaturates (4). A plastic fat is usually workable at room temperature when solid-fat

content lies between 20 and 38% (5). It is generally assumed that the presence of water droplets does not greatly influence the consistency of a product (5,6).

Margarine is composed by three phases: a continuous oily phase, triglyceride crystals, and drops of water, the latter two being dispersed in the first. Triglyceride crystals associate with each other by means of primary and secondary bonds (6,7), leading to a three-dimensional structure that retains the liquid state. As a result of the presence of a fat crystal network, plastic fats exhibit a yield value. The fat behaves like a rigid solid until the deforming stress exceeds the yield value, and the fat starts flowing like a viscous liquid (8). As the shear rate is increased, no significant deformation takes place until the resulting stress reaches the static yield value. This is followed by a decrease in stress, which is attributed to structure breakdown in the sample. The observed behavior indicates the thixotropic character of this type of products (9). At stresses beyond the yield value, bonds are breaking and reforming. The characteristic flow curve for thixotropic fluid is called a hysteresis loop. The classic evaluation of this property comprises the measurement of the area enclosed by the hysteresis curves (10), which requires an arbitrary set of experimental conditions to be fixed, such as final shear rate, time at final shear rate, and gradient of shear rate. Such variable conditions complicate comparisons and analysis of results.

In this work, a kinetic model is proposed for commercial margarine that allows the interpretation of its flow properties as a function of time at constant shear rate. Because the model has less variables to fix it makes the interpretation of the differences in texture of margarine formulated with different water contents possible.

MATERIALS AND METHODS

Studies were carried out on commercial margarine with 82% fatty phase and on samples prepared in a pilot plant with different water contents (15–25% and 45%). All commercial samples were provided by a local manufacturer.

Rheometric studies. For these studies, a Haake Rotovisco RV2 viscometer (HAAKE Mass-Technik GmbH u. Co., Karlsruhe, Germany) was used with a plate and cone system of 0.3° conicity and 20 mm diameter (PKI, 03). Five repli-

*To whom correspondence should be addressed at Centro de Investigación y Desarrollo en Criotecnología de Alimentos (CIDCA), Consejo Nacional de Investigaciones Científicas y Técnicas, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Calle 47 y 116 (1900) - La Plata, Argentina.

ates of each experimental run were made at 15°C, the exception being those experiments conducted to determine the temperature effect on parameters of the proposed model. To minimize alterations of the product structure during handling prior to experimental runs, the loading operation of the viscometer was performed in a systematic way. Samples were obtained with a glass tube of 6 mm i.d. and 3 cm length. The sample was forced out slowly by means of an embolus. The first centimeter was not used, and a 1-mm long wheel was cut from the middle part. Then, it was placed in the center of the plate. The plate was compressed against the cone and was kept compressed for a minute. This time is necessary for the plate and cone to come in contact with each other. The cone was loosened to start the run. Samples were subjected to a shear rate ($\dot{\gamma}$) of 320 s⁻¹.

Data treatment. Data obtained from the rheometric experiments were subjected to regression with the SYSTAT statistical software (Systat, Inc., Evanston, IL).

RESULTS AND DISCUSSION

Several shear stress vs. time curves at constant shear rate were obtained for several types of commercial margarine samples. A typical example of such curves is given in Figure 1. Two zones can be identified in this curve, AB and BC. The first zone (AB) represents the system's transient regime, which ends when the required constant value of the shear rate is reached. In this region, the increase of the shear stress, due to increasing shear rate, is added to the stress decrease caused by alterations in the product structure. In the BC zone, i.e., at constant shear rate, the decrease of the shear stress is exclusively the result of modifications of the structure. Only the second zone of the above described curve was mathematically interpreted. The results that were obtained indicated that a

first-order kinetic model did not describe the observed destruction process of the structure in an adequate manner. Thus, the possible existence of two structures with different destruction rates was postulated. In this model, each structure would contribute to a part of the shear stress necessary to deform the margarine sample. On these grounds, the following kinetic model was selected:

$$\tau = \tau_i + a e^{-k_1 t} + b e^{-k_2 t} \quad [1]$$

where τ_i is the shear stress necessary to keep the sample flow, once the thixotropic effects fade away. The value of τ_i corresponds to that of the Casson constitutive equation for the shear rate used (9); k_1 and k_2 represent the different specific destruction rates (destruction rate constants) of each of the proposed structures; a and b symbolize the contributions of each structure to the initial ($t = 0$) shear stress; and $t =$ time.

Figure 2 displays the goodness of fit of the proposed model. This curve is the result of fitting sample (Table 1) with the model. It must be pointed out that the determination of the rheometric curves for different commercial margarine samples leads to different absolute values of model parameters. However, the proposed kinetic model fits every experimental curve and therefore is valid for all cases.

The relationship between model parameters and temperature was then studied, and results are presented on Figure 3. The figure shows that, for decreasing temperatures, an exponential increase of τ_i , a linear increase of the b parameter and an increase of the a parameter up to a point, beyond which it remains constant, take place. On the other hand, constants k_1 and k_2 did not show significant variations within the experimental temperature range. The change of τ_i with temperature is in agreement with the behavior previously described by Andrade (11):

$$\tau_i = a e^{(E/RT)} \quad [2]$$

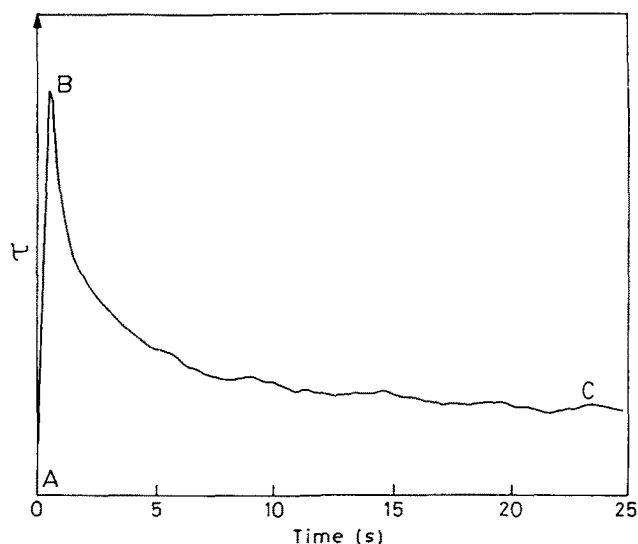


FIG. 1. Shear stress as a function of time at constant shear rate for a commercial margarine.

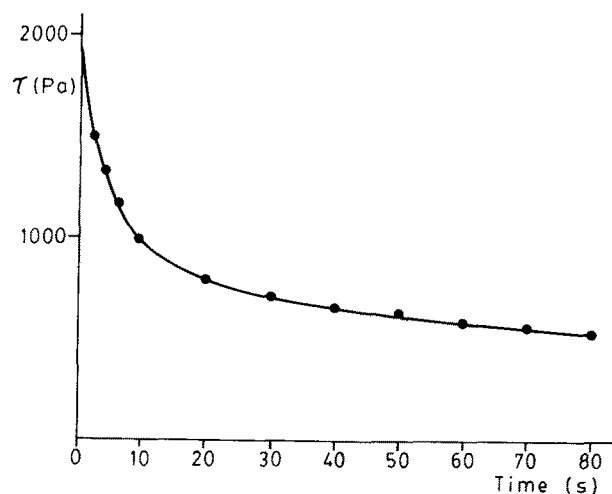


FIG. 2. Comparison between experimental data and predictions of the theoretical model for sample 1 (Table 1).

TABLE 1

Average Values of the Fitting Parameters of the Proposed Model for Different Commercial Margarine Samples

Sample	τ_i (Pa) ^a	a (Pa)	k_1 (s ⁻¹) ^b	b (Pa)	k_2 (s ⁻¹)
1	429.3	918.9	0.175	493.6	0.019
2	450.5	1351.4	0.195	838.3	0.020
3	407.4	1378.8	0.175	885.3	0.021
4	376.0	669.8	0.201	489.6	0.021
5	423.0	869.6	0.260	528.8	0.018
6	427.0	814.8	0.174	579.7	0.020

^aPascals.

^bSeconds.

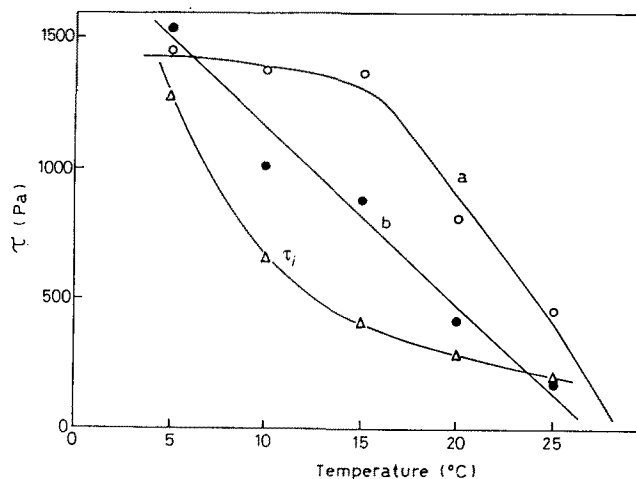


FIG. 3. Variation of model parameters with temperature. ○, *a* parameter; ●, *b* parameter; △, τ_i parameter.

When the sample is cooled, the crystallized triglyceride content increases, which in turn raises not only the number of existing bonds among crystals but also the stress required to destroy the tridimensional structure of the product. Among the parameters subjected to analysis, *b* changes linearly with the solid-fat index of the sample at the experimental temperature (Fig. 4). This fact suggests that the third term of the proposed model essentially represents the rupture of primary structures among triglyceride crystals. However, the solid-fat index does not represent the amount of solids present at each temperature in a realistic way.

The fact that the *a* parameter, at decreasing temperatures, reaches a particular value and then (i.e., at lower temperatures) remains constant, suggests that the number of bonds involved in maintaining the structure does not increase despite a rise in the number of triglyceride crystals. Thus, further bonds among crystals and other types of margarine components, whose quantities do not vary with a decrease of the temperature, are possible. To verify if the dispersed aqueous phase is related with this type of bonds, rheometric experiments of margarine samples, formulated with a fixed fatty phase but containing different amounts of water, were performed. Results thus obtained are presented in Figure 5, which shows that the three samples under analysis exhibit dif-

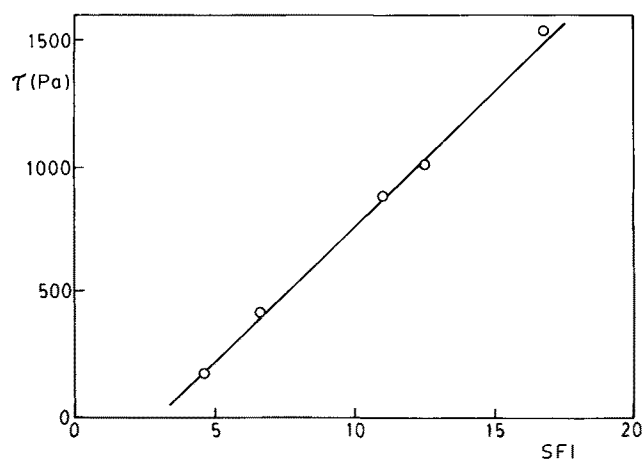


FIG. 4. Variation of *b* parameter with the solid-fat index (SFI) of the sample.

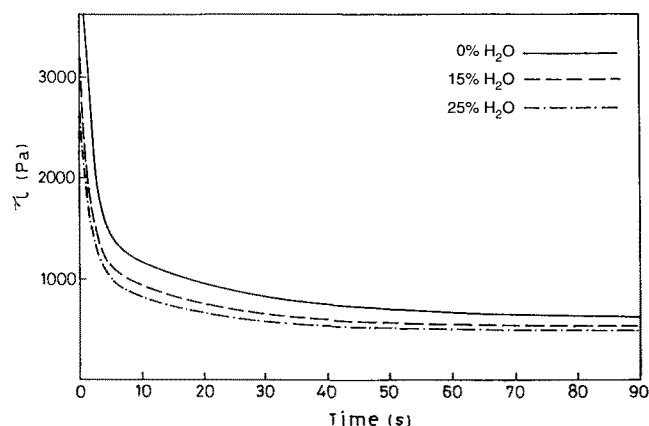


FIG. 5. Effect of water content on the shear stress.

ferent behavior and that a greater hardness is detected at greater water contents.

For these samples, the variation of parameters of the selected kinetic model with temperature was also analyzed. Results obtained (Fig. 6) show that τ_i increases, at any selected temperature, with increasing aqueous phase content of the sample. This behavior can be interpreted by considering the margarine as composed of a "continuous" fatty phase and a dispersed aqueous phase, the latter assumed as being shaped as water spheres. In this way, a larger content of the aqueous phase is represented by a larger number of dispersed spheres, thus increasing the possibilities of interaction among them, which in turn leads to decreased fluidity of the system.

The *b* parameter is not significantly affected by the amount of aqueous phase in the sample (Fig. 6b). Because the fatty phase is identical for the three samples under analysis, this is expected because, as was previously mentioned, the *b* parameter represents the interactions among triglyceride crystals.

On the other hand, the *a* parameter (Fig. 6c) reaches higher values for decreasing temperatures and for higher contents of the aqueous phase. To interpret this behavior, it must be con-

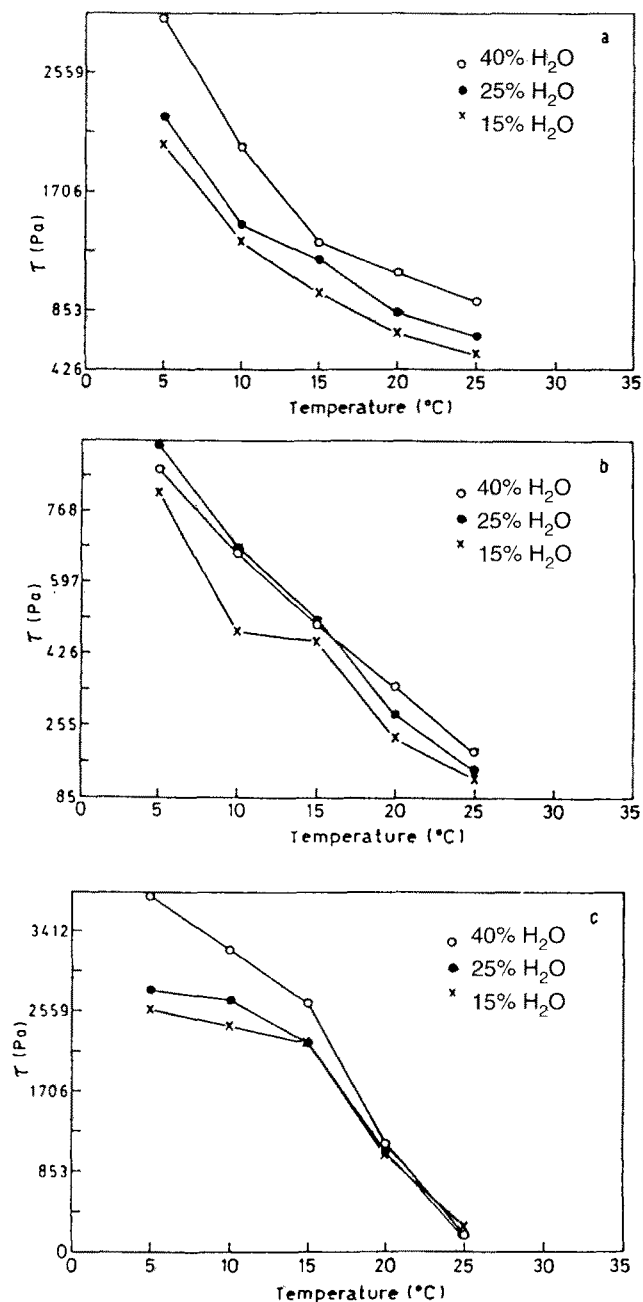


FIG. 6. Effect of water content on the variation of model parameters with temperature: (a) τ , parameter, (b) b parameter, (c) a parameter.

sidered that the number of triglyceride crystals increases with decreasing temperatures, as reflected by the variation of the solid fat index, and that the a parameter, as mentioned above, is dependent on the interactions between triglyceride crystals and drops of the dispersed phase.

At the highest temperatures (20–25°C), the number of triglyceride crystals becomes small and creates a shortage of

them with respect to the aqueous phase (lower water content) and, as a consequence, to the area exposed by the spheres of the dispersed phase. Thus, under these conditions, the interactions between crystals and H₂O are not affected by variation of the aqueous phase content. For decreasing temperatures, the solid content and the amount of aqueous phase become progressively limiting, so a particular value of temperature is reached beyond which the a parameter becomes constant. The temperature at which this phenomenon becomes apparent decreases with greater contents of the aqueous phase. In turn, the final value of the a parameter is higher at larger aqueous phase contents, due to a greater number of interactions between crystals and the aqueous phase.

Results shown in this work indicate that the rheological behavior of a margarine can be interpreted by a three-term kinetic model. This model takes into account the simultaneous existence of two structures, which are destroyed at different rates. The first structure is formed by interactions between triglyceride crystals (fatty phase) and the dispersed phase, while the second is defined by bonds between triglyceride crystals. The a parameter represents the first structure and the b parameter the second one.

At the temperature range within which the product is used (10–25°C), the interactions between crystals and water are more important than the interactions established in the fatty phase (crystal–crystal). Finally, the kinetic model can be employed to perform studies on the influence of different parameters of margarine formulation and manufacture (preparation conditions of the pre-emulsion, type, and content of emulsifying agents, etc.), on rheologic behavior.

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[Received April 3, 1994; accepted October 27, 1994]