

Study of Rheological Properties of Margarine

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ABSTRACT

Margarines from the rheological point of view are thixotropic plastic semisolids that change their plastic character with changes in the portions of the fat and aqueous phases. Contrary to lard and shortening, the emulsions containing ca. 85 and 15% of the fat and aqueous phases, respectively, follow the Casson equation (similarly as butter), whereas those containing 40 and 60%, respectively, satisfy the Herschel-Bulkley equation, which affects remarkably the way of evaluating experimental data. A new precise, and objective rheometrical method was developed for evaluating flow properties, which enables one to check quality and stability of margarines over a wide temperature interval just in the course of their production, and this may be helpful during the optimization of technology processes and standardization of product quality.

INTRODUCTION

Certain important qualitative parameters of margarine, such as consistency or spreadability, are closely associated with its flow properties. During the last few years, many edible fats have been produced to be used as cold spreads where good spreadability at ca. 5°C (i.e., at refrigerator storage temperature) is essential. This is also expressed in slogans advertising these products, such as, "It spreads straight from the fridge." Also, in margarines used for mass production of dough, ever growing emphasis is put on suitable consistency over a certain temperature interval. Perfect knowledge of flow properties enables one to choose an optimum technology regime and to preserve stable product quality.

Empirical and semiempirical methods of evaluating the consistency of margarines used until now, such as with the help of penetrometers, hesionometers, sectilometers, extruders, or panimeters (1), make possible only its qualitative determination in a limited temperature range. Thus, an approach was sought that would enable one to perform a quantitative determination of basic rheological characteristics. Based on experiences with measuring similar types of emulsions, rotation rheometry was employed to study margarine flow properties, since it is the only method that allows their rapid and objective evaluation over wide temperature and shear rate intervals.

As known from the literature available, the rheological properties of margarines have not been studied with the help of rotation rheometry to this extent up to the present time. Only Shama and Sherman (1,2) used a parallel plate viscoelastometer for studying viscoelastic properties of margarines. In contrast, Søltoft (3) and Smidt, et al. (4) used a variable pressure capillary viscometer, which seems to be inconvenient to us with respect to the thixotropic properties observed.

EXPERIMENTAL PROCEDURES

A number of margarine samples with different composition were measured. Let us present four samples by way of typical examples whose characteristics are summarized in Table I. These margarine emulsions of the type W/O may be divided into two groups on the basis of their composition.

Emulsions with a larger portion of fat phase and smaller portion of aqueous phase (ca. 15% aqueous phase) fall in group A. Group B contains the so-termed low caloric value fats, with a reverse fat to aqueous phase ratio (ca. 60% aqueous phase).

From the standpoint of rheology, margarines are generally considered plastic semisolids (1,5,6). On the other hand, Naudet (7) calls them pseudoplastic fluids. However, this may be due to nonuniform terminology. In the Anglo-Saxon literature (8), the non-Binghamian plastic fluids are often referred to as pseudoplastic fluids with a yield value.

For obtaining useful data, it is necessary to choose experimental conditions that are as close as possible to those encountered in practical applications. As far as the spreadability of margarines is concerned, the maximum shear rate when spreading them by a knife can be approximately determined on the basis of the following consideration. When the average spreading rate $v = 0.3$ m/s and final thickness of the spread layer $y = 0.001$ m, then $\dot{\gamma} = v/y = 0.3/0.001 = 300$ s⁻¹. Thus, the shear rates during the spreading process will be of the order of magnitude of about zero (initial state) to $\sim 10^2$ s⁻¹ (terminal state). Thus, margarines were investigated in this range.

The measurements were carried out with the Ferranti-Shirley Cone and Plate Viscometer (Ferranti Ltd., Hollinwood, England) with automatic flow curve recording unit and X-Y Autoplotter. The cone size was of 70 mm diameter and of angle 1°. Flow curves were measured in the shear rate interval 0-667 s⁻¹, i.e., 0-100 rpm of the cone. The rpm value was continuously increased from the rest to a maximum value for 30 s; the same time was necessary to return the cone to the rest (sweep time 60 s). This "loading cycle" was repeated with respect to the thixotropic properties of the samples measured until we achieved coincidence of the downward curve with the upward one. In most cases, it was necessary to use four of these "cycles." For establishing the stability of the emulsions of interest, the samples were measured over a shear rate range of 0-1,300 s⁻¹.

The samples were measured at temperatures of 5.0, 15.0, and 25.0°C (± 0.02 °C) each time 1 week after their manufacture. Constant temperature was kept with the help of the Ultra-cryostat MK 70 (VEB Prüfgeräte-Werk Medingen, GDR) and checked by a chromel-alumel thermocouple and MT 100 digital voltmeter (Metra Blansko, CSSR).

The samples were stored in enclosed vessels at ca. 5°C. Each individual measurement was repeated five times, always with a fresh sample, and the deviations did not exceed $\pm 5\%$.

A knife was used to slice the samples and to place them on the plate of the viscometer. Each sample rested in the instrument for 20 min before starting measurements. Samples were disturbed as little as possible and had enough time to fully recover.

RESULTS AND DISCUSSION

Let us outline generally the way of evaluating the flow curves and explain differences in their courses for the two types of emulsions. As mentioned above, in terms of rheology, the margarines represent thixotropic plastic bodies. This also determines a manner of evaluating experimental data.

Figures 1a and 1b show flow curves of margarines, group

TABLE I
Characteristics of the Margarine Samples Measured

Sample	Water content (%)	Melting point of the margarine fat (C)	Fatty acid composition in the margarine fat (%)										Content of trans bonds (%)			
			8:0	10:0	12:0	14:0	16:0	18:0	20:0	22:0	16:1	18:1	18:2	20:1	22:1	
A 1	15.4	29.1	-	-	-	0.2	10.0	12.3	0.7	1.8	0.4	33.0	37.6	0.8	3.2	18.2
A 2	16.0	31.8	3.2	2.1	2.8	1.2	10.0	8.2	1.4	-	0.4	22.5	47.5	0.7	-	1.8
B 1	59.7	26.9	0.4	0.5	8.7	3.7	8.6	5.9	0.5	0.4	0.3	30.3	38.7	0.6	1.4	8.0
B 2	59.8	27.3	-	-	0.6	0.6	14.6	7.5	2.1	-	0.6	39.6	33.4	1.0	-	18.3

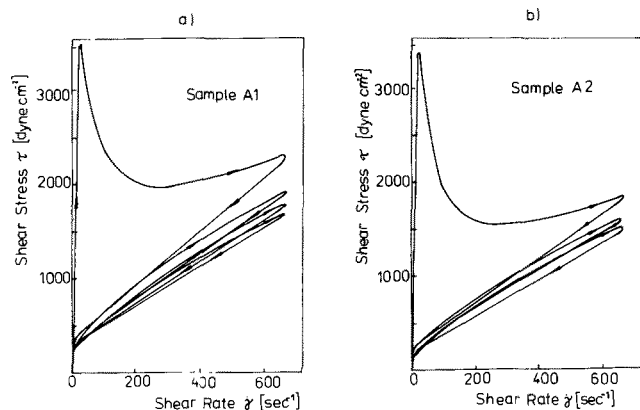


FIG. 1. Flow curves for margarines in group A (25 C) (Ferranti-Shirley Viscometer, large cone, sweep time 60 sec, > upward curve, < downward curve).

A, measured at 25 C. It is obvious from these curves that the shear stress remains at zero value for a certain time, then increases rapidly and drops again. The height of this peak can be considered a "static yield value" (9). It is actually a critical yield value that should be overcome in order that plastic flow could occur in the material. This is a significant criterion for evaluating values of margarines important for their use. Individual samples differed mutually first of all just in this value that reflects the internal structure of the emulsion and depends on the temperature and method of measurement.

Further course of the flow curves indicates that the downward curve (measurement with continuously decreasing shear rates) is always situated below the upward curve (measurement with continuously increasing shear rates), and a curve of each "loading cycle" is situated below the curve of the preceding "cycle." The two branches of the curve coincide only after several "cycles." The two branches form a so-called "hysteresis loop." Since this loop was also observed during measurements after certain intervals (already after several minutes) of so-called "recovery time," i.e., after stopping the stress of the original sample directly in the rheometer, the thixotropic behavior of the emulsions of interest was unambiguously demonstrated. The area of the hysteresis loop can also serve as a measure of the thixotropy, which represents a further important criterion that defines the value of the product. Generally speaking, the larger thixotropy of the product, the better spreadability will be achieved.

The "apparent viscosity" can be essentially evaluated at any point of the flow curve as a ratio of the values of the shear stress and shear rate. However, in thixotropic materials, the data on the apparent viscosity should be complemented by the shear rate and time of the stress acting. It is usually evaluated at a maximum stress—at the origin of its action and after disappearance of the thixotropy.

It is also obvious from the flow curves in Figures 1a and 1b that their downward curves are not completed at the origin but at a certain non-zero value of the shear stress. The point of intersection of the extrapolated part of the flow curve with the axis of ordinates (shear stress axis) can be considered as so-called "dynamic yield value," which is a further important criterion for evaluating flow properties of margarines (9).

Figure 2 offers a functional dependence $\sqrt{\tau} = f(\sqrt{\dot{\gamma}})$ for the samples of group A, where the values τ and $\dot{\gamma}$ were read off from flow curves in Figures 1a and 1b. The linear course of this dependence demonstrates unambiguously that margarines containing ca. 15% aqueous phase follow in the investigated range of shear rates the Casson equation (10)

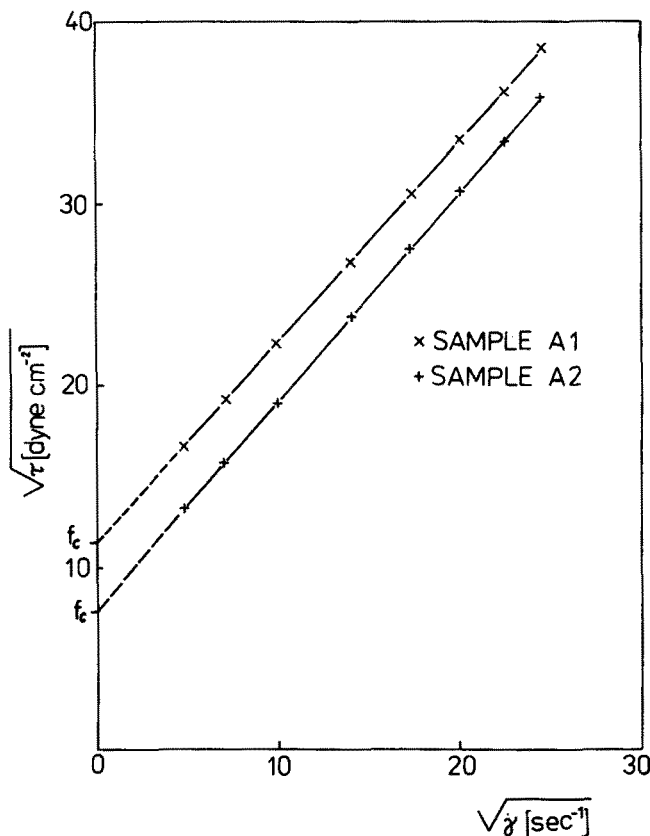


FIG. 2. $\sqrt{\tau}$ as a function of $\sqrt{\dot{\gamma}}$ for margarines in group A (25 C) (f_c = Casson Yield Value).

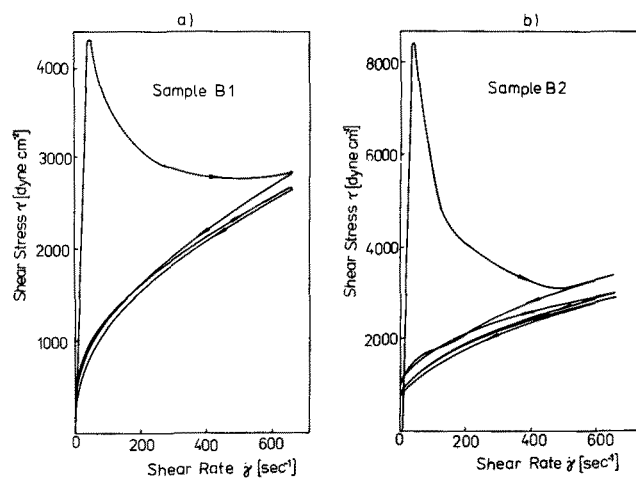


FIG. 3. Flow curves for margarines in group B (25 C) (Ferranti-Shirley Viscometer, large cone, sweep time 60 sec, > upward curve, < downward curve).

$\sqrt{\tau} = \sqrt{f_c} + \sqrt{\eta_c} \sqrt{\dot{\gamma}}$. This finding remarkably facilitates the measurement and evaluation of results, since as a matter of fact it is sufficient to measure the shear stress at three different shear rates for plotting the flow curve. The line slope of the straight line in Figure 2 can be used for numerical or graphical determination of the Casson plastic viscosity $\eta_c = (\sqrt{\tau} - \sqrt{f_c})^2 / \dot{\gamma}$, and the point of intersection of this straight line with the axis of ordinates indicates the Casson yield value f_c .

Somewhat more different courses of the flow curves of margarine samples from group B (low caloric value fats) can be seen from Figures 3a and 3b. Those are also thixotropic plastic semisolids, and just as for the above-mentioned margarines from group A, their static and dynamic yield value and apparent viscosity may be evaluated. However, a

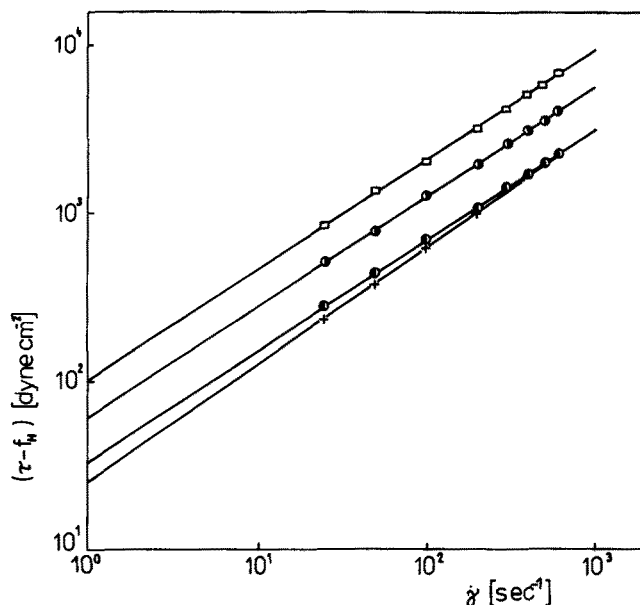


FIG. 4. $\log(\tau - f_H)$ as a function of $\log \dot{\gamma}$ for margarines in group B (f_H = Yield Value and n = exponent in the Herschel-Bulkely equation). \square - sample B1, 5 C, $n = 0.65$; \bullet - sample B1, 15 C, $n = 0.65$; \circ - sample B1, 25 C, $n = 0.65$; $+$ - sample B2, 25 C, $n = 0.70$.

difference is immediately obvious in the downward flow curves, particularly after disappearance of the thixotropy. While in emulsions from group A, which contain larger portions of the fat phase and which satisfy the Casson equation, very flat curves, nearly straight lines were observed (see Figs. 1a and 1b), remarkably larger curvatures were met with in the case of the margarines from group B which contain larger portions of the aqueous phase. Thus, a suitable equation was sought that could describe their behavior.

Figure 4 shows a functional dependence of $\log(\tau - f_H)$ on $\log \dot{\gamma}$ for margarines from group B. The linear course of this dependence indicates that low caloric value fats unambiguously satisfy in the investigated range of the shear rates a more general Herschel-Bulkely equation (11) $\tau = f_H + k_H \dot{\gamma}^n$, where the line slope of the straight line defines the value of the exponent in the Herschel-Bulkely equation n , and its point of intersection with the axis of ordinates shows the value of the constant k_H , which has the dimensions of viscosity when $n = 1$. It is of interest to note that the value of the exponent n is independent of the temperature. As can be seen from Figure 4 for low caloric value fat B1, $n = 0.65$ for temperatures of 5 and 15 C as well as 25 C; for low caloric value fat B2, $n = 0.7$ (at 25 C).

The result that low caloric value fats satisfy the Herschel-Bulkely equation means that in these cases it is insufficient to measure the shear stress only for three different shear rates (as can be done for fats with larger portions of the fat phase). However, when designing the flow curve, more shear stress values have to be measured in the shear rate range selected.

Differences in rheological behavior of both types of margarines investigated give the evidence of their different structure. From the flow curves shown on Figures 1 and 3, it is obvious that for margarines from group B, low caloric value fats (see Fig. 3), a stronger dependence of the apparent viscosity on shear rate is manifested in comparison with the margarines from group A.

From our previous experimental results (12) with butter (17.9% of water, 29.1 C melting point of the butterfat, i.e., approximately with the same amount of water as for margarines of group A), the flow properties were found to be described by Casson equation as for margarines of group A,

the only differences being in absolute values of the yield value and apparent viscosity. This means that the flow properties of emulsified fats depend not only on the shape and quantity of the fat crystals but particularly on the composition and structure of the emulsion. The different shape and amount of fat crystals have an effect on the absolute magnitude of the yield value and of the apparent viscosity only, and not on the form of the rheological equation. The amount of the water phase in the emulsion directly influences the shape of the flow curve, i.e., the course of the shear stress–shear rate functional dependence.

This claim is confirmed by the experimental results of Davis (13), who measured lard and shortening at 25 C with Ferranti-Shirley Cone and Plate Viscometer over the shear rate interval 0-1,500 s⁻¹. These anhydrous fats exhibit, in contradistinction to emulsified fats, dependencies of the shear stress on the shear rate approaching Bingham equation (1). The higher the water content of the plastic fat, the more pronounced departure from the Binghamian fluid is observed.

Butter, margarine, lard, chocolate, etc., composed of either animal or vegetable oil, are classified as plastic fats. According to Muller (6), below yield value, fats show elastic properties, but it appears that these are not of great technological importance. Above the yield value, both the yield value magnitude and the plastic viscosity are of importance. According to the literature, up to the present time the yield value has been studied almost exclusively. Haighton (14) introduces an interesting and, from the practical point of view, important psychological assessment of fat in relation to its yield value.

The values determined according to our procedure (i.e., the static yield value, dynamic yield value, and apparent viscosity in dependence on temperature varied from 5 to 25 C) make it possible to fully characterize the rheological properties of emulsified fats, and this has a direct relation to their serviceability. The identification of appropriate rheological equations may be of importance for construction of the nozzles (tubes) of filling machines. The method is sufficiently sensitive so that it makes it possible to distinguish not only a variety of fats but also the effects of the margarine fat formulation and of the change of important conditions (temperature of emulsifying process and

subsequent cooling) during processing. These aspects are under our continuing investigation.

For establishing the stability of the emulsions of interest, the samples were also measured in the shear rate interval 0-1,300 s⁻¹. The moment when the emulsion is completely destroyed due to the shear stress (i.e., the moment of the separation of the fat and water phases) can be very precisely determined with the help of rotation viscometry. As a result of the sudden jump in apparent viscosity of the emulsified fat, a sharp change in the trend of the flow curve becomes visible.

It was found that in low caloric value fats of group B, fat and aqueous phases were separated already at $\dot{\gamma} = 700$ s⁻¹, whereas in margarines of group A with a larger portion of the fat phase, this phenomenon did not occur even at higher shear rates (to 1,300 s⁻¹).

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