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Food Chemistry 64 (1999) 221–226

Food Chemistry

Flow properties of table margarine prepared from lipase-catalysed transesterified palm stearin:palm kernel olein feedstock

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Received 6 March 1998; received in revised form and accepted 1 May 1998

Abstract

The flow properties of an experimental table margarine prepared from *Rhizomucor miehei* lipase-catalysed transesterified palm stearin:palm kernel olein (PS:PKO) blend at 40:60 was stored for 3 months at test temperatures of 20 and 30°C and determined using a controlled-rate rheometer. A commercial table margarine was used as a comparison. The shear stress-shear rate data was represented well by the Herschel–Bulkley model ($r > 0.99$). The mean yield stress values during storage were the highest for the experimental table margarine. However, the effect of storage on the mean yield stress was insignificant ($p > 0.001$). The Power Law model with a yield stress also represented the margarine flow well ($r > 0.99$) and the Power Law intercepts and slopes were also the highest for the experimental margarines, indicating a higher degree of firmness in the experimental samples. Storage effect was also insignificant ($p > 0.05$).

Keywords: Enzymatic transesterification; Table margarine; Flow properties; Yield stress; Power Law; Commercial margarine

1. Introduction

Margarine was initially developed as a butter substitute. The product was designed to meet butter shortages caused by increasing urban populations during the Industrial Revolution, as well as to produce a table spread with satisfactory keeping qualities for the armed forces (Chrysam, 1996). However, over the years, margarine has established its own image and is used by consumers for a variety of purposes. Today, there has been considerable diversification of the product. Palm oil and palm oil products are excellent raw materials for the formulation of margarine.

Structurally, margarine consists of a continuous liquid fat phase with fat globules, crystalline fats and aqueous phase dispersed in it (Juriaanse & Heertje, 1988). Under certain conditions, fat globules are capable of extreme elongations without rupture (indicating the elastic nature of the membrane that surrounds the globule) and are, therefore, approximated by a Maxwell element. Liquid fat surrounding the globule acts as a viscous fluid and flows on application of stress (Diener & Heldman, 1968). Margarine, thus exhibits viscoelastic (VE) characteristics. Of primary importance to the rheological behaviour of fat, is the amount of crystalline fat and type of crystals present in the fat crystal network (De Man, 1976).

Characteristics which determine margarine quality, such as spreadability and consistency, are important (Segura, Herrera, & Añon, 1990). Thus, rheology, the study of flow deformation of material, became a valuable technique in characterizing and understanding the structure of margarine (Kawanari, Hamann, & Hansen, 1981). For example, the force or stress required to initiate the flow of fluid or semi-solid products play an important role in the storage, transfer, packaging and end-use performance of those materials (Rao & Steffe, 1997). The stress level required to initiate flow is defined as 'yield stress'. This value is related to the internal structure of the material which must be destroyed (overcome) before flow can occur. Contrarily, the stoppage of flow once stress is removed relates to the rebuilding of structure. The destruction and rebuilding of structure are kinetic processes with characteristic relaxation times. Hence, the time frame of test, and the sensitivity of the instrument used to determine yield stress, may influence the value obtained. As a result, the

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0308-8146/98/$—see front matter
PII: S0308-8146(98)00138-1

yield stress determined is usually referred to as the 'apparent yield stress'. Although the 'apparent yield stress' may not represent the theoretically accurate value, it is still extremely useful in comparing and predicting the behaviour of material.

In this study, the flow properties of an experimental table margarine prepared from *R. miehei* lipase-catalyzed transesterified palm stearin (PS):palm kernel olein (PKO) blend at 40:60 ratio during storage for 3 months were examined. A commercial table margarine was used for comparison purposes. A controlled-rate approach was used. Using this approach, movement (yielding) actually has to occur before measurement can be made. Hence, apparent yield stress can only be measured by back extrapolation from a finite level of motion to the point of 'zero motion' or yielding which was done using the software provided by the manufacturer. Results obtained from this work will be helpful in optimizing the flow properties of the experimental table margarine formulation for future studies.

2. Materials and methods

2.1. Materials

Refined, bleached and deodorised hard palm stearin (PS) (Slip Melting Point, 54.5°C) was obtained from Ngo Chew Hong Oils and Fat (M) Pte. Ltd. while palm kernel olein (PKO) was obtained from Southern Edible Oil (Malaysia) Ind. Pte. Ltd. The fats were stored at 0-4°C. Prior to use, palm stearin was melted at 60°C in the oven. *R. miehei* lipase (Lipozyme 1M60) was obtained in the immobilized form (moisture content: 2–3%) from Novo Nordisk Ind. (Copenhagen, Denmark).

2.2. Transesterification reaction

A minimum of 50 kg of *R. miehei* catalysed transesterified blends of PS:PKO at 40:60 ratio was prepared for the fat phase. The reaction blend (100g PS:PKO/g Lipozyme) was agitated in flask on an orbital shaker at 200 rpm at 60°C for 6 h. The same enzyme, after removal from the reaction mixture, was used to esterify a total of five changes of fresh substrate. The transesterification reaction was according to the method described by Ghazali, Hamidah, and Che Man (1995).

2.3. Processing and storage conditions

The production of the table margarine was carried out using the Palm Oil Research Institute of Malaysia (PORIM)'s pilot plant, 'Kombinator' (Schröder, Lubeck, Germany), that is basically made up of two rotators and a blender. The composition of the experimental table margarine was in compliance with the definition of margarine (81% transesterified fat, 16% water, 0.4% soy lecithin emulsifier, 0.003% colouring, 0.03% flavour, 2% salt and 0.02% antioxidants). Commercial margarine [Unilever (M) Holdings Pte. Ltd.] samples were purchased from a local supermarket in Kajang, Malaysia. Information on the label states that it contained palm oil and palm kernel oil. Knowledge of the age and past history of the sample was minimal. The experimental table margarine was stored in covered plastic containers (base dia., 9.3 cm; top dia. with cover, 11.7 cm; height, 7.5 cm) while the commercial table margarines were stored in its original metal containers (250 g/container). The samples were immediately stored at different test temperatures (20 and 30°C) for 3 months and analysed weekly for rheological changes. The initial weeks of storage for both the margarines were termed as Week 0 (Day 0–7) and subsequent weeks as Weeks 1–12 (Days 8–90). The commercial margarine, stored at 20 and 30°C, was abbreviated CM20 and CM30, respectively, while the experimental margarine was designated EM20 and EM30, respectively.

2.4. Viscosity measurements

All viscosity measurements were performed on a Haake RS100 controlled-rate rheometer (Haake GmbH, Karlsruhe, Germany). The instrument has a stabilised low inertia air bearing and a high resolution digital encoder. Temperature control was maintained by a Haake F3 circulator waterbath with an accuracy of ± 0.02°C (Haake GmbH, Karlsruhe, Germany).

The viscosities of the samples were evaluated at 20 and 30°C with a 35 mm diameter and 4° angle cone and plate (C35/4) geometry. Shear rates from 0.1 to 10 s^{-1} were ramped for 200s and used for commercial samples stored at 20 and 30°C and experimental samples stored at 30°C while shear rates of 0.1 to 20 s^{-1}, ramped for 300 s, were used for the experimental samples stored at 20°C. Each measurement was repeated twice, using a fresh sample each time. The samples were allowed to rest to decay the compressive force and to attain temperature equilibrium before measurements. All the viscosity data were analysed with the software provided by the manufacturer.

3. Results and discussion

Log shear stress–shear rate curves for all samples are shown in Fig. 1(a)–(d). Pseudoplastic behaviour was exhibited by all samples with the existence of yield stress. The 'Best Fit' routine was also used and the Herschel–Bulkley model was fitted. This model is the most complex among the shear stress/shear rate models and also the most flexible when it comes to fitting data.

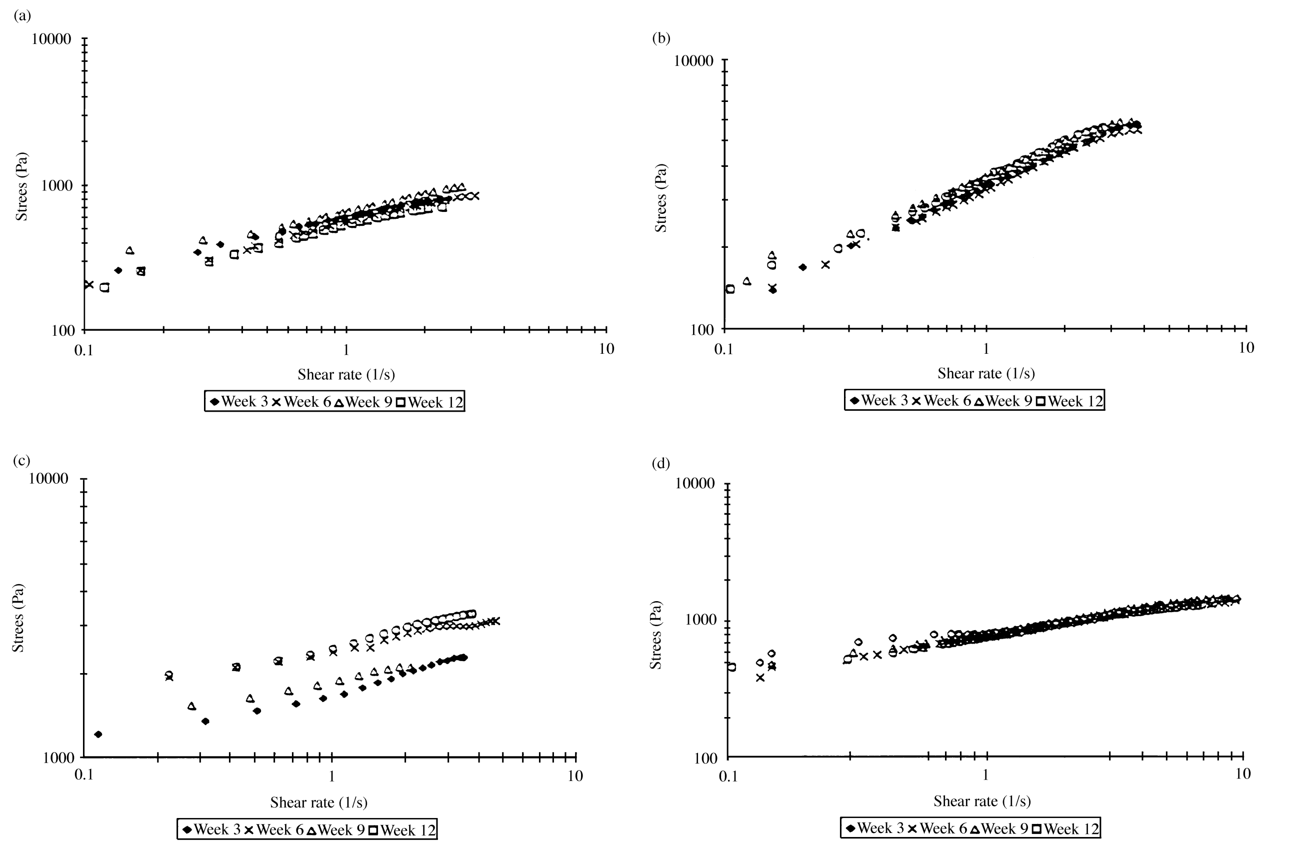

Fig. 1. Log stress vs log shear rate of commercial table margarines stored at (a) 20°C and (b) 30°C. Log stress vs log shear rate of experimental table margarines stored at (c) 20°C and (d) 30°C.

The equation for the Herschel–Bulkley model is given below:

$$\tau = \tau_y + K(\gamma)^n$$

where : τ_y = yield stress
K = consistency coefficient
n = shear rate index

Regression coefficients, r were > 0.99 for all the samples, indicating goodness of fit. The presence of a yield stress denotes a minimal stress which must be exceeded prior to flow occurring due to shear. This has been intepreted as the existence of a network structure, the bonds of which must be broken to allow flow (Sone, 1972). If the structure is considered to be composed of reversible or irreversible types of bonds, then it appears that only reversible types of bonds are broken with extended shearing. This implies that residual viscosity after shearing and yield stress may be proportional to the irreversible bond sites in the structure (Parnel-Clunies, Kakuda, & De Man, 1986). No hysteresis (time dependent behaviour) studies were done in this work.

Fig. 2 shows the mean yield stress values obtained from the Best Fit Herschel–Bulkley Model for all the samples stored from weeks 3 to 12. EM20 samples showed the largest yield stress mean, τ_o, followed by EM30, CM20 and CM30 samples, indicating a highly structured EM20 sample. The mean τ_o of the CM30 sample was 8.5 times less than the EM20 samples. At 20°C, the mean τ_o of the experimental and commercial margarines were 2.6 and 1.8 times more than their counterparts at 30°C, respectively. However, the effect of storage on the mean τ_o of the samples showed no

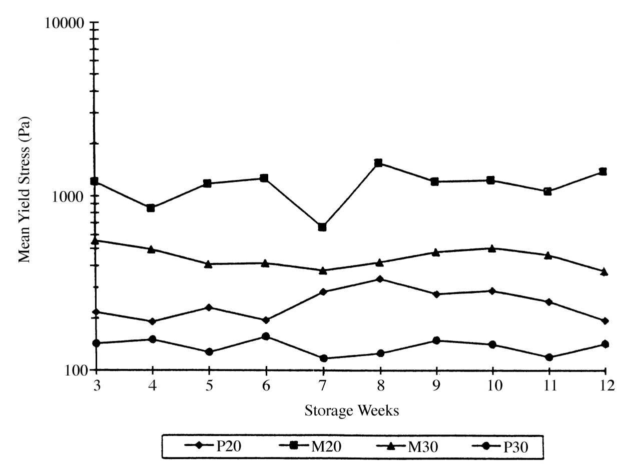

Fig. 2. Mean yield stress vs storage weeks for the experimental and commercial table margarines.

significant difference ($p > 0.001$). There were, however, significant differences in the means of the samples ($p < 0.001$). Moreover, the New Multiple Range Duncan test showed that samples CM30 and CM20 were not significantly different and neither were CM20 and EM30. However, the EM20 samples were significantly different from the others ($p < 0.001$).

Fig. 3(a)–(d) show the more common plot for a flow curve, namely viscosity vs shear rate, on log axes for all the samples. The flow curves for the samples analysed weekly overlapped; thus to ease interpretation of results, only flow curves for weeks 3, 6, 9 and 12 are shown. The mean of viscosity for all the samples at 1 s^{-1} shear rate is shown in Fig. 4. Statistical analysis indicated no significant differences between CM30 and CM20 or among CM20, CM30 and EM30 samples. EM20 was significantly different from the others ($p < 0.001$). Flow behaviour (viscosity vs shear rate) relates to 'spreadability' and although all the products exhibited shear-thinning characteristics [Fig. 3(a)–(d)] within the shear rate ranges used, the relative viscosities at shear rate 1 s^{-1} indicated that CM30 spreads more easily than the others.

The flow properties of many foods can be described by the Power Law equation which is fitted to relate log viscosity (η) to shear rate (γ) and slope (n) and intercept (k) values; it is obtained from the relationship:

$$\eta = k\gamma^{n-1}$$

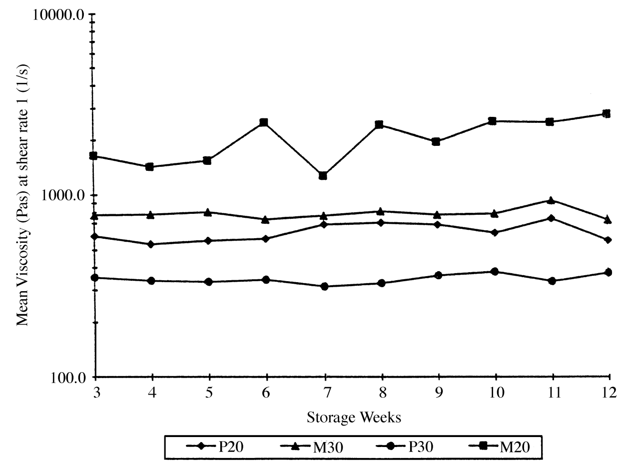

Fig. 4. Log mean viscosity at shear rate 1/s for commercial and experimental table margarines during storage.

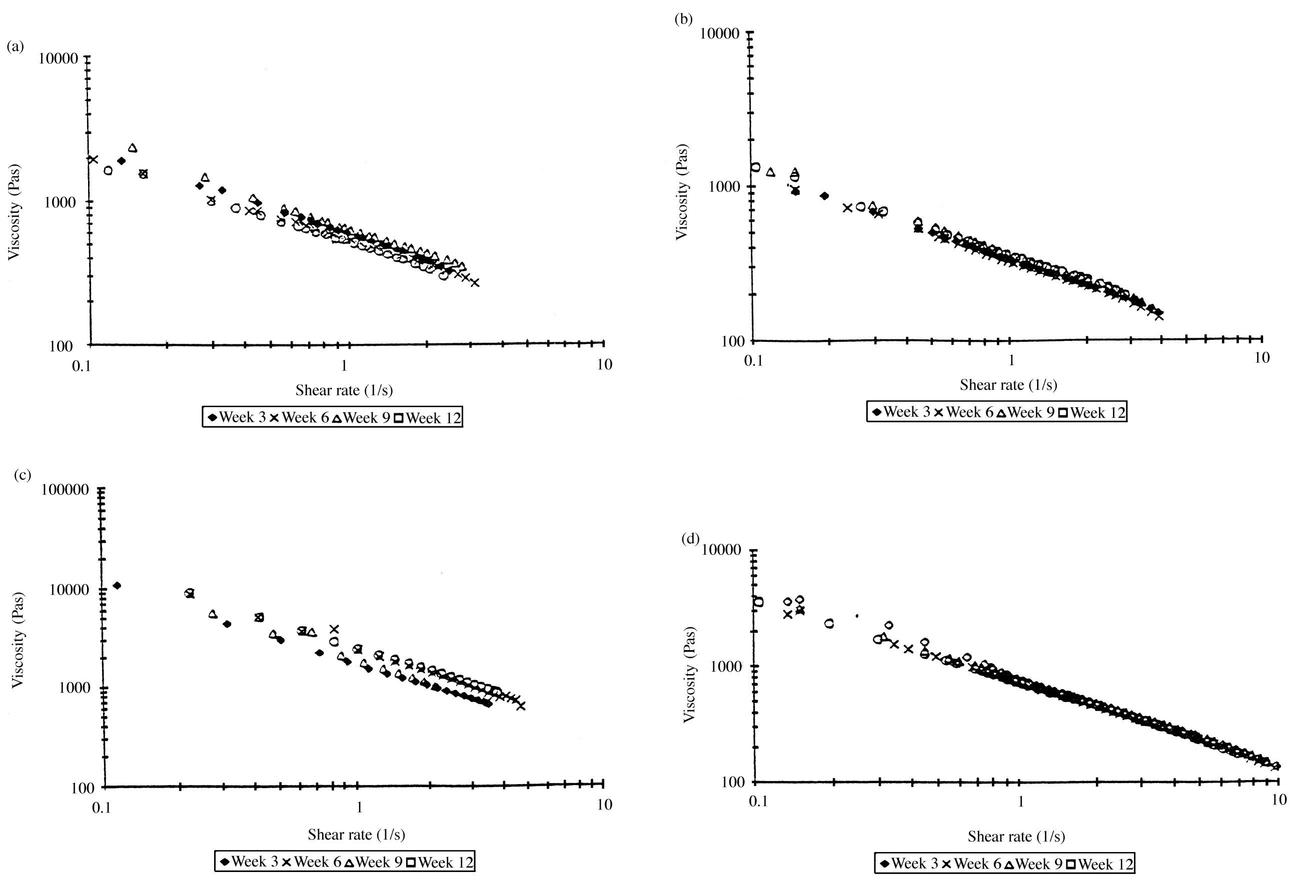

Fig. 3. Log viscosity vs log shear rate of commercial table margarines stored at (a) 20°C and (b) 30°C. Log viscosity vs log shear rate of experimental table margarines stored at (c) 20°C and (d) 30°C.

where k and n are Power law constants. k is the consistency coefficient and n is the shear rate index. For Newtonian fluids, $n = 1$ and k is the viscosity coefficient. Regression coefficients, r were > 0.99 for all the samples, indicating once again, the goodness of fit. The Power Law intercept, k, represents the values of η at shear rate of 1 s^{-1}. The k (consistency coefficient) and n (shear rate index) derived from the model are given in Tables 1 and 2, respectively. The results are consistent with the observed plot, i.e. a shear-thinning line that has a decreasing gradient ($n < 1$) i.e. their η decreases with increasing shear. Hence the samples can be spread when pressure is applied. The effect of storage on the k values showed no discerning trend ($p > 0.05$) for all the samples (Table 1) except for EM20. The k value was the highest for EM20 followed by EM30, CM20 and finally CM30 samples. Higher levels of Power Law intercepts indicate a higher degree of firmness of the samples.

Table 1
Mean k (consistency coefficient) obtained from the Power Law Model

	Mean k value (consistency coefficient)			
	Storage temperatures			
	20°C		30°C	
Storage weeks	Experimental	Commercial	Experimental	Commercial
3	1745.6	587.7	764.9	348.9
4	1507.2	549.2	799.7	338.4
5	2141.6	559.6	809.1	337.0
6	1797.6	564.9	727.3	341.1
7	1177.6	688.1	771.3	313.6
8	2424.8	717.2	817.3	330.4
9	1935.2	686.2	785.8	364.4
10	2332.0	604.4	795.3	379.6
11	2398.4	702.6	914.6	334.6
12	2448.8	545.1	730.0	373.7

Table 2
Mean n (shear rate index) obtained from the Power Law Model

	Mean n value (shear rate index)			
	Storage temperatures			
	20°C		30°C	
Storage weeks	Experimental	Commercial	Experimental	Commercial
3	0.8607	0.5713	0.7277	0.5991
4	0.8278	0.5379	0.7499	0.6174
5	0.8796	0.5511	0.7379	0.5619
6	0.8700	0.5404	0.7015	0.5693
7	0.8643	0.5538	0.7421	0.4383
8	0.9075	0.6538	0.7219	0.5677
9	0.8617	0.6067	0.7090	0.5707
10	0.9779	0.5804	0.7443	0.5659
11	0.8109	0.6069	0.7361	0.5439
12	0.9246	0.5691	0.7025	0.5595

The shear rate index (n) shows no significant discerning trend on storage with most values between 0.54 and 0.75 for samples stored at 20°C and between 0.44 and 0.98 for samples stored at 30°C ($p < 0.001$) (Table 2). The flow behaviour index measures the departure from Newtonian flow and results were consistent with pseudoplastic flow for which n is less than 1. However, higher slope (n) value for EM20 samples indicated a firmer product than the others. An analysis of the means indicated that CM20 and CM30 samples were not significantly different from each other while the EM30 and EM20 samples were significantly different from the others ($p < 0.001$).

Results of the mean yield stress obtained from this study show that the experimental margarine was more highly structured and firmer than the commercial margarine. There was, however, no significant effect of storage on the mean yield stress values ($p > 0.001$). A comparison of the relative viscosities at shear rate 1/s also indicates that the commercial margarine spread more easily than the experimental table margarine. This is confirmed by the lower values of Power Law intercepts and slopes (n) obtained for the commercial margarine than the experimental margarine. The flow data results suggest that the amount of palm stearin in the transesterified PS:PKO (40:60) blend should be lowered somewhat, possibly in the region of 20–30%. This would still be higher than the amount of palm stearin commonly used to produce a standard table margarine (Teah, 1982).

Acknowledgement

The authors acknowledge the financial support received from the Malaysian Government through the IRPA programme (No: 03-02-04-0025) awarded to H. M. Ghazali.

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