Viscoelastic Properties of Plastic Fat Products

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ABSTRACT

An instrument is described for the creep analysis of plastic fat products. The instrument records the deformation of a sample under constant force. Deformation is sensed by a displacement transducer. Instantaneous elasticity, retarded elasticity and plastic flow can be calculated. The extent of instantaneous elasticity of plastic fat products was found to be dependent on loading time. At longer loading times, the instantaneous elasticity as a percentage of total deformation decreased, with a corresponding increase in permanent deformation. The effects of temperature, magnitude of force and work softening were investigated. The results are discussed in relation to the nature of the crystal network structure in plastic fat products.

INTRODUCTION

Certain important aspects of quality of plastic fat products such as consistency are closely associated with their flow properties. A number of empirical methods of evaluating the consistency of plastic fat products include the use of penetrometers, extruders and sectilometers. Relatively few studies have been reported in which attempts have been made to study viscoelastic properties of plastic fat products. Shama and Sherman (1) used a parallel plate viscoelastometer to study the rheological characteristics of butter and margarine. Stern (2) used a plate and cone viscometer for margarine. Elliot and Ganz (3) used a Weissenberg rheogoniometer. Dynamic rheological moduli have been determined by Nederveen (4) using the principles of free torsional vibrations and bending vibrations.

In plastic fat products such as butter, margarine and shortening, the rheological properties of the product are determined mainly by the nature and strength of the crystal network they contain.

In this study, a simple creep analysis instrument was developed. This instrument measures strain under constant stress as a function of time and makes it possible to determine the elastic and viscous components of the rheological behavior of fats and other plastic food materials.

EXPERIMENTAL

The instrument (Fig. 1) consists of a cantilever beam (A) which slides up and down on two vertical guide rods (B) on linear recirculating ball bearings. Thus, friction during movement of the beam is negligible. The beam is attached to a counterweight (D) by means of a nylon line passing over a ball bearing pulley. This enables the beam to be positioned at any height without exerting a downward force. The cantilever beam is also connected to a displacement transducer (E). The sample is placed underneath the end of the beam. At time 0 the load (weight C) is placed on top of the beam to apply a selected force (range 4.9N to 19.6N; expressed in newtons, N) to the sample, and then removed at selected time t. Calibration of the displacement transducer is done by placing accurately machined metal blocks under the beam. The transducer is connected to a model 300D transducer amplifier-indicator equipped with a model 70 differential transformer input module (Daytronic Inc., Dayton, Ohio). The output signal was recorded on a 10mV strip chart recorder with full scale deflection calibrated to read 2 mm.

Cylindrical samples 2.3 cm in diameter were prepared by means of a stainless steel boring tube and trimmed to a length of 2.0 cm by a stretched stainless steel wire. Cubic samples (20 mm each side) were made by means of a wire cutting device.

Samples tested were butter and margarine obtained from local supermarkets and stored at 5 C until analyzed.

Viscoelastic parameters calculated from the loading and unloading curves were as follows: Instantaneous elasticity = loading stress/instantaneous elastic strain (expressed in Pascals, Pa); retarded elasticity = loading stress/retarded elastic strain (expressed in Pa); viscous flow = loading stress x time of flow/permanent strain (expressed in Pa.s). In addition to these viscoelastic parameters, it was found useful to express instantaneous elasticity, retarded elasticity and permanent deformation as a percent of the total deformation. Loading time was 10 min, unless otherwise indicated.

Work softening of butter and margarine was achieved by intensive mixing in a machine consisting of an auger continuously feeding the product into a cage rotating at 100 rpm. Product residence time was about 60 sec. No air was incorporated during the working.

RESULTS AND DISCUSSION

The creep and recovery behavior of butter subjected to a constant force at 5 C is shown in Figure 2. It is apparent that the instantaneous strain (A) developed under stress is much greater than the strain instantaneously recovered after unloading (B).

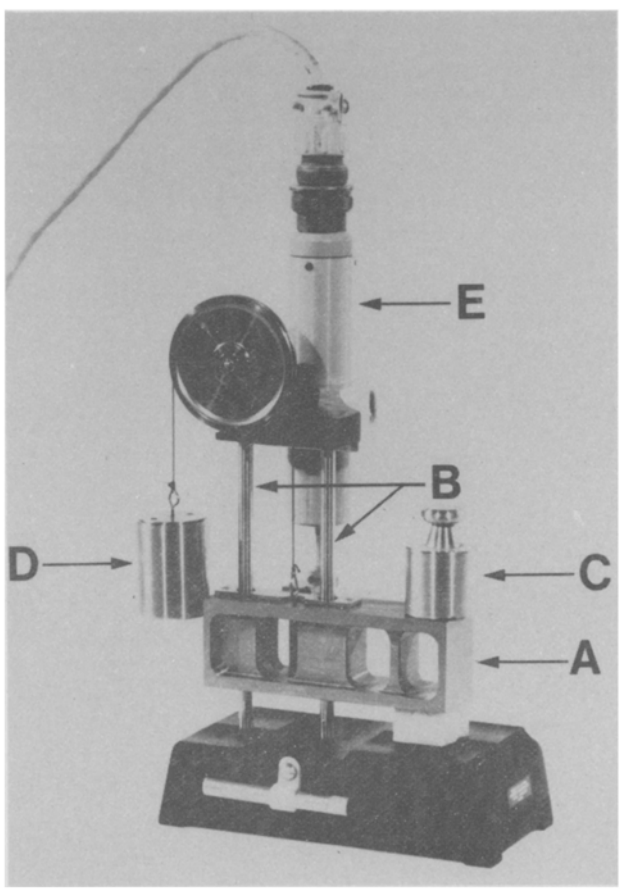

FIG. 1. Instrument for creep analysis. A, cantilever beam; B, guide rods; C, weight; D, counterweight to balance mass of beam, and E, displacement transducer.

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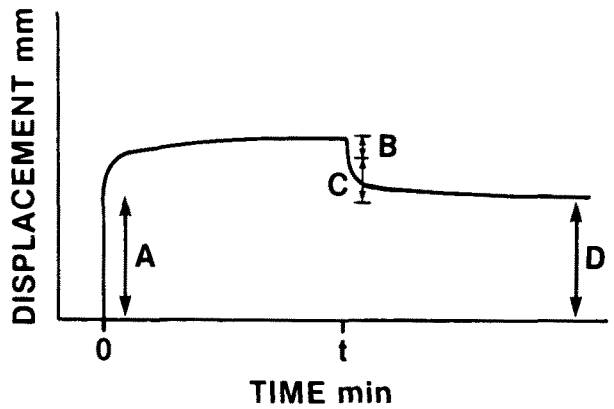

FIG. 2. Creep curve for butter. A, instantaneous deformation at loading; B, instantaneous recovery at unloading; C, time dependent recovery; D, permanent deformation.

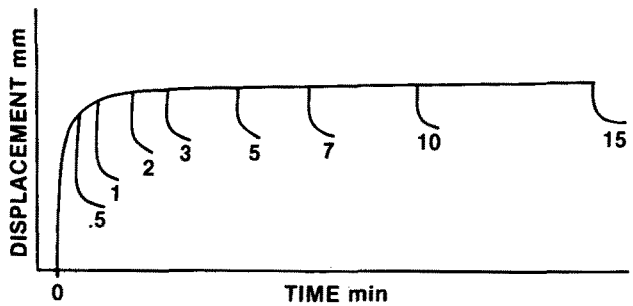

FIG. 3. Effect of loading time on creep behavior of butter.

TABLE I

Effect of Time on Viscoelastic Parameters of Butter at 5 C

Time min	Instantaneous elasticity %	Retarded elasticity %	Permanent deformation %
0.5	43.6	19.8	36.6
1.0	31.6	21.1	47.4
2.0	20.0	20.0	60.0
3.0	17.1	16.1	66.8
5.0	14.3	16.2	69.5
7.0	12.0	18.5	69.4
10.0	9.9	19.4	70.7
15.0	7.5	18.0	74.6

This behavior differs from that suggested by Mohsenin (5) for viscoelastic materials in which the instantaneous strain is equal to the instantaneous recovery of strain. It was found that the magnitude of instantaneously recovered strain of fat products is time dependent. Figure 3 shows the creep curves of butter with loading times ranging from 30 sec to 15 min. The change in distribution of viscoelastic deformation is illustrated in Table I. The proportion of the total deformation attributed to instantaneous elasticity decreased from 43.6% at 30 sec to 7.5% at 15 min. The retarded elasticity showed relatively little change. In this study, retarded elasticity was calculated from the unloading part of the curve as indicated in Figure 3. It appears that initially the network structure of the plastic fat products shows elastic response to stress but, as the time of loading increases, the structure collapses and the elastic component is converted to permanent deformation. The decrease of instantaneous elastic recovery is similar to the stress decay in a relaxation test. If the decrease in instantaneous elasticity is expressed as "decay time," defined as the time in which the instantaneous elasticity decreases to 1/e or 36.7% of its original value, then the decay time for this sample equals 42 sec. This points to a rapid collapse of the network structure under an applied stress greater than the yield value. A double logarithmic plot of instantaneous elasticity and permanent deformation time yields straight lines with the regression equations as indicated in Figure 4. The regression equation for permanent deformation is y = 1.67 + 0.2005x, where y is permanent deformation and x is time, and for instantaneous elasticity y = 1.485 − 0.502x where y is instantaneous elasticity and x is time.

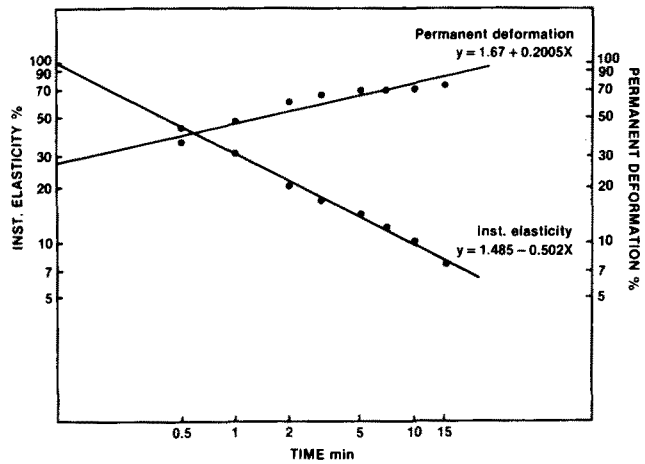

FIG. 4. Double logarithmic plot of instantaneous elasticity and permanent deformation vs time of loading.

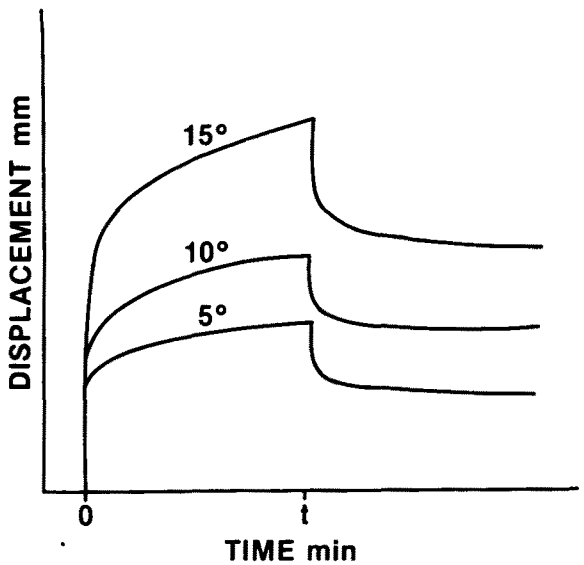

FIG. 5. Effect of temperature on creep behavior of margarine. Test results obtained at 5, 10 and 15 C.

The effect of temperature on the creep behavior of margarine and butter is very pronounced (Figs. 5 and 6). For the calculated viscoelastic parameters, both elastic and viscous components decreased rapidly with temperature (Table II).

The effect of using different forces is demonstrated for a sample of butter in Table III. The values of the elastic and viscous parameters are dependent on the applied force. The value for instantaneous elasticity is affected more than that for retarded elasticity and viscous flow. However, when expressed as percentage of the total deformation, the relative proportions remain fairly constant. These results emphasize

TABLE II

Viscoelastic Parameters of Butter and Margarine in Creep Analysis at Different Temperatures

Sample	Temp. C	Instantaneous elasticity	Retarded elasticity	Viscous flow	Deformation % of total[a]		
		$Pa.10^{-4}$	$Pa.10^{-4}$	$Pa.s.10^{-8}$	Inst.	Ret.	Perm.
Butter	5	1637.5	1192.4	1199.0	12.6	16.7	70.7
Butter	10	517.3	435.5	1153.9	21.8	27.2	51.0
Butter	15	238.4	267.1	593.6	26.6	22.8	50.6
Margarine	5	579.2	482.6	1336.5	13.8	28.4	57.9
Margarine	10	366.4	403.3	736.4	14.5	17.8	67.7
Margarine	15	170.3	141.9	243.3	14.8	19.3	65.9

[a]Instantaneous, Retarded, Permanent.

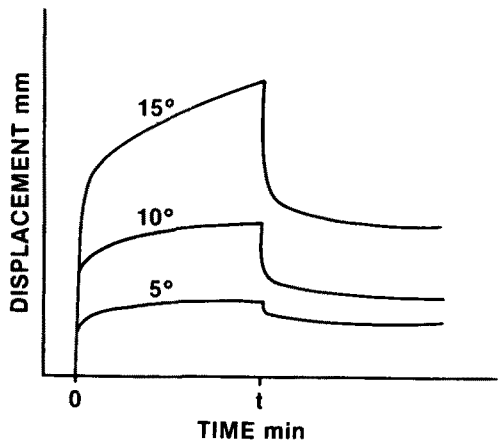

FIG. 6. Effect of temperature on creep behavior of butter. Test results obtained at 5,10 and 15 C.

TABLE III

Viscoelastic Parameters of Butter under Different Forces at 5 C

Force N	Instantaneous elasticity	Retarded elasticity	Viscous flow	Deformation % of total[a]		
	$Pa.10^{-4}$	$Pa.10^{-4}$	$Pa.s.10^{-8}$	Inst.	Ret.	Perm.
9.8	3048.6	2282.3	2493.8	14.5	16.1	69.4
14.7	1539.5	1902.7	2098.4	16.2	13.9	69.9
19.6	1432.4	1443.3	2002.6	18.4	18.4	63.2

[a]Instantaneous, Retarded, Permanent.

the importance of making comparisons of viscoelastic parameters of fats under identical conditions. In practice, the force selection range is limited; very small forces result in very small deformations, which may be insufficient for meaningful analysis, and large forces result in the formation of cracks in the sample.

Viscoelastic parameters of two samples of butter and two samples of margarine (Table IV) illustrate the differences in magnitude between different products. The ratio of elastic to permanent deformation at the usual loading time of 10 min indicates that the level of permanent deformation is in the range of 50-70% of the total deformation.

The effect of work softening is illustrated in Table V. Working results in a dramatic decrease in elastic and viscous parameters, but an apparent restructuring takes place on subsequent storage which results in a gradual increase in all parameters. However, even after seven days, the values are still considerably lower than those of the unworked sample. Working resulted in a change in deformation ratios. Four hr after working, both butter and margarine had a considerably lower proportion of instantaneous elasticity. Seven days after working the stored samples were still showing an increase in instantaneous elasticity. However, the viscoelastic characteristics had not returned to the values found prior to working.

The creep behavior of different food products has been studied (6,7,8). It is apparent from the present study that care has to be exercised in the interpretation of the data as loading time is an important variable in the creep analysis of plastic fat products.

Creep analyses of the viscoelastic properties of margarine and butter confirm the existence of an easily destroyed network, and another component which is more permanent and is related to the retarded elasticity. Further study is required to relate these network structures to crystal particle interactions in plastic fat products.

TABLE IV

Viscoelastic Parameters of Butter and Margarine at 5 C

Sample	Instantaneous elasticity	Retarded elasticity	Viscous flow	Deformation % of total[a]		
	$Pa.10^{-4}$	$Pa.10^{-4}$	$Pa.s.10^{-8}$	Inst.	Ret.	Perm.
Butter A	1539.5	1902.7	2098.4	16.2	13.9	69.9
Butter B	927.6	836.7	1853.6	21.1	25.8	53.2
Margarine A	622.3	592.9	1774.0	22.7	24.9	52.4
Margarine B	994.3	767.3	2073.5	19.2	25.1	55.7

[a]Instantaneous, Retarded, Permanent.

TABLE V

Effect of Work Softening on Viscoelastic Parameters of Butter and Margarine at 5 C

Sample	Treatment	Instantaneous elasticity	Retarded elasticity	Viscous flow	Deformation % of total[a]		
		$Pa.10^{-4}$	$Pa.10^{-4}$	$Pa.s.10^{-4}$	Inst.	Ret.	Perm.
Butter	Before working	1539.5	1902.7	2098.4	16.2	13.9	69.9
Butter	4 hr after working	834.5	503.1	782.3	8.0	18.5	73.5
Butter	7 days after working	987.3	591.3	1093.2	13.4	22.3	64.4
Margarine	Before working	994.3	767.3	2073.5	19.2	25.2	55.7
Margarine	4 hr after working	248.4	143.8	208.3	8.5	19.4	72.1
Margarine	7 days after working	405.7	356.1	506.8	13.6	16.3	69.8

[a]Instantaneous, Retarded, Permanent.

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♣Capillary Gas Chromatographic Analyses of Headspace Volatiles from Vegetable Oils[1]

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ABSTRACT

Eight different vegetable oils obtained commercially were analyzed for volatiles by capillary gas chromatography (GC). Volatiles generated in a GC static headspace sampler at 180 C were injected automatically onto a chemically bonded capillary column. Only a small number of GC peaks of low intensity were observed in the fresh samples, which varied in peroxide values from 0.2 to 3. Several major peaks were evident in the oils aged eight and 16 days at 60 C with peroxide values ranging from 16 to 65. Thirty-four GC peaks were identified on the basis of relative retention time of reference compounds and on the basis of gas chromatography-mass spectrometry (GC-MS). Volatile compounds identified were those expected from the autoxidaion of principal unsaturated fatty acid components of each vegetable oil tested. The relative concentrations of volatile components increased with the level of oxidation as determined by peroxide value.

INTRODUCTION

Different GC methods for the determination of volatile compounds formed in heated vegetable oils have been reviewed by Waltking and Goetz (1). However, there is a lack of quantitative studies using fats of different origins. Methods using GC with packed columns have been limited by the instability of the liquid phase, resulting in bleeding and poor reproducibility of peak retentions. Although capillary GC has been used for the analysis of volatiles in different foods (2), very little work has been reported on its application to analysis of volatiles in vegetable oils. Newly developed capillary GC systems with chemically bonded stationary phase have diminished problems with column bleed and afforded more reproducible peak retention than GC with packed column (3). Quantitative headspace analysis of volatile compounds by pneumatic sampling has been achieved (4). A headspace GC technique also has been developed to measure changes in light oxidized soybean oil (5). This work has been aimed at developing a reproducible capillary GC method to analyze headspace volatiles in different vegetable oils and to identify volatile components producing GC peaks by GC-MS.

[1]Presented at the AOCS Meeting in Chicago, May 1983.

EXPERIMENTAL PROCEDURES

Commercially processed canola, corn, cottonseed, olive, peanut, safflower, soybean and sunflower seed oils were obtained from various industrial sources or purchased at local stores, and analyzed initially for volatiles (zero-time). Each sample was subjected to accelerated oxidation by a modified Schaal oven test (6) by storing 50 g of oil at 60 C for eight days in 8-oz clear glass bottles containing air in the headspace by using loosely stoppered corks lined with cellophane paper. Twenty g of the aged oils were analyzed and the remaining 30 g were again stored at 60 C for eight additional days. Fatty acid composition of each oil was determined by GC analysis of the methyl esters with a Silar-10C column (50 m × 0.4 mm). Peroxide values were determined by AOCS Method CD 8-53 (7).