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Rheology of Plastic Fats

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With 4 figures

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In plastic fats, the crystals of the high-melting triglycerides form a three-dimensional network in the remaining liquid oil. Rheological properties of these systems show strong resemblance to those of other gel systems, containing a network of solid particles, such as dispersions of metal soaps or carbon black in oil, or of clay particles in water. Deformation of a gel under the influence of a stress is determined by the elastic deformation of the network structure, and by the gradual breakdown of this structure after a sufficiently long time at sufficiently high load. Evidence has been presented to show that deformation of such gel systems takes place in restricted locations rather than uniformly throughout the mass (1). The deformation of a gel should, therefore, be described in terms of the formation of locations where the network structure has been disrupted sufficiently to allow undisturbed regions of the network to move past each other. Such locations will be called "cracks", though it is recognized that in many cases these cracks may not become visible at the surface of the sample, and they may sometimes be healed within the time of an experiment.

Strictly speaking, the formation of a crack is not a rheological phenomenon. Since it appears, however, that an important group of materials deforms by breaking up into a number of regions which can move past each other without changing their internal structure, a description of the rheological properties of these materials requires the introduction of the concept of rupture. Recently, even the deformation of liquids has been described by assuming the formation of cracks in the body of the liquid, followed by rapid re-orientation of the molecules to a relaxed state (2).

The present paper describes the results of measurements carried out on simple model systems, consisting of crystals of glyceryl tristearate in paraffin oil. The properties of these gels have been studied in creep

experiments at low stress values, and in a concentric cylinder viscometer at very low rates of shear.

The samples were investigated without prior destruction of the network structure of fat crystals. The measurements relate, therefore, to the structure as obtained by the crystallization process used. Results of measurements are explained in terms of the formation of cracks, which process has been studied both in its initial stage and in the final stage where coherence in the sample is lost.

Experimental

Gels containing 25% of glyceryl tristearate (m. p. 71–72°C) in paraffin oil were mainly used. Substitution of various triglyceride oils for the paraffin oil produced no noticeable change in the properties of the gels.

At temperatures in excess of its melting point, the tristearate is completely miscible with the oil, whereas its solubility at room temperature can be neglected. Cooling of the hot solution under controlled conditions produces a plastic material, the consistency of which may be varied between that of a soft, semi-liquid paste and a hard, brittle solid, depending upon the rate of cooling, and other factors.

In the creep experiments, a hollow cylinder of the material was subjected to torsion by applying a couple to the upper surface, while keeping the lower surface stationary. The inner radius of the cylinder was 2 cm, wall thickness 1 cm, height between 3 and 4 cm. The forces were transmitted to the material by means of riffling metal discs. Rotation of the upper surface was measured by means of an optical lever, allowing measurement of changes in shear as small as $3 \cdot 10^{-5}$.

The viscometer consists of two concentric cylinders with riffling surfaces, between which the sample is sheared. The inner radius of the sample is 2.25 cm, and its effective thickness 0.5 cm. Shear rates in the sample

could be varied between 10^{-3} and 10^{-5} sec. $^{-1}$. Apparatus and technique of measurements were similar to those described by Trapeznikov (3).

Temperature variations of a few degrees had little effect on the properties of the gels, so long as the temperature remained below the point where the solubility of the tristearate becomes noticeable. Measurements were carried out at 20°C.

Results

Typical results of four subsequent creep experiments carried out with a single sample are shown in figs. 1 and 2. It is evident that the behaviour is far from linear in this region of stress values. The first measurement has resulted in hardening of the material, whereas a visible crack, formed after about 27 minutes in the third measurement, results in overall softening and complete disruption

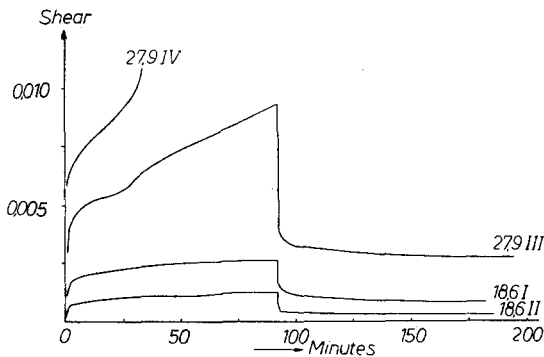


Abb. 1. Creep and recovery of a single sample in successive experiments with increasing stress. (The values against the curves denote shearing stress in g/cm 2 and number of experiment)

in a subsequent experiment. In the semi-logarithmic plot of fig. 2 each curve consists of a series of straight lines, the slope of which suddenly increases after specific time intervals. The pronounced change in slope of curve III after 27 minutes corresponds to the formation of a visible crack. It is postulated that the changes in slope which were invariably found in the semilogarithmic creep curves of both soft and strong gels are always due to the formation of cracks as defined above. The linearity of the relation between deformation and log (time) over long time intervals shows that *uniform* viscous flow is negligible. The permanent deformation, which invariably remains after recovery has been allowed to proceed for a very long time, is due to the presence of

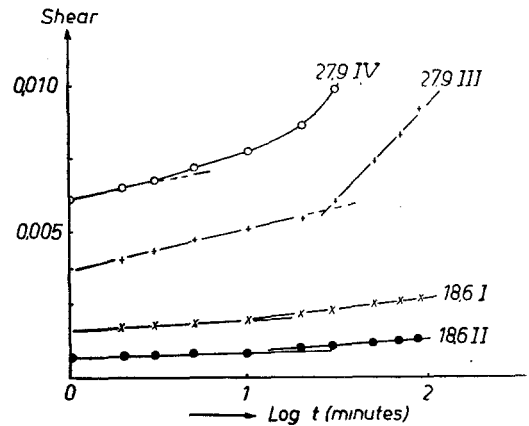


Abb. 2. Creep and recovery (semi-logarithmic plot) of a single sample in successive experiments with increasing stress. (The values against the curves denote shearing stress in g/cm 2 and number of experiment)

cracks, and has been used in calculating an "apparent viscosity".

The shear γ under constant stress S increases with time according to the relation:

$$\gamma = \frac{S}{G_1} + \frac{S}{G_2} \log t \quad [1]$$

where G_1 and G_2 may be termed the "rapid" and "retarded" elastic modulus. The relation holds both during the loading and during the recovery period, for times longer than about one minute. The time-dependent modulus G_2 shows sudden changes after specific time intervals.

The effect on the properties of successive experiments with increased stress is illustrated in fig. 3. The hardening resulting from

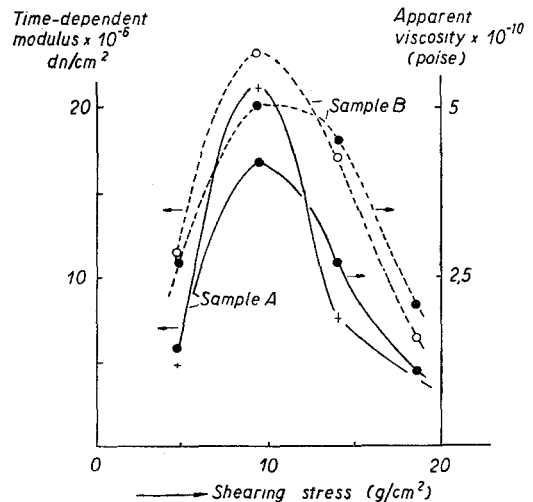


Abb. 3. Effect of successive measurements with increasing stress on gel properties

the first measurement rapidly changes to considerable softening in succeeding experiments. A completely similar behaviour is found in cyclic experiments, in which a constant stress is alternately applied and removed for periods ranging between a few minutes and several hours. The number of cycles necessary to produce the maximum of the modulus and apparent viscosity decreases rapidly with increasing stress. With a sufficiently high stress, the drop in apparent viscosity which immediately precedes complete breakdown of the sample may be effected in the first measurement. The value of the stress necessary to cause complete breakdown in the first measurement indicates the "breaking strength" of the sample. Values found in this way are in the range between 5 and 50 g/cm².

In a hard and brittle gel, complete breakdown occurs by the formation of a number of large cracks. Such cracks are not visible in the soft, liquid-like gels even after breakdown has proceeded to the stage where the drop in apparent viscosity amounts to several decades. In view of the close similarity in behaviour of those gels under the influence of a stress, it is held that the same mechanism is responsible for the deformation of both soft and hard gels. Moreover, gels of intermediate properties can easily be prepared by proper control of the crystallization conditions.

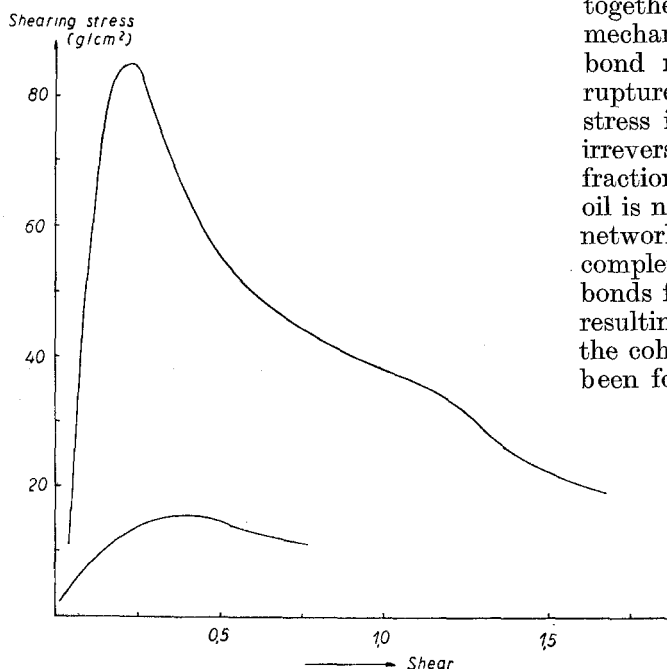


Abb. 4. Typical stress-strain curves of plastic fats containing 15% glyceryltristearate in paraffin oil. Rate of shear $1.9 \times 10^{-4} \text{ sec}^{-1}$

The gels used in the present investigation invariably show permanent deformation, even after loading for a short time with the smallest stress producing a measurable deformation. It follows that cracks are formed even by deformations of the order of 0.0001. Complete breakdown with loss of coherence requires deformations of from 0.15 in brittle samples to 0.60 in very soft samples.

The conditions resulting in complete breakdown have been studied by subjecting the gels to shear at a constant rate. Fig. 4 shows the results obtained with a hard and with a fairly soft sample. The maximum stress indicates the force necessary to break the gel along the wall of the inner cylinder, in a time interval of from 15 to 30 minutes. This corresponds to the strength of the crystal network (4).

Discussion

The properties of the network of fat crystals are determined by the density of junction points between crystals, and by the strength of the bonds in those junctions. The bonds between fat crystals may be of two types. Weak but reversible bonds are due to *Van der Waals* attraction between neighbouring crystals, and stronger but irreversible bonds exist where crystals have grown together during their production, or are mechanically interlinked. Deformation of a bond may be purely elastic, or result in rupture after a definite time interval. The stress is distributed over all reversible and irreversible bonds in each cross-section; the fraction of the stress carried by the liquid oil is negligible so long as breakdown of the network structure has not become virtually complete. The presence of the two kinds of bonds follows from the permanent softening resulting from strong kneading, and from the coherence in a sample where cracks have been formed.

A reversible bond which has been broken under the influence of a stress will re-form in another, relaxed position; this is the process which gives rise to retarded elastic behaviour. The relaxation of the reversible bonds causes an increasing part of the stress to be carried by the irreversible bonds. Even with the rather low stress values used in creep experiments, breaking of irreversible bonds will

occasionally occur. Rupture of one irreversible bond results in a suddenly increased load on the remaining bonds in the same cross-section, which increases their probability of rupture. This auto-catalytic character of the breaking of irreversible bonds (5) is responsible for the sudden formation of cracks, and is manifested in the suddenly decreased values of the time-dependent modulus.

The formation of a crack is thus considered to result from the breaking of all irreversible bonds in a cross-section, whereas coherence of the sample may in that case be maintained by the reversible bonds. The process can be studied by observing the changes in slope of the creep curves in the semi-logarithmic plot, and also by measurement of the permanent deformation which is entirely due to the presence of cracks.

The properties of this model have been treated more quantitatively by application of the absolute reaction rate theory, where it is assumed that the bonds can deform independently of each other. If the stress is sufficiently low to ensure that no irreversible bonds will be broken at a certain stage of a creep experiment, a relation between deformation and time can be derived (6) which is identical with equation (1). It is concluded that the straight portions of the creep curves in the semi-logarithmic plot are due to a deformation mechanism in which no irreversible bonds are broken.

The effect of a preceding deformation, as given in fig. 3, may be explained by assuming that shearing causes primarily an increased number of cross-links between fat crystals, because of some re-orientation of the particles. At the same time, however, the deformation causes the irreversible formation of cracks, resulting in an overall softening on a macroscopic scale. In creep experiments at low stress values, the hardening is found to predominate. This simply means that the size of the sample is still comparable to the size of the undisturbed regions. At higher stress values, or after a longer time interval, the sample is broken up by the formation of cracks. The properties of the sample as a whole now correspond to those of a much weaker material, though the undisturbed regions are, actually, still harder than in the original sample.

At the higher shear rates used in the concentric cylinder viscometer, the breaking of a gel at a predetermined location involves mainly rupture of irreversible bonds. The phenomenon shows some resemblance to the breaking of a filament under specified conditions of loading, and may be treated along the same lines (6, 7).

Acknowledgement

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Summary

A plastic material is obtained by rapid cooling of a solution of glyceryl tristearate in paraffin oil. The fat crystals produced form a three-dimensional network structure, which is mainly responsible for the rheological properties of the material.

The properties have been investigated by means of creep measurements at deformations not exceeding a few percent, and in a concentric cylinder viscometer at very low shear rates.

Results of measurements are discussed in terms of the properties of the three-dimensional network of fat crystals.

Zusammenfassung

Eine plastische Substanz wird durch rasches Abkühlen einer Lösung von Glyceryltristearat in Paraffinöl erhalten. Es entstehen dabei zusammenhängende Fettkristalle, welche eine feste Struktur bilden. Die rheologischen Eigenschaften des Materials werden hauptsächlich durch diese vernetzte Struktur der festen Teilchen bestimmt.

Die Messung der Eigenschaften erfolgte mittels Kriechversuchen bei sehr kleinen Deformationen und im Rotationsviskosimeter bei sehr niedrigem Geschwindigkeitsgefälle. Die Ergebnisse dieser Messungen werden an Hand von den Eigenschaften der vernetzten Struktur der Fettkristalle diskutiert.

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