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Determination of the plastic and viscoelastic properties of a metallic soap by a hot hardness measurement

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An analysis of an indentation test in the case of mixed plastic–viscoelastic behaviour, as is met in metallic soaps, is described. The viscoelastic part of the strain is described in terms of a Burgers model whose five rheological parameters are then a yield stress, σ_0, two elasticity moduli, G_0 and G_1, and two viscosities, η_0 and η_1. This analysis is applied to a hot hardness experiment on a compacted metallic soap, calcium stearate, between 20 and 130° C. By fitting the model to the experimental curves, values of σ_0, η_0, η_1, G_0 and G_1 as a function of temperature, have been derived. It is shown that plastic strain is much greater than viscous strain at low temperature, since η_0 is very high. The material is therefore a solid. It is also shown that, as temperature increases, viscous strain increases and plasticity vanishes (above a transition temperature, $\sigma_0 = 0$, and only viscoelasticity remains). The curves $\eta_0(T)$, $\eta_1(T)$, $G_0(T)$ and $G_1(T)$ have marked slope changes at about 90° C (which is the crystal–crystal phase transition temperature of calcium stearate), and the viscosities fall at 123° C, which is the first crystal mesomorphic phase-transition temperature. This test seems to be a good simple rheological measurement for bodies exhibiting simultaneous plasticity and viscosity or viscoelasticity.

1. Introduction

Few materials exhibit, as temperature increases, such a succession of varied crystalline or mesomorphic structures as metallic soaps [1–3]. It seems useful to try to relate the rheology and the crystalline structure. Unfortunately, the use of classical rheological measurements is extremely difficult because:

(a) at low temperatures the very high strength and viscosity of soaps results in too high extrusion or shearing efforts for classical rheometers;

(b) at higher temperatures, the soaps slip against the walls of capillaries, the shear rate is not known and the results are meaningless; and

(c) at temperatures higher than 250° C, soaps begin to burn.

This explains why few studies of the rheology of metallic soaps have been undertaken until now [4–6]. The present authors noticed the influence of the shear rate on the "viscosity" of the product, but no attempt was made to quantify this phenomenon. Given this feature, a relatively simple mechanical test seemed of great interest, i.e., the hardness test, of which theoretical interpretations exist, relating the geometry of the indentation to the rheology of the indented material for the rigid plastic [7] and elasto-plastic [8] cases.

The purpose of this article is firstly to present a theoretical interpretation of this test for a more complex rheological behaviour, and secondly, to discuss the results obtained for calcium stearate between 20° C and 130° C.

2. Experimental procedure

2.1. Description of the apparatus

No available apparatus known to the authors met the necessary requirements, which were the availability of low loads, below one kilogram, since the yield stresses to be measured are between 0.1 and 1×10^7 Pa, and the existence of a heating

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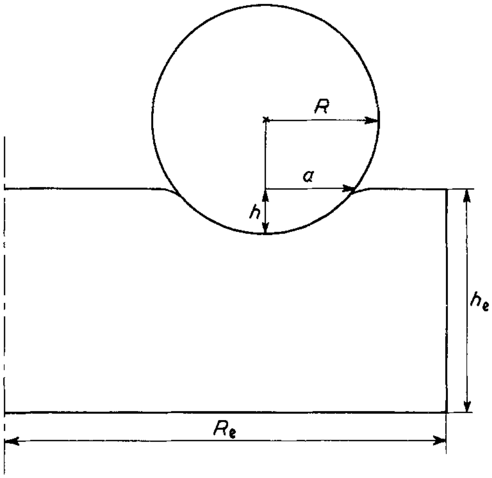

Figure 1 Geometry of the indentation.

system, giving temperatures of up to 250° C. This is why an indentation machine possessing these characteristics was designed and built.

The sample is obtained by compacting soap powder in a cylindrical mould with a radius, R_e, of 22 mm, under a pressure of 6.6×10^7 Pa, which is much greater than the yield stress, σ_0, and ensures a thorough compaction everywhere in the sample. The resulting height of the sample, h_e, is 10 mm. The surfaces of the sample must be strictly parallel, so that they are normal to the indentation axis. Moreover, the surfaces must be very smooth. This requires the use of fine grain-size powder ($\leqslant 200\,\mu$m) and a low roughness of the mould (CLA roughness, $R_a \leqslant 1\,\mu$m). To ensure good reproducibility of the results it is necessary to wait a day after compaction of the samples. The sample is put into a cylindrical electric heater giving a controlled temperature between room temperature and 250° C, with a precision of ± 1° C. A particularly important point is the thermal insulation of the upper side of the sample on which the hardness is to be measured. In the apparatus used, the support of the indentor and its guiding system, which is in close contact with the sample, acts as an insulator.

Previous measurements [9] showed that the thermal diffusivity of calcium stearate varies between $1 \times 10^{-7}\,\text{m}^2\,\text{sec}^{-1}$ at 20° C and $0.5 \times 10^{-7}\,\text{m}^2\,\text{sec}^{-1}$ at 150° C. It has been calculated that, neglecting heat losses, it takes 15 min for the sample to reach a steady homogeneous temperature. To take losses into account, a heating time of 30 min was used. The eccentricity of the indenter axis with respect to the sample axis allowed for about 20 measurements on the same sample by rotating the heater containing the sample (see Fig. 1).

The experiment consisted of, recording as a function of time, t, the depth of penetration, h, of a rigid tungsten carbide ball, with a radius, R, of 1 mm, using a linear displacement transducer,

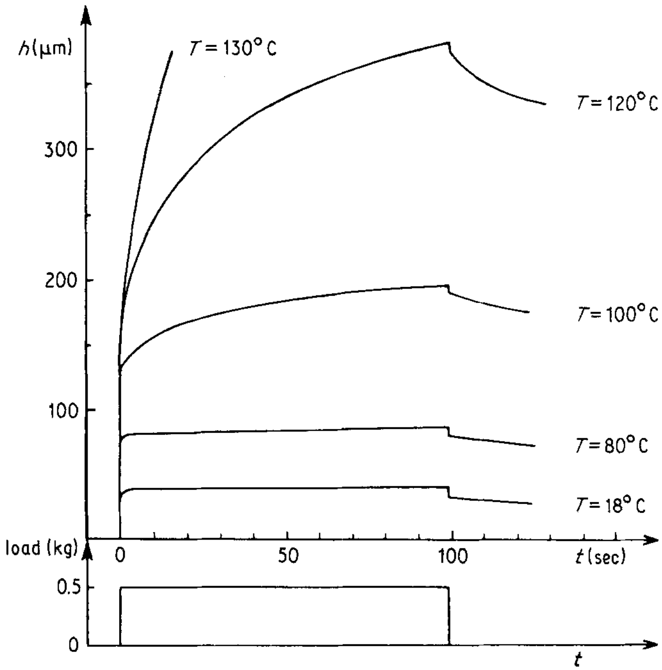

Figure 2 Typical indentation curves of h against t at various temperatures for calcium stearate.

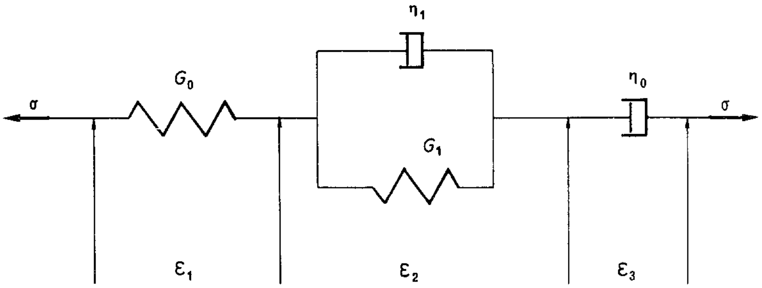

Figure 3 Burgers' model.

capable of measuring displacements between 1 μm and 10 mm. For precision, a load, M, giving displacements between 20 μm and 1 mm was chosen. As values of the yield stress, σ_0, between 0.1 and 1×10^7 Pa were expected, the usual loads were 0.5 or 1 kg. To measure lower yield stresses, it may be necessary to increase R and to diminish M.

2.2. Theoretical analysis

Fig. 2 shows some typical experimental curves for h against t. After the instantaneous deformation (elastoplastic), the soap goes on flowing. It can be seen that the viscous behaviour exhibited at high temperature still exists at room temperature, and becomes more and more important as the temperature increases. After the loading is removed from the sample, an instantaneous recovery of the strain is seen, followed by a more delayed recovery.

This leads us to superimpose on the rigid plastic strain, a visco-elastic strain. For the latter, the one-dimensional rheological model of Burgers has been used (Fig. 3), which takes into account an "instantaneous" elasticity, G_0, responsible for the strain, ϵ_1, a "delayed" elasticity, $G_1 + \eta_1$, responsible for the strain ϵ_2 and a viscosity, η_0, responsible for the strain ϵ_3.

Under a stress, σ, the system flows according to the following equations,

$$\epsilon_1(t) = \sigma(t)/G_0, \tag{1}$$

$$\sigma(t) = \eta_0 \dot{\epsilon}_3(t), \tag{2}$$

$$\epsilon_3(t) = \frac{1}{\eta_0} \int_0^t \sigma(\tau)\,\mathrm{d}\tau \tag{3}$$

and

$$\sigma(t) = G_1 \epsilon_2(t) + \eta_1 \dot{\epsilon}_2(t) \tag{4}$$

or

$$\epsilon_2(t) = \frac{1}{\eta_1} \exp(-t/\theta_1) \int_0^t \exp(\tau/\theta_1)\sigma(\tau)\,\mathrm{d}\tau \tag{5}$$

with $\theta_1 = \eta_1/G_1$.

The total strain is then given by

$$\epsilon(t) = \epsilon_1(t) + \epsilon_2(t) + \epsilon_3(t). \tag{6}$$

Fig. 4 shows the theoretical curve when the stress, σ, is constant. The resemblance to the experimental curve justifies the choice of the model. This model relates two scalar functions, ϵ and σ. However, strictly speaking, the flow under the indentor is three-dimensional and therefore ϵ and σ should be second order tensors. To use the

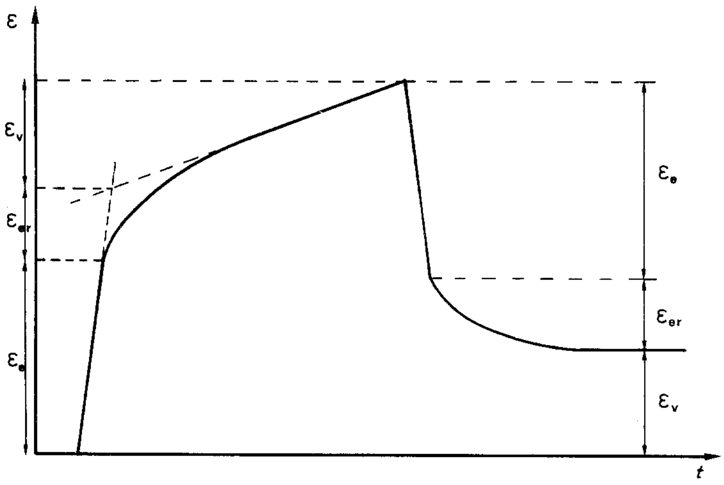

Figure 4 Theoretical curve of ϵ against t for Burgers material strained at constant stress, σ.

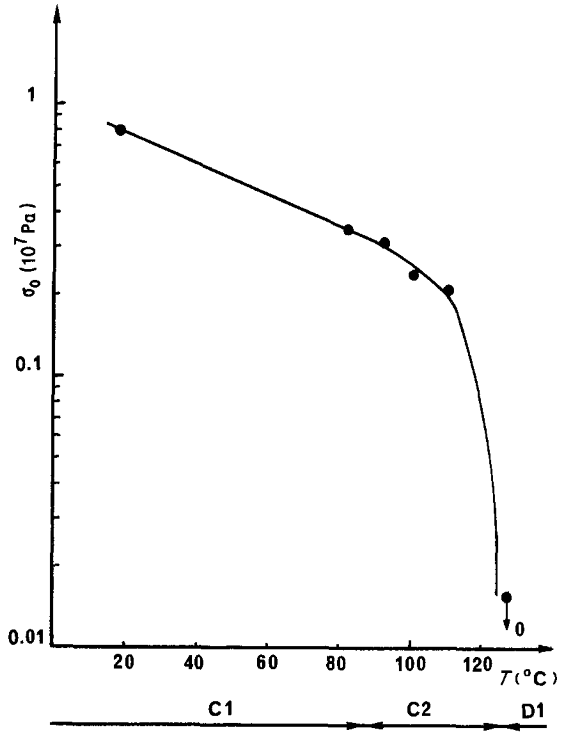

Figure 5 Yield stress, σ_0, of calcium stearate as a function of temperature T. C_1, C_2: crystalline phases, D_1: mesomorphic disc phase (taken from [2]).

Burgers model, these tensors should be replaced by "equivalent" strain and stress.

As an equivalent stress, the mean pressure under the ball will be used,

$$\sigma(t) = Mg/\pi a^2, \tag{7}$$

where a is the radius of contact between the ball and the soap sample and g is the acceleration due to gravity. Since,

$$a^2 = h(2R-h), \tag{8}$$

then

$$\sigma(t) = \frac{Mg}{\pi h(2R-h)}. \tag{9}$$

An approximate equivalent strain under the ball is given by [7]

$$\epsilon(t) = \frac{0.2a(t)}{R}, \tag{10}$$

and therefore

$$\dot{\epsilon}(t) = \frac{0.2\dot{a}(t)}{R}. \tag{11}$$

This leads to $\dot{\epsilon}(t) \leqslant 10^{-3}\ \text{sec}^{-1}$ for this experiment. The viscosities we find are then given for a

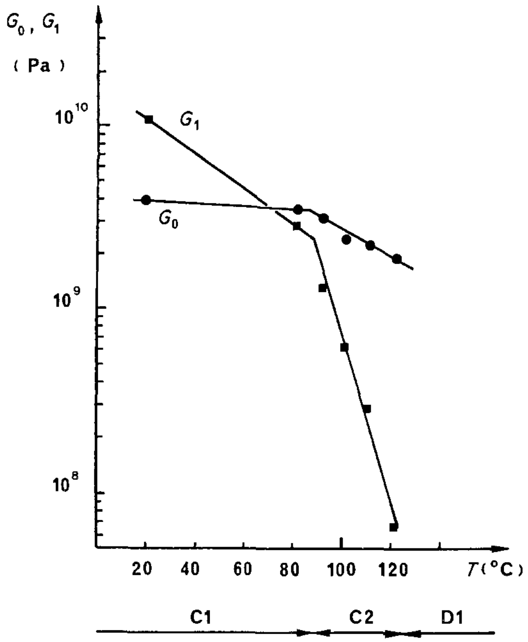

Figure 6 Elasticity moduli G_0 and G_1 of calcium stearate plotted against T.

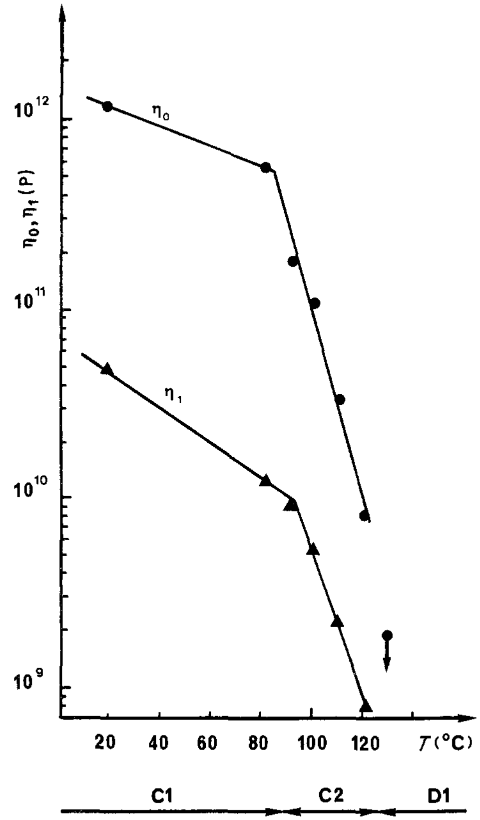

Figure 7 Viscosities η_0 and η_1 of calcium stearate plotted against T.

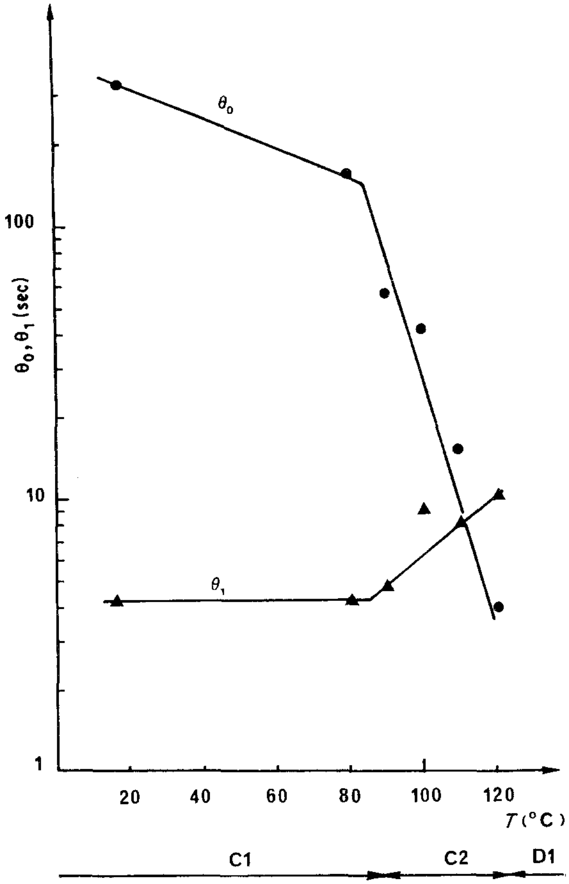

Figure 8 Relaxation times, $\theta_0 = \eta_0/G_0$ and $\theta_1 = \eta_1/G_1$, of calcium stearate plotted against T.

virtually zero shear rate. The parameters σ_0 and G_0 are calculated directly from the plastic and elastic strains shown on the curve in Fig. 2:

$$G_0 = \frac{\sigma_f}{\Delta\epsilon_e} \qquad (12)$$

and

$$\sigma_0 = \frac{Mg}{\pi a_p^2}, \qquad (13)$$

where σ_f is the final stress, i.e., the stress just before unloading, $\Delta\epsilon_e$ is the elastic recovery and a_p is the radius of the contact zone corresponding to plastic deformation (instantaneous deformation). G_1, η_0 and η_1 (and consequently θ_0 and θ_1 where $\theta_0 = \eta_0/G_0$) were calculated by fitting Equation 6 to the experimental curves.

3. Rheological behaviour of calcium stearate

The calcium stearate used was 96.3 wt% pure. It contained 1.5 wt% calcium palmitate, 1.4 wt% calcium arachidate, 0.5 wt% calcium oleate and traces of shorter-chain calcium soaps.

The hardness tests were carried out at increasing temperatures, from 18 to 120° C. A measurement at 130° C failed to give useful results because of the too low viscosity and strength of the soap. Figs 5, 6 and 7 show the temperature dependence of the rheological parameters. It is interesting to note that the changes of slope observed are in good agreement with phase observations by X-ray studies [2]. All parameters fall strikingly at the crystal–mesomorphic phase transition, but only G and η are sensitive to the crystal–crystal transition. Above 120° C, the fall of consistency makes it impossible to measure the parameters and the model cannot be used any longer. There is no instantaneous strain, which means that plasticity has vanished; $\sigma_0 = 0$, only viscoelasticity remains.

Fig. 8 shows the temperature dependence of the relaxation times θ_0 and θ_1.

4. Conclusion

This method, considering its comparative ease of use and the lack of sophisticated instruments required, seems to be very useful in characterizing the rheological behaviour of simultaneously visco-elastic and plastic bodies.

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