

extremes there may be bodies which contain both these features to varying extents, and which may therefore be either 'brittle' or 'ductile' according to circumstances of the test.

J. B. MURGATROYD.

Research Laboratory,
Rockware Glass Syndicate,
Greenford, Middx.

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Place-Exchange Theory of Plastic Flow, as Applied to Polymers

THE place-exchange theory of plastic flow was originally developed by Becker¹, to account for the flow of metals. More recently a somewhat similar theory has been advanced by Eyring² to account for flow in polymeric materials. In the latter theory the flow process is regarded as the movement of a molecule, or segment of a molecule, from one position in the plastic to a neighbouring one, under the influence of thermal energy. If E be the potential barrier separating two positions, and f the stress, then the activation energy for the process is written as $E - bf$, where b is a constant involving the dimensions of the 'unit of flow'. The rate of flow θ may then be written

$$\theta = \text{const. } e^{-(E-bf)/RT} \quad \dots \quad (1)$$

It can be shown from (1) that for very low stresses the system will show Newtonian behaviour, that is, for $bf \ll RT$, $\theta \propto f$, and Eyring has treated simple liquids along these lines³. For $bf > RT$ the following behaviour is predicted

$$\ln \theta = a + b'f \quad \dots \quad (2)$$

(The equations are given in their simplest form.)

We have recently completed an extensive series of measurements on a plasticized cellulose derivative over a stress range 2-160 kgm./cm.² and temperature range 16-100° C. The methods used were compression of cylinders and extension of rods, care being taken to analyse the total strain into its plastic (non-recoverable) and elastic components. In this note we are concerned solely with the plastic flow.

The important result of our work is that equation 2 is followed only at the lower stresses, that is, up to a certain stress value f_0 which is itself a function of temperature. In this range, $f < f_0$, we have further checked, in a qualitative way, the main assumption of the theory; thus we have found that the 'activation energy' for flow falls from c. 30 kcal. at 4.6 kgm. cm.⁻² to c. 11 kcal. at $f \geq f_0$. For values of the applied stress above f_0 we find that the activation energy is independent of stress. In fact, the flow may be described by the equation originally used by Bingham to describe the flow of solid-liquid dispersions through capillary tubes.

$$f \geq f_0, \quad \theta = A(f - f_0) \quad \dots \quad (3)$$

This equation could not have been predicted by the place-exchange theory as it stands. Its application gives hope for a simpler analysis of flow problems in industrial processes than could be achieved by equation 2. We should mention that similar results were obtained by Dillon and Johnston⁴ for the extrusion of compounded rubber. Their work, however, by itself, is not directly comparable with ours owing to the presence of 'fillers' in many of their rubbers

(that is, they are not dealing with a simple polymer system), and the possibility of 'plug-flow' at the lower stresses. In fact, it might be argued that their rubber-filler systems were analogous to the Bingham solid-liquid paste systems. However, our results would suggest that rubber without fillers may follow equation 3 at high stresses, and there are indications, in the paper quoted, that this may well be so.

It is of interest that we found no indication of a true yield-value, and we may hazard the opinion that in our system, whether or not a yield-value is observed is purely a question of duration of experiment and sensitivity of observation. In fact, it is possible to observe flow in our sensitive extension apparatus at stresses much below the apparent yield-value obtained in our compression plastometer. It is, of course, possible that if the plasticizer content were reduced, a true-yield value would appear. It is of interest that to a reasonable approximation, over a temperature interval of 40° C., the 'mobility constant' A has the same temperature dependence as the intercept f_0 , namely,

$$A = A_0 e^{-11000/RT} \quad f_0 = f_{00} e^{11000/RT}.$$

A further feature of our results was that at the very low stresses, in extension, the material showed strain-hardening, θ falling 20-30 fold over the initial 3-4 per cent extension, reaching an apparently steady value, very similar to the behaviour reported by Andrade for metal wires⁵. At the high stresses used in compression, we could not detect any such behaviour. Whether this was due to instrumental limitations we cannot at present say. It does, however, seem likely that any strain-hardened structure which may be formed initially cannot withstand the large shearing forces produced by the high stresses operative in the compression measurements.

It would seem that a critical attitude is required to the application of place-exchange theories in their present form, not only to the flow of plastics at high stresses, but also to the normal viscosity phenomena in liquids. Granting the application of the theory to plastics at relatively low stresses, it might be surmised that at the higher stresses the flowing molecules may pass over several energy barriers, and that the rate of flow is then determined by the rate of exchange of momentum, as visualized by Van der Waals' and Andrade's theories of liquid viscosity⁶. If this is so, it would argue for the possible application of the momentum exchange theory to the behaviour of simple liquids. It is hoped in the future to make experimental and theoretical investigations of this question.

Approval for publication has been granted by the Director-General of Scientific Research and Development, Ministry of Supply.

D. D. ELEY.
D. C. PEPPER.

Colloid Science Department,
University, Cambridge.
May 12.

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