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The Rheological Behavior of a Filled Viscoelastic Material

R. T. SPURR, *Ferodo Ltd., Chapel-en-le-Frith, England*

Introduction

Leaderman[1] observed that creep recovery data obtained at various temperatures on a viscoelastic material could, when plotted, be superimposed by horizontal translation of the time axis in such a way that all the experimental points fell on a single master curve. Tobolsky[2] and Ferry,[3] with their co-workers, developed the theory of the superposition principle and verified it for a number of materials. The principle was found to apply, in the first place, to amorphous polymers. Measurements described below show that the principle also holds for a filled viscoelastic material and that changing the proportion of filler to matrix is equivalent to shifting the time axis.

Experimental Details

The material concerned was a bitumen or pitch and the filler was asbestos. Specimens were simply made, by stirring the asbestos into the melted pitch in the required proportions and pouring the mixture into a mold. It was found difficult to make up specimens containing more than about 30% by volume of asbestos. The properties of the specimens measured were the indentation and rebound hardnesses. To measure the indentation hardness p_m a steel ball was mounted on one end of a pivoted counterweighted beam, a load hung from the beam, and the resulting penetration of the ball into the specimen measured by a dial gauge reading to 0.0001 in. The specimen was mounted on a microscope heating stage and could be heated to temperatures of up to about 45°C.; at higher temperatures it was difficult to keep the whole specimen at a uniform temperature.

To measure the rheological behavior of the specimen at much smaller times, the ball was dropped on the specimen and the diameter of the impression was measured, the surface first being dusted with very fine powder.

Results and Discussion

A $^1/_4$ in. ball was indented into pitch specimens containing 0, 5, 12, 17, and 30% by volume of asbestos, with a load of 100 g., and the penetration Z was measured after 7.5, 15, 30, 60, 120, and 240 sec. at temperatures of 20, 25, 30, 35, and 40°C. Typical results are shown in Figure 1 where

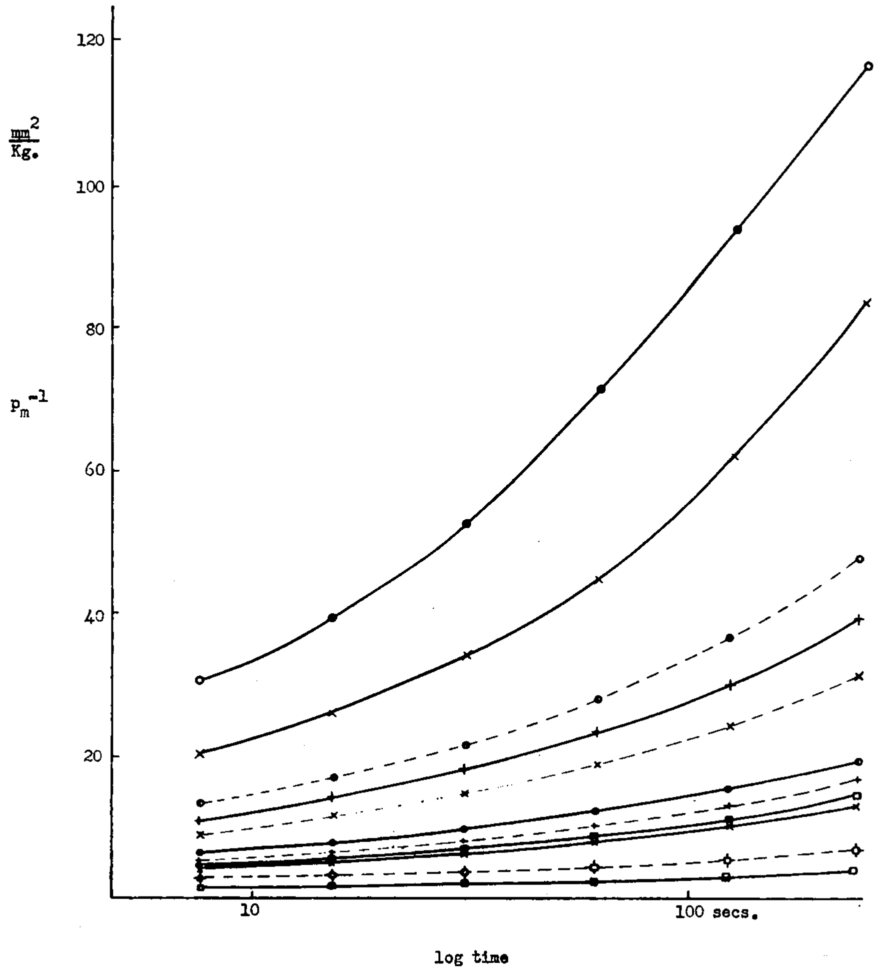

Fig. 1. Penetrations at 20, 30, and 40°C. into specimens containing asbestos, in per cent: (○) 0; (×) 5; (□) 12; (+) 30. (symbols ○, ×, □, +, respectively).

the area A of the indentation ($A = \pi RZ$) divided by the load (i.e., p_m^{-1}) is plotted against log time. Figure 2 shows how the curves of Figure 1 can be displaced along the time axis in such a way that they all fall on the one master curve, and the necessary displacements to give such superposition are shown.

Small amounts of filler had quite surprisingly large effects on the creep behavior. The nature of the filler was also important; for example, long-fiber asbestos had more effect than short-fiber asbestos, which in turn was much more effective than spherical mineral particles, the same volume percentage of filler being compared in each case. Two specimens containing the same nominal proportion of (long-fiber) asbestos could therefore give rather different results, but their creep curves would still fall on the master

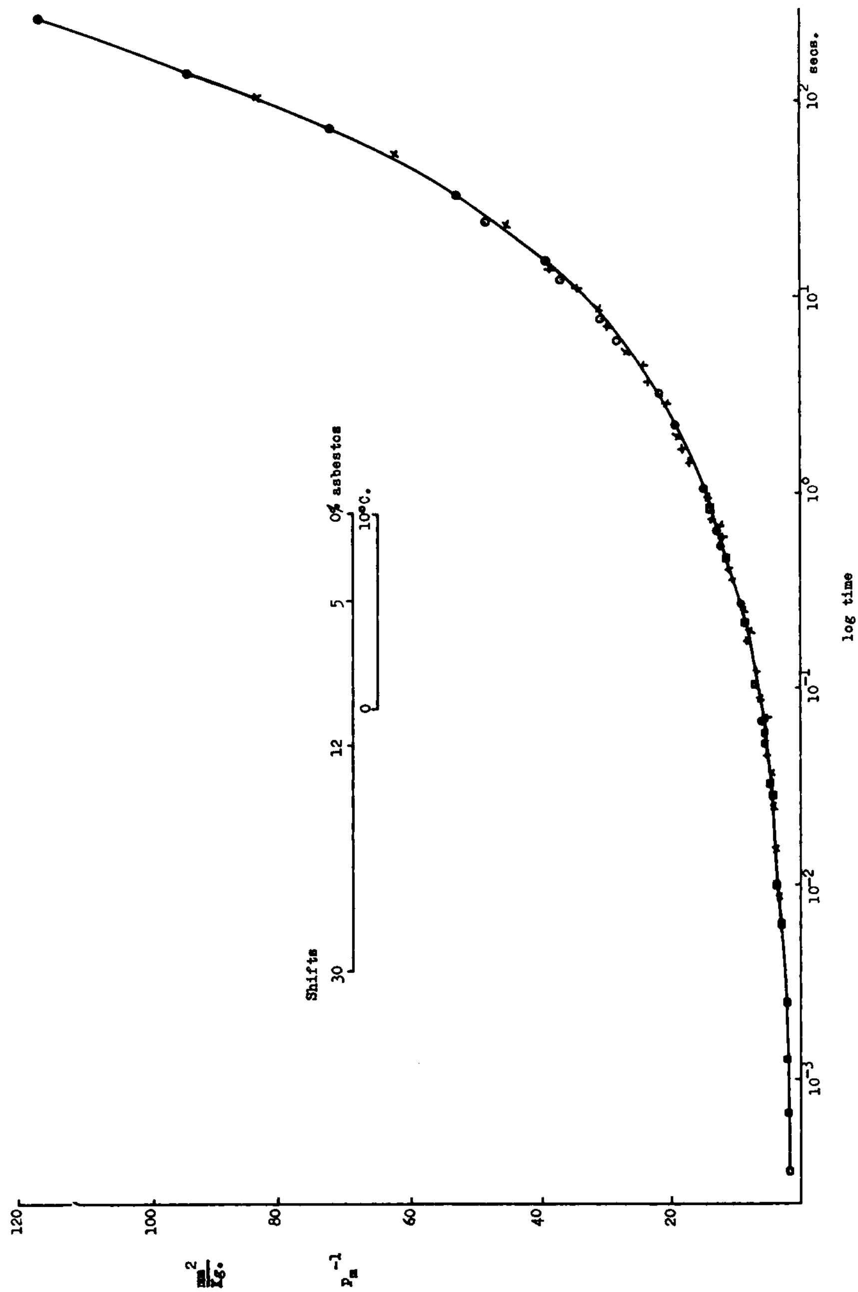

Fig. 2. Shifts required to superpose curves of Figure 1.

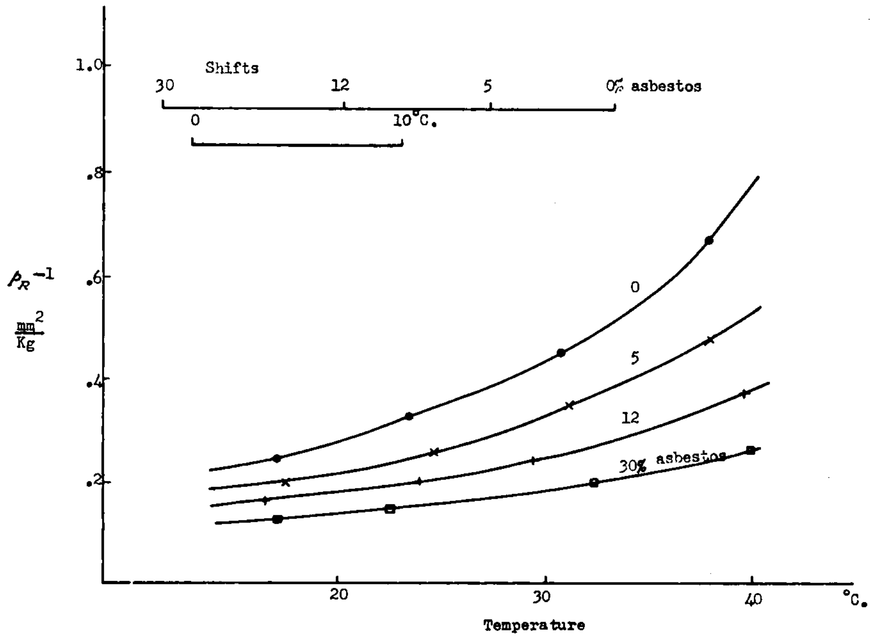

Fig. 3. Shifts required to superpose rebound curves.

curve though slightly displaced along the log time axis. Consequently, there was some scatter in the shifts.

The deformation stresses involved in penetration measurements are complex. The indentor drags down part of the surface not in contact with it, and for a spherical indentor indenting an elastic body $Z/z = 2.0$ where Z is the total penetration of the ball and z the depth of ball actually in contact with the surface.[4] The ratio Z/z is independent of E, etc. At any instant the deformation of a viscoelastic solid should be given by the Hertzian equations with the use of the relevant instantaneous modulus. With the $^1/_4$ in. ball Z/z was constant and about 1.9, and it did not vary with load, composition of specimen, or temperature. Consequently, we can assume that the specimens were viscoelastic and not, for example, plastic. Values of p_m could be converted into appropriate elastic moduli but the simple p_m will be retained here.

Rebound measurements were made to check that extrapolation of the creep curves to small times was justified. The total duration of impact in the rebound measurements was measured by a decade counter which counted only where the steel ball completed the circuit between two very fine wires lying on the surface of the specimen. The duration was of the order of 10^{-4} sec. or less (unfortunately, the counter could not count less than 10^{-4} sec.) for a $^1/_4$ in. ball dropped from a height h of 300 mm. The time t taken for the ball to reach maximum penetration Z is given by $\Delta t = Z/\sqrt{2gh}$ assuming the deceleration is constant, where h is the height from which the ball is dropped. The work done during penetration $\int_0^Z \bar{p}A\ dz =$

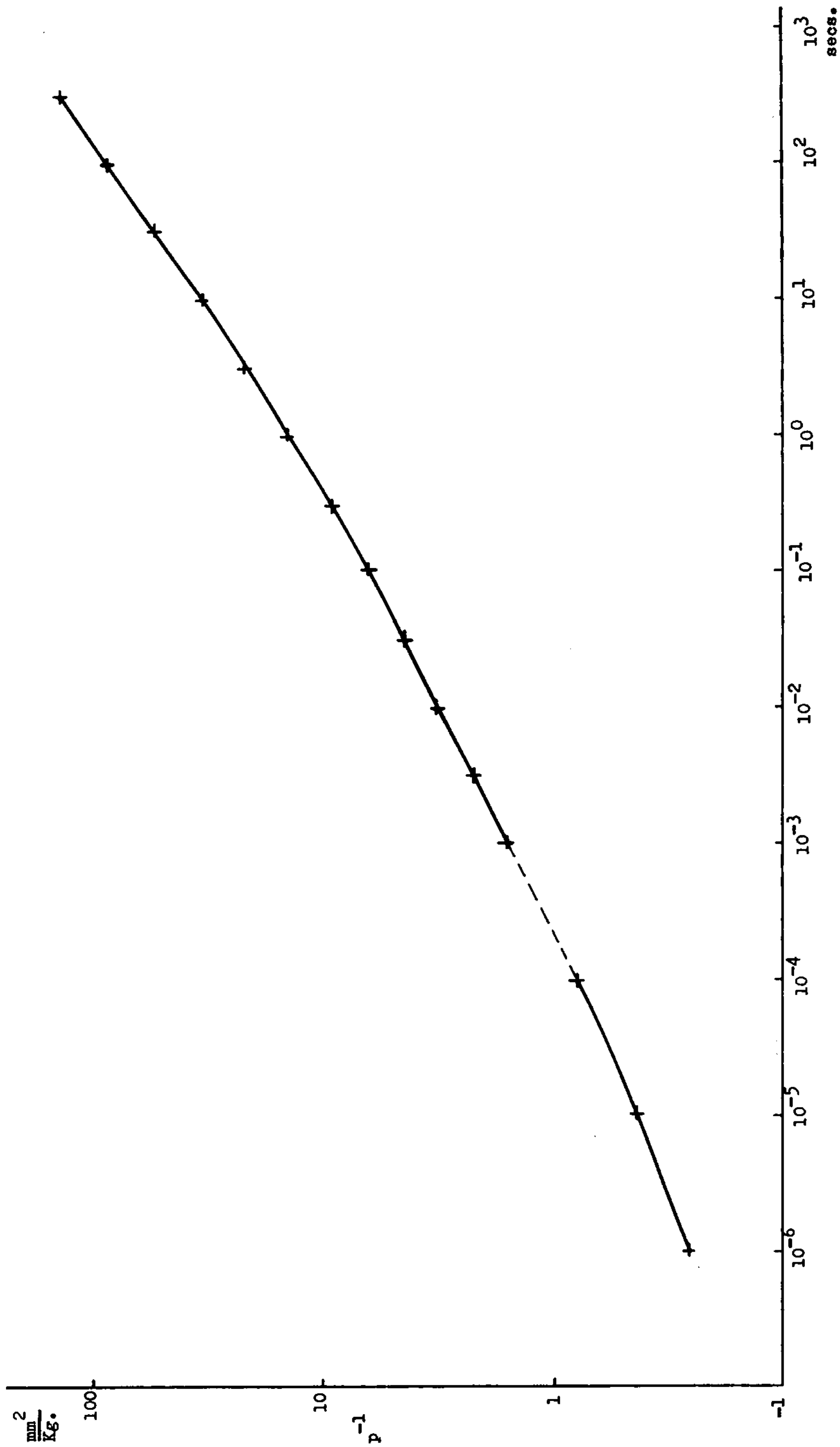

Fig. 4. Rebound and penetration master curves on common axes.

mgh so $\bar{p} = mgh/V$ where $\bar{p}$ is the mean pressure over the instantaneous projected area (assumed constant during indentation) and V is the maximum volume of the indentation of the ball of mass m.

Assuming the surface is dragged down in the same way as in the creep measurements $\bar{p} = mgh/2V$ and $\Delta t = \sqrt{2z}/\sqrt{gh}$ we put $\bar{p} \simeq \bar{p}_R$ the rebound hardness.

The $^1/_4$ in. ball was dropped from a height of 300 mm. and the area of contact was measured. Measurements were made on the same specimens and at the same temperatures as the creep measurements. The times Δt were estimated from the equation given and, by assuming that the time and temperature shifts for the rebound measurements were the same as for the creep measurements, the values of p_R^{-1} were plotted against temperature, the temperatures being adjusted to give a constant time Δt. Typical results are shown in Figure 3, together with the necessary shifts to give superposition; these shifts are similar to the penetration shifts. In Figure 4 log p_m^{-1} and log p_R^{-1} are plotted, with the same units, against log time for the 100% pitch at 40°C., the curves being obtained by applying the appropriate shifts to the master curves. Unfortunately, the curves do not overlap, but it can be seen that they can be extrapolated to merge into one another.

Thus both the creep and rebound curves appear to fall on a common master curve, and the shifts along the log time axis necessary to give superposition for a given change in filler content are approximately the same for both curves.

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Synopsis

The time-temperature superposition principle appears to apply to filled materials, a change in the proportion of filler being equivalent to a shift along the time axis.

Résumé

Le principe de superposition semble s'appliquer aux matériaux porteurs de charges; un changement dans la proportion de la charge est équivalent a un glissement le long de l'axe du temps.

Zusammenfassung

Das Superpositionsprinzip lässt sich auf füllstoffhaltige Systeme anwenden; eine Anderung des Anteils an Füllstoff ist einer Verschiebung entlang der Zeitachse äquivalent.

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