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Pressure Relaxation

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SUMMARY

Data on relaxation properties of elastomers may be obtained by a method based on the measurement of compressed air leakage pressure at a point on a flat face of a compressed test piece. This pressure can be measured without removing the test piece holder from any conditioning medium and by means of very simple apparatus, details and use of which are described.

Some discussion is made of a possible qualitative relationship between stress and pressure relaxation.

Examples of results obtained on test pieces in most common environments are given and discussed.

1. INTRODUCTION

There are many suggested methods for an evaluation of viscous and permanent deformation of elastomeric vulcanizates giving results useful for comparing life and operation of articles in various applications.

For instance, stress relaxation in compression[1] is normally indicated as the most appropriate test method for sealing articles, to assess the permanence of a sealing stress adequate to prevent fluid leakages; sometimes a service life of 20 or more years must be

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provided, and because of this experimental data were extended by Meier *et al.*[2] up to 16 years. The nature and temperature of the fluid may have a significant effect on stress relaxation itself; as a consequence results in conditions more closely resembling the application should be obtained, as stated by Derham,[3] by carrying out such measurements with the elastomer contacting the fluid involved.

However, the application of compression stress relaxometers, an extensive review of which may be found in a paper by Brown and Bennett[4] or in the textbook by Brown,[5] has been delayed because of the cost of such devices, frequently involving the use of an electronic dynamometer and sometimes special conditioning cabinets, and because of operational difficulties such as friction or erratic electrical contacts.

In fact one of the criteria of selection of such methods is, for obvious economic reasons, their simplicity. This is why the compression set test at high[6] and low[7] temperatures is very widely used whilst compression stress relaxation has only a limited application, in spite of the different meaning of the two tests.

It occurred to us that, instead of measuring the total compression force on the end of a cylindrical test piece, the measurement of the local pressure at one point, e.g. its centre, could be made with less expensive equipment, as frequently as necessary and in various environments.

2. PRINCIPLE OF OPERATION

As a practical procedure for measuring local pressure on the centre of the circular end of a compressed cylinder a method, formerly developed by Minotti[8] for measurement of pressure in moulds, has been used.

It consists essentially (Fig. 1) in supplying compressed air, finely controlled through a needle valve, to a precision pressure gauge connected by thin tubing to a small hole facing the end of the compressed test piece. As soon as air leaks out of the hole, the valve is closed leaving on the gauge the reading of leakage pressure.

The equipment beyond the valve up to the test piece must be perfectly airtight and its internal volume must be kept as small as possible (e.g. less than 50 cm^3). This volume not being negligible,

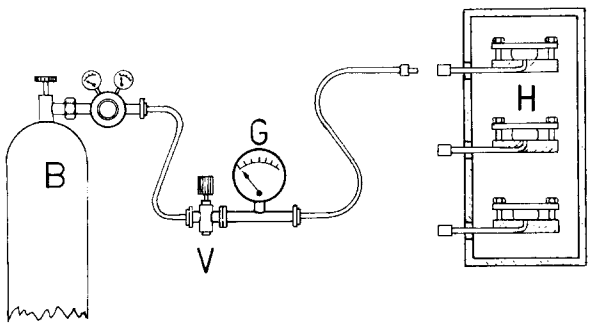

Fig. 1. Layout of the measuring device: B, compressed air bottle and pressure reducer; V, needle valve; G, pressure gauge; H, test piece holders in conditioning cabinet.

and also because of the possibility of some surface effect, the leakage of air between test piece and metal compression plate does not stop immediately when the valve is closed; there is a 'trail', which is normally of short time constant.

To obtain reproducible readings on the gauge a definite time must elapse between valve closure and gauge reading; a convenient value of this time has been found to be 1 min, and this has been used throughout.

The same equipment, including compressed air bottle, needle valve, pressure gauge and tubing, may be successively switched on to many test pieces, compressed in suitable holders, by means of releasable or 'rapid' couplings. The test piece holders, provided with the necessary lengths of tubing, may be kept in any conditioning cabinet or container of liquid.

3. TEST PIECES AND HOLDERS

The test pieces could take various forms, including finished articles, e.g. O-rings, but for general-purpose vulcanizate characterization the well-known compression set[6] cylindrical test pieces in their large (29 mm diameter; 12·5 mm height) and small (13 mm diameter; 6·3 mm height) types seem the most suitable. The applied compression strain may take the customary standard values of 25% or 40%.

The corresponding holders may accommodate single or multiple test pieces, one hole and tubing per piece being necessary. In the

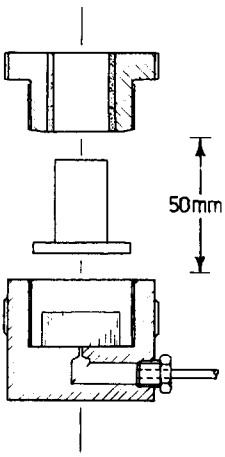

Fig. 2. Single-place adjustable test piece holder.

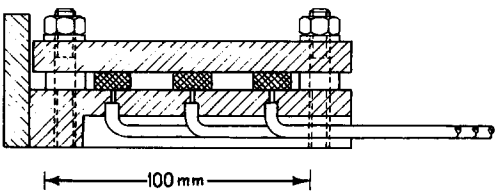

Fig. 3. Three-place test piece holder.

following experiments two forms of such holders have been designed and used.

The first (Fig. 2) is for a single large or small test piece and has one sliding compression plate adjustable by means of a fine pitch thread; this allows measurements in a dynamometer of total force and its correlation with pressure, but is less convenient for pressure measurements because of the friction torque in closing and opening.

The other (Fig. 3) is for three test pieces; it consists of two plates with spacers and closing bolts; a simple mask is needed for centering small test pieces during closure. The long edges can be rounded to facilitate introduction into cylindrical containers or tubular ovens.

The end holes facing the test pieces are 0·5–1 mm diameter, connected to copper tubing (3 mm outer diameter).

The difficulty which bears upon compression set and compression stress relaxation measurements is uncertainty as to the homogeneity of the deformation in a compressed cylinder. Attempts to avoid it variously by bonding or using sandpaper or lubricants have been made, but it is not removed by the proposed type of measurement; lubrication may be applied to the ends to facilitate their expansion or, on the contrary, blocking seats may be used. Comparisons may be made only with similar testing conditions.

As regards temperature conditioning in air, it must be noted that the holder, as in compression set and stress relaxation tests, has a

mass approaching 2 kg of steel, and if introduced cold to the oven needs an appreciable time (3–4 hours) before the test pieces reach a steady-state temperature.

If the holder has been preheated and the introduction of test pieces requires only a short time (less than 5 min), the time to steady state may be substantially reduced (down to about 1 h); if the holder is immersed in a thermostatted liquid, with which the thermal exchange is much more effective, 10–20 min are sufficient.

4. RANGE OF PRESSURES

The reading which is taken after 1 min is, for the initial state of a vulcanizate, loosely dependent (Fig. 4) on hardness and strain; the following successive readings show the relaxation due to compression and environment.

For most cases the measured values go from about 0·05 MPa to about 3 MPa; consequently it is convenient to provide gauges for a few different full scale ranges.

It has to be noted that, when making a single measurement, an overpressure is always reached before the leakage of air takes place, because of sticking between rubber and metal; this overpressure is

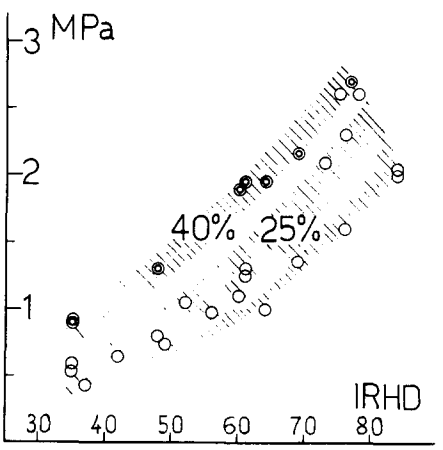

Fig. 4. Range of initial pressures for vulcanizates of different hardnesses and for 25% or 40% compression strain.

normally 10–20% higher than the final measured value, but in some cases overpressures of 50% have been needed.

To cover most practical cases a maximum pressure of 10 MPa of compressed air supply is advisable; the volume of air used being very limited, an ordinary bottle may last for some hundreds of measurements.

5. COMPARISON WITH STRESS RELAXATION

It has already been noticed that compression stress relaxation tests imply generally expensive equipment and difficulties in obtaining precise and reproducible results.

Notwithstanding that this pressure relaxation test is being suggested as an alternative to compression stress relaxation, no strict comparison can be expected between the two tests, mainly because of the well-known indetermination in the strain distribution of a compressed cylinder. The importance of this fact deserves further consideration.

The ends of unstrained large and small cylindrical test pieces (Fig. 5) have a nominal surface area A_0 of, respectively, 660 mm^2 and 133 mm^2.

Applying the hypothesis of perfectly free ends and homogeneous strain e, the surface area under strain becomes:

$$A_f = A_0/(1-e)$$

For $e = 25\%$ and the same test pieces, A_f is, respectively, 880 mm^2 and 177 mm^2.

The other extreme hypothesis is the one in which the ends are fixed. In this case an apparent area A_b can be obtained as the ratio of the total force to pressure at the centre of the test piece. The approximate method developed by Gent and Lindley[9] which provides a pressure distribution as the sum of a constant term and a parabolic term gives, for a cylinder of diameter D and height H, this result:

$$A_b = A_0 \frac{D^2 + 8H^2}{2D^2 + 8H^2}$$

For the test pieces this is, respectively, 470 mm^2 and 99 mm^2.

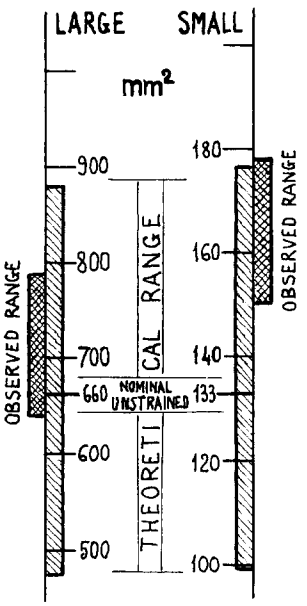

Fig. 5. Apparent area of large and small test pieces.

Experimentally, an attempt to evaluate the importance of this phenomenon has been made using the test piece holder with sliding plate (Fig. 2). The measurement of force showed some hysteresis, whilst the simultaneous measurement of pressure was neat and more reproducible.

The range of results observed on a few vulcanizates are shown in Fig. 5; this range is only an indicative one because of uncertainties in measurement of force in the cupped lateral shape of small test pieces and the limited number of tests.

In addition, it must be noted that an initial determination of apparent area would not be sufficient for a reasonably precise calculation of successive values of force from pressure, because the end of a test piece facing the hole tends, after repeated air leakages, to increase somewhat in diameter, the effect being greater in the presence of a swelling liquid.

Summarizing, whilst the behaviour of vulcanizates tested for stress or pressure relaxation is qualitatively similar, the same cannot be said of quantitative results and it appears convenient to treat the two methods of test separately.

6. SURFACE EFFECTS

As in other physical determinations erratic and ill-defined surface effects may appear.

It has previously been noted that, when pressure is applied for the measurement, an overpressure is reached before leakage. This has been ascribed to a sticking between rubber and metal which is lost when overpressure is sufficient and recovered shortly after the needle valve is closed. This recovery is fairly definite in most cases, but at low temperatures, probably because of freezing of slight surface exudates or extraneous matter, the recovery is much delayed. Of course, even in those cases, by reading 1 min after closure a definite value is obtained.

Occasionally, for vulcanizates showing significant sticking, some stray values have been obtained, but repetition of measurement has permitted these to be recognised. It does not seem, at least in most cases, that high or low surface sticking prevents regular measurements of pressure relaxation.

Some tests have been performed with ground test piece ends in order to assess the effect of surface finish. A larger variability of results does appear and it seems preferable to use test pieces with moulded ends.

7. APPLICATIONS

The method described for measuring pressure relaxation may be applied to various kinds of environment and to different temperatures and also to any time/environment sequence.

Some examples are collected in the following paragraphs. They refer sometimes to the large, and more frequently to the small, compression set test piece and to a nominal strain of 25%. It has not been thought worthwhile to take into account small differences in height of test pieces, the behaviour of those having different height being substantially parallel.

A logarithmic scale of times is used for the diagrams, as is customary in relaxation and creep phenomena, when time is the independent variable.

7.1. Constant deflection in air at room temperature

This is the simplest application and there are no delays for steady-state temperature of test pieces. For times of up to about

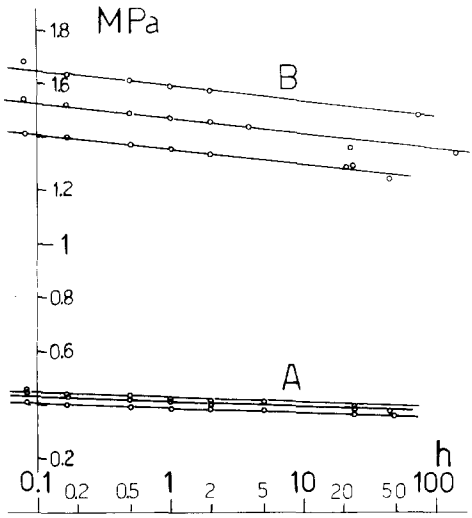

Fig. 6. Pressure relaxation at 23 °C of large test pieces of vulcanizates: A, NR-based, 37 IRHD and B, NR-based, 76 IRHD.

100 h the pressure relaxes (Fig. 6) following an approximately semilogarithmic law.

Instead of a full diagram, a relative pressure decay over a definite time:

$$\Delta = (p_f - p_i)/p_i$$

(p_i = initial pressure; p_f = final pressure) may summarize the results. The diagrams, referring to a logarithmic decade of time, give 4·5% per decade for vulcanizate A and 3·8% per decade for vulcanizate B.

7.2. Constant deflection in air at high temperature

The pressure relaxation in this case cannot, at least for fairly long times (some hundred hours), be approximated with a semilogarithmic law; the results in Fig. 7 generally show a definite curvature.

It would be possible to develop an appropriate analytical representation of the experimental data; if these are referred to several temperatures, they very probably can be treated by the reduced variable method, as has been done for stress relaxation.[2] Further, a single value can be derived from values of pressure at three different

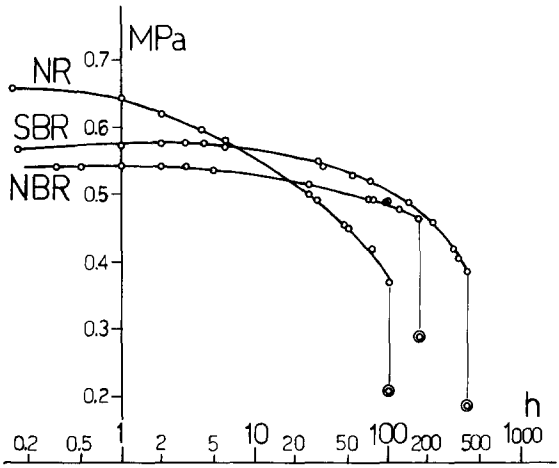

Fig. 7. Pressure relaxation at 100 °C in air of three vulcanizates based on different elastomers. Averages of three small test pieces. Points at lower right were obtained after cooling to 23 °C.

times (e.g. 2, 20 and 200 h):

$$\Delta = \frac{(p_2 - p_{200}) - \left(p_{20} - \frac{p_2 + p_{200}}{2}\right)}{\frac{p_2 + p_{200}}{2}}$$

to take account of the curvature. The diagrams reported (Fig. 7) give respectively 13% for NBR, 21% for SBR and 67% for NR.

The pressure relaxation may be followed when the test pieces are returned to ambient temperature: a further strong decrease in leakage pressure takes place. As would be expected, a partial recovery may be obtained by releasing and restraining the test pieces.

7.3. Constant deflection in oil at high temperature

In this case both relaxation and swelling take place with different intensities and times.

The example reported (Fig. 8) shows that, after a period during which an effective pressure relaxation appears, there is an increase of pressure due to swelling. Here also when the temperature is lowered there is a strong decrease of leakage pressure.

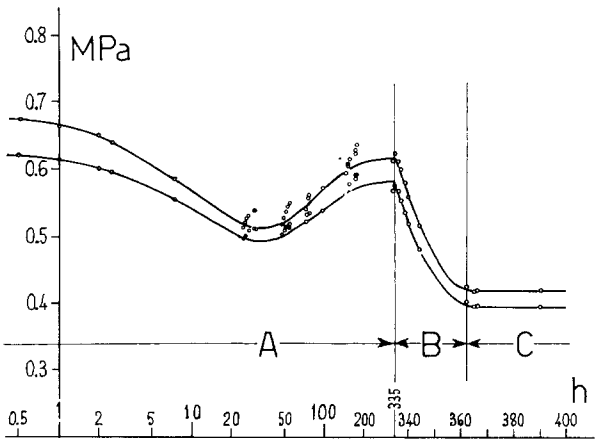

Fig. 8. Pressure relaxation in oil (ASTM No. 3) for two SBR small test pieces: A, relaxation and swelling at 100 °C; B, cooling from 100 °C to 23 °C in oil; C, relaxation at 23 °C in air.

It has been observed that, when swelling overcomes relaxation, a frequent repetition of measurements increases the leakage pressure over an average behaviour; the phenomenon may be viewed like a 'pumping' of oil in rubber, but it has not been investigated further. In addition, there is a very noticeable asymmetry of swelling, which is larger on the ends of test pieces subjected to air flow.

7.4. Constant deflection at low temperature

Using an ethanol/dry ice bath it has been possible to measure leakage pressure variation at low temperatures with the present method.

Two vulcanizate compounds have been used, one based on a polybutadiene and one based on EPDM. The small test pieces were compressed to 25%, kept at ambient temperature for 1 h and then put in the bath at −65 °C. The temperature of the bath was then slowly increased so as to reach +30 °C in about 5 h. Some relaxation may have taken place during this time, but the main effect is due to glass transition and the results (Fig. 9) show rather different behaviour of the two vulcanizates.

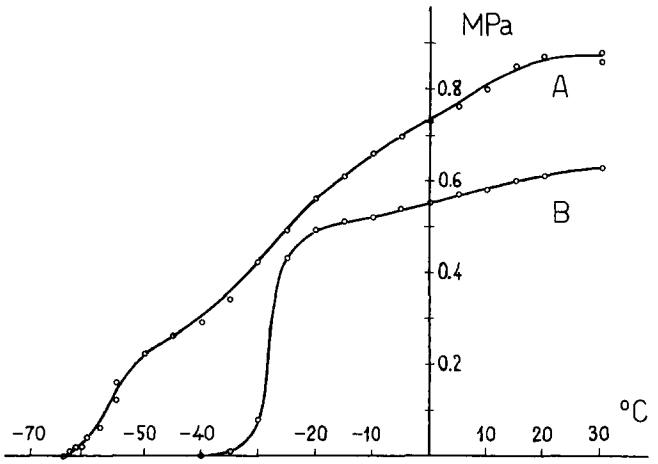

Fig. 9. Leakage pressure recovery by increasing temperature for vulcanizate A (EPDM based) and B (PB based). Averages of three small test pieces.

Two observations may be in order. The first is the shortness of time needed to reach steady state at each temperature, due to the contact of pieces and holders with a strongly stirred bath. The other is the more stringent need, as noted before, to make the readings with the definite 1 min delay after valve closure.

8. CONCLUSIONS

The tests made to measure leakage pressure and to follow its behaviour in different conditions have shown the simplicity and flexibility of the equipment used.

The repeatability of the measurement is fair, but a longer and diversified experiment is needed to investigate the effect of surface sticking and end swelling in the comparison of different vulcanizates. This experimentation should assess the effective technological value of pressure relaxation; it does not seem that this value should be inferior to, for example, that of compression set.

The features of remote measurement and inexpensive equipment warrant a further testing programme, chiefly for those cases where compression stress relaxation is important but difficulties of environment and equipment are present.

9. ACKNOWLEDGEMENTS

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