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New Static and Dynamic Stiffness Testers

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Synopsis

Instruments have been developed for the testing of stiffness of polymers in various gaseous environmental "atmospheres" over a large range of temperatures. They are based on the cantilever principle, where a small strip of a specimen is deflected statically or periodically. Changes in stiffness are measured as function of the bending force or power input, respectively. The dynamic instrument responds very sensitively to the onset of cracking in specimens due to ozone exposure. The static instrument is well suited for measuring the onset of rapidly increasing stiffness as temperatures are lowered.

DYNAMIC STIFFNESS TESTER

Apparatus

The dynamic instrument is shown in Figure 1. It consists essentially of an eccentric rotor (E) made of Teflon, which bends periodially a strip of polymer (S) as it rotates. The rotor and sample are housed in a glass container (J); the rotor is suspended in this container from an aluminum plate serving as a lid; gas tightness is obtained by Viton O-rings (L) between the flange of the glass container and the metal lid which are pressed together by a metal collar and screws. The glass container is provided with a gas inlet (M) and outlet (L) and also with a tube reaching down inside the container for a thermocouple to be located near the specimen. The lower part of the glass container can be removed so that the specimen can be easily replaced by another one. The shaft (D), carrying the rotor (E), is rotated by a d.c. motor (Globe Industries, Inc., Dayton, Ohio, nominal operating voltage 27 V; the motor has a gear arrangement); this shaft runs in Teflon sleeves (H). The whole instrument is thermostated in an air bath to ±1.0°C, only the motor is located outisde this bath at room temperature. Any desired gas "atmosphere" can be supplied (e.g., O_3 plus air, NO_2 plus air, etc.). Other parts of the apparatus are indicated in Figure 1 (see also Fig. 2a).

A constant d.c. voltage is maintained on the motor by a constant voltage supply unit (Harrison Laboratories, Inc., 0–18 V, 0–1.8 amps). The current from the source is kept constant by a Sola transformer. The speed of rotation remains constant for any one applied voltage (800 to 850 rpm for 15 V; 550 to 580 rpm for 12 V; measured with a stroboscope). However,

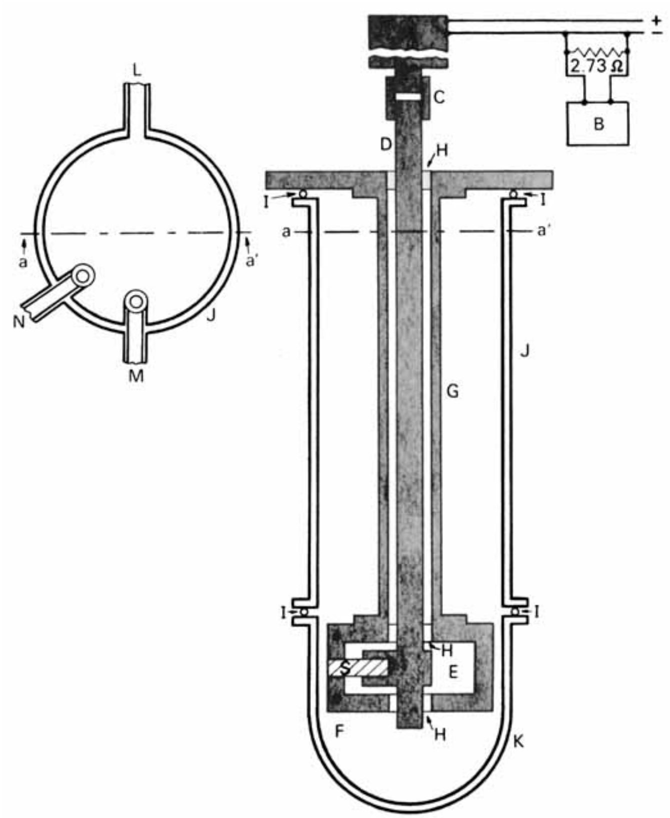

Fig. 1. Dynamic stiffness tester.

the current changes with the applied load. This change in current (in effect in watts) is taken as a measure of changing stiffness. A resistance ($R = 2.73\ \Omega$; see Fig. 1) is inserted parallel with the circuit leading to the motor, and the voltage across this resistance is measured with a Sanborn recorder Model 150. This voltage has a magnitude of ca. 10 to 20 mV. The relative rotor and sample positions are indicated in Figure 2a.

The stiffness of a polymer specimen can be evaluated as follows: Young's modulus E is given for maximal bending by

$$E = \frac{4L^3F_{\max}}{\lambda_{\max}BD^3}\ \text{kg/cm}^2 \qquad (1)$$

where L, B, and D are the length, width, and thickness of the sample, in cm; F is the force for maximum bending, in kg; $\lambda_{\max}$ is the corresponding bending arc, in cm, taken as a straight line (eccentricity of rotor 0.6 cm); and $\lambda_{\max}$ is an apparatus constant. Further,

$$F_{\max}\left(\frac{dS}{dt}\right)_{s_{\max}} = \frac{EBD^3\lambda_{\max}}{4L^3}\left(\frac{dS}{dt}\right)_{s_{\max}} \qquad (2)$$

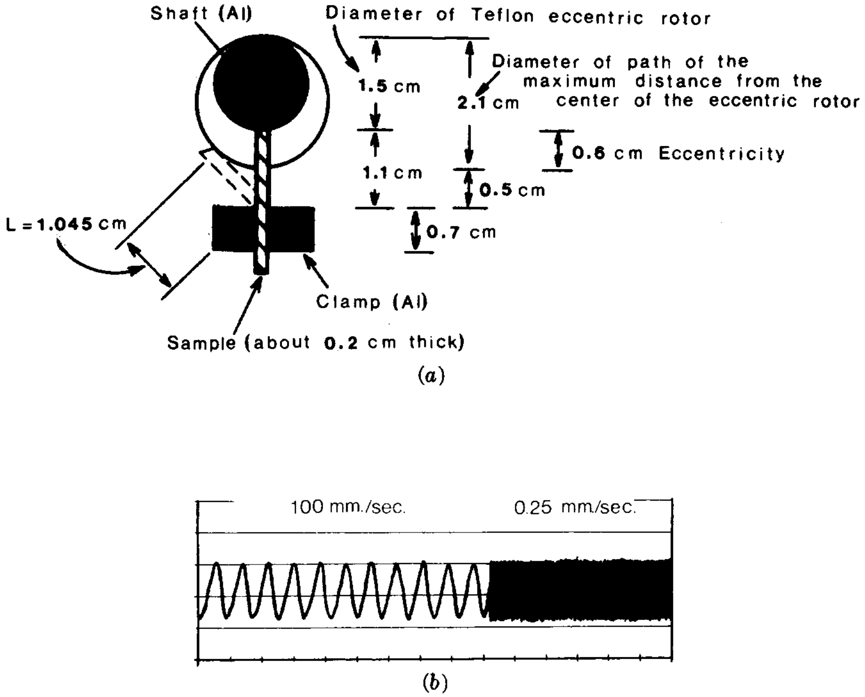

Fig. 2. (a) Details of eccentric rotor and sample. (b) Recording trace of dynamic tester.

here $(dS/dt)_{S_{\max}}$ is the linear rate of bending at very near maximal bending. Equation (2) can be written in terms of watts,

$$W_{\max} = F_{\max}\left(\frac{dS}{dt}\right)_{S_{\max}}$$

Hence,

$$E\left(\frac{dS}{dt}\right)_{S_{\max}} = \frac{4L^3W_{\max}}{\lambda_{\max}BD^3}.$$

As $\lambda_{\max} \approx L \cdot \alpha_{\text{radians}}$ and α_{radians} = constant, one obtains

$$\text{measure of stiffness} = E\left(\frac{dS}{dt}\right)_{S_{\max}} \alpha_{\text{radians}} = \frac{4L^2W_{\max}}{BD^3}. \tag{3}$$

As 10.2 watts = 1 kg-cm/sec, eq. (3) can be expressed as

$$E' = E\left(\frac{dS}{dt}\right)_{S_{\max}} \alpha_{\text{radians}} = \frac{4L^2P}{BD^3}\text{ kg/cm-sec} \tag{4}$$

where P is the power used at maximum bending in kg-cm/sec at exposure time t; all lengths are expressed in cm.

Experimental Results

E' has been plotted versus time of exposure for some typical samples for a number of temperatures in the presence of air and air plus ozone, respectively, in Figures 3 to 5. Watts were experimentally obtained as follows:

$$\text{watt} = \text{I}\cdot\text{V} = \frac{(\text{maximum height of recording trace, in mm})\cdot 2 \times 10^{-3}\ \text{v}}{2.73\ \Omega}\cdot\text{voltage applied to motor}$$

where V and I are the voltage applied to the motor and its current, respectively (see recording trace Fig. 2b). The height of the recording trace is measured 40 sec before and 40 sec after the time of E' at time t. Standard deviations are indicated in the various figures. The polymer best suited to check the proper functioning of the apparatus is Goodrich's Natural Rubber Compound 45016-3. This elastomer is chosen as it is very sensitive to small

TABLE I

Dimensions of Samples, Experimental Temperatures and Applied Voltages

Specimen sample	Width B, cm	Thickness D, cm	Temp., °C	Applied voltage, V
14	1.32	0.1850	−20	15.0
15	1.39	0.1877	23	11.8
19	1.47	0.1851	1	15.15
	± 0.01 cm	± 0.005 cm	± 1°C	± 0.1 V

[a] L was in all cases 1.045 cm.

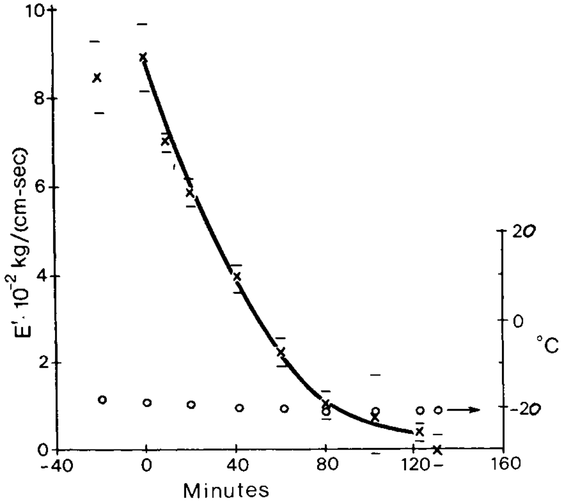

Fig. 3. Natural rubber compound (Goodrich 45016-3) exposed to ozonized air at −20°C (O_3 ca. 59 ppm, dynamic stiffness tester); "negative" times are periods before exposure, O_3 is introduced at t = 0; (×) points derived from heights of tracings, (—) standard deviations; (O) indicates temperatures (right ordinate).

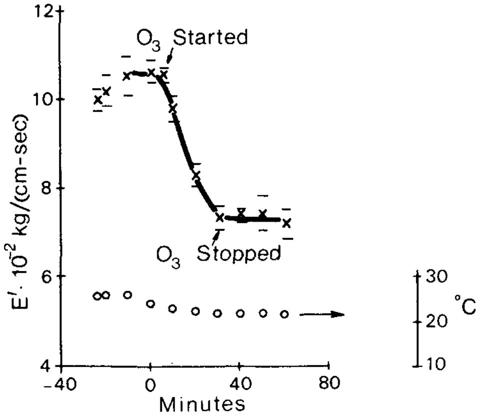

Fig. 4. Same as Fig. 3; + 23°C, shows effect of stopping O_3 supply.

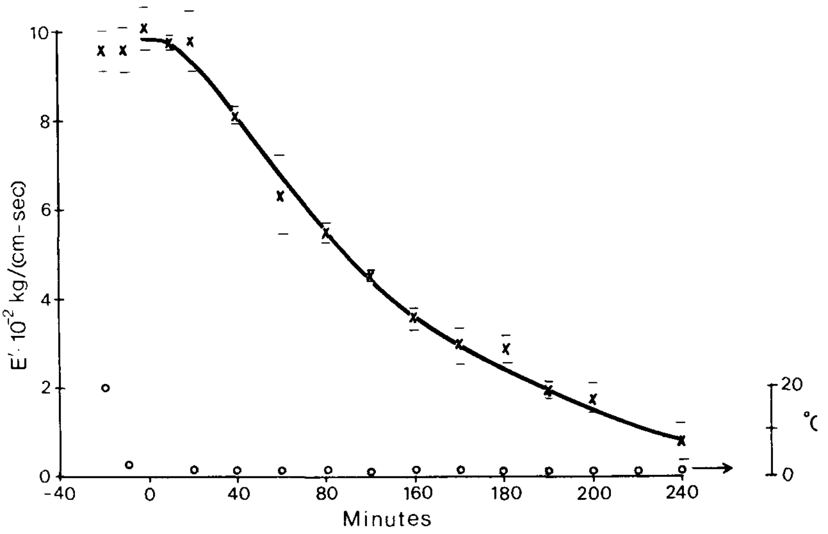

Fig. 5. Same as Fig. 3; + 1°C.

amounts of ozone in the air, and the response of the apparatus to changes in stiffness can therefore be properly tested with this polymer. The dimensions of some of many specimens of this polymer which were investigated are in Table I; applied voltage and temperatures are also included.

E' depends also on the speed of rotation as is shown below,

Sample no.	rpm	*E'*, kg/cm-sec[a]
11	800-850	229
15	550-580	159

[a] Measured at 20% deterioration.

Speeds of rotation decrease by about 10% when a load is applied. E' values for 50% deterioration (decrease of initial E' by $^1/_2$) are given below:

Testing temp., °C	23	20	10	1	−10	−20
$E'_{1/2}$, kg/cm-sec	136.9	123.4	70.2	77.8	74.4	147.9

The $E'_{1/2}$ values pass through a minimum with temperature.

Samples crack on exposure to ozone. The crack always starts at the edge where the specimen is clamped for temperatures of −10°C and −20°C. The crack spreads from this location to a distance of ca. 5 mm from this edge at temperatures of 1°C, 10°C, 20°C, and 23°C. A sample tested at 1°C (Fig. 5) showed a large crack at the edge of the clamp and some cracks in the neighborhood. The onset of cracking at the edge of the clamp manifested itself at once in a sudden decrease in E'. As soon as ozone is removed, further deterioration of the sample (i.e., decrease in E) ceased (see Fig. 4). The open circles indicate the temperature near the specimens; temperatures decreased (negative times) until at zero time the desired temperature was reached when the air was replaced by ozonized air.

du Pont's EPDM compound 5109D-4420 proved remarkably stable in the presence of ozone (ca. 59 ppm) at 26°C and 630 rpm; no detectable change in E' values could be observed during an exposure of 1321 min.

STATIC STIFFNESS TESTERS

Apparatus

The essential principle of the apparatus is as follows. A small strip of a polymer sample is bent (cantilever) by a definite amount. The force needed to accomplish this is measured and the changes in this force due to environmental effects are recorded as a function of time. Simultaneously, the sample experiences a certain amount of permanet set. These measurements are carried out as a function of temperature, pollutant concentration, and time. Stiffness of the polymer (Young's modulus) can be deduced from such experiments. The apparatus is depicted in Figure 6. It is contained in a glass jacket, part of which can be removed for insertion of new samples. This container is thermostated to better than ±1°C. It is provided with a gas inlet and outlet in order to provide the desired atmospheric environment. A thermocouple is located near the test sample which is clamped tightly at one end. A Statham transducer No. G10B-0.3-350 is used for measuring the force and bending distances applied to the specimen via a glass tube (ca. 3 g). The transducer is connected to a Sanborn recorder Model 150.

The mode of operation of the instrument is as follows: the transducer is moved vertically down by a special device applying a micrometer screw. In the present experiments, this movement amounted to 0.5 mm (the micrometer screw can be read to within ± 0.005 mm). This movement is distributed between bending of the polymer sample and movement of the trans-

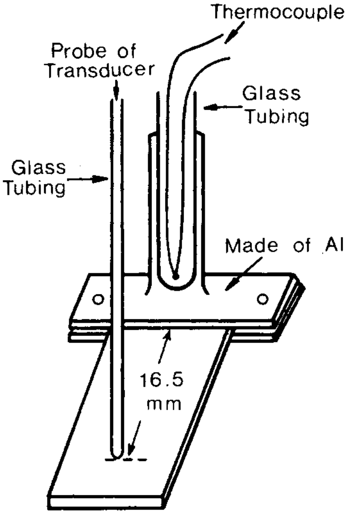

Fig. 6. Static stiffness tester.

ducer probe in an upward direction. The transducer is calibrated in terms of force (grams versus scale divisions) and also in terms of actual movement at the point of contact between the probe and glass tube as a function of force. The calibrations result in linear relations. The following distances are involved:

distance of transducer = distance of probe + distance of sample
A = B + C

Stiffness E (Young's modulus) can be evaluated as follows: For a cantilever beam, one has

$$E = \frac{4FL^2}{BD^3\alpha_{\text{radians}}} \text{ kg/cm}^2 \tag{5}$$

where F is the applied force, in kg; L, B, and D are the length, width, and thickness of the specimen, in cm; $\alpha_{\text{radians}} = \lambda'/L$ where λ' is the bending arc taken as a straight line because of the very small extent of bending.

If the moment is always expressed as that pertaining to 100 scale divisions the recorder (i.e., M'), eq. (5) becomes

$$E = \frac{4L}{BD^3} \times \frac{M' \cdot \text{(scale divisions recorded)}}{100\ \alpha_{\text{radians}}} \text{ kg/cm}^2. \tag{6}$$

The initial load on a specimen was always of the order of 10 g.

Experimental Results

Dimensional details of some of the many polymer samples investigated are given in Table II. All samples show a permanent set after bending; this is also indicated.

TABLE II
Dimensions and Per Cent of Permanent Set of Typical Samples[a]

Name	Width, cm	Thickness, cm	% of Permanent Set (av.)
Goodrich's 45016-3	1.02	0.186	13
du Pont's EPDM 5109D-4420	1.00	0.231	27
Linear polyurethane	1.00	0.042	17

[a] Distance L between the point of clamping and the point of contact of the glass tube, 1.65 cm, for all samples. All samples were tested in pure air as function of temperature.

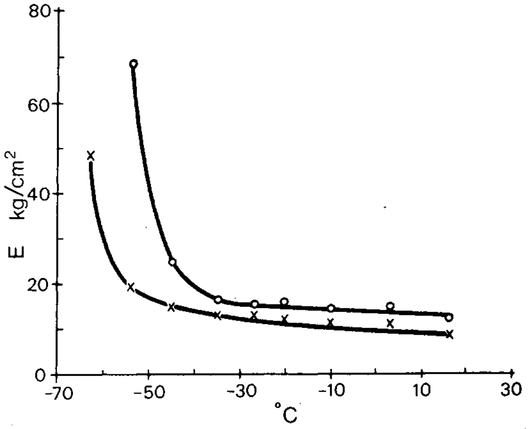

Fig. 7. Natural rubber compound (Goodrich 45016-3) exposed in air over a range of temperatures (static stiffness tester): (O) measurements made immediately after bending (4 to 5 sec); (×) 5 min after bending.

Stiffness E, in kg/cm^2, plotted as a function of temperature is given in Figures 7 to 9. Points drawn as open circles have been measured at $t = 0$, i.e., immediately after bending the sample, which takes 4 to 5 sec; crosses represent measurements after 5 min of bending.

All curves are characterized (except Fig. 9, polyurethane) by a rapid increase in stiffness over a definite range of low temperatures. This increase indicates that the material becomes quite brittle as the temperature decreases beyond a certain value.

The best of the materials investigated from the point of view of stiffness as function of temperature is Goodrich 45016-3, closely followed by du Pont EPDM compound 5109D-4420 (this does not indicate anything concerning characteristics in deleterious environments). These samples start to increase rapidly in stiffness at temperatures around −40°C and −30°C, respectively. Goodyear's H-369 and H-384 (not shown), for instance, show rapid increases already around 0°C and +10°C, respectively. Thus, these tests screen the materials as far as stiffness as function of temperature is concerned.

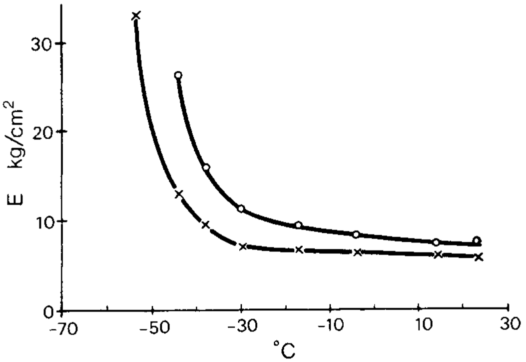

Fig. 8. du Pont EPDM 5109D-4420; same as in Fig. 7.

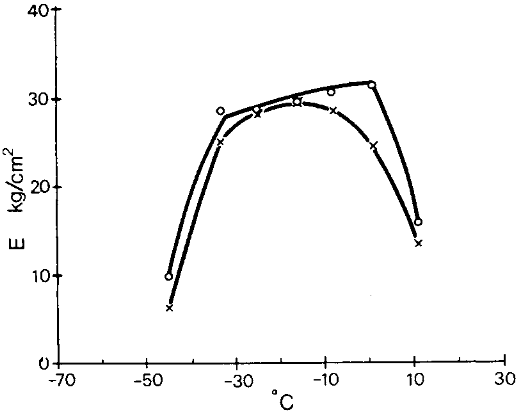

Fig. 9. Linear laboratory polyurethane; same as in Fig. 7.

Linear polyurethane, prepared in our laboratory[2] shows characteristics different from those of the commercial materials (see Fig. 9). The curves are similar to those obtained previously for tensile strengths as function of temperature, except that the maxima are shifted from about +10°C for tensile strength to ca. −10°C to −20°C for the stiffness values.[1]

Figure 10 shows the effect of ozone (ca. 500 ppm) on Goodrich's Natural Rubber compounds 45016-3. As soon as the container is filled with O_3-containing air, the stiffness rises, eventually reaching a plateau. The surface of the sample showed a grayish appearance after exposure, which consists probably of a protective oxide layer.

CONCLUSIONS

The static and dynamic instruments described here perform satisfactorily over a wide range of temperatures and in various gaseous "atmospheres." The static stiffness tester is especially suited for the indication of the onset of rapid increase in stiffness with decreasing temperature in a pure air

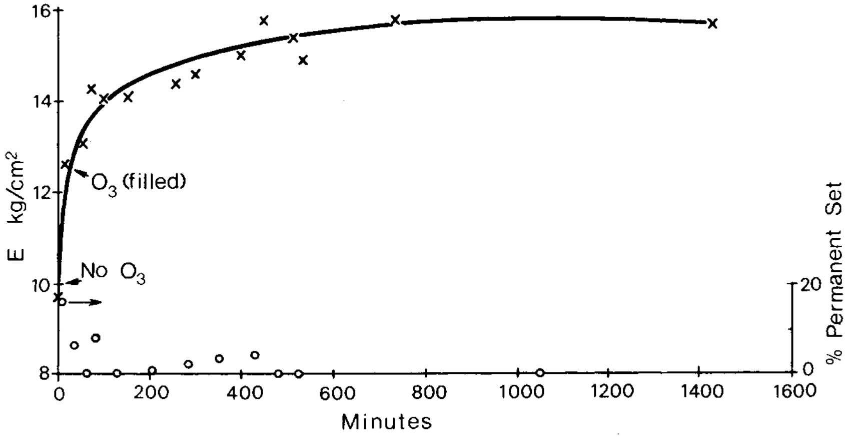

Fig. 10. Effect of ozone on Goodrich's Natural Rubber compound 45016-3, 25°C (static, (O) % permanent set; (X) stiffness; — = 1.70 cm, B = 1.03 cm, D = 0.1682 cm, O_3 ca. 500 ppm). Stiffness measured 5 min after bending.

atmosphere, while the "dynamic" tester is very sensitive in its response to the start of cracking of specimens due to ozone exposure. The effect of ozone is known to be due to chain scission and crosslinking of specimens where continuously new surface is exposed, i.e., where the oxide layer is formed due to the action of ozone is continuously broken by periodic movements.[3]

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