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Characterization of high-loss viscoelastic elastomers

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The behaviour of a variety of high-loss viscoelastic elastomers is described. Measurements were conducted using a novel micromechanics apparatus which is capable of creep, constant load rate, subresonant dynamic and resonant dynamic experiments in bending and torsion upon a single specimen. The range of equivalent frequency is from 10^{-6} Hz to several kilohertz under isothermal conditions.

1. Introduction

Elastomeric materials are used in a great variety of applications, some of which make use of the damping properties of these materials [1]. Several polyurethane compositions have been developed, with very high viscoelastic damping over a range of temperatures [2]. Materials of this type, as well as materials with improved compositions [3] have been found to be useful as impact absorbers in athletic footwear. Viscoelastic behaviour of some of these materials has been determined at a single frequency as a function of temperature, as well as over a narrow range of frequency at different temperatures [4]. Viscoelastic loss in these polyurethanes is high over a relatively wide range of temperatures.

Most available experimental methods for characterizing viscoelastic materials are applicable over rather restricted portions of the time and frequency domains [5]. In the case of thermorheologically simple materials, such a limitation can be circumvented by performing a series of tests at different temperatures and computing a "master curve" of effective viscoelastic behaviour. In cases for which a master curve is to be verified or in thermorheologically complex materials, direct measurements over many decades of time/frequency are required. The present work makes use of an experimental method by which viscoelastic measurements can be performed upon a single specimen, in a single apparatus, over more than nine decades of time and frequency.

2. Experimental method

The apparatus is a modified version of a micromechanics apparatus used earlier for study of microsamples of foams and composites [6]. The apparatus and data reduction techniques are described in more detail elsewhere [7–9]. The apparatus is capable of torsion or bending tests upon cylindrical specimens; torque is generated by a magnetic field acting upon a high-intensity samarium cobalt magnet fixed to the specimen end. This small cylindrical magnet (5 mm diameter, 1.5 mm thick), was found to produce a torque of 3.00×10^{-5} Nm per ampere of coil current. A thin, square mirror, 3 mm × 3 mm, was cemented on to the magnet to reflect a laser beam for angular displacement measurement. This unit, in turn, was cemented as accurately as possible on to the centre of a precision-cut plexiglas® (polymethyl methacrylate) endpiece of 6 mm diameter and 0.5 mm thick, which was cemented to one end of the specimen. The other end was cemented to a vertical brass rod in the apparatus framework. Angular displacement was measured by laser interferometry, as shown in Fig. 1. In this study, both creep and dynamic experiments in torsion were performed. Creep tests involved torque histories of risetime less than 1 sec. Data were taken from chart recorder tracings beginning at 10 sec. Control of the torque as well as a logarithmic drive signal for the recorder were provided by a Z-80 microcomputer programmed in FORTH. Creep tests were conducted over periods from 1 to 3 days. Data from dynamic tests at or below 0.1 Hz were recorded as chart recorder tracings; above 1 Hz, data were taken from an oscilloscope. Recently, a digital oscilloscope has been added to the apparatus to facilitate data collection in the intermediate frequency range 0.1 to 10 Hz. Results from creep and dynamic tests were plotted on a common frequency scale; the time, t, in creep was converted to equivalent frequency, ν, by the relation $\nu = 1/2\pi t$. As the materials examined in this study exhibited relatively little creep, no attempt was made to refine the equivalent frequency plot by Fourier transformation.

A new scheme of data analysis was applied, which permits viscoelastic results to be obtained from data taken in the vicinity of specimen resonances. At low frequencies well below any resonance, the quasistatic relation between applied torque M^* (in which the

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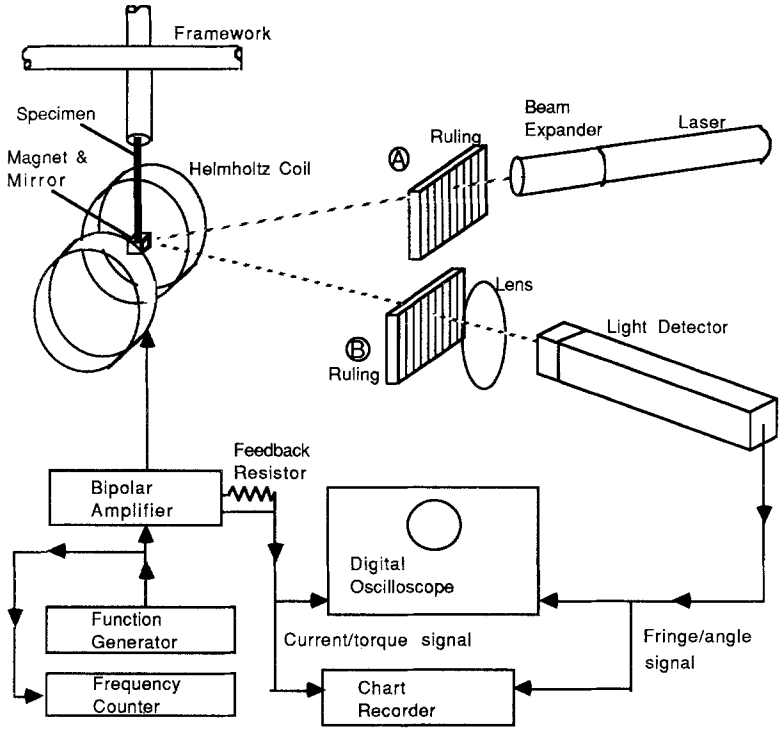

Figure 1 Experimental apparatus.

complex notation incorporates the phase relation) and observed specimen end angular displacement, Φ, in torsion is such that the complex shear modulus, G^*, is given in terms of the specimen diameter, d, and length, h, by

$$G^* = [32h/\pi d^4]M^*/\Phi \quad (1)$$

Data reduction in the vicinity of a specimen resonance was based on the following theoretical relationship [10] for the dynamical rigidity R^* at a frequency v, of a rod subjected to a sinusoidal torque M^* applied at one end and fixed at the other end.

$$R^* = M^*/\Phi = I_{sp}\varrho\omega^2 h[\cot\Omega^*/\Omega^*] - I_{at}\omega^2 \quad (2)$$

in which Φ is the end angular displacement, I_{sp} is the polar moment of inertia of the specimen, ϱ is the mass density of the specimen, ω is the angular frequency, $\omega = 2\pi v$, h is the length of the specimen, $\Omega^* = [\varrho\omega^2 h^2/G^*]^{1/2}$, and I_{at} is the mass moment of inertia of the end attachment.

Data reduction in the case of small loss, i.e. tan $\delta \ll 1$, is straightforward and is the basis for a wide variety of experimental methods [5]. For small loss, Equation 2 becomes considerably simplified in the vicinity of resonance

$$3^{1/2} \tan\delta \cong \Delta\omega/\omega_{res} \quad (3)$$

in which $\Delta\omega$ is the full width at half maximum of the dynamic compliance curve near resonance. The present experiments, however, include tests upon high-loss materials for which such an approximation is not warrantable. Consequently, the exact expression is to be dealt with in a data reduction scheme. To this end, an algorithm has been developed which can numerically invert Equation 2 using Newton's method to obtain from experimental data the complex shear modulus, G^*, of viscoelastic materials. The input data consisted of the complex shear rigidity $R^* = M^*/\Phi$, against frequency, as well as the specimen material density and the value of any attached inertia. The analysis scheme is suitable for situations in which the specimen exhibits one resonance or multiple resonances. The maximum errors in the shear modulus and loss tangent were also calculated based on the estimated errors in the attached inertia, I_{at}, and in the observed phase angle, θ. The uncertainties in G^* and tan δ were computed for display as error bars in the final results. The estimated error increases with frequency in the vicinity of resonance as a result of uncertainty in the value of the attached inertia.

In the current series of experiments upon viscoelastic elastomers, special efforts were made to reduce the inertia to the end of the specimen. Reduction in the end inertia resulted in an increase in the specimen resonant frequency and also improved the accuracy of the computed specimen material properties in the vicinity of a resonance. Because data were collected at frequencies from 0.001 Hz to beyond the lowest resonance, any reduction in end inertia resulted in an increase in the usable frequency range. End inertia was reduced by (i) using a small, high-intensity samarium cobalt magnet, 5 mm diameter and 1.5 mm thick, to generate the torque, (ii) using the smallest possible mirror to reflect the laser light to measure angular displacement, and (iii) using a thin end-piece, 0.5 mm thick, of polymethyl methacrylate (PMMA) to connect the specimen to the magnet. For comparison, a typical specimen was 6 mm diameter and from 6 to 60 mm long.

Experiments at temperatures above and below room temperature were performed as follows. A temperature probe was placed within the specimen chamber to monitor the specimen during testing. Dry nitrogen was forced at low pressure through copper tubing immersed in a bath of ethylene glycol (antifreeze). The bath was heated or cooled under temperature control with an electric 500 W heating probe or a mechanical refrigeration cooling probe. The

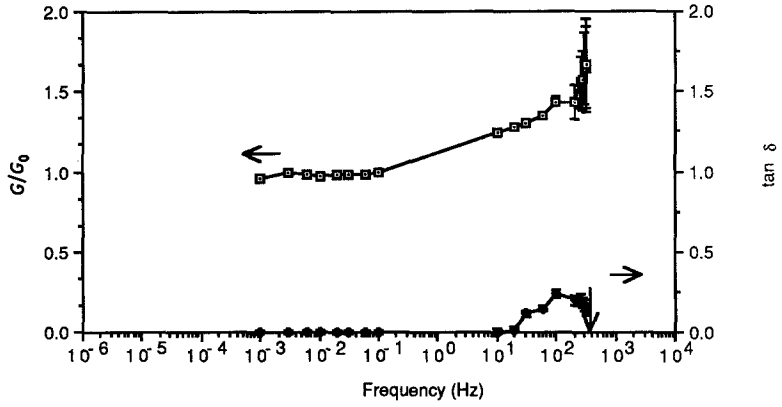

Figure 2 Viscoelastic behaviour of a silicone rubber.

temperature-controlled nitrogen was then directed via an insulated hose, to the specimen chamber.

3. Materials

The following commercially available viscoelastic elastomers were used in these experiments: RTV silicone rubber (Dow Corning, Inc), Sorbothane® (Bostik, Ltd), Viscolite® (Polymer Dynamics, Inc) and Wingfoot® (Goodyear, Inc). Materials were kept at room temperature for at least 2 weeks prior to testing to allow pre-aging.

Sorbothane is a polyurethane elastomer of nominal composition described by Hiles [2]. Viscolite polyurethane elastomers [3] are based on a mixture of linear and branched poly-oxypropylene polyols and 4,4′-diphenylmethane diisocyanate, reacted in proportions that leave a significant number of terminal hydroxyl groups untouched, but available for hydrogen bonding. The materials can contain plasticizers and fillers, depending upon the desired end properties.

Silicone rubber specimens were cast in the laboratory in cylindrical moulds of 1/8 in. diameter. Viscolite specimens were prepared by casting in 1/4 in. diameter cylindrical moulds. They were received from the manufacturer in sealed polyethylene bags where they remained until testing. Sorbothane and Wingfoot specimens were cut from sheets with a scalpel into prismatic bars of rectangular cross-section. Specimens were cut to length using either a scalpel or a device which consisted of two razor blades fixed parallel to each other. Each specimen was cut very slowly to produce end surfaces as flat as possible, then its mass and dimensions were recorded. The density was then calculated. Hardness was measured using Shore (oo) and Shore A durometers at several temperatures.

4. Results

Figs 2 to 6 contain results from isothermal studies at room temperature (26° C ± 1° C). These results were derived from creep studies from 10 sec to as long as several days as well as from the dynamic modulus and loss tangent, from 0.001 Hz to more than 1 kHz. Moduli derived from creep and from dynamic measurements were plotted using the same shape data points on a common frequency scale. Results from creep overlap those from dynamic modulus measurements in the range 0.001 to 0.016 Hz. The specimen resonance frequency is indicated by a downward pointing arrow above the frequency axis. Error bars are based on the analysis described above; where no error bar is shown, the estimated error is smaller than the thickness of the data points. Shear moduli were normalized to the value at 0.1 Hz. These moduli, as well as specimen density and Shore hardness, are presented in Table I. The Shore hardness test involves a non-destructive indentation of the material. Shore hardness values correlate well with the elastic properties, e.g. the shear modulus, of materials.

The viscoelastic behaviour of a specimen of RTV silicone rubber is shown in Fig. 2. This material exhibited relatively small viscoelastic loss and little dispersion of the modulus. The loss tangent derived from the width of the compliance peak near resonance (Equation 3) was tan δ = 0.14 at 356 Hz. This is in reasonable agreement with the loss obtained near resonance by the present data-reduction scheme based on the exact Equation 2, as seen in Fig. 2. The approximation in Equation 3 is warranted in this case because the loss is relatively small. The viscoelastic elastomers by contrast, exhibited large loss tangents and significant dispersion of the modulus in the range

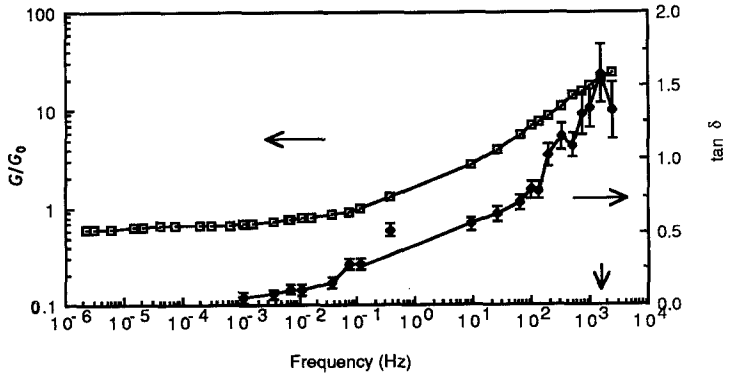

Figure 3 Viscoelastic behaviour of a polyurethane (Viscolite 13B).

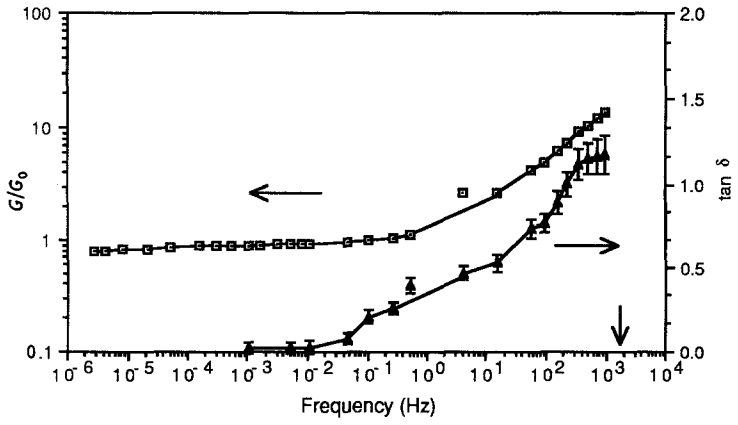

Figure 4 Viscoelastic behaviour of a polyurethane (Viscolite 180587).

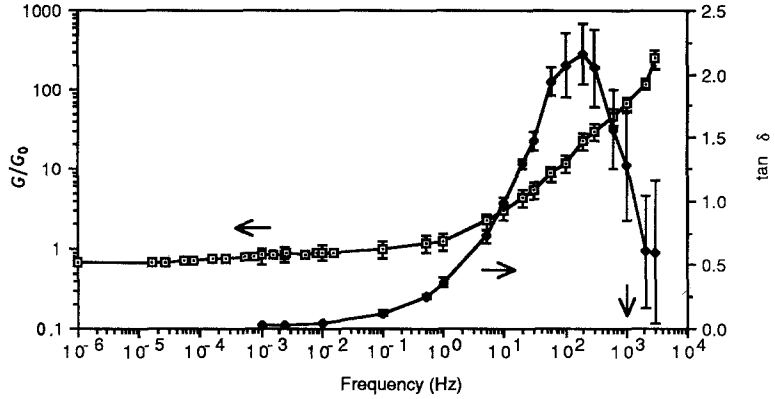

Figure 5 Viscoelastic behaviour of Wingfoot elastomer.

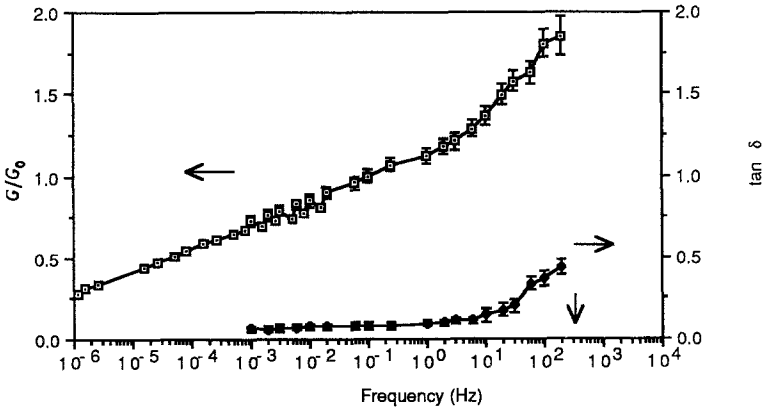

Figure 6 Viscoelastic behaviour of Sorbothane.

1 Hz to 1 kKz, as shown in Figs 3 to 6. The Sorbothane also showed a large amount of creep, while the Viscolite and Wingfoot exhibited minimal creep. Wingfoot exhibited a relatively narrow maximum in its loss tangent curve, with a full width at half maximum of about two decades. The loss curves for the Sorbothane and Viscolite were broader, and no relative maximum was found within the available frequency range.

Temperature dependence of the modulus and loss of Viscolite and Wingfoot at 1 Hz is shown in Figs 7 and 8, respectively. The Viscolite is seen to be less temperature dependent than the Wingfoot in the relatively limited range examined. Durometer results over a wider temperature range are shown in Table I. The difference between the materials is particularly marked at −13° F (−25° C). The Wingfoot has undergone a transition to its glassy state, with board-hard consistency, while the other elastomers have retained their flexibility.

TABLE I

Material	Shore hardness, 10 sec			Density ($g\,cm^{-3}$)	Shear modulus G_0 (MPa), 0.1 Hz, 77° F (25° C)
	77° F (25° C)	40° F (4.5° C)	−13° F (−25° C)		
Silicone rubber	74oo/26A	76oo/28A	76oo/30A	1.06	0.34
Viscolite 13B	80oo/35A	87oo/45A	98oo/83A	1.15	0.58
Viscolite 180587	72oo/22A	77oo/23A	95oo/80A	1.07	0.15
Sorbothane	60oo/14A	65oo/17A	78oo/28A	1.3	0.32
Wingfoot	75oo/26A	87oo/32A	10oo/99A	1.09	0.35

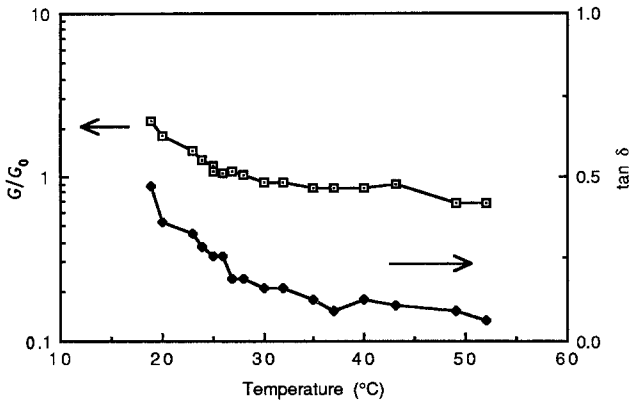

Figure 7 Viscoelastic behaviour of Viscolite 13B at 1 Hz over a range of temperatures.

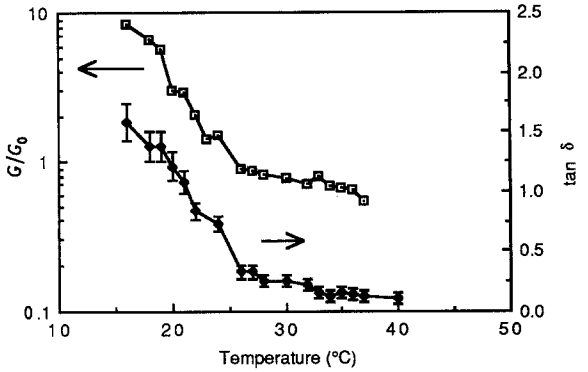

Figure 8 Viscoelastic behaviour of Wingfoot at 1 Hz over a range of temperatures.

5. Discussion

5.1. Material behaviour

All elastomeric materials exhibit large loss tangents and large dispersions of stiffness in some part of the frequency domain. Hevea rubber, for example, attains a peak value of more than 1 in its loss tangent at about 100 MHz at room temperature [5]. At lower frequencies, the loss is much less, e.g. less than 0.1 at 1 kHz and about 0.01 at 10 Hz. Viscoelastic elastomers, by comparison, exhibit large loss in the range 1 Hz to 1 kHz and above. Such materials are therefore useful in a variety of applications for which viscoelastic loss is important, e.g. shock absorption, vibration damping, and sound attenuation. In most of these applications, a large loss tangent is desirable above 10 Hz, and creep should be minimal for time longer than 10 sec.

The viscoelastic elastomers examined in this study were obtained from commercial sources. The chemical composition of the materials may be inferred from the patent literature; however, the actual composition of the manufactured specimens may differ. For example, Sorbothane is said to be manufactured according to the description given by Hiles [2]. Attempts to make viscoelastic elastomers in the laboratory in this way were unsuccessful in that the resulting material was a liquid or a semi-solid with the consistency of chewing gum [11].

In the experimental approach, we observe that more than nine decades of time and frequency are covered in the present method. This is sufficient to tune through part of (in Viscolite and Sorbothane) or most of (in Wingfoot) the rubber–glass transition at room temperature. By contrast, the time–temperature superposition approach, which is commonly used for this type of study, is limited to materials which are thermorheologically simple. In the case of Viscolite, deviations from superposition can exceed 50% [4].

5.2. Applications

Several of the viscoelastic polyurethanes examined in this study have been used as shock absorbing inner soles for athletic shoes. Material properties in the frequency range 1 to 100 Hz are relevant in this application. The effect of viscoelastic shock absorbers on human gait in healthy people and those with clinically degenerative joints was studied by Voloshin and Wosk [12]. The control group was tested with accelerometers at a normal gait with and without viscoelastic inserts in both shoes. The results indicated a 42% reduction in shock wave amplitude upon the locomotor system due to the presence of viscoelastic inserts. The clinical patients wore viscoelastic shoe inserts every day for 18 months prior to testing. It was found that 78% of the clinical symptoms had disappeared, and 17% had satisfactorily improved. Other investigators have also suggested that shock absorbing footwear may alleviate symptoms of clinically degenerative joints [13, 14].

Design of elastomeric damping components for systems subjected to a range of temperatures can be difficult, owing to the temperature sensitivity of these materials. The introduction of new materials, e.g. Viscolite, with reduced sensitivity to temperature, should facilitate such designs.

6. Conclusion

It is concluded that the present method for characterizing viscoelastic materials permits successful measurements over a wide range of time and frequency with a single apparatus. The viscoelastic elastomers Viscolite, Sorbothane, and Wingfoot exhibit large loss tangents and significant dispersion of the modulus in the range 1 Hz to 1 kHz, a range of frequency associated with vibration, noise, and mechanical shock. Of these materials, Viscolite and Wingfoot offer both a large loss tangent and minimal creep, which are desirable characteristics in many applications. Moreover, Viscolite is comparatively insensitive to temperature.

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