ARCHIVES OF ACOUSTICS
3, 1, 35-48 (1978)

VISCOELASTIC RELAXATION IN A SERIES OF FLUOROPROPYLMETHYLSILOXANE FLUIDS

RYSZARD PŁOWIEC

Institute of Fundamental Technological Research, Polish Academy of Sciences
(00-049 Warszawa, ul. Świętokrzyska 21)

MIN GON KIM

University of Rhode Island Kingston (Rhode Island 02881, Department of Physics)

The paper presents the results of measurements of the shear impedance for samples of synthetic oil with different length of molecules for the shear frequencies 10, 30 and 450 MHz over a range of temperatures from −100° C do 50° C. It was found that the results of measurements of the shear impedance are well described by LAMB's liquid model with the high-frequency approximation for the DAVIDSON-COLE term

$$J^*_{j\omega} = J_\infty\left(1+\frac{1}{j\omega\tau_m}\right)+\frac{2KJ_\infty}{(j\omega\tau_m)^\beta}.$$

It has been shown that the coefficient $2K$ in this term is a function of the viscosity of the examined liquid. The results obtained have been interpreted as the superposition of two relaxation processes, one of high-frequency viscoelastic relaxation and one of low-frequency retardation related to the three-dimensional orientation of the molecules. The values of the individual relaxation times have been determined with the aid of ROUSE's theory.

1. Introduction

In recent years a number of lubricating liquids have been commonly used. These are mostly either oils with an addition of polymers which modifies their temperature viscosity characteristics, or completely synthetic oils. Amongst the latter are the most popular silicone liquids due to their small temperature viscosity coefficient and the comparatively low temperature of transition into a glassy state.

In order to know more closely the behaviour of oils as a function of the strain frequency the viscoelastic properties of a selected silicone oil (trifluoropropylmethylsiloxane) were investigated using ultrasonic shear strain. For these investigations oil samples with different lengths of macromolecular chain have been used to determine the influence of the chain length on the rheological properties of the oil.

Similar measurements of the viscoelastic properties have been made with polydimethylsiloxane oils [1]. However, because of the occurrence of crystallization during the cooling of the samples, neither the measurement of their limiting shear elasticity nor the investigation of the high-frequency part of the viscoelatic relaxation process was possible. Instead, the full range of the viscoelastic relaxation in poly-n-butylacrylates and poly-ethylacrylates has been examined. It was found in these liquids that at high frequencies the process of the viscoelastic relaxation can be described by means of a phenomenological formula for the compliance of the liquid to shear $J_{j\omega}$, in the form

$$J^*_{j\omega} = J_\infty\left(1+\frac{1}{j\omega\tau_m}\right)+\frac{2KJ_\infty}{(j\omega\tau_m)^\beta}, \tag{1}$$

where $J^*_{j\omega}$ is a complex compliance at an angular frequency $\omega = 2nf$, J_∞ $(= 1/G_\infty)$ is the limiting high frequency shear compliance, and τ_m is the Maxwell relaxation time, equal to ηJ_∞, with η being the static viscosity of the liquid. The coefficients β and K are numerical parameters.

Equation (1) was proposed by Lamb and others [3] for the purpose of describing the results of measurements of the shear compliance of plain liquids ($K = 1$ and $\beta = 0.5$) and liquid mixtures ($K \neq 1$ and $\beta = 0.5$). Subsequent measurements made on polymer liquids have shown that the parameter β is a function of the distribution of the liquid relaxation times and may vary from 0 to 1 [4, 6].

The last term of (1) is a modification of the empirical high frequency equation stated by Davidson-Cole [5] who have made measurements of the dielectric permittivity of a liquid $\varepsilon^*_{j\omega}$ as a function of the frequency ω. They described the results of their measurements by an equation of the form

$$\varepsilon^*_{j\omega} - \varepsilon_0 = \frac{\varepsilon_0-\varepsilon_\infty}{(1+j\omega\tau)^\beta}, \tag{2}$$

where ε_0 is the value of the static dielectric constant of the liquid, ε_∞ is the limiting value at very low frequencies, τ is the dielectric relaxation time, β is the selected numerical parameter and ω is the angular frequency.

If the stress induced in a liquid does not come from an electric field as in the measurements by Davidson-Cole, but instead is caused by mechanical shear waves, the mechanical compliance of the liquid $J^*_{j\omega}$ can be described in a similar manner,

$$J^*_{j\omega} = J_\infty+\frac{J_r}{(1+j\omega\tau_r)^\beta}, \tag{3}$$

where τ_r is the time of retardation related to the reconstruction of the space orientation of the liquid molecules, and J_r is the retardation susceptibility.

The mechanical shear stress, in addition to the space reorientation of molecules also compels them to perform translational motion. If we describe this motion by the Newtonian susceptibility, Eq. (3) takes the form

$$J^*_{j\omega} = J_\infty + \frac{1}{j\omega\eta} + \frac{J_r}{(1+j\omega\tau_r)^\beta}. \tag{4}$$

For the majority of the examined polymer liquids, with medium and large viscosity coefficients, $\tau_r > \tau_m$. This permits the value of unity to be neglected in relation to the value $\omega\tau_r$. Equation (4) thus reduces to equation (1), with

$$J_r = 2KJ_\infty \left(\frac{\tau_r}{\tau_m}\right)^\beta. \tag{5}$$

2. The method of measurement

The method of measurement consist in defining the mechanical shear impedance of the liquid using transversel ultrasonic vibrations of frequency ω. The relation between the impedance $Z^*_{j\omega}$ and the complex modulus of elasticity of the liquid at this frequency $G^*_{j\omega}$ is of the form

$$Z^*_{j\omega} = \varrho G^*_{j\omega}, \tag{6}$$

where ϱ is the density of the liquid.

The mechanical shear impedance is preferably determined by the measurement of the amplitude refraction coefficient k and of the phase θ of the ultrasonic wave at the interface of two media, i.e. of a solid and a liquid. With a plane wave normally incident onto the interface, the mechanical shear impedance of a liquid is equal to

$$Z^*_{j\omega} = Z_Q \frac{1-k^2+j2k\sin\theta}{1+k^2+2k\cos\theta}, \tag{7}$$

where Z_Q is the impedance of the solid.

For most of the liquids the phase shift of a wave related to the reflection is small since the impedance of a liquid $Z < 0.1\,Z_Q$. Thus it can be assumed that $\cos\theta = 1$. Equation (7) then takes the form

$$Z^*_{j\omega} = R + jx = Z_Q\left(\frac{1-k^2}{(1+k)^2} + j\,\frac{2k\sin\theta}{(1+k)^2}\right). \tag{8}$$

The error caused by assuming $\cos\theta = 1$ is smaller than 1%. Equation (8) permits the evaluation of the real part of the impedance knowing only the amplitude reflection coefficient:

$$R = Z_Q \left(\frac{1-k}{1+k} \right). \tag{9}$$

Knowing the values R and X of the components of the shear modulus of elasticity of the liquid $G^*_{j\omega}$ can be evaluated from (6):

$$G'_\omega = \frac{R^2 - X^2}{\varrho}, \tag{10}$$

$$G''_\omega = \frac{2RX}{\varrho}. \tag{11}$$

In this paper measurements were made at frequencies of 10, 30 and 450 MHz. The measuring system and more particulars related to the measurements at the frequencies 10 and 30 MHz can be found in a previous paper [7], while those for the frequency 450 MHz elsewhere [8].

3. Specification of the samples investigated

The oil to be tested was trifluorpropylmethylsiloxane (FS 1265), a product of Midland Silicone Limited (U. K.) with a structural formula $(CH_3)_3SiO(CH_3SiO(H)_2CF_2)_nSi(CH_3)_3$. This liquid is a linear polymer, free of main chain branches. The measurement involved four samples of this oil which differed only in their chain lengths (i.e. the value of n in the structural formula).

The static viscosity at room temperature (20°C), then mean numerical molecular mass $\overline{M}_n$ and the ratio $\overline{M}_w/\overline{M}_n$, of the individual oil samples were

sample	η [P]	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
A	1.72	1720	1.12
B	30.0	9050	1.19
C	179.0	20000	1.41
D	8120.0	72600	1.84

A mixture comprising samples B and C in the ratio 0.3 B + 0.7 C was also tested. The viscosity of this sample at room temperature was BC 113.0 poises.

The measurement of the molecular mass and its distribution in the four main liquid samples was performed by the Rubber and Plastics Research Association (RAPRA) at Screwbury in Great Britain. The spectra of the distribution of the molecular mass of the individual samples as obtained by RAPRA are shown in Fig. 1.

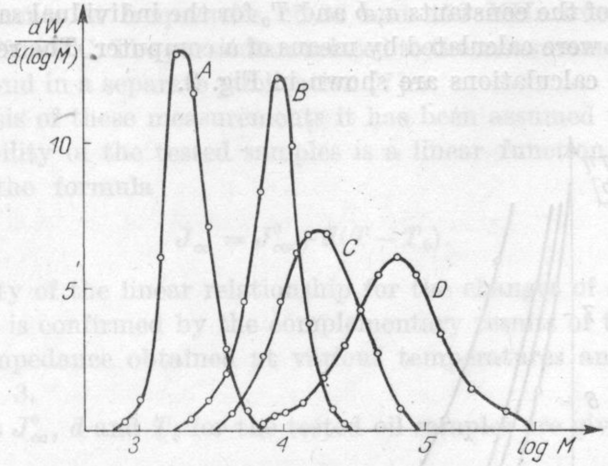

Fig. 1. The spectrum of the distribution of the molecular mass $\overline{M}$ of the samples A, B, BC, C and D of the tested oil

4. Experimental results

4.1. *Measurements of the density as a function of temperature.* These were made using a picnometer. It was found that there was a linear relationship of the density changes of the tested samples over a temperature range from −70°C to 50°C in agreement with the equation

$$\varrho_{(T)} = \varrho_0[1-\alpha_0(T-T_0)]. \tag{12}$$

The values of ϱ_0 α_0 and T_0 for particular oil samples are given in Table 1.

Table 1

Sample	$\alpha_0(\times 10^4)$	a	b	$J^0_\infty \times$ $[10^9 \mathrm{m}^2/\mathrm{N}]$	d	T_0[K]
A	1.3515 7.4	−6.03	932.1	0.2	0.112	151.6
B	1.3707 5.83	−4.58	1100.4	0.154	0.125	156.0
C	1.3945 6.02	−2.62	1016.1	0.297	0.0627	163.0
BC	1.391 6.04	−3.45	1116.7	0.118	0.1523	156.6
D	1.4315 6.99	−1.12	997.6	0.331	0.057	166.6

4.2. *Measurements of the viscosity as a function of temperature.* The measurements were made with the aid of a capillary viscosimeter over a temperature range from −50°C to 50°C. It was found that that changes in the viscosity of the tested samples as a function of temperature can be described using the equation

$$\ln\eta = a + \frac{b}{T - T_0}. \tag{13}$$

The values of the constants *a*, *b* and T_0 for the individual samples are given in Table 1. They were calculated by means of a computer. The results of the measurements and calculations are shown in Fig. 2.

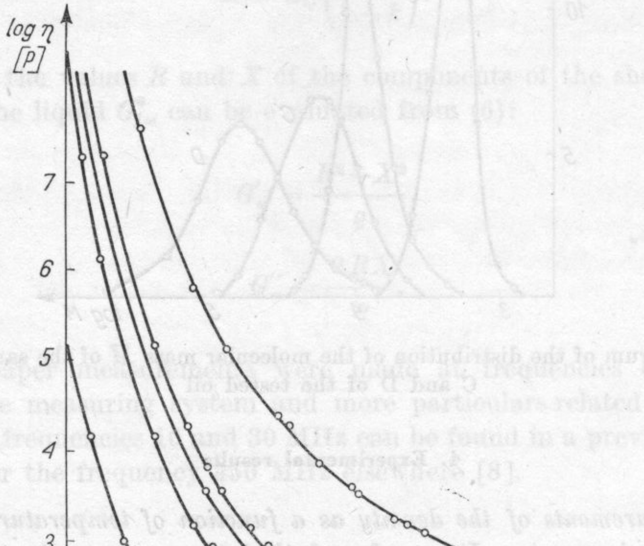

Fig. 2. The results of measurements and calculations (continuous line) of the viscosity η of the tested oil samples as a function of temperature

4.3. *Measurement of the limiting shear compliance as a function of temperature.* With satisfactorily high frequencies the reaction of a liquid to shear strain is purely elastic, whereas the shear modulus of elasticity (known as the limiting modulus) is comparable with the modulus of elasticity of a solid. This area is accessible for measurement over a temperature range in which the liquid is super cooled state i.e. between the temperature of the transition into a glassy state and the temperature at which the viscoelastic relaxation becomes predominant.

The limiting value of shear elasticity G_∞, and strictly speaking the inverse of this magnitude, the limiting shear compliance J_∞ was defined from ultrasonic measurements at frequencies of 30 and 450 MHz over a temperature range from -100 to 0°C. The particulars related to the measurement of this magnitude can be found in a separate publication [7].

On the basis of these measurements it has been assumed that the limiting shear susceptibility of the tested samples is a linear function of temperature, according to the formula

$$J_\infty = J_\infty^0 + d(T - T_0). \tag{14}$$

The validity of the linear relationship for the changes of J_∞ as a function of temperature is confirmed by the complementary results of the measurement of the shear impedance obtained at various temperatures and frequencies as shown in Fig. 3.

The values J_∞^0, d and T_0 for the tested oil samples are given in Table 1.

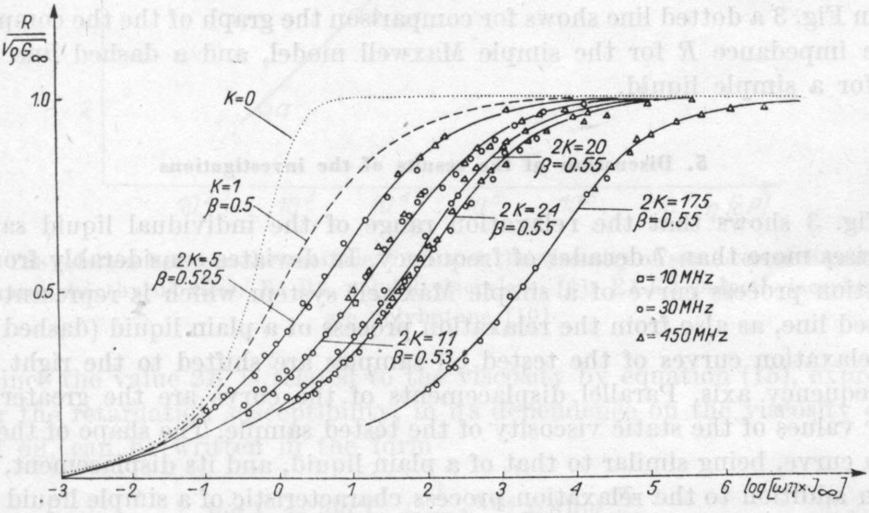

Fig. 3. Comparison of the results of the real impedance R_L in a normalized scale. Continuous and broken lines are plotted from equation (1). Notation can be found in the text

4.4. *Measurement of the real component of the impedance.* The measurement of the real component of the acoustic shear impedance was made at frequencies of 10, 30 and 450 MHz over a temperature range from -50°C to 50°C. For each temperature two measurements of the refraction coefficient k were made, the first for a quartz bar with a free end and the second with the end of the bar immersed in a liquid sample. The difference in attenuation of the first ten pulses that are echoes of repeated reflections in the bar are defined by comparison with a standard pulse of controlled amplitude. The values of the resistance were then defined from formula (9). The accuracy of measurement of R was ± 400 [g/s cm^2] for a frequency of 450 MHz and ± 2400 [g/s cm^2] for the frequencies 10 and 30 MHz.

The results of these measurements are shown in Fig. 3. For the purpose of an orderly presentation of the results use has been made of the method of the replacement of variables [9]. This makes it possible to present the results of measurements made at various frequencies and temperatures in the form of one curve as a function of frequency normalized to the relaxation frequency of the Maxwell model ($1/\omega_0 = \eta J_\infty$). Thus changes in the impedance of a liquid over a wide frequency range and easy comparison of the results obtained for various liquids can be presented.

Also for this reason the values of the component of the impedance R on the vertical axis have been referred to the acoustic impedance in the limit of infinitely large frequencies (i.e. equal to $\sqrt{\varrho G_\infty}$). The continuous lines that approximate the results of measurements have been calculated from formula (1) by selecting on the computer the corresponding values of k and β for the individual oil samples. These values are given in Table 2.

In Fig. 3 a dotted line shows for comparison the graph of the the component of the impedance R for the simple Maxwell model, and a dashed line shows that for a simple liquid.

5. Discussion of the results of the investigations

Fig. 3 shows that the relaxation range of the individual liquid samples comprises more than 7 decades of frequency. In deviates considerably from the relaxation process curve of a simple Maxwell system which is represented by a dotted line, as also from the relaxation process of a plain liquid (dashed line). The relaxation curves of the tested oil samples are shifted to the right along the frequency axis. Parallel displacements of the curve are the greater with higher values of the static viscosity of the tested sample. The shape of the relaxation curve, being similar to that of a plain liquid, and its displacement, show that in addition to the relaxation process characteristic of a simple liquid there also occurs and additional factor which causes the displacement of the measuring points to the right on the frequency scale. The amount of this displacement is defined by the coeficient $2K$ in formula (1). A good approximation to the value of this coefficient, when β is near to 0.5, is given by equation (15) [13]

$$\log 2K = k\eta^{0.146}, \qquad (15)$$

where η is the static viscosity in centipoise, k is a constant coefficient equal to one third for the oil samples tested. It was found that the relationship (15) is also valid for polybutane polymers [10] when $k = 1/8$, and for polyacrylate polymers [2] when k is near to 1/6. This is shown in Fig. 4. The point $E2$ for a sample of polyacrylate polymer is beyond the straight line, probably because of its large molecular mass ($M_n = 22\,000$) and because of some entanglement resulting from this. This consideration also applies to sample D of the tested oils ($M_n = 72\,600$).

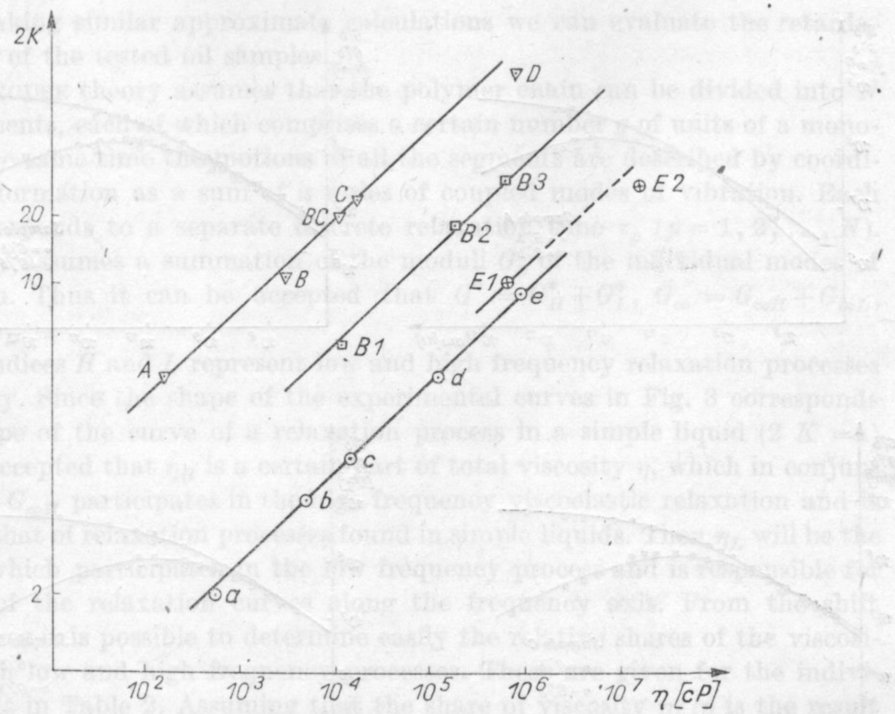

Fig. 4. The relation between the coefficient $2K$ and the viscosity of some tested liquids. A-D trifluorpropylmethylsiloxane, B1-B3 polybutylacrylate [2], E1-E2 polyethylacrylate [2], a-e polybutane [10]

Since the value $2K$ is related to the viscosity by equation (15), expression (5) for the retardation susceptibility, in its dependence on the viscosity of the tested oil, can be written in the form

$$\log J_r = \log J_\infty + \frac{1}{3}\eta^{0.146} + \beta \log \frac{\tau_r}{\tau_m}, \tag{16}$$

φ_r can be defined on the basis of ROUSE's theory.

With the measured values of the real component of the impedance as a function of temperature and frequency, and with the value of imaginary component of the impedance it is possible to calculate the dependence of the components of the modulus of elasticity G' and G'' as functions of frequency. The results for the particular samples are shown in succession in Figs. 5-8. On the vertical axis are values of the moduli normalized by means of the coefficient b, while on the horizontal axis are values of frequency which have been normalized by means of the coefficient a. Practical reasons support the use of such normalization which was introduced by FERRY [9]. The normalization coefficients are

$$b = \frac{\varrho T}{\varrho_* T_*}, \quad ab = \frac{\eta}{\eta_*}, \tag{17}$$

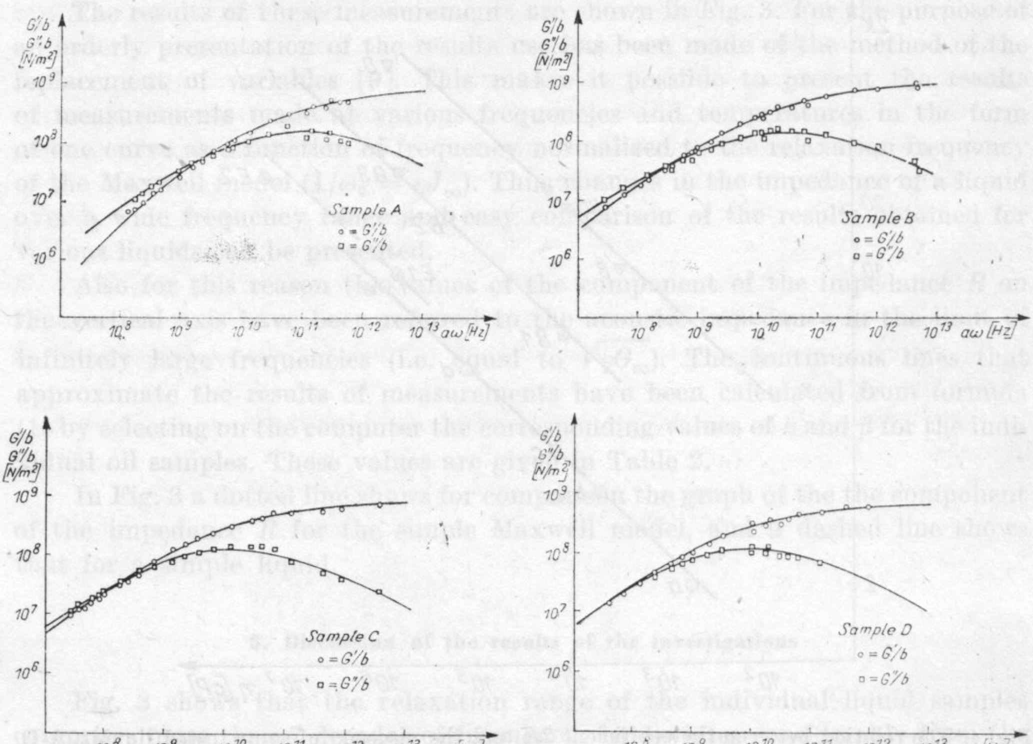

Fig. 5-8. The dynamic modulus G' and the loss modulus G'' of the individual oil samples as functions of frequency. The continuous line is the curve of equations (1) and (6), *a* and *b* are normalization coefficients

where ϱ, T and η are the density, the temperature (in deg. Kelvin) and the viscosity respectively, while the magnitudes with an asterisk are the values at the reference temperature. It has been assumed that this is a temperature of 20°C (293.1 K). For this temperature the coefficients *a* and *b* are equal to unity.

Figs. 5-8 show that the values of the conservative modulus G' increase asymptotically with increasing frequency up to 10^9 N/cm², whereas the loss modulus G'' attains a maximum. The highest value of the loss modulus is one order of magnitude smaller than the limiting of the conservative modulus. The intersection of the curves, at which the values of both moduli become equal ($\tan\delta = 1$) shifts towards lower frequencies with increasing viscosity of the tested sample. This is probably attributable to the increase in retardation when the length of a molecule increases.

The behaviour of a molecule in the range of retardation relaxation can be represented in a similar way to that accepted for the previously tested polydimethylsiloxane oil [1]. To describe the results use was made there of ROUSE's theory. Making similar approximate calculations we can evaluate the retardation times of the tested oil samples.

The Rouse theory assumes that the polymer chain can be divided into N equal segments, each of which comprises a certain number q of units of a monomer. At the same time the motions of all the segments are described by coordinate transformation as a sum of a series of coupled modes of vibration. Each mode corresponds to a separate discrete relaxation time τ_p $(p = 1, 2, \ldots, N)$. This theory assumes a summation of the moduli G_p of the individual modes of the motion. Thus it can be accepted that $G^* = G_H^* + G_L^*$, $G_\infty = G_{\infty H} + G_{\infty L}$, $\eta = \eta_H + \eta_L$.

The indices H and L represent low and high frequency relaxation processes respectively. Since the shape of the experimental curves in Fig. 3 corresponds to the shape of the curve of a relaxation process in a simple liquid ($2\,K = 1$) it can be accepted that η_H is a certain part of total viscosity η, which in conjunction with $G_{\infty H}$ participates in the high frequency viscoelastic relaxation and is similar to that of relaxation processes found in simple liquids. Then η_L will be the viscosity which participates in the low frequency process and is responsible for the shift of the relaxation curves along the frequency axis. From the shift of the curves it is possible to determine easily the relative shares of the viscosities in both low and high frequency processes. These are given for the individual liquids in Table 2. Assuming that the share of viscosity η_L/η is the result of the existence of p Rouse modes, it is possible to determine the value of p for the individual oil samples. The values of p have been calculated on a computer and are also given in Table 2.

Table 2

Sample	$2\,K$	β	p	η_L	η_L/η	η_H
A	5	0.525	2	1.23	0.715	0.49
B	10.5	0.53	7	27.6	0.92	2.4
C	24	0.55	30	175.4	0.98	3.58
BC	20	0.55	20	109.8	0.9717	3.14
D	175	0.55	500	8115.5	0.99944	4.5

The values stated in Table 2 permit to evaluation of the high frequency relaxation times τ_H, and the low frequency relaxation times τ_L for the individual liquid samples, as well as the value of the retardation compliance J_r. The values of τ_L have been calculated from formula (11),

$$\tau_L = \tau_{p_i \ldots N} = \frac{\pi^2}{4N^2} \frac{\eta \bar{M}_n}{\varrho RT \sum_p \frac{1}{p^2} \sin^2 \frac{p\pi}{2N+1} \left(\frac{\bar{M}_w}{\bar{M}_n} \right)} \tag{19}$$

for liquid samples A and B, while for the other samples in view of the satisfactorily large number, N, of the Rouse modes, use has been made of the simplified formula

$$\tau_{p_i} = \frac{6\eta M_i}{\pi^2 p^2 \varrho RT(M_w/M_i)}. \tag{20}$$

In both cases $M_w = \Sigma M_i W_i$ is the mean (by weight) molecular mass of the polymer, ϱ is the density of liquid, R is the gas constant, T is the temperature in degrees of Kelvin, and $N = pq$.

In the computations it has been assumed that the number of monomer units $q = 5$ corresponding to 7 atoms of silicon in a segment. This value is assumed for the bonds Si-O which exhibit an exceptionally high susceptibility to bending [12]. However, it can be proved that the value of q is not critical in the computations.

The values of the relaxation times and of the compliance calculated from formulae (19) and (20) are given in Table 3. Since the spectrum of the Rouse modes is a discrete spectrum, and the spectrum of Lamb liquid model is a continuous spectrum [10], it is difficult to illustrate the superposition of both spectra. However, it can be noticed that in each case the relaxation times of the Rouse modes are considerably lower than the high frequency relaxation times.

Table 3

Sample	$\varphi_H(\times 109)$	φ_{r_1}	$\varphi_{r_N}(\times 109)$	J_r/J_∞	J_r	φ_r/φ_m
A	0.165	1.1×10^{-7}	140	110	3.7×10^{-8}	196
B	0.677	7.8×10^{-6}	240	410	1.2×10^{-7}	925
C	0.977	5.1×10^{-5}	57	900	2.5×10^{-7}	1000
BC	0.88	2.0×10^{-5}	49	852	2.3×10^{-7}	667
D	1.22	1.4×10^{-3}	8	5900	2.8×10^{-6}	640

The identical shape of the curve in the range of viscoelastic relaxation in simple liquids (i.e. with comparatively short molecules) can be explained by the fact that at high frequencies the only motions likely to occur in the long molecule are vibrations of the side groups of a polymer chain.

Thus it seems to be justified to accept that the retardation time τ_r corresponds to the longest time of relaxation (τ_{L_i}) in the Rouse modes of vibration since in this case all of the molecule participates in the process of reorientation.

It should also be noticed that as the length of the polymer chain increases there is also an increase in the polymer susceptibility to bending and the ratio J_r/J_∞ (Fig. 9). This is physically substantiated. The limiting compliance J_∞ is determined by the high frequency properties of liquid and is a characteristic magnitude for a given liquid, whereas the retardation compliance J_r is defined by the depth of the potential barier between polymer molecules. This potential barrier depends on the length of the polymer chain and reduces

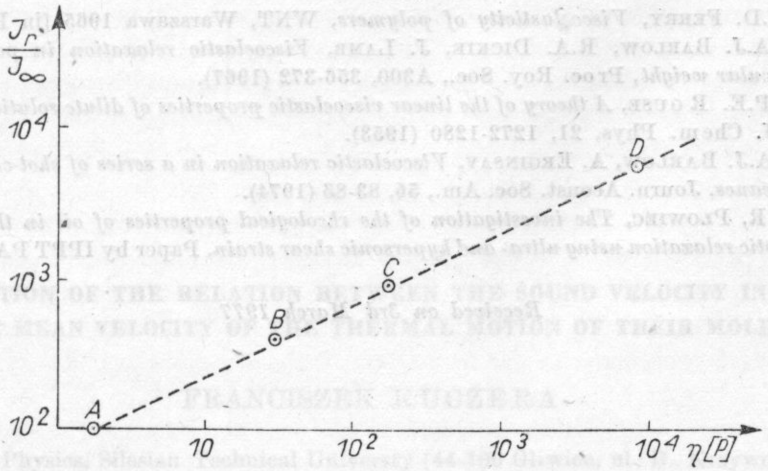

Fig. 9. The relation between the ratio J_r/J_∞ and the viscosity of the tested oil samples

with the increasing chain length. Consequently, J_r is higher for longer polymer chains. The character of the changes in J_r with increasing viscosity is defined directly by the coefficient $2K$ which is related to the viscosity of the tested samples by equation (15) since both the limiting compliance J_∞ and the ratio of the time of retardation to the time of relaxation differ only a little for the individual oil samples.

The execution of the above-decsribed measurements in the ultrasonic laboratory of the University of Glasgow (G. Britain) was made possible with the assistance of prof. J. Lamb for which one of the authors (R. P.) would like to express his sincere gratitude.

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Received on 3rd March 1977