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RHEOLOGICAL PROPERTIES OF EPOXY RESINS IN AN SHEAR ULTRASONIC FIELD

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Ultrasonic shear measurements were perfomed on epoxy resins: araldit *F* and epidian 5 in a temperature range from -30 to 80°C and a frequency range from 10 to 800 MHz. Using reduced variables a "master curve", following the *BEL* model, was determined for $K = 1.8$ and 1.6, and $\beta = 0.47$ and 0.44, respectively. Both elasticity moduli and dynamic viscosity are given as frequency functions. It was found that rheological properties of both resins are close each other in an ultrasonic shear field.

1. Introduction

Hardened epoxy resins find a wider and wider application in electrical engineering and electronics. These applications are accompanied by scientific research, also with application of ultrasound [1], [2], which are used to determine either the kinetics of epoxy resin polymerization or ultrasonic parameters related to the degree of hardening of resins [3]–[5].

The recognition of the stock, i.e. non-hardened resins, is a significant element of the process of hardening. This paper will present results of ultrasonic measurements of rheological properties of non-hardened resins. Professional literature does not give results of such measurements. Presented research will lead to the determination of the reaction of the resin to shear strain in a wide ultrasonic frequency range through the measurement of acoustical impedance to shear. This parameter allows us to calculate the changes of the shear modulus, the loss modulus and dynamic viscosity, as well as the viscoelastic relaxation range.

In ultrasonic measurements conducted with a transverse wave, the epoxy resin is used as a coupling layer, because here oil can not be applied although it finds wide application in investigations conducted with a longitudinal wave. This property of the resin can be explained through the determination of the moduli of elasticity in terms of frequency.

In order to establish the ultrasonic difference, two types of epoxy resins were chosen: epidian 5 from the Sarzyna works (Poland) and araldit *F* produced by Ciba-Geigy (Switzerland).

2. Measuring method

The mechanical shear impedance of the resin was determined with the application of transverse vibrations with a ω frequency. The relation between the impedance $Z^*_{j\omega}$ and the complex modulus of elasticity of a liquid $G_{j\omega}$ for this frequency, ω, is expressed by

$$(Z^*_{j\omega})^2 = \varrho G^*_{j\omega}, \tag{1}$$

where ϱ is the liquid density

$$Z^*_{j\omega} = R + jX, \quad G^*_{j\omega} = G' + jG''.$$

The mechanical shear impedance is most oftenly determined from the measurement of the amplitude reflection coefficient, k, and phase, θ, of the ultrasonic wave on the boundary of two media, i.e., solid body and liquid. The mechanical shear impendance of a liquid in the case of a plane wave inciding perpendicularily to the boundary surface, is:

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

where Z_Q is the impedance of the solid body.

For most liquids the wave phase shift related to the reflection is small, as the impedance of a liquid $|Z| < 0.1 < |Z_Q|$; therefore, it can be accepted that $\cos\theta = 1$. Then equation (2) has a form as follows:

$$Z^*_{j\omega} \cong Z_Q\left(\frac{1-k^2}{(1+k)^2} + j\frac{2k\sin\theta}{(1+k)^2}\right) = R + jX. \tag{3}$$

The error due to the assumption that $\cos\theta = 1$ does not exceed $1^0/_0$. Using equation (3) the real part of the impedance can be calculated with the knowledge of the amplitude reflection coefficient, solely:

$$R = Z_Q\left(\frac{1-k}{1+k}\right). \tag{4}$$

Having R and X the components of the shear modulus of a liquid, $G^*_{j\omega}$, are

$$G'_\omega = \frac{R^2-X^2}{\varrho}, \quad G''_\omega = \frac{2RX}{\varrho} \tag{5}$$

while the dynamic viscosity is expressed by equation

$$\eta'_\omega = \frac{2RX}{\omega\varrho}.$$

Investigations were performed on measuring set-ups built at the Department of Physical Acoustics of the IFTR for frequencies: 10 and 30 MHz [6], 400 and 800 MHz [7]. An apparatus produced by "MATEC" was used for control measurements performed at a frequency of 50 MHz.

The echo method was applied in measurements of the pulse reflection coefficient. A delay line made from fused quartz was used for frequencies of 10, 30 and 50 MHz. Measurements for frequencies of 400 and 800 MHz were done with the use of a tuned resonant cavity with a crystal of lithium niobate as the delay line.

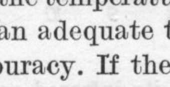
For every individual temperature the reflection coefficient, k, was measured twice; first measurement for an unloaded delay line, second – for a delay line loaded with measured medium. The attenuation difference of first ten reflections of the line was determined through the comparison with a standard pulse with a controlled amplitude. Then the value of resistance was calculated from equation (4).

Considering the tendency of epoxy resins to form conglomerates and resulting layer heterogeneities, the investigated samples, before every series of measurements, were heated to the temperature of 95°C and then measurements were done on samples cooled to an adequate temperature. This procedure gave a satisfactory measurement accouracy. If the scatter of results was too great, measurements for that temperature were repeated several times and the average value was calculated.

Generally it can be stated that the epidian 5 epoxy resin gave a greater scatter of results than the araldit F resin.

3. Characteristic of investigated samples

An epoxy resin is a linear polymer with the average specific gravity, M_n, in the range 340–382 [8]. The epoxy group is the characteristic element of the resin structure. It is a there-part oxycycloproprane ring consisting of two carbon atoms and one oxygen atom



The general formula of a resin with characteristic epoxy groups at the ends is presented in Fig. 1.

Investigations of non-hardened epoxy resins include structure identification with chemical and spectral methods, quantitative analysis of typical functional groups: epoxy and hydroxyl, and estimation of organically bound chlorine, α-glycol groups and ionic chlorine, which occur due to the imperfection of the synthesis process.

Physical properties, such as: molecular weight, viscosity, density, have been also determined. The two last properties are of special interest in the course of ultrasonic investigations with shear waves. Because the density and stationary viscosity, and their changes with regard to temperature, have to be known in order to determine the rheologic properties of the resin and to state

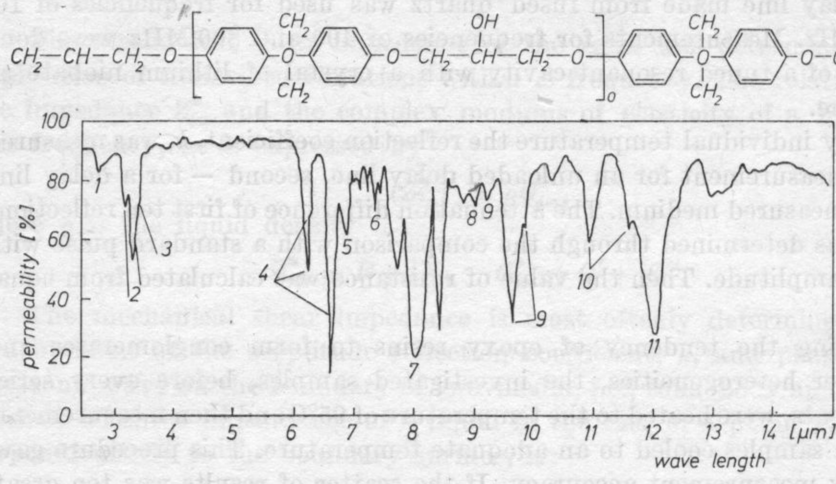


Fig. 1. The epoxyresion formula and its infrared spectrum. The numbers mark groups: *1* – hydroxyl, *2* – methyl, *3, 5* – methylene, *4, 9, 11* – substitution in the aromatic ring, *7* – etheral, *8* – diphenyl ethers, *10* – epoxy

changes of dynamic viscosity and moduli of elasticity in terms of the strain frequency, described by equations (5) and (6). These quantities (especially viscosity) differ for various resin in dependence on the producer and on the imperfection of the synthesis process.

Viscosity

Standard viscometers, such as the Engler, Ford or Hoepler viscometers, can be used in viscosity measurements. However, the Brookfield rotary viscometer is used particularily frequently in control measurements, for its measurement simplicity in a range from several to several milion mPa·s. Therefore, resin viscosity data on the package refer to measurements conducted with the described viscometer.

A Ferranti-Shirley type cone-plate viscometer or a Weissenberg rheoviscometer are used in laboratory measurements. A liquid sample in these viscometers (approx. 0.5 cm³) is subjected to shearing between a fixed flat plate and a cone rotor. The viscous resistance of the liquid, which acts on the rotating cone is the source of the momentum transmitted to a precise mechanic-electric dynamometer with an indicator calibrated in viscosity units. The Weissenberg viscometer beside the tangent component of stress, allows also the measurement of the normal component, which characterizes viscoelastic liquids.

Fig. 2 presents the epidian 5 viscosity in terms of temperature [9], measured with the rotary viscometer. Viscosities given by Ciba-Geigy [10] and measured with a Ferranti-Shirley viscometer at the Materials Quality Assaurance Directorate (England) have been also denoted in the diagram.

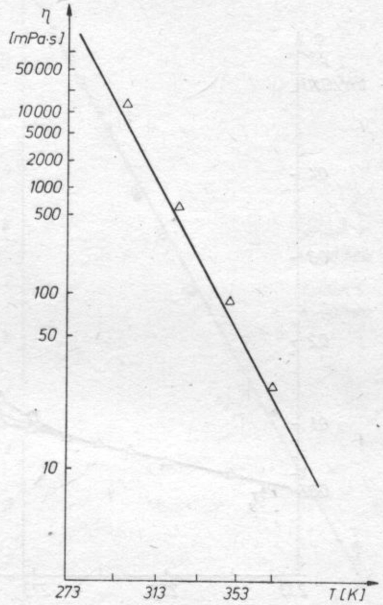


Fig. 2. Changers of the epidian 5 epoxy resin viscosity in terms of temperature [9]. The points mark the viscosity of araldit *F*, given by the producer [10]

Density

Considering the small density influence on the calculation results of the moduli of elasticity and the relaxation spectrum, it has been assumed that the density of both resins changes with temperature in the same manner and accordingly to data reported in literature [11]

$$\varrho = 1.229(1-6.8\cdot 10^{-4})t-20°\mathrm{C}.$$

4. Measurement results

Measurement of the high frequency limiting shear compliance, J_∞

The measurement of the shear compliance, J_∞, was done for araldit *F* at frequencies: 30 and 800 MHz, and for epidian 5 for frequencies 30 and 400 MHz.

Measurement results are given in Fig. 3 in the forms of a quotient $\varrho/R^2 = J_\infty$.

The transtion from the viscoelastic behaviour of the resin to the elastic behaviour, where the compliance changes linearly with temperature, can be clearly seen. The arrow marks the temperature of glass transition T_g.

Within the limit of error it can be accepting that compliance changes of both resins, in terms of temperature, are alike.

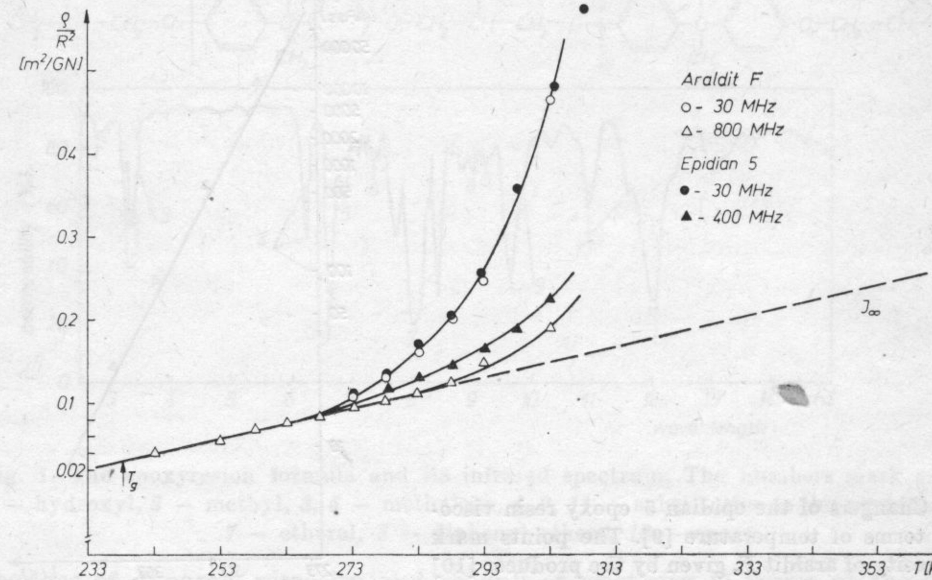


Fig. 3. Changes of the shear compliance, J_∞, in terms of temperature. Araldit F: ○ – 30 MHz, △ – 800 MHz, Epidian 5: ● – 30 MHz, ▲ – 400 MHz

Measurement of the real component of the acoustical impedance of resins

Fig. 4 presents measurement results of the real component of the acoustical shear impedance of the resin, done at a frequency of 10 MHz, while Fig. 5 presents those done at the frequency of 30 MHz.

For comparative purposes, measurements of the araldit F resin at the frequency of 50 MHz have been additionally performed with the application of the American "Matec" apparatus.

5. Discussion

Presentation of measurement results

Applying the principle reduce variable [12], the results of described above impedance measurements performed for various frequencies and at various temperatures have made up one "master curve" which marks impedance changes of both resin samples as a function of frequency ω. This frequency has been related to the relaxation frequency $\omega_m = 1/\tau_M$ of a simple Maxwell model. These curves are presented in Fig. 6.

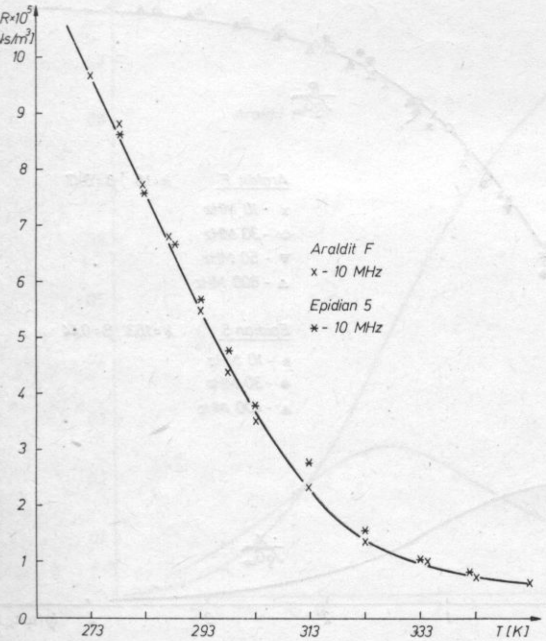


Fig. 4. Measurement results of the real component of impedance in terms of temperature for araldit (X) and epidian (*) for the frequency of 10 MHz

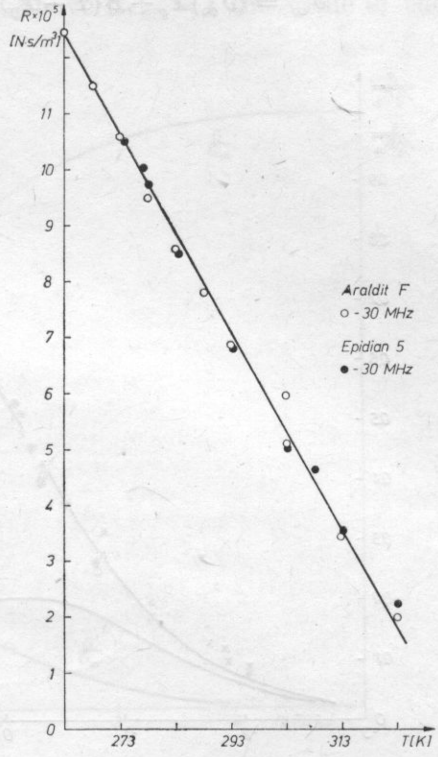


Fig. 5. Measurement results of the real component of impedance in terms of temperature for araldit (○) and epidian (●) for the frequency of 30 MHz

Such a presentation of the results is generally accepted in literature, for it allows the presentation of impedance changes in a vide range of frequencies and an easy comparison of results obtained for various liquids. The reduction of the results on the vertical axis is done through relating the measured impedance for a given value ω to the boundary impedance (equal to $\sqrt{\varrho G_\infty}$, i.e. the impedance for an infinitely great frequency).

Discussion

Presented in Fig. 3 measurements of the boundary shear compliance (J_∞) did not vary significantly for both resins. In both cases the glass transition temperature of the resins was estimated at $T_g = -35°C$, with an error of $\pm 5°C$, resulting from the difficulties of viscosity measurements in the range of negative temperatures. It can be proved that the changes of the boundary shear compliance, J_∞, with temperature can be expressed by the equation:

$$J_\infty = (J_\infty)T_g + B(T-T_g) = 3.4\cdot10^{-11} + 1.89\cdot10^{-12}(T-238.1).$$

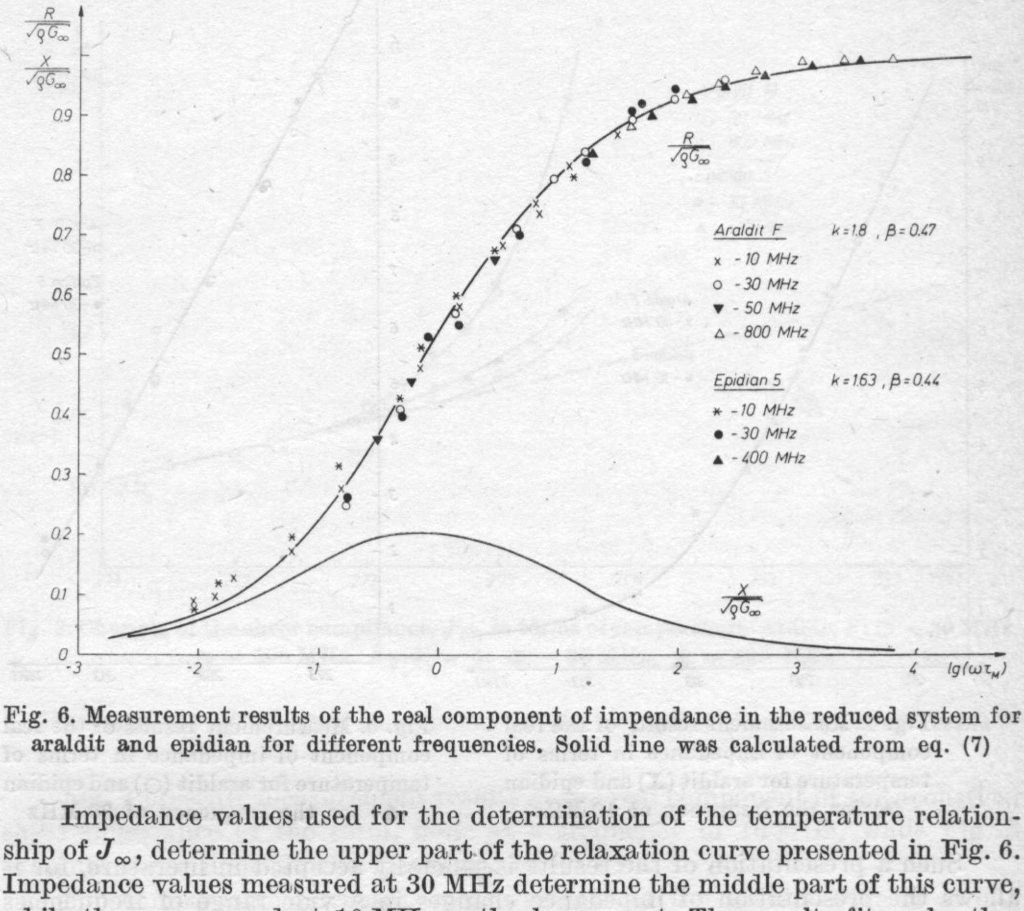


Fig. 6. Measurement results of the real component of impendance in the reduced system for araldit and epidian for different frequencies. Solid line was calculated from eq. (7)

Impedance values used for the determination of the temperature relationship of J_∞, determine the upper part of the relaxation curve presented in Fig. 6. Impedance values measured at 30 MHz determine the middle part of this curve, while those measured at 10 MHz – the lower part. The results fit each other confirming the use of reduce variable. The relaxation curves for both resins include four frequency decades. The full line marks the theoretical curve which has been calculated for a generalized BEL liquid model. This model expressed by the equation:

$$\frac{1}{G^*} = \frac{1}{G_\infty} + \frac{1}{j\omega\tau} + \frac{2K}{G_\infty(j\omega\tau)^\beta}. \tag{7}$$

Parameters, K and β, which approximate the theoretical curve to the measurement results in araldit, equal $K = 1.8$, $\beta = 0.47$. While these parameters for epidian 5 equal $K = 1.6$, $\beta = 0.44$.

Fig. 7 presents curves of the reduced modulus of elasticity, G'/G, and the loss modulus, G''/G_∞, in the relaxation range in terms of the reduced frequency, for araldit F. The loss modulus has its maximum at $\omega\tau = 3$–5. Below $\omega\tau = 1$ the value of the loss modulus is higher than the value of the modulus of elasticity, what proves viscous character of the resin. Above $\omega\tau_M = 1$ the value of the

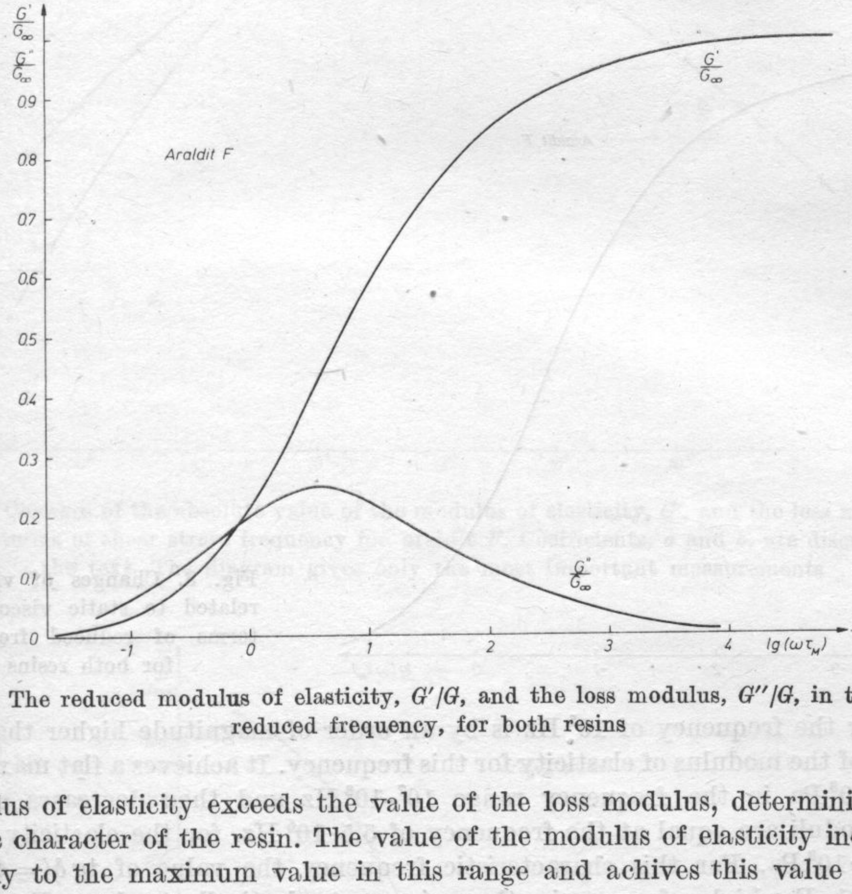


Fig. 7. The reduced modulus of elasticity, G'/G, and the loss modulus, G''/G, in terms of reduced frequency, for both resins

modulus of elasticity exceeds the value of the loss modulus, determining the elastic character of the resin. The value of the modulus of elasticity increases quickly to the maximum value in this range and achives this value within the range of four frequency decades.

The viscous character of the resin and the rate of decrease of viscosity in terms of frequency can be clearly seen in Fig. 8. At $\omega\tau = 2.5$ the resin viscosity constitutes hardly one tenth of its maximal value.

Functions presented in Fig. 7 and Fig. 8 characterizing resins in terms of the reduced frequency, can be related directly to the measured frequency. This can be done considering resin viscosity and density changes as functions of temperature in the form of the following coefficients:

$$ab = \frac{\eta}{\eta^*}, \quad b = \frac{\varrho T}{\varrho^* T^*},$$

where the values of these coefficients for the reference temperature (accepted at 293.1) are equal to 1. The moduli changes in terms of frequency are presented in Fig. 9 for both resins.

The value of the modulus of elasticity, G', for the frequency of 10^5 Hz equals 10^6 Pa and increases with the rise of frequency achieving a maximal value of $1.25 \cdot 10^9$ Pa for the frequency of 10^{11} Hz. The loss modulus value,

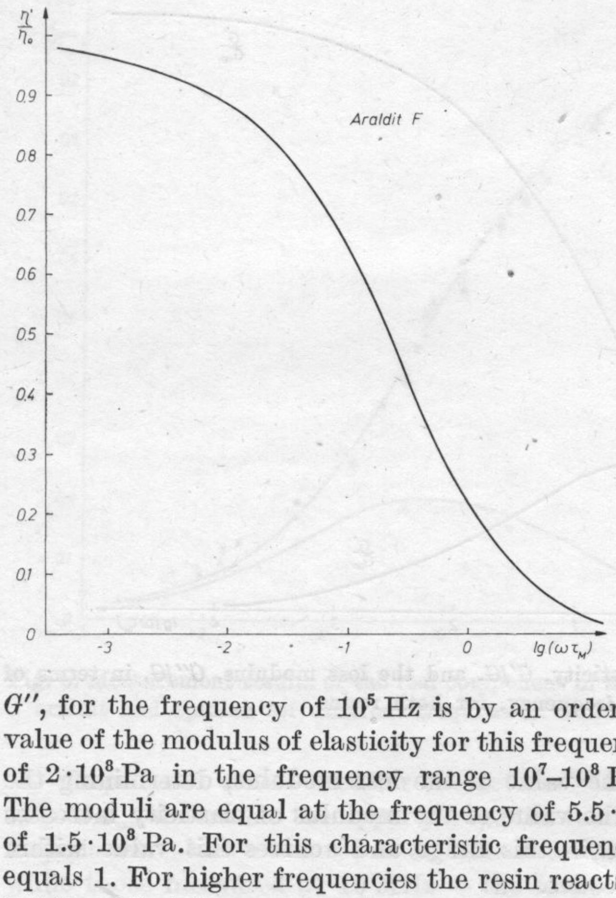


Fig. 8. Changes of viscosity related to static viscosity in terms of reduced frequency for both resins

G'', for the frequency of 10^5 Hz is by an order of magnitude higher than the value of the modulus of elasticity for this frequency. It achieves a flat maximum of $2 \cdot 10^8$ Pa in the frequency range 10^7–10^8 Hz and then decreases slowly. The moduli are equal at the frequency of $5.5 \cdot 10^6$ Hz, for the elasticity value of $1.5 \cdot 10^8$ Pa. For this characteristic frequency the value of $\operatorname{tg}\delta (= G'/G'')$ equals 1. For higher frequencies the resin reacts elastically to shear. From this it follows that the epoxy resin used as a coupling layer, can perform its function for frequencies exceeding the value of 5.5 MHz. The value of this frequency is by an order of magnitude lower in comparison with mineral oils [15] and synthetic oils [16].

Fig. 10 presents the changes of the absolute value of the dynamic viscosity for araldit F in terms of a quantity proportional to frequency (af). The static viscosity in the temperature of 20°C equals 180 mPa·s. For the shear frequency of 10^5 Hz the dynamic viscosity amounts to 144 mPa·s and quickly decreases with the rise of the shear frequency, because for the frequency of 10^8 Hz it equals only 3 mPa·s. The run of the curve for epidian 5 is very close to araldit F.

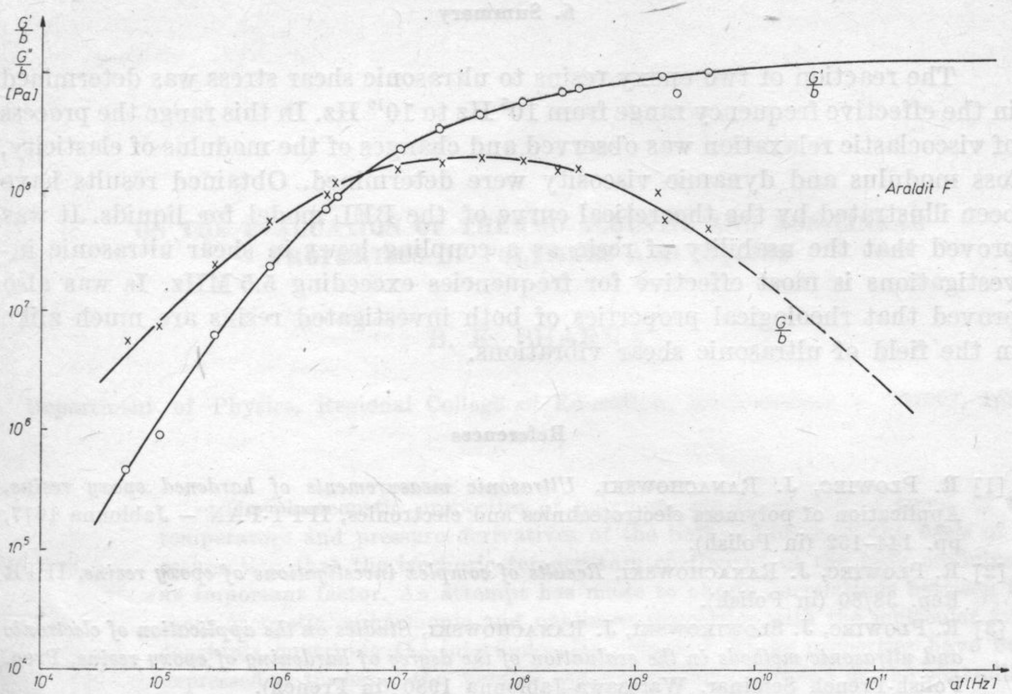


Fig. 9. Changes of the absolute value of the modulus of elasticity, G', and the loss modulus, G'', in terms of shear strain frequency for araldit F. Coefficients, a and b, are discussed in the text. The diagram gives only the most important measurements

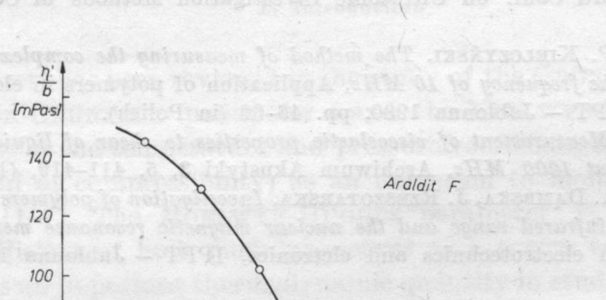


Fig. 10. Changes of the absolute value of the dynamic viscosity in terms of frequency, for araldit F. The diagram gives only the most important measurements

6. Summary

The reaction of two epoxy resins to ultrasonic shear stress was determined in the effective frequency range from 10^5 Hz to 10^{10} Hz. In this range the process of viscoelastic relaxation was observed and changes of the modulus of elasticity, loss modulus and dynamic viscosity were determined. Obtained results have been illustrated by the theoretical curve of the BEL model for liquids. It was proved that the usability of resin as a coupling layer in shear ultrasonic investigations is most effective for frequencies exceeding 5.5 MHz. Is was also proved that rheological properties of both investigated resins are much alike in the field of ultrasonic shear vibrations.

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