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MEASUREMENT OF DYNAMIC PROPERTIES OF SILICONE RUBBERS[1]

László MOLNÁR and Antal HUBA

Department of Precision Mechanics and Optics
Technical University of Budapest
H-1111 Budapest, Hungary
Phone: + 36 1 463-2602
email: lmolnar@antares.fot.bme.hu, huba@antares.fot.bme.hu

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Abstract

The application of silicone rubbers is not new in precision engineering and in the medical practice. However, the role of them has increased lately, so they are often applied as structural materials. The load of the mechanical constructions is often of dynamical type. To analyse exactly the constructions we have to know the dynamic behaviour of the material of the construction. The behaviour of the analysed material, of the silicone rubbers can be written only with complex quantities. The dynamic characteristic data depend on the frequency and temperature. This article presents two methods to define the dynamic properties of silicone rubbers. Firstly the classical dynamic mechanical analysis (DMA) is demonstrated then a direct measurement is shown to determine the frequency-dependent dynamical characteristic data. As a conclusion it can be proposed that the direct measurement gives the more reliable result in case of silicone rubbers.

Keywords: dynamic mechanical analysis, Williams-Landel-Ferry equation.

1. Dynamic Mechanical Analysis of the Silicone Rubber

1.1. Dynamic Mechanical Analysis

The most often used type of the dynamic analysis is the Dynamic Mechanical Analysis (DMA) to define the thermomechanical curve. During the measurement of the thermomechanical curves the answer of the polymer is measured by different temperatures at the excitation of the polymers. The excitation of the polymer is a sinusoidal function with angular frequency ω and a constant amplitude. The type of the load is a force excitation and so the answers are the deformation and the phase lag δ.

The function of the examination:

$$F(t) = F_{\mathrm{st}} + F_{\mathrm{din}} \cdot \sin \omega t, \tag{1}$$

where: F_{st} is the static force; F_{din} is the dynamic force; ω is the angular frequency.

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The loading types of the Dynamic Mechanical Analysis are

- bending
- tension
- pressure.

From the loading types the three-point bending was applied to measure the silicone rubbers. The two other loading types are used for fibers, films and dusty materials. The static force provides that the vertical exciter stays in contact with the specimen during the analysis. The sinusoidal component comes still to the static force. To avoid the separation between the vertical exciter and the specimen the parameters have to fulfil the next condition, $F_{\mathrm{st}} > F_{\mathrm{din}}$.

During the examination the parameters of the analysis were: $F_{\mathrm{st}} = 95.27$ mN, $F_{\mathrm{din}} = 59.54$ mN, $\omega = 4\pi \frac{\mathrm{rad}}{\mathrm{s}}$. The thermomechanical curves can be measured in wide temperature-domain with the method of DMA. This analysis shows very sensitively the inside change of the state of the polymers, so the transformation temperatures can be determined exactly. The temperature was increased by a heating velocity of $5\frac{^\circ\mathrm{C}}{\mathrm{min}}$ from -160 °C up to $+75$ °C. Two thermomechanical quantities, the storage modulus (E') and the loss factor (tg δ) will be shown in the answer diagram depending on the temperature. The loss modulus (E'') can be calculated with E' and tg δ from *Eq.* (2).

$$\mathrm{tg}\,\delta \frac{E''}{E'}. \tag{2}$$

The further thermomechanical quantities can be calculated by the help of the above quantities.

The most important thermomechanical quantities are:

The complex modulus:

$$E^* = \sqrt{E'^2 + E''^2}. \tag{3}$$

The complex viscosity:

$$\eta^* = \frac{E^*}{\omega}. \tag{4}$$

The storage viscosity:

$$\eta' = \frac{E'}{\omega}. \tag{5}$$

The loss viscosity:

$$\eta'' = \frac{E''}{\omega}. \tag{6}$$

The analysis was made for three types of silicone rubbers with different hardness. These are:

- 30 Sh hardness /vulcanization type additive/silicone rubber (30 A)
- 40 Sh hardness /vulcanization type peroxide/silicone rubber (40 P)
- 80 Sh hardness /vulcanization type peroxide/silicone rubber (80 P)

1.2. The Equipment for the Dynamic Mechanical Analysis

The measurement was taken in the laboratory of the Dept. of Polymer Eng. and Text. Technology. The dynamic analyser consists of three main units. The first is a computer, which makes the calculation of the measured data and the graphical display. The second is a control unit, which is responsible for the thermic analysis control. The third unit is a dynamic mechanical analyser.

The equipment is shown in *Fig. 1*. The type and units of the equipment are:

1. computer
2. control unit (Thermic Analyser Controller, TAC 7/DX, Perkin Elmer)
3. dynamic mechanical analyser (DMA 7e, Perkin Elmer)
4. cooling room (cooling agent: liquid nitrogen)
5. heating element

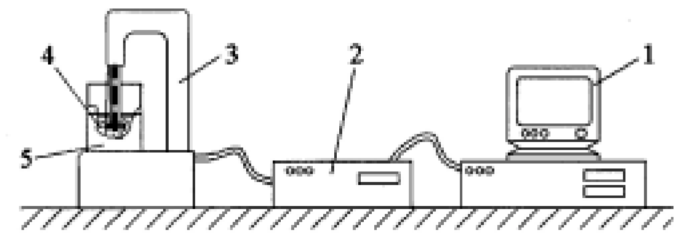

Fig. 1. The equipment of the Dynamic Mechanical Analysis

The examination effect is provided for the specimen by a vertical exciter. The precise fixing of the exciters into the grippers is a very important operation because of the hyperelastic behaviour of the silicone rubbers. In the opposite case the measuring results can be false. The specimens have a block form with a fixing distance of 15 mm. The exciter and the gripper for the three-point bending are illustrated in *Fig. 2*.

1.3. The Results of the Dynamic Mechanical Analysis

The analysed silicone rubbers have a well definable glass transition. The glass temperatures (T_g) are:

- at 30 A silicone rubber: $T_g = -38\,°\mathrm{C}$
- at 40 P silicone rubber: $T_g = -35\,°\mathrm{C}$
- at 80 P silicone rubber: $T_g = -30\,°\mathrm{C}$

The storage modulus decreases two orders of magnitude from 10^9 [Pa] to 10^7 [Pa] in the glass transition. This behaviour and the glass temperature are shown at 30 A and 40 P silicone rubbers in *Fig.* 3 and in *Fig.* 4. The hardness of silicone rubbers influences the glass temperature since the segmental motion already starts at lower temperature in the softer materials than in the hard materials. This proves the measurements because the glass temperature of 40 P silicone rubber is lower than 80 P silicone rubber.

Fig. 2. The vertical exciter

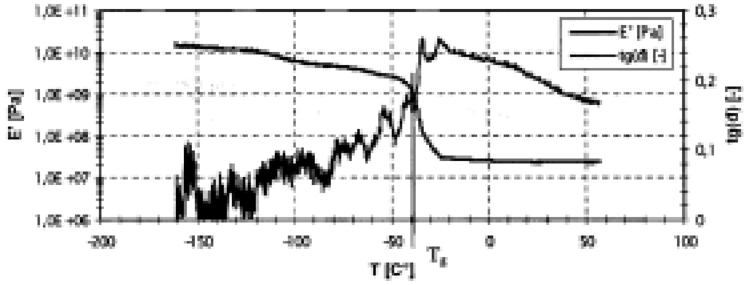

Fig. 3. The thermomechanical curves of 30 Sh A silicone rubber

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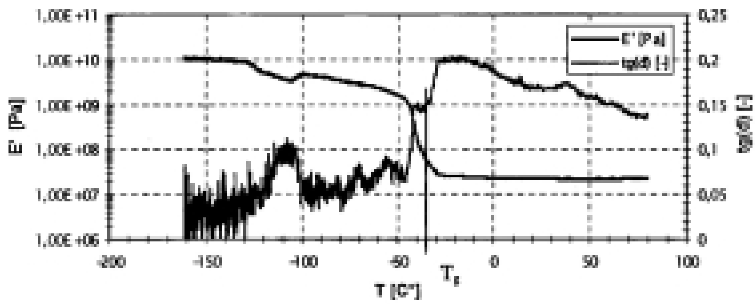

Fig. 4. The thermomechanical curves of 40 Sh P silicone rubber

2. The Expression of the Frequency-Dependent Dynamical Characteristic Data according to the Time–Temperature Equivalence

Time–temperature equivalence in its simplest form implies that the viscoelastic behaviour at one temperature can be related to the behaviour at another temperature by the change in the time-scale only. Williams, Landel and Ferry found an approximately identical relation between the shift factor and the temperature for all amorphous polymers, which could be expressed as

$$\ln a_T = \frac{c_1 \cdot (T - T_0)}{c_2 + (T - T_0)}, \tag{7}$$

where: c_1 and c_2 are constants; T_0 is a reference temperature.

Lots of experiments prove that the c_1 and c_2 constants are the same for most of polymers and if $T_0 = T_g$, c_{1g} and c_{2g} are in temperature domain of $\{T_g; T_g + 100\ [^\circ\mathrm{C}]\}$:

$$c_{1g} = -17.44 \frac{1}{^\circ\mathrm{C}},$$
$$c_{2g} = 51.6\ ^\circ\mathrm{C}.$$

Choosing of $T_0 = T_g$ is advantageous because the thermic mobility of the segments in the polymers is prevented at the temperature of T_g. Thus, if the temperature is increased in the same rate over the glass temperature at different polymers, the mobility of the polymer segments will be the same. The shift factor can be defined as

$$a_T = \frac{t}{t_0} = \frac{\omega_0}{\omega} = \frac{f_0}{f}, \tag{8}$$

where: t is the load duration; ω is the load angular frequency; f is the load frequency. The applied equation to determine the curves of $E'(f)$ and tg $\delta(f)$ from the thermomechanical curves (*Fig. 3*, *Fig. 4*) can be written

$$\ln \frac{f_0}{f} = \frac{c_{1g} \cdot (T - T_g)}{c_{2g} + (T - T_g)}. \tag{9}$$

Applying the *Eq.* (9) the next frequency-dependent characteristics can be got at $T_0 = T_g$ reference temperature.

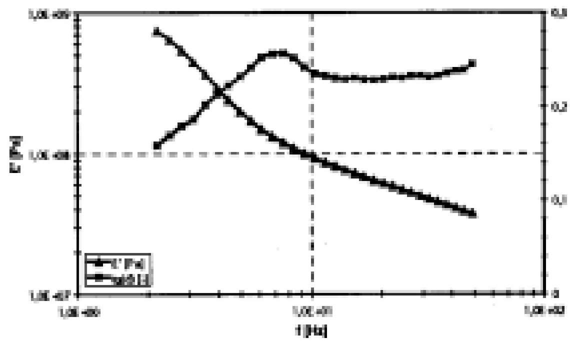

Fig. 5. The storage modulus and the loss rate of 30 A silicone rubber depending on frequency at $T_0 = T_g$

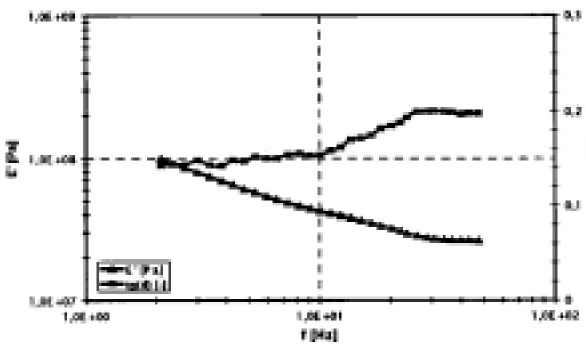

Fig. 6. The storage modulus and the loss rate of 40 P silicone rubber depending on frequency at $T_0 = T_g$

Let us analyse the frequency-dependent behaviour of silicone rubbers by the help of WLF equation reference to $T_0 = 20\,°\text{C}$.

See the conclusions in Chapter. 4.

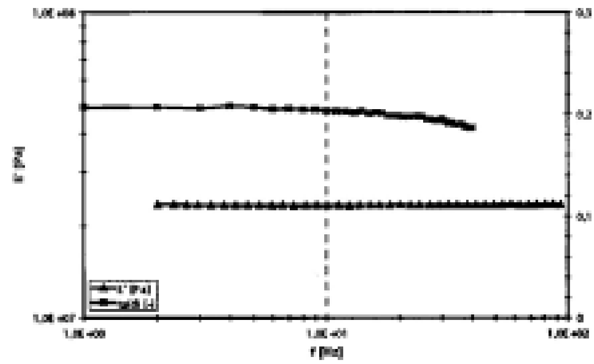

Fig. 7. The storage modulus and the loss rate of 30 A silicone rubber depending on frequency at $T_0 = 20$ °C

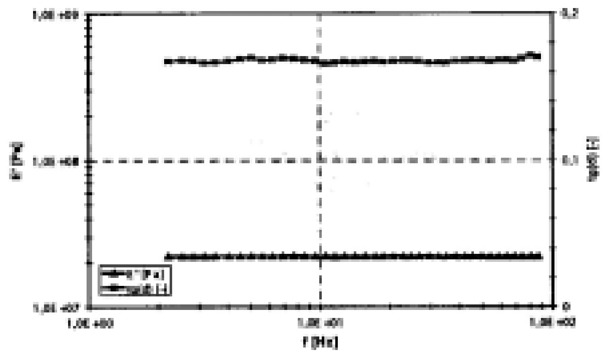

Fig. 8. The storage modulus and the loss rate of 40 P silicone rubber depending on frequency at $T_0 = 20$ °C

3. Direct Measurement of the Frequency-Dependent Dynamical Characteristic Data

The measurement can be made with the same equipment as the Dynamic Mechanical Analysis. The type of loading was also the same. If we hold the temperature at a constant value ($T = 20$ °C) and measure the storage modulus and the loss rate at different frequencies, we obtain the next characteristics:

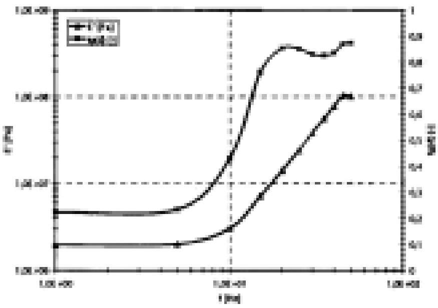

Fig. 9. The storage modulus and the loss rate of 30 A silicone rubber depending on frequency at $T = 20$ °C

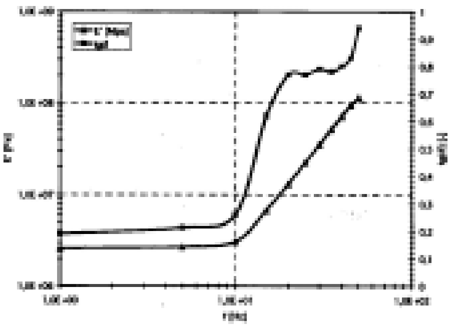

Fig. 10. The storage modulus and the loss rate of 40 P silicone rubber depending on frequency at $T = 20$ °C

4. Conclusions

Comparing the two methods to define the frequency-dependent Dynamical Characteristic Data of silicone rubbers it can be declared that they show high difference. *Figs.* 5 and 6 (in Chapter 2) illustrate that the silicone rubbers show a frequency-dependent behaviour near to the glass temperature. *Fig.* 7 and *Fig.* 8 try to prove the behaviour of silicone rubbers as over the glass temperature their behaviours are frequency-insensitive. The direct measurements verify the frequency-dependent behaviour and *Fig.* 9 and *Fig.* 10 show fast same characteristic as *Figs.* 5 and 6 particularly the characteristic of the loss rate.

The high difference between the two methods can be interpreted with the limited using of the WLF equation for silicone rubbers since it is firstly applied to amorphous polymers; nevertheless, it is used for other polymers, too.

Acknowledgement

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