STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLIII, 1-2, 1998

THERMORHEOLOGICAL BEHAVIOUR OF SILICONE OIL (AK 10^6)

ADINA GHIRI¯ AN* and B. HOCHSTEIN**

ABSTRACT. The rheological measurements have been made to determine the behaviour of silicone oil AK 10^6. It was determined the viscoelastic temperature dependence properties. A value of 43 kJ/mol for the energy of activation has been determined.

INTRODUCTION

Rheological measurements are carried out on materials having industrial interest for one of the following reasons: quality control of raw materials, ingredients and final product; to study the influence of recipe ingredients or modifications on rheological properties and to supplement the information provided by the product behaviour during practical use. The motivation for any rheological study is often the hope that observed behaviour in industrial situations can be correlated with same easily measured rheometrical function. The conditions under which the measurements are carried out depend on the information which is required.

Two different methods are available for determining the rheological behaviour of silicone oil that was tested in our experiment: static and dynamic [1].

Static tests involve the imposition of a step change in stress (or strain) and the observation of the subsequent development in time of the strain (or stress).

In the rheological context the term "dynamic measurement" refers to an experiment in which either the stress or the strain (and usually both) varies harmonically with time. The dynamic tests are: oscillatory strain, wave propagation by using high frequency studies and stady flow.

Compared to steady shear experiments, dynamic tests generally are performed at small strain amplitudes so that they result in only a slight or neglijable disruption of the material microstructure. This feature of oscillatory measurements is on particular advantageous when studying multi-phase materials.

The use of oscillatory methods increased considerably with the development of comercial rheometers. The avantage of oscillatory tests is that a single instrument can cover a very wide frequency range.

MEASUREMENT PRINCIPLES

When dynamic tests are to be carried out on viscoelastic fluids, like silicone oil, the material is usually confined between cylinders, cones or plates as in steady rotational rheometry (Figure 1).

Torsional rheometers (like Cone-Plate and Plate-Plate are used for oscillatory measurements in dynamic experiments for high viscosity fluids and suspensions.

* *"Babeş-Bolyai" University Cluj-Napoca, Department of Chemical Engineering.*

*** University of Karlsruhe, Institut fur Mechanische Verfahrenstechnik und Mechanik.*

Two parameters have to be selected for an oscillation measurement: frequency and stress. The frequency values can be selected. The selected range depends on the sample and the properties which are studied.

A common deformation made for investigating linear viscoelastic behaviour of viscoelastic materials is oscillatory frequency sweep. For oscillatory measurements the sample is subjected to a sinusoidal deformation $\gamma(t)$ with an amplitude at an angular frequency $\omega = 2\pi f$ (Equation (1)), where f is the frequency of oscillation, [2], and the response is sinusoidal too, but with a difference $\delta(\omega t)$ (Figure.2), (Equation (2)).

The ***Oscillatory Frequency Sweep*** program has been used to analyse the thermodynamic of rheological behaviour of silicone oil AK 10^6.

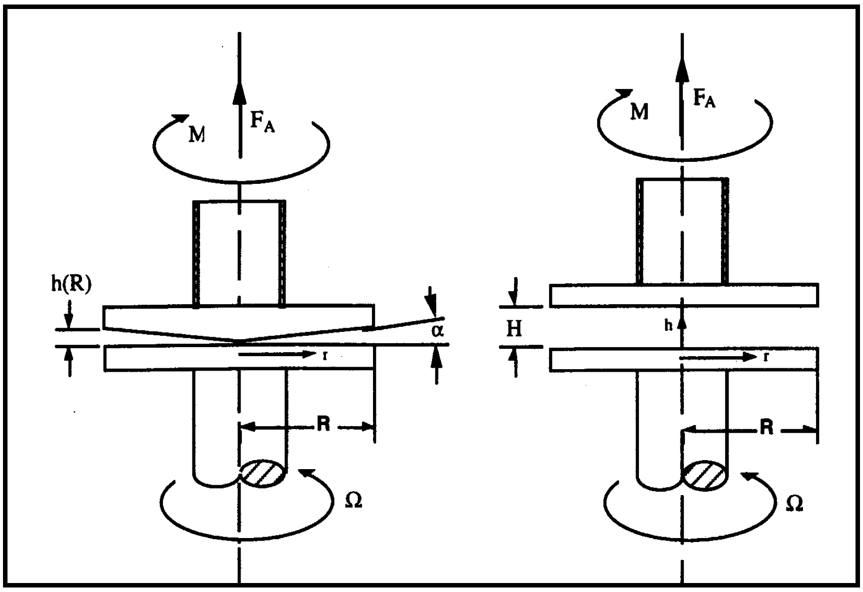
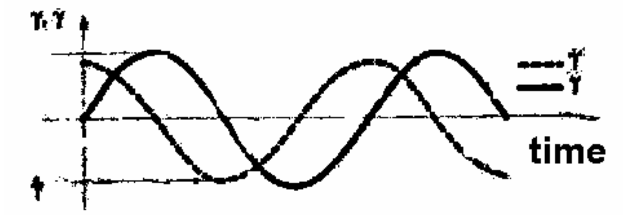
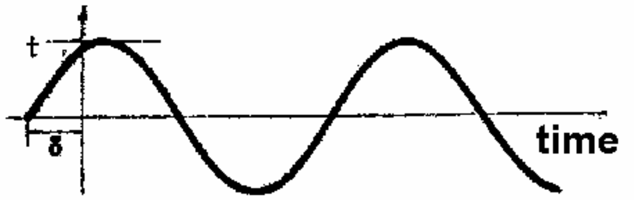


Fig.1. Schematic representations of two rotational viscometers (a. Cone - Plate; b. Plate - Plate).



$$\gamma(t) = \gamma \bullet \sin(\omega t) \quad \textbf{(1)}$$



$$\tau(t) = \tau \bullet \sin(\omega\, t + \delta) \qquad \textbf{(2)}$$

Fig.2. Strain, shear rate and shear stress during a dynamic experiment.

The calculated values in oscillatory tests are dynamic viscosity, phase shift, storage, loss and complex modulus. They can be measured as a function of frequency, time and temperature. This type of measurement gives information about a sample's structure and elasticity or behaviour at gelation or crystallisation.

It is a convention to plot results of oscillatory tests in terms of the dynamic viscosity **η'** and dynamic rigidity **G'**.

For more understanding of the oscillatory method which have been used to discuss the response of viscoelastic material the following terms have been considered:

- the "complex shear modulus" **G*(ω)** (Equation (3)):

$$\left|G^*(\omega)\right| = \frac{\tau(\omega)}{\gamma} \qquad \textbf{(3)}$$

The complex shear modulus **G*(ω)** can be separated in to two component material functions, the "storage modulus" **G'(ω)** and the "loss modulus" **G''(ω)** [3]. The "storage modulus" **G'(ω)** is a measure of the elasticity energy stored by the material, while the "loss modulus" **G"(ω)** is proportional to the energy dissipated (i.e. the viscous portion). The "complex shear" modulus can be calculated from the storage and loss moduli, (Equation (4)).

$$\left|G^*(\omega)\right| = \sqrt{G'(\omega)^2 + G''(\omega)^2} \qquad \textbf{(4)}$$

- the "complex viscosity" **η*(ω)** has been determined by frequency sweep method, at a constant strain amplitude (Equation 5)):

$$\left|\eta^*(\omega)\right| = \frac{\left|G^*(\omega)\right|}{\omega} \qquad \textbf{(5)}$$

The thermorheological measurements suggest that we should give attention to the temperature as an inherent rheological variable.

The effect of temperature on the rheological properties (in particular on the viscosity) has been used to characterize the rheological behaviour of silicone oil AK 10^6 [4].

A new relation has been introduced, relation of Arrhenius (Equation (6)). It has the following form for two different temperatures:

$$\eta_o(T) = \eta_o(T_o)\exp\left[\frac{E_o}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)\right] \qquad \textbf{(6)}$$

where η_o is the viscosity at the zero shear rate.

In this relation the specific parameter which can characterize the material behaviour is the activation energy E_o (kJ/mol). R is the gas constant (R = 8.314 10^{-3} kJ/mol.K) and T is absolute temperature.

The proportional representation of null viscosity introduces a new constant called "factor of the displacement with the temperature" or "shift factor" [5] and noted a_T (Equation (7)).

$$a_T = \frac{\eta_o(T)}{\eta_o(T_o)} \qquad \textbf{(7)}$$

The value of a_T may be found empirically by shifting the curve for temperature T sideways until the overlopping part matches to T_o curve (reference temperature).

Ferry [5] discusses a particular very widely used empirical expression for a_T, the WLF equation introduced by Williams, Landel and Ferry [6] (Equation (8)).

$$\log a_T = -\frac{C1(T - To)}{C2 + T - To} \qquad \textbf{(8)}$$

where the constants C1 and C2 depend on the choise of reference temperature To.

The validity of Equation (6) draws to a Arrhenius curve in semilogarithmic scale, where the coefficient a_T is represented against the reciprocal of absolute temperature (1/T). The straight line plot has the slope s. The activation energy of the flow, (Equation (9)) is proportional with the slope s:

$$Eo = R \bullet s \bullet \ln 10 \qquad \textbf{(9)}$$

EXPERIMENTAL

We have determined the rheological behaviour of silicone oil AK 10^6 using a Haake RheoStress RS 150 with a cone-plate system.

The test material has been contained between the cone and the plate with an angle of 4^o (Type: C35/4H). The bottom member, the plate, (the imput) undergoes forced harmonic oscillations about its axis and this motion is transmitted through the test material to the top member, the cone, (the output) the motion of which is contrained by a torsion bar. Since both members move, the shear rate is proportional to tha relative velocity between them.

The Hakee rheometer RS 150 is used in combination with a computer working with a MS - Windous software. The software is used to send the measurement conditions to the instrument and calculate and present the received data. The following parts complete the apparatus: air filter (with max 4 bar), regulator power box, monotor cooler and an external temperature regulator.

RESULTS AND DISCUSSION

The experimental data have been presented in forms of graphs.

To illustrate the using of the time dependence we have plotted the values of storage modulus **G'** and loss modulus **G''** against **ω** on a logarithmic scale, and the values of complex viscosity **η*** against the **ω** (rad/s).

Figure 3 shows the storage modulus **G'** and loss modulus **G''** versus frequencies for silicone oil AK 10^6 at 20^oC at two different stresses. (50 Pa, OSC-1RMD and 250 Pa, OSC-2RMD, noted in graph). The curves are similar that meaning that for the same range of frequencies the deformation of the sample for the two different stresses is insignificant.

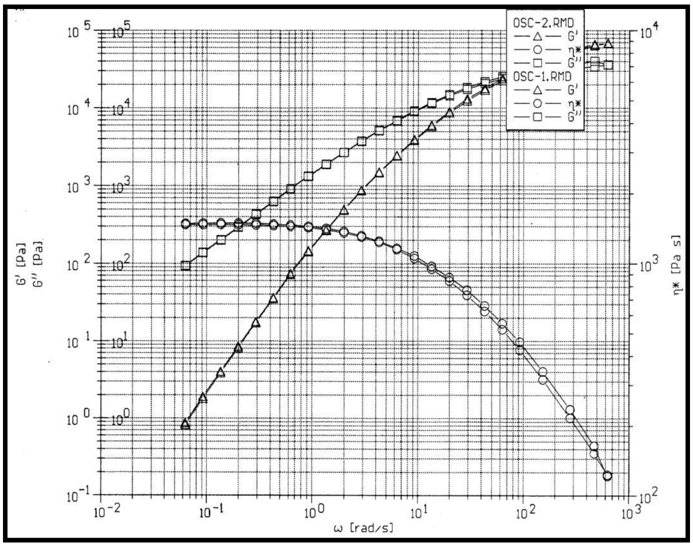


Fig.3. Dependence of the storage, loss moduli and complex viscosity on angular frequency ω (rad/s^{-1}).

To obtained the thermodynamic parameters $\mathbf{a_T}$ and **Eo** which can show us the behaviour of the silicone oil tested the complex shear modulus **G*** was presented as a function of various angular frequencies **ω** (Figure 4) at different temperatures (5^oC, 10^oC, 20^oC, 40^oC, 60^oC and 80^oC). Each temperature determination gives a different curve (Figure 4).

At a constant value of the complex shear modulus (i.g. **G*** 4 10^4 Pa) we have read the $\boldsymbol{\omega_i}$ values, which corresponds to different curves. With these values and with $\boldsymbol{\omega_0}$ for the standard temperature (20^oC) we have calculated the "shift factor" $\mathbf{a_T}$ and then have plotted these values against 1/T (with T-absolute temperature) (Figure 5)

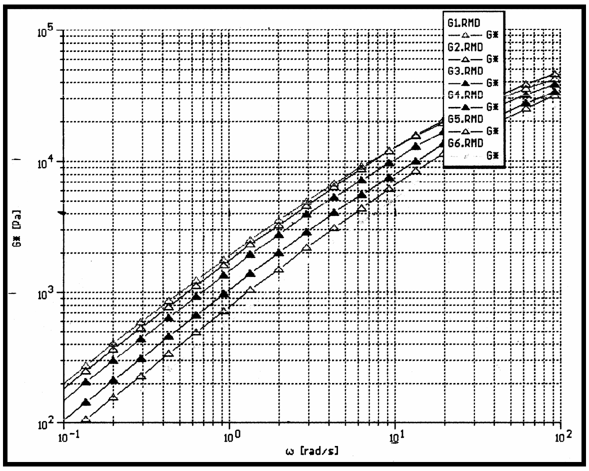


Fig.4. Dependence of the complex modulus on angular frequency ω(rad/s^{-1})

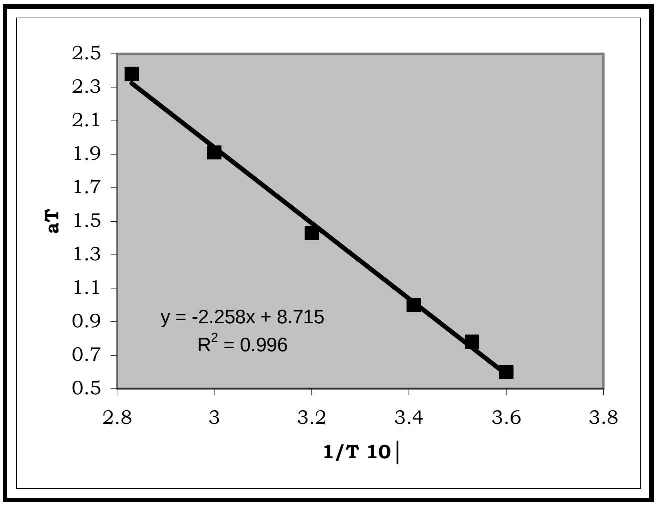


Fig.5. Determination of the activation energy (dependence of a_T on temperature 1/T)

The linear dependence shows a linear viscoelasticity behaviour of the silicone oil AK 10^6 tested (simple fluid). This line can be esed to determine the value of the "shift factor" or coefficient for another temperature (e.g., we calculated 50^0C the value of $\mathbf{a_T}$ = 1.75 and ω_i = 5.25s^{-1}).

The value Eo calculated by equation (9) is:

Eo = R s ln 10 = 8.314 10^{-3} 10^3 2.258 ln 10 = 43.2 kJ/mol.

REFERENCES

1. H. A. Barnes, J. F. Hutton and K. Walters, *An Introduction to Rheology*, Edn. Elsevier, 1989.
2. B. Hochstein and W. Gleissle, *Rheology 95*, 1995, 72-79.
3. M. Pahl, W. Gleissle and H. Martin Laun, *Praktishe Rheologie der Kunststoffe und Elastomere*, VDI-Verlang Gmblt, Dusseldorf, 1991.
4. Harry H. Hull, *An Approach to Rheology Through Multi-Variable Thermodynamics*, Cold-Comp. , Pittsburg, PA 15222, 1981.
5. J.D.Ferry, *Viscoelastic Properties of Polymers*, 2nd Edn.John Wiley & Sons, 1970.
6. M. L. Williams, R. F. Landel and J. D. Ferry, *J.Amer.Chem.Soc*., 1955, 77, 3781.