Shear-wave speeds and elastic moduli for different liquids
Part 3. Experiments-update

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Abstract: Tables of values of shear-wave speeds, shear moduli and relaxation times for 18 new liquids are presented, supplementing the tables for 51 liquids given in Part 2. A brief discussion of errors and analysis of the oscilloscope traces is presented. The relation of the effective moduli measured on the wave-speed meter to independent measurements using phase-modulated birefringence and delayed die swell is discussed. A method of measuring wave speeds and rigidities for sheared media is proposed.

Key words: Shear-wave speed, effective shear modulus, relaxation time, wave-speed meter

1. Introduction

In our earlier work we presented a theory [1] of effective wave-speeds for shear waves into regions at rest and developed the idea of an effective rigidity (shear modulus) and viscosity. A device, the wave-speed meter (U.S. patent 4,602,502), was described and used to measure wave speeds and effective rigidities in 51 liquids [2]. An effective relaxation time for these liquids may be formed as the ratio of the static viscosity upon the rigidity.

The wave-speed meter is a Couette apparatus with two independently rotatable cylinders. The outer cylinder is set into rotation suddenly. This creates a shear wave at one liquid boundary. The wave propagates through the liquid and turns the inner cylinder as it arrives. We measure the lapse time between the onsets of both rotations for a given gap size and determine the transit speed. The onset of motion is detected by two laser beams which are reflected from each cylinder and are focused onto photodiodes before the measurement is started. The drop of the photovoltage indicates the motion of the cylinders as explained in the Appendix. Voltage versus time diagrams are recorded on an oscilloscope. The time of onset of motion of inner and outer cylinder may be accurately determined from the oscilloscope trace. The difference in onset times gives the lapse time, and the transit speed is then obtained as the ratio of gap size to lapse time. In [2], and here, we show that the measured transit times are more or less constant for different gap sizes. In [2] we showed that our data were consistent with data taken from step-in-strain experiments and dynamic measurements, though in fact, different quantities are measured in each of these experiments.

G. G. Fuller, of the Department of Chemical Engineering at Stanford University has recently carried out some measurements of wave speeds using a method of his own which is based on a phase-modulated birefringence technique (see [4] and [5]). At the date of this writing he has obtained wave speeds for two liquids, 0.75% and 1% aqueous solutions of poly(ethylene oxide) (WSR-301). His values 10.8 cm/s and 18.2 cm/s are in good agreement with values 11.6 cm/s and 18.3 cm/s (0.9% solution) reported in [2]. Fullers method works for liquids which exhibit optically anisotropic properties under shear.

The concept of an effective modulus developed in [1] seems to be supported by measurements in [2], here and those of Fuller. Additional support for these ideas in a flow context come from recent measurements of delayed die swell [3]. In those experiments it was established that there is a general critical condition associated with die swell. This condition is defined by a critical speed which is the area average velocity, the extrusion velocity, at the exit of the pipe when the swell is first delayed. The delayed swell ratio and delay distance first increase for larger, post-critical values of the extrusion velocity; then the increases are terminated either by instabilities or by smoothing. The maxi-

Table 1. Wave speeds and rigidities. The columns contain the following data: $\tilde{\mu}$ zero-shear viscosity, $\bar{c}$ average shear-wave speed, G_c effective shear modulus, λ relaxation time, h gap size, c shear-wave speed for each gap size, T temperature, ϱ density

Fluid	$\tilde{\mu}$ [Pas]	$\bar{c}$ [10^{-2} m/s]	G_c [Pa]	λ [s]	h [10^{-3} m]	c [10^{-2} m/s]	T [°C]	ϱ [kg/m^3]
1% PMMA in DEM (Poly(methyl-methacrylate) in diethyl malonate) MN ≅ 1,000,000	0.426	12.9	17.4	0.55	1.38 2.38	14.0 ± 1.3 11.7 ± 1.1	23 24	1,050
2% PMMA in DEM	2.58	25.0	66.8	0.039	1 2 3	25.8 ± 2.0 26.6 ± 1.3 22.5 ± 1.5	22 23 23	1,071
1% PIBM in BIS 2 (Poly(isobutyl-methacrylate) in bis (2-ethyl-hexyl) hydrogen phosphate) MN ≅ 5,500,000	0.065	20.3	38.3	0.0017	0.38 1 2	21.2 ± 4.6 21.2 ± 2.3 18.5 ± 2.7	23 24 24	930
5% K-125 in DEM (copolymer of 80% PMMA and 20% poly(ethyl-butyl-acrylate)) MN ≅ 1,900,000	1.17	46.7	231	0.0051	1 2 3	45.4 ± 3.4 46.1 ± 1.9 48.5 ± 4.4	26 25 26	1,060
Fluorinert FC 5312	2.43	11.3	24.6	0.098	0.25 0.5	10.4 ± 2.9 12.2 ± 4.3	25 24	1,930
1.3% CMC in Water (Carboxy methyl cellulose) MN ≅ 160,000	10.8	48.1	231	0.047	3 6.75	48.0 ± 1.4 48.1 ± 1.4	24 27	999
0.7% CMC in Water	0.598	28.9	90.6	0.0066	1 2 3	32.6 ± 2.9 29.8 ± 1.7 27.9 ± 2.7	23 24 24	1,000
1.3% CMC in 48.7% Water and 50% Glycerin	129	80.8	744	0.074	1.38 6.13	81.2 ± 6.4 80.3 ± 4.7	23 23	1,140
1.2% CMC in 48.8% Water and 50% Glycerin	23.4	57.9	379	0.062	3 6.75	58.8 ± 8.0 57.1 ± 1.0	24 25	1,130
0.8% CMC in 49.2% Water and 50% Glycerin	5.77	48.8	269	0.022	1 2 3	49.0 ± 4.6 47.2 ± 1.9 50.1 ± 2.1	22 23 22	1,130
6% PIB in Decalin (Poly(isobutylene)) MN ≅ 1,000,000	11.0	90.1	730	0.015	1 3 6.75	88.9 ± 5.8 93.6 ± 4.6 87.6 ± 2.7	23 23 23	899
6% PIB in Toluene	41.0	116	1,160	0.035	1.38 2.38	114.2 ± 4.1 116.9 ± 2.6	24 24	868
5.5% PIB in Toluene	5.44	60.6	332	0.016	1.38 2.38	53.3 ± 5.4 67.9 ± 1.2	23 23	903
4% PIB in Toluene	0.88	53.5	244	0.0036	1 2 3	48.4 ± 6.9 56.2 ± 3.4 55.9 ± 1.9	24 24 27	854
2.5% Polyox in Water (Poly(ethylene oxide) WSR-301) MN ≅ 3,000,000	62.8	51.2	302	0.21	1 3 6.75	48.6 ± 3.5 53.8 ± 1.2 51.2 ± 0.1	24 25 24	1,150
Cherry EP 258 # 1 (Pillsbury)	474	117	1,490	0.32	6.75	117.2 ± 4.5	25	1,090
Cherry EP 258 # 4 (Pillsbury)	456	117	1,740	0.26	3 6.75	121.2 ± 16.6 113.0 ± 4.8	26 26	1,270
Cherry EP 258 # 5 (Pillsbury)	423	124	1,620	0.26	3 6.75	131.4 ± 5.6 117.1 ± 3.4	25 24	1,050

mum post-critical velocity at the pipe exit was always greater than the shear-wave speed measured on the wave-speed meter. The post-critical area average velocity at the position of maximum swell before termination was always less than the shear-wave speed. There were always points in the region of swelling where the ratio of the local velocity to the shear-wave speed, the viscoelastic Mach number, was unity. The liquids with the shortest time of relaxation appeared to have a large effective viscosity, with a much greater degree of smoothing. The tight correlation between critical velocities measured in the die swell experiment and the wave speeds is noteworthy. The two experiments are completely independent, there are no parameters to adjust. Nevertheless correlations hold for all fluids tested, over hundreds of measurements, with wave speeds varying over a decade.

2. Table of wave speeds and rigidities

Various material parameters for 18 different liquids are listed in table 1. These supplement tables 1 and 2 in [2] where data for 51 fluids were given. All the wave speeds reported here were computed from oscilloscope traces. The average wave speed, over different gap sizes is called $\bar{c}$ and is used to compute the effective shear modulus $G_c = \varrho \bar{c}^2$, where ϱ is the fluid density. $\tilde{\mu}$ is the zero-shear or static viscosity measured in a cone-and-plate viscometer and λ is a relaxation time given through $\lambda = \tilde{\mu}/G_c$.

An error in c is given in the table for each gap size. It corresponds to one standard deviation over about 10 transit time readings. This error contains errors in reading transit times off the oscilloscope and variations due to changes of input at the outer cylinder. Typically the value for $\Delta c/c$ is smaller than 10%. Thus we find for the relative error in $G_c \Delta G_c/G_c \mathrel{\widehat{=}} 22\%$ when we estimate the relative error in the density measurements as $\Delta\varrho/\varrho \mathrel{\widehat{=}} 2\%$. Other possibly systematic errors of our apparatus can not jet be estimated and are not included here.

3. Development of a wave-speed meter for shear waves into stressed media under shearing

The speed of sound depends on the thermodynamic condition of the gas. In the same way the speed of shear waves in a viscoelastic fluid is a point function of the state of stress at the respective point. In the case of small unsteady shearing perturbations of steady shear with shear rate $\dot{\gamma}$ one finds wave speeds in the form

$$c(\dot{\gamma}) = \sqrt{G(\dot{\gamma})/\varrho}\,,$$

where ϱ is the density of the fluid and $G(\dot{\gamma})$ the rigidity of the stressed fluid. In fact, $G(\dot{\gamma})$ is the instantaneous value (at $\tau = t$) of a relaxation function $G(\dot{\gamma}, t-\tau)$, and $G(0, t-\tau)$ is the relaxation function relative to a state of rest, with effective rigidity $G_c = G(0, \varepsilon)$. The effective rigidities G_c for different liquids are given in [2]. An effective-moduli theory for $G(\dot{\gamma}, t-\tau)$ can be developed along exactly the same lines laid down in [1] and leads to effective rigidities $G_c(\dot{\gamma})$.

We are proposing a device to measure $c(\dot{\gamma})$ and $G_c(\dot{\gamma})$. This device combines the experiment on stress relaxation after sudden removal of steady shearing with the measurements of wave speeds into regions at rest.

Appendix: A remark on the measuring system

Further study of the wave-speed meter should include the influence of the input upon the form of the wave front arriving at the inner cylinder and the measured wave speed. This can be done when we relate the recorded voltage drop on the oscilloscope to the motion of each cylinder. The analysis of both motions will provide the desired information.

Corresponding to the intensity distribution of the laser beam we record a variation of the normalized photovoltage with the angle θ

$$V(\theta) = \exp(-\beta\theta^2)\,. \tag{1}$$

The response of the electronic circuit including photodiode and oscilloscope can be determined as the laser beam is cut off fast in front of the photodiode. We model this as

$$V(\theta, t) = \exp(-\beta\theta^2 - t/\sigma)\,. \tag{2}$$

The dynamic response of the measuring system has been recorded for different constant angular speeds $\dot{\theta}$:

$$V(\theta, \dot{\theta}, t) = \exp(-\beta\theta^2 - b(\dot{\theta})\,t^2)\,, \tag{3}$$

where $b(\dot{\theta}) = \alpha\dot{\theta}^2$. A relation which satisfies all three equations above is

$$V(\theta, \dot{\theta}, t) = \exp(-\beta\theta^2) \cdot [\exp(-\alpha\dot{\theta}^2 t^2) + (1 - \exp(-\alpha\dot{\theta}^2 t^2))\exp(-t/\sigma)]\,, \tag{4}$$

where (1) and (2) are limiting conditions

$$\lim_{\dot{\theta}\to 0} V(\theta, \dot{\theta}, t) = \exp(-\beta\theta^2)\,,$$

$$\lim_{\dot{\theta}\to \infty} V(\theta, \dot{\theta}, t) = \exp(-\beta\theta^2 - t/\sigma)\,.$$

During the measurement θ and $\dot{\theta}$ vary with time and we assume for the $V(t)$-diagram recorded on the oscilloscope

$$V(t) = V(\theta(t), \dot{\theta}(t), t)\,. \tag{5}$$

This is a differential equation for $\theta(t)$ with $\theta(t=0) = 0$. We neglect the effects due to the electronic circuit when t is such that $\exp(-t/\sigma) \ll 1$ which is the case for small times since

$\sigma < 2 \cdot 10^{-6}$ s. $V(t)$ shall be modelled as

$$V(t) = \exp(-\gamma t^4), \tag{6}$$

and we can solve for $\theta(t)$:

$$\theta(t) = \sqrt{\frac{\gamma}{4\alpha + \beta}}\, t^2 \cong \sqrt{\frac{1 - V(t)}{4\alpha + \beta}}, \tag{7}$$

with $\alpha = 2 \cdot 10^6$ and $\beta = 2 \cdot 10^7$. With this formula we can analyze the motion of both cylinders from the $V(t)$-diagrams recorded on the oscilloscope.

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