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ORIGINAL CONTRIBUTION

A new instrument for measuring the viscoelastic properties of dilute polymer solutions

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Abstract A new oscillating capillary viscometer has been developed and used for measuring viscoelastic flow properties of dilute polymer solutions. These flow properties are determined from measurements of the pressure to volume flow relationships for sinusoidal flow in cylindrical glass capillaries. The theory for this measurement procedure is based upon the known theory for oscillatory flow of a viscoelastic fluid in circular tubes and which is presented with a few supplementations in this paper.

The oscillatory flow is generated by a piezoelectric driver which is dipped directly into the aqueous solution. The advantage of this driver is that the excitation voltage for the piston is a direct measure of the motion of the piston. Changes in pressure are measured with a sensitive low-pressure quartz transducer.

The viscometer was tested with aqueous glycerol solutions and a gelatin gel. The viscoelastic flow properties of dilute polymer solutions (gelatin, gelatin/color-coupler, polyacrylamide) were then investigated in the frequency range 5 Hz to 150 Hz at very small volume flow amplitudes. The results presented illustrate the suitability of the method. The results are also evaluated with regard to the stabilizing action of slightly viscoelastic gelatinous coating liquids in the high-speed coating process in the manufacture of photographic materials.

Key words Oscillatory capillary viscometer – viscoelastic flow properties – polymer solutions – high-speed coating process

Introduction

Aqueous solutions of polymers are mainly viscoelastic. Their complicated flow characteristics reflect not only the properties of the particular polymer molecules, but also the interactions between each other, with other components and with the solvent. The relevance of viscoelastic flow properties to many technological and biological processes is well-known, especially the viscoelastic flow properties of blood which have been extensively investigated by Thurston [1–3].

Many steady shear viscosity measurements have been made but they do not give the same extent of physical insight into the mechanical properties of the fluid as can be obtained from oscillatory shear flow studies.

The most commonly used oscillatory shear flow experiments are:

– the Weissenberg rheogoniometer with cone and plate geometry: It has been extensively used for the measurement of oscillating normal stress difference. However, many experiments have shown that at low shear rates of about $\dot{\gamma} = 4\ s^{-1}$ disturbances in form of vortices appear in the gap [4]. In these cases care must be taken not to exceed the limitations of the method.

– Couette type viscometers with coaxial cylinders: Here the measurements are limited to low frequencies because at higher frequencies inertia forces become significant.

– Oscillating capillary rheometer: A polymeric liquid in a circular tube is made to oscillate by means of a sinusoidally varying pressure gradient. The measurements should be carried out at small volume amplitudes so that nonlinear effects are not significant.

An apparatus for oscillatory tube flow measurements of the effect of frequency on the viscoelasticity of dilute polymer solutions was developed and described by Thurston [5–7]. The hydrodynamic theory for axial sinusoidal oscillation of a viscoelastic fluid in a circular tube was given by Thurston and Chmiel and Walitza [8, 9].

We have developed a new oscillating capillary rheometer because of the unavailability of appropriate instrumentation for measurements of the flow properties of slightly viscoelastic solutions, especially the viscoelastic flow properties of gelatinous coating liquids used in the high-speed coating process in the manufacture of photographic materials. In this process where multiple layers of coating liquids are applied simultaneously to a moving web with a slide hopper type coating apparatus, the liquid bridge, formed between the lower edge of the slide hopper and the moving web has to be stabilized against oscillations. Oscillations of the liquid bridge were observed when a critical wet film thickness of about 30 μm was reached. The stabilizing effect of a suction to the lower surface of the liquid bridge and the stabilizing action of added anionic surfactants are known [10]. An additional stabilizing effect of viscoelastic flow properties was found by coating experiments. These coating experiments showed that for viscoelastic solutions with a small angle of viscoelasticity, Φ, $3° \leq \Phi \leq 5°$, the stability of the liquid bridge is markedly improved [11]. The degree of viscoelasticity was modified by adding small amounts of a water-soluble polyacrylamide to the gelatinous solutions.

Experimental method

Measurements of the oscillatory tube flow of viscoelastic fluids were carried out using an apparatus in which the flow is generated by a sinusoidal oscillating piezoelectric driver attached to the measuring chamber. A schematic representation of the apparatus is shown in Fig. 1. At the bottom of the chamber a sensitive low pressure quartz transducer (10 mV/Pa) is mounted. Its electrical signals are measured to obtain the amplitudes of the pressure, and the phase difference between the motion of the driver and the sinusoidal changes of the pressure in the chamber.

All solutions (about 40 ml) are contained in a brass measuring chamber. Inserted in the chamber is a cap with three identical parallel glass tubes, each of length 4.0 cm and radius 0.066 cm. The brass chamber is jacketed for temperature control.

In order to test the frequency characteristics of the piezoelectric driver the measuring chamber was filled with water and the capillaries were sealed with a plug. The piston was made to oscillate with a constant alternating voltage in a frequency range of 2 Hz to 300 Hz. Table 1 shows the normalized pressure amplitudes and the phase difference between the excitation voltage at the driver and the pressure response.

The main advantages of the piezoelectric driver are:

I) The normalized pressure amplitude depends only slightly on frequency. The slight increase observed in the pressure amplitude with frequency is considered in the evaluation of the volume amplitude.

II) At a fixed frequency of 80 Hz there is a linear relationship between the driver oscillation amplitude and

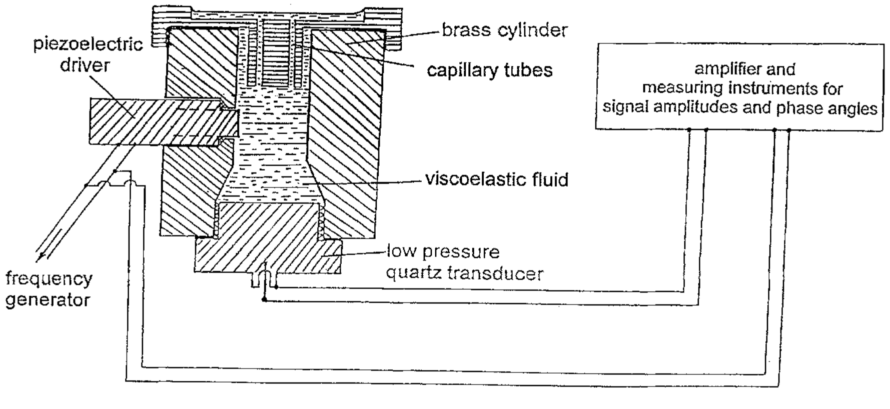


Fig. 1 Schematic diagram of the oscillatory capillary viscometer

Table 1 Frequency characteristic of the piezoelectric driver

Hz	U piezometer (V ~)	Difference of phase (deg)
2	0.94	– 0.4°
3	0.95	– 0.5°
5	0.955	– 0.7°
10	0.96	– 0.4°
25	0.96	– 0.1°
50	0.97	0.3°
75	0.995	0.6°
100	1.005	0.7°
125	1.01	0.6°
150	1.01	0.5°
200	1.015	0.6°
250	1.01	0.4°
300	1.015	0.7°

the excitation voltage. These measurements were carried out with sealed capillaries. The results are given in Fig. 2.

III) As shown in Table 1 the phase difference between the excitation voltage and the motion of the piston is negligible, therefore it was not necessary to develop a device for monitoring the driver motion.

The driver piston oscillates with a very small amplitude of about 0.5 μm to 1.0 μm. This corresponds to a flow amplitude of about 10 μm. All measurements were carried out at very low shear rates of about $\dot{\gamma} = 10$ to $20\,\mathrm{s}^{-1}$ a region where nonlinear effects are insignificant.

Oscillatory flow theory

The simplest mechanical model which describes the flow properties of a viscoelastic fluid is called a Maxwell material. If one assumes that the disturbance of the entrance can be neglected because the capillary is long enough, then the velocity vector of the flux is given by

$$v_x = v(r,t) = i\omega s(r)e^{i\omega t}, \quad v_r = v_\varphi = 0 \ , \tag{1}$$

where $s(r)$ describes the oscillation amplitude of the volume elements, and x,r,φ are the cylinder coordinates. Then the stress tensor has the components $\sigma_{xx} = -p$ and σ_{xr}. Using the Maxwell model the following relations can be obtained [12]

$$\sigma_{xr} + \lambda \frac{\partial}{\partial t}\sigma_{xr} = \eta \frac{\partial v}{\partial r} \tag{2}$$

or in the case of oscillation

$$\sigma_{xr} = \eta^* \frac{\partial v}{\partial r} \tag{3}$$

with

$$\eta^* = |\eta^*|e^{-i\Phi} = \eta' - i\eta'' = \frac{\eta}{1 + i\lambda\omega} \ . \tag{4}$$

That means

$$\tan\Phi = \omega\lambda = \frac{\eta''}{\eta'} \tag{5}$$

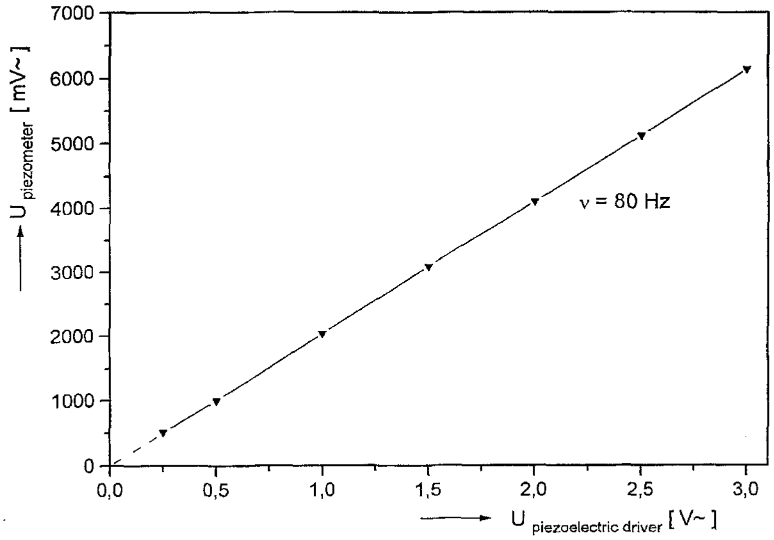
and

$$\eta = |\eta^*|(1 + \lambda^2\omega^2) \ . \tag{6}$$

The divergence of the stress tensor leads to a special form of the Navier–Stokes equation

$$-\frac{\partial p}{\partial x} + \eta^* \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial v}{\partial r}\right) = \rho\frac{\partial v}{\partial t} \tag{7}$$

Fig. 2 Amplitude characteristic of the piezoelectric driver at a fixed frequency



with the known solution

$$v(r,t) = -\frac{i}{\rho\omega}\frac{\partial p}{\partial x}\left(\frac{J_0(kr)}{J_0(ka)} - 1\right), \tag{8}$$

where a is the radius of the capillary, ρ the density, and k a complex material parameter

$$k = \sqrt{-i\frac{\omega\rho}{\eta^*}} = \sqrt{\frac{\omega\rho}{|\eta^*|}}\, e^{i(\Phi/2 - \pi/4)} . \tag{9}$$

After integration over the cross-section of the tube, we obtain for the quotient of the oscillation functions the formula

$$\frac{\Delta V}{\Delta p} e^{-i\alpha} = -\frac{m\pi a^2}{l\omega^2\rho}\left(\frac{2}{ka}\frac{J_1(ka)}{J_0(ka)} - 1\right). \tag{10}$$

$\Delta V(\omega)$ is the amplitude of the volume deformation, $\Delta p(\omega)$ the amplitude of the pressure oscillation and α the phase shift between deformation and pressure. The number of capillaries used is m, and l is their length. By a fitting procedure the values of $|\eta^*(\omega)|$ and $\phi(\omega)$ can be determined which satisfy Eq. (10). For this procedure the Bessel-functions $J_n(z)$ of complex arguments are used

$$z = ka = |z|\exp[\Phi/2 - \pi/4] . \tag{11}$$

If the Womersley parameter, $|z|$, where

$$|z| = a(\omega\rho/|\eta^*|)^{1/2} \tag{12}$$

is smaller than 5, we apply the known potential series

$$J_n(z) = \left(\frac{z}{2}\right)^n \sum_{k=0}^{\infty} \frac{(-1)^k}{(k+n)!(k)!}\left(\frac{z}{2}\right)^{2k} \tag{13}$$

and in the other area the following asymptotic development

$$J_n(z) = \frac{1}{2}\sqrt{\frac{2}{\pi u}}\,(G(iu)e^{i\varphi} + G(-iu)e^{i\varphi}) \tag{14}$$

with

$$G(u) = 1 + \frac{1}{8}\left(\frac{1}{u} - \frac{5n^2}{3u^3}\right) + \frac{1*3}{8^2}\left(\frac{3}{2u^2} - \frac{77n^2}{9u^4} + \frac{385n^4}{54u^6}\right), \tag{15}$$

$$\varphi = u - n^* \operatorname{arctg}\left(\frac{u}{n}\right) - \frac{\pi}{4}, \tag{16}$$

and

$$u = z \quad \text{for } n = 0, \qquad u = \sqrt{z^2 - 1} \quad \text{for } n = 1. \tag{17}$$

Here one must bear in mind the many-valuedness of the complex function. Equation (14) also gives good results for the Bessel functions of the first kind (not for the second one) if the conditions for the asymptotic development are not fulfilled.

Results and discussion

When a viscoelastic material is subjected to an oscillatory tube flow the following quantities are observed: the deformation of the volume $\Delta V = \pi a^2 \Delta s$, the pressure amplitude Δp and the phase angle α between deformation and pressure. If the response of the material is in phase with the deformation ($\alpha = 0$), the material is purely elastic. For Newtonian fluids the pressure curve is in phase with the shear rate $\dot{\gamma} = \partial v/\partial r$. Neglecting the acceleration term in [7] the viscoelastic phase angle Φ is given by

$$\Phi = (\pi/2) - \alpha$$

Most polymeric materials respond in a manner which is neither purely elastic nor purely viscous; the materials are therefore viscoelastic [13, 14].

The values of Φ as a measure of the elastic component were determined. For a purely viscous liquid like glycerol $\Phi = 0$.

Experimental determinations of the complex coefficient of viscosity η^*, the viscous and the elastic component of η^*, η' and η'' as well as the viscoelastic phase angle have been carried out for an aqueous solution of glycerol, aqueous gelatin solutions and a gelatin gel. To test the measurement procedure, measurements were performed using (I) a Newtonian fluid having known viscous properties and (II) a gelatin gel having nearly elastic properties. The glycerol/water mixture (I) with a viscosity of 29.9 mPa*s was used for testing the apparatus. As shown in Table 2 the values of η^* show good correlation. Glycerol shows no elastic effects and no change of viscosity with frequency. The viscoelastic phase angle Φ of these Newtonian test solution is practically zero.

For testing the apparatus the values of the complex coefficient of viscosity η^*, the storage modulus $G' = \omega * \eta''$ and the viscoelastic phase angle Φ, of a gelatin gel were determined. The measuring chamber was filled with a 5.3% gelatin solution at a temperature of 313 K. Measurements were made after cooling to 295 K. The aging time after cooling was about 1 h. The average molecular weight of the gelatin used was about 320 000, determined with the aid of gel chromatography. The results are shown in Table 2.

At low frequencies the storage modulus G' of the gelatin gel increases slowly with frequency. In a frequency range of about 5 Hz to 20 Hz the course of the storage modulus with the frequency is almost horizontal.

Table 2 Frequency dependence of complex viscosity and viscoelastic phase angle for glycerol/water and a gelatin gel

	Glycerol/water at 295 K		5.3% Gelatin (gel) at 295 K		
Hz	η^* (mPa *s)	$\Phi°$	η^* (mPa *s)	$\Phi°$	G' (N/m^2)
5	30.2	1.6	1173	85.9	36.7
10	29.6	− 0.1	591	86.6	37.0
20	29.3	0.8	302	87.2	37.8
40	29.7	0.3	209	87.1	52.4
60	30.1	0.5	168	87.6	63.3
80	29.7	0.8	127	87.7	64.2
100	30.5	0.9	104	88.2	65.1

Table 3 Frequency dependence of complex viscosity and viscoelastic phase angle for several liquids

Hz	15% Gelatin at 313 K		5% Gelatin + 1% color coupler at 313 K		7% Gelatin + 0.16% polyacrylamide at 313 K	
	η^* (mPa *s)	$\Phi°$	η^* (mPa *s)	$\Phi°$	η^* (mPa *s)	$\Phi°$
5	31.9	1.4	17.8	1.7	26.6	18.4
10	32.1	0.8	18.0	1.4	23.2	18.0
20	31.8	− 0.4	17.7	1.0	17.9	18.2
40	31.6	0.8	17.9	1.2	14.6	17.3
60	31.9	0.5	18.3	0.8	14.9	16.8
80	32.2	0.7	18.5	0.6	15.2	16.5
100	32.5	1.0	18.3	1.1	15.4	16.9

Many investigations of gelatin can be found in the literature. Some of them are concerned with the viscoelastic behavior of gelatin gels. te Nijenhuis [15] investigated the elasticity of gelatin gels at low frequencies using a dynamic rheometer which consisted of two concentric cylinders. The inner cylinder oscillated sinusoidally in a frequency range of 0.0001 to 100 rad/s which corresponds to a maximum frequency of 16 Hz. In this frequency range the increase of the storage modulus G′ was very small, too.

Table 2 shows that in a frequency range of about 20 Hz to 60 Hz the storage modulus increases rapidly from about 38 N/m^2 to 63 N/m^2. Above a frequency of 60 Hz the storage modulus increases very slowly again.

The rheological properties of gelatinous coating liquids are of great importance for the stability of the liquid bridge in the high-speed coating process in the manufacture of photographic films and papers. The effect of a slightly viscoelastic gelatinous coating liquid ($\Phi = 3°–6°$) on the stability of the liquid bridge has been investigated previously by means of coating experiments [11]. Instabilities of the liquid bridge create wave-like changes of the coating thickness.

Here the flow properties of three different gelatinous liquids used in the coating experiments [11] were investigated (Table 3) in a frequency range of 5 Hz to 100 Hz at a temperature of 313 K.

The 15% gelatin solution behaves like a Newtonian fluid showing no change of viscosity with frequency. The viscoelastic phase angle Φ was found to be close to 0° and the storage modulus G' was approximately 0.005 N/m^2. Measurements with a gelatin/color coupler solution gave similar results. The hydrophilic color coupler used shows surfactant properties. The hydrophobic part consists of the chromophoric system with a hydrocarbon chain (C_{18}) and is attached to a hydrophilic functional group ($-SO_3$). Investigations on the interaction between gelatin and the color coupler used showed that in the gelatin/color coupler system, 90–95% of the added amount of coupler is bound to the gelatin. The binding isotherms were determined using a surfactant–selective electrode [16]. The strong interaction between gelatin and color coupler causes a drastic increase in viscosity. This raises the question of whether viscoelastic properties are created as a consequence of the formation of intermolecular cross bonds.

From the results it can be seen that gelatin and gelatin/color coupler solutions behave like purely viscous liquids showing no remarkable viscoelastic properties. In order to obtain a low degree of viscoelasticity, small amounts of a water soluble polyacrylamide were added to the gelatin solution. The effect of the addition of 0.16% of a water–soluble polyacrylamide to a 7% gelatin solution is shown in the right column of Table 3. The addition of polyacrylamide generates viscoelastic flow properties and leads to an increased stability in the liquid bridge against oscillations in coating experiments [11]. In a further experiment the flow properties of the polyacrylamide used in the coating experiments were investigated. Measurements were carried out in order to determine the viscous and elastic components of oscillatory flow in a frequency range of 5 Hz to 100 Hz for 0.52% polyacrylamide, at a temperature of 295 K. The results are shown in Fig. 3. The elastic component η'' of the complex viscosity of the polyacrylamide solution used is of considerable magnitude, especially at higher frequencies. This solution shows typically viscoelastic flow properties. The values of G' increase from 0.81 N/m^2 (5 Hz) to 5.15 N/m^2 (100 Hz) with increasing frequency. At low frequencies the changes in both viscosity components are significant. The viscous and the elastic component decrease with increasing frequency. It is seen that η' and η'' become constant at higher frequencies. The viscoelastic phase angle Φ increases at frequencies less than 30 Hz and levels off to a value of about 45° at higher frequencies.

Viscoelastic fluids with $\Phi > 15°$ are not favorable in the coating process. In these cases longitudinal streak formation which is a coating defect was observed. The

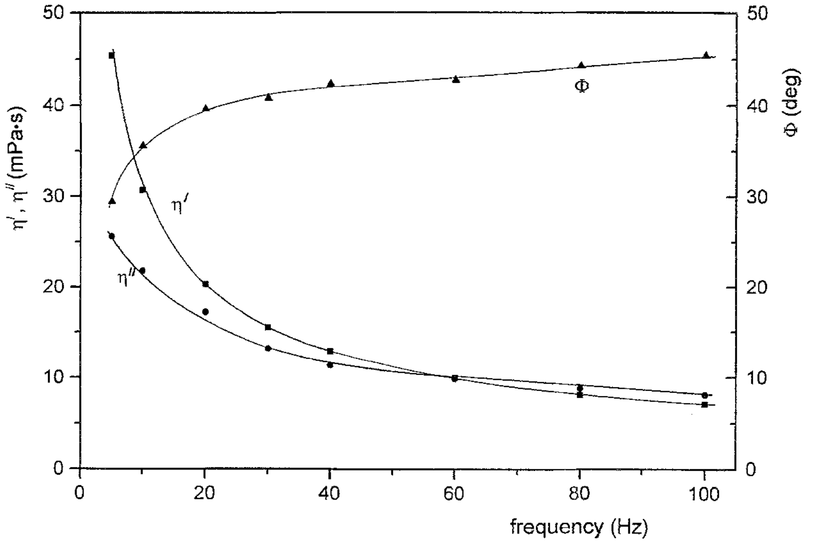


Fig. 3 Viscosity components η' and η'' and viscoelastic phase angle Φ versus frequency for 0.52% polyacrylamide

fine-banded streak formation in the coated layer is probably a consequence of the appearance of normal stresses within the liquid bridge.

The results show that the new device can be used to study slightly viscoelastic polymer solutions ($\Phi \geq 3°$) in the frequency range of 3 Hz to 150 Hz. Measurements were carried out up to 150 Hz. Quantitative evaluation was carried out up to 100 Hz because the measured viscosity data of the solutions used are independent of frequency above 100 Hz.

At frequencies above 150 Hz inaccurate results are obtained, especially with low-viscous solutions. This is due to the effect of inertia which increases quadratically with increasing frequency, whereas viscous effects increase linearly. At frequencies above 150 Hz the viscous pressure component is less than 10% of the total pressure, and the phase angle α is primarily determined from the inertia of the oscillating column of liquid.

For this reason the method is not appropriate for measurements >150 Hz. At very low frequencies ($\nu <$ 3 Hz) the pressure amplitudes are very small and the results are also inaccurate. The use of capillaries with smaller radii and higher amplitudes of ΔV is required for measurements in this frequency range.

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