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Theoretical basis for elasticity measurements of polymer melts and rubbers

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ABSTRACT

A review is presented of techniques that are used for the measurement of the viscoelasticity of fluids, concentrating on those most suited for polymer melts and rubbers. The review focuses on the assumptions made in the analyses and on the advantages and disadvantages of the techniques, rather than on a detailed examination of the theory needed to interpret the data obtained from them. The report primarily covers the techniques of oscillatory rheometry, stress relaxation, creep recovery and extrudate swell for the measurement of linear viscoelasticity properties. For the measurement of normal stress differences the steady shear rotation, exit pressure and hole pressure techniques are examined.

The report is intended to guide those with limited understanding of rheology through the complexities of the measurement of viscoelasticity, and to direct those who wish to seek further information. It is the first of two reports on the measurement of viscoelasticity. The second report (1) focuses on the experimental application of the techniques to the characterisation of the viscoelasticity of polymer melts and rubbers.

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1. INTRODUCTION

The objective of this report is to review the theoretical basis of techniques that can be used for the measurement of the viscoelasticity of polymer melts and rubbers. The review focuses on the advantages and disadvantages of these techniques and on the assumptions made in the derivation of the analyses that are needed to interpret the experimental data, rather than on a detailed analysis of the theory that can be obtained elsewhere (2,3,4).

The report is intended to guide those with limited understanding of rheology through the complexities of the measurement of viscoelasticity, and to direct those who wish to seek further information. It is suggested that the reader first reads the Discussion and Conclusions, Sections 3 and 4 respectively, and then to progress to remainder of the report, Sections 2.2 - 2.5, on a selective basis or for reference. Some of the terminology that is used herein is defined in Section 2.1.

This report is the first of two on the measurement of viscoelasticity. The second (1) reviews the experimental application of the techniques described herein to the measurement of the viscoelasticity of polymer melts and rubbers. The techniques covered in this report are not restricted to these materials but can be used for other substances, for example paints, waxes and foods.

Before progressing with an examination of techniques for the measurement of viscoelasticity it is desirable to identify the needs for such measurements. In a recent report on the industrial needs for viscoelasticity data for polymer melts and rubbers (5) it was concluded that many processing problems are related, at least in part, to the elastic behaviour of the material. Elastic stresses can be induced into the material being processed by shear deformation or extensional deformation, or more likely by a complex combination of the two. Elasticity induced by extensional deformation is particularly relevant to polymer processing as the majority of processes, for example extrusion, blow moulding and thermoforming involve significant extensional flows. Additionally, polymer processes typically involve large deformations. Thus viscoelasticity data obtained under similar conditions, namely of large deformations in both shear and extension, are required for the purpose of modelling industrial processes. This is particularly desirable if one is to avoid or minimise the necessary extrapolation of data that have been obtained under other conditions. Nevertheless, viscoelastic measurements using small amplitudes of deformation are of value for characterising materials as such techniques are more suited to resolving small differences in their behaviour.

2 THEORETICAL BASIS FOR ELASTIC MEASUREMENTS

2.1 GENERAL

Before proceeding with this review it is desirable to clarify what is meant by elasticity. All polymer melts exhibit a viscoelastic response when subjected to a deformation or force. A viscoelastic response comprises a viscous or non-recoverable component, and an elastic or recoverable component. The ISO standard on terminology for plastics, ISO 472 (reference 6), defines *viscoelasticity* as "*The stress response of a material acting as though it were a combination of an elastic solid and a viscous fluid with flow dependent on time, temperature, load, and rate of loading*". Also, ISO 472 defines *elasticity* as "*The property of recovering original size and shape when deforming forces are removed*", and *viscosity* as "*The property of resistance to steady flow exhibited within the body of a material*".

Viscoelasticity can be subdivided into two categories, namely linear viscoelasticity and non-linear viscoelasticity. A linear viscoelastic material can be defined as that which has a linear relationship between stress and strain. By definition a Newtonian fluid that has a viscosity that is independent of shear rate is a linear *viscous* fluid. For a linear viscoelastic fluid the superposition principle can be used, for example, to determine the net effect of two independent strains by summing the effects of the individual strains. This principle is used in the analysis of flow in testing, but it is limited to the range of conditions over which the fluid exhibits linear viscoelasticity. However, for many liquids the flow range over which their behaviour can be described, within the limits of experimental error, as being linear is restricted. For polymer melts the upper limits of stress and strain are usually very small. The limit of the range of linear behaviour can be determined relatively easily using oscillatory rheometry techniques as described in Section 2.2.

A non-linear viscoelastic material can be defined as that for which the stress is a non-linear function of strain. An example of non-linear behaviour is shear thinning which is commonly exhibited by polymer melts particularly under the conditions of flow that are typical of processing. Compared with linear viscoelasticity it is a more complex description of fluid behaviour. Barnes et al (7) comment that the subject of non-linear viscoelasticity is a "much more difficult subject" than linear viscoelasticity. However, the use of non-linear viscoelastic constitutive equations is more likely to yield accurate modelling of the flow of polymers in processing conditions. The measurement of properties in the non-linear regime is therefore desirable, if not essential.

Dynamic testing is widely used to characterise the viscoelastic behaviour of fluids. It is particularly useful for identifying structural changes and differences between materials. In this section only methods that are oscillatory in which the applied stress or strain varies harmonically (sinusoidally) with time are considered. The principle of dynamic testing is that the sample is subjected to an oscillatory stress of known amplitude and the resultant strain is measured. Alternatively a known strain can be applied and the resultant stress measured. These are commonly referred to as "controlled stress" or "controlled strain" modes respectively. A variety of test geometries can be used (2,8), the more common of which are parallel plates, cone and plate and concentric cylinders.

For a linear viscoelastic fluid subjected to an applied harmonic stress σ where

$$\sigma = \sigma_0 \cos \omega t \quad [1]$$

resulting in an harmonic strain γ given by

$$\gamma = \gamma_0 \cos (\omega t - \delta) \quad [2]$$

where σ_0 and γ_0 are the amplitudes of the stress and strain respectively, ω is the angular frequency of oscillation (rad/s), δ is the phase shift or lag (rad) and t is time, the following quantities can be defined:

$$\text{shear storage modulus } G' = \sigma_0 \cos \delta / \gamma_0 \quad [3]$$

$$\text{shear loss modulus } G'' = \sigma_0 \sin \delta / \gamma_0 \quad [4]$$

$$\text{complex shear modulus } G^* = G' + iG'' \quad [5]$$

$$\text{dynamic viscosity } \eta' = G'' / \omega \quad [6]$$

$$\text{out of phase component of the dynamic viscosity } \eta'' = G' / \omega \quad [7]$$

$$\text{complex viscosity } \eta^* = \eta' - i\eta'' \quad [8]$$

where i denotes the complex number defined by $i^2 = -1$.

Furthermore, from equations 5 - 8 it can be shown that

$$G' = \eta' \omega \quad [9]$$

The terminology used is that proposed by The Society of Rheology (9). As mentioned above, the equipment for dynamic testing of fluids can take many forms, and the oscillation can be either resonant or non-resonant (forced) (2). The method most commonly used for dynamic testing of fluids is probably the forced oscillation mode using a parallel plate geometry. In this the sample is held between two parallel circular plates of known diameter with a specified gap (or plate separation). One plate is oscillated relative to the other at a fixed amplitude of angular displacement or torque (controlled strain or controlled stress respectively) and the resultant torque or displacement is measured. From the magnitudes of the applied and measured parameters of torque and angular displacement and the phase shift δ between their harmonic forms (equations 1 and 2) the dynamic modulus and viscosity parameters listed above can be determined. The theory for the determination of these moduli and viscosities is well established for the parallel plate geometry and for other geometries in both forced (non-resonant) and resonant oscillation (2,3,8). The reader is referred to these texts for a more detailed examination of the theory.

For forced oscillation the equation of motion governing the flow, following Marin (8), is given by

$$T_o = -I\omega^2 \theta_o \exp(-i\delta) + A[G'(\omega) + iG''(\omega)]\theta_o \exp(-i\delta) + B\theta_o \exp(-i\delta) \quad [10]$$

where T_o is the torque, I is the inertia of the moving plate, θ_o is the maximum amplitude of the angular displacement, A is a geometry term, and B is related to the compliance of the machine. For a parallel plate geometry and assuming linear viscoelastic behaviour of the fluid being tested the factor A is given by

$$A = \pi R^4 / 2h \quad [11]$$

where h is the plate separation and R is the radius of the plates. For a cone and plate geometry the geometry factor is given by

$$A = 2\pi R^3 / 3\alpha_o \quad [12]$$

where R is the radius of the plates and α is the cone angle (radians) which is assumed to be

small ($\alpha < 4^\circ$). For concentric cylinders the geometry factor is given by

$$A = 4\pi h R_1^2 R_2^2 / (R_2^2 - R_1^2) \quad [13]$$

where R_1 is the radius of the inner cylinder, R_2 is the radius of the outer cylinder and the axial length of the gap is h . The following discussion on the use of the parallel plate geometry also largely applies to the use of the cone and plate and concentric cylinders geometries.

The inertia and compliance terms are normally small such that equation 10 can be reduced to

$$T_o = A[G'(\omega) + iG''(\omega)]\theta_o \exp(-i\delta) \quad [14]$$

These approximations are particularly valid when low frequencies of oscillation are used and when the sample being tested is of low stiffness relative to the stiffness of the machine. However, software is often incorporated into modern rotational rheometers to correct for the inertia term. Correction for the compliance of the machine can also be applied to measured data (10) where this has not been incorporated into the rheometer's analysis software.

The assumptions made in the derivation of equations 10 and 11 are that the fluid is assumed to deform in a linear viscoelastic manner, that the inertia of the sample is negligible, and that edge effects are also negligible (ie surface tension and velocity field perturbations at the edge of the plate). The assumption that the fluid's behaviour is linear viscoelastic is made as the shear strains and shear strain rates vary from a value of zero at the centre of the plates to a maximum at the edge. From geometric considerations it can be shown that the shear strain at radius r is given by

$$\gamma = \theta r / h \quad [15]$$

where θ is the amplitude of the oscillation in radians. In testing of polymer melts the amplitude of oscillation must be kept small, with maximum strains of the order of a few percent if this assumption is to be valid. The linearity of the fluid's behaviour can be relatively easily checked, for example, by reducing the stress or strain amplitude of oscillation and determining whether the modulus and/or viscosity values thus measured differ from the values obtained at the higher amplitude of oscillation. If the values differ then the testing has been carried out in the non-linear region with the values of stress and strain being too

high. A torque or angular displacement sweep will more comprehensively identify the linear viscoelastic region of the fluid's behaviour (the region over which G' and G'' are constant) and thus define the range of conditions over which testing should be carried out. A further check that can be made during testing is that if the fluid's behaviour is non-linear then the measured output function of torque or displacement will not be harmonic (sinusoidal). This check assumes that the input function of displacement or torque was harmonic (a prerequisite of the test) and that the necessary raw data can be obtained from the rheometer.

Corrections can be made for the effect of sample inertia which is most significant in testing of low viscosity fluids at high frequencies (3,11). In reference 11 it was concluded that the effect of fluid inertia was most significant when using a concentric cylinder geometry. Also, the effect of fluid inertia was negligible when using a cone and plate geometry and was not important when using parallel plate geometries, except when using large gaps and testing very mobile liquids. Edge effects can be investigated by using different size sample geometries: a reduction in the ratio of gap size to plate diameter will reduce any edge effect.

Other dynamic techniques are reviewed by Whorlow (2) and Marin (8) and include the orthoganol rheometer (or eccentric rotating discs), the Kepes balance rheometer and the use of eccentric cylinders. These are not considered here as according to Whorlow (2) the recent technical developments in standard oscillatory rheometers have resulted in their capability surpassing the advantages once offered by the above listed techniques, with the consequence that the equipment is no longer widely available, if available at all.

In using oscillatory rheometers to measure non-linear viscoelastic behaviour the reader is referred to Walters (3). For this type of measurement the mathematics is particularly complex and proper interpretation of the data requires prior knowledge of the constitutive equation that is to be used to describe the rheological behaviour of the material. However, Walters (3) reported that interpretation of non-linear measurements on the basis of linear viscoelastic assumptions has been made by various researchers. Walters (3) also refers to the measurement of normal stress differences using non-linear oscillatory techniques but comments that such measurements are subject to large errors due in particular to the difficulty of measuring small transient normal stress differences.

In attempting to correlate dynamic and steady shear viscosity values it can be shown (3) that the following relation holds as both the frequency (rad/s) and shear rate (s^{-1}) tend to zero.

$$\eta'(\omega)|_{\omega \rightarrow 0} = \eta(\dot{\gamma})|_{\dot{\gamma} \rightarrow 0}$$

[16]

This is obviously of limited use as the frequencies and shear rates at which this relation is approximately valid will be small. In contrast Cox and Merz (12) identified that the empirical relation

$$|\eta^*(\omega)| = \eta(\dot{\gamma}) \text{ for } \omega = \dot{\gamma} \quad [17]$$

between the complex viscosity and the steady shear viscosity was valid over a higher range of frequencies and shear rates than [16]. It has been demonstrated that this relationship holds for a limited range of unfilled materials (13, 14).

2.3 STRESS RELAXATION AND CREEP RECOVERY

Creep testing at constant stress, or stress relaxation at constant strain can be used to characterise the viscoelastic behaviour of polymer melts. The principle of creep testing is to stress a polymer sample in shear or in extension and to measure the change in strain of the sample with time. In stress relaxation testing two modes can be used. In the first (case A) the sample is deformed "instantaneously" and held at that value of strain (or position). The subsequent reduction of stress with time is then measured. In the second case (case B) the sample is subjected to a constant rate of deformation prior to the start of the test, eg steady shear. This deformation is then stopped "instantaneously" and the strain held. The subsequent reduction of stress with time is then measured. Creep testing can be used to simulate, for example, the deformation of the polymer in film blowing in which a pressure is maintained to deform the material. Stress relaxation testing can be used to simulate, for example, the process of die swell in extrusion.

In carrying out relaxation or creep testing it is important that the creep rate or relaxation time of the fluid is slow compared with the rate at which the material was either loaded (creep testing), strained (case A, relaxation testing) or the deformation stopped (case B, relaxation testing). If this is not the case then critical data will be lost during the early phase of the test. The inertia of the measuring system will affect the rate at which the sample can be loaded. This can be investigated by changing the inertia of the measuring system, for example by adding weights, and checking whether this has had any influence on the results obtained.

The Deborah number is a parameter that is used as a measure of the elasticity of flow. It is

defined as the ratio of the characteristic time of the material to the characteristic time of the event (7). The characteristic time of a material is a measure of how quickly stress relaxation occurs. The Deborah number is dimensionless. In the context of creep testing for example, if the characteristic time of the event is taken to be the time to load the sample then the testing must be carried out at high Deborah numbers so that creep of the sample during the loading phase is minimal.

Creep and relaxation testing of polymer melts can be carried out in the linear or non-linear viscoelastic region depending on the initial applied stress or strain. For the purposes of interpreting the data it is necessary to know in which region testing has been carried out. To check that testing has been carried out in the linear viscoelastic region the modulus and viscosity values determined from testing should be independent of the applied test conditions.

The analysis of the creep or stress relaxation behaviour normally assumes a prior knowledge of the constitutive form to be used to describe the material's behaviour. However, Soskey and Winter (15) have proposed a method for the analysis of large strain, non-linear relaxation measurements which does not require that a specific type of non-linear constitutive equation is assumed.

Simple linear viscoelastic analysis can be made on the basis of assuming a spring and dashpot model (2). In the simplest form this can be a Maxwell element consisting of a spring and dashpot in series, but this does not accurately describe polymer melt behaviour. A more realistic model for fluids exhibiting the type of behaviour shown in Fig 1 is that of a parallel spring and dashpot element that is in series with a spring and a dashpot, also shown in Fig 1. The behaviour of this model in creep can be represented by

$$\gamma(t) = \sigma_0 J_0 + \sigma_0 t / \eta_0 + \sigma_0 J_1 (1 - e^{-t/\tau}) \quad [18]$$

where γ is the strain, σ_0 the applied stress, τ is the relaxation time and t is time. J_0 and J_1 are the compliances of the spring elements and η_0 and η_1 are the viscosities of the dashpots of the model, Fig 1. (The compliance is the reciprocal of the modulus for a purely elastic element, see equations 31 - 32). For this model the relaxation time τ is given by

$$\tau = \eta_1 J_1 \quad [19]$$

If further parallel spring and dashpots elements are added in series, Fig 2, then

$$\gamma(t) = \sigma_0 J_0 + \sigma_0 t/\eta_0 + \sigma_0 \sum_1^n J_n (1 - e^{-t/\tau_n}) \quad [20]$$

where the contribution of the $n-1$ additional elements are included in the summation in accordance with the principle of linear superposition. J_n and τ_n are the compliances and relaxation times of the individual elements. The inclusion of further spring and dashpot elements results in a spectrum of relaxation times. This spectrum can be represented as a continuous compliance density function $L(\tau)$ where

$$J(t) = \gamma/\sigma_0 = J_0 + t/\eta_0 + \int_{-\infty}^{+\infty} L(\tau)(1 - e^{-t/\tau}) d\ln\tau \quad [21]$$

Similar analyses for stress relaxation cases A and B can be performed (2). For stress relaxation a modulus distribution function $H(\tau)$ can be defined, equivalent in concept to the compliance density function. After the application of an instantaneous strain γ_0 (case A) the stress $\sigma(t)$ is given by

$$\sigma(t) = \gamma_0 \int_{-\infty}^{+\infty} H(\tau) e^{-t/\tau} d\ln\tau \quad [22]$$

or, after instantaneously stopping steady state flow at constant strain rate $\dot{\gamma}_0$ (case B) it is given by

$$\sigma(t) = \dot{\gamma}_0 \int_{-\infty}^{+\infty} \tau H(\tau) e^{-t/\tau} d\ln\tau \quad [23]$$

For linear viscoelastic behaviour the compliance distribution function $L(\tau)$ and the modulus distribution function $H(\tau)$ are related to dynamic data by the following functions

$$\text{Creep compliance :} \quad J(t) = J_0 + t/\eta_0 + \int_{-\infty}^{+\infty} L(\tau)(1 - e^{-t/\tau}) d\ln\tau \quad [24]$$

$$\text{Relaxation modulus after sudden strain:} \quad G(t) = \int_{-\infty}^{+\infty} H(\tau) e^{-t/\tau} d\ln\tau \quad [25]$$

$$\text{Relaxation modulus after steady flow:} \quad \sigma(t) = \dot{\gamma}_0 \int_{-\infty}^{+\infty} \tau H(\tau) e^{-t/\tau} d\ln\tau \quad [26]$$

$$\text{Storage modulus:} \quad G'(\omega) = \int_{-\infty}^{+\infty} H(\tau) \omega^2 \tau^2 / (1 + \omega^2 \tau^2) d\ln\tau \quad [27]$$

$$\text{Loss modulus:} \quad G''(\omega) = \int_{-\infty}^{+\infty} H(\tau) \omega \tau / (1 + \omega^2 \tau^2) d\ln\tau \quad [28]$$

$$\text{Storage compliance:} \quad J'(\omega) = J_0 + \int_{-\infty}^{+\infty} L(\tau) / (1 + \omega^2 \tau^2) d\ln\tau \quad [29]$$

$$\text{Loss compliance:} \quad J''(\omega) = 1/\omega\eta + \int_{-\infty}^{+\infty} L(\tau) \omega \tau / (1 + \omega^2 \tau^2) d\ln\tau \quad [30]$$

where

$$J^*(\omega) = 1/G^*(\omega) = J'(\omega) - iJ''(\omega) \quad [31]$$

and hence

$$J' = G'/(G'^2 + G''^2) \quad [32]$$

and

$$J'' = G''/(G'^2 + G''^2). \quad [33]$$

For a purely elastic element ($G'' = 0$) it can be seen from equation 32 that $J' = 1/G'$. Using these relationships it is possible, in principle, to predict the results of one type of test given the results of another, for example to predict stress relaxation behaviour given the dynamic shear behaviour (8). This is best done numerically although a few analytical solutions exist. The form of the distribution function normally needs to be specified if this is to be done. However, some predictions without knowledge of the functional form are possible. The benefit in being able to predict dynamic properties from short term transient tests, ie creep and stress relaxation, is that the behaviour of unstable systems, eg curing or degrading polymers, can be determined rapidly. The converse of this is that relaxation spectra that have been determined from dynamic testing can be validated against stress relaxation data, thus giving a measure of the ability of the constitutive equation selected to predict flow in other flow regimes.

2.4 NORMAL STRESS DIFFERENCES

2.4.1 General

Normal stresses are the components of stress acting perpendicular to the surface under consideration. For steady shear flow of a Newtonian fluid the normal stresses are equal to each other and equivalent in magnitude to the pressure (tensile stresses are assigned to be positive and thus a pressure is equivalent to a negative stress). It is customary to work in terms of normal stress differences as this removes the contribution due to the isotropic pressure. The first and second normal stress differences in steady shear flow, N_1 and N_2 respectively, are given by

$$N_1 = \sigma_{xx} - \sigma_{yy} \quad [34]$$

and

$$N_2 = \sigma_{yy} - \sigma_{zz} \quad [35]$$

where x is the direction of flow, y is in the direction of the velocity gradient and z is in the neutral direction (alternatively defined by the velocity vectors $v_x = \dot{\gamma}y$, $v_y = v_z = 0$). Normal stress differences in shear flow are thus a measure of the anisotropy of the flow and can be caused by elasticity effects (non-zero normal stress differences can also occur in purely viscous extensional flows). In steady shear flow the first and second normal stress coefficients $\Psi_1(\dot{\gamma})$ and $\Psi_2(\dot{\gamma})$ are often used to characterise the flow and are defined by

$$\Psi_1(\dot{\gamma}) = N_1(\dot{\gamma})/\dot{\gamma}^2 \quad [36]$$

and

$$\Psi_2(\dot{\gamma}) = N_2(\dot{\gamma})/\dot{\gamma}^2 \quad [37]$$

where $\dot{\gamma} = dv_x/dy$.

It is possible to theoretically demonstrate that the following relation holds between the shear storage modulus and the first normal stress difference as both the frequency and shear rate tend to zero

$$G'(\omega)/\omega^2|_{\omega \rightarrow 0} = N_1(\dot{\gamma})/2\dot{\gamma}^2|_{\dot{\gamma} \rightarrow 0} \quad [38]$$

However, relations between normal stress differences and dynamic properties at higher shear rates and frequencies are not well established. The empirical relation

$$|G_c(\omega)| = N_1(\dot{\gamma})/2 \quad \text{for } \omega = \dot{\gamma} \quad [39]$$

has been proposed by Al-Hadithi et al (16) where

$$|G_c| = G' \{1 + [(\eta_0 + \eta')G'/2\omega(\eta')^2]\}^{0.5} \quad [40]$$

and η_0 is the zero shear viscosity and other terms are as previously defined. A further

empirical relationship observed for the first normal stress difference is that a plot of $\ln(N_1)$ as a function of $\ln(\text{shear stress})$ has a unique curve of gradient of approximately 2 and that this curve is independent of temperature. It is also noted that N_2 is usually small compared with N_1 , and this assumption can be used to simplify the analysis of experimental data as reported below.

2.4.2 NORMAL STRESS DIFFERENCES IN ROTATIONAL TECHNIQUES

The theory for the use of cone and plate and parallel plate geometries in rotational rheometry is well established (3). In continuous rotation mode the normal stress differences can be determined from the measurement of the pressure gradient within the test region or by measurement of the force normal to the plates, ie the force trying to separate the plates. The use of these two geometries are considered in further detail below.

Cone and plate

It is assumed that the cone angle is small (not greater than 4°), that edge effects are negligible and that the apex of the cone makes contact with the flat plate (in practice the cone is often truncated). It can be shown that the variation in pressure p acting on the plate with radius r is given by

$$dp/d(\ln r) = -[N_1(\dot{\gamma}) + 2N_2(\dot{\gamma})] + 3\rho\Omega^2 r^2/10 \quad [41]$$

where ρ is the density of the fluid, Ω is the angular speed (rad/s). The shear rate $\dot{\gamma}$ is given by

$$\dot{\gamma} = \Omega/\theta_0 \quad [42]$$

where θ_0 is the cone angle (rad). The last term on the right of equation [41] describes the contribution due to the inertia of the fluid. Thus from the measurement of the variation in pressure on the plate with radius the value of the expression $N_1(\dot{\gamma}) + 2N_2(\dot{\gamma})$ can be determined. Furthermore it can be shown, by integration of the pressure over the plate, that the total normal force F trying to separate the plates is given by

$$F = N_1(\dot{\gamma}) \pi R^2/2 - 3\rho\Omega^2 R^4/40 \quad [43]$$

where R is the radius of the plate (3). Thus from the measurement of the force F the first normal stress difference N_1 can be determined. The second normal stress difference can then be determined from the measurement of the radial pressure gradient between the plates (equation 41) and the value determined for N_1 .

Parallel plate

The parallel plate geometry can be used in continuous rotation to determine the difference in the first and second normal stress differences according to the relation

$$(N_1 - N_2)|_R = 2F/\pi R^2 [1 + 1/2 (dF/d\ln\dot{\gamma}_R)] \quad [44]$$

where $(N_1 - N_2)|_R$ indicates that the term $N_1 - N_2$ is determined for the shear rate $\dot{\gamma}_R$ at the edge of the plate. To correct for inertia effects F can be substituted by F_c where

$$F_c = F + 3\pi\rho\Omega^2 R^4/40 \quad [45]$$

The parallel plate geometry cannot be used to yield values for the individual normal stress differences N_1 and N_2 , unless it is assumed that N_2 is negligible. However, from measurement of the plate separation force F obtained using both the cone and plate and parallel plate geometries the values for N_1 and N_2 can be separately determined using equations 43 and 44.

Experimental problems are encountered in measuring the pressure with radial position in the cone and plate geometry. Flush mounted transducers are necessary to avoid hole pressure errors and the resolution of the measurements, related to the size of the plate and that of the transducers, will be poor. Hole pressure errors that occur when not using flush-mounted pressure transducers can lead to significant errors in the thus determined normal stress difference values. In fact, hole pressure error measurements have been used to determine normal stress differences (see Section 2.4.4). However, for the cone and plate geometry the shear rate is constant everywhere and consequently the hole pressure error is also constant. Thus when using the cone and plate geometry the determination of the pressure gradient in the radial direction can be assumed to be unaffected by the hole pressure error. Such measurements of pressure cannot be used however to calculate the normal force F .

In using equations 43 and 44 to determine N_2 the error is potentially large. N_2 is small

compared with N_1 and consequently it is calculated from the small difference between two large numbers that have been determined from separate measurements. Thus any error in each of the individual experiments will be magnified in the calculation of N_2 .

Ohl and Gleissle (17) have reviewed methods for measuring the second normal stress difference. They report on a new and reportedly improved procedure for analysing results obtained using the separated cone and plate method but this procedure assumes that the ratio N_1/N_2 is independent of shear rate. Measurements on filled systems using this technique are also reported. Whorlow (2) has reviewed other methods for normal stress measurement include re-entrant cone, cone and plate with central air bubble, and Lodge's truncated cone design. The reader is referred to Whorlow (2) for further details.

2.4.3 EXIT PRESSURE AND JET THRUST MEASUREMENTS

Whorlow (2) comments that there has been some degree of success in calculating extrudate swell using constitutive equations that reasonably describe the behaviour of polymer melts. However, he concludes that there seems little prospect that materials parameters, particularly normal stress differences, will be derivable from jet-thrust or die swell measurements on slowly flowing viscoelastic liquids in the foreseeable future. Other techniques are available for measuring normal stress differences in slow flows as described in Section 2.4.2. However, for higher rate flows few other methods are available and thus there is perhaps greater need to consider exit pressure, jet thrust and extrudate swell techniques. The latter technique is considered separately in Section 2.5.

For high flow rates in cylindrical dies if the approximation is made that the flow is viscometric up to the exit plane (ie fully developed) then the normal stress differences N_1 and N_2 are given by

$$N_1(\tau_w) = P_{(a,L)} + \tau_w/2 [\partial/\partial\tau_w P_{(0,L)}] + 1/2\pi a^2\tau_w[\partial/\partial\tau_w(\tau_w^2 T_L)] \quad [46]$$

and

$$N_2(\tau_w) = \tau_w \partial/\partial\tau_w [P_{(a,L)} - P_{(0,L)}] \quad [47]$$

where $P_{(a,L)}$ is the pressure on the tube wall at the exit plane and $P_{(0,L)}$ is the isotropic pressure on the axis of the tube at the exit plane. T_L is the reduction in thrust given by $T_L - T_E$ due to

the elasticity of the fluid, where T_I is the thrust of an inelastic fluid having the same density and viscosity as the elastic fluid and T_E is the thrust for the elastic fluid. The wall shear stress τ_w in the viscometric region is given by

$$\tau_w = ap/2 \quad [48]$$

where a is the radius of the cylinder, p is the pressure drop per unit length.

Particular problems associated with implementing this technique are the determination of the pressures $P_{(a,L)}$ and $P_{(0,L)}$ and the reduction in thrust T_L . By combining equations 46 and 47 the term $P_{(0,L)}$ can be eliminated to yield

$$N_1 + 1/2 N_2 = 1/2\pi a^2 \tau_w \partial/\partial \tau_w [\tau_w^2 T_L + \pi a^2 \tau_w^2 P_{(a,L)}] \quad [49]$$

Furthermore the assumption can be made that $N_2 \ll N_1$ to yield approximate values for N_1 .

The expression for slit dies, equivalent to equation 46, is

$$N_1(\tau_w) = P_{(b,L)} + \tau_w \partial/\partial \tau_w (P_{(b,L)}) + 1/hb [\partial/\partial \tau_w (\tau_w T_L)] \quad [50]$$

where $P_{(b,L)}$ is the wall pressure at the exit plane and h and b are the die thickness and width respectively. According to Walters (3) the slit die cannot be used to measure second normal stress difference values.

The use of equations 49 and 50 require that the wall exit pressure and the reduction in jet thrust due to elasticity are known. The thrust for an inelastic fluid may be calculated numerically and subtracted from that measured for the elastic fluid to determine the reduction in thrust. However, further assumptions about the flow are necessary in carrying out the numerical modelling. Alternatively, an inelastic fluid of the same density and viscosity could be tested but the likelihood of a suitable material being available is remote. The pressure on the wall at the exit can be determined by extrapolation to the exit of values measured along the length of the die. However, errors are incurred in the extrapolation due to viscous heating, pressure dependence of viscosity and also hole pressure errors where flush mounted transducers have not been used, as is not normally possible when using circular dies. Furthermore slit dies of large aspect ratio are required if the 2-D assumptions that are made in the derivation of the equations are to be reasonably valid. Thus significant theoretical assumptions have to be made and potentially significant experimental errors are

incurred in the measurement of normal stress differences using the jet thrust technique.

For low Reynolds number flows, ie flows dominated by viscous rather than inertial forces such as polymer flows, the thrust term can be assumed to be negligible. Thus equations 46-49 can be simplified such that for cylindrical flow

$$N_1(\tau_w) = p_{(a,L)} + \tau_w/2[\partial/\partial\tau_w P_{(0,L)}] \quad [51]$$

and

$$N_2(\tau_w) = \tau_w \partial/\partial\tau_w(p_{(a,L)} - P_{(0,L)}) \quad [52]$$

or combined as in equation 49 to yield

$$N_1 + 1/2 N_2 = p_{(a,L)} + 1/2 \partial/\partial\tau_w(\tau_w p_{(a,L)}) \quad [53]$$

Similarly, for flow in a slit die geometry equation 50 reduces to

$$N_1(\tau_w) = p_{(b,L)} + \tau_w \partial/\partial\tau_w(p_{(b,L)}) \quad [54]$$

The first and second normal stress differences can be separately determined directly using the capillary die equations 51 and 52 but this involves the measurement of the centre-line pressure $P_{(0,L)}$. By using both the capillary and slit die geometries, equations 53 and 54, the term $P_{(0,L)}$ can be substituted. Consequently only the measurement of the wall pressure at the exit as a function of wall shear stress is required. Thus the first and second normal stress difference can be determined through this combination of measurements following this treatment of the experimental data that was proposed by Boger (18) based upon theory initially developed by Han (19). It is noted that capillary and slit die exit pressure values are needed at the same values of wall shear stress. Obtaining such data can present experimental difficulties as, for a given flow rate and temperature, the shear rates in a slit die are lower than those in a capillary die where the diameter of the capillary die is similar to that of the thickness of the slit die.

Vlachopoulos and Mitsoulis (20) and Tuna and Finlayson (21) have investigated one of the major assumptions of the exit pressure method using numerical models, namely the effect of the assumed fully developed (viscometric) flow up to the exit. Both references indicate that the method gives reasonably accurate estimates of the first normal stress difference.

However, it is noted that the numerical analyses used were isothermal, as far as could be determined. In comparison Carreau et al (22) concluded that the velocity rearrangement at the exit and thermal dissipation effects cannot be ignored in the determination of the first normal stress difference from exit pressure values. For a polymer solution the authors (22) claim that viscous dissipation effects represented 90% of the exit pressure value. Boger and Denn (23) have presented theory incorporating the rearrangement of the velocity profile at the exit and show that the assumption of fully developed flow up to the exit results in a significant error in the determination of normal stress differences. For a balanced view of the technique the reader is referred to Baird (24) in which a critique of the exit pressure method is presented along with a response supporting the technique by C.D. Han.

As described by Whorlow (2) a further technique for measuring the second normal stress difference involves the axial flow of an elastic liquid along an annular channel between two concentric cylinders. By measuring the difference in pressure on the two cylinder walls a value for N_2 can be determined. However, a relationship between the N_2 and the shear rate needs to be assumed in order to analyse the experimental data. Furthermore, experimental difficulties are encountered that potentially lead to large errors in results. The technique has been investigated by Tanner (25). The same geometry has been used by Osmer and Lobo (54) to measure the first normal stress difference but with the melt flowing circumferentially rather than axially between the concentric cylinders. Again a relationship between N_1 and shear rate needs to be assumed in order to analyse the experimental data.

The interpretation of entrance pressure drops in capillary dies in terms of elasticity has been carried out by several workers (26 - 31). However, this approach is questioned (32) as it ignores the potentially significant contribution due to viscous extensional flow in the entry region.

2.4.4 HOLE PRESSURE MEASUREMENT

The hole pressure effect is best visualised by means of the streamline shown in Fig 3. Stretching of the streamline of an elastic fluid in the hole region results in a component of tension acting out of the hole, and thus a reduction in the pressure measured at the bottom of the hole compared with the pressure measured at the wall if no hole existed. The hole pressure P_H is defined as this reduction in pressure. For various geometry holes the following expressions for normal stress differences as a function of hole pressure have been established for creeping flows, ie negligible inertia (34)

$$\text{circular hole:} \quad N_1 - N_2 = 3nP_H \quad [55]$$

$$\text{slot parallel to the flow:} \quad N_2 = -Np_H \quad [56]$$

$$\text{slot transverse to the flow:} \quad N_1 = 2nP_H \quad [57]$$

where

$$n = d(\ln P_H)/d(\ln \sigma) \quad [58]$$

and the values N_1 , N_2 and σ are determined at the die wall in fully developed flow. However, the validity of the assumptions made in deriving these equations is questioned (7). For example, at high flow rates the inertia of the fluid which is not considered in the derivation has the effect of reducing the hole pressure difference and causing an asymmetry of the flow lines in the hole region. It is indicated (35) that correction for inertia effects could be made by testing an equivalent inelastic liquid having the same viscosity and density as the elastic liquid. The contribution due to inertia could then be removed from the hole pressure for the elastic liquid. The validity of this correction procedure is questioned even if a suitable equivalent inelastic liquid could be identified as it is likely that the flow fields for the two fluids will be different. However, it might provide a suitable first order correction. Barnes et al (7) comment that the technique has no theoretical justification except at low flow rates and that its use at higher flow rates must be on an empirical rather than theoretical basis. Nevertheless, Lodge (35) comments that encouraging results have been obtained for polymer melts up to reasonable shear rates.

2.5 EXTRUDATE SWELL

The relationship between extrudate swell (which is also often referred to as die swell) and the viscoelastic parameters describing the fluid is complex. In addition to the rheological considerations many others factors including melt compressibility, inertia, gravity, heat transfer, wall slip and surface tension potentially contribute to the magnitude of the extrudate swell. To illustrate this point, extrudate swell is not restricted to elastic fluids. A Newtonian fluid exhibits extrudate swell of x1.13 in the axisymmetric case and x1.19 in the planar case at limiting low Reynolds numbers (the values given are multiplication factors on the die size). As the Reynolds number increases the effect of inertia increases and results in a reduction in the magnitude of the extrudate swell. Tanner (36) has shown, using a simple two-layer

extrusion model, that thermal effects also contribute to the extrudate swell behaviour of a fluid that has a temperature dependent viscosity.

Tanner (34) in summarising the relation of rheology to swelling comments that both the shear and extensional behaviours contribute to the magnitude of the extrudate swell. In recent numerical modelling work (37) it was concluded that extrudate swell was strongly influenced by the second normal stress difference. However, it is noted that the second normal stress difference and the extensional viscosity were not independent parameters in the constitutive model used. Thus the extrudate swell could not be attributed solely to either one of the parameters. On this evidence it is therefore perhaps somewhat optimistic to expect to be able to quantitatively determine material parameters from measurement of its extrudate swell behaviour, particularly as the mechanisms of extrudate swell still require further elucidation. Nevertheless, there is perhaps some potential merit in following the simplistic approach of relating extrudate swell behaviour to the elastic properties of the material.

Tanner (36), for example, has shown that for a material exhibiting a behaviour described by the KBKZ constitutive model that has a single relaxation time and a zero second normal stress difference value, the extrudate swell χ in the axisymmetric case (cylindrical die) is given by

$$\chi = [1 + 1/8 (N_1/\sigma)_w^2]^{1/6} \quad [59]$$

and in the planar case (slit die of infinite width to thickness ratio)

$$\chi = [1 + 1/12 (N_1/\sigma)_w^2]^{1/4} \quad [60]$$

where the suffix w indicates that the values are determined for the conditions at the wall. The analysis assumes that the material previously underwent steady shear flow. Tanner reported that agreement with some experiments on polymer melts was obtained.

Lodge (38) has demonstrated that the ultimate shear recovery (under constrained normal force conditions) following steady shearing flow of a "rubber-like" liquid that exhibits a constant shear viscosity and positive N_1 and zero N_2 values is given by

$$\gamma_\infty = N_1/2\sigma. \quad [61]$$

This term is defined as the *recoverable elastic strain* (the factor of 2 is sometimes absent from

the definition) and its value can be determined from steady shear experiments. Thus a correlation has been identified between the predicted extrudate swell for a KBKZ type fluid, equations 59 and 60, and the recoverable elastic strain which can be measured using a rotational rheometer.

Utracki et al (39) have reviewed other models relating extrudate swell to the recoverable shear strain (40-49). Of these models the authors comment that the experimental evidence fitted the relationship due to Tanner (equation 59) and good agreement was obtained between the values of shear recovery calculated from extrudate swell measurements and those values measured by rotational rheometry. Similar extrudate swell models have since been developed by others (33, 50, 51-53). Pearson and Trottnow (33) have modified the analysis of Tanner (36) to take into account some of the shortcomings, with the result that an analysis using a Maxwell fluid constitutive model showed no significant differences in predictions to those of the Tanner model. Furthermore, analysis was also carried out for extrudate swell from a short die with the mechanism based on extensional sink flow in the entry region (33). Again it was reported that the predictions of extrudate swell were very similar to those obtained using the Tanner model. Huang et al (50) have also developed a model for predicting extrudate swell from short dies with the mechanisms based on the extensional rather than the shear flow behaviour of the material. For the limited results presented there was reasonable agreement of predictions with experiments for polystyrene.

Tanner (34) has calculated the swell ratios for a range of constitutive equations and a value of 1 for the recoverable elastic strain using a numerical model of extrusion. The swell ratio values varied from 1.12 for a Leonov constitutive model to 1.38 for an Oldroyd-B model. This perhaps demonstrates the futility of determining elastic parameters from extrudate swell behaviour.

It is clear that, on their own, recoverable elastic strain data are insufficient to reliably predict extrudate swell behaviour. Thus the inverse problem of determining such data from extrudate swell measurements can be only qualitative at best. Nevertheless the approach has potential to indicate the relation between the material properties determined in shear with the extrudate swell behaviour, in particular for flows in which the elastic behaviour dominates.

3 DISCUSSION

Polymer melts generally behave in a linear viscoelastic manner when undergoing small deformations and in a non-linear viscoelastic manner when undergoing large deformations. Techniques that utilise small deformations and thus operate in the linear viscoelastic regime are of value for characterising materials as the techniques can effectively probe deeper into the structure of the material. Thus such techniques are more likely to be able to discriminate between similar materials. However, polymer melts undergo large and therefore non-linear viscoelastic deformations in commercial processing. The primary requirement for characterising the non-linear viscoelastic behaviour is to obtain parameters to fit constitutive equations for use in modelling. Thus techniques to measure in the non-linear region are essential if one is to characterise the materials adequately. Measurements in the linear viscoelastic region can also be used to determine the parameters of the constitutive equations for use in flow modelling. However, if this is the sole method by which such parameters are to be obtained then it is likely that extrapolation of data to larger deformations will be necessary for modelling processing behaviour, which is likely to lead to poor agreement between the models and the processing behaviour.

Dynamic testing using oscillatory rheometers can be used to characterise the linear viscoelastic behaviour of melts at small amplitudes of deformation. Such techniques can also be used to determine the range of the linear viscoelastic behaviour of materials. The technique and the theory behind linear viscoelastic measurements is well established and corrections for the inertia of the sample and test equipment and for the compliance of the equipment can be made. Such testing can also be used to measure non-linear viscoelastic behaviour. However, correct interpretation of such experimental data is complex and requires assumptions to be made concerning the rheological behaviour of the material being tested.

Stress relaxation and creep recovery measurements can also be interpreted on the basis of linear viscoelastic theory. This limits testing to the region of linear viscoelastic behaviour and again this assumption can be checked relatively easily by carrying out simple testing. Testing can be carried out in the non-linear region but correct interpretation requires a prior knowledge of the rheological behaviour of the material. Correlations have been established between dynamic and stress relaxation or creep testing such that, for example, given results from dynamic testing then the creep behaviour is predictable. This can be used to assess the accuracy of the constitutive equation and materials parameters under different flow conditions from those used to determine the parameters.

Normal stress differences are a characteristic feature of large deformation, non-linear viscoelastic behaviour. Normal stress differences can be determined using rotational rheometers for which the theory is well established. However, the measurements tend to be at low shear rates. In particular the measurement of the second normal stress difference is subject to large errors. Normal stress difference measurements can be made at higher shear rates using exit pressure and hole pressure measurement techniques. However, assumptions made in the derivations of the analyses for the techniques have been shown to be suspect, particularly at the higher shear rates of interest to polymer processors. These assumptions potentially result in very significant errors in the thus determined normal stress difference values. Also, considerable experimental difficulties need to be overcome to reduce experimental errors to a minimum.

The ability to be able to characterise the elasticity of materials through measurement of their extrudate swell behaviour is of considerable potential merit. For quantitative characterisation of the elastic behaviour it has little to commend it as there are many factors in addition to the rheological considerations that contribute to the extrudate swell of a polymer. However, it is anticipated that, with care, qualitative viscoelastic data could be obtained from extrudate swell measurements that could be of use to the processor.

4 CONCLUSIONS

- 1 The measurement of linear viscoelasticity is well established in oscillatory rheometry and in creep and stress relaxation. However, this necessarily restricts measurements of polymer melts to small deformations for the linear viscoelastic assumption to be valid.
- 2 The measurement of non-linear viscoelasticity is less well developed and often requires that the constitutive behaviour of the fluid is known prior to testing to enable proper interpretation of the experimental data to be made.
- 3 The measurement of normal stress difference values at small shear rates using rotational rheometers is well established. However, the error in the measurement of the second normal stress difference is large compared with the first normal stress difference.
- 4 Normal stress difference values can be measured at higher shear rates using exit

pressure and hole pressure measurement techniques. However, the validity of both of these techniques is questioned due to the assumptions made in the interpretation of the experimental data.

- 5 The use of extrudate swell measurements to characterise the viscoelastic behaviour of materials is perhaps suited for qualitative comparison of similar materials but it is not recommended for use as a quantitative measure.

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$$\gamma(t) = \sigma_0 J_0 + \frac{\sigma_0 t}{\eta_0} + \sigma_0 J_1 (1 - e^{-t/\eta_1 J_1})$$

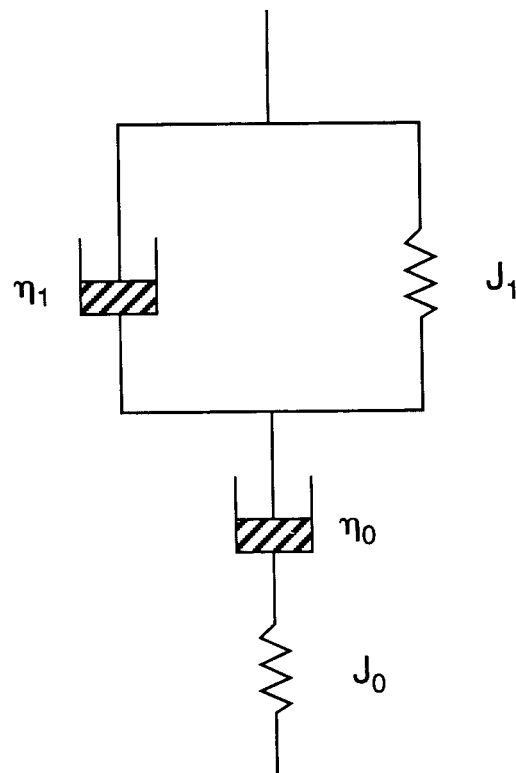
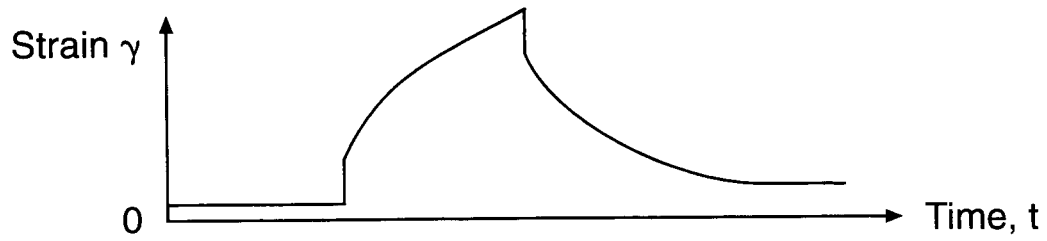
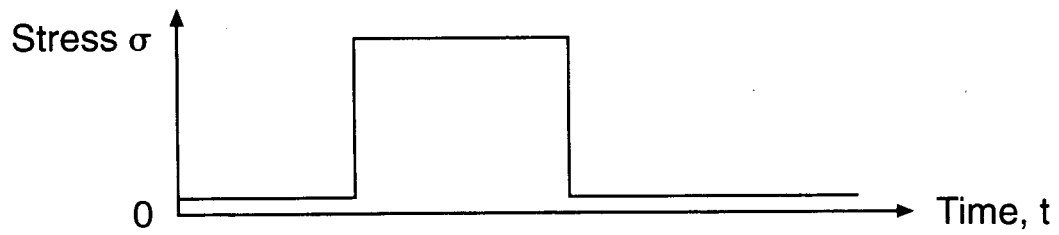


Figure 1 Creep and stress relaxation behaviour of a simple spring and dashpot model

$$\gamma(t) = \sigma_0 J_0 + \frac{\sigma_0 t}{\eta_0} + \sigma_0 \sum_{n=1}^n J_n (1 - e^{-t/\tau_n})$$

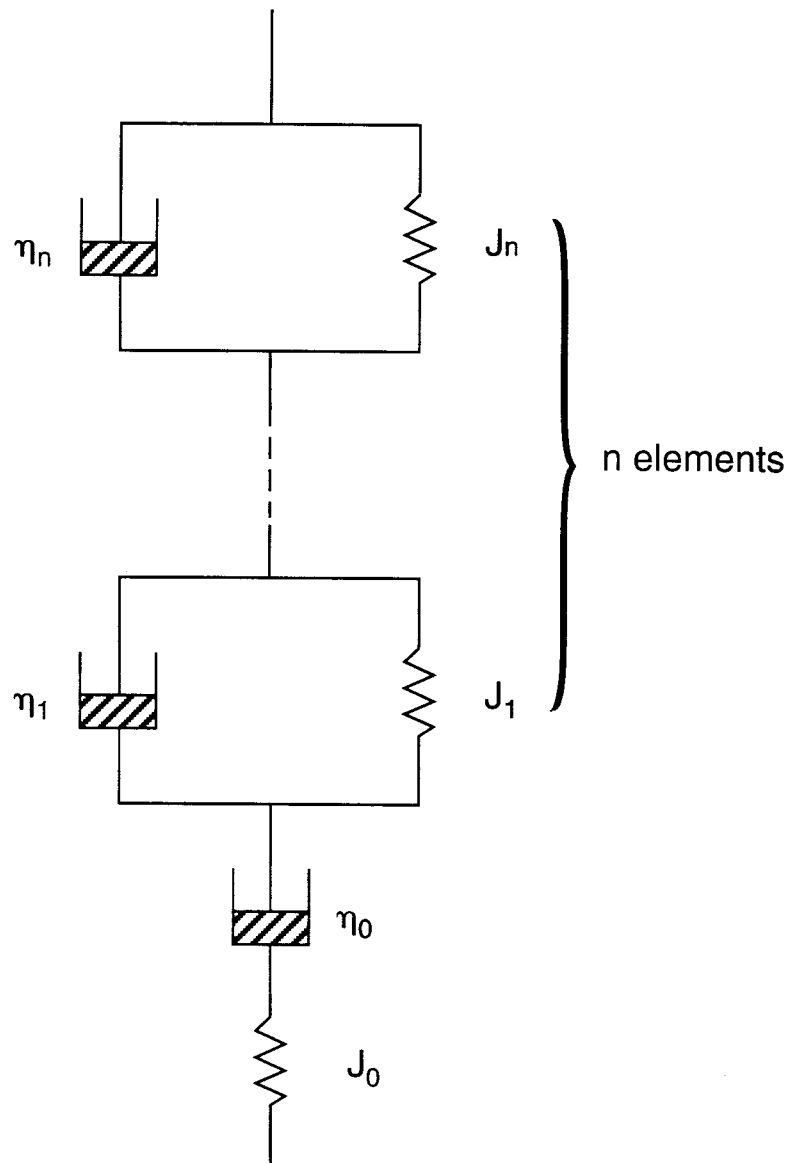


Figure 2 Multiple spring and dashpot model exhibiting a relaxation time spectrum

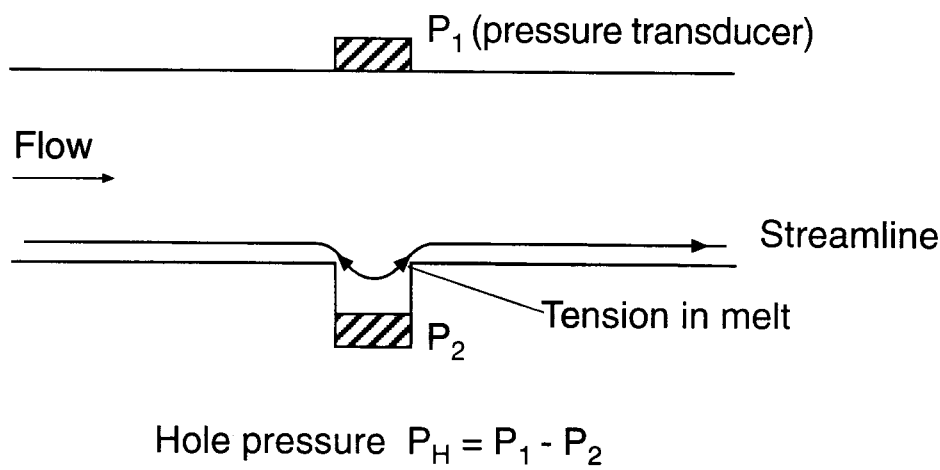


Figure 3 Hole pressure effect