NONLINEAR VISCOELASTIC PROPERTIES OF POLYSTYRENE SOLUTIONS

by

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NONLINEAR VISCOELASTIC PROPERTIES

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POLYSTYRENE SOLUTIONS

ABSTRACT

Polymeric liquids are often subjected to high shear rates in plastics processing operations. These materials exhibit nonlinear behavior under these conditions. The Boltzmann superposition principle, which governs linear behavior, cannot be applied and other constitutive equations that take into account nonlinear phenomena have to be used to describe the flow behavior of polymers subjected to large, rapid deformations.

In this work the nonlinear behavior of concentrated polystyrene solution was examined using sliding plate rheometer developed at McGill University. In this rheometer a novel transducer is used to measure the shear stress and an optical system is used to measure birefringence during flows involving high shear rates.

A reliable technique for preparing concentrated polystyrene solutions in diethylphthalate was developed. The importance of the parallelism of the plates of the sliding plate rheometer was demonstrated. The shear stress was measured directly, and the third normal stress difference was calculated using the stress-optical law.

A relaxation spectrum was inferred from small amplitude oscillatory shear experiments and found to be very narrow. Start-up of steady shear with rates ranging from 0.01 s⁻¹ to 70 s⁻¹ were performed. The steady shear stress was found to be independent of shear rate at high shear rates. The viscosity and the third normal stress coefficient were examined. The effect of the solution concentration on the power law parameters was studied. The transient behavior during these experiments was also studied. The Cox-Merz rule was found to be valid for concentrations less than 0.199 g.cm⁻³, but a deviation from the rule was observed for higher concentrations. Sigmoidal damping functions, based on both the shear stress measurements and the birefringence measurements, were determined. Exponential shear experiments were also performed. The exponential stress coefficient and the third normal stress difference were calculated from experimental data for different values of exponential rate constant and different strain scale factor. The exponential rate constant was shown to have a strong influence on both the exponential stress coefficient and the third normal stress difference.

The experimental results of start-up for steady shear and exponential shear were compared with the predictions of Wagner's model. Wagner's model cannot predict the nonlinear behavior of the solution used here. Wagner's model only predicts small deviations from linear behavior.

RESUME

Les liquides polymèriques sont souvent soumis à de forts taux de cisaillement lors de la fabrication de matières plastiques. Sous ces conditions, ces matériaux montrent un comportement non linéaire. Le principe de supperposition de Boltzmann, qui gouverne les phenomènes non linéaires, ne peut être appliqué et d'autres équations constitutives qui tiennent compte de la non linéarité doivent être employées afin de pouvoir caractèriser les écoulements de polymères soumis à des déformations fortes et rapides.

Dans cette étude, le comportement non linéaire de solutions concentrées de polystyrène a été examiné grace à un rhéomêtre à plaques parallèles developpé à l'Université McGill. Ce rhéomêtre est équippé d'un transducer, pour mesurer la contrainte de cisaillement, et d'un système optique, pour mesurer la biréfringence, lorsque les polymères sont soumis à de fortes déformations.

Une technique fiable pour préparer des solutions concentrées de polystyrène dans du diéthylphthalate fut développée. L'importance du parallèlisme des plaques du rhéomêtre à plaques parallèles fut démontrée. Les contraintes de cisaillement furent mesurées directement et la troisième différence de contraintes normales fut calculée grace à la loi optique-contrainte.

Un spectre de relaxation fut dérivé à partir des résultats expérimentaux de cisaillements oscillatoires à faible amplitude. Des démarages de cisaillement à taux de cisaillement constant (le taux de cisaillement étant compris entre 0.01 s⁻¹ et 70 s⁻¹) furent exécutées. La contrainte de cisaillement du régime permanent fut trouvée indépendante du taux de cisaillement pour des taux de cisaillement élevés. La viscosité et le coefficient de la troisième différence de contraintes normales furent examinées. L'influence de la

concentration sur les paramêtres de la loi de puissance fut étudiée. Le régime transitoire pendant ces expériences fut aussi étudié. La règle de Cox-Merz fut trouvée valide pour des concentrations de moins de 0.199 g/cm³, mais une déviation à la règl^a fut observée pour des concentrations plus élevées. Des fonctions d'amortissement sigmoidales, basées, et sur les mesures de contraintes de cisaillement, et sur les mesures de troisièmes différences de contraintes normales, furent déterminées. Des expériences à taux de cisaillement exponentiel furent aussi performées. Le coefficient de contrainte exponentiel et la troisième différence de contraintes normales furent calculés à partir des données expérimentales pour différentes valeurs de la constante de cisaillement exponentiel et pour différentes valeurs du facteur de déformation. Il fut montré que la constante de cisaillement exponentiel avait une forte influence à la fois sur le coefficient de contrainte exponentiel et sur la troisième différence de contraintes normales.

Les résultats expérimentaux pour le démarage de cisaillement à taux de cisaillement constant et les expériences à taux de cisaillement exponentiel furent comparés avec les prédictions du modèle de Wagner. Le modèle de Wagner ne peut pas prédire le comportement non linéaire des solutions utilisées dans cette étude. Le modèle de Wagner prédit seulement les petites déviations du comportement linéaire.

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Yes, but....

That is how I feel when I write this thesis, which is a gathering of all the helps I received from everyone. I remember when I used to run to the office of someone "screaming my head off".

· I think it will never work, anyway, I know it since the beginning the thing will never work...

And eventually, I finished !!!!! Thanks to the moral support and help of many people.

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Imagine there's no heaven It's easy if you try No hell below us Above us, only skies Imagine all the people Living for today

Imagine there's no countries It isn't hard to do Nothing to kill or die for And no religion too Imagine all the people Living life peace

You may say I'm a dreamer But I'm not the only one Hope some day you'll join us And the world will be one

Imagine no possession I wonder if I can No need for greed or hunger A family of men Imagine all the people Sharing all the world

You may say I'm a dreamer But I'm not the only one Hope some day you'll join us And the world will be one

John Lennon

1. INTRODUCTION

1. INTRODUCTION

1.1 Rheology

Rheology is the science that studies the deformation of a material in response to an applied force. The development of synthetic polymers and the processing of plastics have raised many interesting problems for rheologists. A better understanding of the properties of melts and polymer solutions subjected to various flow histories is urgently needed. In rheology two major areas are of particular interest. The first is the rheological characterization of a particular polymer; it is necessary to find relationships between the deformation (strain) and the resultant stress in the polymer. These relationships are generalized in so-called "constitutive equations". The second area of interest in rheology is the study of the influence of various molecular parameters and of the chemistry of the polymer on rheological behavior.

1.2 Presentation of the problem

The behavior of a polymeric liquid subjected to a deforming force is intermediate between that of a viscous liquid and that of an elastic solid. For this reason, polymers are classified as viscoelastic materials. When the deformation is very small or very slow, the response is linear. Linear viscoelastic behavior, which is governed by the Boltzmann superposition principle, is a very useful tool for characterizing polymer molecules in their equilibrium state. In polymer processing operations, however, polymeric liquids are subjected to very high rates of deformation, and linear viscoelasticity is no longer observed.

An important property of deformed polymers is the molecular orientation and its dependence on time and temperature. With the help of the "stress-optical" law, a relationship between the molecular orientation, measured by means of birefringence, and the components of the stress tensor, can be established.

A newly developed apparatus, the sliding-plate rheometer, makes it possible to measure simultaneously the shear stress in the polymer, using a shear-stress transducer, and the birefringence, during transient shearing deformations involving high shear rates. Thus, it is possible to carry out experiments, such as single or multiple step strains, steady high shear rates, large-amplitude oscillatory shear, and exponential shear, using concentrated solutions of high molecular weight polymers or melts.

The synthesis of linear, high molecular weight, narrow-molecular weight distribution polystyrene is presently possible. Measurements are often performed on concentrated solutions of polystyrene because it is an amorphous polymer, it can be easily synthesized or purchased, and because it is strongly birefringent. However, preparing concentrated solutions is a time consuming and difficult step, and a special technique for this had to be developed.

1.3 Objectives of the work

The objectives of the work were:

- To develop a technique for preparing concentrated solutions of high molecular weight polystyre ne. The solution should be homogeneous and the molecular weight of the polymer should not be affected by the dissolution process.

- To evaluate the sliding plate rheometer as a tool for the study of nonlinear viscoelasticity of polymeric liquids and to make a thorough analysis of possible sources of error.

- To study the nonlinear viscoelastic behavior of concentrated polystyrene solutions involving the measurement of stress and birefringence.

The experiments to be performed were the following:

- Small amplitude oscillatory shear
- Steady shear
- Step shear
- Exponential shear

- And finally to compare the experimental results with the predictions of Wagner's constitutive equation.

1.4 Organization of the thesis

Chapter II reviews existing theories of the rheological behavior of polymeric liquids. The different models and constitutive equations are then described. Chapter III gives the theoretical basis of the experimental techniques used in this study. Chapter IV describes the equipment and experimental procedures. The results are reported and discussed in Chapter V. Predictions and computations according to Wagner's model are presented in Chapter VI and compared with the experimental results. Chapter VII is a summary of the conclusions reached during the research and recommendations for future work. An extensive literature review was conducted during this research, and this has been incorporated directly into the appropriate chapters. A list of the nomenclature used is given at the end of the thesis. 2. THEORETICAL BACKGROUND

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2. THEORETICAL BACKGROUND

Chapter outline

Some theoretical background is given in this chapter. The rheological material functions used in this work are first defined. Then several constitutive equations used to describe the flow of a polymer solution are presented. The chapter ends with typical results of the experiments performed in this study.

2.1 Introduction

2.1.1 Generalities

In experimental rheology the commonly used flows are divided into two classes: extensional and shear flows. The shear flows can be divided into two categories: pressuredriven flow and drag flow. The first includes capillary flow and slit flow, both types occurring often in melt processing, for example in dies and in injection molding. In pressure-driven flows it is possible to measure the viscosity at very high shear rates. In drag flow are included the concentric cylinder, sliding cylinder, cone and plate, parallel disk and sliding plate geometries. Drag flow is easy to generate in the laboratory by means of rotational rheometers, but these devices are restricted to use at low shear rates¹.

2.1.2 Steady simple shear

Steady simple shear is the easiest flow to generate and the most commonly used type of deformation for measurements in rheology. The simplest example of steady simple flow is when the fluid that fills the gap between two parallel plates is sheared by the linear motion of one plate relative to the other at constant speed. During the deformation the gap between the plates remains constant.

For the discussion given below the following coordinates are used: the direction of the flow is x_1 , the direction of the velocity gradient is x_2 , and x_3 is the direction perpendicular to the shear plane (O_1x_1,x_2) (see figure 2-1).



Figure 2-1 Simple shear

The shear strain γ is defined by:

I

$$\gamma = x/h$$
 2-1

where x is the displacement of the moving plate, and h is the gap between the plates. The shear rate is given by the derivative of the shear strain:

$$\dot{\gamma} = V/h$$
 2-2

where V is the velocity of the moving plate. The stress components generated by this motion have been shown by Lodge(2, p.62) to be:

$$\left(\begin{array}{ccccc}
\sigma_{11} & \sigma_{12} & 0 \\
\sigma_{21} & \sigma_{22} & 0 \\
0 & 0 & \sigma_{33}
\end{array}\right)$$
2-3

This tensor is obviously symmetric. Three independent material properties can thus be measured in simple shear:

The shear stress:
$$\sigma = \sigma_{12} = \sigma_{21}$$
 2-4

The first normal stress difference: $N_1 = \sigma_{11} - \sigma_{22}$ 2-5

The second normal stress difference: $N_2 = \sigma_{22} - \sigma_{33}$ 2-6

Adding 2-5 and 2-6 we can define another property, the third normal stress difference:

$$N_3 = \sigma_{11} - \sigma_{33} \qquad 2-7$$

According to Criminale⁴ σ , N₁, and N₂ are sufficient to describe completely the response of any incompressible fluid to steady simple shear.

Using the above four quantities it is possible to define four rheological material functions:

The viscosity:
$$\eta = \sigma/\dot{\gamma}$$
 2-8

The first normal stress coefficient: $\Psi_1 = N_1/\gamma^2$ 2-9

The second normal stress coefficient:
$$\Psi_2 = N_2/\dot{\gamma}^2$$
 2-10

The third normal stress coefficient
$$\Psi_3 = N_y / \gamma^2$$
 2-11

Only two of the latter three are independent.

The shear stress is relatively easy to measure, but N_1 , N_2 and N_3 cannot be measured directly. In cone-plate or parallel-disk rheometers, N_1 , which was first discussed by Weissenberg³, can be measured. However, these rheometers are restricted to use at very low shear rates because of secondary flows or edge effects⁴⁷.

Many researchers have tried to establish a precise relationship between the viscosity and the first normal shear stress difference, but these attempts have not really been succesful^{1,1,10}.

2.2 Rheology of viscoelastic liquids

2.2.1 Generalities

The behavior of a polymeric liquid subjected to deformation is qualitatively similar to that of a "Maxwell element". This mechanical analogy consists of a linear dashpot and a linear spring. The force resulting from an elongation X_{\circ} of the assembly is given by

$$F(t) = K_*X_{\circ} \left[\exp(-K_*t/K_*) \right]$$
2-12

where K_{\star} is the spring constant and K_{\star} the dashpot constant.

2.2.2 Linear viscoelasticity

2.2.2.1 Relaxation modulus

Linear viscoelasticity is the simplest viscoelastic theory. (see for example Ferry¹¹ for a more complete description of linear viscoelasticity). In this theory the structure of the material is considered to be unaffected by deformation. This assumption is only valid for deformations that are very slow or very small.

The relaxation modulus, for a "stress relaxation experiment" is defined as:

$$G(t) = \sigma(t)/\gamma$$
 2-13

where G(t) is the stress relaxation modulus, $\sigma(t)$ the stress and γ the strain. During a stress relaxation experiment the polymer is suddenly subjected to step strain and the stress is recorded as a function of time after the deformation.

It is possible to calculate the stress for any kind of deformation, as long as the response is linear, by using the Boltzmann cuperposition principle. This can be written as follows:

$$\sigma(t) = \int_{-\infty}^{t} G(t-t') \gamma(t') dt'$$
2-14

2.2.2.2 The relaxation spectrum

Using the Maxwell element analogy, the shear stress can be expressed as:

$$\sigma(t) = G_{o\gamma_{o}}[\exp(-t/\lambda)]$$
²⁻¹⁵

. . .

where G_o is analogous to K, and λ is analogous to K,/K. The so-called "Maxwell model" is then defined by:

$$\sigma_{ij}(t) = \int_{-\infty}^{t} G_{o}[\exp(-(t-t')/\lambda)] \gamma_{ij}(t') dt'$$
2-16

and the "generalized Maxwell model" is defined by:

$$\sigma_{ij}(t) = \int_{-\infty}^{t} \sum_{k=1}^{N} G_k[\exp(-(t-t')/\lambda_k)] \gamma_{ij}(t') dt'$$
2-17

where σ_{ij} is a component of the stress tensor and γ_{ij} is a component of the infinitesimal strain tensor.

The Maxwell model can be represented by an assembly of i Maxwell elements in parallel. The relaxation modulus is then given by:

$$\mathbf{G}(t) = \sum_{i=1}^{N} \mathbf{G}_{i} \left[\exp(-t/\lambda_{i}) \right]$$
 2-18

where G_1 and λ_1 are the ith relaxation strength and the relaxation time corresponding to each Maxwell element.

The set of values (G_{i},λ_{i}) constitutes the "discrete spectrum" of the material. The longest relaxation time t_{1} is called the "terminal relaxation time".

2.2.3 Non linear viscoelastic theory

2.2.3.1 Introduction

The linear theory cannot be applied when large and rapid deformations occur, which is normally the case in flows of industrial importance. The response to the deformation then depends on:

- 1) The size of the deformation
- 2) The rate of the deformation
- 3) The kinematics of the deformation

No general theory can predict the response for nonlinear behavior. The rheological constitutive equations generally used are empirical in nature.

2.2.3.2 The Lodge network theory

Lodge^{13,14} proposed a single-integral constitutive equation for nonlinear viscoelasticity based on ideas from the theory of rubber elasticity. It can be looked upon as a generalization of the Maxwell model. This constitutive equation is:

$$\sigma_{ij}(t) = \int_{-\infty}^{t} m(t-t')B_{ij}(t,t')dt'$$
2-19

where $B_{ij}(t,t')$ is the Finger tensor's and m(t-t') is the "memory function". It can be demonstrated that

$$m(t-t') = dG(t-t')/dt' = \sum_{i=1}^{N} G_i/\lambda_i \exp[-(t-t')/\lambda_i]$$
 2-20

which gives

$$\sigma_{ij}(t) = \int_{-\infty}^{t} \sum_{i=1}^{N} G_i / \lambda_i \exp[-(t-t')/\lambda_i] B_{ij}(t,t') dt'$$
2-21

Unfortunately, this model does not give quantitatively correct predictions. It predicts that the viscosity is constant and that $N_2=0$, which contradicts experimental observation¹⁵⁻¹⁹. N_2 has been shown to be negative and between 10% and 30% of the absolute value of N_1 .

2.2.3.3 Wagner's model

The Lodge network model has been modified by Wagner and others²⁰ in order to improve its predictions. This modification takes the form:

$$\sigma_{ij}(t) = \int_{-\infty}^{t} M B_{ij}(t,t') dt'$$
2-22

where M is a nonlinear memory function depending on time and on the two scalar invariants of the Finger tensor, I_1 and I_2 . Thus:

$$M = M[(t-t'), I_1(B_{ij}), I_2(B_{ij})]$$
2-23

This equation is a special case of the well-known BKZ²¹ equation.

Wagner² proposed the separability of the memory function, which can then be expressed as a product of the memory function for linear behavior m(t-t') and a "damping function" $h(I_1, I_2)$. This results in the following constitutive equation:

$$\sigma_{ij}(t) = \int_{-\infty}^{t} m(t-t') h(I_1, I_2) B_{ij}(t, t') dt'$$
2-24

However, this model still predicts that the second normal stress difference is zero. To correct this Wagner² later proposed another constitutive equation given by:

$$\sigma_{ij}(t) = \int_{-\infty}^{t} m(t-t') h(I_1,I_2) [(1+\beta)C^{-1}_{ij}(t')+\beta C_{ij}(t')]dt'$$
 2-25

where C_{ij} is the Cauchy tensor, and β is the ratio of the second normal stress difference to the first normal stress difference.

In the cases of simple shear and simple extensional flow, I_1 and I_2 , the scalar invariants of the Finger tensor, and thus the damping function, are only functions of γ , the shear strain, and ϵ , the Hencky strain respectively. The damping function $h(\gamma)$ takes into account the destruction of the polymer network when it is deformed. $h(\gamma)$ decreases as the strain increases; at zero strain h(0)=1.

Wagner¹¹ proposed a single exponential function for the damping function in order to fit experimental data. Osaki²⁴ fitted his experimental shear data with a sum of two exponentials. Papanastasiou²⁵ proposed a sigmoidal form for the damping function:

$$h(\gamma) = 1/(1+a\gamma^2)$$
 2-26

2.2.3.4 Theory of entanglements

Entanglement theories have been developed in order to explain the unique flow behavior of melts and concentrated polymeric solutions. In concentrated solutions and melts there are strong interactions between the molecules. These local interactions result from the inability of the chains to pass through each other and are often imagined as entanglements between the long molecular chains. During the flow, these entanglements are continuously destroyed and created.

2.2.3.5 Doi-Edwards theory

Edwards²⁴ was the first to propose that in a dense polymeric system, entanglement constraints act like an open-ended confining tube, enclosing each macromolecular chain along its average contour. The relaxation of the molecule after a deformation is then restricted to reptation out of its tube. Doi and Edwards^{27.30} introduced the concept of reptational motion (de Gennes³¹) into a dynamic model of the nonlinear viscoelasticity of concentrated systems of flexible macromolecules under macroscopic deformations. They derived a rheological constitutive equation considering the motion of a single polymer molecule in the mean field imposed by other chains.

According to the Doi-Edwards theory, linear behavior is governed by two relaxation times, λ_{\bullet} "the equilibration time" and λ_{\bullet} the time for "disengagement". At very short times $(t < \lambda_{\bullet})$, there is a reorganization of the segments between entanglements. Once this is finished the molecule begins to "reptate" out of its tube. This diffusion process is very slow.

When $t > \lambda_{e}$, the Doi-Edwards theory predicts that the relaxation modulus is given by:

$$G(\gamma,t) = h(\gamma)G(t)$$
 2-27

and that the first normal stress difference in a step strain experiment is given by:

$$N_1 = \dot{\gamma}\sigma \qquad 2-28$$

Unfortunately, the theory does not give an analytical function for $h(\gamma)$, but it predicts that $h(\gamma)$ is independent of chemical structure. Equations 2-27 and 2-28 have been found to be valid for a low density polyethylene.

The Doi-Edwards theory also predicts that $N_2(t,\gamma)/N_1(t,\gamma)$ is negative and varies with the strain, γ , following a relationship that is valid for all linear monodispersed entangled polymers. The relationship predicted by the theory depends on whether the "independent alignment assumption"³⁹ is used. The independent alignment assumption states that the orientation of each chain segment does not change during the relaxation process.

Osaki et al.³² have found that for polystyrene solutions, at strain magnitudes up to 4.0, the observations are in good agreement with the predictions of the Doi-Edwards theory. These researchers also observed that the ratio of the longest relaxation time t_1 to the equilibration time t_e is equal to the ratio of the molecular weight to the molecular weight between entanglements³³. The molecular weight between entanglements M_e is the average molecular weight spacing between entanglement points (12, p. 243).

2.3 Several rheological tests

A description of the theoretical background of the rheological tests used in this work is presented here.

2.3.1 Small amplitude oscillatory shear

In order to determine a discrete relaxation spectrum, small amplitude oscillatory shear experiments were carried out. The strain for this test is given by:

$$\gamma(t) = \gamma_{\circ} \sin(\omega t)$$
 2-29

where γ_0 is the amplitude of the strain, and ω the frequency. If the rate of strain is sufficiently small the induced stress $\sigma(t)$ is:
$$\sigma(t) = \sigma_0 \sin(\omega t + \delta)$$
 2-30

where σ_{o} is the stress amplitude and δ is the mechanical loss angle.

The results of oscillatory shear experiments are usually described using two moduli defined as follows:

$$G'(\omega) = \sigma_0/\gamma_0 \cos \delta \qquad 2-31$$

$$G''(\omega) = \sigma_0/\gamma_0 \sin \delta \qquad 2-32$$

called respectively the "storage" and the "loss" modulus. The stress $\sigma(t)$ can then be expressed as:

$$\sigma(t) = \gamma_{o}[G'(\omega)\sin\omega t + G''(\omega)\cos\omega t]$$
 2-33

Two alternative material functions can also be defined:

$$\eta'(\omega) = \sigma_0 / \gamma_0 \sin \delta = G'' / \omega$$
 2-34

$$\eta''(\omega) = \sigma_o/\gamma_o \cos \delta = G'/\omega \qquad 2-35$$

The stress $\sigma(t)$ can be represented as follows in terms of these functions:

$$\sigma(t) = \dot{\gamma}_{\sigma}[\eta'(\omega)\cos\omega t + \eta''(\omega)\sin\omega t]$$
 2-36

From those two material functions the complex viscosity η^* is defined:

$$\eta^*(\omega) = \eta'(\omega) - i\eta''(\omega)$$
 2-37

and

$$\eta^* = \sqrt{(\eta')^2 + (\eta'')^2} = \sigma_0/\gamma_0$$
 2-38

In order to determine a discrete relaxation spectrum, Laun³⁴ used a linear regression procedure to determine (G_k, λ_k) by means of:

$$\{[G'(\omega_k)-G'_k]^2 : [G''(\omega_k)-G''_k]^2\} = minimun \qquad 2-39$$

where

$$G'(\omega_k) = \sum_{i=1}^{N} G_i(\omega_k \lambda_i)^2 / [1 + (\omega_k \lambda_i)^2]$$
 2-40

$$G''(\omega_k) = \sum_{i=1}^{N} G_i(\omega_k \lambda_i) / [1 + (\omega_k \lambda_i)^2]$$
 2-41

First Laun selects values of λ_1 to have values equal to integer powers of ten from 10⁴ to 10⁹ and then calculates G₁ from 2-39.

However, inferring the relaxation spectrum from experimental data in this way has some disadvantages, since there is no unique solution and sometimes the relaxation times are found to be negative. Baum_baertel and Winter³⁵ have developed a nonlinear regression method that calculates simultaneously the values of the relaxation strengths and the relaxation times.

2.3.2 Steady shear experiments

2.3.2.1 Typical results

During steady shear experiments the sample is subjected to a constant shear rate $\dot{\gamma}$. The shear stress and the first and second normal stress differences can in principle be measured during such an experiment. The shear stress growth coefficient, $\eta^+(\dot{\gamma})$, the first normal shear stress coefficient, $\Psi_1^+(\dot{\gamma})$ and the second normal shear stress coefficient $\Psi_2^+(\dot{\gamma})$, can thus be calculated from experimental data. The strain, shear stress and first normal shear stress difference are shown in figure 2.2.

From figure 2.2b it can be seen that the shear stress, after an initial overshoot, becomes steady. This steady value is plotted as a function of shear rate to give the viscosity curve which normally includes a zero shear viscosity at low shear rates and a power law



Figure 2.2 Steady shear experiment

region at high shear rates. The first normal stress difference also reaches a steady value after an initial overshoot as is shown in figure 2.2c.

The maximum value of the first normal shear stress difference N_t , occurs at a time t_N , that is larger than the time t_S , at which the maximum value of the shear stress occurs.

i Fr Osaki³⁴ found that $t_s = a/\gamma$ with a≈3. Depending on the form of the damping function used it was found according to Doi-Edwards theory that $2 < t_N/t_s < 3^{37}$. However, the precise values of t_N and t_s are very difficult to determine experimentally. Some researchers have even found in some cases the presence of an undershoot after the overshoot³⁶.

2.3.2.2 The Cox-Merz rule

A relationship between the viscosity function and the complex viscosity is the Cox-Merz rule³⁹ which is given by:

$$\eta(\dot{\gamma}) = \eta^{*}(\omega) \qquad (\dot{\gamma} = \omega) \qquad 2-42$$

However, this "rule" is based only on empirical observations and is not universally valid^{40,41}. For example, Osaki⁴² reported the failure of this rule for polystyrene solutions when $cM > 10^{4}$ (c=concentration in g/cm³, M=Molecular weight).

2.3.3 Single-step strain experiment

2.3.3.1 Introduction

Single step shear strain is the test most widely used to study nonlinear viscoelastic behavior. In figure 2.3 is shown the strain versus time curve for an ideal step strain and for a typical actual deformation. Ideally, the material is deformed instantaneously, as shown by curve 1 in figure 2.3. In practice, however, it is not possible to generate such a deformation. The actual strain is usually a ramp during which the total strain is given by $\gamma(t) = \gamma_0 \Delta t$, followed by a steady value, as represented by curve 2 in figure 2.3.

2.3.3.2 The damping function

The Doi-Edwards theory can be used to predict the relaxation modulus $G(t,\gamma)$, for times greater than λ_{t} . The predicted relaxation modulus is the product of the linear modulus and a damping function:

$$G(t,\gamma) = h(\gamma)G(t)$$
 2-43

This equation states that for different values of γ the relaxation modulus $G(t,\gamma)$ will vary by a factor equal to $h(\gamma)$. Linear behavior is obtained as $\gamma \rightarrow 0$. Osaki⁴ found that the behavior of polystyrene solutions is linear up to values of strain of 0.57.



Figure 2-3 Single-step strain experiment

2.3.3.3 Behavior of type I and type II solutions under single step shear strain

Osaki and Kurata^{*a*} proposed a classification of polystyrene solutions according to their behavior in a step shear experiment. In particular they compared their experimental results with the prediction of the Doi-Edwards theory. For type I solutions the separation of the relaxation modulus into two functions given by equation 2-43 was observed at times greater than λ_k , this time being proportional to M². For type II solutions the separation was observed only in the terminal zone of G(t). Type I behavior was observed by Osaki and Kuruta when cM<10⁶ and type II behavior at higher values of cM. The critical value of cM corresponds to about 50 entanglements per molecule. Einaga et al.⁴ and Fukuda et al.⁴ found that the relaxation times did not depend on the strain. When separable behavior is not observed, i.e for $t < \lambda_{b}$, Osaki et al.⁴ proposed the use of two damping functions $h_{1}(\gamma)$ and $h_{2}(\gamma)$, expressing the relaxation modulus as follows:

$$G(t,\gamma) = \sum_{i=1}^{N} \lambda_{i} h_{i}(\gamma) G_{i} \exp(-t/\lambda_{i})$$
2-44

2.3.4 Exponential shear

The strain generated by "exponential shear" is given by:

$$\sigma(t) = A \left[\exp(\alpha t) - 1 \right]$$
 2-45

where α is the exponential rate constant and A the strain scale factor. Because of its exponential form, this deformation is a "strong flow" that has a tendency to stretch molecules".

To represent the results of this type of experiment, the "exponential viscosity" has been defined by Zülle et al.⁴ as follows:

$$\eta^{e}(\mathbf{t},\boldsymbol{\alpha},\mathbf{A}) = \sigma(\mathbf{t},\boldsymbol{\alpha},\mathbf{A})/\dot{\gamma}(\mathbf{t})$$
 2-46

Doshi and Dealy" also defined another material function as follows:

$$\eta_{\rm P}(t,\alpha,A) = \sqrt{\left(N_{\rm i}^2(t) + 4\sigma^2(t)\right)/\dot{\gamma}} \qquad 2-47$$

They suggest that this is more appropriate to characterize the role of the molecular stretching and orientation.

At small times the behavior of the sample under exponential shear strain follows linear behavior. At large times, the flow generates very rapid disentanglement, and the behavior is very nonlinear.

The sliding-plate rheometer has been found to be very convenient to generate exponential shear^{49,50}.

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3. THEORETICAL BASIS OF EXPERIMENTAL TECHNIQUES USED

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3. THEORETICAL BASIS OF EXPERIMENTAL TECHNIQUES USED

Chapter outline

In this chapter the sliding-plate rheometer is discussed first. The principle of operation of this rheometer, the principal sources of errors, and a way to avoid some of these errors are presented. In a second part the birefringence technique is discussed. The stress-optical law, and the derivation of the relationship between birefringence and stress are given.

3.1 The sliding-plate rheometer

3.1.1 Introduction

The rheometer geometries that are most used to measure viscoelastic properties are of three types:

- 1. Cone and plate
- 2. Parallel disk
- 3. Concentric cylinder

A good review of these is given by Dealy¹. Unfortunately, these types of rheometer cannot be used by the rheologist to perform experiments at high shear rates because of secondary flows, edge and end effects and non-uniform shear rates. The errors resulting from these effects have been reviewed by several authors¹³. In particular, none of these rheometers is useful for the study of nonlinear viscoelasticity.

However, a new sliding-plate rheometer designed at McGill³⁴ which incorporates a shear stress transducer, makes it possible to measure simultaneously the shear stress and the birefringence during deformations involving high shear rates. In contrast to rotational rheometers, however, the total strain is limited by the length of the plates.

3.1.2 Principle of operation

100

The sliding plate rheometer, which generates a flow with a uniform velocity gradient, consists of two plates: one stationary and one movable. In the gap between the plates the polymeric sample undergoes simple shear (as shown in figure 2.1) when the sliding plate moves. For this rheometer the shear stress σ , the shear strain γ and the shear rate γ are given by equations 3-1, 3-2, and 3-3 respectively.

$$\sigma = F/A \qquad 3-1$$

$$\gamma = X/h$$
 3-2

$$\dot{\gamma} = V/h$$
 3-3

where F is the force required to move the sliding plate, A is the wetted area, X is the displacement of the sliding plate, h is the distance between the two plates, and V is the velocity of the moving plate.

3.1.3 Sources of error

Some possible errors associated with the use of the sliding-plate rheometer are described in the following paragraphs.

- Gap imperfection

If the plates are not perfectly flat or are not parallel, the gap between them will not be uniform. The effect of non-uniform gap can be seen in figure 3.1. Figure 3.1a shows non-parallel plates with a varying gap. Figure 3.1b shows the stress obtained for start-up of steady shear using truly parallel plates and figure 3.1c shows the case when the plates are not parallel. Comparing figures 3.1b and 3.1c, it can be seen that in the case of nonparallel plates the stress does not reach a steady value.



Figure 3.1 Parallelism of the plates of the sliding-plate rheometer

- Edge and end effects

These effects are due to surface tension and to the difference in rheological properties between the sample and the surroundings. They result from a mismatch between the state of the stress in a homogeneously deformed sample and the hydrostatic stress in the surrounding fluid. It has been shown that these effects are larger when the material is subjected to high shear rates⁵⁴. Edge and end effects can also induce secondary flows.

- Shear wave propagation

When transient tests are performed, errors can be produced as a result of shear wave propagation. Because of the inertia of the sample, the sudden motion of the plate does not result in an instantaneous acceleration of every element of the sample. This shear wave propagation can also result in a stress overshoot. This source of error mainly occurs for liquids of low viscosity and is minimized when the gap is small. In the experiments conducted in this work the solutions studied have a high viscosity, and the gap is small. Thus, errors due to shear wave propagation are assumed to be negligible.

- Slip phenomenon

When concentrated polymer solutions and melts are subjected to very high shear stresses the no-slip boundary condition at the wall may no longer be valid, and slip may occur?.

- Bubbles

Zones of non-contact resulting from gas bubbles trapped between the sample and the plate can induce errors. Such bubbles can also promote a cohesive failure between the sample and the plate.

- Viscous heating

The deformation of the sample causes viscous heating and this will result in a thermal gradient in the sample. This problem is more severe for high shear rates, high viscosities and large gaps.

- Errors associated with sample deterioration

An additional source of error is sample inhomogeneity due to the loss or absorption of water or solvent or to degradation.

To overcome some of these problems, particularly edge and end effects, shear wave propagation and sample deterioration, Dealy and Soong^{43,10,11} developed a shear-stress transducer. Using this device the shear stress can be measured locally, at the center of one page, where the flow is uniform.

3.2 Birefringence

3.2.1 Why use light?

Matter is composed of charged particles. A beam of light, which can be understood as an oscillating electric field propagating through space, can be altered when passing through a material. (For more details see references 12-14). Rheoptics is the science that uses light to evaluate rheological properties. The advantages of using light can be summarized as follows:

- No physical contact between the light and the matter and therefore no perturbation of the flow field.
- Measurements can be carried out on small samples.
- Fast time response.

3.2.2 Definition of birefringence

When a light beam passes through a material, its velocity decreases. The refractive index, n, is defined as the ratio between the speed of light in vacuum and the speed of light through the sample. The birefringence¹⁵ is the difference between the refractive indexes in two perpendicular directions for a given material.

Ward¹⁶ describes in his book the three types of birefringence. They are:

- Orientation birefringence observed in anisotropic materials.
- Deformation birefringence, which can be caused by an external deformation in isotropic or anisotropic materials.

- Form birefringence, which occurs when the medium contains more than one phase.

3.2.3 The stress-optical law

Brewster¹⁷ observed that the light passing through a stressed glass plate in the direction of applied stress was polarized into two waves: one in a direction perpendicular to the stress and the other in the direction of the stress. He also noticed that the velocity of the wave in the stress direction was greater than the velocity of the wave in the stress direction perpendicular to the stress. Other researchers have proposed that if light passes irough a plate of thickness, d, of material in a direction perpendicular to a simple tension P applied to the plate, the two polarized waves are retarded by the factors r₁ and r₂ given by:

$$\mathbf{r}_1 = \mathbf{C}_1 \mathbf{P} \mathbf{d} \qquad \mathbf{r}_2 = \mathbf{C}_2 \mathbf{P} \mathbf{d} \qquad 3-4$$

where C_1 and C_2 are constants for the two polarized waves. The "relative retardation" is then given by:

$$\mathbf{r_1} \cdot \mathbf{r_2} = \mathbf{CPd}$$
 3-5

where C is the stress-optical coefficient. Later, Maxwell and Newmann¹⁸ showed that if the material is subjected to two perpendicular stresses, P and Q, the two factors are given by:

$$r_1 = (C_1P + C_2Q)d$$
 $r_2 = (C_2P + C_1Q)d$ 3-6

and therefore the relative retardation is:

$$r_1 - r_2 = (C_1 - C_2)(P - Q)d = C(P - Q)d$$
 3-7

More than a hundred years later, Lodge¹⁹ suggested that birefringence could be used to measure stresses in polymeric solutions. He formulated the stress-optical law according to which the stress is proportional to the birefringence.

$$\Delta n_{ij} = C \sigma_{ij} \qquad 3-8$$

where C is the stress-optical coefficient, which is a function of the chemical structure of the polymer. Experimental values of C for polymers can be found in the tabulations of experimental data on polymer melts by Janeschitz-Kriegl²⁰ (section 1.2.3.2) and by Van Kevelen²¹.

This law does not take into account light absorption and scattering. These can result in a deviation from the law. Also, it has been noticed in injection molding that a change in the temperature affects the birefringence²².

3.2.4 Relation between the stress and the birefringence

If the light beam is propagated in the x, direction, perpendicular to the shear plane, we have:

$$\sigma_{11} - \sigma_{22} = \Delta n_{12} / C \left[(\sin \chi)^2 - (\cos \chi)^2 \right]$$

= $\Delta n_{12} / C \cos 2\chi$ 3-9

where Δn_{12} is the birefringence, C the stress-optical coefficient and χ the stress-optical angle. The stress-optical angle is the smaller angle between the shearing plane and the vibration plane of the polarizers.

If the light is propagated in the x_2 direction (direction of the velocity gradient) we have:

$$(\sigma_{11} - \sigma_{33}) \mathbf{C} = \Delta \mathbf{n}_{13} \qquad 3-10$$

If the light is propagated in the x_1 direction (direction of motion), we have:

Deviations from the stress optical law have been observed in high-stress, extensional, flows for both polystyrene²³ and polyethylene²⁴. It was suggested by Wales²⁵ that the stress-optical law remains valid up to values of stress of 10⁷ N/m².

3.2.5 Measurement of birefringence

Birefringence is most often measured by the light intensity method. As shown in figure 3.2 the optical train usually used to measure birefringence is composed of: a light source, a polarizer, a test sample, an analyzer and a detector. The incident beam is polarized in a direction perpendicular to itself. The test sample retards one component of the polarized light. The analyzer recombines the light. The analyzer is rotated at 90° with respect to the polarizer. More information about optical components can be found in the books by Azzam¹² or Schurcliff¹⁴.

Bühler²⁴ developed an apparatus to measure birefringence with a double laser beam to allow a more sensitive determination of birefringence. Another method used to measure



Figure 3.2 Optical train

birefringence is the compensator method. It is reviewed in detail in the Encyclopedia of Polymer Science (15 p45).

After passing through the polarizer, the two perpendicular waves of light are retarded when they pass through the birefringent medium subjected to deformation. The retardation is proportional to the thickness and the normal stress difference. The light is then recombined by the analyzer. The light intensity measured by the detector is:

$$I = I_{o} \sin 2\alpha^{2} \sin \pi r / \lambda^{2}$$
 3-12

where I_{α} is the incident intensity measured when the polarizer and analyzer are parallel, α is the smallest angle made between the direction of one of the waves and the direction of one of the stresses. As can be seen, I is proportional to the birefringence. The derivation of this equation is given in Jessop's book²⁷.

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4. EQUIPMENT AND EXPERIMENTAL PROCEDURES

4. EQUIPMENT AND EXPERIMENTAL PROCEDURES

Chapter outline

This chapter describes the experimental equipment. First, the characteristics of the samples are given. Then, descriptions of the two rheometers and of the optical apparatus used in this work are provided. The experimental procedures are also explained in this chapter.

4.1 Polystyrene solutions

Measurements were performed on concentrated solutions of a high molecular weight polystyrene. A wide range of nonlinear phenomena could thus be observed.

4.1.1 The polymer

The polystyrene used here had a molecular weight of 2.84×10^6 and a polydispersity index, M₄/M₅, of 1.09. The polymer was synthesized by Toyo Soda Manufacturing Company. It has the appearance of raw cotton. Since polystyrene with a high molecular weight is not necessarily stable the samples were stored in a refrigerator.

4.1.2 The solvent

The solvent used was diethylphthalate (Boiling point = 296 °C, vapor pressure at 20 °C = 0.05 mmHg). This solvent was chosen because it is relatively safe to handle (Chiara'). It also had been used by other researchers, and therefore the results of the present work could be directly compared with those obtained elsewhere.

4.1.3 Solution preparation

4.1.3.1 Previous work

It is important that the solution be homogeneous and that the molecular weight not be affected by the dissolution process. Solution preparation techniques had been previously investigated by Chiara' and by Doshi². Chiara proposed to make the solutions of more than 30% by weight in three steps, adding 10% each time, heating to a temperature in the range of 50-70 °C, and employing a low stirrer speed (around 10-20 rpm). The dissolution of polystyrene occurs very slowly. Therefore, another method was used by Osaki³ to prepare an 8% polystyrene solution in chlorinated byphenyl. He added dichloromethane (a solvent with a low boiling point) to the mixture of polymer and solvent to prepare the solution; when the polymer was completely dissolved, the solution was heated to 50 °C under vacuum to eliminate the dichloromethane. The addition of dichloromethane accelerates the dissolution of polystyrene.

4.1.3.2 Method used

For the present study, solutions with concentrations ranging from 0.188 g/cm^3 to 0.206 g/cm^3 were made. Each solution was prepared using 4g of polystyrene and about 22.8g of diethylphthalate. This provided enough material for two experiments on the sliding-plate rheometer and one on the Rheometrics Mechanical Spectrometer. The polystyrene and diethylphthalate were added in four steps. In the first three steps 1g of polystyrene was added to 7g of diethylphthalate, and in the fourth step the remaining polystyrene and diethylphthalate were added to obtain a solution containing 4g of polystyrene and 22.4g of diethylphthalate.

The solutions were prepared in a 150 ml beaker and stirred at a speed of 5-6 rpm. To obtain such a low speed a rheostat was installed in series with the motor. The solutions were heated to about 50 °C. The temperature should not exceed 100 °C, which is the glass transition temperature of polystyrene and the temperature above which degradation may take place.

Between every addition of polymer and solvent the solution loses about 0.1 g due to evaporation. Therefore, the final concentration had an uncertainty of 2.5%. However, two solutions of the same nominal concentration tested on the sliding plate rheometer gave good reproducibility for a steady-shear experiment (cf chapter V, section 5.2).

4.1.4 Solution storage

The solutions were also stored in the refrigerator. It is important that all the solutions used be stored under the same conditions for the reproducibility of experiments. The effects of storage conditions on polystyrene solutions have been studied by Moore et al.⁴³.

4.2 The Rheometrics Mechanical Spectrometer

Dynamic measurements were done on a Rheometrics Mechanical Spectrometer (RMS-605). More information about this rheometer can be found in the operating manual⁴. Two parallel discs with diameters of 25 mm were used to shear the samples in this study. The torque and normal force were measured in response to the deformation imposed during the experiment by the "sensitive shear stress-transducer" model T-100. A microprocessor connected with the rheometer calculates the rheological properties from the torque and normal force data.

The polystyrene solution had to be heated to 50 °C for one hour or more in order to become fluid-like. This operation had to be done in an oven in order for the heating to be uniform. The sample was then squeezed between the two discs in a slow and gradual manner by increments of 20 μ m until the gap between the plates was 1 mm (see figure 4.1). Before starting the "squeezing operation" the sample was left at rest in the rheometer for twelve hours to assure its uniformity.

The relaxation spectrum was calculated using a commercial software package (IRIS⁷) developed by Baumgaertel and Winter⁴.

4.3 The sliding-plate rheometer

Most of the experiments in this study were performed on a sliding-plate rheometer developed at McGill University. The sliding-plate rheometer is equipped with a servohydraulic actuator and a shear-stress transducer to measure the local stress. The servohydraulic system is controlled (MTS 4132 Control) by a MTS Model 442 controller and



Figure 4-1 Parallel disc geometry

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a DEC PDP-11 microcomputer system. The rheometer is also equipped with an optical set-up for birefringence measurements in the 1-3 plane of the sample.

The rheometer consists of an upper stationary plate and a lower moving plate. The lower plate rides on linear bushing bearings. A gap of either 0.365 mm or 0.65 mm was maintained between the plates using shims. In this gap the polymer was subjected to simple shear (see figure 4.2). A shear stress transducer is mounted in a cavity in the upper plate (see Figure 4.3). The shear stress transducer measures the deflection of a beam in a direction parallel to the flow. This deflection is caused by the shear stress acting on the end of the beam. The face of the transducer, including the shear-sensitive end of the beam, is flush with the surface of the upper plate. The deflection of the beam is monitored by an MTI Accumeasure capacitance probe and amplifier 1023-PA.

The optical system used to measure birefringence is described in a separate section (4.3.3).

4.3.1 Experimental procedures

The two plates of the sliding-plate rheometer were cleaned carefully with acetone and petroleum ether to remove any remaining sample from a previous experiment. The glass windows used for the measurement of birefringence were polished using an optical cleaning cloth. After careful cleaning, the transducer housing was mounted and fastened tightly in position. It is very important that the shear-sensitive surface be flush with the surface of the plate. Also, the capacitance probe face must be parallel to the cantilever beam but must not touch the beam. The hot (50 °C) polystyrene solution was then poured on the glass window of the lower plate. The solution was left resting for 24 hours in order to allow air bubbles to escape (see figure 4.4). The upper plate and the shims fixing the thickness of the gap were mounted in place and carefully screwed down in order for the pressure on the polymer to be evenly distributed. The polymer was finally left resting for an additional 12 hours before the beginning of an experiment. The shear stress transducer was calibrated using standard weights suspended by a system of pulleys and wires.



Figure 4.2 The sliding-plate rheometer



Figure 4-3 The shear-stress transducer with micrometer for positioning the capacitance probe



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Figure 4-4 Polystyrene solution resting

4.3.2 Flatness of the plates

It is important that the gap be uniform, and that the plates be parallel to avoid the errors described in section 3.2.2. Figure 4.5 shows the stress for a steady shear experiment using parallel and non-parallel plates under the same operating conditions. The importance of the flatness of the plates can be readily seen. Callipers were used to evaluate the flatness of the plates.



Figure 4-5 Experimental evidence of non parallelism of the plates

- The lower plate

The optical glass was removed and its flatness was checked. A variation in flatness of 2.56% of 0.3 mm for the whole length was found. In order to improve the flatness, the lower plate was redesigned. In the new design, adjustable screws located under the glass can be used to correct small imperfections when the glass is not parallel to the upper plate (see figure 4.6).

- The upper plate

The variation of flatness of the upper plate was verified to be less than 5%.



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Figure 4-6 The lower plate

4.3.3 The optical system

The sliding-plate rheometer incorporates an optical system for measurement of birefringence that was originally designed by Haghtalab?

4.3.3.1 Description

The major components are shown in Figure 4.7 and described below:

1. A 0.5 mW helium-neon laser and power supply (Optikon company, LS-.5).

2. A laser beam expander (Optikon, 16X laser beam expander with spatial filter, 31-4054).

3. A polarizer and an analyzer consisting of two polarizing prisms (Oriel corporation of America, 2520-2).

4. An U-V extended visible diffuser head (Oriel, 7062).

5. A photomultiplier photometer (Oriel, 7070).

6. A laser line filter (Oriel, 5272, 1 in diameter).

7. Tubular optical bench, carriers, rod holders, polarizer rotators and adaptors.

In order to measure birefringence the laser light beam is first expanded by the beam expander, passes through a polarizer and a filter, and is then transmitted through the sample. The filter is used to prevent too much light from going into the detector. The transmitted light goes through the analyzer and is measured by the photomultiplier. The laser line filter allows only light with the same wavelength as the laser to reach the detector. The diffuser is used to reduce the influence of the angle of incidence of the light. The photocurrent generated in the photomultiplier is proportional to the intensity of the light reaching the detector. The output voltage signal, which is digitized and stored on the PDP-11, is proportional to the intensity of light reaching the detector.

4.3.3.2 Experimental procedures

The laser and the light detector were switched on 24 hours prior to an experiment to assure steady state. Before carrying out the experiment, all the optical components were



Figure 4-7 The optical train

aligned. The experiments were conducted in a dark room to avoid interference of ambient light.

At the beginning of an experiment, I_{o} , the value of the incident light was measured. The sample was in the rheometer, and the polarizer and analyzer were parallel. This gave the maximum intensity. During the experiment, the polarizer was rotated to have a 45° angle with the flow. The analyzer was rotated to make a 90° angle with the direction of the polarizer. Thus, the polarizer and analyzer were crossed. The accuracy of this step was checked by seeing if the light reaching the detector was at its minimum. The intensity, I, during an experiment was then measured. The birefringence is related to the intensity by:

$$\Delta n = \lambda d/\pi \arctan[(I/I_o)/\sqrt{1-(I/I_o)^2}]$$
4-1

where Δn is the birefringence, d is the gap between the moving plate and the stationary plate, I_{o} is the incident intensity, I is the intensity during an experiment, and λ is the wavelenght of the laser light.

The results were analyzed using a microcomputer and software developed previously.

4.3.4 Control of the temperature during the experiments

A thermocouple was placed on the upper surface of the upper plate of the rheometer and connected to a chart recorder to measure fluctuations of the temperature during the experiments. The thermocouple was also necessary to check that the temperature of the rheometer, which was warmed by the nearby hydraulic pump, had reached a steady value before starting the experiment. To study the effect of temperature on birefringence, the output voltage from the light detector was also recorded on the same chart recorder.

All the experiments performed with both the Rheometrics Mechanical Spectrometer and the sliding-plate rheometer were done at room temperature, because there was no temperature control system for these rheometers.
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5. RESULTS AND DISCUSSION

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5. RESULTS AND DISCUSSION

Chapter outline

In this chapter the results of the research are presented and discussed. In the first part the results of the small amplitude oscillatory shear experiments are presented, and the relaxation spectrum is determined. The results of the steady shear experiments are given in the second part. The third part deals with the results of the step-shear experiment and the determination of the damping function. Finally, the results of the exponential shear experiments are presented in the fourth part.

5.1. Small amplitude oscillatory shear experiments

5.1.1 Determination of the material functions

The loss modulus G', the storage modulus G", and the complex viscosity η^* were determined for a 0.199 g/cm³ solution over four decades of frequency. Six measurements per decade were made. Parallel disc fixtures were used in the Rheometrics Mechanical Spectrometer. The radius of the discs was 25 mm and the gap between them was 1 mm. The experiments were performed at a temperature of 23 °C. The loss modulus, G', the storage modulus, G", and the complex viscosity, η^* , are plotted versus the frequency, ω , in figure 5.1. The straight line for $\omega > 0.316$ rad/s was obtained by least-square linear regression. The equation for this line is:

$$\log(\eta^*) = 1.66 - 1.03 \log(\omega)$$
 5-1

The data points for 0.01 rad/s < ω < 0.316 rad/s were simply connected by straight line segments.

The curve of $\eta^*(\omega)$ shows a power law region ($\omega > 0.316$ rad/s). In this apparatus the lowest possible frequency was 0.01 rad/s, which was not low enough to give the zero



Figure 5.1 Complex viscosity and storage and loss moduli versus frequency for a 0.199 g/cm³ solution, at a temperature of 23 °C

shear viscosity η_{0} . Osaki¹ obtained a value for η_{0} of 3 10° Pa s by using frequencies of less than 10³ rad/s. For frequencies above 5 rad.s⁻¹ the storage modulus becomes constant. It can be seen there is a broad plateau. The value of the plateau modulus, G_{N} , can thus be evaluated. An average of the values of the modulus for frequencies ranging from 1 rad/s to 100 rad/s gives a plateau modulus G_{N} of 3924.1 Dyne/cm² = 392.41 Pa. At frequencies above 3 rad/s, the loss modulus is too small to be measured, which indicates a very elastic material. A cross-over point between G' and G'' was observed at a frequency of about 0.01 rad/s.

5.1.2 Determination of the relaxation spectrum

The discrete relaxation spectrum was determined from the dynamic mechanical data using a commercial software package (IRIS). The fundamentals of the method used have been described by Baumgaertel and Winter². The results obtained from the computation are listed in table 5.1.

| G, (Pa) | λ _ι (s) | |
|------------|-----------------------|--|
| 77 | 1.587 | |
| 121.5 | 12.01 | |
| 164.6 | 66.50 | |
| | | |

Table 5.1 Relaxation times and strengths as determined using IRIS

5.1.3 Linear relaxation modulus

The linear relaxation modulus can be calculated from the relaxation spectrum using equation 2-18.

$$G(t) = \sum_{i=1}^{N} G_i \exp(-t/\lambda_i)$$
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Figure 5.2 Linear relaxation modulus versus time for a 0.199 g/cm³ solution

for $\omega^{1} = \langle t < \omega^{1} \rangle$ where ω_{in} is the minimum frequency and ω_{in} is the maximum frequency at which measurements were made. λ_{i} and G_{i} are the ith relaxation time and the corresponding relaxation strength respectively.

Figure 5.2 shows the linear relaxation modulus as a function of time. The longest relaxation time, t_1 , was determined by the slope of the asymptotic straight line in the plot of log[G(t)] versus time at long times and was found to be equal to 66.5 s. It should be noted that the linear relaxation modulus at small times is equal to the plateau modulus at high frequencies.

5.2 Steady shear experiments

5.2.1 Raw data

Steady shear experiments were performed for shear rates ranging from 0.01 s^{-1} to 70 s⁻¹. The solution tested was a 0.199 g/cm³ solution. The gap used was 0.365 mm, and the temperature was 25.7 °C. Figures 5.3a and 5.3b present the shear stress results for four shear rates. These four rates represent the four types of behavior found using 17 different shear rates. Each of these types of behavior is described below.

- From 0.01 s¹ to 0.3 s¹

The shear stress does not reach a constant value after the maximum even at long strains. This case is illustrated in figure 5.3a for $\dot{\gamma}=0.01$ s⁻¹.

- From 0.3 s⁻¹ to 0.5 s⁻¹

The shear stress as a function of shear strain shows an overshoot and becomes steady at higher shear strains. This case is illustrated in figure 5.3a for $\dot{\gamma}=0.3$ s⁻¹.

- From 0.5 s^{-1} to 5 s^{-1}

An initial overshoot (at $\gamma = 2.5$) is followed by an undershoot (at $\gamma = 10$) and another overshoot (at $\gamma = 17.5$) before becoming steady. This case is illustrated in figure 5.3b for $\dot{\gamma}=1$ s⁻¹.

- Above 5s⁻¹

Only one overshoot is found. This case is illustrated in figure 5.3b for $\dot{\gamma} = 5s^{-1}$.



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Figure 5.3a Start-up of steady shear; shear stress versus strain for a 0.199 g/cm³ solution at two shear rates: 0.01 s⁻¹, 0.3 s⁻¹ at a temperature of 25.7 °C



Figure 5.3b Start-up of steady shear; shear stress versus strain for a 0.199 g/cm³ solution at two shear rates: 1 s⁻¹, 5 s⁻¹ at a temperature of 25.7 °C

In figures 5.4a and 5.4b is presented the intensity of light detected by the photomultiplier as a function of strain for four shear rates: 0.05, 0.7, 5, and 10s⁻¹. Again among the 17 shear rates used, four types of behavior were observed:

- From 0.01 s⁻¹ to 0.3 s⁻¹

The intensity increases as a function of strain and levels off. This case is illustrated in figure 5.4a for $\dot{\gamma} = 0.05 \text{ s}^{-1}$.

- From 0.3 s¹ to 1.5 s¹

The curve of the intensity as a function of strain displays an overshoot before becoming steady. This case is illustrated in figure 5.4a for $\dot{\gamma} = 0.7 \text{ s}^{-1}$.

- From 1.5 s⁻¹ to 10 s⁻¹

An initial overshoot (at $\gamma = 9$) is followed by an undershoot (at $\gamma = 21$) and a second overshoot (at $\gamma = 30$). This case is illustrated in figure 5.4a for $\gamma = 5 \text{ s}^{-1}$.

- Above 10s⁻¹

Only one overshoot is found, and after this the intensity decreases continuously. This case is illustrated in figure 5.4b for $\gamma = 10$ s⁻¹.

5.2.2 Viscosity

In order to obtain the viscosity defined by equation 2-8

$$\eta = \sigma/\dot{\gamma}$$
 2-8

the steady-state stress value at each shear rate was used. The steady stress value represents an average over the range of strains during which the value of stress fluctuated less than 3%.

Figure 5.5 shows the viscosity as a function of shear rate on a log log plot. It can be seen from this figure that the zero-shear viscosity was not reached even at very low shear rates. The power law constants were determined using linear regression. The resulting power law equation is:



Figure 5.4a Start-up of steady shear; light intensity versus strain for a 0.199 g/cm³ solution at three shear rates: 0.05 s⁻¹, 0.7 s⁻¹, 2 s⁻¹ at a temperature of 25.7 °C



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Figure 5.4b Start-up of steady shear; light intensity versus strain for a 0.199 g/cm³ solution at a shear rate of 10 s⁻¹ at a temperature of 25.7 °C



Figure 5.5 Viscosity versus shear rate for a 0.199 g/cm³ solution at a temperature of 25.7 °C

$$\log(\eta) = 2.37 - 1.01 \log(\dot{\gamma})$$
 5-2

which implies that

$$\eta(\text{Pa s}) = 237 \ (\dot{\gamma})^{-101}$$
 5-3

The steady-state stress is thus essentially independent of shear rate:

$$\sigma = \eta \dot{\gamma} \approx 237 \text{ Pa}$$
 5-4

Figure 5-6 shows the steady-state stress as a function of shear rate. For the rates corresponding to the power law region the stress is constant. This behavior has also been observed by Osaki³ at lower shear rates (0.4 s⁻¹ < γ < 1 s⁻¹) for a 0.166 g/cm³ polystyrene solution. The molecular weight of the polystyrene was 3-10⁶ g/mol.

5.2.3 Third normal stress coefficient

The third normal stress difference was calculated from:

$$N_3 = \Delta n_y / C \qquad 3-15$$

where C is the stress-optical coefficient measured by Philipoff⁴ (C = 5.8.10⁹ m²/N) and Δn_{B} is the birefringence given by:

$$\Delta n_{13} = \lambda d/\pi \arctan\left((I/I_o)/(\sqrt{I - (I/I_o)^2})\right)$$
4-1

where λ is the laser wavelength, d is the thickness of the gap, I is the intensity measured during the experiment when the polarizer and analyzer are crossed, and I_o is the intensity measured at the beginning of the experiment when the polarizer and analyzer are parallel.



Figure 5.6 Steady shear stress versus shear rate for a 0.199 g/cm³ solution. at a temperature of 25.7 °C

Two values of the intensity were considered in detail for each experiment at a given shear rate: the maximum and the steady state values. In the experiments where no steady state value of intensity was observed only the maximum intensity was considered. The third normal stress difference corresponding to the maximum intensity, N_{3m} , and the third normal stress difference corresponding to the steady value of intensity, N_{3m} , were evaluated. The third normal shear stress coefficients corresponding to N_{3m} and N_{3m} are then given by:

$$\Psi_{3m} = N_{3m} / \gamma^2$$
 5-5

$$\Psi_{3a} = N_{3a}/\dot{\gamma}^2 \qquad 5-6$$

Figures 5.7 and 5.8 show Ψ_{3m} and Ψ_{3m} as functions of shear rate. The straight lines were obtained by linear regression. The equations for these lines are:

$$\log(\psi_{30}) = 4.02 - 1.14 \log(\dot{\gamma})$$
 5-7

$$\log(\psi_{3x}) = 3.64 - 1.76 \, \log(\gamma)$$
 5-8

where Ψ is in Pa s² and $\dot{\gamma}$ is in s⁴.

5.2.4 The transient behavior

The curves of stress and intensity as functions of strain show overshoots at shear rates greater than 0.3 s⁻¹. The time at which the maximum value of stress, t_n, occurs and the time at which the maximum value of intensity, t_n, occurs are shown as functions of $1/\gamma$ (inverse of the shear rate) in figure 5.9 on a log-log plot. Straight lines were obtained by linear regression of the data for rates from 0.3 s⁻¹ to 10 s⁻¹. The equations of these lines are as follows:

$$t_{r} = 3.03 /\dot{\gamma}$$
 5-9
 $t_{r} = 8.62 /\dot{\gamma}$ 5-10



Figure 5.7 Maximum value of the third normal stress coefficient versus shear rate for a 0.199 g/cm³ solution at a temperature of 25.7 °C







Figure 5.9 Time of overshoot versus reciprocical of the shear rate for a 0.199 g/cm³ solution. Lines correspond to Equations 5-9 and 5-10

Thus, the overshoot occurs at constant strain independent of shear rate. This is in agreement with the results of Osaki³ for polystyrene solutions and Sakai et al.⁵ for solutions of poly(α -methylstyrene). At higher rates (above 10 s⁻¹) equations 5-11 and 5-12 are no longer valid, and the times at which the overshoots occur are greater than those predicted by equation 5-11 and 5-12.

5.2.5 Reproducibility of the data

The reproducibility of the data is better than 5% for five repeats. To evaluate reproducibility, two solutions, 1 and 2, with a nominal concentration of 0.193 g/cm³, were prepared simultaneously and were used in two series of steady-shear experiments with shear rates ranging from 0.05 s⁻¹ to 70 s⁻¹ at a temperature of 27 °C. The rheometer gap was 0.365 mm.

Figures 5.10 and 5.11 show the viscosity and the third normal stress coefficient corresponding to the maximum value of light intensity as functions of shear rate on a log-log plot for solutions 1 and 2. It can be seen that the results for the two solutions are essentially the same. The best fitting for the power law regions gave:

| Solution 1: | |
|--|-------|
| $\log(\eta) = 2.30 - 1.04 \log(\dot{\gamma})$ | 5-11a |
| $\log(\Psi_{3m}) = 3.26 - 1.17 \log(\dot{\gamma})$ | 5-11b |

| Solution 2: | |
|--|-------|
| $\log(\eta) = 2.27 - 1.03 \log(\dot{\gamma})$ | 5-12a |
| $\log(\Psi_{3m}) = 3.10 - 1.11 \log(\dot{\gamma})$ | 5-12b |



Figure 5.10 Reproducibility of the shear stress measurement as indicated by results of viscosity for two solutions at a temperature of 27 ℃



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Figure 5.11 Reproducibility of third normal coefficient measurements for two solutions at a temperature of 27 °C

From this it can be concluded that the method of preparing the solutions as well as the rheological data are quite reproducible.

These results can be compared with the results for the 0.199 g/cm³ solution given above. The power law constants for $\eta(\dot{\gamma})$ and $\Psi_{3m}(\dot{\gamma})$ are the same for the three solutions within 2% and 5% respectively. For the 0.199 g/cm³ solution the ordinate values at the origin are larger, which results from the difference in concentration.

5.2.6 Effect of concentration

Figure 5.12 shows the viscosity as a function of shear rate for a 0.204 g/cm³ solution and a 0.199 g/cm³ solution. The values of viscosity in the power law region were fitted using linear regression. The resulting equations are:

$$C = 0.204 \text{ g/cm}^3 \log(\eta) = 2.45 - 1.156 \log(\dot{\gamma})$$
 5-14

$$C = 0.199 \text{ g/cm}^3 \quad \log(\eta) = 2.37 - 1.010 \log(\dot{\gamma})$$
 5-2

The slope for the straight line in the power law region for the 0.206 g/cm³ solution is greater than the one for the 0.199 g/cm³ solution. Osaki³ also observed that when the concentration of the solution increases, particularly, when it is a type II solution, the power law index increases.

5.2.7 Comparison with oscillatory shear experiments

Figure 5.13 shows the complex viscosity as a function of angular frequency and the viscosity as a function of shear rate for the 0.199 g/cm³ solution. The equations for the straight lines in the power law regions had been obtained previously:

$$\log(\eta^*) = 1.66 - 1.03 \log(\omega)$$
 5-1

$$\log(\eta) = 2.37 - 1.01 \log(\dot{\gamma})$$
 5-2



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Figure 5.12 Viscosity versus shear rate for 0.199 g/cm³ and 0.204 g/cm³ solutions at a temperature of 25.7 °C



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Figure 5.13 Comparison between complex viscosity and viscosity for 0.199 g/cm³ solution



Figure 5.14 Comparison between complex viscosity and viscosity for 0.204 g/cm³ solution

The two curves are essentially the same. The horizontal shift can be explained by the difference between the temperatures at which the experiments were performed. Therefore, for this solution the Cox-Merz⁶ rule is valid.

Figure 5.14 shows the same curves for the 20.4 g/cm³ solution. The dynamic experiments for this solution were run at 22 °C. The equations for the two straight lines are given below:

$$\log(\eta^*) = 2.69 - 0.93 \, \log(\omega)$$
 5-15

$$\log(\tau_i) = 2.45 - 1.16 \log(\dot{\gamma})$$
 5-14

It can be seen from this figure and from equations 5-14 and 5-15 that the Cox-Merz rule is not valid. Osaki et al.⁷ also observed deviations from the Cox-Merz rule at higher concentrations, particularly for type II solutions.

5.3 Step-shear experiments

5.3.1 Results

Stress relaxation experiments were carried out with a solution of concentration 0.199 g/cm³. The strain varied from 0.30 to 20 strain units. The relaxation of both shear stress and birefringence were also studied for a 0.204 g/cm³ solution. In this case the strain varied from 0.1 to 15 strain units. For all these experiments, the gap used was 0.365 mm, and the temperature was 26 °C.

The relaxation modulus, $G(t,\gamma)$, was calculated from the shear stress according to

$$G(t,\gamma) = \sigma(t,\gamma)/\gamma$$
 2-13

Another material function, here called the third relaxation modulus, was calculated from the third normal stress difference as follows:

$$G_{3}(t,\gamma) = N_{3}(t,\gamma)/\gamma^{2}$$
 5-16

where N_3 is determined from the birefringence:

$$N_3(t,\gamma) = \Delta n_{13}/C \qquad 2.15$$

and the birefringence is determined from the light intensity:

$$\Delta n = \lambda d/\pi \arctan[(I/I_o)/(\sqrt{I - (I/I_o)^2})]$$
4-1

Figure 5.15 shows the shear stress relaxation modulus for the 0.199 g/cm³ solution for various strains. In this figure is also shown the linear relaxation modulus calculated from the discrete spectrum according to

$$G(t) = \sum_{i=1}^{N} G_i \exp(-t/\lambda_i)$$
 2-18

Figures 5.16 and 5.17 show the relaxation modulus and the third relaxation modulus respectively as functions of time for the various strains. The curves were obtained by averaging the raw data to eliminate noise. The sampling frequency of the data acquisition system was 10 samples per second. The data points in figures 5.15 to 5.17 are averages of 20 data points.

5.3.2 Discussion

Tables 5.2 and 5.3 give the rise time for the two series of experiments. According to Laun⁸ the influence of the rise time, Δt_{o} , is negligible for measurements taken at times t greater than Δt_{o} . The largest rise time in the experiments performed here was 0.20 s. The first data points taken into consideration here were at t = 2 s; therefore, the influence of Δt_{o} was considered negligible.



Figure 5.15 Relaxation modulus versus time for a 0.199 g/cm³ solution at a temperature of 26 °C



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Figure 5.16 Relaxation modulus versus time for a 0.204 g/cm³ solution at a temperature of 26 °C



Figure 5.17 Third relaxation modulus versus time for a 0.204 g/cm³ solution at a temperature of 26 °C

The curve of the linear relaxation modulus calculated from the discrete spectrum and the curve of the relaxation modulus obtained from the step shear experiment for small strain should be the same. Those two curves are shown on figure 5.15; the two curves are parallel but differ by 30%. This difference results from the fact that the dynamic experiments, from which the discrete spectrum was inferred, were performed at 23 °C while the step shear experiments were performed at 26 °C. Those two curves can be brought together by a time-temperature (horizontal) shift. The shift factor a_t was evaluated and found to be equal to 3.2. No birefringence was observed for strains less than 0.82. Thus for strains of less than 0.82 the behavior of the melt can be considered linear.

| Table 5.2 Rise time for step-shear performed with a 0.199 g/cm ³ solution. | | Table 5.3 Rise time for step-shear performed with a 0.204 g/cm ³ solution. | | | |
|---|-----|---|-------|-----|-------|
| γ. | γ. | Δt | γ. | γο | ∆t |
| 0.16 | 4 | 0.04 | 0.10 | 4 | 0.025 |
| 0.36 | 8 | 0.045 | 0.31 | 8 | 0.038 |
| 0.52 | 12 | 0.043 | 0.42 | 12 | 0.035 |
| 0.74 | 16 | 0.046 | 0.62 | 16 | 0.038 |
| 0.99 | 20 | 0.049 | 0.83 | 20 | 0.041 |
| 1.41 | 30 | 0.047 | 1.27 | 30 | 0.042 |
| 1.92 | 40 | 0.048 | 1.86 | 40 | 0.047 |
| 3.94 | 60 | 0.066 | 3.88 | 60 | 0.065 |
| 5.96 | 75 | 0.079 | 5.78 | 75 | 0.071 |
| 7.97 | 160 | 0.080 | 7.84 | 100 | 0.078 |
| 9.95 | 100 | 0.099 | 9.75 | 100 | 0.097 |
| 14.90 | 100 | 0.149 | 14.65 | 100 | 0.146 |
| 19.88 | 100 | 0.20 | | | |

5.3.3 Superposition

The relaxation moduli as functions of time are parallel curves for different strains.

This is valid both for the relaxation function defined in terms of shear stress as well as that for the third normal stress difference. The curves for the different strains could be superposed by means of a vertical shift. Figures 5.18 and 5.19 show the curves of $\sigma(t)/\gamma$ and $N_3(t)/\gamma^2$ after shifting. The curves are superposable for $t_t>4s$ within experimental error.

According to Osaki⁹ the molecular weight between entanglements for polystyrene solutions is given by:

$$c^{14} M_e = 1.23*10^4 (g/cm^3)$$
 if $c < 0.3g/cm^3$ 5-17

Therefore, for c = 0.199 g/cm³:

$$M_e = 1.18 \times 10^3$$
 5-18

The ratio M/M_e is then equal to 22.1 and is comparable to the ratio t_1/t_x (where t_1 is the longest relaxation time and t_x is the time after which the superposition of the relaxation modulus curves is possible) which is equal to 16.7. Osaki⁹ also found that

$$M_{\star}/M \approx t_{i}/t_{k}$$
 5-19

5.3.4 Determination of the damping function

The values of the damping function $h(\gamma)$ were determined from the shift factor required to superpose the curves of Figures 5.15 and 5.16. The shift factor required to bring the curves of Figure 5.17 together gave the values of another damping function, called here $h_3(\gamma)$.

The experimental data for the damping functions $h(\gamma)$ and $h_3(\gamma)$ are plotted as functions of strain in Figure 5.20. The lines represent the best fit to equation 2-26. The subroutine used to fit the experimental data was EDLIN from the IMSL library. This



Figure 5.18 Relaxation modulus curves superposed for a 0.199 g/cm³ solution, at a temperature of 26 °C



A.

Figure 5.19 Third relaxation modulus curves superposed for a 0.204 g/cm³ solution, at a temperature of 26 °C



Figure 5.20 Damping function of polystyrene solution. The solid curve is for Equation 5.20, while the dashed curve is from Equation 5.21 at a temperature of 26 °C
subroutine is based on least squares regression. Thus, the two functions $h(\gamma)$ and $h_3(\gamma)$ for the 0.192 g/cm³ solution are:

$$h(\gamma) = 1/(1+0.22\gamma^2)$$
 5-20

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$$h_3(\gamma) = 1/(1+0.18\gamma^2)$$
 5-21

The shear stress damping function for the 0.199 g/cm³ solution was:

$$h(\gamma) = 1/(1+0.216\gamma^2)$$
 5-22

A comparison of equations 5-20 and 5-22 shows the good reproducibility of the data.

5.3.5 Ratio of N₂ to N₁

According to Wagner¹¹ we should have

$$G(t,\gamma) = h(\gamma) G(t)$$
5-23

and

$$N_{i}(t,\gamma) = h(\gamma) G(t) \gamma$$
5-24

The function measured here was:

$$h_3(\gamma) = N_3(t)/\gamma G(t)$$
 5-25

If the ratio between the first and second normal stress differences is equal to β , the ratio between the third and the first normal stress differences is $(1-\beta)$. From this it follows that:

$$h_{3}(\gamma) = h(\gamma)(1-\beta)$$
 5-26

The ratio β can then be determined as a function of γ from the experimental data. Figure 5.21 shows β as a function of strain. It can be seen that the ratio N₂/N₁ is not constant. This is in disagreement with the results of Wagner¹², Christiansen and coworkers¹³, and Tanner¹⁴, who found that β is constant, although these authors studied different solutions.

5.4 Exponential shear

5.4.1 Results

Exponential shear experiments were conducted using a 0.192 g/cm³ solution. The gap between the two plates was 0.365 mm. Experiments were performed for an exponential rate constant, α , ranging from 0.02 to 6 (with a scale factor equal to 1) at a temperature of 27 °C and for a strain scale factor, A, ranging from 0.1 to 10 (with an exponential rate of 0.5) at a temperature of 25 °C. For all these experiments the exponential shear stress coefficient and the birefringence were evaluated. The exponential shear stress coefficient η_e is defined as:

$$\eta_{\bullet}(t,\alpha,A) = \sigma(t)/\dot{\gamma}(t)$$

$$\eta_{\bullet}(t,\alpha,A) = \sigma(t)/\alpha A \exp(\alpha t)$$
5-27

using the shear rate, $\dot{\gamma}(t)$, given by equation 2-45.

However, the exponential shear stress coefficient was not calculated according to 5-27. It was evaluated from the measured value of the strain rate since the actual strain history always deviates to some extent from ideal strain history, so that $\alpha Aexp(\alpha t)$ and $\dot{\gamma}(t)$ are not equal in practice.

Figure 5.22 shows the exponential shear stress coefficient, η_{er} as a function of strain for an exponential rate constant, α , of 0.02 and a strain scale factor, A, of 1. Figures 5.23 and 5.24 show the exponential shear stress coefficient, η_{er} as a function of shear strain, for values of the exponential rate constant, α , ranging from 0.1 to 6 and for values of the strain scale factor, A, ranging from 0.1 to 10 respectively. Figures 5.25 and 5.26 show the



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Figure 5.21 N₂'N₁ versus strain for a 0.204 g/cm³ solution, at a temperature of 26 $^{\circ}$ C



Figure 5.22 Exponential shear coefficient versus strain ($\alpha = 0.02$, A = 1) for a 0.192 g/cm³ solution at a temperature of 27 °C



Figure 5.23 Influence of the exponential rate constant on the exponential stress coefficient for a 0.192 g/cm³ solution, at a temperature of 27 °C

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Figure 5.24 Influence of the strain scale factor on the exponential stress coefficient for a 0.192 g/cm³ solution, at a temperature of 25 °C



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Figure 5.25 Influence of the exponential rate constant on the third normal stress coefficient for a 0.192 g/cm³ solution, at a temperature of 27 °C



Figure 5.26 Influence of the strain scale factor on the third normal stress coefficient for a 0.192 g/cm³ solution, at a temperature of 25 °C

normal stress difference, N_3 , as a function of shear strain, for values of the exponential rate constant, α , ranging from 0.1 to 6 and for values of the strain scale factor, A, ranging from 0.1 to 10 respectively.

The curves were obtained by averaging the raw data to eliminate noise. The sampling frequency of the data acquisition system was 70 measurements per second, and the points shown in Figures 5.22 to 5.26 are averages of 5 data points.

5.4.2 Discussion

Figure 5.22 shows the behavior of the exponential stress coefficient for a very small value of exponential shear rate constant, α . In this case the behavior of the polymer during the flow follows linear viscoelasticity over a significant part of the experiment. The exponential stress coefficient, η_{α} increases monotonically as a function of shear strain. It can be seen from Figures 5.23 and 5.24 that η_{α} as a function of strain has a maximum. The maximum occurs at about the same value of strain for every value of the exponential rate constant, α , and for every value of the strain scale factor, A. It occurs at a total strain of 6.5 strain units. After the maximum the function decreases continuously without reaching a steady value. It can be seen that both α and A have a strong influence on the results. When α or A increases, η_{α} decreases. This is not in agreement with the prediction of the Giesekius¹³ theory discussed by Schieber¹⁶ which is that $\eta_{\alpha}/\eta_{\alpha}$ is relatively insensitive to a variation in A.

The influence of α , the exponential shear rate constant, and of A, the strain scale factor, on the third normal stress difference can be seen in figures 5.25 and 5.26 respectively. For $\alpha < 1$, the third normal stress difference as a function of time increases continuously until reaching a maximum value. It stays constant at this maximum value thereafter. For $\alpha > 1$ the maximum in the third normal stress difference is reached at a higher strain. After the maximum the value of the third normal stress difference decreases sharply. It can be seen from Figure 5.26 that A does not have a strong influence on the results. For 0.1 < A < 4 the third normal stress difference increases, finally reaching a steady value. For A=10, N₃ as a function of strain displays a maximum and then decreases. The parameter α has a larger influence than A on the third normal stress difference.

5.5 Effect of temperature

It was noticed that heat from the nearby hydraulic pump increased the temperature of the rheometer over long periods of time. The temperature of the upper plate was measured by means of a thermocouple. Before running any experiment it was established that this temperature had reached a steady value. During the experiments it was verified that the temperature of the melt varied by less than 0.1° C. When the experiment was finished and the pump was stopped the temperature of the upper plate decreased until room temperature was reached. This temperature was measured simultaneously with the intensity of light reaching the photodetector. Figure 5.27 shows the temperature and intensity of light passing through the polymer as functions of time. It can be seen on this graph that a decrease in the temperature causes a increase in birefringence.



Figure 5.27 Influence of temperature on light intensity

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6. COMPARISON WITH THEORETICAL MODEL

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6. COMPARISON WITH THEORETICAL MODEL

Chapter outline

This chapter presents a comparison of the experimental data for steady shear experiments and exponential shear experiments with the predictions of Wagner's model. In the first part the model is presented. The calculations necessary for using Wagner's model are presented in the second part. The comparisons of the experimental results and predictions from the model are presented and discussed in a third part.

6.1 Introduction

The results of the steady shear experiments and exponential shear experiment for a 0.199 g/cm³ solution were compared with the predictions of Wagner's constitutive equation. This equation expresses the state of stress in the polymer as a function of the flow history (kinematics of the flow) and the material properties of the polymer. Wagner's constitutive equation is given below:

$$\sigma_{ij}(t) = \int_{-\infty}^{t} m(t-t')h(I_{i},I_{2})[(1+\beta)B_{ij}(t,t')+\beta C_{ij}(t,t')]dt'$$
6-1

Each of the functions in the integral are defined bellow.

6.1.1 The memory function

The memory function, m(t,t'), is given by:

$$m(t-t') = \sum_{i=1}^{N} G/\lambda_i \exp((t-t')/\lambda_i)$$
 2-18

with G_i being the ith relaxation modulus and λ_i the ith relaxation time. The relaxation modulus and relaxation times for the polystyrene solution considered here are given in

table 5.1. These parameters come from the discrete spectrum calculated using smallamplitude oscillatory shear data.

6.1.? The damping function

The damping function, $h(\gamma)$, used here is given by:

$$h(\gamma) = 1/(1+0.216\gamma^2)$$
 5-22

6.1.3 The kinematics

 $B_{ij}(t,t')$ and $C_{ij}(t,t')$ are the components of the Finger and Cauchy tensors respectively, and β is the ratio of the second normal stress difference to the first normal stress difference.

6.2 Predictions of Wagner's model

6.2.1 Start-up of steady shear

In steady shear flow the fluid is deformed by the motion of the upper plate moving at a constant velocity. The flow history is given by:

$$\gamma(t) = 0 \qquad t < 0$$

$$\gamma(t) = \dot{\gamma}t \qquad t > 0 \qquad 6-2$$

Substituting 5-22 and 2-18 into 6-1 we obtain:

$$\sigma_{12}(t) = \int_{-\infty}^{1} \int_{-\infty}^{N} G_{i} / \lambda_{i} \exp(-(t-t^{2}) / \lambda_{i}) [1/(1+0.22\gamma^{2})] [(1+\beta)B_{12}(t,t^{2}) + \beta C_{12}(t,t^{2})] dt^{2} dt^{2} dt^{2}$$

The components of the Finger and Cauchy tensor are as follows:

For t' < 0
$$B_{12}(t,t') = \dot{\gamma}t$$
 6-4a

$$\mathbf{C}_{12}(\mathbf{t},\mathbf{t}') = -\dot{\boldsymbol{\gamma}}\mathbf{t} \tag{6-4b}$$

For t' > 0
$$B_{12}(t,t') = \dot{\gamma}(t-t')$$
 6-4c

$$C_{12}(t,t') = -\dot{\gamma}(t-t')$$
 6-4d

Substituting 6-4 into 6-3:

$$\sigma_{12}(t) = \int_{-\infty}^{t} G_{i} / \lambda_{i} \exp(-s/\lambda_{i}) \left[1/(1+0.216(\dot{\gamma}t)^{2}) \right] (\dot{\gamma}t) ds + \int_{-\infty}^{t} \int_{-\infty}^{N} G_{i} / \lambda_{i} \exp(-s/\lambda_{i}) \left[1/(1+0.216(\dot{\gamma}s)^{2}) \right] (\dot{\gamma}s) ds$$
6-5

where s = t-t'.

In a similar way, the first normal stress difference $[N_1(t) = \sigma_{11}(t) - \sigma_{22}(t)]$ can be expressed as follows:

$$N_{1}(t) = \int_{-\infty}^{t} \int_{i=1}^{N} G_{i}/\lambda_{i} \exp(-s/\lambda_{i}) \left[\frac{1}{(1+0.216(\dot{\gamma}t)^{2})} (\dot{\gamma}t)^{2} ds + \int_{-\infty}^{N} \int_{i=1}^{N} G_{i}/\lambda_{i} \exp(-s/\lambda_{i}) \left[\frac{1}{(1+0.216(\dot{\gamma}s)^{2})} (\dot{\gamma}s)^{2} ds \right]$$
6-6

The second and third normal stress difference $N_2(t)$ and $N_3(t)$ are then given by:

$$N_2(t) = \beta N_1(t)$$
 6-7

and

$$N_{3}(t) = \sigma_{33}(t) - \sigma_{22}(t) = (1+\beta) N_{1}(t)$$
 6-8

6.2.2 Exponential shear

The strain history for exponential flow is given by:

$$\gamma(t) = 0$$
 $t < 0$
 $\gamma(t) = A [exp(\alpha t) -1]$ $t > 0$ 6-9

where α is the exponential rate constant and A is the strain scale factor. The stress is then evaluated from equation 6-3 where the components of the Finger and Cauchy tensors are as follows:

For
$$t' < 0$$
 $B_{12}(t,t') = A [exp(\alpha t)-1]$ 6-10a

$$C_{12}(t,t') = -A [exp(\alpha t)-1]$$
 6-10b

If
$$t' > 0$$
 $B_{12}(t,t') = A(\exp(\alpha t) - \exp(\alpha t'))$ 6-10c

$$C_{12}(t,t') = -A \left(\exp(\alpha t) \cdot \exp(\alpha t') \right)$$
 6-10d

Substituting 6-10 in 6-3 we obtain:

$$\sigma_{12} = \int_{-\infty}^{t} A \sum_{i=1}^{N} G_{i} / \lambda_{i} \exp(-s/\lambda_{i}) (\exp(\alpha t) - 1) [1/(1 + 0.216A^{2}(\exp(\alpha t) - 1)^{2})] ds$$

+
$$\int_{-\infty}^{t} A \sum_{i=1}^{N} G_{i} / \lambda_{i} \exp(-s/\lambda_{i}) \exp(\alpha t) (1 - \exp(-\alpha s)) [1 + 0.216A^{2}\exp(2\alpha t)[1 - \exp(-\alpha s)]^{2}] ds = 6-11$$

The exponential shear stress coefficient, which can be evaluated from equation 6-11, is defined as follows:

$$\eta^{*}(t) = \sigma(t)/\alpha Aexp(\alpha t)$$
 5-27

In a similar way the first normal shear stress difference can also be found:

$$N_{1}(t) = \int_{\infty}^{t} A^{2} \sum_{i=1}^{N} G_{i} / \lambda_{i} \exp(-s/\lambda_{i}) (\exp(\alpha t)1)^{2} \{1/[1+0.216A^{2}(\exp(\alpha t)-1)^{2}]\} ds$$

+
$$\int_{-\infty}^{t} A^{2} \sum_{i=1}^{N} G_{i} / \lambda_{i} \exp(-s/\lambda_{i}) \exp(2\alpha t) (1-\exp(-\alpha s))^{2} \{1+0.216A^{2}\exp(2\alpha t)[1-\exp(-\alpha s)]^{2}\} ds \ 6-12$$

The second and third normal stress differences are given by equations 6-7 and 6-8.

The shear stress, the third normal stress difference, and the exponential shear stress coefficient were computed according to Wagner's model using an IMSL library subroutine (DQDAG). The programs used here are available in the Polymer Engineering Laboratory of McGill University.

6.3 Results and comparison with experimental data

6.3.1 Start-up of steady shear

Wagner's predictions were compared with the experimental data performed with a 0.199 g/cm³ solution at a temperature of 25.7 °C. Figures 6.1 to 6.4 show the stress as a function of strain $\gamma(t)$ for both the experimental data and the predictions of Wagner's model for four different shear rates ranging from 0.01 s⁻¹ to 5 s⁻¹. It can be seen from figures 6.1 and 6.2 that the experimental data are in good agreement with the predictions of Wagner's model for small shear rates ($\gamma < 0.3 \text{ s}^{-1}$). However, for rates larger than 0.3 s⁻¹ the steady stress predicted by Wagner is smaller than the one obtained experimentally. For a shear rate of 1 s⁻¹ the experimental stress signal displays an undershoot and a second overshoot that are not predicted by Wagner's model. This discrepancy increases as the shear rate increases.

The steady shear stress as a function of shear rate for both the prediction according to Wagner's model and the experimental data are shown in figure 6.5. For shear rates greater than 0.2 s⁻¹ the experimental steady stress starts to level off after reaching a maximum. Wagner's predictions are in good agreement with the experimental data for rates up to 0.3 s⁻¹. Then the predicted stress decreases and tends toward zero for very high shear rates. The discrepancy between experimental data and theoretical predictions is due to the



Figure 6.1 Start-up of steady shear ($\dot{\gamma} = 0.01s^{-1}$), shear stress versus strain







Figure 6.3 Start-up of steady shear ($\dot{\gamma} = 1s^{-1}$), shear stress versus strain



Figure 6.4 Start-up of steady shear ($\dot{\gamma} = 5s^{-1}$), shear stress versus strain



Figure 6.5 Steady shear versus shear rate; comparison between experimental data for a polystyrene solution and Wagner's model prediction

very narrow relaxation spectrum of the solution.

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To illustrate the importance of the spectrum in the behavior of the steady shear stress, Figure 6.6 shows the steady stress as a function of shear rate according to Wagner's predictions .or a high-density polyethylene melt which has a broad relaxation spectrum (the relaxation strengths, G_{ij} , the relaxation times, λ_{ij} are those of table 6.1) (the data are these of Tony Samurkas¹) and the sigmoidal damping function given below:

 $h(\gamma) = 1/(1+0.15\gamma^2)$ 6-13

Table 6.1

Relaxation strengths and Relaxation times for a high-density polyethylene melt

| G _i (Pa) | λ, (S) |
|-----------------------|-----------------------|
| .1027 105 | .6816 104 |
| .9346 10 ^s | .4106 101 |
| .2057 105 | .5051 10° |
| .4545 104 | .3171 10 ¹ |
| .9322 103 | .7496 10 ¹ |
| .1001 104 | .2688 102 |
| .1922 10 ³ | .2787 103 |
| | |

It can be seen from figure 6.6 that the stress does not decrease.

Figure 6.7 shows t, (the time at which the stress overshoot occurs) as a function of the inverse of the shear rate on a log-log plot. The equations of the straight lines obtained by linear least square regression are:

$$t_{se} = 3.01/\dot{\gamma}$$
 5-9
 $t_{sp} = 2.20/\dot{\gamma}$ 6-14



Figure 6.6 Steady shear stress versus shear rate; Wagner's model prediction for a high-density polyethylene melt with a broad relaxation spectrum. The damping function and relaxation spectrum used are those of Samurkas (1).



Figure 6.7 Comparison between experimental and theoretical (Equation 6-14) times of overshoot

where t_{w} is the time at which the stress overshoot occurs for the experimental data, and t_{w} is the time at which the stress overshoot occurs according to Wagner's predictions. From these two equations it can be seen that the strain at which the experimental stress overshoot occurs is not in agreement with Wagner's predictions. It can also be seen in figure 6.7 that the deviation from equation 5-9, discussed previously and observed experimentally is not predicted by Wagner's model.

In Wagner's model if the memory function is expressed with a single relaxation time and the damping function is expressed as a single exponential as follows:

$$h(\gamma) = \exp(-a\dot{\gamma}t)$$
 6-15

the stress is predicted to be:

$$\sigma_{12}(t) = \int_{-\infty}^{t} \frac{G}{\lambda} \exp(-(t-t')/\lambda) \dot{\gamma}t \exp(-a\dot{\gamma}t) dt' + \int_{-\infty}^{\infty} \frac{G}{\lambda} \exp(-(t-t')/\lambda) \dot{\gamma}(t-t') \exp(-a\dot{\gamma}(t-t')) dt'$$
 6-16

From equation 6-16 the time at which the stress overshoot occurs is found to be:

$$t_{s} = 1/a\dot{\gamma} \qquad 6-17$$

To be in agreement with equation 5-9 "a" should be equal to 0.34. Figure 6.8 shows the damping function determined experimentally, the single exponential form calculated above and the experimental data. It can be seen from this figure that this single-exponential form is also in good agreement with the experimental data. However, the calculation above has been done for a single relaxation time and a single relaxation strength.

Figures 6.9 to 6.12 show the third normal stress difference as a function of strain $\gamma(t)$ for both the experimental data and the predictions of Wagner's model for four



Figure 6.8 Exponential and sigmoidal damping function.



Figure 6.9 Start-up of steady shear ($\dot{\gamma} = 0.1 \text{ s}^{-1}$), third normal shear stress difference versus strain



Figure 6.10 Sart-up of steady shear ($\dot{\gamma} = 0.7 \text{ s}^{-1}$), third normal shear stress difference versus strain



Figure 6.11 Start-up of steady shear ($\dot{\tau} = 2 s^{-1}$), third normal shear stress difference versus strain



Figure 6.12 Start-up of steady shear ($\dot{\gamma} = 10 \text{ s}^{-1}$), third normal shear stress difference versus strain

shear rates ranging from 0.1 s⁻¹ to 10 s⁻¹. The presence of a third normal stress difference is characteristic of nonlinear behavior. For a rate of 0.1 s⁻¹ the measured third normal stress difference increases much more than predicted by Wagner's model. It can be seen from figures 6.9 and 6.10 that Wagner's model does not predict the overshoot and undershoot observed experimentally, but for a rate between 0.7 s⁻¹ and 2 s⁻¹ the measured steady value is in fair agreement with the predicted values. However, when the rate is increased to 10 s⁻¹ it can be seen than even for the steady value the experimental values are much larger than the predicted values.

6.3.2 Exponential shear

Wagner's model predictions were compared with the experimental data from an exponential shear experiment for a 0.192 g/cm³ solution. Figures 6-13 to 6-16 show the exponential shear stress coefficient, η^{e} , as a function of strain for values of the exponential rate constant, α , ranging from 0.5 to 6 (the strain scale factor, A, is constant and equal to 1). The experimental data curves have the same shape as Wagner's predictions curves for α ranging from 0.5 to 6 but quantative discrepancy between experimental data and theory increases as α increases.

It can be seen from figure 6.17 that the strain at which the exponential stress coefficient η^{e} displays a maximum is the same for every theoretical curve but is different from the one observed experimentally.

Figure 6.18 shows the theoretical curves of the exponential shear stress coefficient for a constant value of the exponential rate constant and a strain scale factor ranging from 0.1 to 10. The experimental data (See Figure 5.24) show that η^e displays a maximum at the same strain for every value of the scale factor A. On figure 6.18 it can be seen that depending on the value of the strain scale factor the maxima occur at different shear strains.

Figures 6.14, 6.19 and 6.20 show the exponential shear stress coefficient as a function of strain for the same exponential rate constant, α , and for A equal to 1, 0.1, and



Figure 6.13 Exponential stress coefficient versus strain (A = 1, α = 0.02), comparison between experimental data and Wagner's model prediction



Figure 6.14 Exponential stress coefficient versus strain (A = 1, α = 0.5), comparison between experimental data and Wagner's model prediction



Figure 6.15 Exponential stress coefficient versus strain (A = 1, α = 1), comparison between experimental data and Wagner's model prediction







Figure 6.17 Wagner's prediction of the exponential stress coefficient for different values of the exponential rate constant



Strain Figure 6.18 Wagner's prediction of the exponential stress coefficient for different values of the strain scale factor



Figure 6.19 Exponential stress coefficient versus strain (A = 0.1, α = 0.5), comparison between experimental data and Wagner's model prediction



Figure 6.20 Exponential stress coefficient versus strain (A = 10, α = 0.5), comparison between experimental data and Wagner's model prediction

10 respectively. The discrepancy between the experimental data and the theory increases as A increases.

Figures 6.21 to 6.23 show the third normal stress difference for values of the exponential rate constant ranging from 0.02 to 6 (the strain scale factor is constant and equal to 1). It can be seen from figure 6.21 that for α very small (linear behavior) the experimental data are in good agreement with the theory up to values of strain of 6 which corresponds to:

$$t = \log(6+1)/0.02 = 97.29 s$$
 6-18

and

$$\dot{\gamma} = 0.7 \, \mathrm{s}^{-1} \tag{6-19}$$

At this shear rate the behavior of the polystyrene solution was nonlinear. For steady shear experiments a discrepancy between the experimental data and theoretical curves could be seen for $\dot{\gamma} = 0.7 \text{ s}^{-1}$ (see figure 6.10).

It can be seen from figures 6.22 and 6.23 that the overshoot observed experimentally in the third normal stress difference is not predicted by Wagner's model. It can also be seen that the discrepancy between experimental data and the theory increases with increasing α .

Figures 6.24 and 6.25 show a comparison between the experimental data for exponential shear with A ranging from 0.1 to 10 and an exponential rate constant of 0.5. It can be seen from those figures that the discrepancy between theory and experiments increases as A decreases.

To summarize, Wagner's predictions are not in good agreement with the experimental data for exponential shear for our solutions.



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Figure 6.21 Exponential shear ($\alpha = 0.02$, A = 1), third normal shear stress difference versus shear strain, comparison between experimental data and Wagner's model prediction





Figure 6.23 Exponential shear ($\alpha = 6$, A = 1), third normal shear stress difference versus shear strain, comparison between experimental data and Wagner's model prediction.


6.3.3 Conclusions

Wagner's model does not predict the stress for steady shear experiments performed at high shear rates ($\dot{\gamma} > 5s^{-1}$) for the solutions used here, neither does it predict the third normal stress difference for steady shear experiments performed at high shear rates. Wagner's model also fails in the prediction of the exponential stress coefficient and the third normal stress difference for exponential shear. Therefore, it can be concluded from 'he results mentioned above that Wagner's model cannot predict the nonlinear behavior of the solutions used here. Wagner's model is only valid for small deviations from linear behavior. Wagner's model seems to fail for solutions of very narrow relaxation spectrum.

REFERENCE

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1 Samurkas T., Ph.D. Thesis, Chemical Engineering Department, McGill University, 1991.

7. CONCLUSIONS

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7 CONCLUSIONS

7.1 Summary of accomplishments and findings

Nonlinear viscoelastic properties of polystyrene solutions were studied with the sliding-plate rheometer and compared with the predictions of Wagner's model.

A technique to make polystyrene solutions was developed and was shown to give good reproducibility in the measurement of rheological properties.

The sliding-plate rheometer was evaluated as a tool to study nonlinear viscoelasticity of polymeric liquids. The possible sources of error were reviewed. In particular it is very important to assure parallelism between the upper fixed plate and the lower moving plate in order to avoid errors in the shear-stress measurement. The lower plate was redesigned in order to assure precise parallelism.

Measurements of shear stress during transient shearing deformations involving high shear rates were made possible by using a shear stress transducer. Birefringence measurements in the plane perpendicular to the direction of the velocity gradient were performed to evaluate the third normal stress difference.

Start-up of steady shear was performed with the polystyrene solutions for higher shear rates than any previously reported. The transient behavior of the fluid was studied, and the presence of an undershoot and a second overshoot for both the shear stress and birefringence were observed. The power law region in the viscosity curve had a slope of -1 indicating that the steady-state stress is independent of shear rate. For concentrations of polystyrene higher than 20 g/cm³ the absolute value of the slope increased to 1.18.

Single-step shear experiments with large step strain were performed. A damping function was evaluated from the measurements of the relaxation modulus and fitted with an empirical sigmoidal function. A different damping function was inferred from the measurement of the relaxation of the third normal shear stress difference. The ratio of the second normal stress difference to the first normal shear stress difference was estimated from these two functions and was found not to be constant as a function of strain.

The exponential shear stress coefficient and the third normal stress difference were evaluated for exponential shear experiments. These two rheological functions were shown to depend strongly on the exponential rate constant.

Small-amplitude oscillatory shear experiments were also performed. A relaxation spectrum was inferred from the experimental data and found to be very narrow. The complex viscosity was compared with the steady shear viscosity. Two types of behavior were observed: for low concentrations (less than 20 g/cm³) the Cox-Merz rule was obeyed whereas it was not obeyed for more concentrated solutions.

It was shown that temperature has an influence on the birefringence. A decrease of 7 °C in temperature doubles the light intensity signal.

The experimental data were compared with the predictions of Wagner's constitutive equation. It was shown that for very high shear rates Wagner's predictions and experimental data were clearly distinct. The results of this comparison can be summarized as follows:

- Above a rate of 0.2 s⁻¹ the measured steady shear stress is constant as a function of shear rate. Wagner's model predicts a steady shear stress that decreases with shear rate.
- 2. The transient behavior (undershoot and second overshoot) was not predicted by Wagner's model.
- 3. When the shear rate was further increased, the discrepancy between experimental data and the theory became even more pronounced.
- 4. For exponential shear the predictions of Wagner's model were found to be in complete disagreement with the experimental data.

7.2 Recommendations for future work

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What follows are recommendations for future work based on the present research:

- 1. The heating used to dissolve polystyrene in diethylphthalate should be reduced to avoid evaporation of solvent during the preparation of solution.
- 2. The influence of the product cM (c = concentration in g/cm³, M = molecular weight) on the results of the experiments performed at very high shear rates and large strains should be studied by varying either the concentration of the solution or the molecular weight of the polystyrene sample.
- 3. Further study of the effect of temperature on birefringence should be done.
- 4. Other theoretical models such as the Doi-Edwards and Phan-Thien Tanner should be compared with the experimental data to see if they can describe the behavior of solutions with a narrow relaxation spectrum.
- 5. The sliding-plate apparatus should be modified to improve the control of temperature.

NOMENCLATURE

- A = Strain scale factor
- $B_{ij} =$ Component of the Finger tensor
- C = Stress optical coefficient
- C_1 = Stress optical coefficient for the first wave
- C_2 = Stress optical coefficient for the second wave
- C_{ij} = Component of the Cauchy tensor
- F = Force
- G = Relaxation modulus
- G_{\circ} = Third relaxation modulus
- $G_k = k^{th}$ relaxation strength
- G' = Storage modulus
- G'' = Loss modulus
- $K_e = Spring constant$
- $K_{\star} = Dashpot constant$
- I = Intensity of light
- I_{o} = Incident intensity of light
- $I_1(B_{ij}) =$ First invariant of the Finger tensor
- $I_2(B_{ij})$ = Second Invariant of the Finger tensor
- M = Molecular weight

 $M[(t-t'),I_1(B_{ij}),I_2(B_{ij})] = Memory function$

- M_{\bullet} = Molecular weight between entanglement
- N_1 = First normal stress difference
- N_2 = Second normal stress difference
- N_3 = Third normal stress difference
- P, Q = Stresses

- V = Velocity of the upper plate
- X = Displacement of the upper plate
- $X_{\circ} = Elongation$
- c = Concentration of the polystyrene solution
- d = Size of the gap
- h = Gap between the plates of the sliding-plate rheometer
- $h(\gamma)$ = Damping function defined with the shear stress
- $h_3(\gamma)$ = Damping function defined with third normal stress difference
- m(t-t') = Memory function
- n = Refractive index
- $\mathbf{r}_1, \mathbf{r}_2 = \text{Retardation paths}$
- t = Time
- t_N = Time at which the maximum of third normal stress difference occurs during star-up of steady shear
- t_s = Time at which the maximum of shear stress occurs during start-up of steady shear
- t_1 = Terminal relaxation time
- x = Displacement
- $x_1 = Direction of the flow$
- x_2 = Direction of the velocity gradient
- x_3 = Direction perpendicular to plane (O, x_1 , x_2)
- $\Delta n = Birefringence$
- Δn_{ij} = Component of the birefringence tensor
- Ψ_1 = First normal stress coefficient
- Ψ_2 = Second normal stress coefficient
- Ψ_3 = Third normal stress coefficient
- Ψ_{3m} = Maximum of third normal stress coefficient during start-up of steady shear

 $\Psi_{3\alpha}$ = Steady value of the third normal stress coefficient

 α = Exponential rate constant

 $\beta = N_2/N_1$

- γ = Shear strain
- $\dot{\gamma}$ = Shear rate
- $\delta =:$ Mechanical loss angle
- ϵ = Hencky strain
- $\eta = \text{Viscosity}$

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- η_{\bullet} = Exponential stress coefficient
- $\eta_{\rm P}$ = Material function defined by Dealy et Doshi
- $\eta(\dot{\gamma}) =$ Steady viscosity
- $\eta^*(\omega) =$ Complex viscosity
- λ = Relaxation time
- λ_d = Disengagement time
- $\lambda_{\bullet} =$ Equilibration time \cdot
- $\lambda_k = k^{th}$ relaxation time

 σ = Shear stress

- σ_{ij} = Component of the stress tensor
- χ = Stress optical angle
- ω = Frequency