

The Dynamic Behavior and Stress Relaxation of Polymer Melts

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Polymer melts exhibit a decrease in apparent viscosity as a function of decreasing time scale of shearing. In order to obtain an understanding of the mechanisms giving rise to this non-Newtonian behavior studies have been made of the dynamic linear viscoelastic response, the limit of linear viscoelastic behavior and the stress relaxation in polymer melts after steady state shearing. The results of these experiments are analyzed with respect to shear induced changes in the relaxation spectrum and the effect of these changes on the apparent viscosity.

INTRODUCTION

Understanding of the viscoelastic behavior of polymer melts is essential to the development of improved methods and procedures for processing. Determination of the relationship between melt flow behavior and molecular structure produces the insight and understanding requisite to the development of improved polymers. The research described herein is directed to furthering this understanding.

When a shear stress, τ , is applied to a liquid, flow, or continued deformation with time, takes place at a rate which may be defined by a shear rate, $\dot{\gamma}$. Figure 1 illustrates the simplest possible flow, Newtonian, as continuous deformation at a shear rate which is directly proportional to shear stress. In this ideal flow the rate of relative motion of molecules or molecular segments is directly proportional to the applied shear stress and the flow behavior may be defined by a single coefficient of viscosity, η . For a polymer melt the application of shear stress results in flow at a shear rate which is not directly proportional to stress, resulting in a non-linear relationship, Non-Newtonian. The application of incremental increases in applied stress produces incremental increases in the strain rate that are larger than in Newtonian response. In this form of Non-Newtonian flow the rate of relative motion of molecules or molecular segments increases at an increasing rate as the stress is increased. The flow takes place more easily than in Newtonian response at higher stresses, and it must be concluded that the stress or the flow processes

resulting from the stress changes the internal structural response mechanisms in such a manner that flow can take place more easily than in the Newtonian case.

Non-Newtonian flow behaviors are often described by an apparent viscosity where:

$$\eta_{app} = f(\tau, \dot{\gamma})$$

A typical plot of apparent viscosity as a function of

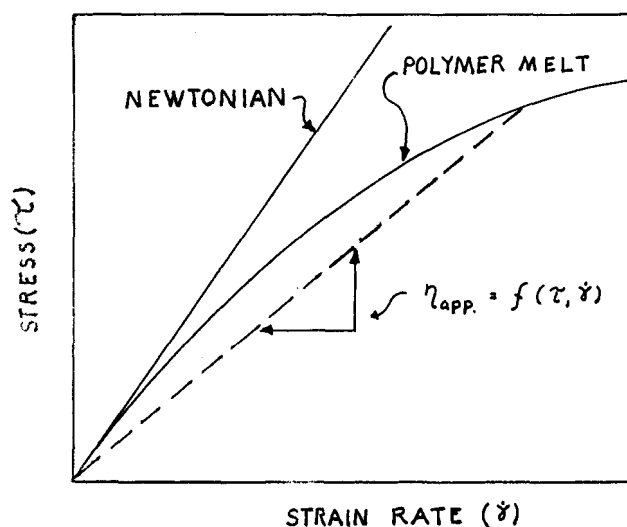


Figure 1. Definitions of Newtonian and Non-Newtonian viscosity.

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shear rate, $\dot{\gamma}$, is shown in Figure 2. At low shear rates a region of shear rate independent (Newtonian) viscosity is often found. At shear rates above the limit the decreasing slope of the stress vs strain rate curve produces a decreasing apparent viscosity. In practical fabrication operations this decrease in apparent viscosity results in reduced energy requirements for the flow of polymer melts compared to that which would be required if these materials behaved in a Newtonian manner. On the other hand the Non-Newtonian behavior of polymer melts make difficult the calculation and prediction of flow behavior in complicated flow regimes. Because both the energy requirement reduction and the ability to predict flow behavior have importance to the fabrication and processing of polymers, the subject of Non-Newtonian flow has been the center of extensive research.

Viscoelastic behavior may be broadly classified into two general categories, linear viscoelastic response, and non-linear viscoelastic response. It should be borne in mind that both linear and non-linear viscoelastic response can give rise to Non-Newtonian flow. For the purposes of this discussion, linear viscoelastic response may be defined as a response in which the relationship of stress to strain or stress to strain rate may be described by a single constant provided the time scale of application or observation of the stress or strain is held constant. That is for a linear viscoelastic material, constants, somewhat similar to a Hookean modulus or a Newtonian viscosity in that they are single valued, will describe the behavior of the material for any given specific time scale of loading or observation provided the time scale of loading or observation is held constant even though the linear viscoelastic material is itself a time rate dependent rheological body. Materials that do not exhibit this single constant effect are defined as being non-linear viscoelastic.

When a polymer in the solid or glassy state is subjected to a mechanical stress the internal structure responds by molecular motions or molecular segment motions that have been found to be linear viscoelastic in nature (1). For example the in-phase elastic modulus, E' , is independent of stress or strain magnitude up to some limiting value, if the time scale of loading, for example frequency, is held constant. If the time scale of loading is decreased the response is still linear viscoelastic but the in-phase modulus increases and visa versa. That is, an increase in the resistance to deformation is observed with shorter time scales of loading or higher frequency. This increase in resistance in solid polymers to deformation with increasing deformation rate appears, in some aspects, to be contrary to the observed decrease in apparent viscosity in melts with increase in shearing rate. The explanation appears to lie in differences in internal structural response between the solid case and the melt or flow case.

When a solid polymer is deformed the cohesive forces, Van der Waals and dipole forces, restricting internal structural motion, such as chain uncoiling

or molecular segment motion, resist motion in a manner related to the time scale of action of the applied deformation. The longer the time scale of application of deformation the greater the relaxation of internal cohesive forces. Accordingly the longer the time of application of deformation the greater the amount of relaxation. Therefore the linear viscoelastic response of a solid polymer at any given specific temperature may be described in its time dependence by a spectrum of relaxation times. On the other hand a fluid or polymer melt when subjected to a shearing stress may exhibit increasing elastic response with increasing shear rate (3) but the flow process itself will change the internal structure and its cohesive mechanisms in such a manner that flow can take place more easily. This flow induced change in structure precludes the description of the viscoelastic response by a single specific relaxation spectrum and indicates that a spectrum of relaxation spectra is required to understand the flow process.

EXPERIMENTAL

In order to study this flow induced change in linear viscoelastic response the polymer melt must be studied in a shear field where the time scale of loading and the steady state shearing rate are controlled in a homogeneous stress and strain field. The orthogonal rheometer (2) provides such a shear field in which both the forces in the direction of flow and in the direction of displacement may be measured. Detailed descriptions and analysis of the orthogonal rheometer have appeared elsewhere (3, 4, 5, 6). For the purposes of the current work it is sufficient to say that this instrument measures the stress in the direction of flow, in-phase stress, τ_x , the stress in the plane of shear at 90° to the in-phase stress, out of phase stress, τ_y , in a shear field in which the polymer melt is sheared through a circular closed path at

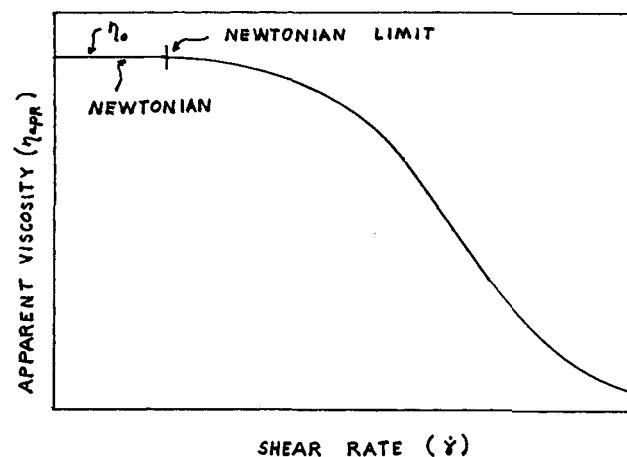


Figure 2. Apparent viscosity as a function of shear rate.

controlled rotational frequencies, ω . The following equations give the needed relationships.

$$\psi = \frac{a}{t}$$

$$\gamma = 2\pi\psi$$

$$\dot{\gamma} = 2\pi\psi\omega$$

$$G' = \tau_y/\psi$$

$$G'' = \tau_x/\psi$$

$$\eta' = \tau_x/\dot{\gamma}$$

where a = the radius of the circular path of shear, t = the thickness of the melt specimen, ψ = the non-dimensional deformation or strain if we consider the specimen as a solid, γ = magnitude of the non-dimensional deformation per cycle if we consider the specimen to be a flowing liquid, $\dot{\gamma}$ = the rate of non-dimensional deformation if we consider the specimen to be a flowing liquid, G' = the in-phase modulus, G'' = the loss or out-of-phase modulus, η' = the in-phase viscosity.

Table I presents the molecular characteristics of the two samples of branched polyethylene (I, II) used in studies in this research. In addition a third branched polyethylene, III, was used to confirm one specific result. All tests were performed at 140°C.

In the orthogonal rheometer it is possible to control the time scale of loading by controlling the frequency, ω , while varying the strain magnitude, γ , or shearing rate $\dot{\gamma}$ by varying the radius, a , of the circular path of shear. This permits the determination of whether or not the polymer melt exhibits linear viscoelastic response. Figure 3 displays the results obtained on polymer I when tested at a constant frequency, $\omega = 0.0715$ cycles per second. The points were obtained by applying increment increases of strain, γ , of approximately 0.01 and measuring the resulting in-phase stress, τ_x . Over the first

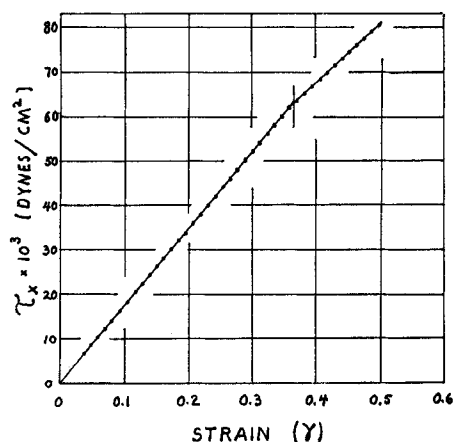


Figure 3. Linear viscoelastic response of polyethylene I at 140°C, frequency equals 0.0715 cycles per second.

Material	I	II
Weight Average Molecular Weight	800,000	550,000
Number Average Molecular Weight	55,000	31,400
Methyl Groups per 100 carbons	2.1	2.0
Density	0.919	0.922
Melting Point	112°C	112°C

29 increments of strain the points fall on a straight line. We may therefore conclude that this polymer melt exhibits true linear viscoelastic response to a strain magnitude limit of approximately 0.37. Above the limit another range of linear response is observed thereby facilitating the precise location of the break in the curve at the limit of linear viscoelastic response.

Confirmation of this linear viscoelastic response is shown for polymer III in Figure 4. Again we see the region of linear viscoelastic response up to the limit, again followed by another linear region of lower slope, and in this case a second break in the curve to another linear region of still lower slope. It should be noted that these plots, Figures 3 and 4, are related to the definitions of viscosity, Figure 1, simply by multiplying the strain, γ , by 2π times the constant frequency to obtain the strain rate $\dot{\gamma}$. In other words the viscoelastic melt, below the limit of linear viscoelastic response, exhibits a stress vs. strain rate relationship that can be described by a single constant thereby permitting the measurement of single valued frequency dependent viscosities, $\eta(\omega)$. The result is that by holding the time scale of loading constant ($\omega = \text{constant}$) a linear relationship between stress, τ , and strain rate, $\dot{\gamma}$, is obtained for a linear viscoelastic material similar to

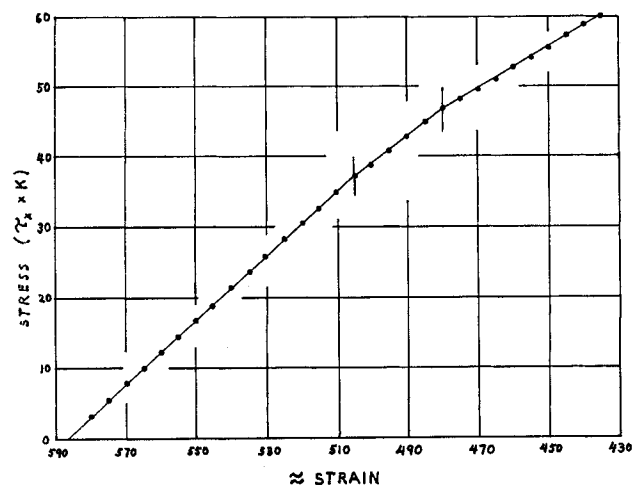


Figure 4. Linear viscoelastic response of polyethylene III.

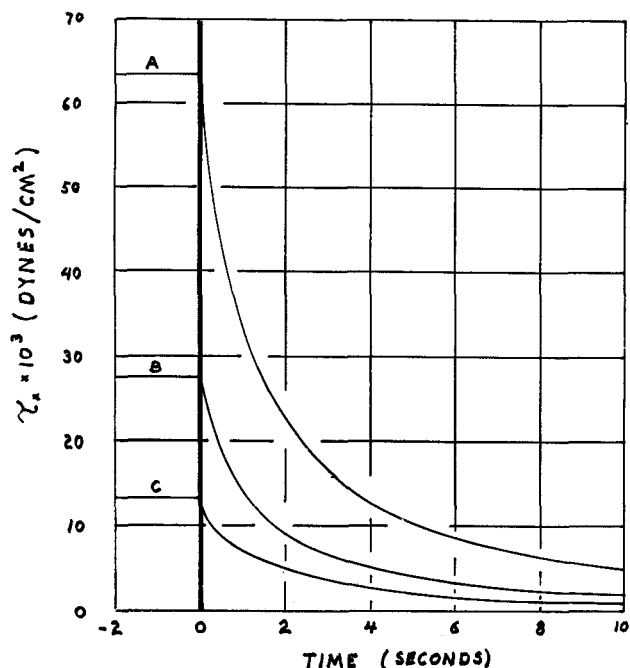


Figure 5. Stress relaxation curves of polyethylene I after shearing at 0.0715 cycles per second and three levels of strain magnitude.

the linear relationship found for a time independent Newtonian response.

Many other polymer melts of a wide variety of chemical species and molecular weights have also been investigated in this manner. All have exhibited linear viscoelastic response, some to much higher magnitudes of strain. As the frequency, ω , is increased the slope of the stress, τ , vs strain rate, $\dot{\gamma}$, plot decreases thereby producing a decreasing frequency dependent viscosity, $\eta(\omega)$, as frequency is increased (6) which in form is very similar to the decreasing shear rate dependent apparent viscosity, $\eta_{app}(\dot{\gamma})$, of Figure 2.

One way of studying this shear induced decrease in viscosity is by investigation of the relaxation behavior of melts after steady state shearing. The procedure simply involves the instantaneous stopping of the shearing process and the measurement of the stresses as they relax with time. Figure 5 displays the results of three such tests on polyethylene I at 140°C. Time zero is the time at which the steady state shearing is stopped. Prior to time zero the melt is continuously subjected to shear at, in this case, a frequency of 0.0715 cycles per second for curves A, B, C. The constant valued in-phase viscous force, τ_x , corresponding to the in-phase frequency dependent viscosity, $\eta(\omega)$, is shown prior to time zero. At time zero the shearing is instantaneously stopped and the in-phase viscous force, τ_x , decays with time. It should be noted that in this case each relaxation curve was obtained after previous shearing at the same frequency ($\omega = 0.0715$) but

that the strain magnitude, γ , in the linear viscoelastic range was selected so that the relaxation took place from various stresses, $A = 63,000$ dynes/cm², $B = 27,500$, $C = 13,000$. The rate of relaxation appears to be much more rapid at the higher initial stresses, τ_x .

It is common practice in the studying of stress relaxation to plot the stress, τ , vs time on a logarithmic scale in order to make the short time responses more apparent. Figure 6 presents the relaxation data of Figure 5 as a semi-logarithmic plot. Two points should be noted: 1) Because in this type of stress relaxation test a steady state shearing prior to stress relaxation produces a steady state stress prior to time zero, the measurement of the stress values at short times of relaxation is facilitated. There is no difficulty with a high speed recorder in determining the relaxing stress after such short times as 0.01 seconds. 2) The more rapid rate of decay of absolute value stress previously mentioned for relaxation from higher values of strain, γ , is again observed. We may conclude that the stress relaxation is dependent on the shearing experience prior to stress relaxation for flowing polymer melts.

The important question now becomes what are the parameters of flow which determine the stress relaxation behavior? The determining parameters may include stress, τ , strain, γ , strain rate, $\dot{\gamma}$, or frequency, ω . In order to establish whether or not the shear stress, τ , prior to stress relaxation is the determining factor a series of stress relaxations from a stress, τ_x , of approximately 22,000 dynes/cm² but at various frequencies and therefore various strains, γ , and strain rates, $\dot{\gamma}$, were conducted on polyethylene II. The results are shown in Figure 7. The in-phase viscous stress has been normalized to the stress at time zero to eliminate small differences in the steady state shear stress. Curve D was from a frequency of $\omega = 0.0103$, E from $\omega = 0.027$, F from $\omega = 0.0735$ and G from $\omega = 0.20$. It is apparent that although the steady state shear stresses prior to

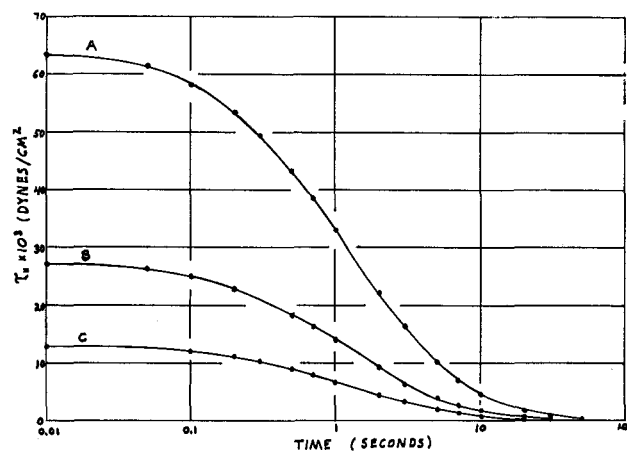


Figure 6. Data of Figure 5 replotted vs log time.

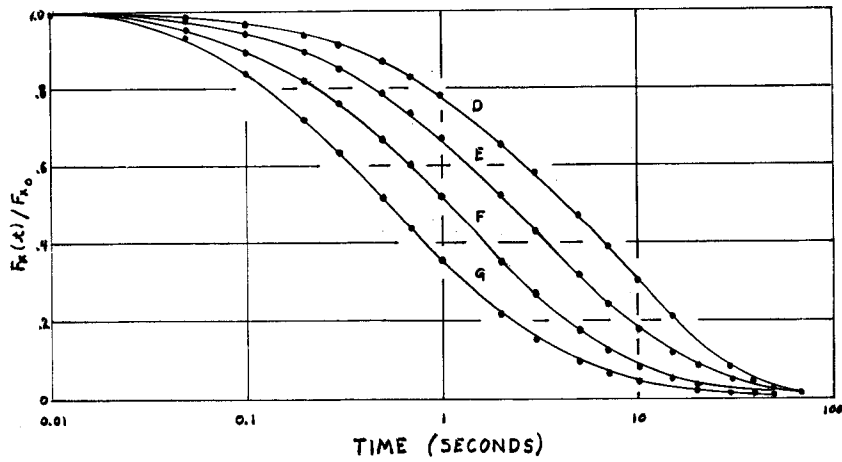


Figure 7. Stress relaxation of viscous force of polyethylene II from steady state shear stress of 22,000 dynes/cm². Frequency of D = 0.0103, E = 0.027, F = 0.0735, G = 0.20.

stress relaxation were all approximately the same, the relaxation behavior is not explicitly a function of previous shearing stress. Apparently the relaxation behavior is a function of the previous shear magnitude, γ , or the previous shear rate, $\dot{\gamma}$, or the previous shearing frequency, ω .

It has been previously shown (6) that the melt viscosity as determined in the orthogonal rheometer is not explicitly a function of shear rate but rather is directly a function of frequency. For this reason it seems reasonable to consider the frequency dependence of the stress relaxation characteristics after steady state shearing. Figure 8 shows the in-phase modulus of polyethylene I expressed as reduced time dependent modulus, $G'(t)/G'_0$, at four different frequencies. We see that as the frequency of the steady state shearing prior to relaxation is increased the

relaxation takes place more rapidly.

Curves J and K display double sets of data. For each curve both sets of data were taken at the same frequency but at different magnitudes of stress, τ , (and therefore strain, γ) prior to relaxation. The absolute magnitudes of the stresses prior to relaxation differed by a factor of approximately 2.5. The important point is that if the frequency is held constant the relaxation response is independent of the stress and therefore independent of the strain, γ , and strain rate, $\dot{\gamma}$, but is explicitly dependent only on the frequency in the linear viscoelastic range.

To confirm the above conclusion the out-of-phase relaxation modulus, $G''(t)$, of polyethylene I was determined after steady state shearing at a frequency of 0.0715 cycles per second at three different magnitudes of stress, τ_x . The results are shown in Figure

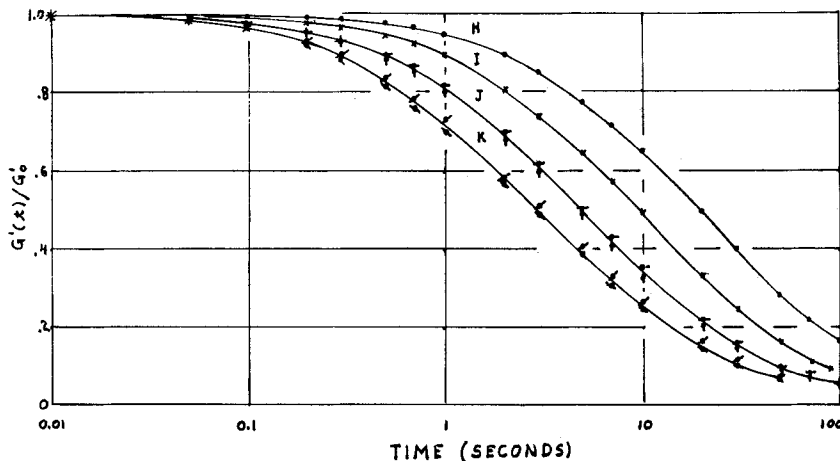


Figure 8. In-phase relaxation modulus of polyethylene I from various stresses. Frequency of H = 0.0108, I = 0.0265, J = 0.0715, K = 0.182.

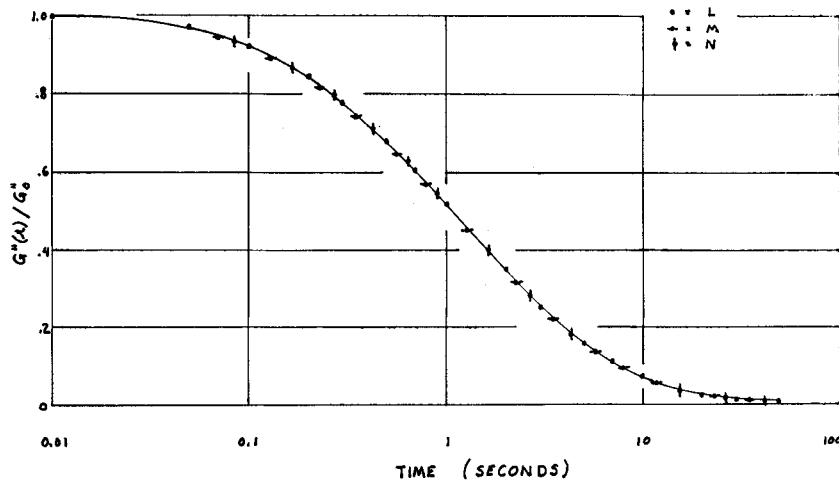


Figure 9. Out-of-phase relaxation modulus of polyethylene I after shearing frequency of 0.0715 and various shearing stresses, $L = 13,300$, $M = 27,300$, $N = 63,400$ dynes/cm².

9 as reduced time dependent out-of-phase relaxation modulus, $G''(t)/G''_0$. The stresses prior to relaxation were: $L = 13,300$, $M = 27,300$ and $N = 63,400$ dynes/cm². Even over this wide a range of stresses we see that at constant frequency prior to relaxation the relaxation behavior is independent of stress, strain and strain rate. We must conclude that the stress relaxation behavior is explicitly a function of the frequency only.

Since frequency has been shown to be the factor that determines the relaxation behavior, it then becomes possible to compare the relaxation of the in-phase response and the relaxation of the out-of-phase response by determining each at the same frequency. Such a comparison is made in Figure 10 in which both relaxation curves were determined after shearing at $\omega = 0.0715$. We see a distinct difference in the two relaxations. The out-of-phase modulus is

determined from the force in the direction of shearing, this means that the force in the direction of flow (viscous force) relaxes more rapidly than, τ_y , the elastic force.

The observed dependence of the relaxation behavior on the frequency of previous shearing raises the question, does the previous frequency of shearing change the shape of relaxation spectrum or simply shift the relaxation spectrum along the time scale? Since the relaxation spectrum is directly related to the negative slope of the time dependent stress, τ , vs log time curve this question can be resolved by shifting the relaxation curves along the time axis to see if they superimpose. Figure 11 is the result of shifting the relaxation curves of Figure 8 horizontally to superimpose on curve K. A very good fit is found indicating that an increase in frequency of prior shearing simply moves the relaxation spec-

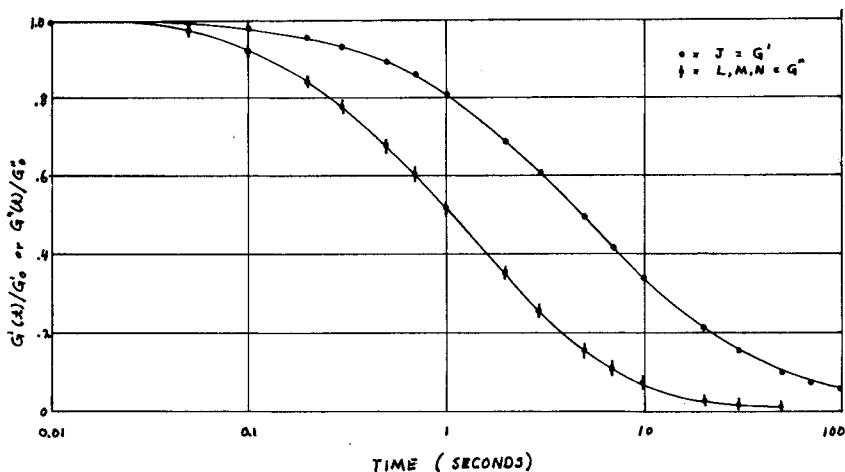


Figure 10. Comparison of in-phase, J , and out-of-phase, L, M, N , relaxation moduli.

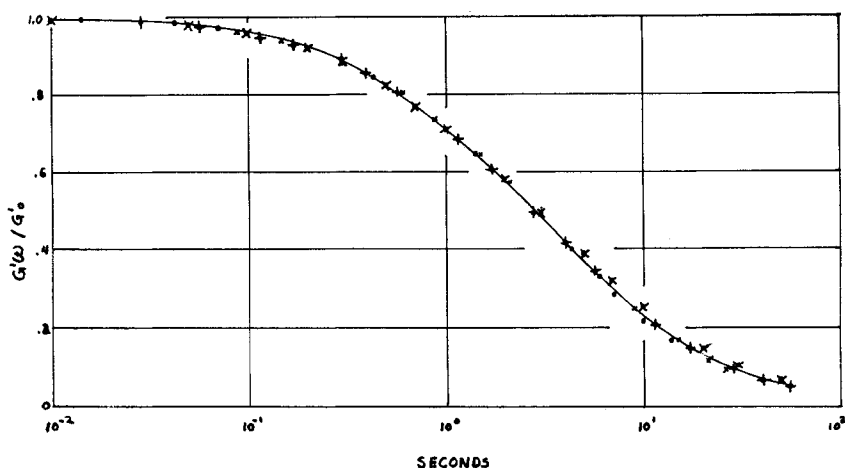


Figure 11. Data of Figure 8 shifted on log time axis to superimpose.

trum to shorter times in the linear viscoelastic range studied.

DISCUSSION

The frequency of application of a mechanical stress or strain interacts with the relaxation mechanisms of the material to produce a time dependent (i.e., viscoelastic) response. The results reported above indicate that the frequency of applied loading *itself* changes the relaxation mechanisms of the polymer melt in such a manner that stress may relax more rapidly if the polymer has been subjected to a high frequency mechanical loading thus giving rise to a reduced viscosity with frequency.

In the conventional picture of polymer melt flow the reduction of viscosity with shear rate is attributed to the orientation and molecular disentangling processes associated with the large strains involved in the flow process. The surprising aspect of the results presented here is that frequency can change the relaxation mechanisms regardless of how small a strain is applied since the response is linear viscoelastic and therefore frequency can control viscosity by controlling the relaxation mechanisms without the large strains associated with orientation and disentanglement.

CONCLUSIONS

1. Polymer melts exhibit linear viscoelastic response.
2. In the orthogonal rheometer the stress relaxation

of polymer melts after steady state shearing is a function of only the previous frequency of shearing and not dependent on the shear stress, the shear strain or the shear rate in the linear viscoelastic range.

3. The out-of-phase modulus, $G''(t)$, relaxes more rapidly than the in-phase modulus, $G'(t)$.
4. The frequency of shearing prior to relaxation shifts the relaxation spectrum to shorter times with increased frequency but does not change its shape.
5. By shifting the relaxation spectrum an increase of frequency of shearing can reduce melt viscosity regardless of how small the magnitude of shear in the linear viscoelastic range.

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