

Determination of the Elastic Component for Polymeric Melt under Steady Shear Flow

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SYNOPSIS

Steady state shear flow in rectilinear coordinates can be generated by a direct shear rheometer. The rheological behavior of polymeric melts under shear flow can be characterized by the inception of steady shear flow and stress relaxation after cessation of steady shear flow. Experiments were performed for bisphenol A polycarbonate with various mol wts. The elastic components, such as the primary normal stress differences and the elastic recoverable shear strain of the polymeric melts, can be determined from the shear moduli.

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INTRODUCTION

Characterization of the rheological behavior of polymer melt under steady shear is necessary in order to understand how the melt behaves during processing and fabrication. In this study, the steady shear rheology of bisphenol A polycarbonate (PC), with melt flow rates of 3, 10, and 80, are characterized, using a direct shear rheometer (DSR). This rheometer is based on simple shear flow geometry and the local stress for a given shear deformation is monitored by a shear stress transducer, developed by Dealy of McGill University, Canada.¹⁻⁴ The experimental procedure involved a steady shear flow type in which the stress growth and relaxation were also monitored. From both the stress growth and stress relaxation, the shear modulus and the primary normal stress differences can be determined and used to calculate the elastic recoverable shear strains.

STRESS GROWTH UPON INCEPTION OF STEADY SHEAR FLOW

A polymer melt sample between two parallel plates is at rest. At a certain time, $t = 0$, one plate is moved

at a constant speed, v_0 . If the shear stress is monitored as a function of time, then for a Newtonian fluid, the shear stress increases instantaneously to a finite constant value. For a Hookian solid, the shear stress will grow monotonically with increasing time. Polymer melts, however, exhibit an intermediate response. The shear stress will grow as a function of time, during shear, until it reaches a constant level. This plateau in shear stress is the steady state level for a given shear rate. The behavior of stress, developing during the start-up of the steady shear flow, is a characteristic property of the polymer melt at that shear rate. This is known as the stress growth upon inception of steady shear flow.

Upon inception of steady shear flow, the macromolecules are stretched elastically. The response of the polymer melt is thus analogous to the solid state response and the initial slope of the shear stress vs. the shear strain curve is the shear modulus, G :

$$G = \lim_{t \rightarrow 0} \left(\frac{d\tau_{12}}{\dot{\gamma}_{12} dt} \right) \quad (1)$$

where τ_{12} is the shear stress and $\dot{\gamma}_{12}$ is the strain rate.

Furthermore, the stress growth can be characterized by the following material function:^{5,6}

$$\tau_{12} = -\eta + \dot{\gamma}_{12} \quad (2)$$

$$N_1 = \sigma_{11} - \sigma_{22} = -\psi_1 \dot{\gamma}_{12}^2 \quad (3)$$

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where N_1 is the primary normal stress difference. The subscripts and superscripts used here conform with conventional notation as described by Bird et al.⁵

STRESS RELAXATION AFTER CESSATION OF STEADY SHEAR FLOW

After steady shear flow has been attained, the shearing motion is stopped and stress relaxation is monitored as a function of time. For linear viscoelastic behavior, the stress at any time, t , can be predicted by:

$$\tau_{12}(t) = -\dot{\gamma}_{12} \int_{-\infty}^t G(t-t') dt' \quad (4)$$

where $G(t-t')$ is the relaxation modulus function.

If the relaxation modulus function is known for a given polymer system, then, eq. (4) can be integrated to predict the relaxation process. Various models have been proposed to describe the relaxation behavior of polymers, such as the simple Maxwell model. This model consists of a Hookian elastic spring with spring constant, G , and a viscous dashpot with arbitrary viscosity, η . The relaxation shear stress, τ_{12} , is then:

$$\tau_{12}(t) = G\lambda\dot{\gamma}_{12}e^{-t/\lambda} \quad (5)$$

where $\lambda = \eta/G$, is known as the relaxation time constant.

However, most polymer relaxation behavior cannot be described adequately with a single Maxwell element model. The behavior can be better described with n Maxwell elements placed in parallel, the generalized Maxwell model. The relaxation stress is then:

$$\tau_{12}(t) = \sum_{i=1}^n G_i \lambda_i \dot{\gamma}_{12} e^{-t/\lambda_i} \quad (6)$$

For polymer melts, three to four elements are usually sufficient to describe the relaxation process.⁶

For polymers with broad mol wt distributions, the relaxation time distribution is correspondingly broad and, in a limited time domain, the relaxation modulus can be approximated by a power-law function⁷:

$$G(t) = G(t_0) \left(\frac{t}{t_0} \right)^{-m} \quad (7)$$

where $G(t_0)$ is the relaxation modulus at time t_0 and m is the power-law index and is less than unity.

Most models, however, exhibit the same form of the function describing the relaxation modulus, $G(t)$:

$$G(t) = G_0 \sum_{i=1}^n x_i e^{-t/\lambda_i} \quad (8)$$

where G_0 is the relaxation modulus at time $t = 0$ and $\sum_{i=1}^n x_i = 1$.

In this study, eq. (8) is used to obtain the relaxation spectrum and the shear modulus at relaxation time $t = 0$.

THE PRIMARY NORMAL STRESS DIFFERENCES

The total stress tensor is characterized by three stress components in the simple shear deformation history:

1. Shear stress, $\tau_{12} = \tau_{21}$,
2. The primary normal stress differences, $N_1 = \sigma_{11} - \sigma_{22}$, and
3. The secondary normal stress differences, $N_2 = \sigma_{22} - \sigma_{33}$.

For relaxation after cessation of steady shear flow, $\dot{\gamma}_0$, if the fluid is a simple fluid, the primary normal stress differences can then be estimated by^{8,9}:

$$N_1 = -2\dot{\gamma}_0 \int_0^{\infty} \tau_{12}(t) dt \quad (9)$$

The elastic recoverable shear strain, γ_r , can then be estimated from the shear modulus, G , and the primary normal stress differences, N_1 , according to eq.¹⁰:

$$N_1 = 2G\gamma_r^2 \quad (10)$$

EXPERIMENTAL

A predried injection-molded cylindrical disk specimen, with a radius of 3.81 cm and a thickness of 0.125 cm, was placed in a nitrogen-purged oven. The sample was preheated to 200°C for about 5 to 10 min to minimize the moisture content in the specimen. When the sample softened, it was then placed

Table I Materials and Testing Conditions

	MFR = 3		MFR = 10		MFR = 80
Temperature (°C)	250	280	250	280	250
Shear Rate (sec ⁻¹)					
Minimum	1	5	5	20	20
Maximum	200	500	300	500	500
Strain Level					
Minimum	2	5	5	10	10
Maximum	10	10	20	10	10

between the parallel plates of the direct shear rheometer and was slowly compressed to 0.5 mm. The sample was then heated up to the desired testing temperatures of 250 and 280°C. When the temperature equilibrated, testing was done on the sample using the steady shear flow test mode. The shear stress, obtained from the shear transducer and the crosshead travel distance, was measured as a function of time. After reaching steady state flow, the flow was stopped and the stress relaxation was monitored as a function of time. Each sample was tested for various shear rates at given temperatures.

Materials used in this study were polycarbonate, manufactured by the Dow Chemical Company, with 3 different weight average mol wts: 39,000 (3 MFR), 28,000 (10 MFR), and 17,000 (80 MFR). Testing conditions for these specimens are shown in Table I. The mol wts were determined using GPC and polycarbonate standards.

THE DIRECT SHEAR RHEOMETER (DSR)

The direct shear rheometer used an MTS load frame and the local shear stress was measured directly by a shear stress transducer. The rheometer was based on simple shear flow geometry. For polymer melt studies, the DSR had a limiting temperature of 300°C. No low temperature limits were published, however, the limit was probably relative to the lower temperature capability of the transducer capacitance, the cable connecting the shear transducer to the amplifier outside of the environment chamber, and the brittle temperature of the material of the transducer.

Regarding the displacement, the travel distance was limited to the amount of sample (in this case, 11.3 cm) that was used, or the length of the plates. Even though the shear stress transducer can be made to handle high shear stress, the limitation on the load frame must also be considered. If the force required to move the plate is larger than, or equal to,

the capability of the stroke actuator, then the motion of the piston to a given applied stroke function is not correct or, in some cases, pump cavitation may occur. In these experiments, the maximum load exerted to the frame was 32 MPa (5000 psi).

The deformation rate, that is, plate velocity, was controlled by the MTS load frame function generator. Limitations of generating shear history are thus limited to the MTS capability (12.7 cm stroke) and the dimension of the DSR plates. For steady shear flow experiments, using the 0.5 mm plate spacing, the maximum shear rate was found to be 300 sec⁻¹ for polycarbonate tested at 250 and 280°C. Above this shear rate, the steady state condition was not achieved before reaching the limit of the applied strains. This was due to the amount of material filling between the gap (11.3 cm).

Reproducibility of the DSR was found to be within 10% after performing 5 runs using the same material and conditions. However, the reproducibility can only be achieved when the plates are cleaned thoroughly after each sample change.

RESULTS

A polymer sample was tested under steady shear flow and the shear stress was monitored as a function of time. From one experimental run, three distinct portions can be identified. At initial start up, the shear stress growth was measured, assuming that inertia effects were negligible. At long times of shearing, the shear stress approached a constant level and steady state was achieved. When the applied shear rate was small, the shear stress grew monotonically to a constant steady state value. However, for large applied shear rate, the shear stress grew quickly and overshoot the constant steady state value. After the overshoot, the shear stress decayed as a function of time to the steady state value. Steady shear flow was achieved only when the shear stress became constant (with the stipulation that

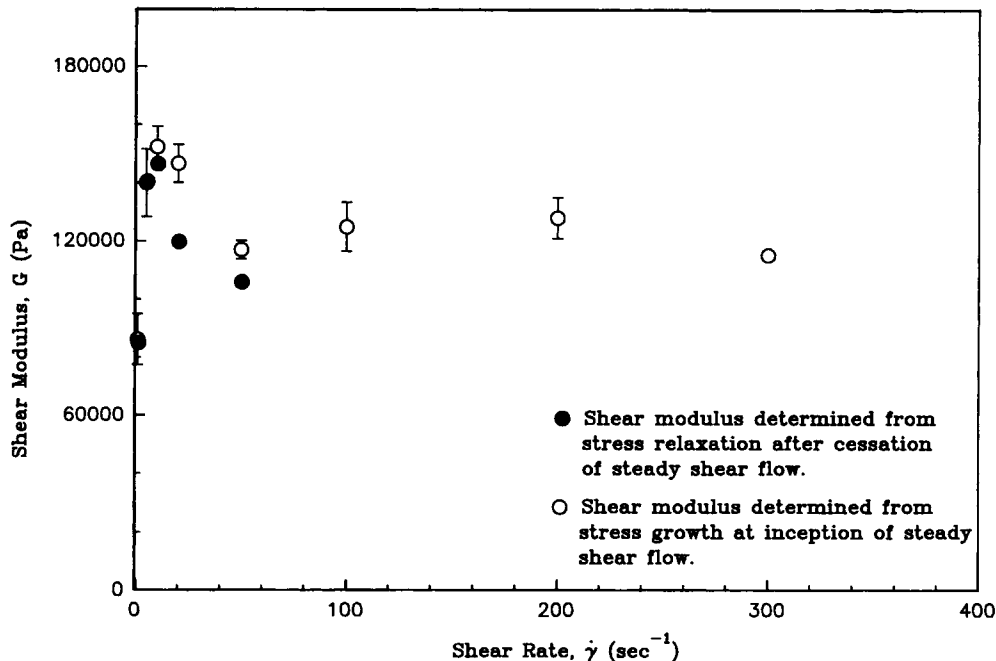


Figure 1 Shear modulus as a function of applied shear rate for polycarbonate MFR = 3 at 250°C.

there was no chemical reaction occurring during shear, such as degradation of the polymer). When the steady state condition had been achieved, the shearing action was stopped and the stress relaxation after cessation of steady shear flow was observed. From the stress growth and stress relaxation portion, rheological parameters can be estimated.

The shear modulus, G , of the melt is determined using two methods. In the first method, G is estimated from the initial slope of the shear stress–shear strain curve, generated from the short time during the stress growth portion of the experiment. This is in accordance with eq. (1). In the second method, G is estimated by fitting the stress relaxation curve by a 3 to 4 element generalized Maxwell model and the sum of all the individual shear moduli is the shear modulus of the melt, in accordance with eq. (6). The shear moduli, G , for polycarbonate 3 MFR, 10 MFR, and 80 MFR, at 250 and 280°C, as a function of shear rates, are plotted in Figures 1–5. As illustrated, the shear moduli determined from both methods agreed.

The shear modulus increased with increasing rate of shear deformation and approached a constant value at high shear rates. This is expected, since at low shear rates relaxation times can be smaller than the characteristic experimentation time and thus yield a smaller value of shear modulus. As the applied shear rate is increased, at a value where the characteristic experimentation time is equivalent to

the characteristic relaxation time of the polymer, the shear modulus will then plateau to a constant value. However, as illustrated in Figures 1–5, the shear moduli at high shear rates for all specimens tested were not constant, due to mol wt degradation at high temperature, and were accelerated, in part, by impurities introduced from the plate-cleaning procedure. This prevented multiple runs with the same specimen. The polycarbonate samples were analyzed for mol wts as shown in Table II, and were found to decrease dramatically after significant time at 280°C.

The primary normal stress difference, N_1 , was estimated from the area under the stress relaxation curve according to eq. (9) and the elastic recoverable shear strain, γ_r , was estimated according to eq. (10). Figure 6 shows the primary normal stress differences for various grades of polycarbonate, and temperatures are plotted against the shear rate. The normal stress differences for these polycarbonates were found to be linear on doubly logarithmic scales and were found to vary with the applied shear rates to a power of 1.5. This slope did not agree with the predicted power of 2 for low shear rates from various rheological models.⁴

One of the processibility parameters of a given polymer is its extrudate swell. Extrudate swell has been studied and has been found to be related to the elastic recoverable shear strain.¹¹ Figure 7 shows the elastic recoverable shear strain as a function of ap-

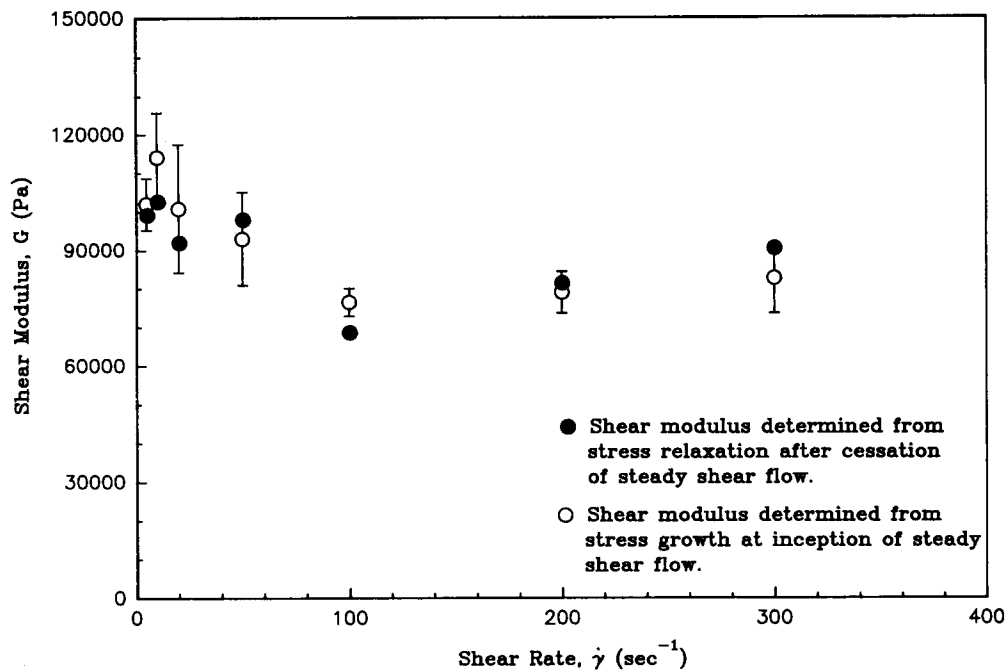


Figure 2 Shear modulus as a function of applied shear rate for polycarbonate MFR = 3 at 280°C.

plied shear rate at various temperatures. As the shear rate increased, the extrudate swell increased, and so did the elastic recoverable shear strain. This trend was observed in this study for the recoverable shear strain. From this result, the elastic recoverable

shear strain, which can be used to represent the elastic energy in the polymer melt under shear deformation, is dependent on mol wt, temperature, and applied shear rate. At a high temperature, the relaxation time is short and therefore the stored energy

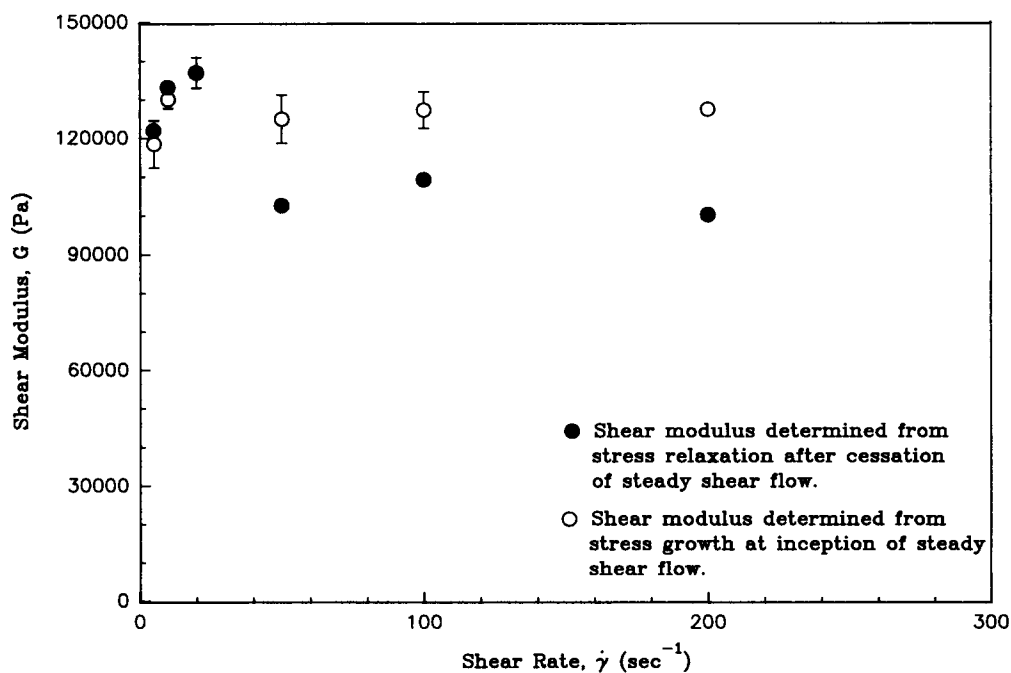


Figure 3 Shear modulus as a function of applied shear rate for polycarbonate MFR = 10 at 250°C.

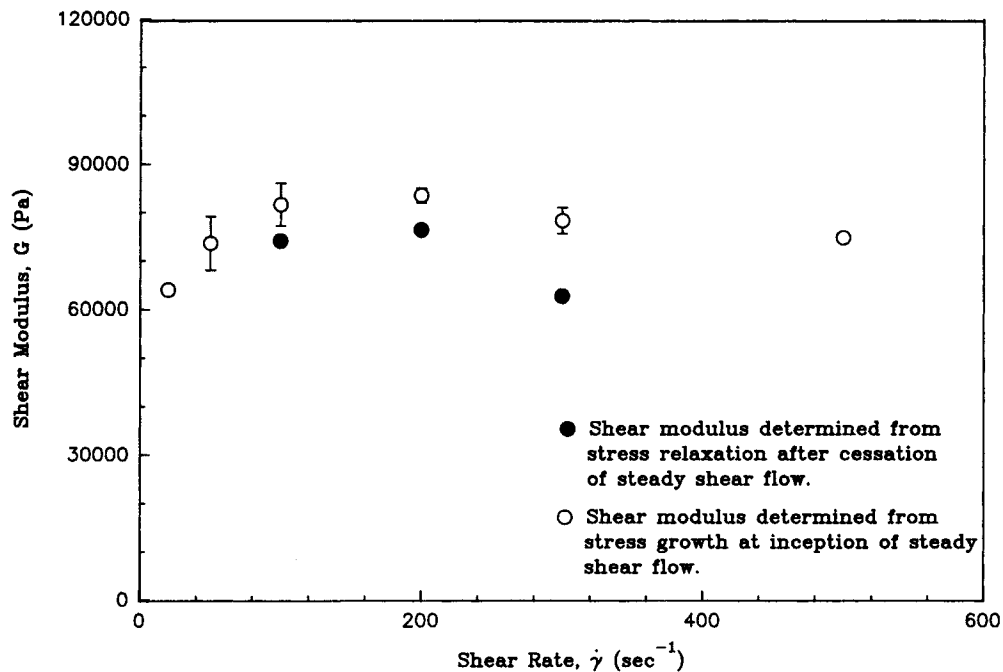


Figure 4 Shear modulus as a function of applied shear rate for polycarbonate MFR = 10 at 280°C.

is less, giving rise to a decrease in elastic recoverable shear strain. Any mol wt degradation will have an adverse effect on this measurement. As mol wt increases, the characteristic relaxation time increases (according to the 3.4 power) and, therefore, the

elastic energy in the system will increase accordingly. Again, this will result in an increase in the elastic recoverable shear strain. The dependence of the elastic recoverable shear strain on the applied shear rate can be explained as analogous to the shear

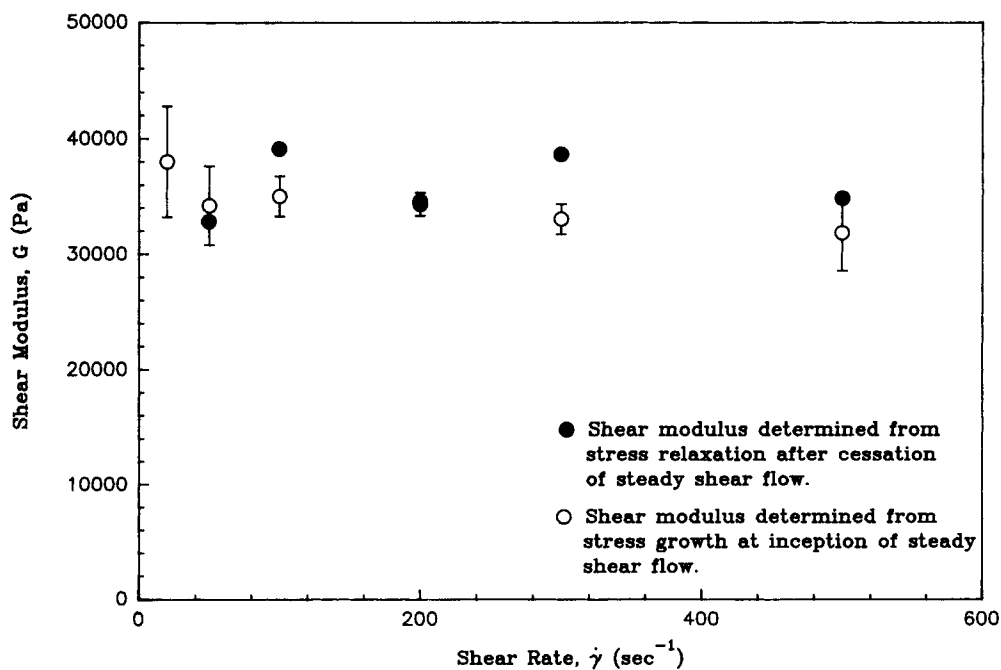


Figure 5 Shear modulus as a function of applied shear rate for polycarbonate MFR = 80 at 250°C.

Table II Molecular Weights of Polycarbonate Before and After DSR Testing

MFR	Before Testing				After Testing			
	M_n	M_w	M_z	PDI	M_n	M_w	M_z	PDI
3	14,500	39,800	64,600	2.75	8700	22,100	39,700	2.55
10	10,500	28,100	45,400	2.68	9400	21,600	34,000	2.31
80	7500	17,300	27,400	2.32	6400	13,700	23,300	2.16

modulus. At a low shear rate, the characteristic experimentation time is longer than the characteristic relaxation time and, hence, the elastic recoverable strain decreases. At high shear rates, the elastic recoverable shear strain should asymptote to a steady value, as shown by Wagner and Laun.¹² In Figure 7, the asymptotic steady elastic recoverable shear strain value can be observed for polycarbonate 3 and 10 MFR tested at 250°C. For high melt flow polycarbonates, this asymptotic value has not been achieved at these testing conditions. The largest recoverable shear strain for polycarbonate, with a mol wt of 39,000 at 250°C, was 2.4. In comparing this number with values for LDPE at 190°C, as reported

by Bagley,¹³ polycarbonate is predicted to have a lower extrudate swell than LDPE.

SUMMARY AND CONCLUSIONS

For proper design of fabrication and processing conditions, a knowledge of the elastic nature of the polymer melt is required. This study utilizes the rectilinear simple shear flow apparatus, which is the direct shear rheometer, to determine these elastic parameters for polycarbonate melts. The elastic parameters considered are the shear modulus, the primary normal stress difference, and the elastic recoverable shear strain. The shear modulus of the

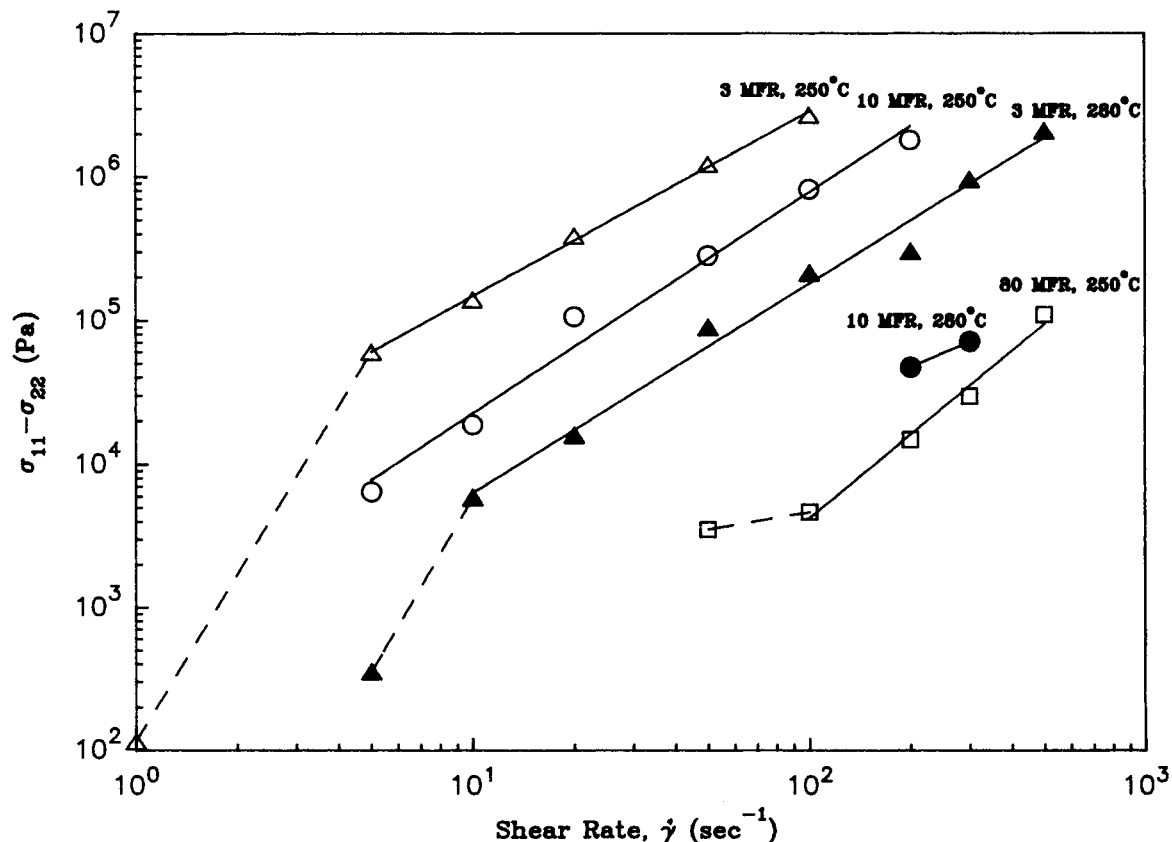


Figure 6 Primary normal stress differences vs. shear rate for polycarbonate.

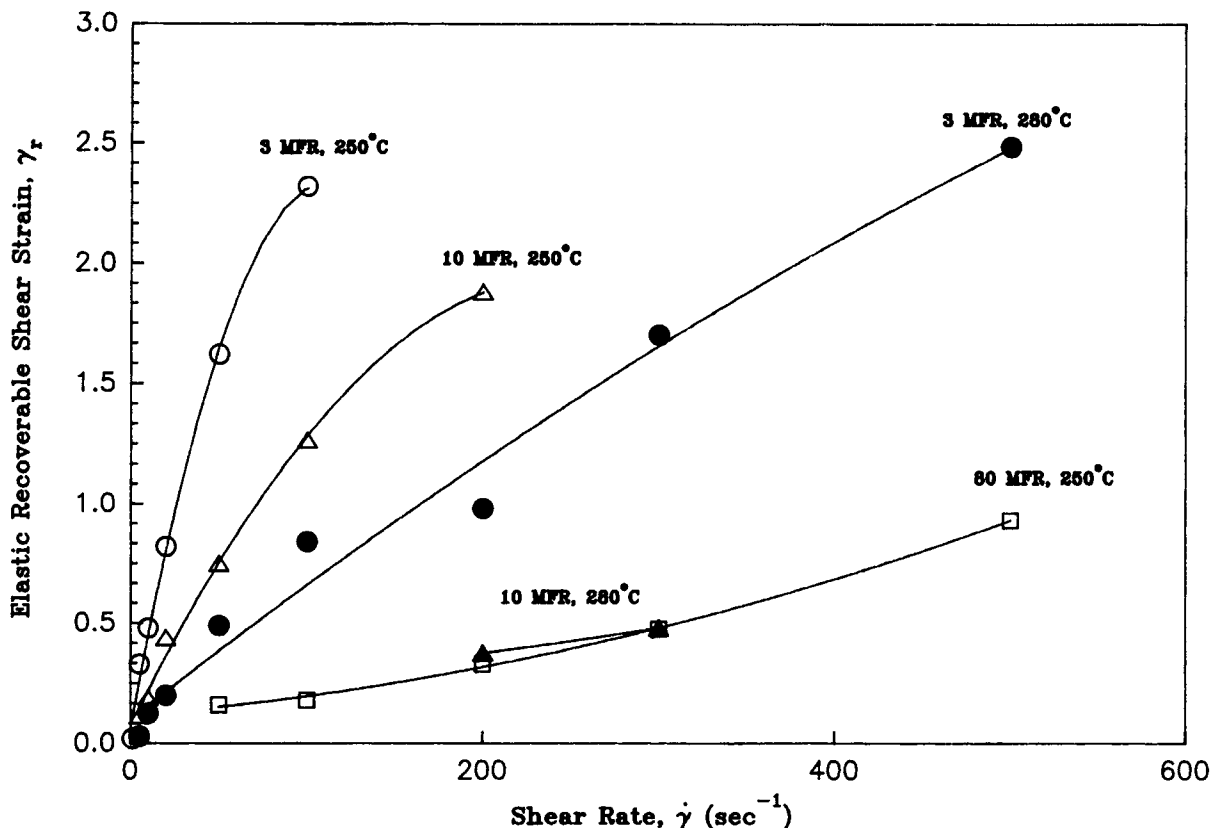


Figure 7 Elastic recoverable shear strain vs. shear rate for polycarbonate.

polycarbonate melt is determined from two methods: the start-up of a steady shear flow and stress relaxation after cessation of a steady shear flow. The shear modulus obtained from both methods agree well with each other. The shear modulus is found to be shear rate dependent at low shear rates and it approaches a constant value at high shear rates. Furthermore, the primary normal stress differences and the elastic recoverable shear strain can also be estimated from such experiments, as illustrated. The primary normal stress difference that was determined was found to increase according to a 1.5 power. This does not agree with the 2 power, as predicted from theory for low shear rates. The elastic recoverable shear strain was the result of these analyses. The elastic recoverable shear strain was found to be dependent on mol wts, temperature, and applied shear rates (low shear). For polycarbonate 3 MFR at 250°C, the elastic recoverable shear strain was estimated to be 2.4.

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