

# Effect of Wall Slip of Polymer Melts on their Relaxation Modulus Behavior

*Dilhan M. Kalyon and Halil Gevgilili*

*Stevens Institute of Technology, Castle Point Station, Hoboken, NJ 07030*

## Abstract

The determination of the relaxation modulus using the step imposition of a strain is an important step in the fitting of the parameters of viscoelastic constitutive equation. In the nonlinear region the true shear strain imposed on a polyethylene melt is found to deviate considerably from the targeted strain due to the presence of wall slip which is documented here. The presence of the wall slip reduces the range of strains for which the strain-dependent relaxation modulus can be determined for the linear polyethylene melt investigated.

## Introduction

Stress relaxation following a step strain, i.e., a sudden shearing displacement is an important but difficult experiment to carry out (1). In this experiment the specimen is held between a cone and a disk or in between two parallel disks under isothermal conditions. A shear strain,  $\gamma$  is introduced at time,  $t = 0$ , by applying a large and presumably constant shear rate for a short duration of time. Upon the sudden imposition of the shear strain,  $\gamma$ , the measurement of the time decay of the shear stress,  $\tau_{12}(t)$ , provides the relaxation modulus  $G(t, \gamma)$ :

$$G(t, \gamma) = \tau_{12}(t)/\gamma \quad (1)$$

In the limit of linear viscoelasticity the linear shear stress relaxation modulus,  $G(t)$ , is independent of the imposed shear strain. The damping function,  $h(\gamma)$  can be obtained as a function of strain,  $\gamma$ , by the vertical shift of the  $G(t, \gamma)$  onto the linear viscoelastic modulus  $G(t)$ :

$$h(\gamma) = G(t, \gamma)/G(t) \quad (2)$$

The accurate determination of the relaxation modulus is an important step in the fitting of the parameters of various non-linear constitutive equations and as we shall show here the collection of the relaxation modulus data is affected by the presence of wall slip.

## Experimental

The step strain experiment was carried-out using the Advanced Rheometric Expansion System (ARES) rheometer with a Force Rebalance Transducer (2K-FRTN1) available from Rheometric Scientific, Inc. of Piscataway, NJ. The test fixtures consisted of stainless steel cones and disks, which were used in the cone-and-plate and parallel disk modes. The rheometer was modified by installing an imaging window into the wall of the environmental chamber. This facilitated the continuous monitoring of the deformation of the specimen at its edge.

A high-speed camera (CR Imager, Model 2000 by Roper Scientific, capable of recording at speeds as high as 2000 frames per second) was also installed to allow the filming of the motion of the moving surface as well as the free surface of the specimen at its edge. During the experiments a straight-line marker line was placed to cover the edges of the fixtures and the free surface of the specimen. This marker line technique was used by Kalyon

and co-workers earlier to document the wall slip behavior of concentrated suspensions in steady torsional and small amplitude oscillatory shear flows and to characterize the wall slip velocity versus the shear stress behavior of such suspensions (2,3). In this technique the initial position of the marker line as well as the configuration it assumes upon the deformation of the sample, are monitored.

## Materials

Representative results will be shown here for one high density polyethylene, which is commercially available from Exxon-Mobil Chemical Company with the designation of HDA 601. The melt index and solid density values of HDA 601 are 0.55 and 0.933 g/cm<sup>3</sup>, respectively.

## Results and Discussion

The typical relaxation modulus versus time and strain behavior of the high density polyethylene melt is shown in Figure 1. These data were collected at 190 °C using cone-and-plate fixtures. Overall, six different targeted strains ranging from 0.5 to 4 were used. Above 0.1 s the apparent relaxation modulus curves are parallel (in a double logarithmic plot) and appear to be amenable to the time-strain separability. At relatively low strains the relaxation modulus is independent of the strain imposed and the relaxation modulus vs. time behavior in this linear viscoelastic region could be predicted accurately with the relaxation spectra obtained from the fitting of the dynamic data. For all of the polymers investigated the relaxation modulus vs. time curves obtained at various strains were parallel suggesting the separability of the memory function to a time-dependent linear viscoelastic memory function and a strain dependent damping function (Equations 1 and 2). Similar data are conventionally used to determine the parameters of various nonlinear constitutive equations for various polymer melts (4-6). However, are such relaxation data accurate?

To check the accuracy of the strain, first the time-dependence of the angular displacement of the cone during the imposition of the step strain was determined using high speed cinematography. From the angular displacement the tangential velocity of the cone during the imposition of the step strain was obtained. It was determined that during the typical imposition of the step strain, the disk first accelerates up to about half the time required for the imposition of the strain, i.e., up to about 8 ms, and then decelerates up to about 18 ms. This is followed by the recoil of the disk which takes place during the next 5 ms.

For a particular run that was studied, the targeted strain of 2.0 would have been reached with an angular displacement of 0.218 radians. However, our experiments indicated that the disk first overshoots to an angular displacement of 0.254 radians and then moves back to the

desired angular displacement of 0.218 radians. This typical motion of the disk during the step strain experiment introduced an error, which was akin to imposing a double strain instead of a single step strain. Thus, a second strain, although relatively minor, was immediately introduced in the opposite direction, following the imposition of the first strain to finally arrive at the targeted angular displacement. The rise time, necessary for the strain of 2 to be imposed, is around 20 ms. For the strain to be approximated as a step strain the interval of time during which the strain is imposed should be small in comparison to the duration of time one waits prior to measuring the decay of the shear stress (7). Thus, the strain could be introduced here sufficiently fast to be considered as a step strain.

Torque vs. time information was collected during the imposition of various strains using cone-and-plate fixtures with 8 and 25 mm. The torque data collected with the 25 mm fixture (but not the 8mm fixture) generally exhibited a torque overload for a broad range of temperatures (the torque reached over 2000 g-cm for a duration of about 100 ms and thus could not be measured in this time interval). Soskey and Winter (8) and Papanastasiou *et al.* (9) also observed such overloading of the transducer. However, the relaxation modulus vs. time data collected with the 8 and 25 mm fixtures agreed well in the time range of interest, i.e., 120 seconds in spite of the prior overloading of the transducer with the 25 mm fixtures. Nevertheless, most of our experiments were carried-out using the fixtures with 8 mm diameter to entirely eliminate the transducer overloading effect.

It was determined that the shear stress grows at a faster rate during the acceleration of the disk, which introduces the strain, in comparison to the rate of growth of the shear stress observed during the deceleration of the disk. Does the motion of the disk generate the targeted strain in the melt? By following the marker line at the edge of the specimen we were able to measure the true shear deformation introduced into the melt at the edge. The marker line experiments generated the major finding of this study which was the revealing of the slip of the polyethylene melt at the walls of the rheometer for both the cone-and-plate and the parallel-disk flows during the step strain experiments.

For all of the data collected in the non-linear regime, the polymer melt was found to slip at both surfaces. The discontinuity in the marker line developing upon wall slip was monitored to generate the slip velocity at the wall (2)

$$V_s = |V_f - V_w| \quad (3)$$

where  $V_f$  is the velocity of the fluid at the wall and  $V_w$  denotes the wall velocity. Upon corrections for the curvature effects, the flow visualization data were utilized to measure the discontinuity of the marker line at the top and bottom surfaces. The time derivatives of the distances of separation between the marker line at the edge of the disk and at the free surface of the fluid, located adjacent to the moving disk, is equal to the slip velocity.

The time dependence of the wall slip velocity during the imposition of the step strain was investigated in detail. The slip of the polymer at the wall occurs almost immediately upon the initiation of the motion of the fixture and continues until the fixture is stationary. The slip velocity increases during the first 6 to 8 ms, during which the moving surface accelerates, followed by the decrease of the slip velocity until the fixture comes to rest.

Recording the motion of the plates and the straight marker line allows the determination of the true strain introduced into the polyethylene melt at the edge during the step strain experiment. The imposed strain is significantly smaller than the strain reported by the data acquisition unit of the rheometer. For example, upon targeting the imposition of a strain of 2.0 at a temperature of 190°C the true strain which could be imposed on the melt was only  $1.1 \pm 0.1$  and thus the imposed strain differed considerably from the targeted strain. The shear stress increases only up to the point where the true strain is fully imposed and then immediately undergoes a monotonic decrease until it eventually becomes negligible.

The slip of the melt at the wall diminishes the strain range over which the relaxation modulus can be possibly determined for linear polyethylene (which was found to be less than 1.4 in our experiments). All of the step strain experiments targeting strains in the 2 to 4 range generate true strains which are in the 1.1 to 1.3 and consequently all of the shear stress relaxation modulus data fall on the same curve (Figure 2). All corrected modulus data then approach the linear viscoelastic relaxation modulus values. The use of the slip-corrected strain in the determination of the relaxation modulus gives rise to shear stress relaxation moduli (Figure 2), which are significantly greater than those determined without the wall slip correction (Figure 1). The damping function values, determined upon slip corrections, are also greater than those not corrected for wall slip.

We also carried out a second set of marker experiments in which the marker line was placed at the surface of the molded specimen where it contacted the disk of the rheometer. Upon deformation the specimen was quenched and removed intact from the rheometer upon the completion of the relaxation experiment and the shape of the marker line, still evident on the surface of the deformed specimen was studied. The objective was to determine whether the deformation in the radial direction was uniform or not. Occasionally discontinuities were observed in the radial direction suggesting that a uniform strain could not be imposed. However, such cases were rare and the strain imposed upon wall slip was found to be generally uniform.

The wall slip of the polyethylene melt observed here is consistent with the molecular weight and concentration dependence of the wall slip of polymer solutions observed in plane Couette flow (10) and cone-and-plate flow (11) upon step shearing. Furthermore, this clearly documented and unambiguous occurrence of wall

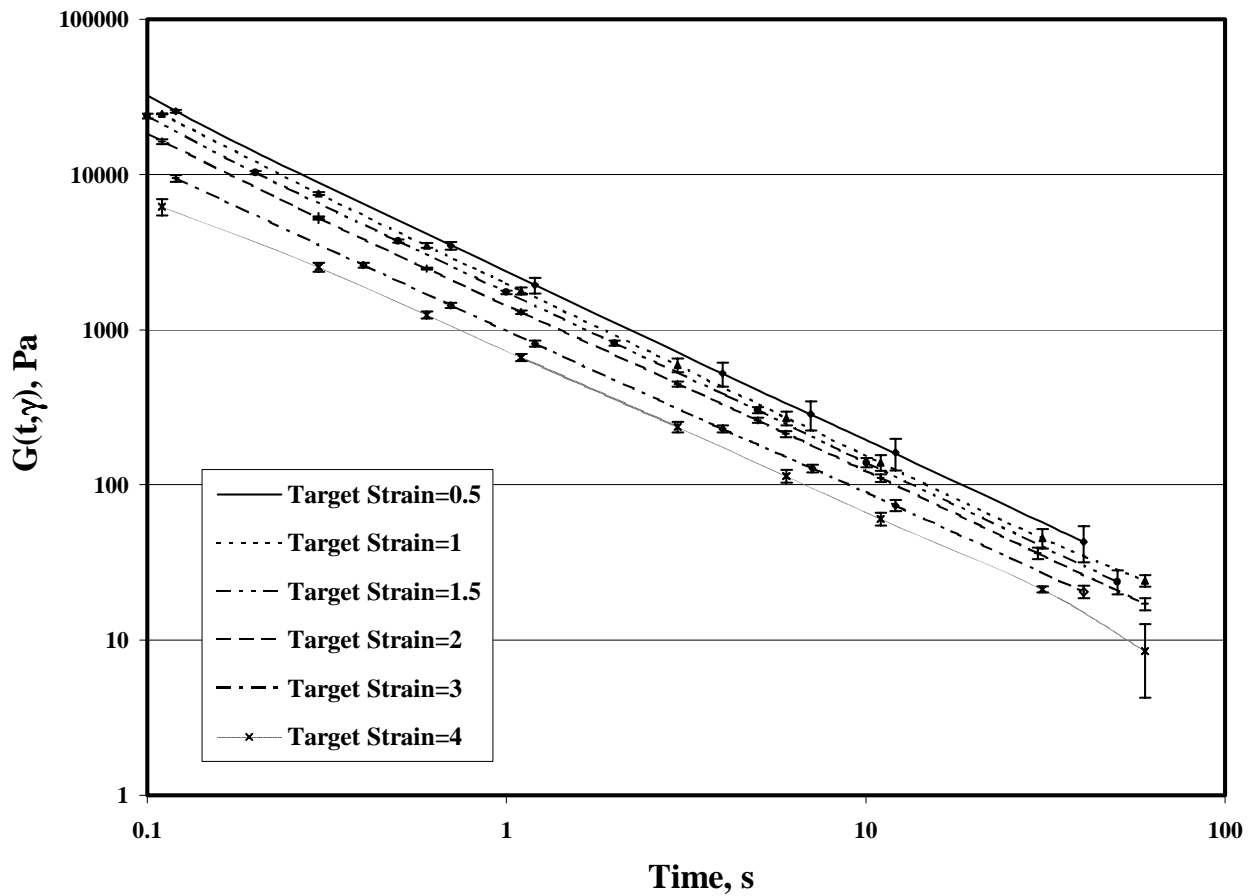
slip of the polyethylene melts upon sudden shearing, in retrospect, is not surprising. The characteristic time for the incorporation of the step strain is only about 20 ms. Such a small characteristic time for deformation for a melt with a high molecular weight and thus a relatively high relaxation time gives rise to a relatively high Deborah number. Under such high Deborah number conditions the behavior of the polyethylene melt will approach the behavior of an elastic solid. In the absence of a relatively high work of adhesion between the polyethylene melt and the wall, polyethylene will slip at the wall.

#### **Acknowledgements:**

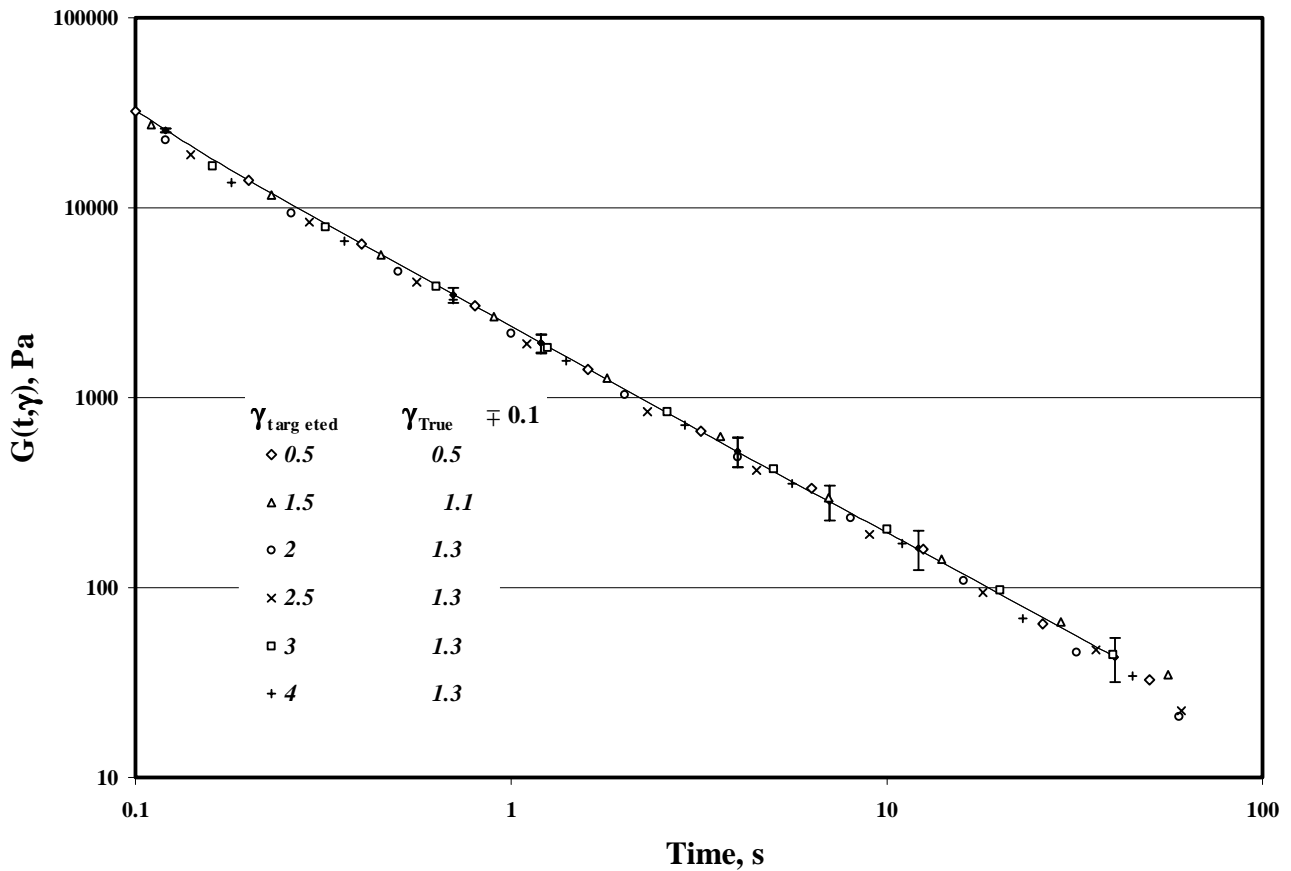
We acknowledge with gratitude the input and suggestions of Dr. Paul Tong of SIT and Dr. Cesar Garcia-Franco of Exxon Mobil Corporation.

#### **References:**

1. Vrentas, C.M. and W. W. Graessley, "Study of shear stress relaxation in well-characterized polymer liquids," *J. Rheol.* **26**, 359-371 (1982).
2. Kalyon, D. M., P. Yaras, B. Aral and U. Yilmazer, "Rheological behavior of a concentrated suspension: A solid rocket fuel simulant," *J. Rheol.* **37**, 35-53 (1993).
3. Aral, B. K. and D. M. Kalyon, "Effects of temperature and surface roughness on time-dependent development of wall slip in steady torsional flow of concentrated suspensions," *J. Rheol.* **38**, 957-972 (1994).
4. Laun, H. M., "Description of the non-linear shear behaviour of a low density polyethylene melt by means of an experimentally determined strain dependent memory function," *Rheol. Acta* **17**, 1-15 (1978).
5. Larson, R. G., "Nonlinear shear relaxation modulus for a linear low-density polyethylene," *J. Rheol.* **29**, 823-831 (1985).
6. Kalyon, D. M., D. Yu and J. Yu, "Melt rheology of two engineering thermoplastics: Poly(ether imide) and Poly(2,6-Dimethyl-1,4-phenylene ether)," *J. Rheol.* **32**, 789-811 (1988).
7. Larson R. G., *Constitutive equations for polymer melts and solutions*, (Butterworths, Stoneham, MA, 1988).
8. Soskey, P. R. and H. H. Winter, "Large step shear strain experiments with parallel-disk rotational rheometers," *J. Rheol.* **28**, 625-645 (1984).
9. Papanastasiou, A. C., L. E. Scriven and C. W. Macosko, "An integral constitutive equation for mixed flows: Viscoelastic characterization," *J. Rheol.* **27**, 387-410 (1983).
10. Archer, L. A., Y.-L. Chen and R. G. Larson, "Delayed slip after step strains in highly entangled polystyrene solutions," *J. Rheol.*, **39**, 519-525 (1995).
11. Mhetar, V. R. and L.A. Archer, "Slip in entangled polymer solutions," *Macromolecules* **31**, 6639-6649 (1998).



**Figure 1: Apparent shear stress relaxation modulus versus time at different targeted strains in the range of 0.5 to 4 at 190 °C using cone-and-plate flow.**



**Figure 2: Slip-corrected shear stress relaxation modulus versus time behavior of linear polyethylene at 190 °C using cone-and-plate flow.**