Fast Determination of Polymer Melt Viscosity by Optical Falling Needle Viscometer

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SYNOPSIS

An optical falling needle rheometer was employed to measure the melt viscosity of high density polyethylene (HDPE) and low molecular weight poly(tetrafluoroethylene) (PTFE). The temperature dependence of the melt viscosity of these two polymers was obtained and described by an empirical Arrhenius relation. At the present time, this method has been confirmed to be a simple and fast (within several tens of seconds for each measurement) approach to determine polymer melt viscosities of up to at least 1×10^5 Pa s. The sample cell containing ~ 2.5 cm^3 materials can be vacuum sealed and disposed of without the need of subsequent cleaning each time, which could be a useful feature. In comparison with HDPE, the PTFE sample melt was found to show a much higher melt viscosity with about the same degree of polymerization. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Low shear rate viscosity is a very important parameter in describing the flow behaviors of polymer melts. This parameter is usually determined by using a rotational rheometer. Similar to a rotational rheometer, a falling needle viscometer can also be used to measure the polymer fluid viscosity at very low shear rates based on the relation:

$$\eta = K_n \frac{\rho_s - \rho_l}{U_\infty} \qquad (1)$$

where ρ_s and ρ_l are the density in g/cm^3, respectively, of the needle and of the liquid, U_∞ is the terminal velocity, and K_n is a needle constant depending only on the dimensions of the system. However, for very high viscosity fluids such as polymer melts there exists an upper limit of the viscosity range for a regular falling needle viscometer because of the long measurement time with estimated periods of even days or months that are not acceptable in practice. Recently, we have developed a magnet-accelerated optical falling needle rheometer that allows us to measure viscosities from 1×10^{-3} Pa s to 1×10^5 Pa s (possibly much higher than this value in principle if we can find an appropriate high viscosity fluid to test the upper limitations of our instrument) at very low shear rates (i.e., in the Newtonian fluid region).[1] The needle travel distance can be reduced up to about 20 microns with an experimental precision of $\leq 1\%$ by using a position-sensitive detector. Meanwhile, the falling velocity of the needle can be accelerated by using a powerful magnet below the sample. Therefore, the measurement time for high viscosity fluids can be extraordinarily reduced from hours to seconds or from days to minutes.

Initial measurements were made on materials with viscosities as high as 50 Pa s.[1] We now report measurements on a conventional high density polyethylene (HDPE) and a low molecular weight poly(tetrafluoroethylene) (PTFE) as a first step in pursuing an ultimate measurement of the viscosity of high M_w materials, such as ultrahigh molecular

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weight polyethylene (UHMWPE) and commercial PTFE. Little viscosity data has been published on PTFE.[2] Measurements were made at high temperatures (as high as 380°C) using our newly developed high-temperature optical falling needle viscometer. The results demonstrate the suitability of this viscometer for many polymer melts.

Materials

HDPE (Alathon 7030) was a linear polymer with a weight-average molecular weight M_w of 8.6×10^4 g/mol and a polydispersity M_w/M_n of 5.1. M_w and M_w/M_n of HDPE were determined by gel permeation chromatography (GPC) at 135°C in trichlorobenzene with universal calibration using polystyrene as the primary standard. Low molecular weight PTFE (PTFE-6 in ref. 2) was prepared by free-radical dispersion polymerization in an aqueous medium. Weight-average molecular weight and distributions estimated from dynamic rheometry and creep measurements[2] were $M_w = 3.4 \times 10^5$ g/mol and $M_w/M_n = 2.8$. Viscosity standards were purchased from Polysciences, Inc. and Cannon Instrument Co.

RESULTS AND DISCUSSION

Figure 1 shows a schematic representation of the high-temperature optical falling needle viscometer. The sample (in powder form) was initially cold pressed into a 1-cm diameter rod with a 0.88-g magnetic needle (1.7-cm length and 0.3-cm diameter) inside. This process minimized void formation before melting. The sample rod, which had its rod axis parallel to the needle long axis, was then fitted into a cylindrical glass sample cell. The cell was evacuated for hours at temperatures below the melting point of the polymer and finally flame sealed. The loaded sample cell was mounted on a translational stage driven by a stepping motor that had a step length of 1.0 μm and inserted into a well-insulated heating brass block with fiberglass cloth wrapping. The setup was then placed in a transparent Dewar bottle. There was a small window in the brass block allowing the observation of the needle. The temperature fluctuation was maintained to within ±0.1°C by means of a proportional temperature controller (Bayley Instrument Co.). When the temperature was above the melting point of the polymer, it became relatively transparent. By projecting the needle
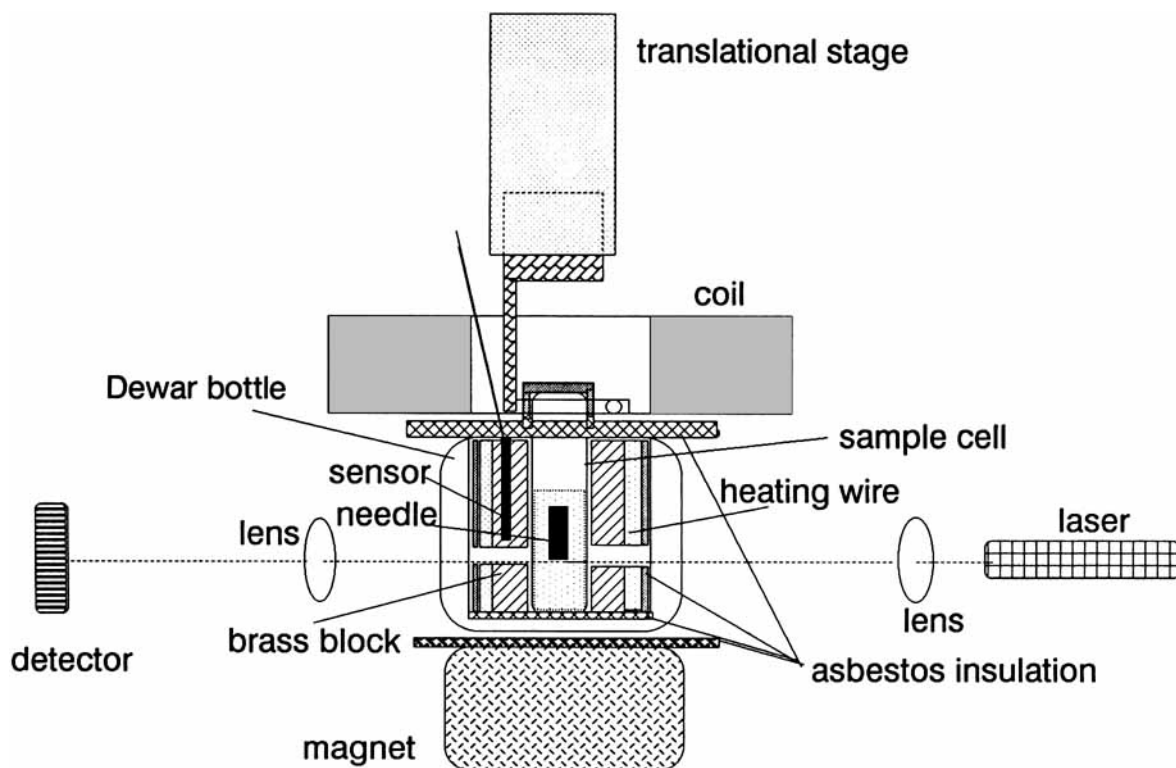

Figure 1   Schematic representation of the high-temperature optical falling needle viscometer.

image to the position-sensitive detector through a simple optical arrangement, the needle movement could be monitored as a function of time. Then the falling velocity was computed directly by the PC/ AT computer that acquired the data from the sensor via an analog/digital converter. For the low viscosity fluids, initially the upper magnetic coil was used to levitate the needle to a null point, and, when necessary, the lower electromagnet was used to accelerate the falling velocity of the needle. The falling velocity was determined on the basis of a short travelling distance (say $\sim$ 20–100 μm) for each measurement and at least 10 consecutive measurements were made to calculate the average value and to ascertain that the terminal velocity was being measured.

Figure 2 shows a log–log plot of the calibration curve for the needle in a set of viscosity standards. From the linear fitting, the needle constant was determined according to eq. (1). Thus, the viscosity of an unknown fluid can be calculated from the falling velocity of the needle using this constant.

Figure 3 shows an Arrhenius plot of melt viscosity versus inverse temperature between 130°C and 320°C for the PE sample. For each data point in this plot, the measuring time was only about several tens of seconds because the needle was set to travel only 100 μm for each measurement. The measurements were also being made in a consecutive manner

in order to ascertain whether the melt was homogeneous and whether the terminal velocity was achieved. A good linear behavior is shown in Figure 3. The solid line is the least-squares fitting curve with a standard deviation of 1.3%, yielding the activation energy of melt viscosity to be 5.72 kcal/ mol. The 1.3% standard deviation refers to the linear fitting deviation that is an average value of the deviation from the theoretical fitting values over all the experimental points. Subsequent standard deviation values have the same meaning. The value of 5.72 kcal/mol is in good agreement with the literature value by using a different rheometer.[3] The empirical equation obtained for the PE is

$$\eta \ (\text{Pa s}) = 7.61 \ \exp\left(\frac{5.72 \times 10^3}{RT}\right) \qquad (2)$$

where R and T are expressed in cal mol^{-1} K^{-1} and °K, respectively. The melt viscosity at 190°C is 3.83 $\times$ 10^3 Pa s (at a shear rate of 4.6 $\times$ 10^{-3} s^{-1}), which is again in agreement with the value of the zero shear rate viscosity (3.47 $\times$ 10^3 Pa s) determined from a rotational rheometer. The consistency would suggest that our present viscometer is suitable for the melt-viscosity measurement of bulk polymers.

The melt-viscosity measurement of a low molecular weight PTFE was undertaken at temperatures between 330°C and 380°C. The melt became opaque
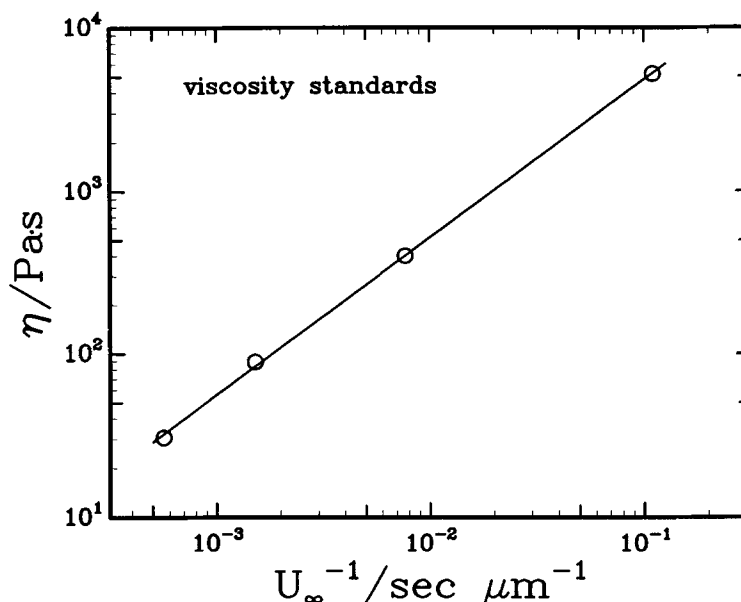

Figure 2 Calibration curve of viscosity versus inverse natural falling velocity for the needle in a set of viscosity standards. Solid line represents the least-squares fitting curve with $K[\equiv K_n(\rho_s - \rho_l)] = 5.0 \times 10^4$ Pa s μm s^{-1}.
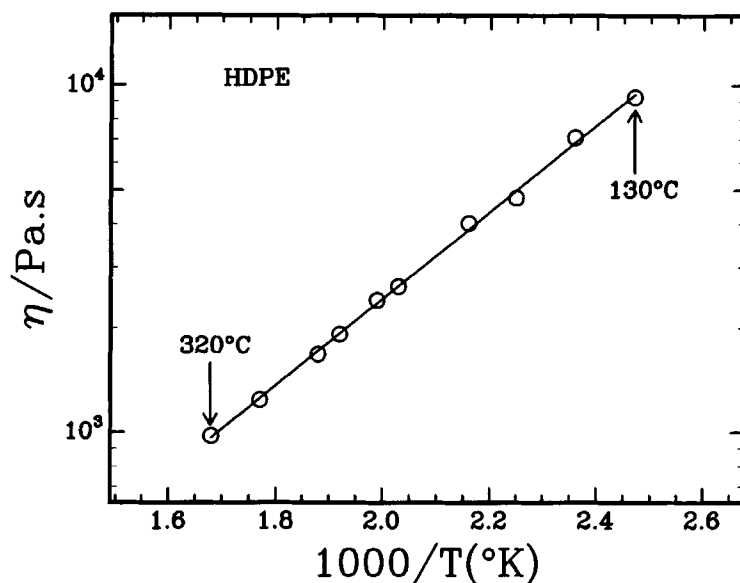
Figure 3 Arrhenius plot of melt viscosity versus inverse temperature for the polyethylene sample (Alathon 7030, Du Pont).

when the temperature was below ~ 330°C via crystallization. Above 400°C, the melt darkened slowly presumably caused by small amounts of organic impurities. An Arrhenius plot of the melt viscosity versus inverse temperature for the PTFE sample is shown in Figure 4. The viscosity value at 380°C (the lowest point in this plot) is 3.2×10^4 Pa s, which is consistent with those values measured using a rotational rheometer.[2] A least-squares fitting (solid

line) of the experimental data with a standard deviation of 2.1% yielded an empirical equation:

$$\eta \, (\text{Pa s}) = 3.73 \times 10^{-2} \exp\left(\frac{1.77 \times 10^4}{RT}\right) \quad (3)$$

with an activation energy of about 17.7 kcal/mol, which was about three times that of the PE sample. In our experimental temperature range the natural
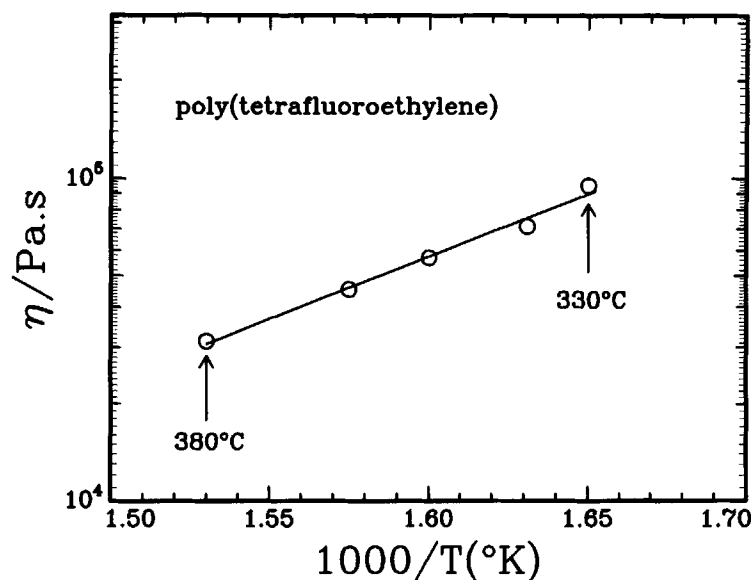

Figure 4 Arrhenius plot of melt viscosity versus inverse temperature for the low molecular weight poly(tetrafluoroethylene) (PTFE-6 in ref. 2).

falling velocity of the needle in the PTFE melt varied from ~ 0.4 μm/s to ~ 1.4 μm/s. In other words, for each measurement it took only ~ 2 min for the needle to fall through a 50-μm distance even at 330°C.

In general, a commercial PTFE is known to demonstrate quite different properties from those of a commercial PE, such as its well-known chemical inertness, high lubricity, and high thermal stability. The differences are considered to be due to the strength of the C — F bond that shields the carbon backbone.[2] However, the commercial PTFE is also notorious for its intractability because of its unusually high melt viscosity. The degree of polymerization (based on M_w) is about 3250 for both the PE and PTFE used here. The melt viscosity of the PE at 380°C was estimated to be 6.27×10^2 Pa s by using eq. (2) obtained over the temperature range of 130°C to 320°C. This value is about 50-fold smaller than that for the PTFE (3.2×10^4 Pa s). This is the same difference in viscosity found in the earlier study.[2] The viscosity of commercial PTFE is many orders of magnitude higher than measured here and is attributed mostly to the effects of higher M_w. However, the somewhat greater viscosity of PTFE when compared with PE, on a constant M_w and temperature basis, might be a result of additional molecular interactions arising from the presence of fluorine, as well as the slightly lower chain flexibility for PTFE.[2,4,5]

Determination of the low shear-rate melt viscosity of much higher M_w samples is considered possible. The ultimate goal is to analyze commercial PTFE and UHMWPE that have expected viscosities of about 10^{14} (380°C) and 10^9 (190°C) Pa s, respectively. Progress toward reaching this goal will be reported in the future.

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