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# Evaluation of polymer rheology from drop spreading experiments

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**Abstract**

In this paper, spreading experiments on "heavy" polymer drops are performed. "Heavy" refers to large polymer drops, i.e., the radius of the drop, $R$, is much larger than the capillary length, $\kappa^{-1}$, so that the spreading is dictated by gravity. The zero-shear viscosity can be found from measurements of the time-dependent drop radius or vice versa. Viscosity values found from spreading experiments compare well with the viscosity values found from dynamic rheological experiments.
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## 1. Introduction

Some industrial processes like "slush" molding, dip coating, and rotational molding rely on the force of gravity to deform a polymer melt (Tadmor and Gogos, 1979). In each process, a thick film of polymer is deposited onto a substrate and flows under the force of gravity. The process is useful in coating metal parts with thick polymer layers (Demarquette et al., 2000; Blunk and Wilkes, 2002) and molding large, thin-walled, hollow parts.

To get useful polymeric products from gravity-driven processes, low viscosity polymers are usually required because of the small gravitational forces involved. Traditional polymers used in these applications include uncross-linked polyesters or epoxies that are cross-linked subsequent to deformation. Polyvinyl chloride (PVC) plastisols are suspensions of PVC particles in plasticizer and the plastisol has a low viscosity. The plastisol can flow under the force of gravity and subsequent heating will expand the PVC particles and allow the plasticizer to enter the particles and "fuse" the material to a flexible PVC (Nakajima et al., 1981). More recent industrial work has focused on rotational molding of polyolefins. However, only low melt viscosity polyolefins can be used. There is no criteria to ascertain what viscosity is suitable for these applications and as more advanced polyolefins are produced it would be advantageous to have a method of screening these products for the low force processes.

There are two major regimes of spreading. The first regime is for small drops where the radius of the drop, $R$, is much smaller than the capillary length, $\kappa^{-1}$, of the fluid, $R < \kappa^{-1}$. In this regime, the drop has the shape of a spherical cap and spreading is driven by capillary forces. Spreading of droplets dominated by capillary forces has been studied extensively in the literature (Tanner, 1979; Zosel, 1993, Cazabat and De Coninck, 1998; Valignat et al., 1999). Spreading of small droplets is characterized by a drop with a spherical cap shape and the drop radius scales with time, $t$, as $R \sim t^{1/10}$. The spreading of small drops has been shown to be highly dependent on the nature of the spreading surface or the liquid/solid interaction (Welgyan and Burns, 1982; Nieh et al., 1996).

The second regime is for large drops, $R > \kappa^{-1}$, where flow is dominated by gravity. The capillary length defines the transition from the first to the second regime

$$\kappa^{-1} = (\gamma/\rho g)^{1/2}, \tag{1}$$

where $\rho$ is the fluid density in g/cm$^3$, $g$ is the acceleration due to gravity, and $\gamma$ is the surface tension. In this regime, gravity makes the drop shape essentially flat with curvature

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near the drop edge. The case of larger drops driven by gravitational forces has received much less attention but still has practical application. Lopez et al. (1976) were the first to extensively describe the spreading of large or "heavy" drops on solid surfaces. Lopez et al. derived an expression for the velocity profile in the spreading "heavy" drop assuming the no-slip boundary condition at the solid–liquid interface and complete wetting, i.e., stronger liquid–solid interactions than liquid–liquid interactions. Lopez et al. showed that the drop radius scales with the spreading time as $R \sim t^{1/8}$ for "heavy" drops.

Brochard-Wyart et al. (1991) greatly expanded on this work by theoretically showing that there are two spreading mechanisms when $R > \kappa^{-1}$. These researchers show that the drop radius can be found from

$$\frac{R^7}{t}\left[\frac{2}{\alpha^{1/2}\kappa}L + \frac{R}{2}\right] = \frac{\kappa^2 V^3 \gamma}{3\pi^3\alpha^2\eta_0}, \tag{2}$$

where $V$ is the drop volume, $\eta_0$ is the zero-shear viscosity, and $L$ is a factor related to the size of the drop relative to a pertinent molecular length scale. The term $\alpha$ is referred to as the "reduced volume" and is the ratio of the drop volume to the volume of a flat disk of the same radius and height as the drop. In practical terms, $L$ and $\alpha$ are fitting parameters. For drop sizes slightly larger than $\kappa^{-1}$, the drop is almost flat with dissipation mainly occurring at the drop edge. Spreading can be described by the left-hand term inside the brackets in Eq. (2). The radius of the drop scales with time as $R \sim t^{1/7}$. Once a critical radius is reached, $R > R_c > \kappa^{-1}$, the case of Lopez et al. exists with dissipation happening in the bulk of the drop. The spreading is described by the right-hand term inside the brackets in Eq. (2).

The problem of the spreading of drops in the capillary and gravitational regimes was considered very recently by Starov et al. (2003). Starov et al. use a similar approach to Lopez et al. and Brochard-Wyart et al. in the gravitational regime. These researchers make the same basic assumptions, namely that the drop is nearly flat, that complete wetting of the solid surface occurs, and that the no-slip boundary condition exists. However, Starov et al. insert a term to describe the spreading of non-Newtonian drops using the shear-thinning parameter. Starov et al. assume that the viscosity of the liquid can be described by the "power" law or Ostwald-de Waele model for shear-thinning of polymeric liquids: $\eta = k\dot{\gamma}^{(n-1)/2}$. However, the Ostwald–de Waele model is empirical and cannot describe the low shear rate region where a zero-shear viscosity would be encountered. The model of Starov et al. is therefore only applicable if the drop spreading rates under the force of gravity are concurrent with the deformation rates where the polymeric fluid would be shear-thinning.

In this study, the change in drop radius with time is measured for large polymer drops. The polymers are high molecular weight polydimethylsiloxanes (PDMS) at room temperature. From the dependence of radius with time, the dominant spreading mechanism can be found. The equation set forth first by Lopez et al. and then by Brochard-Wyart et al. can be used to calculate the zero-shear viscosity of the PDMS melts. This technique could be useful, for instance, in determining the zero-shear viscosity of high molecular weight polymer melts where normal rheological characterization methods may not be able to attain low enough strain rates to reach the zero-shear viscosity regime. Likewise, if the zero-shear viscosity of the melt is known, the spreading area of the melt can be predicted to show if the melt will provide a certain amount of coverage in a specified period of time.

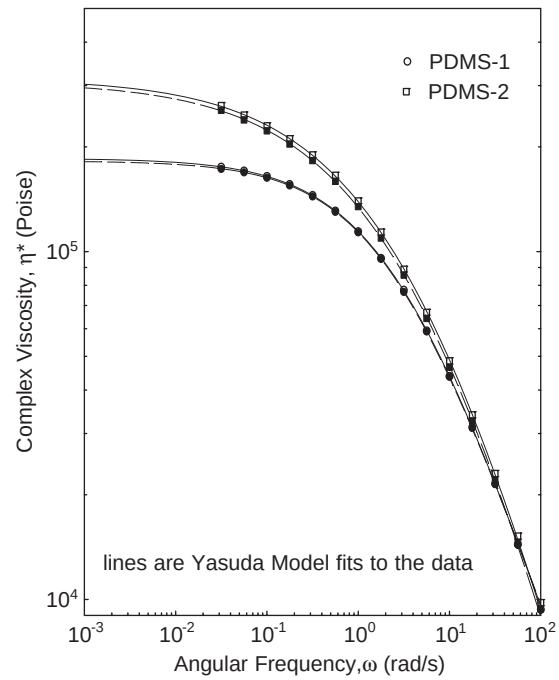


Fig. 1. Dynamic rheological data for PDMS-1 and PDMS-2 obtained at room temperature. The lines are Yasuda Model fits to the data to obtain the zero-shear viscosity, $\eta_0$.

## 2. Experimental

The polymers used are PDMS samples of different viscosity. Both PDMS samples are tested in a Rheometrics RD-SII mechanical spectrometer to assess viscoelastic properties. Experiments are performed at room temperature using 25 mm diameter parallel plates. The applied strain is 5–6% to keep the measured torque above the minimum value of the transducer. The applied angular frequency range is $\omega = 0.032$–$100$ rad/s. The experiments proceed from high to low applied angular frequency. Complex viscosity, $\eta^* = G^*/\omega$, results are shown in Fig. 1. The zero-shear viscosity, $\eta_0$, is found by fitting the frequency-dependent viscosity data to a Yasuda viscosity model

$$\eta^* = \eta_0[1 + (\omega\tau)^a]^{(n-1)/2}, \tag{3}$$

where $a$, $\tau$, and $n$ are somewhat empirical fitting parameters but are dependent on the weight average molecular weight ($M_w$) and polydispersity ($M_w/M_n$) of the polymer. Each experiment is performed twice and the zero-shear viscosity values are 185 261 and 182 170 Poise (P) for PDMS-1 and 314 269 and 307 764 P for PDMS-2 indicating the experimental error for rheological experiments is 2%. The Ostwald–de Waele model used by Starov et al. (2003) cannot accurately describe the shear rate-dependent viscosity behavior of the PDMS samples used because it can only be fit to the viscosity data accurately if the zero-shear viscosity region is ignored.

The spreading experiments are conducted by placing a known mass of PDMS on a clean, flat, glass plate 0.11–0.14 cm thick. The plate is raised slightly off the surface of the table so the bottom of the plate can be accessed from underneath. The plate is checked to make sure that it is level. Spreading proceeds at room temperature, which is 21 °C. The PDMS is formed into spheres or disks, placed onto the glass, and allowed to spread. The initial shape of the PDMS mass is not relevant because after a few minutes (about 100 s) a flat, circular drop is obtained. The change in diameter of the drop is recorded using a ruler placed underneath the glass, directly opposite the side of spreading.

## 3. Results and discussion

### 3.1. Polymer drop spreading experiments

Figs. 2 and 3 show the change in drop radius for the PDMS samples as a function of time for several starting mass values. The average drop radius is plotted because there are small variations in the drop radius as a function of position. The radius variations may be because of irregularities in the glass surface and are represented in the figures by the error bars. Although the spreading surface could have been made smooth, the goal was to use a microscopically rough, high-energy surface typical of most polymer processing techniques.

For each mass of PDMS used, the regime $R \sim t^{1/8}$ is dominant. For high molecular weight PDMS, the density is $\rho = 0.978\,\mathrm{g/cm^3}$ and $\gamma = 21.3\,\mathrm{dyn/cm}$ (Silicones, 1987). The capillary length for high molecular weight PDMS is then $\kappa^{-1} = 0.149\,\mathrm{cm}$. Therefore, the radius values measured are much larger than the capillary length and the case of "heavy" drops is obtained.

The spreading data indicate that spreading velocity is quite low, i.e., on the order of $v \sim 10^{-7}\,\mathrm{cm/s}$ at long spreading time. The drop height at long times, $h$, can be estimated from the conservation of mass and the assumption that the drop is either a flat disk or a percentage of a flat disk, i.e., use the reduced volume approach of Brochard-Wyart et al. A deformation rate in the drop can then be defined as $\dot{\gamma} \sim v/h \sim 10^{-6}\,\mathrm{s^{-1}}$. This means that the spreading of the PDMS drops occurs well within the zero-shear viscosity region of Fig. 1 and there is no shear-thinning of the PDMS as it spreads.

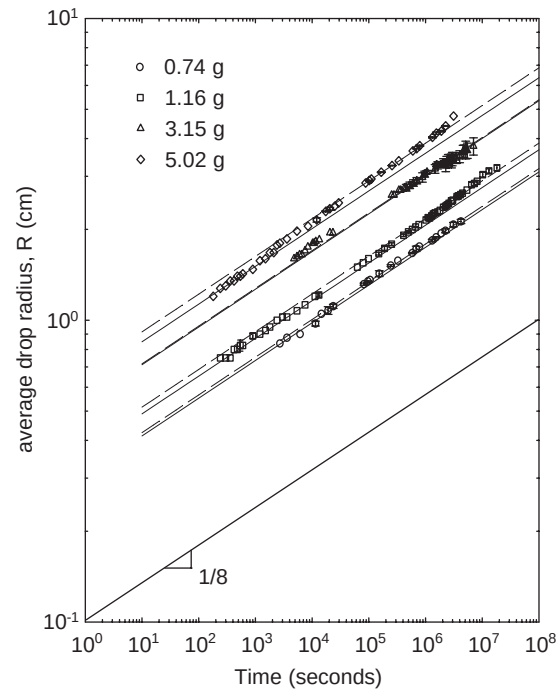


Fig. 2. Data for PDMS-1 drop spreading. Solid lines are radius ($R$) values determined from Eq. (4); dashed lines are zero-shear viscosity ($\eta_0$) values obtained from Eq. (4).

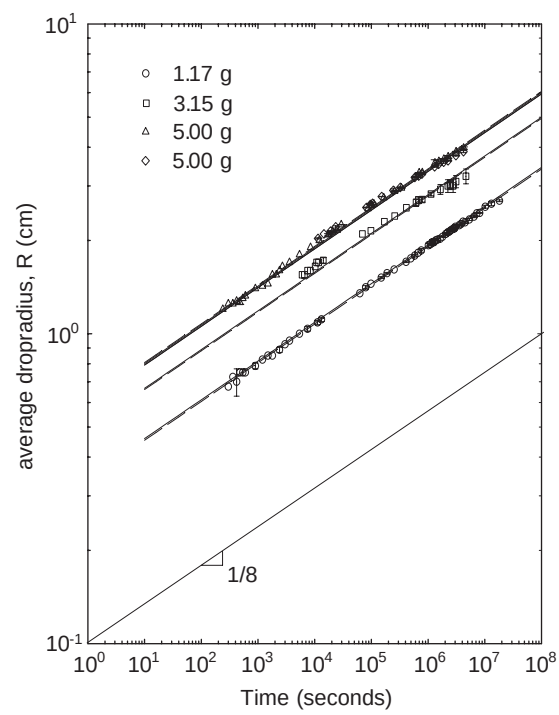


Fig. 3. Data for PDMS-2 drop spreading. Solid lines are radius ($R$) values determined from Eq. (4); dashed lines are zero-shear viscosity ($\eta_0$) values obtained from Eq. (4).

The observed scaling of radius with time is consistent with the regime observed by Lopez et al. Therefore, the measured radii are larger than the critical radius value described by Brochard-Wyart et al., i.e., $R > R_c$. It is possible that the intermediate regime for "heavy" drops described by Brochard-Wyart et al. where $R \sim t^{1/7}$ or $R < R_c$, may exist at low radius values relative to the ones encountered in the spreading experiments. The critical radius for change from the $R \sim t^{1/7}$ regime to the $R \sim t^{1/8}$ regime is found from $R_c \sim cL\kappa^{-1}$, where $L \propto \log(R/a)$, $a$ is a molecular size, and $c$ ranges from 2 to 4. Brochard-Wyart et al. find $L$ to be about 12. This would mean that $R_c$ for the system currently studied is ca. 3.6–7.2 cm. The observed scaling suggests that $c$ and $L$ may be a lot lower than the estimates given.

At $R > R_c$, Eq. (2) can be reduced to

$$R = \left[\frac{2V^3\kappa^2\gamma}{3\pi^3\alpha^2\eta_0}\,t\right]^{1/8} \tag{4}$$

to describe primary dissipation in the drop bulk. Eq. (4) shows that the result of Lopez et al. is recovered. Lopez et al. show similar scaling of $R \sim t^{1/8}$ for polydimethylsiloxane spread on mica surfaces for several sized drops.

### 3.2. Calculation of time-dependent polymer drop radius from zero-shear viscosity

The solid lines drawn through the data in Figs. 2 and 3 are calculated directly from Eq. (4) using the zero-shear viscosity values for each PDMS sample. In the current context, $\alpha$ is the only adjustable parameter in the equation and Brochard-Wyart et al. show that $\alpha$ is low at the beginning of spreading when $R < \kappa^{-1}$. In the early stages of spreading the drop is a spherical cap and deviates greatly from the shape of a perfectly flat disk. In time, $\alpha$ grows to a limiting value of 0.75 at $R > R_c > \kappa^{-1}$. For a perfectly flat drop, $\alpha$ would be 1. In principle, $\alpha$ can be found experimentally if the drop profile can be imaged. This has been done (Bascom et al., 1964; Welgyan and Burns, 1982) for small drops. In keeping with the spirit of simplicity of experimentation for determination of the zero-shear viscosity, the drop profile is not imaged but detailed experiments of the heavy drop profile could be performed with the proper apparatus. For simplicity, $\alpha$ is assumed to be the large radius asymptotic value of 0.75. Fits of the equations using $\alpha > 0.75$ severely under predict the drop radius over all spreading time. According to the theory of Brochard-Wyart et al., $\alpha = 0.5$–$0.6$ in the early stages of spreading. Fits of the equations using $\alpha = 0.5$–$0.6$ give slightly higher drop radius values over all time than the ones observed but it is possible that early stage spreading data is better fitted using $\alpha = 0.5$–$0.6$.

There is good agreement between the experimental and calculated data. The spreading rate can be used to determine, for instance, a desired surface coverage of the melt at a certain temperature after a specified period of time. This would be helpful in determining whether or not a melt is appropriate for gravity-driven flow over reasonable time scales.

Table 1
PDMS-1

| Mass (g) | $\eta_0$ (P) from Eq. (4) | $r^2$ value | % $\eta_0$ difference |
|---|---|---|---|
| 0.74 | 151 224 | 0.9979 | 18 |
| 1.16 | 123 022 | 0.9968 | 33 |
| 3.15 | 175 020 | 0.9934 | 5 |
| 5.02 | 100 708 | 0.9930 | 45 |

Table 2
PDMS-2

| Mass (g) | $\eta_0$ (P) from Eq. (4) | $r^2$ value | % $\eta_0$ difference |
|---|---|---|---|
| 1.17 | 347 134 | 0.9994 | 11 |
| 3.15 | 337 404 | 0.9785 | 7 |
| 5.00 | 271 231 | 0.9984 | 14 |
| 5.00 | 289 495 | 0.9762 | 8 |

### 3.3. Calculation of zero-shear viscosity from time-dependent polymer drop radius

To examine how well spreading experiments can predict zero-shear viscosity, Eq. (4) is fit to the time-dependent radius data. The dashed lines drawn through the data in Figs. 2 and 3 show this result. Tables 1 and 2 include the predicted $\eta_0$ values along with the correlation coefficient values from the regression analysis ($r^2$ values) and the percent difference from the $\eta_0$ values obtained from dynamic rheology.

The trend in calculated $R$ or $\eta_0$ is consistent for PDMS-1 and PDMS-2. The zero-shear viscosity is very sensitive to the measured radius, i.e., $R^8 \sim 1/\eta_0$. For instance, if the measured radius was 5% higher than the actual radius because of experimental error, the calculated viscosity would be 32% lower than the actual viscosity: $(R'/R)^{-8} \sim (\eta_0'/\eta_0) = (1.05)^{-8} = 0.68$ because of the strong scaling. But the spreading experiments do a reasonable job of predicting the zero-shear viscosity values.

Fig. 4 shows the same data in Figs. 2 and 3 for concurrent mass values. However, the PDMS-2 data in Fig. 4 is replotted as a function of reduced time $= t\ (\eta_{0,1}/\eta_{0,2})$ where $\eta_{0,1}/\eta_{0,2} = 0.59$ is the zero-shear viscosity ratio of PDMS-1 to PDMS-2. So the PDMS-1 data is plotted in real time and the PDMS-2 data is shifted relative to the PDMS-1 time. The curves for the two PDMS samples at a given mass fall onto one another. This indicates that spreading is governed by the intrinsic time scale of the polymer, i.e., $\eta_0 \sim \tau^{3.4}$, where $\tau$ is the overall molecular relaxation time of the polymer. In addition, the drop radius axis could be normalized by drop mass$^{3/8}$ or volume$^{3/8}$ to create a master curve. This shows that the kinetics for any size drop are the same. Using more sample does not speed things up but simply provides more surface coverage.

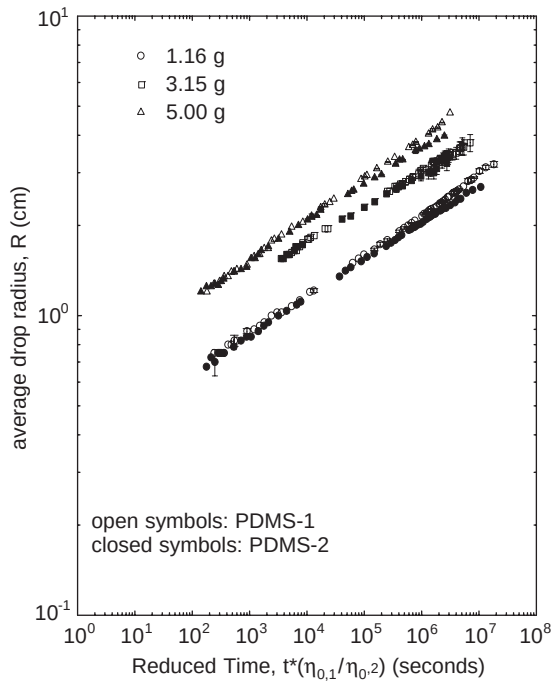


Fig. 4. Drop spreading data for PDMS-1 and PDMS-2 at concurrent mass values. PDMS-2 time space is shifted using the viscosity ratio of PDMS-1 to PDMS-2.

Graessley and Ver Strate (1980) present a simple method to determine the zero-shear viscosity of polymer melts using an extensional deformation method. The spirit of that work is similar to that presented here: to determine the zero-shear viscosity for high molecular weight polymers using nothing more than a simple experimental apparatus. Graessley and Ver Strate also conducted experiments on the gravity-driven deformation of polymer melts at room temperature. The polymers were an ethylene–propylene copolymer and polyisobutylene. The extensional method was able to give reasonable values of zero-shear viscosity at the right experimental conditions.

From a practical standpoint, it appears possible that polymer drop spreading experiments could be performed under a variety of conditions. For polymers intended for gravity-driven processing, it is anticipated that the melt viscosity would be low to facilitate spreading. Therefore, experimental times would be significantly lower than those encountered in this study. For very fast spreading, a more complicated experimental technique may be needed to discern the drop radius with time. The PDMS melts used in this study are chosen because of the relatively slow and easily discernible spreading at room temperature. Although the experiments are conducted for appreciable times, the data shows that, at any given mass, the trend in drop radius persists from very low times ($\sim 10^2$ s) to very high times ($\sim 10^6$ s). This indicates that experiments conducted for several minutes to several hours may be more than sufficient to discern the time-dependent drop radius or zero-shear viscosity. Higher viscosity melts may require experiments for several days.

It also appears possible to perform elevated temperature experiments, perhaps in a convection oven. In the case of the PDMS samples used here, it would speed up the spreading. The initial sample shape does not matter because the polymer quickly assumes the droplet shape on the glass surface. For instance, polyethylene discs could be molded, placed on a flat glass plate in a convection oven, and allowed to spread. The polyethylene drop could be removed periodically, cooled, and the radius measured. The spreading equation would have to include a term to take into account the contraction of the polymer sample upon cooling or simply monitor the drop radius inside the oven.

## 4. Conclusions

In this paper, spreading experiments are used to determine the change in radius of a “heavy” polymer drop with time. The drop is “heavy” because the spreading is driven by gravity. In the experiments used in this study, large polymer drop spreading depends on viscosity only because temperature, mass, and surface tension are kept constant. It is found that the spreading rate can be determined from knowledge of the zero-shear viscosity of the melt or vice versa. This could prove helpful, for instance, in determining whether or not a polymer melt would offer a specific amount of surface coverage after a certain spreading time. Likewise, the low strain rates encountered in spreading experiments could be used to access the zero-shear viscosity regime of polymeric melts, which may prove difficult using more conventional rheological testing equipment.

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