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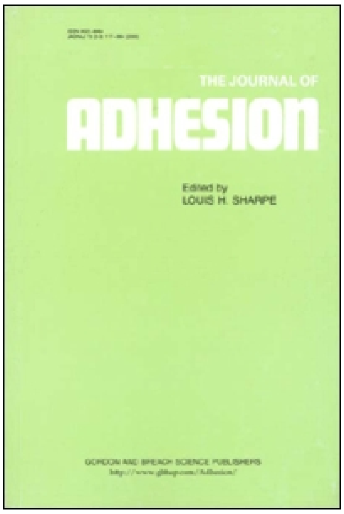

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# Note: The Spreading of Molten Polymers

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Note

# The Spreading of Molten Polymers

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IN PREVIOUS WORK[1-4] on the kinetics of spreading of polymer melts, small drops of molten polymer were observed to be spherical segments. Drops exhibiting a "cap" about the center and a projecting "foot" were suggested by Schonhorn and coworkers[1] but were never observed. We have recently observed such shapes for fluoroalkyl methacrylate polymers spreading on clean glass.

Polymer pellets were heated under nitrogen in a cavity within an aluminum cylinder. The cylinder was provided with viewing windows and a band heater. Except for the viewing windows, the cavity was completely surrounded by a wall of aluminum 3 cm thick. Temperature was measured with thermocouple placed next to the polymer pellet. There were no detectable temperature gradients within the cavity during the measurements. The glass surface (micro cover glass) was cleaned by gentle flaming and was supported within the cavity on the end of a section of glass tubing. The pellets were initially cylindrical in shape; pellet volume was about 0.003 $cm^3$. In each measurement the pellet was placed in the cavity prior to heating the cylinder to the desired temperature. Thermogravimetric analysis indicated no polymer degradation under the conditions of the measurements.

An analytic solution to the heat transfer equation for a cylindrical pellet permitted calculation of the temperature difference between the outer surface and the center of the pellet when the temperature within the cavity just reached the desired point. This difference was negligible under the conditions of the present study. For example, calculations based on the pellet dimensions (0.08 cm. radius; 0.18 cm. high), the heating rate used (11° C/min.), and the thermal conductivity ($6x10^{-4}$ cal./sec. $cm.^2$ deg. C/cm.) and heat capacity (0.25 cal./gm. deg. C) of typical fluoropolymers showed a difference of less than 0.3°C for the highest temperature used. Even if the thermal conductivity of the polymer were one tenth of the above value, the difference would only be 2°C.

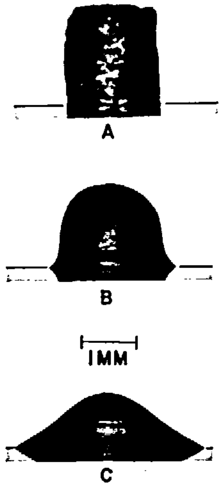

**Figure 1** — Fluoroalkyl methacrylate polymer ($\eta_{inh}$ = 1.01) pellet on glass at 220°C.
A. 3 minutes after reaching temperature
B. 10 minutes
C. 15 minutes

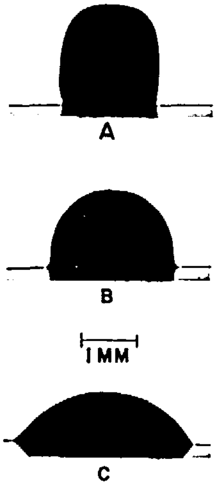

**Figure 2** — Fluoroalkyl methacrylate polymer ($\eta_{inh}$ = 0.62) pellet on glass at 180°C.
A. 10 seconds after reaching temperature
B. 3 minutes
C. 12 minutes

Figure 1 shows profile photographs of a polymer pellet at different stages of spreading at 220°C. This polymer had an inherent viscosity, $\eta_{inh}$, of 1.01 in $CCl_2F$-$CF_2Cl$ (0.5 gm/100 ml) at 30°C[5]. The horizontal line in each photograph is in the plane of the glass surface. Another sample of the polymer having a lower molecular weight ($\eta_{inh} = 0.62$) and therefore a lower melt viscosity, tended to form a spherical segment more readily on heating, but the pellet still showed a projecting foot during spreading. This is shown in Figure 2. A sample of still lower molecular weight ($\eta_{inh} = 0.27$) did form an almost spherical segment on heating. This is shown in Figure 3. However, when observed at a lower temperature (110°C) this polymer had a profile similar to that of Figure 2.

Drop profiles similar to that of Figure 2, but with smaller projecting feet, were also observed with viscous silicone fluids on glass at 25°C. This is shown in Figure 4 for a drop of polydimethylsiloxane (Dow Corning 200 fluid) having a viscosity of $5\text{x}10^5$ centipoises. Observations on silicone fluids having different viscosities indicate that a projecting foot is detectable when the viscosity is as low as $10^5$ centipoises.

There are at least two processes that are significant in determining the rate at which a liquid drop spreads over a solid. The first is the interaction of the liquid with the solid at the solid-liquid-vapor boundary. This interaction causes the liquid to tend to spread out until an equilibrium configuration is attained. The second process is the propagation of the disturbance originating at the three-phase boundary throughout the bulk of the drop. The equilibrium shape is defined, through the Laplace equation, by the surface

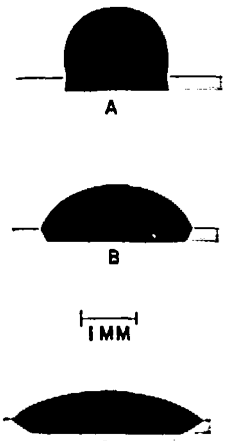

**Figure 3** — Fluoroalkyl methacrylate polymer ($\eta_{inh}$ = 0.27) pellet on glass at 160°C.
A. 10 seconds after reaching temperature
B. 3 minutes
C. 15 minutes

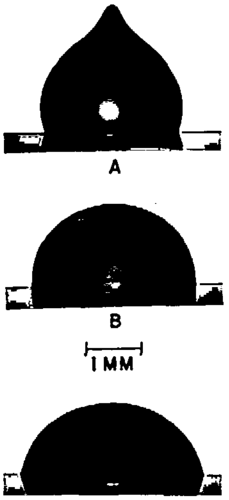

**Figure 4** — Polydimethylsiloxane ($\eta$ = $5 \times 10^5$ centipoises) drop on glass at 25°C.
A. 1 minute after touching surface
B. 2 minutes
C. 3 minutes

tension, the density and the contact angle of the liquid. When the contact angle changes, the liquid surface tension causes the drop to assume a new equilibrium shape while the bulk viscosity of the liquid tends to retard this process. The rate of spreading of the entire drop is primarily determined by the slower of these two processes.

Previous observations[1-4] in which polymer drops spread as spherical segments are examples of systems where spreading is controlled primarily by interaction at the three-phase boundary. In other words, the controlling factor in these systems is the rate of change of the contact angle. In the systems studied in the present work, the equilibrium contact angle is low and the bulk viscous forces offer significant resistance to spreading. This leads to the formation of the observed foot at the base of the drop.

We are indebted to C. R. Antonson of Du Pont who obtained an analytic solution to the heat transfer equation and calculated temperature differences for the polymer pellets.

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