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Kinetics of Wetting of Surfaces by Polymers; Capillary Flow

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The rate of penetration of liquids into capillaries and slits provides an experimental tool with which to study wetting, since capillaries and slits represent models for actual surface irregularities. Classically, equations for the distance penetrated l as a function of time t have been solved with the assumption that the contact angle θ is constant. This condition is not valid for polymer melts. Equations for $l = f(t)$ are obtained for horizontal slits and capillaries taking $\cos \theta_t = (\cos \theta_\infty)(1 - ae^{-ct})$; the importance of terms arising from $\theta(t)$ is demonstrated.

For vertical capillaries and slits with descending or ascending liquid columns, equations for dl/dt are obtained but are not amenable to general solutions in elementary form. In general, the dynamics of flow is controlled by the coefficient $(\gamma_L \cos \theta_t)/g\eta$, where g is a factor which depends on the geometry of the system.

INTRODUCTION

The formation of an adhesive bond between an adhesive or polymer melt and a surface depends on the development of a maximum area of molecular contact and the displacement of air from the microirregularities on the surface. Whereas much attention has been given to the thermodynamics of wetting and adhesive forces, relatively little quantitative work has been carried out on the rate of approach to equilibrium conditions for viscous systems.

The rate of penetration of liquids into capillaries and slits provides an experimental tool with regard to wetting, since capillaries and slits may represent models for surface irregularities. Equations for the dynamics of capillary flow developed in the past have assumed that the rate of wetting or the development of equilibrium contact angles is sufficiently rapid relative to the rate of movement of liquid as not to require consideration.

Recent studies of Schonhorn, Frisch, and Kwei (1) on the spreading of sessile drops of molten polymers indicates that the contact angle θ_t is time dependent. Since in any real experiment with polymer melts the initial contact angle may be far removed from its equilibrium value, it is of interest to consider the influence of a time-dependent contact angle on the classical problem of the penetration of liquids into capillaries.

DISCUSSION

I. Horizontal Capillaries. If we assume Poiseuille's law for the flow of Newtonian liquids through tubes and consider that there is no "slip" at the wall, the fluid moves with a velocity v under a pressure P, according to the following (2):

$$v = \frac{R^2P}{4\eta l}\left[1 - \left(\frac{r}{R}\right)^2\right], \qquad [1]$$

where R is the radius of the tube, r the radial distance from the center, l the tube length, and η the viscosity. The average fluid velocity $\bar{v}$ defined as $Q/\pi R^2$, where Q is the volumetric flow rate, may be shown to be given by

$$\bar{v} = \frac{v_{\max.}}{2} = \frac{R^2P}{8\eta l}. \qquad [2]$$

For a liquid flowing under capillary pressure P_c alone, we may substitute (3)

$$P = P_c = \gamma_L(1/G_1 + 1/G_2), \qquad [3]$$

where G_1 and G_2 refer to the radii of curvature and γ_L is the surface tension of the liquid. In small cylindrical tubes where the meniscus does not depart from a spherical shape, $P_c = 2\gamma_L \cos\theta/R$; θ is the wetting angle at the wall. Combining equations, we have

$$\bar{v} = \frac{R\gamma_L \cos\theta}{4\eta l}. \qquad [4]$$

In the past (4, 5) this has been integrated by assuming that the rate of change of momentum of the contents of the capillary is negligible and the rate of wetting is rapid compared with the rate of movement of the liquid. With this condition, $\cos\theta$ is a constant; substituting $dl/dt = \bar{v}$ and taking $l = 0$ when $t = 0$ leads to the equation[1]

$$l^2 = \frac{R\gamma_L \cos\theta}{2\eta} \cdot t. \qquad [5]$$

Recently, in investigating the spreading of sessile drops on solid surfaces, Schonhorn, Frisch, and Kwei (1) have shown that for polyethylene and poly-(ethylene-vinyl acetate) melts, there is a strong time dependence of the contact angle and that $\cos\theta$ adjusts itself at the interface without regard to the mass of the fluid involved; in other words, the wetting is independent of the stress. It is now of interest to consider the implications of this conclusion on the capillary flow of polymer melts.[2] In this situation, $\cos\theta$ may perhaps be replaced by some suitable function as

$$\cos\theta_t = (\cos\theta_\infty)(1 - ae^{-ct}), \qquad [6]$$

which has the correct boundary conditions

$$t = \infty, \qquad \cos\theta_t = \cos\theta_\infty;$$
$$t = 0, \qquad \cos\theta_t = (\cos\theta_\infty)(1 - a).$$

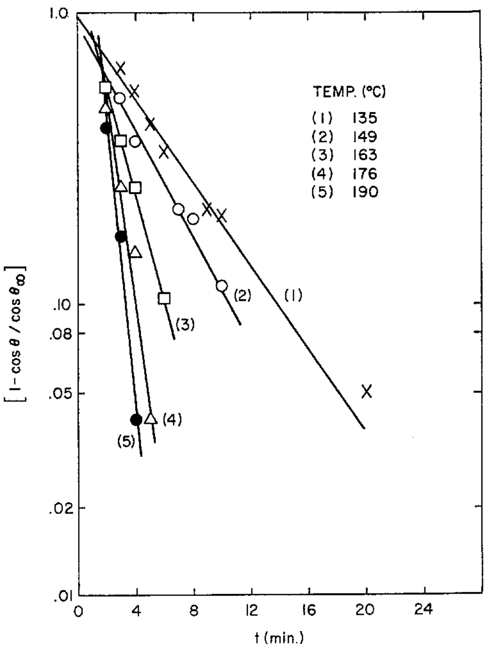

FIG. 1. Rate of wetting of poly-(ethylene-vinyl acetate) (1) on aluminum at different temperatures plotted according to Eq. [6].

TABLE I

VALUES OF THE COEFFICIENT c FOR POLY-(ETHYLENE-VINYL ACETATE) ON ALUMINUM

c (sec^{-1})	T (°C)
16.4×10^{-3}	190
13.3	176
6.6	163
3.3	149
2.7	135

Further justification is found in plotting the experimental data of Schonhorn *et al.* according to Eq. [6]. A glance at Fig. 1 clearly indicates an excellent fit over the entire time range and at all temperatures.

Values of the coefficient c are shown in Table I.

In the experiments of Schonhorn *et al.*, $a \approx 1$ and $\cos\theta_\infty = 1$. Substituting Eq. [6] in [4] leads to the expression:

$$\frac{dl}{dt} = \frac{R\gamma_L(\cos\theta_\infty)(1 - ae^{-ct})}{4\eta l} \qquad [7]$$

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[1] It is of interest to note at this point that rapid wetting is favored by low viscosity, high surface tension, and low contact angles. The latter two conditions are antithetical, however, especially on low-energy surfaces.

[2] In this connection, G. E. P. Elliot and A. C. Riddiford (*J. Colloid and Interface Sci.* **23**, 389 (1967)) find advancing contact angles to be independent of velocity at low velocities.

such that the initial velocity is proportional to cos θ_∞ $(1 - a)$ and the final velocity, to cos θ_∞.

Again taking the boundary condition of $l = 0$ at $t = 0$ results in the integrated form:

$$l^2 = \frac{R\gamma_L \cos \theta_\infty}{2\eta}\left[\left(t - \frac{a}{c}\right) + \frac{ae^{-ct}}{c}\right], \quad [8]$$

which reduces to Eq. [5] when $\cos \theta = \cos \theta_\infty$, that is, $c = 0$ and $a = 0$.

The importance of the terms arising from cos θ_t can be seen by comparing Eq. [8] with Eq. [5] for a real set of conditions. Thus with $\cos \theta_\infty = 1$, and with values of 1 and 0.001 sec^{-1} selected for a and c, respectively, from Table I, $l^2/(R\gamma_L \cos \theta_\infty/2\eta)$ is plotted against t in Fig. 2. At $t < 10{,}000$ sec, Eq. [8] is seen to deviate seriously from the simple dependence on t indicated by a similar plot according to Eq. [5]. On linear coordinates, Fig. 3, it is seen that at short times, an apparently long induction time would be observed in a real experiment with polymer melts. Obviously, neglect of cos θ_t would lead to erroneous results in the calculation of $\gamma_L \cos \theta/\eta$ from experimental data on the penetration distance l as a function of t.

It is especially interesting at this point to note that in comparing the spreading rate of drops at different temperatures, Schonhorn *et al.* find this process to be proportional to γ and inversely proportional to η. Data at different temperatures for cos θ_t/cos θ_∞ or r/r_0, the ratio of drop radius to the radius when $\theta = 90°$, can be combined into a master plot over time and temperature with a shift factor a_T given by the quantity

$$a_T = \gamma_L/\eta L_W .$$

This has a formal similarity to the term $\gamma_L/\eta l$ given in the preceding equations except that L_W is apparently not dependent on drop dimensions but is characteristic of a given polymer-substrate pair. Also, L_W apparently does not depend on substrate roughness. The order

$$(L_W)_{\text{mica}} > (L_W)_{\text{al.}} > (L_W)_{\text{Teflon}}$$

suggests that a friction or "slip" factor may be involved. Both a_T and the coefficient c have the dimensions of reciprocal time and must be related.

II. Vertical Capillaries and Slits. The case for vertical capillaries is well known in the literature (4, 5) and has also been solved with the assumptions that wetting is very rapid and that the rate of change of momentum is negligible. See Section I of the Appendix. For time-dependent contact

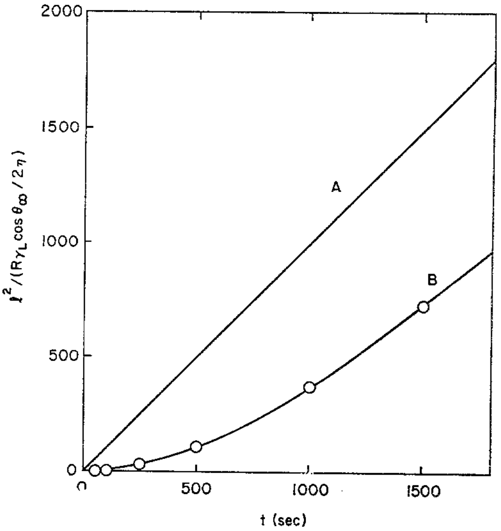

FIG. 3. Similar to Fig. 2 except on a linear plot at short times.

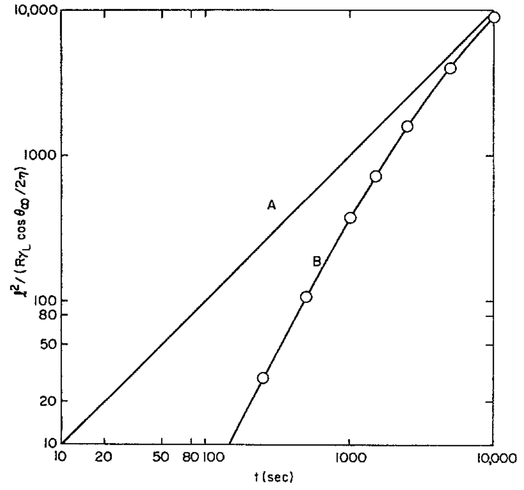

FIG. 2. Calculated data for the penetration distance of a polymer melt into a capillary comparing Eq. [8] with [5] on a log-log plot over long times. $a = 1$, $\cos \theta_\infty = 1$, and $c = 0.001\ \text{sec}^{-1}$.

angles, however, we have

$$l\frac{dl}{dt} = \frac{R^2}{8\eta} \cdot \left[\frac{2\gamma_L(\cos\theta_\infty)(1 - ae^{-ct})}{R} \pm \rho g l\right]. \qquad [9]$$

This equation has no general solution of an elementary form. Special cases may be solved simply. Thus, when $R \ll 1$, the contribution of the hydrostatic term becomes negligible and may be dropped and the equation thereby reverts to Eq. [8]. This, however, is not the case for fine capillaries when $R \approx 0.1$ cm. At very short times, a solution may be affected as in Section I of the Appendix except that $m = R\gamma_L (\cos\theta_\infty)(1 - a)/4\eta$. Also at very long times, $m = R\gamma_L (\cos\theta_\infty)/4\eta$. Intermediate times would require approximate solutions.

With the exception of a change in the numerical coefficient, flow into fine slits is identical in form to capillary penetration. See Section II of the Appendix.

APPENDIX

I. Vertical Capillary; cos θ_∞ *= Constant.* For an ascending or descending column of liquid in a capillary, the capillary pressure is reduced or increased by the hydrostatic pressure $\rho g l$ of the liquid column. Substituting in Eq. [4] leads to

$$\frac{dl}{dt} = \frac{R^2}{8\eta l}\left[\frac{2\gamma_L(\cos\theta_\infty)}{R} \pm \rho g l\right]. \qquad [10]$$

Invoking assumptions previously mentioned and rearranging for $+\rho g l$ leads to

$$\frac{l\,dl}{(m + nl)} = dt,$$

where $m = (R\gamma_L \cos\theta_\infty)/4\eta$ and $n = \rho g R^2/8\eta$. Integration leads to the following when $l = 0$ at $t = 0$:

$$l - \frac{m}{n}\log_e (m + nl) = nt - \frac{m}{n}\log_e m. \qquad [11]$$

For an ascending column, we have by inspection

$$l = \frac{m}{n}\log_e (m - nl) = -nt + \frac{m}{n}\log_e m. \qquad [12]$$

Noting, in this case, that the equilibrium height l_∞ achieved in a vertical column is given by

$$l_\infty = \frac{2\gamma_L \cos\theta_\infty}{R\rho g}$$

and that $l_\infty = m/n$, we can rearrange Eq. [12] to the equivalent form

$$\log_e \frac{l_\infty}{l_\infty - l} - \frac{l}{l_\infty} = \frac{nt}{l_\infty} = \frac{R^2\rho g}{8\eta l_\infty} \cdot t,$$

which is identical to the equation of Ligenza and Bernstein (4). Taking the first two terms for the expansion of $\log_e[l_\infty/(l_\infty - l)]$, leads to the further approximation

$$l^2 = \frac{R^2\rho g l_\infty}{4\eta} \cdot t = \frac{R\gamma_L \cos\theta_\infty}{2\eta} \cdot t,$$

which differs from Ligenza and Bernstein's calculation by a factor of 2 owing to an error in their published manuscript. This last equation is seen to be identical to Eq. [5] for the case of the horizontal capillary.

II. Flow between Slits or Parallel Plates. The capillary flow into slits or parallel plates may offer certain experimental advantages. For a straight horizontal channel of rectangular cross section having width W and height H, the average velocity is given by (2) $(W \gg H)$

$$\bar{v} = \tfrac{2}{3}\, v_{\text{max.}} = \tfrac{2}{3}\left(\frac{H^2 P}{8\eta l}\right),$$

where the capillary pressure is the only driving force, $P = P_c = 2\gamma_L \cos\theta_\infty/H$, and

$$\frac{dl}{dt} = \frac{H\gamma_L \cos\theta_\infty}{6\eta l}.$$

This is similar to the solution given by Bikerman (6) by a different method. With the exception of the coefficient (1/6), this equation is identical to the capillary case and the several solutions developed earlier in the report apply to this problem with a simple change of the numerical factor.

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