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The Rheology of Wetting By Polymer Melts

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ABSTRACT

Theoretically, the rate of capillary penetration of a polymer melt into a slit, a model for a surface irregularity, has been shown to depend on $\gamma \cos \theta / \eta$ where γ refers to the surface tension of the liquid, η its viscosity and θ a time-dependent contact angle. Analytical expressions relating the depth of penetration with time have been experimentally verified by observations of the penetration of molten polyethylene and poly-(ethylene-vinyl acetate) into aluminum channels. Values of η , calculated from the observed data, agree closely with independent determinations of this material parameter. A theoretical treatment has also been developed which describes the velocity of spreading of a liquid drop over a flat surface. Flow equations for the flow of free films were adapted for this purpose. The spreading velocity is predicted to depend on the product of three factors (1) a scaling factor, $(\gamma/\eta R_0)$, where R_0 is the initial radius of curvature, (2) $\cos \theta_e (1 - \cos \theta / \cos \theta_e)$ where θ_e refers to the equilibrium value of θ , and (3) geometric terms. After demonstrating that a drop of molten polymer may be treated as a spherical cap, the predicted dependence of spreading rate on drop size, $\cos \theta_e$ (nature of the substrate) and the scaling factor was experimentally verified. Some discrepancies noted at long times and high temperatures are discussed.

INTRODUCTION

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

Accordingly, the flow of a polymer melt over a surface under the influence of surface tension forces has been studied by observing separately (a) the kinetics of spreading of a drop—to obtain information about the mechanism of surface transport, e.g., viscous flow or surface diffusion, and (b) the rate of penetration into a channel or slit—a system which is a model for a surface irregularity. The important factors controlling the rate of wetting were

studied, and quantitative techniques were developed for analyzing such diverse but important variables as substrate surface energy, polymer melt viscosity, and time and temperature.

THEORY

Penetration of a Liquid Into Horizontal Slits:

Classically, [1] the rate of penetration $\frac{dl}{dt}$, of a liquid into a slit of height

H and width W ($W \gg H$) under the influence of surface tension forces only is:

$$l \frac{dl}{dt} = \frac{H}{6} (\gamma \cos \theta_e / \eta), \quad (1)$$

where θ_e is the equilibrium advancing contact angle; γ , the surface tension of the liquid; η the viscosity; and l the distance penetrated after time t .

Since $\frac{\gamma}{\eta} \cos \theta_e$ is a constant, Equation (1) can be integrated directly to give:

$$l^2 = \frac{H}{3} (\gamma \cos \theta_e / \eta) t \quad (2)$$

Newman [2] has pointed out that Equation (2) is no longer correct when $\cos \theta$ depends on time and is not at its equilibrium value, $\cos \theta_e$. Throughout the remainder of the text, a time-dependent contact angle will simply be designated as θ . Substitution of θ in Equation (1) followed by integration by parts leads to:

$$l^2 = \frac{H}{3} (\gamma \cos \theta / \eta) \cdot t \left[1 - \frac{1}{t \cos \theta} \int_0^t t \left(\frac{d \cos \theta}{dt} \right) dt \right] \quad (3)$$

Since $d \cos \theta / dt$ is positive, the time dependence of the advancing contact angle therefore, is seen to result in a retardation of penetration. As $(d \cos \theta / dt) \rightarrow 0$, $\cos \theta \rightarrow \cos \theta_e$, and Equation (3) reduces to the classical equation.

For experimental purposes, it is more convenient to rewrite Equation (3) in terms of the slope $n(t)$ of a plot of $\log l^2/H$ vs $\log t$:

$$l^2 = \frac{H}{3} (\gamma \cos \theta / \eta) \cdot t / n(t) \quad (4)$$

When $\cos \theta \rightarrow \cos \theta_e$, $n(t) \rightarrow 1$.

The double logarithmic plot of l^2/H vs t also provides an experimental criterion for the validity of the various penetration equations. When $n(t) =$

1, the classical equation holds and γ/η can then be directly determined, provided $\cos\theta_*$ is known. When $n(t) > 1$, Equations (3) and (4) are applicable. In order to evaluate γ/η from such penetration plots, one may resort to either representing the time dependence of $\cos\theta$ by some mathematical function [2] or to more general extrapolation procedures. Utilizing the latter approach, it is readily seen from Equation (3) that the quantity l^2/Ht may be extrapolated to $(1/t) \rightarrow 0$ giving an intercept equal to $1/3(\gamma/\eta)$ if $\cos\theta$ is an inverse function of time. However, if $n(t) \approx 1$, and $\cos\theta_* = 1$, (i.e. the liquid wets the surface) $\cos\theta$ could be taken to be equal to $\cos\theta_*$; this is a satisfactory approximation since the value of $\cos\theta$ changes less than 10% for $\theta < 20^\circ$; γ/η may then be calculated from Equation (4).

The Spreading of a Spherical Drop:

An analytical expression for the velocity of spreading of a sessile drop is not reported. This section develops a treatment which describes the velocity of spreading of a liquid drop based on flow equations developed for the flow of free films [3]. These equations lead to the following expressions for the average velocity $\langle V \rangle$ of a liquid film of uniform thickness, δ , flowing under the influence of a constant pressure, P :

$$\langle V \rangle = \frac{dr}{dt} = \frac{1}{3} \frac{\delta^2}{\eta} \frac{\partial P}{\partial r} = \frac{1}{3\eta} \tau_{\max} \cdot \delta \quad (5)$$

where $\frac{\partial P}{\partial r}$ is the pressure drop in the direction of flow r , τ_{\max} is the maximum shear stress and r the base radius of the drop. The thickness, δ , is a dynamic thickness defined by:

$$\delta = Q/2\pi r \cdot \langle V \rangle \quad (6)$$

where Q is the volumetric flow rate and $2\pi r$ the width of the drop.

To apply these formulae to the spreading of drops, one has to take into account that:

1. the pressure difference causing flow is not constant during spreading.
2. the thickness of the drop is not uniform.

These two factors will affect the magnitude of the shear stress, τ_{\max} , which can be evaluated from the equivalent expression:

$$\tau_{\max} = \frac{\partial P}{\partial r} \cdot \delta = (\text{Force/Vol}) \cdot \delta \quad (7)$$

Since $(\partial P/\partial r)$ is not a constant, we will use the second equality and express the shear stress in terms of $F(t)$, a time dependent force.

If only surface tension forces are considered, it is seen from Figure 1, that the force acting at the liquid/solid interface is given by:

$$F = \gamma_S - (\gamma_{SL} + \gamma \cos\theta) \quad (8)$$

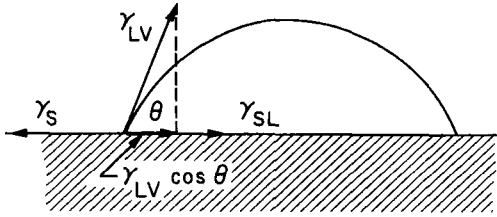


Figure 1. Surface tension forces acting at the perimeter of a sessile drop.

Where γ_S is the surface tension of the solid substrate,* γ_{SL} , the surface tension acting in the solid/liquid interface and γ the surface tension of the liquid in equilibrium with its vapour. At equilibrium one has, from Young's equation:

$$\gamma \cos \theta_* + \gamma_{SL} = \gamma_S \quad (9)$$

hence $F \rightarrow 0$ as $\cos \theta \rightarrow \cos \theta_*$.

The surface tension forces act at the perimeter of the drop. The total force/unit volume acting on a sessile drop of volume $V_o = 2\pi/3(R_o)^3$ is therefore:

$$\begin{aligned} \frac{2\pi r F(t)}{V_o} &= \frac{2\pi r \gamma \cos \theta_*}{V_o} \left[\frac{\gamma_S - \gamma_{SL}}{\gamma \cos \theta_*} - \frac{\cos \theta}{\cos \theta_*} \right] \\ &= \frac{3 r \gamma \cos \theta_*}{R_o^3} [1 - \cos \theta / \cos \theta_*] \quad (10) \end{aligned}$$

The maximum shear stress is therefore:

$$\tau_{\max} = \frac{3 r \gamma \cos \theta_*}{R_o^3} [1 - \cos \theta / \cos \theta_*] \cdot \delta \quad (11)$$

and the velocity of spreading:

$$\langle V \rangle = \frac{\gamma \cos \theta_*}{\eta} [1 - \cos \theta / \cos \theta_*] (r/R_o) (\delta/R_o)^2 \quad (12)$$

It remains to find a suitable expression for δ^2 , the equivalent thickness of the drop. When the drop shape can be approximated by that of a spherical cap, it is possible to determine δ directly by means of Equation (6), since the volume of liquid ΔV that has left the domain of the original hemisphere can be calculated; the volumetric flow rate Q follows by differentiation of ΔV with respect to time. The exact equivalent width, remains, however, still to be determined.

* It is not necessary or possible to specify the surface tension of the solid explicitly, since the exact composition of the substrate surface is not known. Even though the present experiments are carried out on aluminum plates, the surface layer probably consists of hydrated aluminum oxide.

Another possibility is to assume that δ must represent some average thickness $\langle \delta \rangle$ and to let $\langle \delta \rangle$ be proportional to the height, h , of the drop. The proportionality constant may, however, itself be a function of time or drop shape which is characterized by the angle θ . Replacing δ^2 by $\langle \delta \rangle^2$ and assuming:

$$\langle \delta^2 \rangle = a(\theta) \cdot h^2 \quad (13)$$

one obtains the following expression for the reduced spreading velocity $d(r/R_o)/dt$:

$$\langle v \rangle = a(\theta) \frac{\gamma \cos \theta_*}{\eta R_o} (1 - \cos \theta / \cos \theta_*) (r/R_o) (h/r_o)^2 \quad (14)$$

For a spherical cap, the quantities r/R_o and h/R_o are given [1] by the well known equations:

$$\frac{r}{R_o} = [2 \sin \theta (1 + \cos \theta) / (2 + \cos \theta) (1 - \cos \theta)]^{1/3} \quad (15)$$

$$\frac{h}{r} = (1 - \cos \theta) / \sin \theta \quad (16)$$

Separating all the variables in Equation (14) which depend explicitly on θ , we obtain:

$$\frac{d(r/R_o)/dt}{(r/R_o) \cdot (h/R_o)^2 (1 - \cos \theta / \cos \theta_*)} = a(\theta) \frac{\gamma \cos \theta_*}{\eta R_o} \quad (17)$$

The significance of this equation is that (a) the spreading rate is determined by the material quantities $\gamma \cos \theta_* / \eta R_o$; (b) for a given liquid, the spreading rate should depend on the initial radius of the drop, which implies a mass-effect; and (c) the spreading rates of the same liquid on different surfaces is proportional to $\cos \theta_*$ when $\cos \theta = 0$.

EXPERIMENTAL

Two polymer types were investigated, i.e. a low-density polyethylene and a poly-(ethylene-vinylacetate) copolymer. The polyethylene, obtained from Union Carbide Corp., and designated DYLT, has a number-average molecular weight of 7,000 and a density of 0.91 g/cm³ at 23°C. The copolymer of ethylene and vinyl acetate, manufactured by duPont and sold under the trade name of ELVAX 220, has a density of 0.95 g/cm³ at 23°C and a vinyl acetate content of 27-29%. Both samples were extracted for 6 hours in a Soxhlet apparatus with ligroine (B.P. 30-60°C) and anhydrous ethyl ether. The extracted polymers were then dried under vacuum at 70°C for 8 hours. The samples were studied in the "as is" and extracted conditions.

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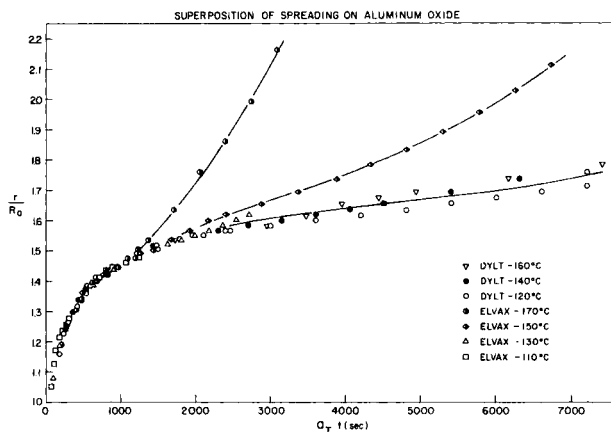


Figure 4. Reduced spreading distance as a function of time for DYLt and ELVAX at various temperatures. Data shifted to that obtained with DYLt at 120°C (Al. surfaces only).

Drop spreading was investigated on clean aluminum, which has a high energy surface and on a fluorinated polymer (Viton B) which has a low energy surface. The aluminum surface was prepared as follows: High purity aluminum (99.9%) was rolled and cut to the size of 1-1/2 in. x 1/2 in. x 1/32 in. After annealing, the aluminum plate was mechanically polished on a grinding wheel to 3 microns and then electropolished in a solution of H₃PO₄ (817 ml), H₂SO₄ (134 ml), H₂O (40 ml), and CrO₃ (40 g) at 70°C in a manner discussed by Thomas [4]. The electropolished aluminum surface was smooth, highly reflecting and free from organic contamination as judged by the observation of zero contact angles with water and glycerol.

The Viton surface was prepared by casting a film on a clean glass surface from a solution of Viton (25 g), triethylenetetramine (0.6 g), and methyl-ethylketone (120 g). The film was air dried and cured at 60°C for 3 days. A contact angle with glycerol of 99 ± 1° was observed on this surface.

Contact angles were measured with a contact angle Goniometer and an environmental chamber built by Ramé-Hart, Inc. This goniometer provides an overall magnification of 15.4 x. Test surfaces were placed in the environmental chamber and heated to the measured temperature monitored by a Chromel-Alumel thermocouple. A weighed polymer pellet (0.003 g) was placed on the test surface and the contact angle of the sessile drop measured as a function of time. Contact angles were measured for DYLt at 120°, 140°, 160°C and for Elvax at 110°, 130°, 150°, and 170°C. In the experiments the environmental chamber was kept open to the atmosphere.

The channels for penetration studies were prepared by mounting two electropolished aluminum plates between uniform thickness washers by means of four screws. The space between the plates was approximately 0.04 cm and was measured separately for each experiment. In the penetration

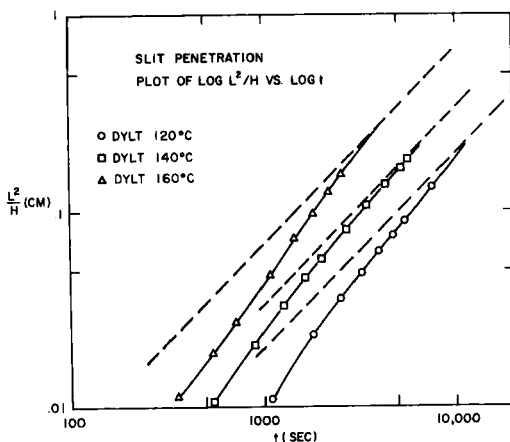


Figure 2. Penetration of polyethylene into an aluminum channel as a function of time plotted according to equation (4) (solid line) and equation (2) (dashed line).

experiment, the aluminum channel was placed horizontally in the environmental chamber. After reaching thermal equilibrium, a thin compression molded sheet of the polymer was placed adjacent to the opening end of the channel and the penetration measured with a cathetometer as a function of time.

Melt viscosities were measured over a range of shear rates with the Instron capillary rheometer at temperatures corresponding to those used above.

RESULTS

Slit Penetration:

To test the previous analysis, the penetration data are plotted as $\log l^2/H$ vs $\log t$ in Figure 2; this figure includes the relationship which would have been observed if the classical equation had been applicable to the data. The retardation of penetration is clearly evident. In Figure 3 the suggested extrapolation of l^2/Ht to $(1/t) \rightarrow 0$ for the determination of γ/η is carried out. The plot is non-linear, and unless the data are obtained over a long time scale, the extrapolation procedure would give erroneous results. If the intercept is indeed equal to $1/3(\gamma/\eta)$, as predicted, then the viscosity calculated from this value, using known values of γ [5], should be equal to the independently measured shear viscosity. This comparison, listed in Table 1, shows that good agreement between these two independent estimates of the viscosity is obtained. It is concluded, therefore, that the extrapolation procedure is self-consistent. Hence, without introducing an explicit function for the time dependence of $\cos\theta$, the value of γ/η can be determined from the penetration data.

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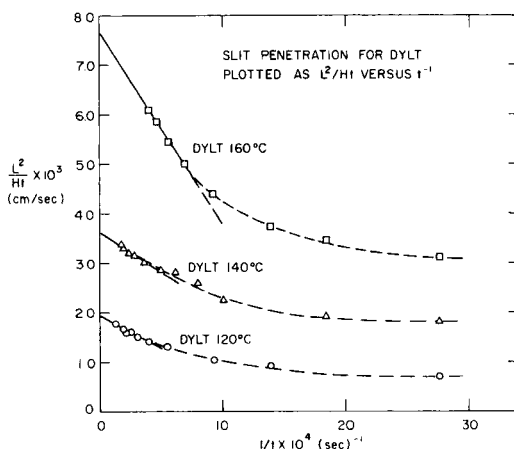


Figure 3. Extrapolation procedure for penetration data.

Drop Spreading:

When the drop shape can be approximated by that of a spherical cap, the base radius r and height h are functions of θ only and may be calculated by means of Equations (15) and (16). Conversely, if at some angles θ the base radius r is measured, a value for R_0 can be obtained. A constant value of R_0 , therefore, implies the validity of the spherical cap geometry. The values of R_0 quoted in this paper were calculated by this procedure and found to be independent of the angle θ .

One may therefore rewrite the expression for the spreading velocity (Eqn. 14):

$$\langle v \rangle = a(\theta) (\gamma/\eta R_0) (\cos\theta_\infty (1 - \cos\theta/\cos\theta_\infty)) \cdot f(\theta) \quad (18)$$

where $f(\theta) = (r/R_0) \cdot (h/R_0)^2$.

This expression has several important implications:

1. For a given value of $\cos\theta_\infty$, curves of r/R_0 vs t can be superposed by means of a shift factor equal to $\gamma/\eta R_0$, since all other terms on the right hand side of Eqn. (18) are functions of θ only.

Table 1. Comparison of Viscosities for DYLT (Poises)

$T(^{\circ}\text{C})$	120	140	160
Penetration ^(a)	4.6×10^3	2.7×10^3	1.2×10^3
Rheometer ^(b)	5×10^3	2.4×10^3	1.3×10^3

^(a) values of γ at the temperature indicated were calculated from data given in reference 5.

^(b) value at 1 Sec⁻¹.

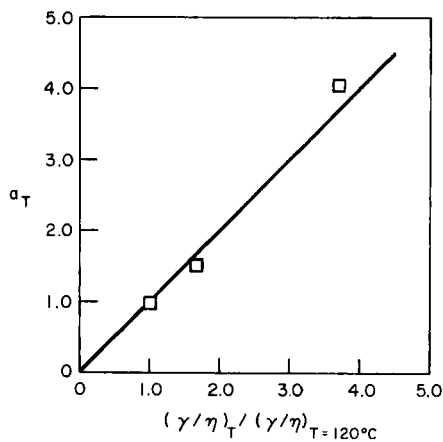


Figure 5. Shift factor a_T versus $(\gamma/\eta)_T/(\gamma/\eta)_{T=120^\circ\text{C}}$ for DYL T (Al. surfaces).

2. The shift factor $\gamma/\eta R_0$ is proportional to $1/R_0$, the initial radius of the drop. This implies a mass-effect since the mass of the drop is equal to $\rho \cdot (2\pi/3) R_0^3$, where ρ is the density of the liquid.
3. Data obtained on surfaces with unequal values of $\cos\theta_0$ do not superpose by means of a shift equal to $\gamma/\eta R_0$.

Furthermore one has to examine the dependence of the proportionality factor $a(\theta)$ on θ . The data will, therefore, be analyzed with respect to superposition and the mass effect, the function $a(\theta)$ and the influence of $\cos\theta_0$ on spreading behavior.

A. Superposition:

In Figure 5 all spreading data on aluminum surfaces, reduced to the data obtained with DYL T at 120°C , are presented in a plot of r/R_0 vs $a_T \cdot t$, where a_T is the shift factor (listed separately in Table 2):

$$a_T = \gamma/\eta R_0 \tag{19}$$

For $\theta > 40^\circ$ the superposition is excellent for both DYL T and ELVAX. The DYL T data reduce over the whole time scale; marked deviations are, however, observed for the ELVAX series for $\theta < 40^\circ\text{C}$. The cause of this is not known, and may be due in part, to degradation of the ELVAX samples at higher temperatures and long times. At 170°C the ELVAX drop discolored slightly in the later stages of the experiment; unextracted ELVAX became dark brown under the same conditions.

Since a plot of r/R_0 vs $\log(a_T \cdot t)$ is linear for $\theta > 40$ with a slope equal to 0.34, the velocity can be calculated by means of the relationship:

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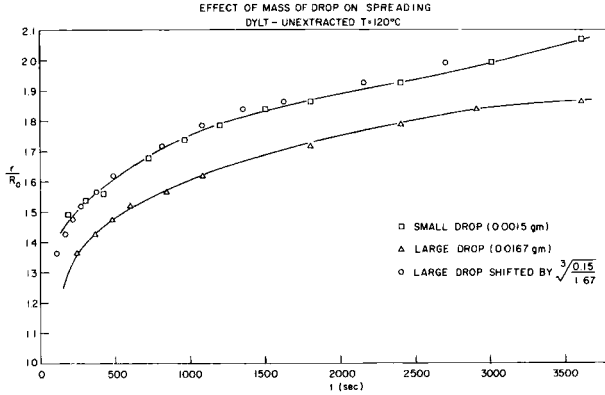


Figure 6. Effect of the mass of the drop on spreading distance for DYL T (unextracted) $T = 120^\circ\text{C}$ (Al. surfaces).

$$d(r/R_0)/dt = 0.34/t. \quad (20)$$

In the subsequent analysis, only the spreading data for $\theta > 40$ are used to establish quantitative relationships.

Having obtained the shift factors, one may now verify the functional dependence of a_r .

In Figure 5 we have plotted the DYL T-shift factors versus the ratio's γ/η , obtained from the slit penetration data. Since R_0 is approximately the same, the plot should be linear, and pass through the origin. This prediction is borne out by the data.

The dependence of the shift factor on R_0 —(mass-effect) is illustrated in Figure 6. It is seen that the two curves superpose over the whole time scale a shift equal to $(m_1/m_2)^{1/3}$ i.e. to the ratio $(R_1/R_2)_0$. This fact provides the strongest evidence for the viscous nature of the drop spreading.

B. The proportionality Factor $a(\theta)$:

In Figure 7 we have plotted the quantity

$$u(\theta) = \frac{d(r/R_0)/dt}{(r/R_0)(h^2/R_0^2)(1 - \cos\theta/\cos\theta_*)} = a(\theta) \cdot (\gamma/\eta R_0) \cos\theta_* \quad (21)$$

as a function of θ using data obtained with DYL T. As Eqn. (21) implies and the data show, this plot allows for a reduced representation for a given value of $\cos\theta_*$. The shift factors (listed in Table 2) are equal to the reciprocal of the r/R_0 vs t shift factor. Figure 7 shows that for $\theta > 60^\circ$, $a(\theta)$ is indeed a constant. Having already determined the value of $\gamma/\eta R_0$ and the shift factors,

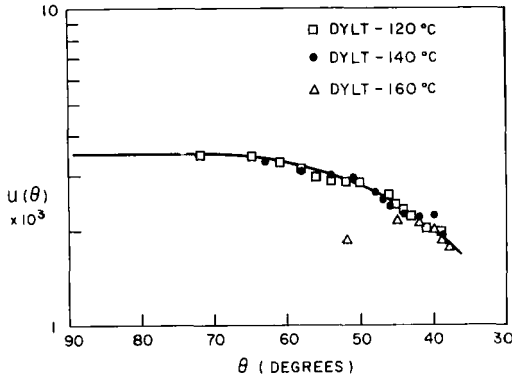


Figure 7. The dependence of $u(\theta)$, equation 21, on the contact angle θ . (Al. surfaces).

the value of a can be calculated. The result, listed in Table 3 shows that $a = 0.064$, which implies $\langle \delta \rangle \sim \frac{1}{4}h$, a physically reasonable value. For $\theta < 60^\circ$ the value of a decreases by a factor of 2.

C. The Influence of $\cos\theta_*$ on Spreading Behavior:

Since it is established that the proportionality factor a is primarily a function of θ , one may verify Eqn. (18) by using it to predict the spreading velocity for a liquid over a surface with a given value of $\cos\theta_*$.

The spreading of ELVAX drops on Viton B, cast as a film on a microscope slide, was measured and the equilibrium contact angle θ_* determined to be

Table 2. Shift Factors for r/R_0 and $u(\theta)$ vs t

ELVAX			DYLTL		
T(°C)	r/R ₀	u(θ)	T(°C)	r/R ₀	u(θ)
110	1	1	120	1	1
130	2	0.5	140	1.5	0.65
150	5.4	0.21	160	4.1	0.22
170	7.6	0.14			

Table 3. Calculation of a for DYLTL

	120°C	140°C	160°C
$a(\gamma/\eta R_0)$	3.50×10^{-3}	5.3×10^{-3}	14.0×10^{-3}
γ/η	6×10^{-3}	10×10^{-3}	22×10^{-3}
R_0 (cm)	0.112	0.115	0.100
a	0.065	0.062	0.064

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equal to $59^\circ (\pm 1^\circ)$. Since $(\cos\theta_*)_{AL} = 1$, the spreading velocity on Viton should be related to the spreading velocity on aluminum by:

$$[d(r/R_o)/dt]_{\text{Viton}} = [(dr/R_o)/dt]_{\text{Al}} [\cos\theta_*(1 - \cos\theta/\cos\theta_*)/(1 - \cos\theta)] \quad (22)$$

Hence from the $\theta - t$ data on aluminum the corresponding velocity at angle θ on Viton can be calculated. By interpolation $(dr/R_o/dt)_{\text{Viton}}$ for the observed θ, t data on Viton is obtained, subsequent integration of the velocities yields the reduced distance r/R_o . The so predicted values of r/R_o are compared to the experimentally observed values in Table 4. Excellent agreement is obtained for both the 110°C and 130°C data. Since the calculation is very sensitive to the value of $\cos\theta_*$ used, the value of θ_* required to achieve the good fit obtained serves as an independent check on the experimentally measured value of θ_* .

Table 4. Prediction of Spreading on VITON for ELVAX

VITON—110°C				VITON—130°C		
t(sec)	θ	$r/R_o(\text{calc})^a$	$r/R_o(\text{exp})$	θ	$r/R_o(\text{calc})^a$	$r/R_o(\text{exp})$
480				80	—	1.088
600	79	—	1.097	76	1.127	1.123
720	76	1.122	1.123	73	1.157	1.151
840	74	1.143	1.142	71	1.179	1.169
960	72	1.161	1.160	69	1.199	1.188
1080	70	1.176	1.178	67	1.214	1.207
1200	68	1.189	1.197	65	1.225	1.226
1500	66	1.213	1.216	63	1.243	1.246
1800	64	1.229	1.236	62	1.255	1.256
2100	63	1.240	1.246	—		
2400	62	1.249	1.256	61	1.271	1.266
3000	60	1.255	1.276	60	1.280	1.276
∞	58	1.297		59	1.286	

(^a) Calculated from equation (22) and subsequent graphical integration.

DISCUSSION

The experimental results presented in the previous section are in good agreement with the theoretical analysis, even though the theory developed is based solely on hydrodynamic considerations. That one is dealing with an essentially viscous process is most clearly evident from the drop spreading data.

The spreading times obey the Scaling Law, derived by Herring [6], for viscous flow. This law states that the times required for a given change of

shape of a series of regularly shaped objects, differing only in size, are related to each other by the expression:

$$\Delta t_2 = R_2/R_1 \cdot \Delta t_1$$

where R_1 is a characteristic dimension of object 1, R_2 that of object 2; Δt_1 the time required for a certain change in the shape of object 1 and Δt_2 , the time required for the same change a shape for object 2. Since the whole r/R_0 vs t curve is shifted by R_2/R_1 , this means also that from the shape of the r/R_0 vs t curve no specific flow mechanism can be inferred.

Even though polymer melts are very non-Newtonian, the effect of a non-Newtonian viscosity has been neglected. This is justified in view of the small shear rates involved. Taking $\langle \delta \rangle \approx \frac{1}{4}h$, one obtains from Eqn. (11) a value of the max shear stress, at $t = 0$, of 225 dynes/cm². For a liquid with a viscosity of 10³ poises, the smallest viscosity encountered in this work, the max. shear rate would be only $\sim 0.2 \text{ sec}^{-1}$. If corrections for non-Newtonian flow are necessary, the equations for the flow of such a film, derived by Biermann [7], should be used.

Comparing the two expressions for the spreading velocity and the rate of penetration into a slit:

$$\langle v \rangle = d(r/R_0)/dt = (\gamma/\eta R_0) \cos\theta_* (1 - \cos\theta/\cos\theta_*) f(\theta) \quad (\text{spreading})$$

$$\langle v \rangle = dl/dt = H/6 (\gamma/\eta) \frac{\cos\theta}{l} \quad (\text{penetration})$$

the question arises whether or not the time dependence of $\cos\theta$ measured in the drop spreading experiment can be used to calculate the rate of penetration. Because of the dissimilar geometries involved—penetration occurs between fixed boundaries, while in spreading there is always one free boundary—the two $\cos\theta$ functions cannot be used interchangeably. Nevertheless, the two $\cos\theta$ functions have a similar shape as can be derived from further analysis of the penetration data, once γ/η is known.

Hence the assumption that $\cos\theta$ is some inverse function of time, which leads to the extrapolation procedure suggested for the penetration data, is justified.

Two explicit empirical formulae for the time dependence of $\cos\theta$ have been suggested, the one by Newman [2]:

$$\cos\theta = \cos\theta_* [1 - ae^{-ct}] \quad (23)$$

and the other by Kwei, Schonhorn and Frisch [8]:

$$\frac{\cos\theta}{\cos\theta_*} = kt/(1 + kt) \quad (24)$$

Such formulae, if generally valid, would simplify many of the calculations. For the drop spreading data these formula imply (a.o.):

$$h/R_o = [2e^{-ct}/3 - e^{-ct}]^{1/3} \quad (\text{Newman, } a = 1) \quad (25)$$

or

$$r/R_o = (1 + 2kt)^{1/2}/(1 + 1.5 kt)^{1/3} \quad (\text{K.S.F. } \cos\theta_* = 1) \quad (26)$$

In practice, for our data at least, the prediction say, of r/R_o vs t using (26) and k from (24), turns out to be rather disappointing; similarly, using $a = 1$ and c obtained from (23) does not permit h/R_o to be described within experimental accuracy. These formulae are therefore best regarded as strictly empirical.

The experimental results obtained in the investigation differ significantly from the earlier data of Schonhorn, Frisch and Kwei [9]. These authors discussed their drop spreading data exclusively in terms of the shift factor, a_τ , required to achieve superposition of r/R_o vs t curves, where

$$a_\tau = \gamma/\eta L_w$$

and L_w a scaling length. L_w was found to be independent of the size of the drop, and increased by a factor 2 when spreading data obtained on Teflon were shifted to the data obtained on Al. Since the present data clearly show a mass effect, the scaling length in the present data is equal to R_o . The increase in scaling length for spreading on a low energy surface can be understood since Eqn. (14) shows that for $t \rightarrow 0$ the shift factor for two dissimilar surfaces is equal to $(\gamma/\eta R_o) \cdot \cos\theta_*$. When $\cos\theta_* < 1$ the apparent scaling length, increases. Furthermore, Eqn. (14) shows that superposition of r/R_o vs t plots by means of a shift along the time axis is not possible for dissimilar surfaces. Hence the kinetics of drop spreading cannot be discussed on the basis of superposition only. As previously shown, however, the velocities can be accurately predicted using the value of $\cos\theta_*$ and the spreading velocities observed on one of the surfaces.

These significant differences are probably due to two major changes in experimental procedure. The aluminum plates in the present work were prepared by electropolishing, water as well as glycerol spreads completely on these surfaces. The aluminum plates used by Schonhorn, Frisch and Kwei were prepared by degreasing and subsequent treatment with a solution of 0.083 M sodium dichromate in 4 M sulphuric acid. As reported, water wets this surface, but the spreading of glycerol requires more than 1 hour [8], whereas on the surfaces used in this study, glycerol spreads in about 1-2 minutes. Secondly, the polymers used in the present investigation were extracted as described in the experimental section. Extraction increases the

viscosity; also the extracted polymers are less susceptible to degradation at 170°C.

One may conclude, therefore, that the particular procedure used in preparing surfaces has a controlling effect on the kinetics of spreading but not, apparently, on the shape of the spreading drop. In the present work, as well as in the earlier work of Schonhorn, Frisch and Kwei [9] the observed shape is that of a spherical cap.

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