AIP Journal of Applied Physics

Kinetics of Wetting of Surfaces by Polymer Melts

H. Schonhorn, H. L. Frisch, and T. K. Kwei

Citation: Journal of Applied Physics **37**, 4967 (1966); doi: 10.1063/1.1708174
View online: http://dx.doi.org/10.1063/1.1708174
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/37/13?ver=pdfcov
Published by the AIP Publishing

JOURNAL OF APPLIED PHYSICS VOLUME 37, NUMBER 13 DECEMBER 1966

Kinetics of Wetting of Surfaces by Polymer Melts

H. Schonhorn, H. L. Frisch, and T. K. Kwei
Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey
(Received 7 July 1966)

The kinetics of wetting of both high-energy (aluminum, mica) and low-energy (FEP Teflon) surfaces by thermostated polyethylene and ethylene–vinyl acetate copolymer melts in air were followed by the rate of approach of the apparent contact angle θ to its final value θ_∞ and the change of the radius of the base of the polymer melt drop, r, with time. The volume of the drops studied varied from 0.006 cm^3 to 0.028 cm^3 and θ could be studied in the interval from about $100° > \theta \geqslant \theta_\infty$. The melted polymer drops maintain the shape of a spherical segment. The reduced dimension r/r_0, where r_0 is the value of r when the contact angle is 90°, is a universal function of the reduced time $a_T t$, a dimensionless quantity. The reduced contact angle $\cos\theta/\cos\theta_\infty$, where $\cos\theta_\infty$ is the value of $\cos\theta$ at infinite time, can be represented by a function of the same variable $a_T t$. The shift factor a_T is given by $\gamma/L_w\eta$, where γ is the surface tension of the liquid, η is the viscosity, and L_w is a length characteristic of the polymer–substrate system.

I. INTRODUCTION

Adhesion concerns the formation of an interface between the liquid adhesive and the substrate. To obtain extensive contact between the liquid and the substrate, air (as well as contaminants) must be displaced from the surface of the solid adherend, i.e., the adhesive must wet the solid.[1] The final extent or degree of wetting is quantitatively expressed by the apparent final contact angle, θ_∞.[1,2] In the case of polymer drops on the surfaces used in our study, θ_∞ was approached, reproducibly after time lags varying from minutes to hours, depending on the temperature and system. The rate of wetting in these cases can be followed by (1) the temporal evolution of the apparent contact angle, $\theta = \theta(t)$, to θ_∞, or (2) by following the *apparent*[3] adherend area covered by the polymeric liquid drop. Drops of low molecular weight liquids, e.g., water, ethyl alcohol, etc., achieve θ_∞ in times smaller than observation times required for measuring the angle θ by means of a protractor mounted in the eye piece of a low-power telescope. Thus only method (2) has been employed to follow the rate of wetting,[1,2] although high-speed cinematography may allow one to follow rapid changes in θ and the drop shape and dimensions.

There is considerable experimental difficulty in following the beginning of the wetting process, about $\theta = 180°$, since stationary, thermally equilibrated drops in point contact with the flat adherend surface are hard to produce. The initial procedure employed by us sufficed only to obtain reliable data for contact angles not much larger than 90°. This is a serious limitation, since there may well be several kinetic stages of wetting. The experimental procedure employed in these measurements as well as the description of the polymers and adherend surfaces which we used are discussed in Sec. III of this paper.

It is generally believed that wetting (i.e., the displacement of air by the liquid) is achieved by capillary forces and retarded by the viscosity or generalized viscosity (consistency) of the liquid.[1,2,4,5] Independently of whether the flow occurred in the bulk of the spreading drop or some surface boundary layer, one would expect to solve for the wetting rate of (apparent) surface area coverage (by the drop) by equating the rate of change of the reversible work due to capillarity to the rate of energy dissipation due to viscous flow. Inertial effects can be neglected for these slow motions. Effects due to gravity are also negligible as long as the initial, lineal dimension of the molten polymer drop l_0 is smaller than

$$l_0 = (2\gamma/\rho g)^{\frac{1}{2}}, \tag{1}$$

where γ is the surface tension of the molten polymer, ρ the density, and g the gravitational acceleration. Thus using drops with $l_0\,[\sim(m/\rho)^{\frac{1}{3}}$, m the mass of the drops$]$ of the order of a fraction to several millimeters, we go from a region where gravity can be neglected to a region where the gravitational stress is of the order of the capillary stress.

If capillary forces balanced by "viscous" resistance were the sole forces acting in the wetting process then a characteristic scaling law would apply.[6] While scaling laws[6] were derived to apply to sintering processes, they are expected to apply equally well in the present context. If A is the wetted area after a duration of time t, then

$$A/l_0^2 = K(\gamma t/l_0\eta), \tag{2}$$

where K is a function of the indicated argument. The plane projection of the drop onto the adherend surface would be expected to be (more or less) circular. To minimize the reversible capillary work, one would expect that the free surface would appear in cross section as shown in Fig. 1(a) rather than 1(b) with a characteristic "cap" about the center of the drop and an advancing, projecting "foot."

---

[1] J. J. Bikerman, *The Science of Adhesive Joints* (Academic Press Inc., New York, 1961).

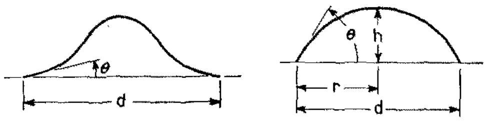
[2] D. D. Eley, *Adhesion* (Oxford University Press, London, 1961).

[3] We dispense from now on with using the adjective "apparent" since only apparent surface entities are susceptible to measurement by macroscopic means.

[4] K. Kanamaru, Kolloid-Z. **192**, 51 (1963).

[5] E. D. Shchukin, Yu. V. Goryunov, G. I. Den'shchikova, N. V. Pertsov, and B. D. Summ, Kolloidn. Zh. **25**, 108 (1963).

[6] C. Herring, J. Appl. Phys. **21**, 301 (1950).



(a) (b)

FIG. 1. (a) Expected cross section of a spreading liquid drop in contact with a planar surface; (b) experimentally observed cross section of the wetting liquid.

Previous attempts[7] to study the approach to θ_∞ in the contact angle of polymer drops with time have not concerned themselves with simultaneous studies of the drop-shape parameters nor the kinetics of wetting as revealed by changes in wetted area with time. The temporal evolution of θ was viewed,[4] at least in its final stages, as a relaxation phenomenon describable by a single constant relaxation time. While at first sight this viewpoint is attractive, we do not believe it suffices to account for what is seen.

In our investigations we considered the following questions:

(1) How are the kinetics of θ related to the kinetics of area-wetting as well as of other parameters determining the instantaneous shape of the drop?

(2) What are the basic physical variables (surface tension, density, melt viscosity, etc.) which enter, and what is the form of the basic scaling law which describes the wetting by various polymer drops of various surfaces over a considerable range in temperature and drop mass?

(3) What is the physical mechanism of wetting? In particular what is the nature of the forces acting in this system?

Our investigations indicate definite answers to the first two questions. They also point the way to an astonishing conclusion concerning question (3) which suggests strongly that we do not really understand the mechanism of wetting.

II. POLYMER SINTERING

Before we proceed to the description of our experiments on wetting we would like to review briefly certain results in sintering of polymers which already suggest that the surface behavior of these materials with large viscosities and only moderate surface tensions may be quite anomalous.

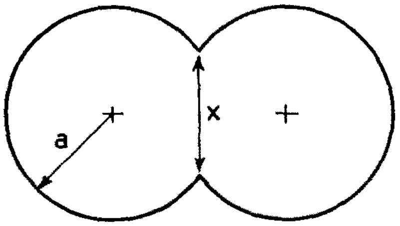


FIG. 2. Coalescence of two adjacent spheres in sintering.

In the classic sintering experiment one observes the coalescence of two adjacent spheres of polymeric material (cf. Fig. 2). The radius of the interface between the two spheres x (Fig. 2) increases in time because of the action of surface tension and when resisted only by viscous flow should satisfy the Frenkel law[7]

$$(x/a)^2=3\gamma t/2\eta a, \tag{3}$$

where a is the initial radius of the polymer spheres. We note that Eq. (3) has the form expected from dimensional scaling [cf. Eq. (2)]. This sintering law has been confirmed by Kuczynski[8] for viscous amorphous materials such as inorganic glasses. On the other hand, Kuczynski and Neuville[9] recognized the inadequacy of Eq. (3) in accounting for the behavior of poly-(methyl methacrylate) which appears to follow an empirical relation

$$(x/a^{3/5})^n=K(T)t \tag{4}$$

with neither the $\frac{3}{5}$ exponent of a, nor the n which varies from 5 at $T=127°\text{C}$ to 0.5 at 207°C, having any phenomenological significance. It is doubtful that non-Newtonian flow explains this behavior. The sintering of polytetrafluoroethylene also does not follow Eq. (3). Lontz[10] has suggested that viscoelastic effects may account for this departure.

III. EXPERIMENTAL

To eliminate effects due to thermal gradients, the test surfaces with a weighed polymer pellet were placed in a tube-type furnace for studying the progress of the wetting. The temperature of the furnace was monitored by a Chromel–Alumel thermocouple placed in the immediate vicinity of the polymer drop. The rear of the furnace was illuminated. The polymer pellet melted in the furnace to form a sessile drop. Simultaneous measurements of the contact angle θ, length of the drop in (apparent) contact with the substrate d, and height of the drop h were recorded as functions of time. These measurements were carried out by using a telescopic device built by the Gaertner Scientific Corporation with a ×10 magnification. The telescope was equipped with an ocular protractor and a micrometer for measuring both contact angle and linear dimensions of the sessile drop, with precisions of ±1.5 min of arc and ±0.00005 in., respectively. The drops were also photographed with a 35-mm Ihagee Exakta camera (magnification ~×2) mounted on the telescope. The beam-splitting lens allows one to see in the eyepiece a duplicate of the image at the focal plane of the camera. A spirit level on the telescope, mounted parallel to its optic axis, allows one to level it. The telescope can

---

[7] J. Frenkel, J. Phys. (U.S.S.R.) **9**, 385 (1945).

[8] G. C. Kuczynski, Trans. AIME **185**, 169 (1949).

[9] G. C. Kuczynski and B. Neuville, Notre Dame Conference on Sintering and Related Phenomena, June 1950.

[10] J. F. Lontz, in *Fundamental Phenomena in the Material Science*, L. J. Bonis and H. H. Hausner, Eds. (Plenum Press, New York, 1964), Vol. 1.

resolve 360 deg about its mounting post. The cross hairs in the eyepiece serve as a reference in leveling of the test specimen.

The method of measuring surface tensions of molten polymers has already been described.[11] The melt viscosities of the polymers were measured at 155°, 170°, and 181°C with a Tinius–Olsen capillary rheometer. The length of the capillary was 0.0313 in. and its radius was 0.02326 in. The applied stresses were varied in each experiment to obtain a range of shear rates from 5 to 100 $\sec^{-1}$. The flow curves indicated that the stress varied linearly with the shear rate at shear rates of about 10 $\sec^{-1}$. The viscosity values η employed by us were all taken at the constant shear rate of 10 $\sec^{-1}$. An Arrhenius plot of $\log\eta$ vs reciprocal absolute temperature was made, from which the viscosities at other temperatures were calculated.

Two polymers were used: (1) Elvax 220, a high-melt-index ethylene–vinyl acetate copolymer developed by duPont. The vinyl acetate content is 27–29 wt% of the polymer. The melt index of the copolymer is 125–175, and it has a density of 0.95 g/cm^3 at 30°C. (2) DYLT is a polyethylene supplied by Union Carbide Plastics Company. It has a number-average molecular weight of 10^4, approximately 45 methyl groups per 10^3 methylene groups, a melt index of 230, and a density of 0.917 g/cm^3 at 25°C. Both polymers appear not to have degraded within the duration of our experiments on all the surfaces employed.

Three surfaces were employed: (1) Aluminum plates $5\times1\times\frac{1}{16}$ in. were degreased and sulfochromated at 65°C. The sulfochromate solution was 0.083*M* sodium dichromate in 4*M* sulfuric acid. The specimen plates were rinsed thoroughly in de-ionized water and air-dried and stored in desiccators. Water spreads completely on these surfaces, $\theta_\infty{}^{25^\circ\mathrm{C}}=0$. (2) Freshly cleaved mica was employed. Water also spread completely on the mica. (3) FEP Teflon was used with no cleansing procedure other than a solvent wipe with trichloroethylene. Water $\theta_\infty{}^{25^\circ\mathrm{C}}=114\pm2^\circ$.

IV. EXPERIMENTAL RESULTS

The wetting kinetics of the ethylene–vinyl acetate copolymer, Elvax 220, was studied on the aluminum surface at temperatures from 118°–170°C; on FEP Teflon at 170°C and 151°C, and on mica at 151°C. Polymer pellets of various masses were employed with l_0 between 0.5–5 mm. The kinetics of wetting of polyethylene on Al was studied at 151°C. In all these cases the drop shape approximated very closely a spherical segment [cf. Fig. 1(b)] in the measured range of contact angles from somewhat larger than 90° to the final contact angle. The final contact angle of both polymers on the aluminum and the Elvax 220 on the mica surfaces was apparently 0°, although measurements could not be accurately carried out below 1°. The final contact angle of Elvax 220 on the FEP Teflon surface was 74°±1° at 170°C and 75°±1° at 118°C. These values conform to what would be predicted using Fowkes equations.[12]

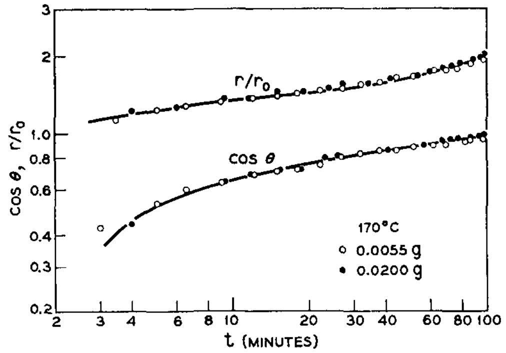


FIG. 3. Kinetics of spreading of Elvax 220 on aluminum.

Figure 3 shows a typical plot of the data. In Fig. 3, we plot $\cos\theta$ and the ratio of the radii at time t, $r=d/2$, to the radius at $t=0$, r_0 ($t=0$ when the contact angle is 90°) as a function of elapsed time, for Elvax 220 on Al at 170°C, for two different drop masses. The data are reproducible at each temperature and the characteristic features of the time dependence of r/r_0 and $\cos\theta$ exhibited in Fig. 3 are shown by all other curves on this and different substrates and temperatures. Thus we can dispense (for the sake of saving space) with showing other individual curves including the wetting rates of polyethylene on Al at 151°C. While for large times t, $\cos\theta$ in all cases appears to approach asymptotically $\cos\theta=1$, it is not clear from our data whether the radial velocity $v=dr/dt$, approaches asymptotically a constant value or a weakly decreasing function of the time.

The radius r_0 of the drop when the contact angle is 90° is directly proportional to l_0 or $m^{1/3}$. Thus, e.g., from the data in Fig. 3, the drop of mass $m_1=0.0055$ has a $(r_0)_1=0.1157/2$ while the drop of mass $m_2=0.0200$ has a $(r_0)_2=0.18/2$ and $(m_2/m_1)^{1/3}=1.54\approx(r_0)_2/(r_0)_1=1.56$. This fact is consistent with our observation that r of a drop is a universal function of θ, closely approximated by

$$r^3/V=(3/\pi)[\sin\theta(1+\cos\theta)/(1-\cos\theta)(2+\cos\theta)], \quad (5)$$

where V is the constant volume of the spreading drop, $V=m/\rho$, ρ the polymer density, which follows from the geometry of a spherical segment. Figure 4 shows a typical plot of the left-hand against the right-hand side of Eq. (5) for Elvax 220 on Al at 151°C and 170°C. Similarly the height of the drop, h, should, for a spherical segment, be related to r by

$$h/r=(1-\cos\theta)/\sin\theta. \quad (6)$$

Figure 5 shows an experimental test of this relation at 170°C; the agreement is satisfactory.

---

[11] H. Schonhorn and L. H. Sharpe, J. Polymer Sci. **3A**, 569 (1965).

[12] H. Schonhorn, Nature **210**, 896 (1966).

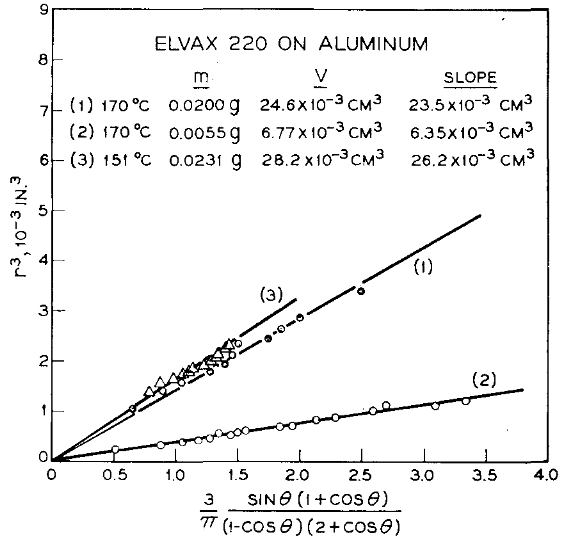


FIG. 4. Test of the spherical segment approximation according to Eq. (5).

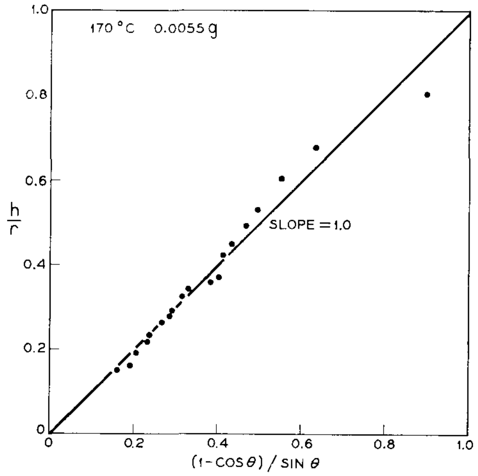


FIG. 5. Test of the spherical segment approximation according to Eq. (6).

The question arises whether there exists a macroscopic precursor "foot" of the drop [cf. Fig. 1a)] which advances ahead of it, but is so thin as not to be measurable. To answer, in part, this question we studied a number of pairs of drops simultaneously wetting an Al surface until they coalesced. Presumably if their precursors existed and met this would affect the wetting kinetics as seen by the approach of $\cos\theta$ to its final value. This did not occur, at least to within spacings between the drops of less than $10\,\mu$. After the drops sintered (i.e., came in contact and rapidly formed an interface between them) such an effect was observed and recorded in a sequence of photographs. What could be observed were stages as those shown in Fig. 6.

Many of the drops used were large enough so that the gravitational bulk stress ($\rho g a$, a the radius of the drop) would be of the order of the capillary stress ($2\gamma/a$). Since gravity is directional, one can study the effect due to the gravitational stress very simply by following the wetting kinetics of an "upside down" drop. Figure 7 shows a plot of $\cos\theta$ vs time for such an Elvax 220 drop on Al at 161°C, the l_0 of this drop was ~3 mm, so that the gravitational stress on this drop is roughly half as large or larger than the capillary stress if it were the "right side up". Also shown in Fig. 7 are the interpolated values of $\cos\theta$ as a function of t of drops "right side up" of the same l_0 which were obtained from data at 170°–151°C. We note that there is no appreciable effect on $\cos\theta$ nor does there appear one in the r/r_0 kinetics which are not shown.

Finally in Fig. 8 we plot $\cos\theta$ as a function of time for drops of Elvax 220 on Al without thermostatting. The data were obtained when the samples were placed on a hot plate in air; we estimate the thermal gradient to be at least the order of 5°–10°C/mm. The rate of wetting in the presence of a thermal gradient appears to be about five times the thermostated rate.

V. DISCUSSION

At the outset of our discussion we must recognize that we only have available data in certain restricted stages of the wetting and ranges of sizes of the polymer-melt drops. Neither the earliest nor the latest stages of the wetting process could be followed conveniently by our procedures. Thus, e.g., we do not know whether wetting stops before a "monomolecular" film is attained, or what is the initial velocity of wetting. Smaller drops could not be easily studied or formed on the surfaces.

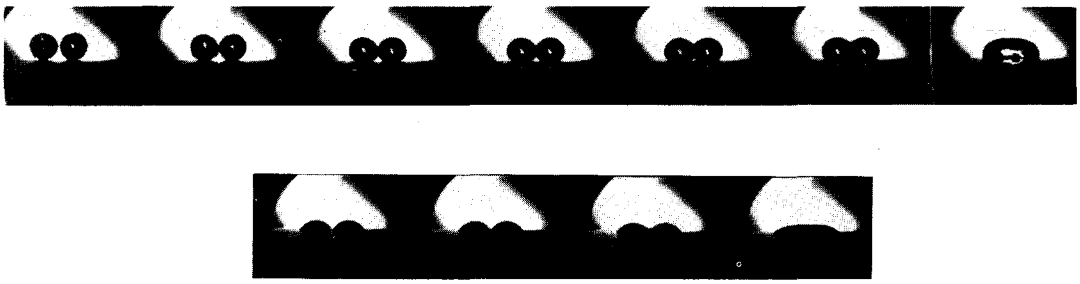


FIG. 6. Coalescence of two sessile drops on a planar surface.

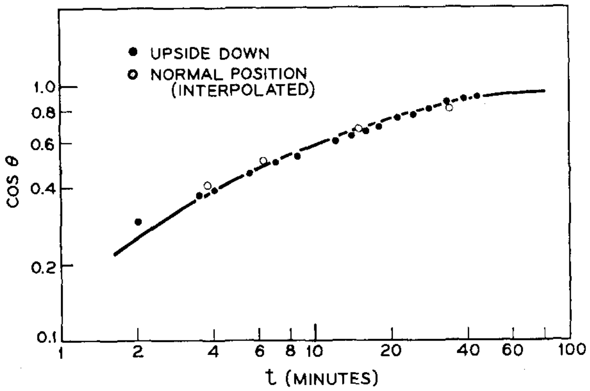


FIG. 7. Effect of gravity on the rate of change of the contact angle of Elvax 220 on aluminum.

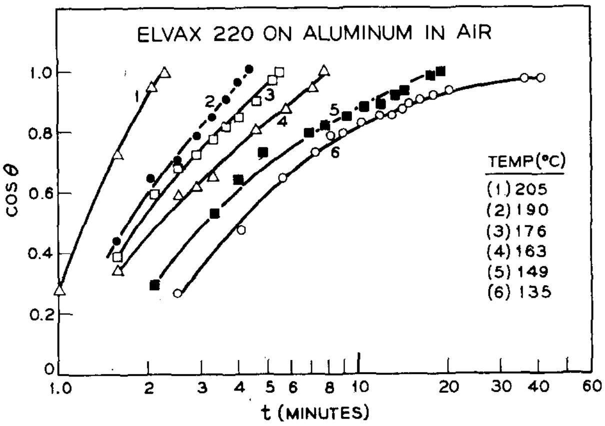


FIG. 8. Rate of wetting of Elvax 220 on aluminum on a hot plate in air.

Within these restrictions, though, we can attempt to answer the questions raised in the Introduction. The melted polymer drops on both high-energy surfaces (Al and mica) and the low-energy surface (FEP Teflon) maintain a definite shape, roughly that of a spherical segment. Geometry thus implies a definite functional relation (G), cf. Eq. (5), relating $\cos\theta/\cos\theta_\infty$ to r/r_0, i.e.,

$$\cos\theta/\cos\theta_\infty = G(r/r_0). \qquad (7)$$

Equation (7) implies that, if r/r_0 is then given by a dimensionless function of reduced time a_Tt,

$$r/r_0 = F(a_Tt), \qquad (8)$$

where the frequency a_T is characteristic of the real velocity of wetting, then, from Eqs. (7) and (8),

$$\cos\theta/\cos\theta_\infty = G[F(a_Tt)] = H(a_Tt). \qquad (9)$$

Thus the kinetics of wetting, when followed by the approach of θ to θ_∞, is characterized by the same characteristic frequency a_T. This answers our first question.

One of the more astonishing features of the curves shown in Fig. 3 is that at fixed temperature both $\cos\theta/\cos\theta_\infty$ and r/r_0 are independent of mass, i.e., l_0 or r_0 of the drop. That both entities show this behavior follows from Eqs. (8) and (9). Furthermore, we can conclude that a_T is not a function of the mass or r_0, l_0. An examination of our data shows that a_T is a function of temperature. From a large number of rough preliminary experiments using a variety of polymer melts on Al at various temperatures, it appears that the rate of wetting correlates with the surface tension of the polymer γ and inversely with the melt viscosity η. The latter varies strongly with temperature. To produce a dimensional group of properties with the dimension of reciprocal time using η and γ, we require a characteristic length L_w. This unknown L_w *cannot* depend on l_0, r_0, m, or ρg (cf. Fig. 7). We assume it is a property of the polymer–substrate system. We shall present strong evidence that it is not a function of T. Thus, tentatively we set

$$a_T = \gamma/L_w\eta. \qquad (10)$$

We can now test two things: (1) Can one superimpose the kinetics of wetting data, i.e., $\cos\theta/\cos\theta_\infty$ and r/r_0 vs t data for all polymer–substrate pairs, drop sizes, and temperatures by only horizontally shifting the time scale in a log–log plot of the data. Figures 9 and 10 show that the answer to this question is affirmative. We choose the unit reduced time so that a_T for Elvax 220 on Al at 170°C is 1. (2) Is the temperature dependence of a_T solely contained in the factor γ/η; i.e., is L_w roughly constant with temperature? This is indeed the case as can be seen from Fig. 11, where we plot

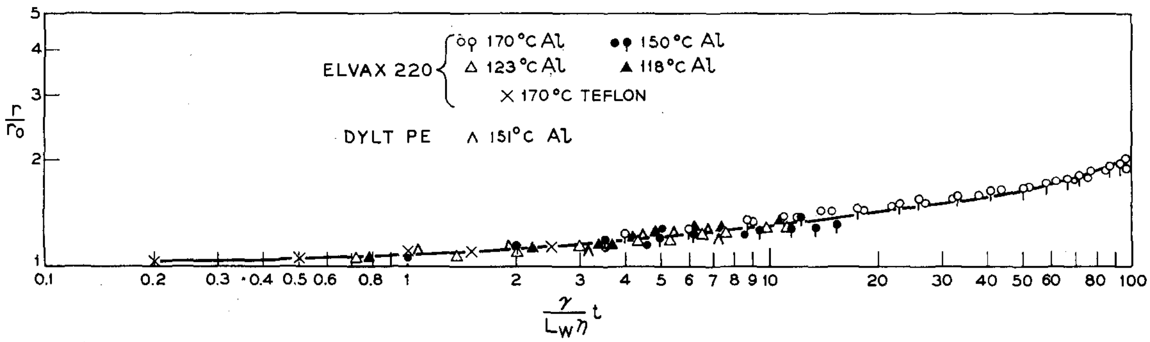


FIG. 9. Master curve of r/r_0 vs a_Tt. ○ 0.005 g, ♀ 0.0200 g, ● 0.0072 g, solid circle with line 0.0231 g.

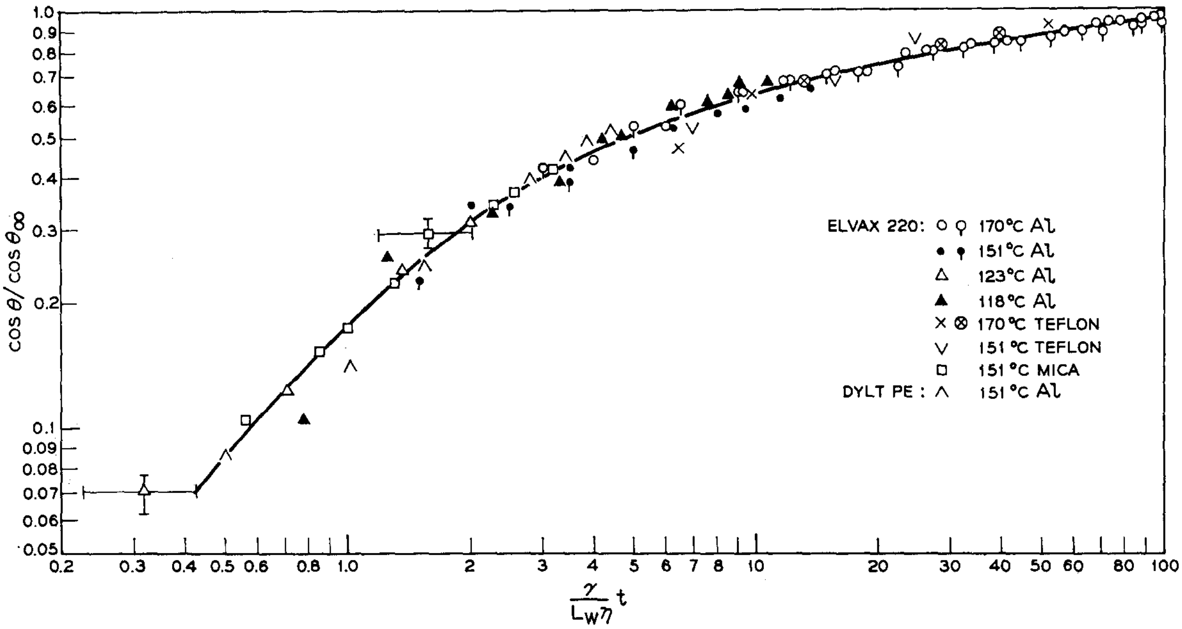


FIG. 10. Master curve of $\cos\theta/\cos\theta_\infty$ vs $a_T t$ (legend same as in Fig. 9).

$(\gamma/\eta)_T/(\gamma/\eta)_{170°}$ vs a_T determined at different temperatures for Elvax 220 on Al. That this is not an artifact of a double logarithmic plot can be seen from the following: The shift factor a_T is 0.478 at 151°C, 0.157 at 123°C, and 0.125 at 118°C; the corresponding values of $(\gamma/\eta)_T/(\gamma/\eta)_{170°}$ are 0.493, 0.148, and 0.119, respectively.

We do not know the magnitude of L_w. We have determined the ratio of L_w's for Elvax 220 on various substrates from the ratio of a_T, at a given temperature. We find that

$$[(L_w)_{\mathrm{Al}}/(L_w)_{\mathrm{Teflon\ FEP}}]_{170°\mathrm{C}}=2.4$$
$$[(L_w)_{\mathrm{Al}}/(L_w)_{\mathrm{mica}}]_{151°\mathrm{C}}=0.30.$$

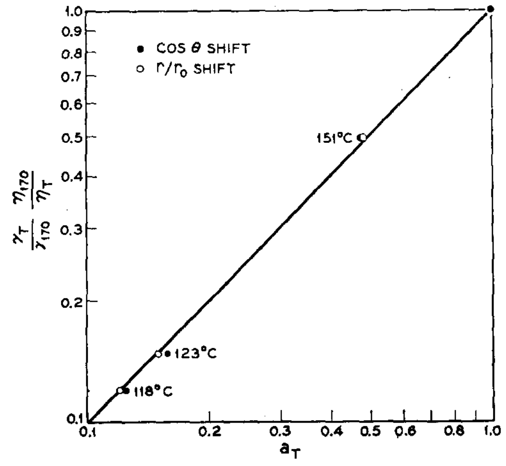


FIG. 11. Relationship between a_T and $(\gamma/\eta)_T/(\gamma/\eta)_{170°}$.

Assuming that L_w is temperature-independent, the ordering for Elvax 220 would be

$$(L_w)_{\mathrm{mica}}>(L_w)_{\mathrm{Al}}>(L_w)_{\mathrm{Teflon}}.$$

This is not the order of surface roughness as determined by a Talysurf trace which gives the order of surface roughness as Al>Teflon>mica. The ratio of $(L_w)_{\mathrm{Al}}$ for Elvax 220 to $(L_w)_{\mathrm{Al}}$ for DYLT at 151°C is ~0.65.

This is as far as we can go at present in answering the second question raised in the Introduction.

We had hoped that the basic physical mechanism of the wetting could be accounted for by conventional, macroscopic hydrodynamics (if necessary of a non-Newtonian, viscoelastic fluid). Our observations are not consistent with that view: (i) The drop shape is roughly that of a spherical segment with no precursor. This would imply that a special mechanism acting at the interfaces determines the drop shape and not bulk flow. (ii) Turning a fairly large drop upside down does not affect the rate of wetting. By turning the drop upside down the bulk stress distribution is changed significantly. The fact that this does not affect the rate of wetting suggests that the latter is independent of the stress. (iii) a_T is independent of the mass or l_0. Granting that the shape of the drop is that of a spherical segment, all attempts to account for the kinetics by flow even of a viscoelastic, somewhat non-Newtonian fluid (even invoking channel or boundary layer flow) lead to a dependence of a_T or L_w on l_0. On the contrary, the drop, by some mechanism [probably residing at the interface, cf. (i)], is able to adjust $\cos\theta$, e.g., without regard to the mass of fluid involved. The phenomenon appears to be "nonlocal."

ACKNOWLEDGMENTS

We are indebted to C. Herring for constructive criticism and valuable discussions in the course of this work, and to F. W. Ryan for his extreme care and patience in collecting the numerous data necessary for this work.

JOURNAL OF APPLIED PHYSICS VOLUME 37, NUMBER 13 DECEMBER 1966

Temperature Dependence of the Widths and Positions of the *R* and *N* Lines in Heavily Doped Ruby

Richard C. Powell
Air Force Cambridge Research Laboratories (OAR), Bedford, Massachusetts

AND

Baldassare DiBartolo,* Behzad Birang,* and Charles S. Naiman*
Mithras, Inc., Cambridge, Massachusetts

(Received 7 July 1966)

The widths and positions of the *R* and *N* lines in heavily doped ruby have been measured at temperatures from 13° up to 450°K. The results for the temperature dependence of the linewidths are explained in terms of microscopic strains, Raman scattering of phonons by the impurity ions, and direct phonon processes. The results for the lineshifts with temperature are due to the absorption and emission of virtual phonons. A Debye model of phonons is used with different effective phonon distributions for the linewidth and lineshift processes. Also the effective phonon distribution for the broadening of pair (*N*) lines is different from that for the broadening of single ion (*R*) lines.

I. INTRODUCTION

We have measured the temperature dependence of the widths and positions of the four most prominent lines in the fluorescence spectrum of heavily doped ruby from 13° up to 450°K. The results for samples containing 2.1 at. % and 0.94 at. % chromium are compared with similar measurements made previously[1] on lightly doped ruby (about 0.05 at. % chromium). The R_1 and R_2 lines are found to be broadened by microscopic strain, Raman processes, and direct processes between their excited states. The N_1 and N_2 lines are broadened by microscopic strain, Raman processes, and direct processes within the ground state manifolds. The thermal lineshift results are consistant with virtual phonon processes involving different Debye temperatures than those used to fit the linewidth data.

II. EXPERIMENTAL

For measurements at room temperature and below, the samples were mounted in a Janis model 8DT cryostat capable of continuous temperature variation from 4.2° up to 300°K. For temperatures above 300°K the samples were mounted in a quartz furnace. The samples were excited by the emission of an air-cooled General Electric BH6 1000-W high-pressure mercury lamp, filtered by 4 cm of saturated $CuSO_4$. The fluorescence observed at 90° to the direction of excitation was chopped and focused onto the entrance slit of a McPherson model 213 one-meter scanning monochromator. At low temperatures the grating was used in second order to achieve a resolution of 0.14 cm^{-1}. The signal was detected by an RCA 7102 photomultiplier tube cooled by liquid nitrogen. The modulated signal was then amplified by a P.A.R. JB-5 lock-in amplifier and displayed on a strip-chart recorder.

III. THEORETICAL CONSIDERATIONS

McCumber and Sturge[1] investigated the thermal dependence of the widths and positions of the absorption *R* lines in lightly doped ruby. They explain the constant width below 77°K as being due to broadening by microscopic strains, and the rapid increase in width with temperature above 77°K as being due to the Raman scattering of phonons by the impurity ions. Kurnit, Abella, and Hartman[2] included a direct process term between the $\bar{E}$ and $2\bar{A}$ levels in the consideration of the R_1 line-

---

* Sponsored by U. S. Army Engineer Research and Development Laboratories, Fort Belvoir, Virginia, under Contract DA-44-009 AMC-1090(T).

[1] D. E. McCumber and M. D. Sturge, J. Appl. Phys. 34, 1682 (1963).

[2] N. A. Kurnit, I. D. Abella, and S. R. Hartmann, *Physics of Quantum Electronics*, P. L. Kelley, B. Lax, and P. O. Tannewald, Eds. (McGraw-Hill Book Co., Inc., New York, 1966), p. 267.