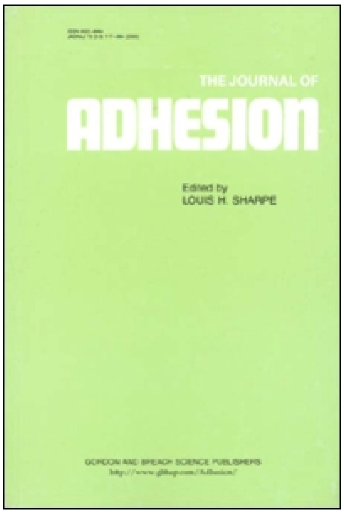
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Spreading of Polydimethylsiloxane Drops on Solid Horizontal Surfaces

V. A. Ogarev[a]; T. N. Timonina[a]; V. V. Arslanov[a]; A. A. Trapeznikov[a]
[a] Institute of Physical Chemistry, Academy of Sciences of the U.S.S.R., Moscow, U.S.S.R.

To cite this Article Ogarev, V. A. , Timonina, T. N. , Arslanov, V. V. and Trapeznikov, A. A.(1974) 'Spreading of Polydimethylsiloxane Drops on Solid Horizontal Surfaces', The Journal of Adhesion, 6: 4, 337 — 355

To link to this Article: DOI: 10.1080/00218467408075037

URL: http://dx.doi.org/10.1080/00218467408075037

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Adhesion, 1974, Vol. 6, pp. 337–355
© 1974 Gordon and Breach Science Publishers Ltd.
Printed in Scotland

Spreading of Polydimethylsiloxane Drops on Solid Horizontal Surfaces

V. A. OGAREV, T. N. TIMONINA, V. V. ARSLANOV and
A. A. TRAPEZNIKOV

Institute of Physical Chemistry, Academy of Sciences of the U.S.S.R., Moscow, U.S.S.R.

Downloaded At: 17:03 22 January 2011

(*Received November 30, 1973*)

Effect of the volume of drops, surface energy and roughness of substrate together with temperature and viscosity on the spreading velocity of polydimethylsiloxane (PDMS) drops on solid horizontal surfaces was studied. Spreading velocity was shown to grow with decreasing drop volume, the effect being more pronounced at high viscosities of polymer. The deviation of shape of the spreading drop from that of a spherical segment is more pronounced the higher the surface energy of substrate, the higher the polymer viscosity and the smaller the drop volume. Spreading on a rough surface is slower than on a smooth one owing to the energy barrier created by surface inhomogeneities: the barrier is to be overcome by the spreading liquid. Based on the experimental results a mechanism of spreading of polymer drops is proposed. Changes in potential energy of a drop and in the free surface energy of the system during spreading were compared, allowing a theoretical evaluation of the influence of gravity on the spreading velocity of drops. A theoretical analysis of spreading kinetics of viscous drops is given. The equation proposed agrees well with the experimental results at $90° > \theta > 0°$.

INTRODUCTION

The degree of wetting of solid surfaces with a liquid is measured by the equilibrium contact angle θ_0[1]. The change of the contact angle in time, i.e. spreading velocity, was first discussed by Kanamaru[2] for the case of viscous compounds on solid surfaces. More detailed studies by Schonhorn *et al.*[3, 4] dealt with spreading of drops of liquids with viscosities from 9 to 200 poises. Spreading velocity is demonstrated not to depend on the volume of drops; spreading drops retain the shape of spherical segments. It was also shown that gravity does not affect the spreading velocity of drops with mass from

Downloaded At: 17:03 22 January 2011

5×10^{-3} to 2×10^{-2} grams[3]. Based on the results obtained, a logarithmic spreading law for viscous drops on solid surfaces is proposed. The law is similar to the expression derived for the sintering of polymers[5].

The present work concerns the results of experiments on polydimethylsiloxane (PDMS) spreading on solid horizontal surfaces of various nature within a broad range of viscosities. Experiments were aimed at determining main physical parameters influencing spreading velocity, and at elucidating a possible spreading mechanism.

MATERIALS AND PROCEDURES

The molecular weight ($\bar{M}$) of linear PDMS was determined in CCl_4 solution according to the formula: $(\eta) = 3.56 \times 10^{-4} \times \bar{M}^{0.63}$ [6]. We used literature data[7] for the viscosities at 22°C of PDMS samples with given $\bar{M}$. The following PDMS samples were studied in this work:

$\bar{M} \times 10^{-3}$	16	19	35	340	708	960
η, poises	5.6	7.1	25.1	28.2×10^3	478.6×10^3	159×10^4

For temperatures differing from room temperature η was calculated from the linear relation in η versus $1/T$ using the known value of the apparent activation energy of viscous flow ($E = 3.8$ kcal/mole)[8]. Density of PDMS in the studied range of $\bar{M}$ was taken equal to 0.98 g/cm^3. Surface tension γ obtained for high $\bar{M}$ by extrapolation[9] lies between 20.9 and 21.2 erg/cm^2; $d\gamma/dT$ equals -0.048 erg/(cm^2 × degree)[10].

The spreading of PDMS was studied on freshly cleaved surfaces of mica, mirror-polished Pyrex surfaces, and polytetrafluoroethylene surfaces prepared according to the Fox and Zisman procedure.[11] Mechanically polished metals were also used: stainless steel, IIIX–15 steel (both having the 10th class of roughness†), and brass (8th class‡).

Glass and PTFE surfaces were treated with boiling potassium dichromate acidic solution, washed in twice distilled water, and air dried. Mica surfaces were used immediately after cleaving. The cleanliness of surfaces was checked by water wetting. Water drops on glass and mica spread completely. θ_0 of water on PTFE (114°) agreed with the earlier work.[11] After treating metals with solvents, such as ether, n-hexane, benzene, carbon tetrachloride, followed by warming to 100°C, immediately or after mechanical polishing, the contact angle of water varied from 75 to 90°. Metal surfaces (e.g. that of IIIX–15 steel) became more hydrophilic after heating in the burner flame

---

† In compliance with the U.S.S.R. standards, the root-mean-square deviation of asperities and depressions from the medium line for this class of roughness equals —0.1 to 0.2 microns (Translator's note).

‡ 0.4 to 0.8 microns (Translator's note).

to 800°C. Nevertheless, after 4 hours' cooling in air, surface properties were restored. A similar result was obtained by White.[12] The author assumes that hydrophobic properties of metal surfaces are due to adsorption of organic substances present in air. However, it is not to be ruled out that hydrophilic and hydrophobic properties of metal surfaces may be related to various modifications of surface oxide films. As the nature of metal surfaces remains unclear, we shall not dwell upon results obtained for them. It is only to be noted that they almost coincide with those obtained for glass surfaces.

Contact angle of the projection of a drop θ, diameter d, area of contact with the surface, and height h of a drop were measured simultaneously by means of a horizontal microscope with goniometric eyepiece having 20-fold overall magnification. Accuracy of angle measurements was $\pm 1°$ for big angles and $\pm 2°$ for small ones. Accuracy of h and d measurements was $\pm 2.5 \times 10^{-3}$ cm.

PDMS apparently does not decompose up to 250°C[13] on all studied surfaces, thus permitting spreading over a broad range of temperatures to be studied. We studied spreading of PDMS drops at temperatures above 22°C using a tube furnace. The temperature was controlled automatically with minimum accuracy ± 2°C. The hot junction of a Chromel/Alumel thermocouple was located in close proximity to a spreading drop. Highly viscous samples of PDMS were prepared in advance in the shape of beads of various diameter. In spite of careful preparation the surface of beads was not perfectly spherical. Therefore, in the initial period, θ-values at different sides of drops were not the same. As a rule, θ of the two projections equalized at 110–120°C and did not differ further on. Thus the systematic measurements were conducted starting from these θ values. Experimental difficulties connected with measuring θ at the first moment of contact of drops with a substrate made it impossible to obtain the total spreading curve. Hence, all the experimental results were reduced to the conventional zero time at $\theta = 90°$ and were expressed in the reduced coordinates $\cos\theta/\cos\theta_0$ and r/r_0, where r_0 and θ_0 stand for the drop radius at $\tau = 0$ and the contact angle of projection respectively measured at $\tau = \infty$. θ_0 of PDMS drops on mica and glass surfaces equals zero and 23° on PTFE, irrespective of polymer viscosity.

RESULTS AND DISCUSSION

Effect of volume and gravity on the spreading velocity of drops. The shape of a spreading drop

Figure 1 shows typical results of spreading measurements for PDMS drops on solid horizontal surfaces in reduced coordinates. For the high-viscosity PDMS sample ($\eta = 159 \times 10^4$ poises) the change of the reduced angle and

Downloaded At: 17:03 22 January 2011

radius depends on the volume of a drop (V_0), spreading velocity falling with increasing V_0. The spreading velocity of low-viscosity PDMS samples (η = 25.1 poises) is independent of V_0 which agrees with [3, 4]. The results of more detailed studies of the relation between V_0 and spreading velocity are given in Figure 2. The data are presented in the following coordinates: time of reaching $\theta = 60°$* *vs.* V_0, and referred to mica and PTFE. It follows that the greater V_0, the longer the time of reaching $\theta = 60°$ in the whole range of V_0. At comparatively big drop volumes $\tau_{60°}$ tends to diminish, probably because of the predominance of gravity. At lower viscosities of PDMS or higher temperatures, the drop volume exerts a weaker influence on $\tau^{60°}$.

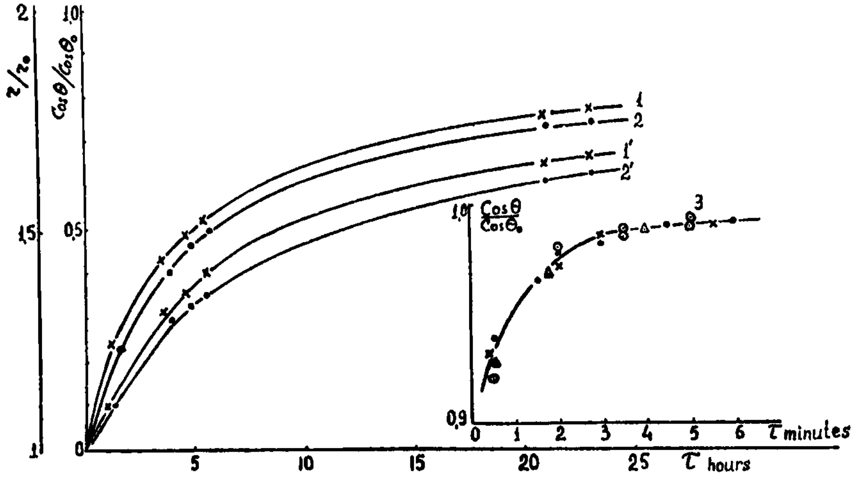


FIGURE 1 Dependence of cos θ/cos θ_0 (curves 1, 2, 3) and r/r_0 (curves 1′, 2′) on τ for PDMS drops on the surface of mica; $\bar{M} = 960 \times 10^3$; 1,1′ – $V_0 = 17 \times 10^{-4}$ cm^3; 2,2′ – $V_0 = 32 \times 10^{-4}$ cm^3; $\bar{M} = 35 \times 10^3$; 3 – $V_0 = (1 - 30) \times 10^{-4}$ cm^3.

The dependence of spreading velocity on the initial radius of drops was noted before[14, 15] but not discussed. This phenomenon cannot be explained by greater inertial resistance at greater V_0, because even low-viscosity PDMS samples (η = 5.6 poises) are characterized by a Reynolds number of the order of 10^{-2}. The Reynolds number was calculated from $Re = 2ur\rho/\eta$, where u is the linear liquid flow velocity, ρ is the density of liquid, and r is the radius of the drop. Presumably, the most straightforward way to account for the decrease in spreading velocity with greater drop columes is to consider the balance of forces affecting the spreading drop. Let spreading be

---

* $\tau_{60°}$ is conventional time chosen for the convenience of comparing PDMS spreading times.

Downloaded At: 17:03 22 January 2011

Downloaded At: 17:03 22 January 2011

connected with the decrease of the surface free energy of the system $(f_1)^{16\text{-}18}$. Then the moving force of spreading can be expressed as $F_1 = 2\pi r f_1$, where r is the radius of contact area of a drop. We shall express the force of viscous resistance of the spreading mass as $F_2 = -\pi r^2 f_2$,[2, 3, 16, 18] where f_2 is a product of viscosity and velocity gradient of viscous flow. Assuming independence of f_2 from r, one may see that spreading velocity should be proportional to $1/r$. Figure 3 shows the time of reaching $\theta = 60°$ *vs.* initial radius of a spreading drop on log–log scale. The data indicate with sufficient accuracy that the spreading time is directly proportional to r_0.

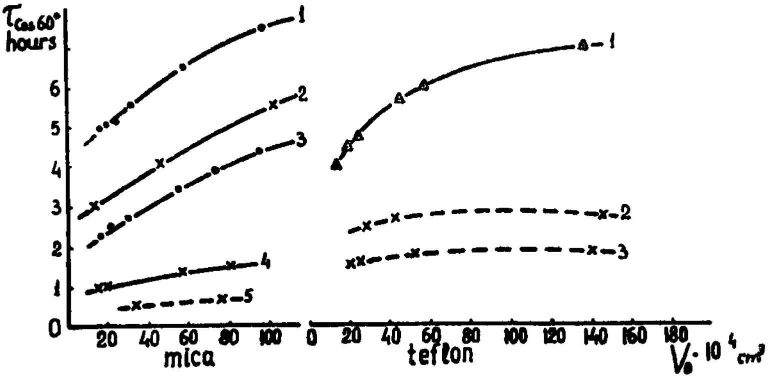


FIGURE 2 Curves $\tau_{\cos 60°}$ *vs.* V_0 for PDMS drops on the surface of mica; viscosities (poises); 1—159 × 10^4; 2—442 × 10^3; 3—478.6 × 10^3; 4—67.6 × 10^3; 5—34 × 10^3; PTFE surface; 1—478.6 × 10^3; 2—133 × 10^3; 3—67.6 × 10^3.

Besides that, the geometric shape of a spreading drop may affect spreading velocity. It was noted that starting from a certain η-value of the polymer, the measured contact surface radius is less than that calculated from the height of a drop: $r = h/\tan \theta/2$. This is indicative of elongation of the drop in the direction normal to the spreading surface when compared to the spherical segment having the same base radius. Figure 4 refers to the experimental results treated in accordance with the sphere formula for one PDMS sample. The higher the viscosity of PDMS and the surface energy and the lower V_0, the greater the deviation of the spreading drop from a spherical segment. For PDMS with $\eta < 35 \times 10^3$ poises, the geometry of drops is satisfactorily described by the sphere equation irrespective of the substrate nature and V_0. It could be seen from Figure 2 that V_0 of drops exerts the most pronounced effect on the spreading time of high-viscosity PDMS samples, i.e. when the shape of drops differs considerably from a spherical segment.

The shape of spreading viscous drops can be approximated by a cone for $90° > \theta > 0°$. Figure 5 gives quite a few experimental data for different

Downloaded At: 17:03 22 January 2011

substrates and at different temperatures, but for the same volume of drops. The data were treated using the cone equation. On the average, the error of drop volume calculations (Figure 5) is 12%. The same data treated with the help of the sphere equation give an error of 25%. The strongest deviation from the straight line in Figure 5 is observed when teaching $\theta = 90°$, for PDMS with $\eta \leqslant 35 \times 10^3$ poises and at high temperatures. No doubt that the cone approximation of the geometry of spreading viscous drops is rough to the same extent as the assumption of their spherical shape (Figure 4). Still the former makes it possible, as we shall see later, to give a theoretical account of the spreading of viscous drops.

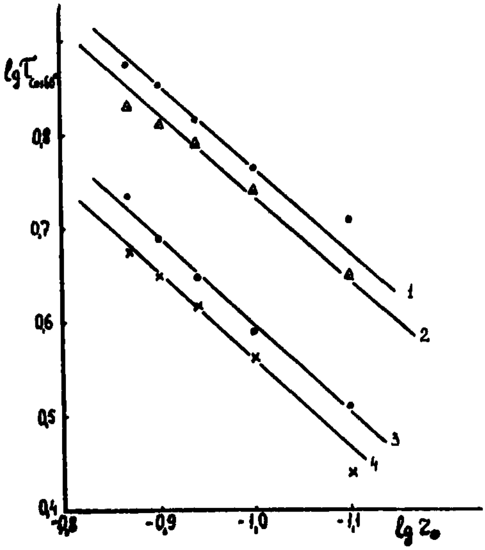


FIGURE 3 Logarithmic dependence of the time of reaching $\theta = 60°$ by a PDMS drop ($\bar{M} = 960 \times 10^3$) on the initial radius of the drop on the surface of mica: 1 — 22°C; 3 — 100°C. Curves 2 and 4 refer to PDMS with $\bar{M} = 708 \times 10^3$ on PTFE (22°C) and glass (100°C) surfaces respectively.

It is accepted[3, 18] that the gravitation force ($\rho g r_0$) only slightly affects the spreading velocity while it is less than or equal to $2\gamma/r_0$. It follows from the equation $r_0 = (2\gamma/\rho g)^{1/2}$ that for PDMS the gravitational force should not exert its influence on spreading velocity for drops with mass less than 36×10^{-3} grams. But the data in Figure 2 infer that the relative decrease in spreading time with growing drop volume is related to gravity even for smaller V_0. As the gravitational force is directed downwards, we can evaluate its influence by studying the spreading of a drop in a normal and an overturned position. Overall results are given in Figure 6 in the same coordinates as in Figure 2. The scatter for overturned drops, particularly at big V_0-values, is due to the difficulties in preparing PDMS samples uniform in

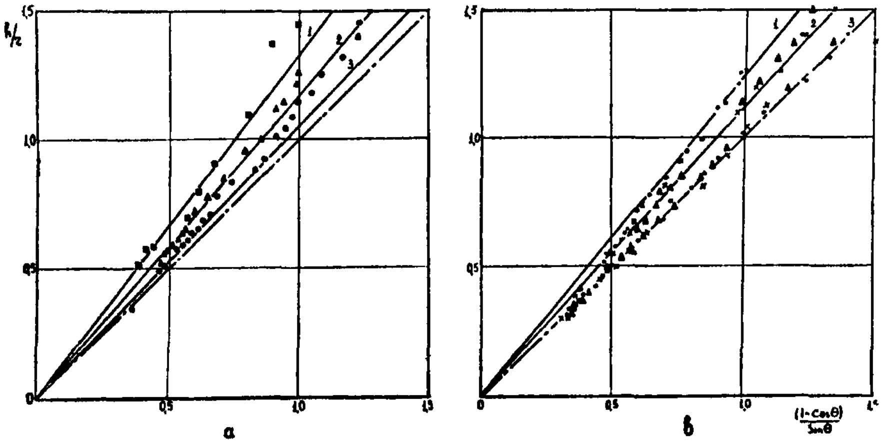


FIGURE 4 Experimental verification of sphericity of segments of PDMS drops ($\bar{M} = 708 \times 10^3$) by the equation $h/r = [(1 - \cos\theta)/\sin\theta]$; (a) mica at 22°C; 1—$V_0 = 17 \times 10^{-4}$ cm^3; 2—$v_0 = 54 \times 10^{-4}$ cm^3; 3—$V_0 = 97 \times 10^{-4}$ cm^3; (b) $V_0 = 54 \times 10^{-4}$ cm^3; 22°C: 1—mica; 2—glass, PTFE; 3—mica, glass, PTFE at 200°C.

shape. In some instances overturned drops did not acquire the regular shape even after having reached $\theta = 90°$, i.e. the beginning of the spreading time reading. This means that at $\tau = 0$ contact surface for drops of the same size may be different. Nevertheless, in any case (with the exception of the smallest drops) the time of reaching $\theta = 60°$ by overturned drops was always noticeably greater than for drops in a normal position. The difference is especially pronounced on the PTFE surface.

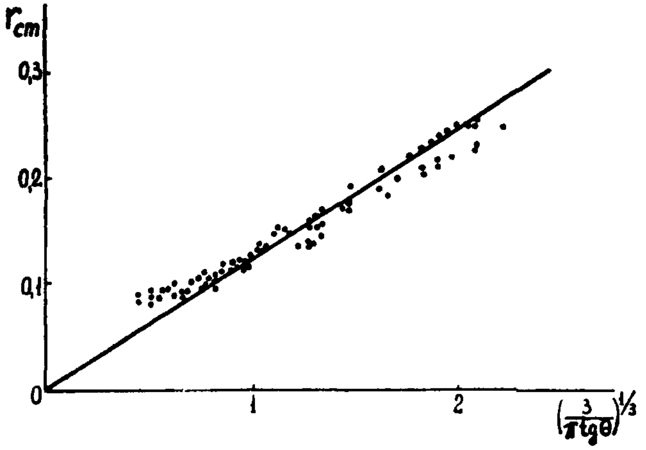


FIGURE 5 Experimental verification of conicity of PDMS drops for various molecular weights at 22° to 250°C by the Eq. $r = (3V_0/\pi \tan\theta)^{1/3}$ for $V_0 = 16 \times 10^{-4}$ cm^3.

Downloaded At: 17:03 22 January 2011

Downloaded At: 17:03 22 January 2011

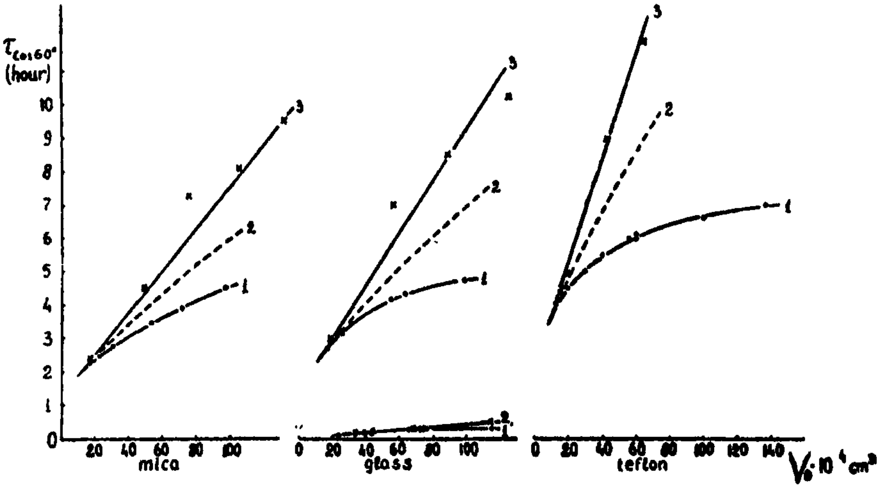


FIGURE 6 Curves $\tau_{\cos 60°}$ versus V_0 at 22°C for PDMS drops ($\bar{M} = 708 \times 10^3$): 1—normal position; 2—without effect of mg; 3—overturned position. $\bar{M} = 340 \times 10^3$; 1'—normal position; 2'—overturned position.

Formally, the effect of mg on spreading velocity can be excluded, if one draws a mean line between the graphs for normal and overturned drops (curve 2, Figure 6). It follows from Figure 6 that mg starts affecting $\tau_{60°}$ at a drop weight about 2 to 3 times less than calculated from the capillary constant equation. The influence of mg on spreading velocity can be calculated from comparing the potential energy changes of a drop $\Delta U = 2\ \mathrm{mg}/5\ (h_2 - h_1)$† with the free surface energy of the system[19]:

$$\Delta G^s = \pi(r_2^2 - r_1^2)(\gamma_{1,3} + \gamma_{1,2} - \gamma_{2,3}) + \pi(h_2^2 - h_1^2)\gamma_{1,2}$$

during the spreading of a drop on a solid surface. Concerning the variation of the contact angle from 90° to 60°, the height h is expressed through the volume V_0 of a drop as $h_1 \approx (V_0/2)^{1/3}$ and $h_2 \approx (V_0/5.4)^{1/3}$, respectively. In spreading on the PTFE surface from 90° to 60°, PDMS drops with $V_0 = 0.01\ \mathrm{cm}^3$ are characterized by $\Delta U = 25\%$ of ΔG^s and those with $V_0 = 0.001\ \mathrm{cm}^3$ by $\Delta U = 5\%$ of ΔG^s. These figures are fairly close to the experimental data presented in Figure 6.

The effect of surface nature, temperature and PDMS viscosity on spreading velocity

Figure 7 shows the spreading curves for the PDMS samples of three molecular weights on mica, glass, stainless steel, IIIX-15 steel, brass and PTFE. At lower $\bar{M}$ of PDMS spreading velocity increases; for any given $\bar{M}$ the spreading

---

† $\frac{2}{5}h$ is the location of the centre of gravity.

velocity is greater for substrates with higher surface energy. The effect of surface nature on spreading velocity decreases for lower molecular weights of the polymer. As it was mentioned above, there are no definite data concerning the nature of metal surfaces. Therefore, it is not clear why spreading velocity on metals is practically the same as on glass (Figure 7).

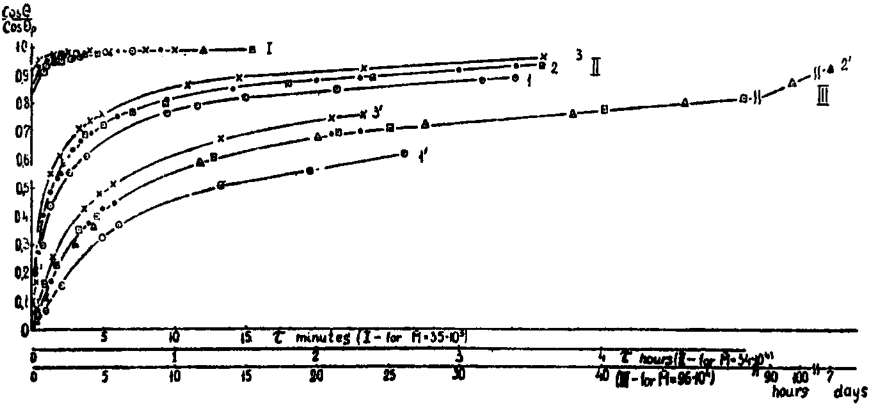


FIGURE 7 Spreading curves of PDMS drops ($V_0 = 25 \times 10^{-4}$ cm^3) at 22°C. Surfaces: 1,1′—PTFE; 2,2′—glass and metals; 3,3′—mica. $\bar{M}$: I—35×10^3; II—340×10^3; III—960×10^3.

Figure 8 refers to the spreading of PDMS drops on rough-surfaced glass ("orange peel" type with maximum level difference 2 microns) and on polished glass covered with dense adsorbed monolayer of the same PDMS applied from n-hexane solution according to the known technique.[20] It is noteworthy that with increasing surface roughness the spreading velocity drops. It is apparent that the total surface of rough glass consisting of a statistical set of macro- and microheterogeneities becomes more inaccessible to relatively big PDMS molecules. This can be attributed to the growth of the spreading energy barrier caused by the increased irregularity of composition and surface roughness.[21] However, considering the spreading of polymers with sufficiently long molecular chains, microheterogeneities could be of no substantial importance owing to the possibility of making "bridges" by long polymer molecules at partial surface filling. In this case the decrease in spreading velocity will be determined, mostly, by the surface heterogeneity, but the work of adhesion must be considerably lower.

The reduction of the spreading velocity of PDMS on a glass surface with adsorbed monolayer of the same polymer (Figure 8, curve 4) is accounted for by the lowered surface energy of the substrate. The adsorbed monolayer of PDMS is known[20] to have the critical surface tension about 22.5 erg/cm^2. This means that the glass surface covered with the adsorbed layer of PDMC

Downloaded At: 17:03 22 January 2011

resembles PTFE surface in its energetic properties. PDMS spreading on a densely absorbed monolayer of the same polymer differs substantially from the flow of drops on a thick polymer layer. The latter has a considerably greater velocity and can be described by the law of sintering of polymer drops.[5]

Figure 8 also presents the temperature dependence of the spreading velocity of PDMS on the surfaces of various nature. The spreading velocity changes in the same manner as in the experiments with samples of decreasing molecular weight although, in this instance, the surface energy of substrate should undoubtedly be falling as well.

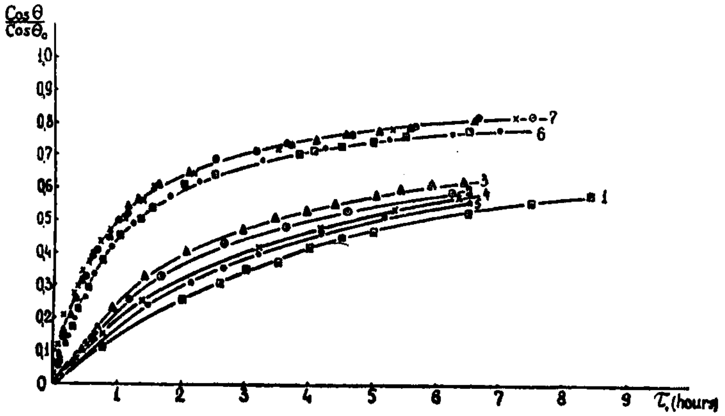


FIGURE 8 Spreading curves of PDMS drops ($\bar{M} = 708 \times 10^3$) at 22°C. Surfaces: 1—PTFE; 2—glass; 3—mica; 4—adsorbed PDMS monolayer on glass; 5—rough glass; 6—PTFE at 200°C; 7—mica at 200°C.

Figure 9 demonstrates the effect of the critical surface tension γ_c, determining surface wettability,[20] upon the time of reaching $\theta = 60°$ for PDMS drops of various viscosity. The values of γ_c for mica and glass are taken from the literature[22] as well as for PDMS on glass and PTFE.[20] The difference in $\tau_{60°}$ for the polymer sample with $\eta \leqslant 28 \times 10^3$ poises (curve 1) on various surfaces is very small. Curves 2 and 3 relate to the systems where the moving force of spreading characterized by γ_c, does not greatly exceed the force of viscous resistance proportional to η. At lower polymer viscosities the curves degenerate into a straight line parallel to the x-axis. The similar degeneration of curves into straight lines parallel to x-axis should be observed for highly viscous polymers. The difference between these two limiting cases consists only in spreading velocities. This velocity is very high in the first case and infinitesimally low in the second. Consequently, in both cases the spreading velocity is practically independent of the surface energy of the substrate

Downloaded At: 17:03 22 January 2011

within the sensitivity of our method. Therefore, the spreading velocity of polymer drops depends to a substantial degree on γ_c only in the region where the moving force of spreading and the force of viscous resistance do not differ greatly.

Figure 9 demonstrates also the data on PDMS spreading ($\bar{M} = 708 \times 10^3$) at 250°C (curve 4). Regardless of the fact that the viscosity of the sample at 250°C falls practically to that of PDMS with $\bar{M} = 340 \times 10^3$ at 22°C (curve 1), spreading time in the first case was considerably greater. Evidently, the moving force of spreading decreases with temperature and outweighs the drop in polymer viscosity. This is supported by Figure 10 where a log-log plot is given for the time of reaching $\theta = 60°$ by a drop versus bulk viscosity of PDMS. Lines 1 and 2 pertain to mica and PTFE surfaces respectively (22°C) and lines 3 and 4 are drawn for elevated temperatures. The slope of the straight lines is actually the same and is close to one thus indicating proportionality between the spreading time and the bulk viscosity of polymer. It follows from the figure that the lines shift towards greater spreading times at elevated temperatures. It was demonstrated[23] that by comparing viscosity axis intercepts one may evaluate the moving forces of spreading on solid surfaces. In the system PTFE/PDMS at 250°C the moving force of spreading falls approximately 1.5–2 times as against 22°C.

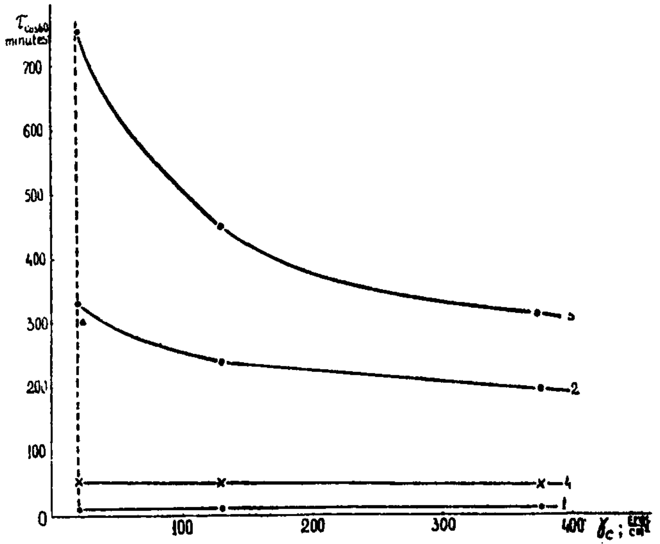


FIGURE 9 Relationship $\tau_{\cos 60°}$ versus γ_c at 22°C for PDMS drop ($V_0 = 55 \times 10^{-4}$ cm³). Viscosities, poises: 1—28.2 × 10^3; 2—478.6 × 10^3; 3—159 × 10^4; 4—30 × 10^3 (viscosity at 250°C of the sample having $\eta = 478.6 \times 10^3$ poises at 22°C).

Downloaded At: 17:03 22 January 2011

The mechanism of spreading of liquids over solid surfaces is not studied in depth though considerable efforts are made in investigating both liquid metals[24] and organic compounds in connection with boundary lubricants,[25] hydrophilizing and hydrophobizing agents,[20] and polymer coatings.[2-4, 26, 27]

Assuming a perfectly smooth surface together with the lack of mutual solubility of the components of the system and the absence of transport of the spreading compound through the gas phase one can conceive two different spreading mechanisms. The first consists in diffusional motion of molecules of the spreading compound on the solid surface. The kinetics of spreading in this case is determined by the tendency of the system to increase its entropy. If the heat of adsorption is high, the molecules of the spreading compound cannot migrate freely over the solid surface. In this second case the compound may spread as a phase, as a result of molecular self-diffusion on the surface or in the bulk. Here the inequality $\gamma_{SV} > \gamma_{SL} + \gamma_{LV} \cos\theta$ where γ is specific surface free energy of a corresponding phase boundary, must be fulfilled.

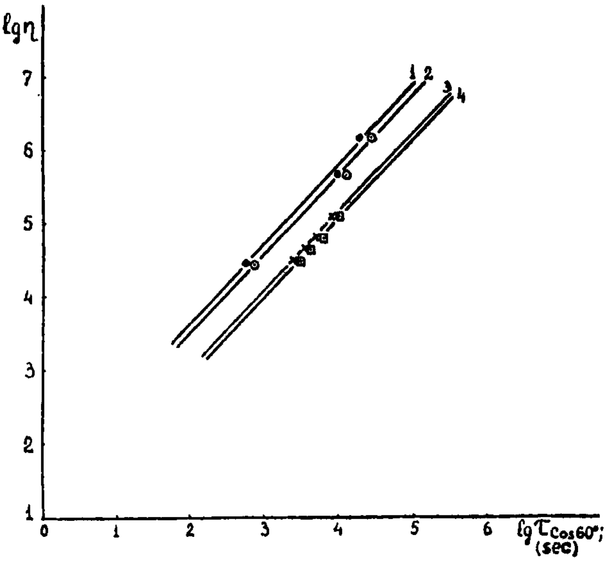


FIGURE 10 Relationship $\log \eta$ versus $\log \tau_{\cos 60°}$ for PDMS drops ($V_0 = 55 \times 10^{-4}$ cm^3). $\bar{M} = 340 \times 10^3$; 708×10^3; 960×10^3; temperature 22°C; surfaces: 1—mica; 2—PTFE. $\bar{M} = 960 \times 10^3$; temperatures 100, 150, 200, 250°C; surfaces: 3—mica; 4—PTFE.

The spreading of high molecular compounds on solid surfaces should, apparently, follow the second mechanism. We are not aware of any direct experiments, but there was an investigation of spontaneous spreading of

Downloaded At: 17:03 22 January 2011

liquid oils.[25] It was shown by means of interference microscopy and ellipsometry that a film with a thickness of about 1000 Å flows from the bulk of a liquid on to a solid surface. No thinner films were observed.

Assuming that the 2-dimensional migration of PDMS molecules on high energy surfaces is hampered due to comparatively high heat of adsorption it can be expected that PDMS spreading follows the second mechanism as well. The question about the existence of a microscopically thin film moving in front of a spreading drop could be partially answered by observing the visible boundaries of two drops spreading towards each other until coalescence occurs. The kinetics of spreading of two PDMS drops on mica surface did not change up to the distance of 20 microns between them. Therefore, at least at this distance from the drop border, there is no microfilm. Similar results were obtained for other systems.[3]

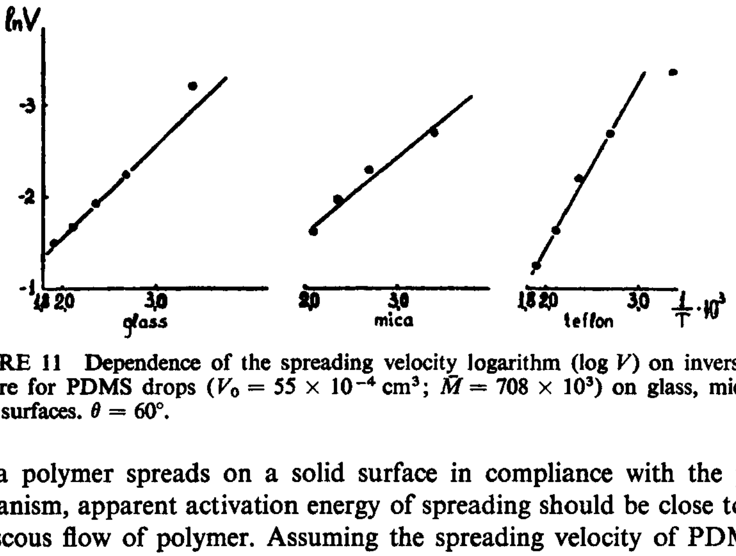


FIGURE 11 Dependence of the spreading velocity logarithm (log V) on inverse temperature for PDMS drops ($V_0 = 55 \times 10^{-4}$ cm^3; $\bar{M} = 708 \times 10^3$) on glass, mica and PTFE surfaces. $\theta = 60°$.

If a polymer spreads on a solid surface in compliance with the phase mechanism, apparent activation energy of spreading should be close to that of viscous flow of polymer. Assuming the spreading velocity of PDMS at $\theta = 60°$ on various surfaces to comply with the exponential law $V = V_0 \, e^{-E/RT}$, where V_0 is a temperature-independent constant, we can calculate apparent activation energy of spreading (E). E values calculated from the data in Figure 11 for spreading on mica, glass, and PTFE surfaces are 1.7, 2.0 and 3.6 kcal/mole respectively as compared with 3.8 kcal/mole for activation energy of viscous flow for high molecular PDMS. The decrease in apparent activation energy of spreading in passing from PTFE to mica surface is undoubtedly caused by the influence of the substrate surface free energy. This may be connected with intensification of self-diffusion of PDMS macromolecules in the zone of contact between a drop and the surface with the increase of the substrate surface energy.

Downloaded At: 17:03 22 January 2011

Spreading equation for viscous drops

The theory of spreading of viscous compounds on horizontal solid surfaces is not sufficiently advanced. Kanamaru[2] regarded time changes of θ for drops of viscous compounds on solid surfaces as a relaxation phenomenon depending on a single constant, namely relaxation time. It was assumed[3] that the spreading velocity is characterized only by the rate of approaching by θ its equilibrium value θ_0. This rate was expressed by a logarithmic law with two unknown constants.[26, 28] it was pointed out[28] that fast spreading of drops should be due to low viscosity of the compound, high surface tension of substrate, and low contact angle. Nevertheless, capillary pressure of surface microirregularities of the substrate was considered as the basic moving force of spreading. It is evident that, in this case, as the surface irregularity disappears so will the moving force. Another mechanism seems to be of more general nature; according to it the moving force of spreading is identified with the decrease of surface free energy of the system[18, 29] in the same way as it was done for spreading of liquid metals.[16, 17] In the implicit form the spreading law for viscous compounds on solid surfaces was given by Yin,[18] but the mathematical method used in this work was justly criticized for the lack of correctness.[30]

Downloaded At: 17:03 22 January 2011

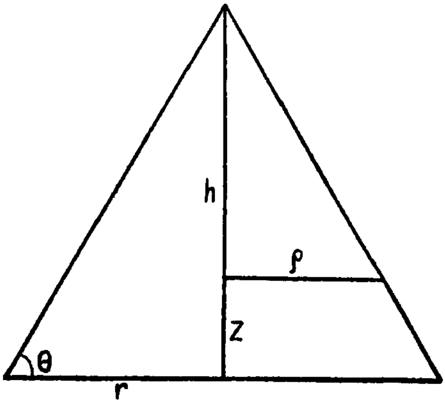


FIGURE 12 Approximated shape of a spreading drop and parameters used in deriving the spreading equation.

Accounting for pertinent comments leads to further complication of the the problem which remains unsolved. Probably in the most physically correct way the problem is formulated by Ruckenstein.[29] The author takes into account the subsurface layer of a spreading viscous drop. Unfortunately, as in the above case,[18] the problem cannot be solved to the end.

In this work we shall consider the case of spreading of a viscous compound on a smooth horizontal surface when the weight of a drop and the substrate

Downloaded At: 17:03 22 January 2011

roughness can be neglected. Besides, basing upon the experimental data discussed above, the shape of a spreading drop is approximated by a cone.

Figure 12 gives the parameters of the cone, used in deriving the spreading equation. Here z and ρ are variable values of height (h) and radius (r) of the contact area of a drop. The variables are limited by $0 \leqslant z \leqslant h$, $0 \leqslant \rho \leqslant r$, and $z = h - \rho \cdot \tan\theta$ where θ is dynamic contact angle.

The moving force of spreading expressed by the change in the free surface energy of the system is expressed as:

$$F_1 = 2\pi\rho f \tag{1}$$

For non-complete spreading of a drop with the equilibrium contact angle θ_0, f can be expressed in the following form:

$$f = \gamma_{LV} \, . \, (\cos\theta_0 - \cos\theta) \tag{2}$$

For complete spreading:[17]

$$f = \gamma_{SV} - \gamma_{SL} - \gamma_{LV}\cos\theta \tag{3}$$

In order to refer the moving force of spreading to all levels of the drop surface from the phase boundary to the top, we must express it in the general form as $F_1' = 2\pi\rho f'$ where $f' = f$ at $z = 0$.

Let viscous resistance of the drop mass written in a form of the Newton law be the force counteracting spreading:

$$F_2 = -\pi\rho^2\eta\frac{dv}{dz} \tag{4}$$

where dv/dz is the velocity gradient of viscous flow in the z direction. The velocity gradient in the ρ direction is neglected by assuming the horizontal flow velocity to be constant.

For a given moment $F_1 = F_2$, i.e.

$$2\pi f\rho = -\pi\rho^2\eta\frac{dv}{dz}$$

consequently,

$$dv = -\frac{2f\,dz}{\rho\eta} \tag{5}$$

Having expressed spreading velocity by the variation of the area of the horizontal section of the drop in time ($ds/d\tau$) and taking into account independence of θ from z for a cone, we obtain:

$$\frac{ds}{d\tau} = \int_0^v 2\pi\rho dv = \int_0^h \frac{4\pi f}{\eta} dz \tag{6}$$

Since at $z = 0$ the velocity reaches maximum and at $z = h$, $v = 0$, integrating of Eq. (6) will give spreading velocity expressed in terms of variation of contact area of drop in time:

$$\frac{ds}{d\tau} = \frac{4\pi f h}{\eta} \tag{7}$$

or

$$d\tau = \eta \frac{ds}{4\pi f h} \tag{8}$$

It follows from Eq. (7) that spreading velocity is directly proportional to the moving force of spreading, i.e. if $f > 0$ spreading will occur.

Let now the contact angle change. We shall express h and ds in terms of θ and the volume of the drop V_0. It follows from Figure 12 that $h = r \tan\theta$, $V_0 = 1/3(\pi r^2 h)$, and $S = \pi r^2$. Hence,

$$\begin{aligned} &h = (3V_0/\pi)^{1/3} \tan^{2/3}\theta;\ r = (3V_0/\pi)^{1/3} \tan^{-1/3}\theta; \\ &dr = -\tfrac{1}{3}(3V_0/\pi)^{1/3} \tan^{-4/3}\theta\, d(\tan\theta);\ ds = 2\pi r dr \end{aligned} \tag{9}$$

Substituting r and dr into the last equation gives:

$$ds = -\tfrac{2}{3}\pi(3V_0/\pi)^{2/3} \tan^{-5/3}\theta\, d(\tan\theta) \tag{10}$$

Substituting Eqs. (9) and (10) into (8) we obtain:

$$\int_0^\tau d\tau = \frac{-\frac{2}{3}\pi\eta(3V_0/\pi)^{\frac{2}{3}}}{4\pi(3V_0/\pi)^{\frac{1}{3}}} \int_\infty^{\tan\theta} \frac{\tan^{-\frac{5}{3}}\theta\, d(\tan\theta)}{f \tan^{\frac{2}{3}}\theta} \tag{11}$$

Integration on the assumption of f being independent of θ and subsequent transformations give:

$$\tau = \frac{\eta(3V_0/\pi)^{\frac{1}{3}}}{8 f \tan^{\frac{4}{3}}\theta} \tag{12}$$

Eq. (12) describes spreading of viscous drops on smooth horizontal surfaces in the interval 90° > θ > 0° bringing together main physical parameters affecting spreading velocity. Time changes of the contact area radius of a drop on the substrate surface are expressed by the equation:

$$r = \left(\frac{24 V_0 f}{\pi\eta}\right)^{\frac{1}{4}} \tau^{\frac{1}{4}} \tag{13}$$

A similar relation between r, V_0, and τ was obtained earlier.[16] It follows from Eq. (12) that spreading time is directly proportional to the bulk viscosity of the spreading phase and the cubic root of the initial volume of a drop and inversely proportional to the variation of the free surface energy of the system. This is in accordance with the experimental results discussed above. A quantitative verification of the deduced equation is done in Figure 13. Tangent

Downloaded At: 17:03 22 January 2011

of the slope of the straight lines serves as an exponent of the corresponding parameter in the equation. For the case of complete spreading of PDMS drops and for the formation of a final contact angle the following equations were considered:

$$\log r - \tfrac{1}{4}\log\left(\frac{\gamma_{SV}-\gamma_{SL}}{\gamma_{LV}} - \cos\theta\right) = \tfrac{1}{4}\log\left(\frac{8\gamma_{LV}}{\eta}\cdot\frac{3V_0}{\pi}\right) + \tfrac{1}{4}\log\tau \qquad (14)$$

at

$$\frac{\gamma_{SV}-\gamma_{SL}}{\gamma_{LV}} = I$$

and

$$\log\tau = \log\frac{\eta(3V_0/\pi)^{\frac{1}{3}}}{8\gamma_{LV}} - [\log(\cos\theta_0 - \cos\theta) + \tfrac{4}{3}\log\tan\theta] \qquad (15)$$

The equations are obtained after transforming Eqs. (12) and (13) and taking logarithms. Tangent of the slope of curve 1 (Figure 2) is 0.28, and Eq. (14) gives 0.25. Three other parameters, η, V_0 and $\tan\theta$, are in a good agreement with Eq. (12).

Downloaded At: 17:03 22 January 2011

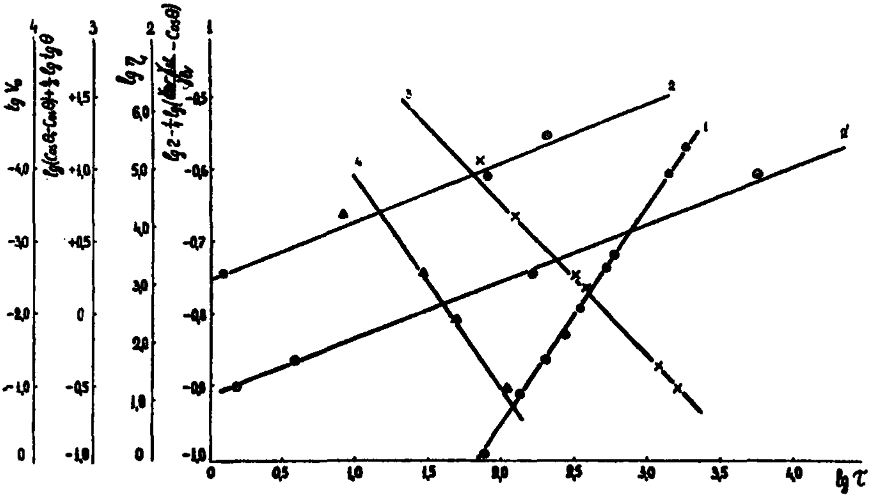


FIGURE 13 Experimental verification of Eq. (12) at 22°C: 1—mica, $\bar{M} = 708 \times 10^3$; $V_0 = 203 \times 10^{-3}\,\mathrm{cm}^3$; 2—$\theta = 70°$, mica, $\bar{M} = 25 \times 10^3$; 38×10^3; 340×10^3 708×10^3; 960×10^3; $V_0(\mathrm{cm}^3) = 1.33 \times 10^{-3}$; 2.14×10^{-3}; 1.93×10^{-3}; 203×10^{-3}; 2′—the same as for 2 but at $\theta = 10°$; 3—PTFE, $\bar{M} = 960 \times 10^3$; $V_0 = 2 \times 10^{-3}\,\mathrm{cm}^3$; 4—glass, $\bar{M} = 340 \times 10^3$; $V_0(\mathrm{cm}^3) = 4 \times 10^{-4}$; 2.64×10^{-3}; 1.17×10^{-2}; 1.09×10^{-1}.

Cherry and Holmes[26] give the following expression for the spreading velocity of a viscous compound on a solid surface:

$$\frac{d(\cos\theta)}{d\tau} = \frac{\gamma_{LV}}{\eta L}(\cos\theta_0 - \cos\theta) \tag{16}$$

All symbols are identical to those used by us except L, an unknown parameter characterizing the couple polymer/substrate and having the dimension of length.[3, 26, 28] Rewriting Eq. (12) in a differential form and substituting f from Eq. (2) we obtain:

$$-\frac{d(\tan\theta)}{d\tau} = \frac{6\gamma_{LV}\cos\theta_0}{\eta(3V_0/\pi)^{1/3}}\left(1 - \frac{\cos\theta}{\cos\theta_0}\right)\tan^{7/3}\theta \tag{17}$$

This expression can be compared with Eq. (16) in the interval 90° > θ > 0° giving:

$$L = \left(\frac{3V_0}{\pi}\right)^{1/3}\Big/6\cos\theta_0. \tag{18}$$

The couple polymer/substrate is characterized here by θ_0; the expression includes the drop volume. For the couple PDMS/PTFE at $V_0 \approx 10^{-3}$ cm^3 L is about 10^{-3} cm. Generally speaking, a similar expression but in a more complex form can be derived by substituting f from Eq. (3) for substrates on which a polymer spreads completely:

The "thermodynamic adhesion work" determined by the Young-Dupré relationship is known not to be a reliable measure of the strength of adhesion bond, particularly for the systems polymer/substrate. There are at least three reasons for that:

1) Breaking of bond causes irreversible processes in the system occurring due to the plastic deformation of the system or the electrification of the surfaces.

2) Cohesion work for high molecular compounds is well above the doubled free surface energy.

3) Adhesion work refers practically always to the interface, with a great number of micro- and macrodefects.

Adhesion force was demonstrated, however, to grow with lower contact angle of a drop,[32-34] and in this context it is assumed[27] that the time of building up the adhesion bond plays an essential role for high viscosity compounds. Indeed, a strong contact requires complete penetration of the spreading compound into all microirregularities of the surface which it spreads on. Otherwise the remaining unfilled cavities will act not only as sites with the lack of adhesion, but as defects favouring the breakdown of adhesive bonds. As a consequence, adhesive force may be many times less than is calculated for perfect surfaces. This case as a special kind of defect of

Downloaded At: 17:03 22 January 2011

the polymer/substrate interface was considered by Bascom *et al.*[35] It was shown[27] that adhesive force correlates better with $\gamma_{LV}/\eta L$ (see Eq. (16)) termed "wetting constant" than with the change of a contact angle of a drop. Taking into account Eq. (17) the constant can be expressed as $6\gamma_{LV} \cos \theta_0 / \eta(3V_0/\pi)^{1/3}$ where, at least for drops, all terms have a certain physical sense.

References

1 D. D. Eley in *Adhesion* (Oxford University Press, London, 1961). P. 52.
2. K. Kanamaru, *Kolloid-Z.* **192,** 51 (1963).
3. H. Schonhorn, H. L. Frisch, T. K. Kwei, *J. Appl. Phys.* **37,** 4967 (1966).
4. T. K. Kwei, H. Schonhorn, H. L. Frisch, *J. Colloid and Interface Sci.* **28,** 543 (1968).
5. J. I. Frenkel, *Fizicheskiy journal* (*Russ.*) **9,** 385 (1945); *J. Experimental. Technicheskoy Fiziki* (*Russ*) **16,** 29 (1946); C. Herring, *J. Appl. Phys.* **21,** 301 (1950).
6. V. N. Zvetkov, R. K. Chander, *Visocomolecular. Soedineniy* (*Russ.*) **11,** N4, 605 (1959).
7. T. Takaoka, S. Ueda, *J. Polymer. Sci.*, **B4,** 317 (1966).
8. V. Bajant, V. Chvalovski, I. Ratouski, *Silicon* (Izdatelstvo Chimicheskoy Literaturi, Moscow, 1960). P. 253.
9. D. G. LeGrand, G. L. Gaines, Jr., *J. Colloid and Interface Sci.* **31,** 162 (1969).
10. R. J. Roe, *J. Phys. Chem.* **72,** 2013 (1968).
11. H. W. Fox, W. A. Zisman, *J. Colloid. Sci.* **5,** 514 (1950).
12. M. L. White, *Clean Surfaces, Their Preparation and Characterization for Interfacial Studies*, Ed. G. Goldfinger (Marcel Dekker New York, 1970).
13. R. F. Willis and R. F. Shaw, *J. Colloid and Interface Sci.* **31,** 397 (1969).
14. H. Van Oene, J. E. Chang and S. Newman, *J. Adhesion* **1,** 54 (1969).
15. S. Strella, *J. Appl. Phys.* **41,** 4242 (1970).
16. E. D. Schukin *et al.*, *Kolloid. Journal* (*Russ.*) **25,** 108 (1963).
17. J. V. Najdich, *J. Phys. Chem.* (*Russ.*) **42,** 1946 (1968).
18. T. P. Yin, *J. Phys. Chem.* **73,** 2413 (1969).
19. J. L. Moilliet, *J. Colloid and Interface Sci.* **32,** 165 (1970).
20. W. A. Zisman, *Advan. Chem.* **43,** 1 (1964); V. A. Ogarev, V. M. Rudoy and A. A. Trapeznikov, *Izvestiy Academy Science USSR* (*Russ.*). **11,** 2788 (1972).
21. R. E. Johnson and R. H. Dettre, *Advan. Chem.* **43,** 113 (1964).
22. V. D. Kuznezov, *Surface Energy of Solid* (*Russ.*). (Gostehizdat, Moscow, 1954). Pp. 185, 205.
23. V. V. Arslanov, T. N. Ivanova and V. A. Ogarev, *Docladi AN USSR* (*Russ.*) **198,** 5 (1971).
24. *Surface diffusion and spreading* (Russ.) Izdatelstvo Nauka, Moscow, 1969).
25. W. D. Bascom, R. L. Cottington and C. R. Singleterry, *Advan. Chem.* **43,** 355 (1964).
26. B. W. Cherry and C. M. Holmes, *J. Colloid and Interface Sci.* **29,** 174 (1969).
27. B. W. Cherry, Snhaela el Muddarris, *J. Adhesion* **2,** 42 (1970).
28. S. Newman, *J. Colloid and Interface Sci.* **26,** 209 (1968).
29. E. Ruckenstein, *Chemical Eng. Sci.* **24,** 1223 (1969).
30. R. V. Duba, *J. Phys.* **74,** 2040 (1970).
31. B. V. Deryagin and S. S. Voyutskii, *Kolloid. Journal* (*Russ.*) **27,** 624 (1965).
32. M. J. Barbarisi, *Nature* **215,** 383 (1967).
33. E. A. Bourcher, *Nature* **215,** 1054 (1967).
34. M. Levine, G. Ilkka and P. Weiss, *Adhesives Age* **7,** 24 (1966).
35. B. W. Cherry and C. M. Holmes, *Brit. J. Appl. Phys.* **2,** 821 (1969).

Downloaded At: 17:03 22 January 2011