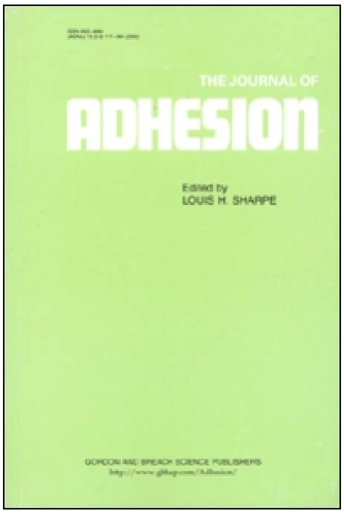

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# Viscoelasticity and Kinetics of Wetting on Rubber

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# Viscoelasticity and Kinetics of Wetting on Rubber*

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The kinetics of spreading of a liquid drop is usually controlled by conversion of capillary potential energy into viscous dissipation within the liquid when the solid is rigid. However, if the solid is soft, a "wetting ridge" near the solid/liquid/vapour triple line can also be a dissipative sink as the wetting front moves. As a consequence, the kinetics of wetting of rubber may be controlled essentially by viscoelastic losses in the polymer rather than by viscous losses in the liquid drops. Therefore, a direct analogy between the kinetics of wetting and adhesion, respectively, for a liquid and a solid on an elastomeric substrate has been recently proposed. In this paper, the superposition of viscoelastic braking and moderate rubber swelling in the drop spreading phenomenon is considered.

KEY WORDS: wetting kinetics; viscoelasticity; rubber; wetting ridge; contact angle; swelling; tricresylphosphate

## I INTRODUCTION

Wetting plays a fundamental role in adhesive bonding in which sufficient contact and coverage of solid substrates must be obtained before adhesive solidification occurs. Wetting phenomena are also important in a number of natural and other industrial processes such as eye irrigation, the application of insecticides, paints and inks, and tertiary oil recovery. Not only the degree of wetting but also the speed of the wetting process is of great importance.

Under classic conditions of wetting on a smooth, horizontal, homogeneous, isotropic and hard solid, the kinetics of spreading is controlled essentially by a dynamic energy balance between the rate of restitution of capillary potential energy and viscous dissipation occurring due to shear motion within the liquid.[1] Thus, if a small axisymmetric sessile drop is placed on a solid surface, the contact angle, $\theta(t)$, before equilibrium is attained, is greater than the static value, $\theta_0$, where the latter satisfies Young's

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[*] One of a Collection of papers honoring Jacques Schultz, the recipient in February 1995 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M*.

equation:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta_0 \tag{1}$$

$\gamma_{ij}$ terms being the interfacial free energies between solid ($S$), liquid ($L$) and vapour ($V$) phases. This capillary imbalance leads to a spreading force of $\gamma[\cos\theta_0 - \cos\theta(t)]$ and as the wetting front moves forward, work is expended and dissipated by viscous shear within the liquid.

However, when liquids are put into contact with soft solids such as rubbers, local deformation will result near the $SLV$ triple line due mainly to the component of liquid surface tension, $\gamma_{LV} = \gamma$, perpendicular to the undisturbed substrate, $\gamma \sin\theta_0$[2,3]. The resulting "wetting ridge", or elastic displacement of the solid has a height, $h$, of the order of magnitude of $\gamma \sin\theta_0/G$, where $G$ is the shear modulus of the solid. Therefore, when spreading occurs on a soft, viscoelastic substrate like a rubber, there exists another dissipative process retarding wetting front movement.[4] As the triple line advances, the wetting ridge accompanies it and the strain/relaxation cycle occurring along the spreading path leads to further energy loss, so that an analogy between the kinetics of wetting and adhesion, respectively, for a liquid and a solid on an elastomeric substrate has been recently proposed.[5,6]

In this study, the superposition of viscoelastic braking and rubber swelling in the drop spreading phenomenon is also presented and discussed.

## II THEORETICAL

The derivation of Young's equation in which forces are equilibrated parallel to the solid surface may be regarded as correct for most purposes. Nevertheless, the component of liquid surface tension perpendicular to the solid surface leads to a reaction in the substrate. Thus, a local deformation of the solid occurs leading to the formation of a wetting ridge[2,3] which has a height of the order of $\gamma \sin\theta_0/G$, as pointed out above.

When the $SLV$ triple line is moving at speed $U$, corresponding to a drop spreading with contact angle $\theta(t)$ decreasing towards $\theta_0$, the wetting ridge moves with the triple line and work, $\dot{E}$, is effected per unit time and per unit length of triple line,[4]

$$\dot{E} = \frac{\gamma^2 U}{2\pi G \epsilon} \tag{2}$$

where $\epsilon$ is a cutoff distance near the triple line, below which the behaviour of the solid is no longer linearly elastic ($\epsilon$ is of the order of a few nanometers).[3] The absence of $\theta(t)$ in equation (2) is, perhaps, surprising but is related to the fact that a horizontal "stretching" term accompanies the wetting ridge and their combined effect essentially eliminates contact angle dependence.[4]

However, most soft solids, and in particular rubbers, are viscoelastic and a fraction, $\Delta$, of the energy expended in equation (2) will be dissipated. Taking the fraction of the work, $\Delta$, to be rate dependent, as has been shown in adhesion experiments,[7-9] we write

$$\dot{E}\Delta = \frac{\gamma^2 U}{2\pi G \epsilon}\left(\frac{U}{U_0}\right)^n \tag{3}$$

where $U_0$ and $n$ are constants and may, thus, define the damping properties of the solid.

The behaviour during spreading of a small axisymmetric drop of a liquid on an ideal, hard solid has been previously described.[1] A dynamic energy balance is observed in which the excess free energy, due to the fact that the drop has not attained capillary equilibrium, is consumed by dissipation within the liquid caused by viscous shear. The rate at which capillary free energy is given up, per unit length of triple line, is given by

$$\dot{F} = \gamma U[\cos\theta_0 - \cos\theta(t)] \tag{4}$$

this equation being obtained by considering the spreading force at the triple line due to Young's equation of equilibrium not being satisfied for contact angle $\theta(t)$, and multiplying this by spreading speed.

This work is consumed, totally for hard solids and partially for rubbers, by viscous dissipation, $T\dot{S}$, taking the form for small contact angles[1] ($\theta(t) \leq 1$ rad)

$$T\dot{S} = \frac{3\eta l U^2}{\theta(t)} \tag{5}$$

where $\eta$ is liquid viscosity and l is a logarithmic factor, approximately constant, involving cutoff distances to the dissipative zone of the drop.

When the solid is a rubber, the wetting ridge near the triple line is also a dissipative sink as the wetting front moves[4-6] and the viscoelastic dissipation, $\dot{E}\Delta$, defined by equation (3), occurs at the wetting ridge. Considering the global energy balance between equation (4) and equations (3) and (5), we obtain

$$\cos\theta_0 - \cos\theta(t) = \frac{3\eta l U}{\gamma\,\theta(t)} + \frac{\gamma}{2\pi G\epsilon}\left(\frac{U}{U_0}\right)^n \tag{6}$$

which is the basic equation governing spreading in the general case. Typically, $n \ll 1$, and, thus, at sufficiently high speeds, the first member on the right hand of equation (6) dominates, while at lower speeds the second member governs behaviour. The latter situation corresponds to the experimental results reported here and, therefore, equation (6) will be recast as

$$\log[\cos\theta_0 - \cos\theta(t)] \approx n \log U + \log\frac{\gamma}{2\pi G\epsilon U_0^n} \tag{7}$$

It is worth noticing that under the same conditions, equation (6) can also be written as

$$\log[(W_0 - W)/\gamma] \approx n \log U + \text{constant} \tag{8}$$

where $W$ and $W_0$ represent the "instantaneous" and equilibrium work of adhesion $[W_{(0)} = \gamma(1 + \cos\theta_{(0)})]$. Equation (8) is very similar, apart from the sign within the left hand member, to the adhesion dynamics equation corresponding to the separation process between a hard substrate and a rubber. As discovered by Gent and Schultz[7] some years ago, the apparent energy of adhesion of an elastomer during separation from its substrate, $W$, greatly exceeds the intrinsic Dupré value, $W_0$($W_0 = \gamma_1 + \gamma_2 - \gamma_{12}$, where $\gamma_1$ and $\gamma_2$ are the surface free energies and $\gamma_{12}$ the interfacial free energy).

Adopting an established form for the separation rate dependence,[9] we have, using our notation,

$$\log[(W - W_0)/W_0] \approx n \log v + \text{constant} \tag{9}$$

where $v$ is the crack speed and the constant $n$ is equal to 0.5–0.6. Therefore, a direct analogy between relations (8) and (9) being evident, a parallel can be drawn between the phenomena of wetting and adhesion involving viscoelastic solids such as rubbery materials.

Although the general phenomenon of wetting dynamics on viscoelastic materials is now well understood,[5, 6] complications may arise in some circumstances, for example when equilibrium conditions for wetting are affected by another interfacial phenomenon such a rubber swelling. In this paper, such a situation will be described and taken into consideration.

## III EXPERIMENTAL

The contact angle, $\theta$, of small sessile drops of tricresylphosphate, TCP, (drop volume 2 μl, viscosity $\eta = 70\,\text{cP}$, surface tension $\gamma = 40.9\,\text{mN}\cdot\text{m}^{-1}$), has been measured with a Ramé-Hart contact angle goniometer as a function of time after deposition, $t$, on flat, smooth, horizontal surfaces of soft and rigid solids at 20°C. Although TCP is a non-volatile liquid at 20°C, solid samples were placed in a closed glass box to obviate any interference from the room atmosphere. Each contact angle given is the average of 5 measurements and the standard deviation is of the order of 0.5 degree or less.

In the case of relatively high modulus solids (Teflon PFA, Du Pont de Nemours, $G \approx 250\,\text{MPa}$, and fused silica, Quartz et Silice, $G \approx 30\,\text{GPa}$), equilibrium contact angles are attained after only *ca.* 15 seconds as shown in Figures 1 and 2. For these two rigid materials, the kinetics of spreading are very similar, although the contact angle on silica is small compared with that on Teflon PFA. This confirms that viscous dissipation (Eq. (5)) is relatively minor, even for small equilibrium contact angles.

Figure 1 also gives the variation of the contact angle, $\theta(t)$, on an elastomer (a two-component silicone rubber, RTV 630, General Electric Co.) having a low shear modulus, $G$, equal to 1.5 MPa. In the first set of experiments, in order to avoid any interference produced by a moderate degree of swelling of the elastomer by tricresylphosphate, the rubber samples were immersed in the liquid for several days prior to the wetting experiments until equilibrium swelling was noted by gravimetry. The samples were then carefully dried before depositing drops of the same liquid on the surface.

Much slower spreading occurs with the rubbery material, 30 minutes being necessary to obtain the equilibrium value of the contact angle. This behaviour is attributed to local deformation of the substrate leading to viscoelastic braking of the spreading of TCP. The hypothesis is corroborated by line 1 of Figure 3 which has been obtained by plotting the difference between the cosines of equilibrium contact angle, $\theta_0$, and the instantaneous contact angle, $\theta(t)$, as function of the liquid spreading speed, $U$ ($U = dr/dt$, where $r$ is the drop contact radius). Verification of equation (7) suggests that the spreading dynamics of TCP on the silicone rubber is effectively governed by the formation of a wetting ridge at the liquid drop periphery and that the value of the gradient $n$ of 0.56 is in good accordance with a phenomenon of viscoelastic dissi-

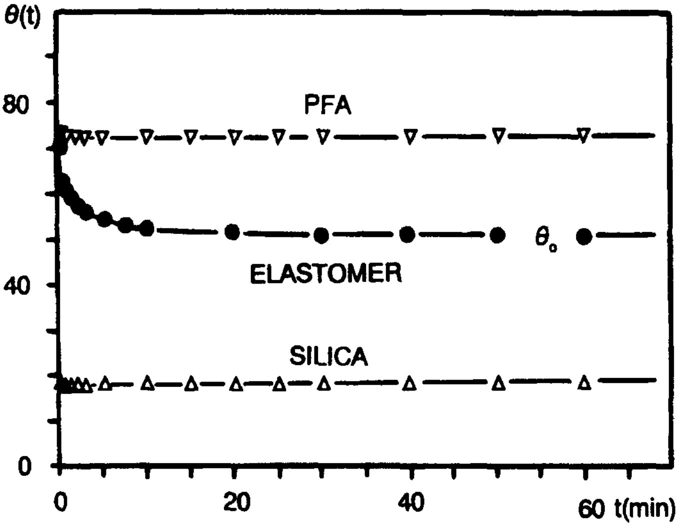

FIGURE 1 Evolution of the contact angle, $\theta(t)$, of TCP on preswollen silicone rubber, Teflon PFA and fused silica.

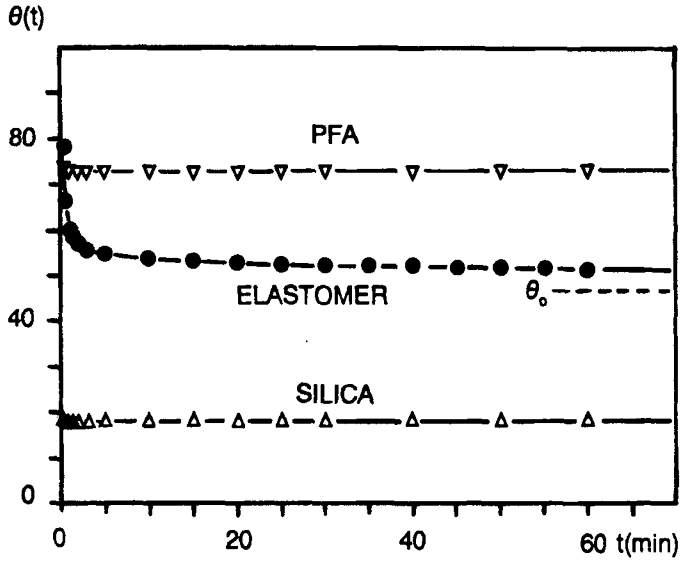

FIGURE 2 Evolution of the contact angle, $\theta(t)$, of TCP on silicone rubber, Teflon PFA and fused silica.

pation[7,9] in the wetting ridge. The dissipative properties of the elastomer have also been determined using the rolling cylinder adhesion test[9-11] and the value of $n$ was found to be 0.55, which is good agreement with the value deduced from wetting kinetic measurements.

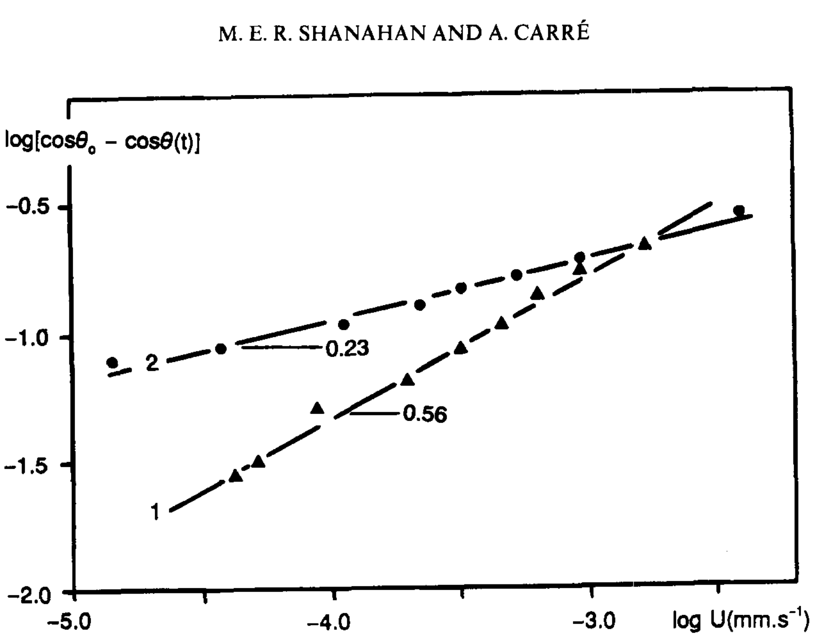

FIGURE 3 Evidence for the hypothesis of viscoelastic braking for TCP spreading on silicone rubber- Line 1 with preswelling, line 2 without preswelling by TCP.

Figure 2 presents the variation of the contact angle, $\theta(t)$, on the same rubber, but this time the elastomer had not been preswollen by TCP. In comparison with the spreading kinetics on rigid solids (Teflon PFA, fused silica), we observe the same behaviour as before, that is a slow variation of the contact angle $\theta(t)$ on the elastomer. However, after the main variation of the contact angle occurring within the first 30 minutes, we observe a very slow, yet continuous, decrease of $\theta(t)$ over a period of several hours before a stable value for $\theta_0$ is obtained (this slow decay of $\theta(t)$ is more clearly visible on curve 2 of Fig. 4).

Application of equation (7) leads to line 2 of Figure 3. This result suggests that the spreading dynamics of TCP on the silicone rubber is again governed by the formation of a wetting ridge; however, the value of the gradient, $n = 0.23$, is rather low in comparison, on the one hand, with values typically found in kinetic adhesion studies[7, 9] and, on the other hand, with the former experiments using the preswollen rubber. It is suspected that moderate swelling of the rubber by TCP (of the order of 1 wt% at equilibrium) may influence the spreading kinetics and be responsible for the low value on $n$. Further evidence for interference due to swelling is the slow and very long decay of $\theta(t)$ for several hours before a stable equilibrium value, $\theta_0$, is reached, this period of time being reduced to 30 minutes when the rubber is preswollen.

## IV DISCUSSION

To dissociate purely viscoelastic effects from swelling effects in the set of experiments reported in Figure 2, a simple model of diffusion of TCP in the rubber substrate has been developed.

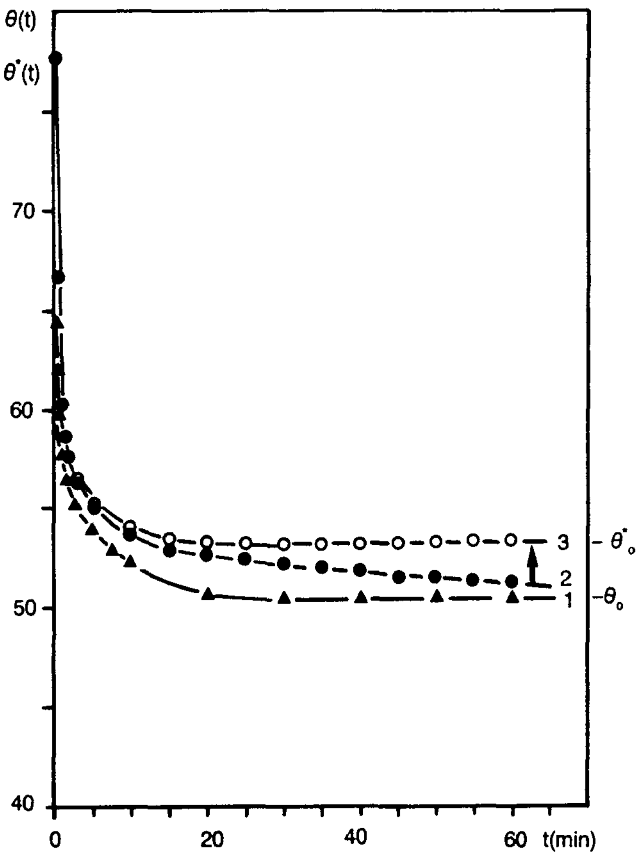

FIGURE 4 Evolution of the contact angle, $\theta(t)$, of TCP on silicone rubber preswollen by TCP (1), silicone rubber (2) and on silicone rubber after allowing for swelling effects (3).

Rubber swelling modifies the liquid/solid work of adhesion, $W_0$, because, in addition to the initial liquid/solid interactions, liquid diffusion into the solid produces supplementary liquid/liquid interactions, liquid molecules having penetrated the solid/liquid interface. Therefore, to the initial work of adhesion in the absence of swelling, $W_0$, an additional term corresponding to a fraction of the cohesion energy of the liquid, $2\gamma$, has to be added. If $t$ is the time of diffusion, the work of adhesion at $t$, $W_0(t)$, can then be expressed as

$$W_0(t) = W_0 + 2\lambda(t)\gamma \tag{10}$$

with $\lambda(t) \ll 1$. In equation (10), neither potential changes of the volume of the liquid and solid phases nor possible variations of the solid/liquid interface area are taken into account, given the low degree of swelling of silicone rubber by TCP ($\leq 1$ wt%) and the relatively minor impact of swelling on contact angle at equilibrium.

To evaluate the time dependent function, $\lambda(t)$, a model of diffusion inspired by the Langmuir adsorption theory is proposed. Considering that liquid molecules having diffused into the rubber are localised on discrete sites (maybe free volume domains), we can deduce the rate of filling of these sites by TCP with time. Only the filling of the first layer of the sites situated below the solid/liquid interface at a distance of the order of the length of intermolecular interaction (a few nm)[12] needs to be considered to estimate $\lambda(t)$.

As in the classic Langmuir adsorption process, we consider that the rate of filling of sites by TCP molecules follows first order kinetics. If N represents the total number of free sites per unit area at $t = 0$ and $N(t)$ the number of free sites at the time $t$, then $dN(t)/dt = -k\,N(t)$, where $k$ is the rate constant. Therefore, $N(t)$ decreases as $N \exp(-kt)$ and the number of sites occupied by TCP molecules at $t$ become $[N - N(t)]$, a quantity which determines directly the parameter $\lambda(t)$ in equation (10), so that $W_o(t)$ can be writren as

$$W_o(t) = W_o + \beta N(1 - e^{-kt})\gamma \tag{11}$$

where $\beta$ is a constant.

Using the Young-Dupré expression, $W = \gamma(1 + \cos\theta)$, and introducing the boundary conditions of $\theta = \theta_o$ for $t = 0$ (contact angle at equilibrium without swelling) and $\theta = \theta_{o\infty}$ for $t \to \infty$ (contact angle at equilibrium with swelling), we obtain

$$\cos\theta_o(t) = \cos\theta_o + (\cos\theta_{o\infty} - \cos\theta_o)(1 - e^{-kt}) \tag{12}$$

The time dependent variation of contact angle on the silicone elastomer and on the silicone elastomer preswollen with TCP is shown in Figure 4 over a period of about 60 minutes. It may be observed that the period corresponding to the major part of the contact angle decrease – the contact angle changes by 20 degrees in the first 10 minutes for both types of sample – is over after 30 minutes of contact with the preswollen elastomer. In addition, after 30 minutes, the contact angle on the non-swollen rubber decreases slowly and approximately linearly up to 60 minutes of contact with a linear fit satisfying the equation $\theta(t) = 53.1 - \alpha t$ ($\theta(t)$ in degrees and $\alpha = 5.24 \times 10^{-3}$ deg. s$^{-1}$ for $t$ between 30 and 60 minutes). This linear part can be derived from the exponential decay of $\cos\theta_o(t)$ (Eq. (12)) with time when the viscoelastic braking regime is over. Considering that $\exp(-kt) \approx 1 - kt$ (for relatively short times) and that $\cos\theta \approx 1 - \theta^2/2$ (for $\theta \leq 1$ rad) allows us to deduce, after some mathematical simplification, an approximate expression of equation (12) in the form:

$$\theta_o(t) \approx \theta_o - \frac{k(\theta_o^2 - \theta_{o\infty}^2)}{2\theta_o} \cdot t \tag{13}$$

This last expression justifies the linear decay of $\theta(t)$ observed between 30 and 60 minutes (Fig. 4). Taking now the experimental values for $\theta_o(t = 0)$ and $\theta_{o\infty}(t \to \infty)$, respectively, as 53.1 and 47 degrees allows us to estimate the rate constant of the diffusion process of TCP, $k$, which we find to be of the order of $9 \times 10^{-5}$ s$^{-1}$. It can be observed that the variation of $\theta_o$ from 53.1 to 47 degrees, attributed to swelling, is minor. This validates the use of several simplifying hypotheses employed in this discussion.

The accuracy of the speed constant, $k$, may be evaluated by comparing the experimental values of $\theta(t)$ with the values deduced from equation (12) for contact times greater than 30 minutes (see Table I). Good agreement between both series of values justifies the simple model of diffusion of TCP into the silicone rubber.

TABLE I

Comparison between experimental values of $\theta(t)_{\mathrm{exp}}$ and theoretical values deduced from Eq. (12), $\theta_0(t)_{\mathrm{th}}$, for $t$ greater than 30 minutes (in Eq. (12) $k$ is equal to $9 \times 10^{-5}\ \mathrm{s}^{-1}$, $\theta_0$ to 53.1 and $\theta_{0\infty}$ to 47 degrees)

| t/sec | 1800 | 2100 | 3600 | 7200 | 10800 | 14400 | $\infty$ |
|---|---|---|---|---|---|---|---|
| $\theta(t)_{\mathrm{exp}}$ | 52.2 | 52.0 | 51.3 | 50.7 | 50.2 | 49.7 | 47.0 |
| $\theta_0(t)_{\mathrm{th}}$ | 52.2 | 52.1 | 51.5 | 50.3 | 49.4 | 48.7 | 47.0 |

Admitting that the evolution of the contact angle after 30 minutes results only from swelling, it now becomes possible to separate purely viscoelastic braking from the swelling effect by taking $\theta^*(t) = \theta(t) + \alpha t$ as being the virtual contact angle in the absence of rubber swelling (curve 3, Fig. 4).

The use of $\theta^*(t)$ in equation (7) is illustrated in Figure 5 where the "swelling free" linear fit (line 3) has presently a gradient, $n$, of 0.59 (in agreement with other wetting and adhesion experiments[5, 6, 9]) and is situated parallel and near to the preswollen data (line 1). This result indicates that the low gradient value of $n = 0.23$ is very probably related to the slight swelling of the silicone rubber by TCP. The swelling produces a slow and small decay of the equilibrium value of the contact angle with time. Considering the equilibrium contact angle as the value obtained after a few hours of liquid diffusion reduces the actual value of $\theta_0$ and leads to an overestimation of the left member of equation (7) and, therefore, to a decrease of the gradient, $n$.

However, not all the mechanisms related to swelling are at present totally understood. For example, swelling affects the damping properties of the elastomer. The small

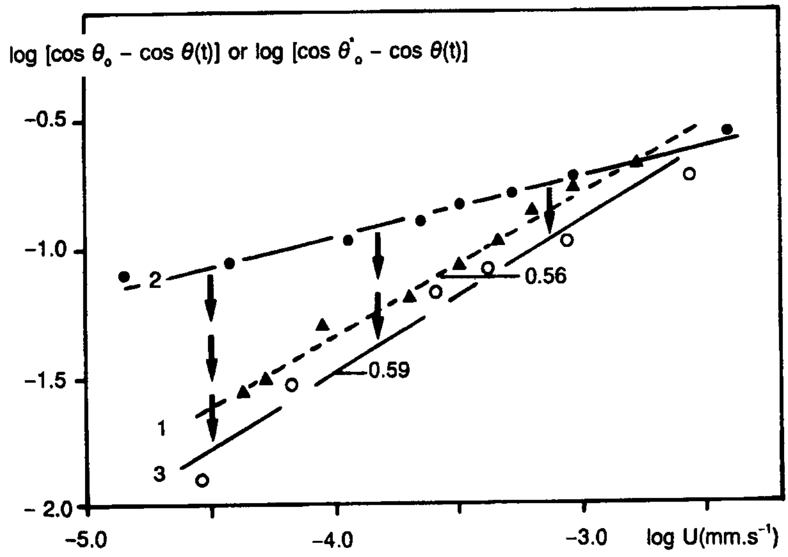

FIGURE 5 Variation of the gradient $n$ (Eq. (7)) with rubber swelling. After correction of swelling effect on $\theta_0$ ($\theta_{0\infty} \rightarrow \theta_0^*$) line 2 becomes 3. Line 1 refers to preswollen rubber.

horizontal shift between lines 1 and 3 of Figure 5 may be due to a reduction of the loss modulus, $E''$, produced by the swelling of the rubber. This slight shift has also been observed with the cylinder adhesion test performed on swollen and non-swollen rubber tracks.

## V CONCLUSION

Wetting experiments performed using a silicone elastomer and tricresylphosphate as a model liquid have shown the existence of two phenomena. Using the elastomer both in its unswollen and preswollen (by TCP) states, it has been shown that the major effect to be observed is a slowing down of spreading after the initial deposition of the liquid drop, as compared with behaviour on rigid solids. This effect is mainly related to viscoelastic dissipation occurring in the "wetting ridge", or local deformation of the substrate in the immediate vicinity of the triple line. Moreover, albeit to a less marked extent, there would also seem to be a modification to spreading kinetics related to swelling of the elastomer by the liquid and subsequent modification of interfacial interactions. This secondary phenomenon increases the time necessary to attain a stable equilibrium value for $\theta_o$. As a result, the value of the factor $n$ of equation (6) *et seq.* is apparently reduced.

The viscoelastic braking of a liquid spreading on a rubbery material can be considerated to be similar to dissipation phenomena in the adhesion of elastomers. It is recognized that, during the separation process of an elastomer from a substrate, the apparent energy of adhesion often far exceeds the thermodynamic value and this excess corresponds essentially to viscoelastic dissipation.[7-9] The dissipative properties of the elastomer used in the present wetting study have also been determined using the rolling cylinder test[9-11] and the value of $n$ found to be 0.55. This is in good agreement with the value obtained for TCP spreading when effects of rubber swelling do not interfere ($n = 0.56$).

Variation of interfacial interactions with time, in our case due to swelling, has a direct impact on $\theta_o$ and on the Dupré work of adhesion at equilibrium, $W_o = \gamma(1 + \cos\theta_o)$ or $W_o = \gamma_1 + \gamma_2 - \gamma_{12}$. An analogous situation may be encountered in the case of solid/solid contact involving a polymer or, more specifically, a rubber for which molecular rearrangements (in the elastomer) above $T_g$ may modify the interfacial free energy, $\gamma_{12}$, with time, as evoked in dwell time effects on rubber adhesion.[13] Although such processes may occur at liquid/polar polymer interfaces,[14] it is thought that, in our experiments, interfacial energy variation results more from liquid diffusion than from molecular orientation, the wetting liquid and solid substrate both being non-polar.

In this study, it has been shown that the kinetics of spreading of a liquid on a rubber may be largely dependent on viscoelastic dissipation in the wetting ridge of the substrate near the triple line. This behaviour may, in practice, be slightly altered by moderate swelling which modifies the solid/liquid interactions for long contact times.

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