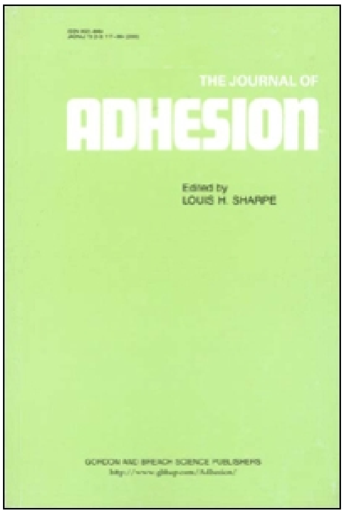


The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Wetting Dynamics of an Oil-accommodating Adhesive

M. Greiveldinger[a][b]; M. E. R. Shanahan[a][c]
[a] Centre des Matériaux P.M. Fourt, Ecole Nationale Supérieure des Mines de Paris, EVRY Cédex, France [b] IRSID, Maizeres-Les-Metz, France [c] Université d'Evry Val d'Essonne, Evry Cédex, France

To cite this Article Greiveldinger, M. and Shanahan, M. E. R.(2001) 'Wetting Dynamics of an Oil-accommodating Adhesive', The Journal of Adhesion, 75: 2, 161 — 174

To link to this Article: DOI: 10.1080/00218460108029599

URL: http://dx.doi.org/10.1080/00218460108029599

J. Adhesion, 2001, Vol. 75, pp. 161–174
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Wetting Dynamics of an Oil-accommodating Adhesive

M. GREIVELDINGER [a, b, *] and M. E. R. SHANAHAN [a, c, †]

[a] *Ecole Nationale Supérieure des Mines de Paris,*
Centre des Matériaux P.M. Fourt, B.P. 87, 91003 EVRY Cédex, France;
[b] *IRSID, B.P. 30320, 57283 MAIZIERES-LES-METZ, France;*
[c] *Université d'Evry Val d'Essonne, Bld. F. Mitterand, 91025 EVRY Cédex, France*

(Received 6 April 2000; In final form 13 July 2000)

Oil-accommodating adhesives are widely used industrially to avoid the necessity of degreasing metals before bonding. We have undertaken a study of the behaviour of drops of an uncured model epoxy adhesive on both degreased and oiled, galvanized, steel sheet during temperature increase. Contact angle, θ, *vs.* time, t, behaviour is significantly different for the two cases. On a degreased substrate, wetting rate initially increases with temperature, therefore time, due to decreasing viscosity, and then becomes reduced as equilibrium is approached. For oiled substrates, there is a central pseudo-plateau in the θ *vs.* t curve, corresponding to a modified capillary balance, itself caused by significant absorption of the oil by the adhesive. This behaviour is modelled semi-quantitatively. In the case of spreading on a degreased substrate, a simplified model is proposed to explain dynamic effects related to reduced viscosity during temperature rise.

Keywords: Absorption; Epoxy resin; Oil; Spreading; Structural adhesive; Thin film; Wetting

INTRODUCTION

Bonding of steel sheet in the automotive industry has become more efficient over recent years, in that direct application of structural adhesives can be made whilst the steel is still coated with the (essentially mineral) oils used both to protect against corrosion and to

---

[*] Present address: Société Michelin, Clermont-Ferrand, France.

[†] Corresponding author. Tel.: 33-1-6076-3022, Fax: 33-1-6076-3150, e-mail: shanahan@mat.ensmp.fr

facilitate the shape-stamping processes. The fact that modern epoxy-based adhesives are capable of penetrating the oil barrier in order to produce durable bonds obviates the need to cleanse the steel sheet and, thus, cuts out a production step, leading to greater efficiency. Work effected over the past 15 years or so [*e.g.*, Refs. 1 – 8] has suggested that the elimination of oil at the interface occurs by various mechanisms, in particular the thermodynamic displacement of oil by the adhesive at the solid surface, and the absorption of oil within the adhesive, thus liberating access for direct adhesive/substrate contact. The former of the two mechanisms was favoured in the early days [1], yet present-day evidence tends to put the emphasis on the latter [9, 10]. Fairly conclusive evidence has been found for the diffusion of oil into the adhesive as being a major mechanism of oil elimination at the interface, at least with the systems studied. The principal technique described in the work mentioned [9, 10] was Fourier transform infrared spectroscopy (FTIR).

In the study described here, another technique has been adopted: that of wetting, or spreading. Clearly, when an adhesive is applied to a substrate, good wetting must take place to obtain good coverage and avoid leaving dry patches (bubbles, voids). An industrial epoxy adhesive is (generally) exceedingly viscous at room temperature and in the heating (curing) process, two things occur: an initial decrease in viscosity leads to better (faster) spreading and, later, the resin starts to gel as crosslinking becomes predominant. Thus, we have considered the wetting dynamics of an epoxy resin on a metallic substrate, both in the presence and in the absence of a thin oil film, whilst the system is being heated.

EXPERIMENTAL

The adhesive used in this study as the spreading liquid was a model epoxy resin, yet sufficiently close to commercial specifications for it to have some bearing on actual industrial processes. A reactive mixture of diglycidyl ether of bisphenol A (DGEBA or BADGE) and dicyandiamide (DDA or DICY), in stoichiometric proportions, was adopted. The substrate used was again of industrial significance: galvanized steel sheet (Extragal Z, Usinor). Wetting experiments were effected either on the clean, degreased galvanized steel (solvent degreasing with ethyl acetate in an ultrasonic bath) or on the degreased substrate that was re-oiled to *ca.* 1–3 gm^{-2} coverage using a dip-coating technique. The oil was an industrial product commonly applied to steel sheet of the present type for its lubricant and anticorrosion properties.

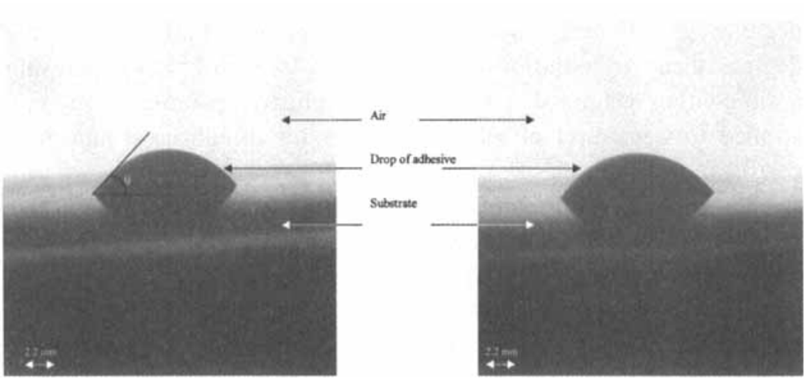
The experimental principle is very simple. Drops of epoxy adhesive of volume of *ca.* 20 microlitres (μℓ) were used. This corresponds to a scale which is manageable experimentally (the adhesive is viscous) yet for which there are negligible gravitational effects in wetting (contact radius $r \sim [\gamma/(\rho g)]^{1/2}$, where γ is the surface tension of the adhesive, ρ its density, and g is acceleration due to gravity). These drops of resin were deposed on the flat, horizontal, galvanized steel (oiled or degreased) and the system heated in air at a constant rate (10°C min^{-1}) from ambient temperature to 180°C. Temperature was maintained at 180°C for a further period until the experiment had run for 30 minutes (corresponding to a typical industrial heating cycle). Using a camera to observe drop profile and a PC system to record the evolution of drop shape, it was possible to consider contact angle before, during and after the heating cycle. Evolving contact angles, $\theta(t)$, functions of time, t, were calculated either by simple trigonometry assuming sphericity:

$$\tan\left(\frac{\theta}{2}\right) = \frac{h}{r} \tag{1}$$

where h is drop height, or from image treatment of data from near the triple line. Good agreement of the results obtained by the approaches obviates further discussion, except to mention that values of θ discussed below correspond to averages taken from the two techniques. Spreading results were found reproducible using typically 5 or 6 drops for separate experiments, but errors are not specifically calculated since they evolve with θ. In addition, they have no bearing on the semi-quantitative model proposed further on.

RESULTS

Figure 1 shows an example of drops of the resin DGEBA/DDA of identical volume posed on the galvanized steel substrate at 20°C, after



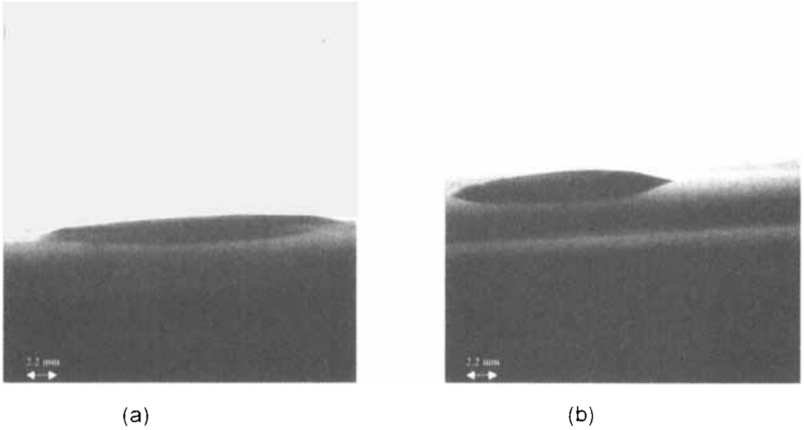
(a) (b)

FIGURE 1 Drops of equal volume (*ca.* 20 μℓ) of uncured epoxy resin on (a) oiled, and (b) degreased, galvanized, steel substrates after 5 minutes of contact at 20°C.

5 minutes of contact time. Figure 1(a) corresponds to a substrate with a thin layer of oil and Figure 1(b) without oil. No significant difference can be observed between the two images. In both cases, the initial contact angle is between 45 and 50°. However, as the heating cycle gets under way, spreading behaviour becomes quite different depending on whether or not the oil film is present. The adhesive spreads more readily on steel sheet in the presence of oil than in its absence, as manifested by Figure 2, showing the behaviour in (a) with oil and in (b) without oil (final state after crosslinking). Contact angle is difficult to ascertain in Figure 2(a), being apparently below 10°, whereas, in Figure 2(b), on the clean substrate, θ (final) is of the order of 15°. Thus, we can see directly from the initial and final states that the presence of an oil film modifies spreading. But what happens between beginning and end?

Analysis of spreading data for each minute elapsed during the heating cycle was effected for both oiled and degreased substrates. Figure 3 presents the evolution of contact angle, $\theta(t)$, as a function of time, t, from the onset of heating. Experiments were repeated several times, and allowed us to confirm the reproducibility of the trends shown in Figure 3.

On the degreased substrate, $\theta(t)$ starts to decrease significantly after *ca.* the third minute, corresponding to $\theta = 48°$ and temperature $T = 49°\text{C}$. This continues up until about the 18th minute ($\theta = 12°$,



(a) (b)

FIGURE 2 State of spreading of drops of epoxy resin (*ca.* 20 μℓ) on (a) oiled, and (b) degreased, galvanized, steel substrates, after crosslinking of the resin (*i.e.*, after heating cycle).

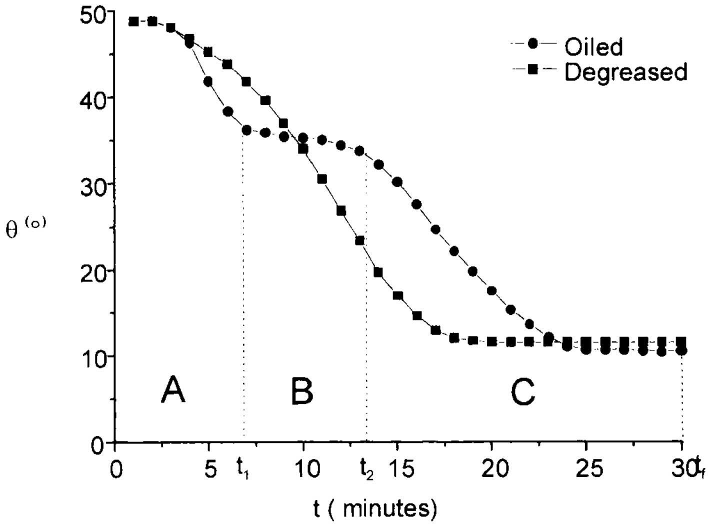


FIGURE 3 Evolution of contact angle, $\theta(t)$, with time, t, during heating cycle (10°C min^{-1} to 180°C, 180°C for remainder of 30 min), for both oiled and degreased, galvanized, steel substrates. A, B and C correspond to 3 domains observed with the oiled substrate (explained in text).

$T = 180°$C since a minute previously). After this, θ is approximately constant. By contrast, contact angle evolution on the oiled substrate is rather more complex. Up until about the 4th minute ($\theta = 46°$,

$T = 62°C$), the behaviour is similar to that for the degreased substrate, but then the rate of decrease of θ becomes greater up until about the 7th minute ($\theta = 36°$, $T = 83°C$). This time we call t_1 (see Fig. 3). There is then a period of stabilisation (slow rate of decrease of θ) until about the 13th minute ($\theta = 34°$, $T = 141°C$, time $= t_2$), followed by a period of greater rate of decrease of θ lasting until something like the 24th minute, corresponding to $\theta \approx 11°$ when the temperature has already been at 180°C for some 7 minutes. On the oiled substrate, spreading is faster for the first 7 minutes but then the period of stabilisation causes a subsequent lag behind the case of spreading on a degreased substrate from *ca.* the 10th minute ($\theta = 35°$, $T = 102°C$). After the period of stabilisation, it is as though the two substrates lead to similar behaviour, apart from the fact that the behaviour on the oiled substrate is "out of phase" and lags behind the other. The "shift" is of the order of 5 minutes. Finally, both systems stabilise at $t > 25$ minutes with the final contact angle (after crosslinking of the adhesive) being a little lower for the oiled system, in qualitative agreement with Figure 2. Nevertheless, it should be noted that the significance and reliability of very small values of contact angle are debateable.

There is, thus, a clear distinction between the trends shown by spreading behaviour on the two substrates, *viz.* with and without a thin oil film (2 – 3 μm). We shall attempt to explain these differences in the following section.

THEORY AND DISCUSSION

Basics

In order to explain observed behaviour, we shall first invoke the dynamic energy balance of spreading involving capillary forces and viscous dissipation [11, 12].

Considering unit length of the triple line solid/liquid/air (vapour) of a spreading drop, there exists a capillary, spreading force, F_S, given by:

$$F_S = \gamma_S - \gamma_{SL} - \gamma\cos\theta(t) = \gamma[\cos\theta_0 - \cos\theta(t)] \qquad (2)$$

where γ_S, γ and γ_{SL} are, respectively, the surface free energies of the solid, and of the liquid, and their common interfacial free energy. The right hand member follows from Young's equation, where θ_0 is the equilibrium contact angle [$\theta(t)$ is the dynamic angle: $\theta(t) \geq \theta_0$].

For relatively low values of contact angle, $\theta(t)$, say less than *ca.* 1 radian, the frictional force resisting F_S, denoted by F_F and due to Poiseuille type, viscous flow in the drop, is given by [12]:

$$F_F \approx \frac{3\eta\ell U}{\theta(t)} \tag{3}$$

where η is liquid viscosity and U is spreading speed. The term ℓ is the natural logarithm of the ratio of a macroscopic distance (*ca.* drop contact radius, r) and a microscopic cut-off (preventing divergence of the shear stress at the triple line). Given the logarithmic (weak) dependence on r, ℓ is treated as a constant.

For dynamic equilibrium, $F_S = F_F$ and, thus, from Eqs. (2) and (3), we have the classic relationship:

$$U = \frac{dr}{dt} = \frac{\gamma\theta(t)[\cos\theta_0 - \cos\theta(t)]}{3\eta\ell} \tag{4}$$

If the contact angle is sufficiently small ($\theta < 1$ radian), the volume, V, of a spherical cap shaped drop may be approximated by:

$$V \approx \frac{\pi}{4}\theta(t)r^3(t) \tag{5}$$

Equations (4) and (5) lead to:

$$\frac{d\theta}{dt} = \frac{K\gamma\theta^{7/3}(t)[\cos\theta(t) - \cos\theta_0]}{\eta} \tag{6}$$

where K groups the numerical constants [$K^3 = \pi/(4V\ell^3)$].

Shape of θ *vs.* t Curve

Let us return to Figure 3. We define 3 zones for the oiled substrate: zone A ($t = 0$ to $t = t_1$) corresponds to the initial rapid decrease of θ, zone B ($t = t_1$ to $t = t_2$) represents the pseudo-plateau, and zone C ($t = t_2$ to $t = t_f$) is the final period of contact angle evolution.

Equation (2) contains γ_S explicitly and Eq. (6) contains it implicitly (in cos θ_0). It was found that the effective value of solid surface free energy, γ_S, in our two systems, *viz.* oiled substrate and degreased substrate, was approximately the same at *ca.* 49–50 mJm^{-2} [9]. Clearly, the surface free energy of the resin, γ, is the same for both systems (neglecting any potentially slight modification following oil absorption). However, the term γ_{SL} of Eq. (2), which also affects $\cos\theta_0$, requires more attention. We shall define the terms γ_{SL}^{O} and γ_{SL}^{NO} to refer to the *effective* values of interfacial free energy adhesive/substrate, respectively, in the cases of oiled and degreased galvanised steel. In the following discussion we shall neglect any direct temperature dependence of surface free energies since (a) these should be relatively small and, anyway, similar in both systems, and (b) our appraisal of the situation will be semi-quantitative.

During the heating cycle, it would seem reasonable, as a first approximation, to neglect any possible variations in γ_{SL}^{NO} when compared with those of γ_{SL}^{O} · γ_{SL}^{O} will undoubtedly be modified during diffusion of the oil into the adhesive (that the oil diffuses into the adhesive in the system studied has been clearly shown elsewhere [9, 10]). Thus, we consider $\gamma_{SL}^{O}(t)$ to be a variable during the heating cycle. With the origin of time, t, being at ambient temperature, at the start of the temperature increase, we shall assume that $\gamma_{SL}^{O}(0)$ has a small value. This is plausible since we have two organic compounds, adhesive and oil, in contact. However, at the end of the heating cycle, $t = t_f$, the vast majority of oil will have diffused and, thus, values of γ_{SL}^{O} and γ_{SL}^{NO} should be comparable. During the cycle, $\gamma_{SL}^{O}(t)$ will increase (by hypothesis) as oil gradually diffuses away from the interface. To summarise, we assume that:

$$\gamma_{SL}^{O}(0) < \gamma_{SL}^{O}(0 < t < t_f) < \gamma_{SL}^{O}(t_f) \approx \gamma_{SL}^{NO}(t_f) \approx \gamma_{SL}^{NO}(0) \qquad (7)$$

Now, in zone A of Figure 3, diffusion of the oil has not really got under way and so considering relations (2) and (7), we may expect F_S to be larger for the oiled substrate than for the degreased system. (Differences in $\cos\theta(t)$ will be relatively small for the 2 cases since $\theta < 1$ radian.) Thus, with a higher spreading force on the oiled substrate, we may expect a higher spreading speed and a more rapid decrease in θ, other things being equal. Indeed, this is what we observe experimentally. (There may also be some lubrication effect of the oil film, which would tend to enhance the observed effect.)

In zone B, with increasing temperature, oil diffusion becomes more significant. Assuming, to a first approximation, a linear relationship between diffusion, the value of $\gamma_{\mathrm{SL}}^{\mathrm{O}}$ and elapsed time t (the adhesive "sees" a "cleaner" metallic surface with time), we postulate:

$$\gamma_{\mathrm{SL}}^{\mathrm{O}}(t) = \gamma_{\mathrm{SL}}^{\mathrm{O}}(t_1) + \alpha(t - t_1) \tag{8}$$

where α is given by:

$$\alpha = \frac{\gamma_{\mathrm{SL}}^{\mathrm{O}}(t_2) - \gamma_{\mathrm{SL}}^{\mathrm{O}}(t_1)}{t_2 - t_1} \tag{9}$$

When Eq. (8) is used in conjunction with Eq. (2), Eq. (6) becomes:

$$\frac{d\theta}{dt} = \frac{K\theta^{7/3}(t)}{\eta}[\gamma(\cos\theta(t) - \cos\tilde{\theta}_0) + \alpha(t - t_1)] \tag{10}$$

where $\tilde{\theta}_0$ corresponds to the (hypothetical) equilibrium contact angle of the adhesive on the oiled substrate under interface conditions equivalent to those found at $t = t_1$. This extra term, $\alpha(t - t_1)$, has the effect of *decreasing* the (absolute) value of the slope $d\theta/dt$. Thus, in the presence of an oil film which is diffusing into the adhesive (at a non-negligible rate), the effective spreading force, F_{S}, is reduced and spreading rate is decreased compared with the behaviour on a degreased substrate. Qualitatively, at least, this is what is observed in Figure 3.

Finally, in zone C, we suppose that most of the oil has diffused into the adhesive leaving the substrate almost as in the case of the degreased substrate. Thus, behaviour with and without oil is similar: there is simply a shift on the time scale of the behaviour of the oiled system due to earlier events.

The above scenario is somewhat tentative, but it does explain the basic shape of the curve, θ *vs.* t, presented in Figure 3. However, further supporting evidence is also available.

In Figure 4 we present contact angle, $\theta(t)$, for the adhesive on the oiled substrate, this time as a function of temperature, rather than elapsed time, during the heating cycle. In addition, we have added results obtained by FTIR analysis [9, 10] which correspond to an estimation of the percentage remaining of the oil originally at the

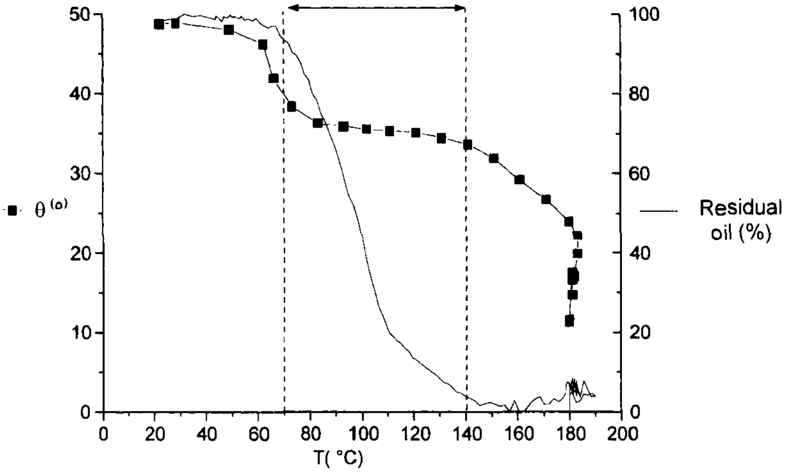


FIGURE 4 Comparison, as a function of temperature, *T*, (heating cycle as for Fig. 3) of the evolution of contact angle, θ, of the epoxy resin on oiled, galvanized steel, with the percentage of (initial) residual oil at the interface (FTIR results from [9, 10]).

adhesive/substrate[1] interface, during the heating cycle. It can be seen from the FTIR data that diffusion starts significantly towards 70°C, corresponding well to the spreading transition between zones A and B. Similarly, oil diffusion is virtually complete at 140°C, which is in good agreement with the transition from the pseudo-plateau of zone B to the final behaviour of zone C. (Note that θ decreases at a constant temperature of 180°C towards the end of the cycle – crosslinking is not yet significant.) This evidence shows clearly that the contact angle barely changes during the phase in which oil diffusion is significant.

Although there are differences in the reasoning, the above semi-quantitative approach to wetting based on variations of interfacial free energy *during spreading* may be compared with the behaviour of reactive liquids on a substrate [13] or to molecular orientation of wetting liquids [14].

---

[1] The substrate in the FTIR analysis was, in fact, *not* the galvanized steel, but similarity in behaviour is reasonably assumed [9, 10].

Effects of Temperature

The above semi-quantitative appraisal in the two cases of spreading on an oiled and on a degreased galvanized steel substrate leads to a plausible explanation of observed phenomena. However, temperature effects on two key parameters are neglected. This is evidenced by Eq. (6) [and, later, Eq. (10)] in which numerical constants are regrouped in K, yet adhesive surface tension, γ, and viscosity, η, remain. (Indeed, these two may be combined to give $\tilde{V} = \gamma/\eta$: a characteristic speed.)

The complete problem is rather complex and the following is, therefore, intended only as an indicative, first, approximate step. We shall restrict our attention to spreading on the degreased substrate only. We shall assume that the temperature dependence of surface (interfacial) free energies is of secondary importance. However, viscosity is another matter. In the case of an epoxy adhesive, two antagonistic effects are related to temperature increase. Initially, temperature increase leads to decreasing viscosity but, later, at the onset of crosslinking, the polymer will gel and viscosity will increase dramatically. We consider only the former effect.

A plausible dependence for resin viscosity on temperature is an Arrhenius type relation [15]:

$$\eta = \eta_0 \exp\left[\frac{E}{\mathrm{R}T}\right] \tag{11}$$

where η_0 is a constant, E an activation energy, R the ideal gas constant and T is, now, absolute temperature. Using Eq. (11) in Eq. (6), we obtain:

$$\frac{d\theta}{dt} = \tilde{K}\theta^{7/3}(t)[\cos\theta(t) - \cos\theta_0]\exp\left[\frac{-E}{\mathrm{R}T}\right] \tag{12}$$

where $\tilde{K} = K\gamma/\eta_0$.

With the heating cycle employed, we may express the temperature of the drop (ignoring slight inertial effects) as:

$$T = T_0 + \phi t \tag{13}$$

where T_0 is ambient temperature (293°K) and ϕ is rate of temperature increase ($\phi = dT/dt = 10\,\mathrm{K\,min}^{-1}$).

In order to exploit Eq. (12), it must be integrated after substituting for T from Eq. (13). Unfortunately, analytical integration is (apparently) impossible, but provided $\phi t/T_0$ is small, say inferior to 1/2, we may approximate for the exponential term:

$$\exp\left[\frac{-E}{\mathrm{R}T}\right] \approx \exp\left[\frac{-E}{\mathrm{R}T_0}\right]\exp[Ct] \tag{14}$$

where the constant $C = E\phi/(RT_0^2)$.

Similarly, for θ small, we have $\cos\theta \approx 1-\theta^2/2$ and, thus, obtain from Eq. (12):

$$\int \frac{\theta^{-7/3}\cdot d\theta}{(\theta_0^2-\theta^2)} \approx \frac{\tilde{K}}{2}\exp\left[\frac{-E}{\mathrm{R}T_0}\right]\cdot\int \exp[Ct]dt \tag{15}$$

The integral on the left hand side is only readily accessible if $\theta_0 = 0$. Our experimental results suggest a small, if non-zero value; therefore, for simplicity we adopt the approximation of $\theta_0 = 0$. Introducing the boundary condition that at $t = 0$, the initial value of θ is θ_i, we may integrate Eq. (15) (approximately) and, after rearrangement, we obtain:

$$\theta(t) \approx \theta_i\left[\frac{3C}{3C + 5\tilde{K}\theta_i^{10/3}\exp(-E/\mathrm{R}T_0)(\exp(Ct)-1)}\right]^{3/10} \tag{16}$$

For use in Eq. (16), and its antecedents, T_0, ϕ and t are taken from experimental conditions and θ_i was measured. The activation energy, E, was obtained by regression analysis of viscosity measurements using Eq. (11). Constant $\tilde{K}$ was also evaluated using regression analysis, this time with Eq. (12). (Values of $d\theta/dt$ were estimated from curves of θ *vs.* t.)

In Figure 5, we present the experimental results of θ *vs.* t for the system DGEBA/DDA spreading on degreased galvanized steel, together with the dependence calculated from Eq. (16) after estimation of the adjustable parameters. Although the agreement between the two certainly leaves room for improvement, the general features of a sigmoidal relationship are present in both curves. It must be emphasised that this is a first, approximate approach for elucidating the spreading behaviour during temperature increase, and discrepancies can be attributed to several things. The simple model and its

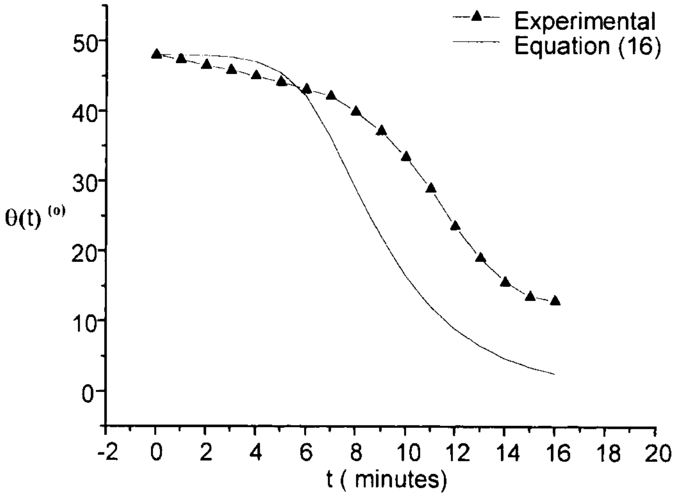


FIGURE 5 Contact angle, $\theta(t)$, *vs.* time, *t*, for the epoxy resin spreading on degreased, galvanized steel. Experimental results are compared to an application of Eq. (16).

application involve various potential sources of error, including the approximation of $\theta_0 = 0$, the difficulty of measuring reliable values of θ less than *ca.* 20°, and mathematical simplifications. Note that, in the temperature range considered, no significant onset of adhesive hardening was apparent – this occurs only after several minutes at 180°C.

CONCLUSIONS

The spreading, or wetting, behaviour of drops of a model epoxy resin on both oiled and degreased, galvanized, steel sheet has been studied during a temperature (increase) cycle. Behaviour for the two substrates is rather different. On the degreased surface, as temperature increases, so the rate of spreading increases with decreasing viscosity until equilibrium is approached, when it slows down. Spreading on an oiled substrate is more complex. A more rapid initial wetting phase is followed by a pseudo-plateau, which itself is followed by an increased rate of wetting, similar to the case without an oil film, but shifted to longer contact times. We have modelled this behaviour semi-quantitatively by invoking the effect of diffusion of the oil into the adhesive, leading to a modified capillary balance. Comparison with data on the amount of residual oil at the interface strongly suggests that the pseudo-plateau corresponds to the phase of significant oil absorption by the adhesive, corroborating the model. A simplified model of spreading on a degreased substrate during temperature rise is proposed.

One aspect which has been overlooked in our simplified model is that of potential lubrication effects facilitating drop spreading "on" the shearing oil film. A more detailed appraisal of this topic has been treated elsewhere in a different, yet related, problem [16]. However, in the context of the semi-quantitative picture presented here, it would seem reasonable to neglect lubrication as a first approximation, since any shear occurring in the oil film takes place over a thickness of *ca.* 3 μm, at most, leading to small displacement rates in the direction of drop spreading.

Although improvements and further work are clearly necessary to obtain a full understanding of the processes involved, the trends observed in spreading are correctly accounted for in this description.

References

[1] Debski, M., Shanahan, M. E. R. and Schultz, J., *Int. J. Adhesion Adhesives* **6**, 145 (1986).

[2] Debski, M., Shanahan, M. E. R. and Schultz, J., *Int. J. Adhesion Adhesives* **6**, 150 (1986).

[3] Commerçon, P. and Wightman, J. P., *J. Adhesion* **22**, 13 (1987).

[4] Foister, R. T., *J. Adhesion* **24**, 270 (1987).

[5] Maeda, S., Asai, T., Fujii, S., Nomura, Y. and Nomota, A., *J. Adhesion Sci. Technol.* **2**, 271 (1988).

[6] Hong, S. G. and Boerio, F. J., *J. Adhesion* **32**, 67 (1990).

[7] Hong, S. G. and Boerio, F. J., *J. Appl. Polym. Sci.* **55**, 437 (1995).

[8] Ogawa, T. and Hongo, M., *J. Adhesion Sci. Technol.* **11**, 197 (1997).

[9] Greiveldinger, M., *Ph.D. Thesis*, Ecole Nationale Supérieure des Mines de Paris (2000).

[10] Greiveldinger, M., Shanahan, M. E. R., Jacquet, D. and Verchere, D., *J. Adhesion* to appear.

[11] Huh, C. and Scriven, L. E., *J. Colloid Interface Sci.* **35**, 85 (1971).

[12] de Gennes, P. G., *Rev. Mod. Phys.* **57**, 827 (1985).

[13] Shanahan, M. E. R. and de Gennes, P. G., *C.R. Acad Sci. Paris* **324**(IIb), 261 (1997).

[14] Shanahan, M. E. R., Houzelle, M. C. and Carré, A., *Langmuir* **14**, 528 (1998).

[15] Glasstone, S., *Textbook of Physical Chemistry*, 2nd edition (D. van Nostrand Company, Inc., Princeton, 1946).

[16] Shanahan, M. E. R., *J. Colloid Interface Sci.* in Press.