

Wetting of Galvanised Steel by An Epoxy Adhesive: Effects of Surface Oil

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ABSTRACT

The wetting properties of an uncured epoxy resin on both clean and oiled, galvanised steel have been studied. Since the polymer is very viscous at ambient temperature, and also with an aim to simulate industrial conditions, the spreading of drops of resin during a heating cycle (temperature increase at 10°C/min) was recorded and analysed. On clean steel, a contact angle, θ , vs time, t , plot shows sigmoidal behaviour, whereas on the oiled substrate, spreading almost ceases in an intermediate stage. This strange behaviour is attributed to significant oil absorption by the polymer.

INTRODUCTION

In the automotive industry, structural adhesive bonding is becoming a current method for the assembly of steel components. Steel sheet, irrespective of surface treatment, is generally delivered with a fine layer of oil on the surface to prevent corrosion and in order to facilitate shape stamping. With modern adhesives, bonding is successfully effected without prior removal of the oil film, yet without disappearance of the oil, poor or zero adhesion would result due to the existence of a weak boundary layer,⁽¹⁾ the oil itself! Clearly the adhesive must penetrate the oil layer to gain contact with the steel, but how? Over the last ca. 15 years, work has suggested various possible mechanisms, of which the more significant are:

1) thermodynamic displacement of the oil

and, 2) absorption of the oil by the adhesive.⁽²⁻⁷⁾ It is now thought that mechanism 2) is predominant.^(8,9) Since wetting of the substrate by the adhesive is a pre-requisite of good adhesion, this study focuses on the pragmatic issue of the polymer spreading on the steel, both in the presence of an oil film, and in its absence, for comparative purposes.

EXPERIMENTAL

A simplified, yet industrially quite representative, adhesive was used: a reactive mixture of diglycidyl ether of bisphenol A (DGEBA) curing with a stoichiometric quantity of dicyandiamide (DDA). The steel substrate was again of industrial significance : galvanised steel sheet (Extragal Z, Usinor). Wetting experiments were done both on the

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clean, degreased steel (ethyl acetate, ultrasonic bath), and reoiled substrates (dip-coating to ca. 2 gm^{-2}). The oil used was an industrial product often used with the present steel for its anti-corrosion and lubricant properties.

Drop of epoxy resin of ca. $20 \mu\text{L}$ were deposited on flat, steel substrates, maintained horizontally, and heating effected at $10^\circ\text{C}/\text{min}$ from ambient to 180°C , with maintenance at this temperature until total elapsed time was 30 minutes. This is fairly representative of an industrial heating cycle. Contact angles of adhesive drops, $\theta(t)$, as a function of time, t , were obtained assuming drop sphericity, with r and h representing contact radius and height:

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

or by image treatment of data near the triple line, polymer/steel/air,

RESULTS

Typical results of $\theta(t)$ vs t are shown in Figure 1, both for spreading on clean steel and on the reoiled substrate. It can be seen that the rate of decrease of contact angle, $|d\theta/dt|$, increases initially, for both substrates, although apparently greater on the oiled steel (stage A). The overall phenomenon is related to viscosity reduction with increasing temperature, whilst the greater effect seen on oiled steel is probably due to a lubrication effect. On clean steel, $|d\theta/dt|$ stabilises before the onset of an asymptotic approach to equilibrium at $\theta \approx 10^\circ$ (stage C). For oiled steel, before this asymptotic approach to equilibrium, spreading "stagnates" (stage B). Although $|d\theta/dt|$ never becomes zero, it is very much reduced. This behaviour has been attributed to oil diffusion within the bulk adhesive, during the

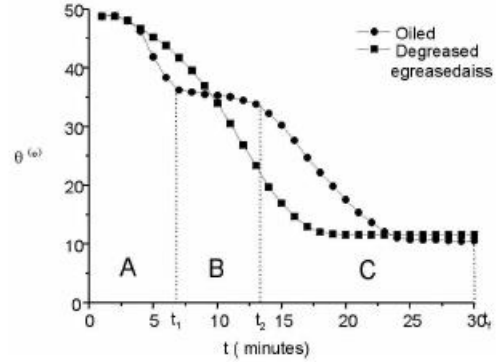


Figure 1. Contact angle, θ , vs time, t , for spreading of $20 \mu\text{L}$ drops of an uncured epoxy resin on oiled and degreased galvanised steel, during heating cycle.

spreading process. In the following, we shall suggest a semi-quantitative theory to explain the observed behaviour. It should be noted that significant crosslinking of the adhesive only occurs after the period of 30 minutes investigated here.

ANALYSIS OF RESULTS

In the hydrodynamic theory of wetting,⁽¹⁰⁾ there exists a dynamic balance between the unequilibrated Young force, F_S , and Poiseuille-type shear friction within the liquid, F_F :

$$F_S = \gamma[\cos\theta_o - \cos\theta(t)] = \frac{3\eta l U}{\theta(t)} \approx F_F \quad (2)$$

where γ is liquid surface tension, θ_o and $\theta(t)$ are respectively equilibrium and dynamic contact angles, η is viscosity, l is a dimensionless constant (of order 10), and U is spreading speed. Rearrangement of Equation(2) and use of a constant volume condition lead to:

$$\left| \frac{d\theta}{dt} \right| = \frac{K\gamma\theta^{7/3}(t)[\cos\theta_o - \cos\theta(t)]}{\eta} \quad (3)$$

where K is a numerical constant. Equation

(3) describes the decrease of contact angle during spreading under usual conditions, but here we have to contend with the possible presence of a thin oil film (lubrication and absorption by the adhesive) and decreasing viscosity due to temperature rise.

Effect of Oil Layer

Let us first consider the influence of the oil film. In stage A, $|d\theta/dt|$ is greater in the presence of oil, probably due to lubrication. This problem has been considered theoretically elsewhere,⁽¹¹⁾ but in essence we arrive at the following conclusion. The total spreading speed is given by the sum of spreading of the resin on the oil film and shear movement of the oil underlayer. In the case of a two-dimensional drop, it has been shown that:

$$\frac{v}{v} \sim \frac{2\gamma l e r}{\eta A} \quad (4)$$

where v and v are respectively oil shear and resin flow contributions to spreading speed, η and η are respective viscosities, oil and resin, e is oil film thickness and r and A are respectively drop half-width and cross-sectional area. With reasonable values of the various parameters, we find that spreading speed should be ca. 10% faster in the presence of an oil film, due to lubrication. The same basic scenario applies for an axisymmetric drop, as studied here, and thus we may explain semi-quantitatively the initially higher value of $|d\theta/dt|$ for an oiled substrate.

At longer times, spreading "stagnates" in the presence of an oil film (stage B). This corresponds to the period of major absorption of oil within the resin. As oil is absorbed, the effective capillary balance at the drop/substrate interface varies with time, modifying θ_o . Taking θ_o to represent

the hypothetical value of θ_o at the beginning of stage B (time t_1), Equation (3) is modified to⁽¹²⁾:

$$\frac{d\theta}{dt} = \frac{K\theta^{7/3}(t)}{\eta} [\gamma(\cos \theta_o - \cos \theta(t)) - \alpha(t - t_1)] \quad (5)$$

where α describes a (linearised) time dependence of interfacial tension during the "stagnation" period. Thus during stage B, the term in α brings $|d\theta/dt|$ virtually to a standstill, during oil diffusion.

Finally, after complete oil absorption (stage C), spreading resumes as if on a clean substrate, simply displaced to longer times.

Influence of Temperature Rise

Sigmoidal behaviour of $d\theta/dt$ vs t , in the case of spreading on a clean substrate, may be explained by rising temperature leading to reduced viscosity of the resin.⁽¹²⁾ A plausible dependence of viscosity on temperature is that given by the Arrhenius Equation⁽¹³⁾:

$$\eta = \eta_o \exp\left[\frac{E}{RT}\right] \quad (6)$$

where η_o is a constant, E is an activation energy and R and T have their usual meanings. When equation (6) is employed in equation (3), we obtain:

$$\left|\frac{d\theta}{dt}\right| = K\theta^{7/3}(t) [\cos \theta_o - \cos \theta(t)] \exp\left[\frac{-E}{RT}\right] \quad (7)$$

where K is a numerical constant. Use of equation (7) with experimental results is a little complicated, but described elsewhere.⁽¹²⁾ However, making a few reasonable approximations, we have found an acceptable agreement between experimental results and the approximate application of equation

(7). The comparison is shown in Figure 2. Although quantitative agreement leaves room for improvement, the main features of the sigmoidal behaviour are well represented: with initially increasing spreading rate, followed by stabilisation and then asymptotic approach to equilibrium.

CONCLUSIONS

The pragmatic problem of wetting, or spreading, of a structural adhesive, on both clean and oiled galvanised steel substrates, has been approached by direct observation and analysis of contact angle vs time data. On oiled steel, initial spreading is faster than on clean steel: a consequence of lubrication. There is then a "stagnation" period of slow movement, which may be explained by absorption of the oil within the adhesive. Finally, asymptotic approach of equilibrium is similar to behaviour on a clean substrate, but simply shifted to longer times. Using a clean, steel substrate, we observed sigmoidal vs t behaviour, which may be explained, semi-quantitatively at least, by viscosity reduction during temperature increase.

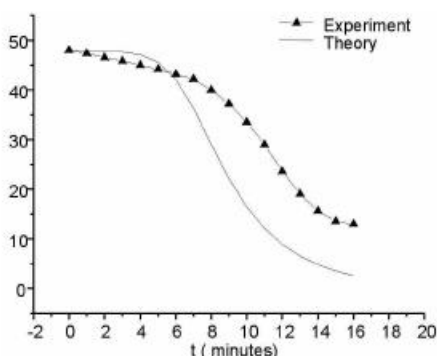


Figure 2. Contact angle, θ , vs time, t , for spreading of $20 \mu\text{L}$ drops of resin on degreased steel (triangles) compared with model based on temperature-dependent viscosity.

REFERENCES

1. J. J. Bikermann, *The Science of Adhesive Joints*, Academic Press, New York (1968).
2. M. Debski, M. E. R. Shanahan, and J. Schultz, *Int. J. Adhesion Adhesives*, **6**, 145 (1986); **6**, 150 (1986).
3. P. Commerçon and J. P. Wightman, *J. Adhesion*, **22**, 13 (1987).
4. R. T. Foister, *J. Adhesion*, **24**, 270 (1987).
5. S. Maeda, T. Asai, S. Fujii, Y. Nomura, A. Nomota, *J. Adhesion Sci. Technol.*, **2**, 271 (1988).
6. S. G. Hong and F. J. Boerio, *J. Adhesion*, **32**, 67 (1990) ; *J. Appl. Polym. Sci.*, **55**, 437 (1995).
7. T. Ogawa and M. Hongo, *J. Adhesion Sci. Technol.*, **11**, 197 (1997).
8. M. Greiveldinger, Ph. D. thesis, Ecole Nationale Supérieure des Mines de Paris (2000).
9. M. Greiveldinger, M. E. R. Shanahan, D. Jacquet, and D. Verchère, *J. Adhesion*, **73**, 179 (2000).
10. P. G. de Gennes, *Rev. Mod. Phys.*, **57**, 827 (1985).
11. M. E. R. Shanahan, *J. Colloid Interface Sci.*, **229**, 168 (2000).
12. M. Greiveldinger and M. E. R. Shanahan, *J. Adhesion* (in press).
13. S. Glasstone, *Textbook of Physical Chemistry*, van Nostrand, Princeton (1946).