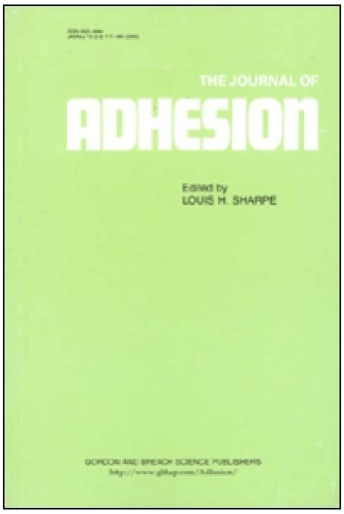

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Wetting Kinetics and the Strength of Adhesive Joints

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ABSTRACT

The work of adhesion, depending solely on the contact angle and surface tension, is unreliable as a guide to the strength of a joint. The kinetics of joint formation, exemplified by the rate of wetting, is also important and can be measured by rate of change of contact angle, a process for which an empirical equation has previously been suggested. A proposed mechanism introduces a viscosity term into the differential form of this equation.

$$(d\cos\phi/dt) = (\gamma_{LV}/\eta L)(\cos\phi_\infty - \cos\phi_t)$$

A series of metal lacquers was prepared from epoxy, U/F and M/F resins in various ratios and also epoxy/P/F and epoxy/acrylic mixtures. Stainless steel substrates, coated with these lacquers were then cemented together using polyethylene as an adhesive. It is shown that joint strength correlates better with a high wetting constant ($\gamma/\eta L$) than with a low contact angle except where this is very low.

INTRODUCTION

THE "thermodynamic work of adhesion", defined by the relationship

$$W_A = \gamma_{LV}(1 + \cos\theta) \tag{1}$$

where γ_{LV} is the surface tension of the liquid adhesive, and θ is the contact angle formed by the adhesive on that adherend is an unreliable guide to the strength of an adhesive joint for two reasons. The breaking of the joint requires irreversible processes such as plastic deformation to take place with a consequent dissipation of energy in bringing about such processes and also the term W_A refers to a defect free interface whereas in practice, there are a large number of flaws at the interface between the adhesive and the adherend.

A number of authors have, however, shown the strength of a joint to increase with decrease in contact angle [1,2,3,4]. Some authors have ascribed

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this increase in strength to the fact that if the contact angle between the adhesive and the adherend is small, then the stress concentrations at the edge of these flaws, where the adhesive has failed completely to wet the adherend, will be reduced[5,6]. The purpose of this communication is to suggest that the kinetics of the joint forming process also have a role to play in the development of the observed relationship between the strength and the contact angle.

If the rate of wetting of the substrate by the adhesive is not sufficiently fast to enable it to penetrate completely all the microfissures in the substrate surface in the time which is allowed for the joint formation process, then small voids left at the substrate/adhesive interface will act as stress raisers and reduce the strength of the joint to a value which may be several orders of magnitude lower than that which could be calculated for a defect free interface[7].

Schonhorn[8] has suggested that the rate of wetting may be determined from the rate at which the contact angle at the edge of a spreading drop approaches its equilibrium value. Newman[9] and independently Cherry and Holmes[10], proposed that this rate of change of contact angle with time could be represented by means of the equation

$$\cos\phi_c = \cos\phi_\infty \cdot [1 - a \exp(-ct)] \qquad (2)$$

where ϕ_t is the contact angle at time *t* and ϕ_∞ is the ultimate contact angle, '*a*' and '*c*' are constants. Newman also suggested that rapid wetting is favoured by low viscosity, high surface tension and low contact angle, and that the last two conditions are antithetical especially on low energy surfaces.

Cherry and Holmes[10] suggested that equation 2 represented an integrated form of

$$(d\cos\phi/dt) = c(\cos\phi_\infty - \cos\phi_t) \qquad (3)$$

and proposed a mechanism for the spreading process which interprets '*c*' as $(\gamma_{LV}/\eta L)$ where 'η' is the viscosity of the spreading adhesive and '*L*' a parameter with dimensions of length which is related to the adhesive/substrate interaction. On the basis of equation 3, 'c' represents a convenient parameter to describe the rate of wetting and is termed the 'wetting constant'. This paper presents preliminary results showing the nature of the dependence of the joint strength on the wetting constant.

When a joint fails, if the substrates remain intact, then failure must take place either by yield or fracture of the adhesive. The third possibility, that of crack propagation along the adhesive/adherend interface, merely represents a special case of the fracture mode of failure and strong arguments have been advanced[11] that such a process is either impossible or very highly improbable; it will not therefore be considered further. Cherry and Holmes[12] have suggested that the mechanical properties of a polymer which is used as an adhesive in a joint system depend upon flaws in the adhesive which can facilitate flow in the polymer when failure is by yield or which can propagate as cracks when failure is by fracture. It seems likely that these flaws may be located at the adhesive/adherend interface and be the result of imperfect wetting of the adherend by the adhesive in the time which was available for joint formation. Since the strength of the joint is therefore a function of the strength of the adhesive any experiments which are designed to examine the effect of the kinetics of wetting on the strength of the joint which is formed, must utilise the same adhesive in all the experiments, and the rate of wetting of the substrate by the adhesive can only be varied by modifying the surface of the substrate. This has been achieved in the series of experiments to be reported, by coating stainless steel substrates with a series of lacquers and characterising the surfaces so formed by measuring the wetting constant for the adhesive on these substrates at the temperature of joint formation.

If equation 3 is written in the full form as proposed by Cherry and Holmes[10]

$$(d \cos\phi/dt) = (\gamma_{LV}/\eta L)(\cos\phi_x - \cos\phi_t),$$

it can be seen that for a liquid which can spread on a series of different substrates, then at a given value of ϕ_t the rate of wetting will increase as the term $(\cos\phi_x/L)$ increases. The factors which determine L are at present unknown. In the previous papers[10,14] it has been shown that the value of L is several orders of magnitude greater than molecular dimensions and so must include other terms in addition to the distance between successive positions of metastable equilibrium for an advancing drop edge. Consequently it is not possible to correlate $\cos\phi_x$ and L; the term $(\cos\phi_x/L)$ may change in a direction opposite to the change in $\cos\phi_x$ when the substrate is changed and therefore it is suggested that the relationship which was put forward by Newman[9] that the rate of wetting increases with decrease in contact angle may not necessarily be universally true. Under such circumstances the rate of wetting may be a better guide to the strength of a joint than the contact angle.

EXPERIMENTAL

A series of lacquers was prepared, based upon an epoxide resin (Epikote 1007—Shell Chemical Company Limited), a urea formaldehyde resin (Beetle Urea Resin BE 640, B.I.P. Chemicals Limited) and a melamine formaldehyde resin (Epok U9190, B.P. Chemicals (U.K.) Ltd.). The ratios of epoxide: urea: melamine are shown in Table 1. Two further lacquers were prepared, an epoxy/acrylic based on Epikote 1001 (Shell Chemical Company Limited) and Acryloid AT 70 (Rohm and Haas Co.) in the ratio of 40:60 and an epoxy phenol formaldehyde based on Epikote 1007 (Shell Chemical Company Limited) and Scadoform L9 (Scado-Archer-Daniels) in the ratio 70:30. The solvents and stoving schedules for these lacquers are all detailed in the manufacturer's literature.

For the formation of joints, stainless steel specimens 20 mm x 60mm x 3 mm were degreased in toluene in a Soxhlet extraction apparatus for twenty minutes. This treatment may not remove all contamination from the metal surface, but ensures that a reproducible surface is obtained. Double sided cellotape was used to stick the specimens on to a rubber sheet, and they were then lacquered using a roller coater. The lacquers were cured according to the manufacturers instructions and the thickness of the lacquer film determined using a Magne-gage (American Instruments Inc.). By this technique it was found possible to prepare coatings whose thickness was between 5μ and 10μ with a standard deviation of less than 6%.

In order to ensure that no further change in the surface took place subsequently to the initial cure, the contact angle made by bromoform on the surface was measured shortly after the stoving cycle recommended by the manufacturers was complete, and again after stoving for a further five hours at 150°C. It was found that in all cases the contact angle changed by less than 1°.

The lacquered specimens were joined together to form a lap shear joint with polyethylene WNC 18 (I.C.I. Ltd.) as the adhesive using the techniques described by Cherry and Holmes[12]. In this technique a square sample of the adhesive 1 mm thick is sandwiched between the over-lapping ends of two substrate specimens, with spacer plates to ensure that the ultimate thickness of the adhesive is 0.75 mm. Heating blocks on either side of the substrate ensure a rapid and uniform temperature increase to the joint formation temperature, 150°C. The joint assemblies were then held at this temperature in an inert atmosphere for thirty minutes and then allowed to cool down overnight. This slow cooling minimized stresses caused by the differential contraction of substrates and adhesive. The joints were then pulled apart on an Instron tensile testing machine at rates of crosshead separation of 22.5 mm $\sec^{-1}$ and 0.45 mm $\sec^{-1}$. Since the joints were so designed that the stress concentration factor[13] was equal to unity, the strengths are reported uncorrected in Table 1.

For the determination of the rate of change of contact angle, a similar piece of stainless steel of dimensions 45 mm x 45 mm x 5 mm was cleaned and coated in exactly similar fashion. The effect of lacquer thickness on the contact angle obtained with bromoform was examined and it was found that changes in the lacquer thickness in the range $5\text{-}50\mu$ had no detectable effect on the contact angle.

Samples of polyethylene WNC 18, were moulded into hemispheres in a cavity in a Teflon (polytetrafluorethylene) plate and were dropped onto the lacquered stainless steel specimen which was maintained at 150°C in an inert atmosphere, as has been described elsewhere[14].

Table 1.

Serial	*Lacquer*	*Wetting Constant (hour^{-1})*	*Equilibrium Contact Angle*	*Joint Strength Tested at 22.5mm min^{-1} (MN m^{-2})*	*Joint Strength Tested at 0.45mm min^{-1} (MN m^{-2})*
	Epoxy/ Urea/ Melamine				
1	70/0/30	1.50	64°	9.0 ± 0.8	7.8 ± 0.5
2	60/20/20	1.12	78°	9.2 ± 0.6	7.9 ± 0.7
3	60/10/30	0.862	72°	9.8 ± 0.7	8.2 ± 0.4
4	60/30/10	0.738	73°	9.3 ± 0.4	6.0 ± 0.3
5	70/30/0	0.352	61°	6.1 ± 0.8	4.9 ± 0.5
	Epoxy/ Phenol-Formaldehyde				
6	70/30	0.367	47°	9.6 ± 0.5	7.3 ± 0.5
	Epoxy/ Acrylic				
7	40/60	0.372	56°	2.7 ± 0.3	1.9 ± 0.2

The ultimate contact angle attained and the value of the wetting constant are recorded in Table 1. The wetting constant was calculated from the slope of a plot of log $(1 - \cos\phi_t/\cos\phi_\infty)$ against t obtained using a least squares method. Readings of $\cos\phi_t/\cos\phi_\infty$ greater than 0.97 were neglected in this calculation since a small error in the angular measurements in this region would cause a disproportionately large error in the final result.

DISCUSSION

The high values observed for the equilibrium contact angle suggests that either the critical surface tensions of the lacquers were less than the surface tension of the polyethylene at 150°C or that true equilibrium had not been established. Schonhorn and Sharpe[16] have reported the surface tension of a similar polyethylene at 150°C as 26.6 dynes/cm. The values of γ_c for the lacquer were not determined at 150°C but the conclusion of Good and Girifalco[17] that the surface energy of a solid is approximated by the critical surface tension, suggests that γ_c at 150°C is considerably lower than its room temperature value.

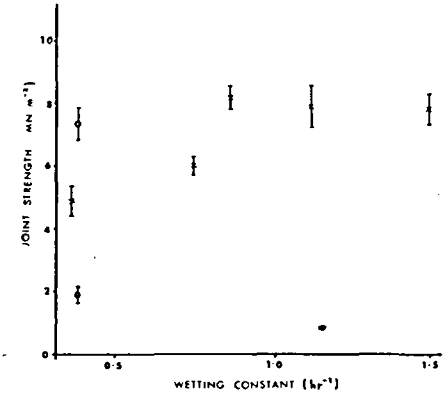

Figure 1. Strength plotted against wetting constant.

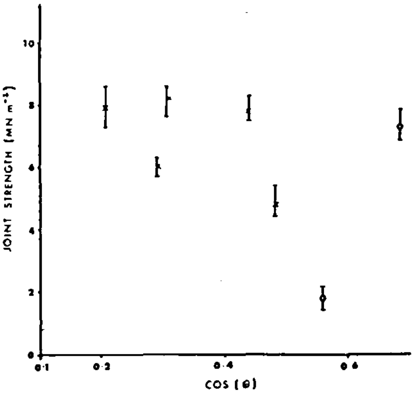

Figure 2. Strength plotted against contact angle.

Even if true equilibrium had not been established, however, the relative initial rates of wetting are indicated by the relative values of the wetting constant in Table 1. It seems likely that during the half-hour which was allowed for joint formation, the equilibrium contact angle would not be established as the adhesive penetrated the micro-fissures in the surface, hence, under these circumstances it was concluded that the integrity of the interfacial region might be more readily correlated with the rate at which the adhesive could penetrate the micro-fissures in the surface, than with the equilibrium constant angle.

In Figure 1 the joint strength when tested at a crosshead separation rate of 0.45 mm min^{-1} is plotted against the wetting constant. By contrast the same joint strengths are plotted against the apparent equilibrium contact angle in Figure 2. The systems based on the epoxy/urea/melamine resins are indicated by a cross, the others by an open circle. For the systems based on epoxy/urea/melamine resins, it can be seen that the strength of the adhesive correlates better with a high wetting constant than with a low contact angle. The major exception to this general behaviour is observed with the system based on the epoxy/phenol-formaldehyde resin. This system had the lowest contact angle of all those measured in this series of experiments. Therefore it is suggested that for this system although the amount of wetting which can take place in the time of joint formation is small, the low contact angle blunts the sharpness of the flaws at the interface and so decreases the stress concentrations and increases the joint strength.

Cherry and Holmes[15] have suggested that failure by yield and fracture may be differentiated by the shape of the stress-strain curve in that if Hooke's law is obeyed up to the point of failure, then failure is by fracture, whereas if there is a pronounced deviation towards the strain axis before failure, then failure is by yield. They have also shown that the fracture strength is considerably less than the yield strength for joints which are at the transition point between these two modes of failure.

For the epoxy/urea/melamine series of joints, it was found that when they were tested at the higher strain rates, failure was by yield for all samples except number five. The wetting constant for this system was the lowest of all the resins in the epoxy/urea/melamine series and it is suggested that the rate of wetting was so slow that micro-fissures were left at the adhesive/adherend interface and propagated as cracks when a stress was applied. The strength of this sample was approximately 66% of that of any of the systems which failed by yield. The results for joints tested at lower strain rates ran parallel to those tested at the higher strain rate except that when the stress-strain curves for these experiments were examined, some slight departure from Hooke's law was observed just prior to failure. This suggests that the demarcation between yield and fracture may not be so definite as postulated previously.

The epoxy/acrylic 40/60 lacquer based systems all failed by fracture at a very low stress, at all strain rates, and this is again interpreted as an example of a low wetting rate causing micro-fissures to be left which could propagate as cracks on application of a stress.

CONCLUSIONS

Neither the thermodynamics of the wetting process as exemplified by the contact angle nor the kinetics of the process as exemplified by the wetting constant are in themselves adequate to explain the dependence of the joint strength on the wetting properties of the adhesive. However, any work which aims to characterize this dependence must take both these factors into account if a quantitative relationship between wetting and strength is to be established.

NOMENCLATURE

a	Constant
c	Wetting constant = $\gamma_{LV}/\eta L$
γ_{LV}	Surface tension of liquid adhesive
η	Viscosity of liquid adhesive
θ	Contact angle of liquid adhesive on adherend
L	Unspecified parameter with dimension of length
W_A	Thermodynamic work of adhesion
ϕ_t	Contact angle at time t
ϕ_∞	Contact angle finally attained

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