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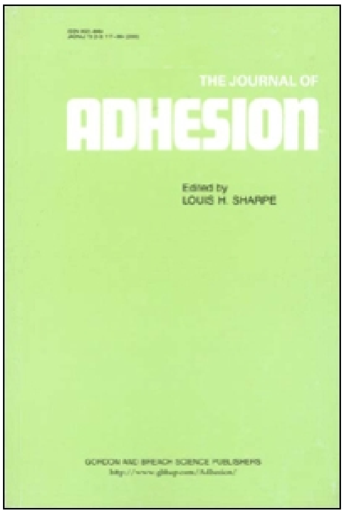

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Adhesion and Crosslinking in Epoxy Resin/Steel Assemblies

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A novel technique has been employed to investigate the development of interfacial bonding between steel and epoxy resins. Whereas such systems are usually rigid, precluding use of the very informative peel test, we have used spring steel as a flexible adherend and peeled this from the (relatively) rigid crosslinked polymers. Peel energy has been assessed for 180° and 90° tests, using a cylindrical former to limit irreversible deformation of the steel. Cure cycles for the resins DGEBA/DDA and DGEBA/DDS have been studied using DSC, and results exploited in such a way that peel tests could be effected on assemblies for which the total degree of polymer crosslinking was standardised, yet polymer/steel contact time during crosslinking was varied. The degree of potential reactivity of the polymers with respect to the steel was thus controlled. It was found, for both polymers, that measured adhesion energy was an approximately linear function of the fraction of crosslinking agent that reacted whilst epoxy/steel contact was maintained. Master curves for the two systems have been plotted, irrespective of cure conditions, the DGEBA/DDS system presenting better adhesion. Although no direct evidence of type and/or number of interfacial bonds is presently available, a simple argument suggests that chemical reactions occurring at *ca.* 1% of available surface sites may markedly improve adhesion.

Keywords: Crosslinking; DGEBA/DDA; DGEBA/DDS; epoxy resin; interfacial bonds; peel; steel

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INTRODUCTION

The study of adhesion is a complex subject because not only surface, or interfacial, forces control the strength of a given joint, but also the local bulk properties of the two phases in contact may play a significant role. Various types of interaction of a physical and/or a chemical nature can be the basis of adhesion, but when separation occurs by the application of external forces there is virtually always accompanying deformation of one or both of the contacting solids in the vicinity of the failure front, which can lead to considerable energy dissipation. In fact, this dissipation, of a viscoelastic or plastic nature generally, can be many times greater than the intrinsic, or thermodynamic, work of adhesion of Dupré [1] required simply for separation at the interface (assuming that failure is strictly interfacial, which is often not the case – this does not, however, change the basic reasoning). Nevertheless, the apparent, or effective, energy of adhesion is, as may be expected, largely controlled by the true strength of the interface (or interphase) – the dissipation can often successfully be considered as an "amplifier" or term multiplying the intrinsic adhesion term [2–5] (see below). One of various test geometries which has been successfully used in establishing the above relationship between interfacial and effective adhesion is the peel test in its various guises. It can be used for continuous assessment of adhesive strength as opposed, for example, to the lap-joint for which usually only force at failure may be exploited. However, the peel test is normally only exploitable when at least one of the adherends is flexible. In many structural adhesive applications, the entire assembly is relatively rigid thus precluding successful use of the peel test which has proved so useful as a fundamental technique for understanding interfacial and bulk contributions to adhesion energy. Although fracture mechanics approaches prove very useful for assessing overall effective energy of adhesion (see, for example Kinloch [6]), it has generally proved difficult to assess the importance of the interfacial bonding itself.

Our interest in the present study is to consider aspects of interfacial bonding in a model system representing a simplification of a common structural adhesive application – that of the bonding of steel by an epoxy resin. Despite the widespread use of epoxy resins to produce structural joints with steels, it would seem that relatively little work on the fundamental interfacial interactions has appeared in the literature, at least in cases where primers are not employed [7]. Although coupling agents are of enormous benefit, our present interest is directed to the simpler case.

The bulk curing process of epoxy resins is already a complex phenomenon, depending on type of resin and/or hardener and competition between linear polymerisation and crosslinking reactions, varying mechanical properties and glass transition temperatures [8–10], but the interface (or interphase of finite thickness) between an epoxy and a metal promises to be yet more complicated. Various surface analytical techniques, such as XPS (X-ray photoelectron spectroscopy), FT-IRRAS (Fourier transform infrared reflection absorption spectroscopy) and SERS (surface-enhanced Raman scattering spectroscopy), have been used to consider the type of bonds forming at metal/epoxy interfaces/interphases but these studies have not looked at quantitative relations between physico-chemical bonding and overall adhesive strength. Nigro and Ishida [11] considered the cure behaviour of very thin epoxy resin films on steel using FT-IRRAS and came to the conclusion that modifications to the resin structure may occur due to the proximity of the steel, but apparently they did not consider the bonds occurring between the two phases, which are our primary concern. Other studies on aluminium/epoxy systems [12–14] and copper/epoxy assemblies [13] suggest strongly a significant modification of cure properties near the interface resulting in a graded structure or *interphase* [15]. Boerio *et al.* have also investigated the interaction between silver and epoxy adhesives [16, 17]. Dicyandiamide is a much used crosslinking agent and infrared studies have been effected on its interactions with zinc (there appeared to be no changes in contact with steel) [18]. These seem to be the nearest studies to our present concern although surface analytical techniques have been applied to other metal (oxide)/polymer interfaces (see Lee [19]).

In this study, our primary concern has been the *development* of interfacial interactions between epoxy adhesives and a simple steel, and their effect on adhesion, rather then direct analysis of the chemical nature of the bonds. Given the difficulties normally associated with the study of rigid structural adhesive assemblies, discussed above, we have opted for a novel technique. Since epoxy adhesives tend to be rather inflexible, at least at usual service temperatures, we have used flexible adherends instead and peeled the adherend away from the adhesive, rather than the reverse which is more usual with, for example, systems involving elastomers. Since the measured energy of adhesion involves an interfacial term and dissipation, the latter depending on polymeric mechanical properties, we have adopted cure cycles for which the adhesives were taken to final, or complete, cure, to preserve given bulk mechanical properties, whilst varying contact time with the steel, thus limiting the potential development of interfacial bonds.

EXPERIMENTAL

Materials

The novelty of this study resides in using a flexible steel adherend which is peeled away from a block of epoxy adhesive. Spring steel, as used for shims, of thickness 30 μm and in the form of bands of width 2.5 cm and length 20 cm were bonded to two types of epoxy resin under various conditions. The steel was a carbon steel, quenched and cold-rolled, presenting a mean surface roughness inferior to 0.5 μm. Surface pre-treatment before bonding with the epoxy materials was limited to vapour degreasing for 30 minutes in trichloroethylene followed by an acetone rinse and drying in warm air.

Two adhesives were employed, both representing model systems to avoid complexities being introduced by the use of standard commercial materials of unknown formulation. The first, kindly supplied by CECA, was a diglycidyl ether of bisphenol A (DGEBA or BADGE) cured by a stoichiometric quantity of dicyandiamide (DDA). This material contained also 8% of fumed silica to improve handling properties before crosslinking by increasing viscosity and $<1\%$ of an (unknown) accelerator. Crosslinking conditions (variable) will be described below.

The second model adhesive was also a DGEBA prepolymer, Dow DER 332, cured with 4,4′-diaminodiphenyl sulphone (DDS) in a stoichiometric ratio. Fumed silica (4%) was added, as above, to increase pre-crosslinking viscosity.

Steel/epoxy resin assemblies were made in specially prepared moulds such that the final adhesive layer was 1 mm thick and one side adhered to an aluminium block acting as a support in the subsequent peel experiments. When curing was effected in contact with the flexible steel, a pressure of *ca.* 1.8 kPa was applied to facilitate interfacial contact.

Differential Scanning Calorimetry (DSC)

Although the essential part of this study resides in peel tests, described below, an initial, and later parallel, constituent was effected using differential scanning calorimetry (DSC). DSC was employed mainly for two purposes: to follow the kinetics of the cure reactions with each adhesive system as a function of temperature, and to ensure that cure cycles adopted for the adhesive assemblies were complete with no residual curing agent present leading to post-cure and potentially modifying mechanical properties of the polymers and, therefore, the adhesion.

A Setaram DSC 92 apparatus was used to heat *ca.* 90 mg samples of adhesive in closed aluminium crucibles at a rate of 10°C/minute up to predetermined temperatures, at which the samples were left for predetermined times before cooling to ambient temperature. This first heating cycle was intended to lead to partial or complete crosslinking of the polymer depending on time and temperature. After cooling, a second heating at a rate of 10°C/minute in the range $-100°C$ to 300°C was effected in order to evaluate the degree of crosslinking obtained during the first heating by considering enthalpy changes. This technique was employed in order to estimate the total time of cure necessary at a given temperature.

Peel Tests

The principal peel test used in this work was that at peel angle, $\theta, = 180°$ (measured between the direction of motion of the applied peel force acting on the separating steel band and the separated rigid epoxy substrate) although some tests were effected at $\theta = 90°$. In both cases, a cylinder (diameter 2 cm) was made to remain in contact with the flexible steel in the zone immediately succeeding peel. The use of such a cylinder effectively limits irreversible deformation occurring to the separated band [20–22]. Tests were effected using suitable jigs on an Instron tensile testing machine and at ambient laboratory temperature and relative humidity. Various peel rates were used initially varying from 5×10^{-2} to $5\,\mathrm{cm \cdot min^{-1}}$. It was found that peel forces and, therefore, apparent energies of adhesion, remained virtually constant for peel speeds in the range of 5×10^{-2} to $2\,\mathrm{cm \cdot min^{-1}}$, for a given system, but that above the latter rate, the force increased. Therefore, in the range up to $2\,\mathrm{cm \cdot min^{-1}}$, it may be concluded that dissipation effects were relatively independent of peel rate. Above $2\,\mathrm{cm \cdot min^{-1}}$, it was observed that the separated steel band did not stay in direct contact with the cylinder – the cylinder was "squeezed out" of the hollow provided by the curved steel, thus allowing the radius of curvature of the latter to decrease, leading to irreversible deformation and supplementary dissipation of energy. These preliminary experiments led to our standardising peel rate in the following to $1\,\mathrm{cm \cdot min^{-1}}$.

The principal interest of this study was to consider the effective energy of adhesion of steel to epoxy resins and the possibility of the development of chemical bonds at the interface during cure of the polymer. As described above, measured adhesion energy has several times been successfully shown to include an energy associated with interfacial failure and an "amplifying" term due to local bulk dissipation. Thermodynamically the components should be considered as additive, but since dissipation is usually (approximately) proportional to the intrinsic energy of adhesion, the dissipative term effectively becomes a multiplier, depending on a number of factors, including (generally) rate and temperature (see below for details). Clearly this multiplying factor will strongly depend on bulk polymer properties. For this reason, we have employed a technique in which final mechanical properties of the polymeric adhesive should remain constant, yet the development of interfacial bonds can be varied [22,23]. The resin was crosslinked without contact with the steel for a period t_1, followed by a period t_2 in contact. For a given temperature, T, the sum $(t_1 + t_2)$ remained a constant. Values of $(t_1 + t_2)$ for a given T were determined by DSC. In the case of the system DGEBA/DDA, it was found that suitable curing conditions were 1560 and 720 minutes, respectively, at 70 and 80°C and 30 minutes for 100, 110 and 120°C, all followed by a post-cure of 30 minutes at 140°C to ensure complete crosslinking. For the system DGEBA/DDS, it was found adequate to use values of $(t_1 + t_2)$ of 900 and 840 minutes at 110 and 120°C, respectively, without ensuing post-cure.

RESULTS AND DISCUSSION

Differential Scanning Calorimetry (DSC)

The Setaram DSC 92 apparatus allowed direct exploitation of results of measured enthalpy changes. As the basis of the following interpretation of the data, we make the reasonable hypothesis that each molecule of DDA, or DDS, depending on the system, delivers its contribution to the enthalpy change when it reacts chemically (exothermically) with the DGEBA [24,25]. The speed of reaction is proportional to the signal obtained. By integrating the enthalpy up to a certain time, at a given temperature of reaction, ΔH (partial), and comparing this with the integral of the total signal corresponding to complete crosslinking, ΔH (total), we may define a degree of advancement of the reaction, α. Similarly, the fraction of the reaction remaining to occur, $\beta = 1 - \alpha$, is related the difference of enthalpy, ΔH (residual) = ΔH (total) − ΔH (partial):

$$\alpha = \frac{\Delta H \text{ (partial)}}{\Delta H \text{ (total)}} \tag{1}$$

$$\beta = 1 - \alpha = \frac{\Delta H \text{ (residual)}}{\Delta H \text{ (total)}} \tag{2}$$

The rate of reaction is given by the equation:

$$\frac{d\alpha}{dt} = K(1 - \alpha)^n \tag{3}$$

where t is time, K a rate constant, depending on temperature, and n a constant.

The reaction between DGEBA and DDA is principally first order, neglecting any side reactions and thus $n = 1$, leading, after integration of Eq. (3) to:

$$\alpha = 1 - \exp(-Kt) \tag{4}$$

In the case of the reaction DGEBA/DDS, the order of the reaction is $n = 2$, thus giving:

$$\frac{1}{(1-\alpha)} - 1 = Kt \qquad (5)$$

Using the DSC results obtained for the system DGEBA/DDA crosslinked at 100°C we have plotted $\ln(1-\alpha)$ *vs* t in Figure 1. Other temperatures, likewise, give satisfactory results confirming the reaction to be essentially first order and leading to the rate constants, K, at the five temperatures studied given in Table I. As may be expected, results near the middle of the range, say $0.1 \leqslant \alpha \leqslant 0.8$, are somewhat more reliable than for small α (inertial effects) and large α (asymptotic behaviour). K can thus be represented by the equation:

$$K = K_0 \exp\left(\frac{-E}{RT}\right) \qquad (6)$$

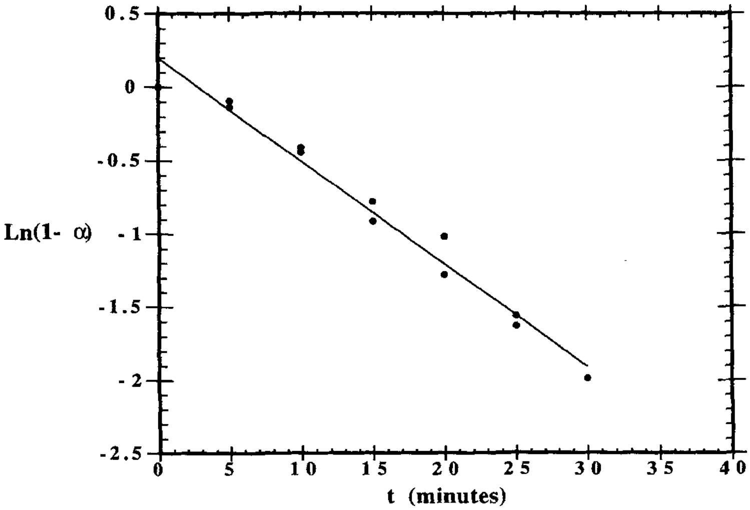

FIGURE 1 $\ln(1-\alpha)$ *vs* t at 100°C for the crosslinking reaction of the system DGEBA/ DDA.

TABLE I Values of rate constant, K, at various crosslinking temperatures, for the system DGEBA/DDA

T(°C)	70	80	100	110	120
$K(\mathrm{s}^{-1})$	3.9×10^{-6}	1.5×10^{-5}	1.2×10^{-3}	1.7×10^{-3}	2×10^{-3}

where $\ln K_0 = 42 \pm 8$ and the activation energy, $E = 155 \pm 24$ kJ·mole^{-1}. (T is, of course, absolute temperature in Eq. (6)).

The DSC results obtained with the system DGEBA/DDS crosslinked at 110°C are given in Figure 2 in the form of $(1-\alpha)^{-1} - 1$ *vs* t, showing satisfactory agreement with Eq. (5), corresponding to second order kinetics. Table II gives K for the temperatures of 110, 120 and 150°C, leading to $\ln K_0 = 4.0 \pm 0.8$ and $E = 39 \pm 5$ kJ mole^{-1} in Eq. (6).

Although use of Eq. (6) suggests plausible temperature dependence of reaction kinetics, some variability (possibly due to modifications in mechanism with temperature) was present and, as such, values of β derived directly from DSC results (Eq. (2)) were used in the following.

With the above analysis of the kinetics of crosslinking of the DGEBA/DDA and DBEBA/DDS systems, it was possible to choose

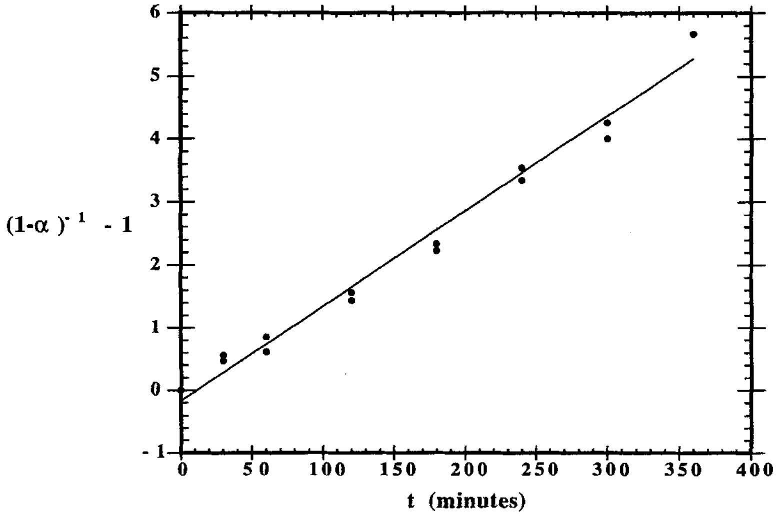

FIGURE 2 $(1-\alpha)^{-1} - 1$ *vs* t at 110°C for the crosslinking reaction of the system DGEBA/DDS.

TABLE II Values of rate constant, K, at various crosslinking temperatures, for the system DGEBA/DDA

T(°C)	110	120	150
K(s^{-1})	2.5×10^{-4}	3.7×10^{-4}	8.0×10^{-4}

suitable values of time without, t_1, and time with contact, t_2, for crosslinking in the presence of steel at various temperatures for the peel study. This allowed suitable control of β at the outset of contact. It should nevertheless be noted, as described in the introduction, that the presence of a steel adherend may potentially modify local curing properties. Notwithstanding complications possibly occurring due to the proximity of the metal, modifying local type and/or degree of crosslinking, we shall in the following make the simplifying assumption that bulk reaction kinetics also apply in the interface/interphase region.

Peel Tests

The general equation relating apparent, or measured, energy of adhesion in a peel test, W, to peel force, F, is:

$$W = \frac{F}{\ell}(1 - \cos\theta) \tag{7}$$

where θ is peel angle and ℓ the width of the peeled band. Thus, for a test at 90°, the energy of adhesion becomes simply F/ℓ. In the case of the 180° test using a cylinder to limit irreversible deformation, allowance must be made for the work expended in lifting the cylinder of weight P and the relation becomes [21]:

$$W \frac{2F - P}{\ell} \tag{8}$$

System DGEBA/DDA

In Figure 3 we present the energy of adhesion, W, as evaluated by Eq. (8) for 180° peel results at a rate of 1 cm·min^{-1} with the DGEBA/

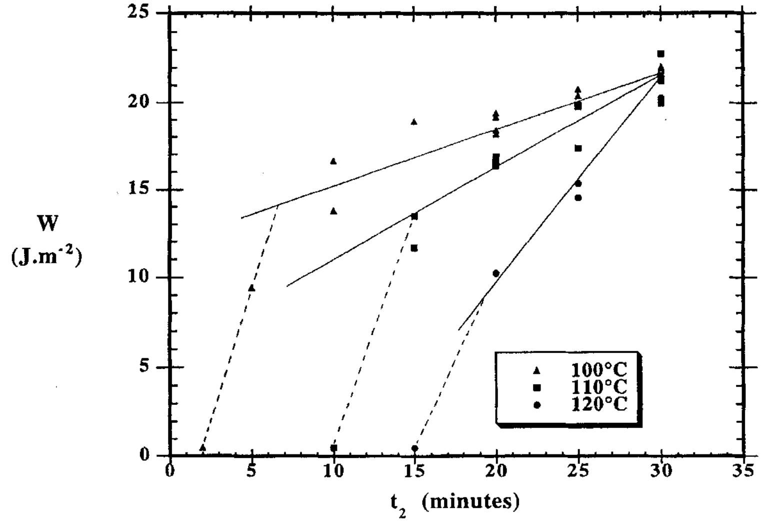

FIGURE 3 Peel test results for $\theta = 180°$ and at a rate of 1 cm.min^{-1} for a flexible steel band adhering to the DGEBA/DDA epoxy system: measured energy of adhesion, *W*, *vs* contact time during crosslinking, t_2, for temperatures of 100, 110 and 120°C.

DDA resin adhering to the steel band. These results correspond to values of contact time, t_2, for the cure temperatures of 100, 110 and 120°C. (Although similar in form, the results for cure at 70 and 80°C are not presented in Fig. 2 since total cure time is considerably longer in these cases). Results at $\theta = 90°$ were virtually indistinguishable, suggesting negligible dissipation in the peeled steel band.

Several observations may be made from these results. Firstly, except for values of t_2 which are too low (for a given temperature), *W* is in the range of *ca.* 10–25 Jm^{-2}. Although these values are quite low, they are too high to represent intrinsic adhesion alone without dissipation, unless virtually all atomic sites on each side of the interface have chemically combined with their neighbours in the contiguous phase – an exceedingly unlikely hypothesis [22]. The fact that a spring steel was used and peeled over a cylindrical former undoubtedly reduced, if not eliminated, energy dissipation in the peeled member, as noted above (independence of peel angle). Nevertheless, in the zone very close to the peel front, the epoxy resin is certainly deformed and this will undoubtedly contribute to the measured energy of adhesion, *W*.

However, this dissipation would seem to be virtually rate independent in the range considered here.

Figure 3 shows that the adhesion increases with decreasing crosslinking temperature, for a given value of t_2. This can be explained by the fact that, for a lower temperature and a given t_2, there remains a higher fraction, β, of chemical interaction of the DDA to occur after resin/steel contact, thus a greater possibility of interfacial bond formation.

When the contact time, t_2 is 30 minutes, *i.e.* crosslinking occurs entirely in the presence of the steel, the measured energy of adhesion is virtually identical at *ca.* 22 Jm^{-2}, whatever the crosslinking temperature. The resin is entirely crosslinked and all potential interfacial bonds have "had the chance" to be formed. Between values of W near 10 Jm^{-2} (depending on the temperature) and the maximum near 22 Jm^{-2}, adhesion seems to increase more or less linearly, the gradient being a function of temperature, with the lines converging. However, for W less than *ca.* 10 Jm^{-2}, there is an abrupt drop in adhesion and for low values of t_2, interfacial strength becomes virtually zero. This corresponds to a value of α of *ca.* 0.8, showing the crosslinking reaction to be well advanced before resin/steel contact. The polymer is already quite rigid and, therefore, the intimate contact necessary for adhesion between the two phases cannot be assured.

Figure 4 represents energy of adhesion, W, *vs* the fraction of adhesive DGEBA/DDA crosslinked in contact with the steel, β (assuming, as stated above, equivalent bulk and surface reaction kinetics). The results correspond to all the crosslinking temperatures considered, *i.e.* 70, 80, 100, 110 and 120°C (plus two results corresponding to 140°C demonstrating "complete" adhesion and unmeasurable adhesion – the two extremes). Results obtained with peel angle $\theta = 90°$ and 180° are included. It can clearly be seen how, for a value of β inferior to *ca.* 0.2, adhesion drops effectively to zero, but above this threshold, whatever the peel angle or crosslinking temperature, the results fall within a convincing band suggesting similar behaviour. Approximating this "master curve" to a straight line, we obtain:

$$W = (11.2 \pm 0.3) + (10.5 \pm 0.7)\beta; \quad \beta \geqslant 0.2 \tag{9}$$

where W is in Jm^{-2} and β is a fraction $(0.2 \leqslant \beta \leqslant 1)$. The correlation coefficient is 0.96.

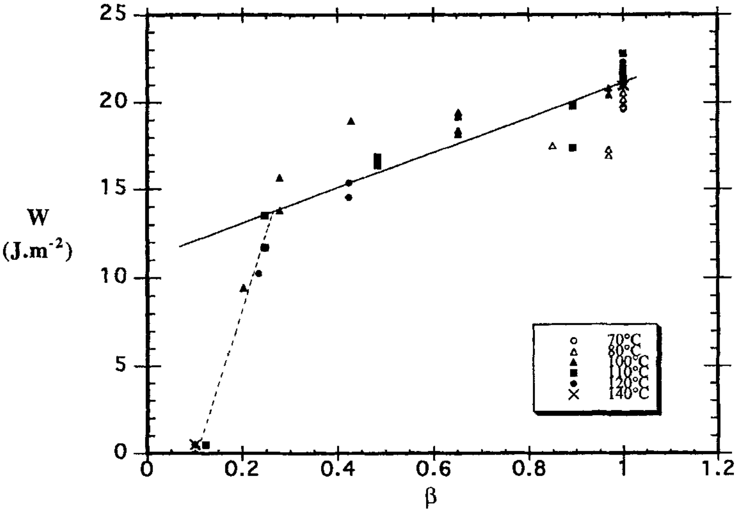

FIGURE 4 Energy of adhesion, *W*, *vs* fraction of DGEBA/DDA crosslinked in contact with steel, *β*.

Neglecting the zone for which *β* is too small for good, intimate contact to be attainable between the already considerably crosslinked resin and the steel, it is clear that apparent adhesion depends closely on the quantity of DDA still to be reacted when resin/steel contact is effected. This suggests, albeit indirectly, that a certain number of chemical bonds form at the interface whilst the resin is still chemically active, and that this number is directly proportional to the number of, as yet, unreacted DDA molecules available. We shall conjecture further after having discussed the second system studied.

System DGEBA/DDS

Figure 5 summarises results of energy of adhesion, *W*, *vs* resin/steel contact time, t_2, for the DGEBA/DDS system. The first observation is that the time scale is very different from that for the DGEBA/DDA system. Indeed, the latter is somewhat delicate to crosslink in a controlled manner since it is relatively lethargic chemically at low temperatures but then accelerates rapidly under hotter conditions. The DGEBA/DDS is more even to control.

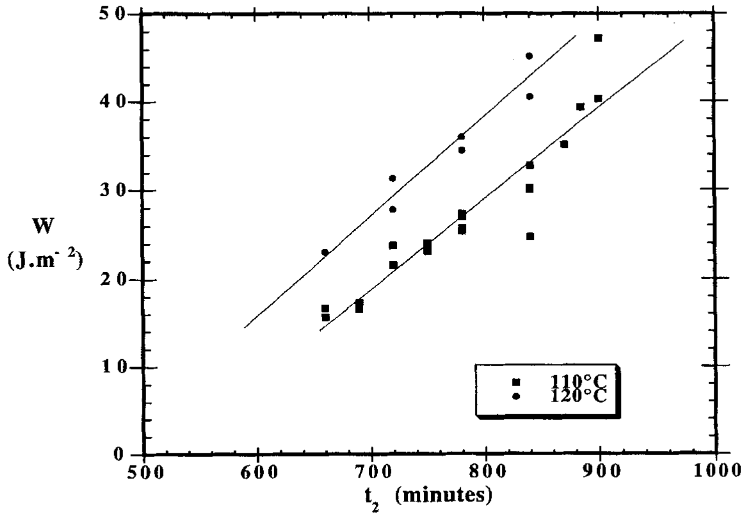

FIGURE 5 As for Figure 3 except adhesive is DGEBA/DDS system, and temperatures are 110 and 120°C. Note very different kinetics compared to the DGEBA/DDA results above.

Figure 6 is the equivalent of Figure 4 for the DGEBA/DDS system showing *W vs* β. Cure temperatures are 110 and 120°C and again it can be seen that a master curve summarises the dependence for *ca.* $0.2 < \beta \leqslant 1$. For β less than *ca.* 0.2, again it was impossible to obtain adequate resin/steel contact for measurable adhesion to be obtained. As before, above this threshold, adhesion energy increases approximately linearly with the fraction of crosslinking agent available after polymer/metal contact, suggesting the active role of DDS in interfacial bond formation. The order of magnitude of the apparent energy of adhesion is rather similar to that obtained with DGEBA/DDA, although somewhat higher values are evident. Thus, the same argument suggesting negligible energy dissipation in the metal but some losses in the polymer near the peel front applies. The energy of adhesion, as a function of β, can be represented by the equation:

$$W = (11.5 \pm 0.5) + (34.0 \pm 0.8)\beta; \quad \beta \geqslant 0.2 \qquad (10)$$

with the same units as Eq. (9). The correlation coefficient is 0.95. The overall findings with DGEBA/DDS are similar to those with DGEBA/DDA but apparent energies of adhesion are somewhat higher.

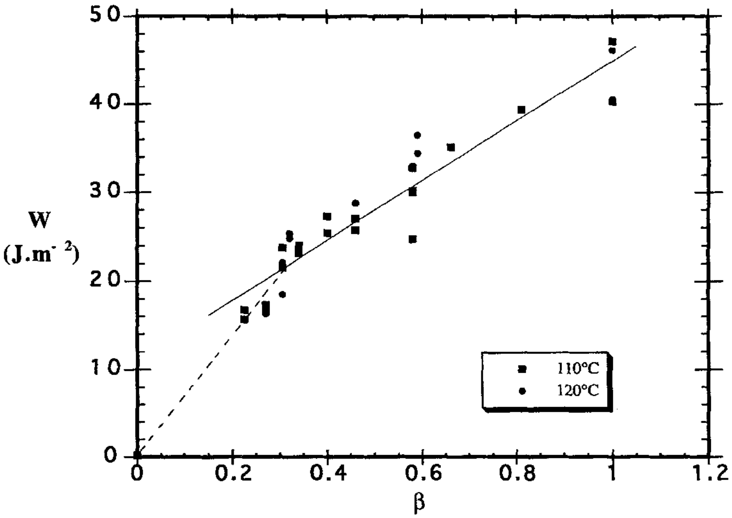

FIGURE 6 As for Figure 4 except adhesive is DGEBA/DDS system.

Comparison of DGEBA/DDA and DGEBA/DDS Systems

The overall behaviour of these two systems in peel is very similar as far as apparent energy of adhesion, *W*, as a function of crosslinking activity, β, is concerned (Fig. 7). Comparing Eqs. (9) and (10) we find that the essential difference is the value of prefactor of β, or gradient. This suggests that the DGEBA/DDS is apt to produce stronger and/or more interfacial bonds with steel. We are not yet really in a position to be able to advance ideas as to the type and/or surface density of interfacial bonds for the moment. Nevertheless, we surmise that the added strength for $\beta > 0.2$ is related to the creation of chemical species during crosslinking. Surface analytical techniques have not, as yet, given direct evidence. Nevertheless, we note that the constant terms in Eqs. (9) and (10) are approximately the same, within experimental error. We shall, therefore, tentatively propose the following argument.

The constant terms in question amount to extrapolations to values of effective energy of adhesion when the adhesives are totally crosslinked before contact with the steel but, hypothetically, when intimate contact is established. We may then reasonably suppose that these extrapolated values of adhesion energy correspond to the destruction of physical interfacial bonding, together with the associated viscoelastic

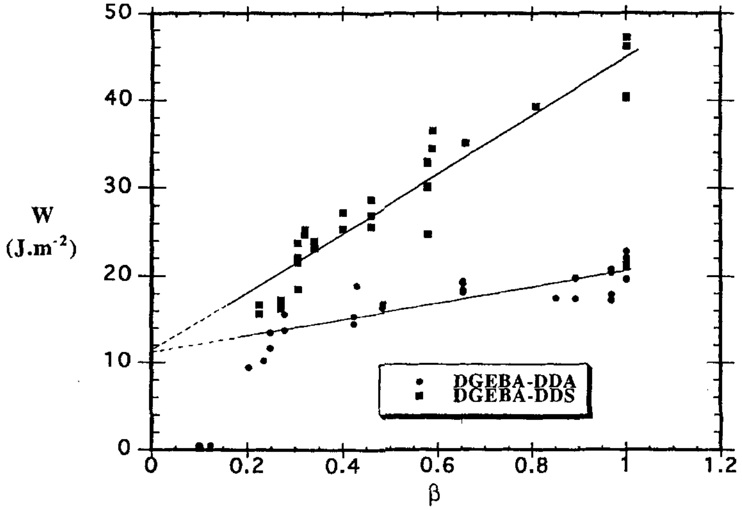

FIGURE 7 Results of energy of adhesion, *W*, *vs* fraction of adhesive crosslinked in contact with steel, *β*, for both DGEBA/DDA and DGEBA/DDS systems.

and/or plastic dissipation occurring in the resin during the separation process. The two terms constituting *W* will be additive. The latter contribution can be considerable, often outweighing the former by a large margin [26] and analysis of the overall situation can be complex [27]. Nevertheless, despite the difference in order of magnitude of the two terms, it seems fairly intuitive that dissipation will increase with intrinsic interfacial strength and successful use of this hypothesis has been made over the years [2–5]. Assuming a linear relation between the two, we have:

$$W = W_I + W_D \approx W_I + W_I f(D) \approx W_I f(D) \qquad (11)$$

for $f(D) \gg 1$, where W_I is equal to the sum of interfacial, intrinsic contributions to the energy of adhesion, W_D is the dissipated component and $f(D)$ is a factor of proportionality, or energy dissipation factor. (Although the two energy sinks are strictly additive, it is as though the dissipation acts as an "amplifier".)

For values of β extrapolated to 0, W_I will *only* contain physical interactions of a van der Waals nature (plus potential hydrogen bonding and/or acid-base interactions). We do not know the value of W_I

($\beta = 0$) in this case but a reasonable estimate would be of the order of $10^{-1}\,\mathrm{Jm}^{-2}$. This indicates that $f(D)$ is of the order of 100 and, apparently, relatively independent of peel rate in the range considered. Thus, for $\beta = 1$, W_I is of the order of $2 \times 10^{-1}\,\mathrm{Jm}^{-2}$ for DGEBA/DDA and $4.5 \times 10^{-1}\,\mathrm{Jm}^{-2}$ for DGEBA/DDS. Despite the clear difference, we shall treat these figures as being similar, from the point of view of orders of magnitude. The hypothesised chemical bonding, W_I^χ, corresponds to something like $2 \times 10^{-1}\,\mathrm{Jm}^{-2}$ where we postulate that:

$$W_I(\beta = 1) = W_I^\phi + W_I^\chi \tag{12}$$

W_I^ϕ being the physical contribution and W_I^χ the maximum potential chemical contribution. Let us now estimate the density of potential chemical bonding [22]. It is probable that any chemical bonds will be of the character C—N, C—O or similar, having bond energies of the order of 250–350 kJ mole^{-1} [28]. Bonds of the form Fe—O are in a similar range (*ca.* 400 kJ mole^{-1}) [29]. A mole of such bonds, representing 6×10^{23} units, when "smeared out" to a monolayer, a typical bond having a cross-section of *ca.* $3 \times 10^{-20}\,\mathrm{m}^2$, will occupy *ca.* $2 \times 10^4\,\mathrm{m}^2$. Complete chemical bonding at the interface then corresponds to something like $W_I^\chi \approx 20\,\mathrm{Jm}^{-2}$. As a result, our simple estimate of $W_I^\chi = 2 \times 10^{-1}\,\mathrm{Jm}^{-2}$ suggests that approximately 1 percent of atomic sites develops a chemical bond. We do not know what type of bonds may be established – for example, the direct interaction of DDA with steel seems to be ruled out [18]. Nevertheless, phenomenological evidence definitely suggests that some sort of chemical interaction is occurring between steel and crosslinking DGEBA and that a relatively low concentration of bonds may markedly improve adhesion. The use of primers, potentially increasing the surface density of chemical interactions and therefore linkages, can thus only be beneficial, as known in practice [7].

CONCLUSIONS

We have studied the development of adhesion between steel and two model epoxy resins corresponding to DGEBA cured with DDA and

DGEBA cured with DDS. In order to circumvent the problem of studying rigid structural assemblies, we have used a spring steel as the adherend and peeled this from a block of adhesive. No coupling agents have been used in this basic study. By ensuring virtually identical mechanical properties of the adhesives after final cure, but by varying contact times during cure with the steel adherends, it has been possible to study the evolution of fundamental adhesion with quantity of curing agent available. The quantitative appraisal of available curing agent was obtained using DSC. It has been shown that, irrespective of cure conditions, final adhesion is a direct, increasing function, approximately linear, of available curing agent, the quantitative relationship differing between DDA and DDS. It is, therefore, hypothesised that chemical reactions occur at the interface during crosslinking and that these increase adhesion. Although no direct evidence of the type and/or density of chemical bands is presently available, a simple argument suggests that chemical reactions occurring at as few as 1% of the atomic sites available can lead to noticeable gains in interfacial strength.

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