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Int. J. Adhesion and Adhesives **16** (1996) 129–135
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0143-7496/96/$15.00

0143-7496(95)00028-3

Effects of plasma treatment on the adhesion of an epoxy composite

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(Accepted 8 August 1995)

Improvements to adhesion between an epoxy composite material substrate and an epoxy structural adhesive can be obtained by plasma treatment of the former. However, quantitative evaluation of the strength increase is often difficult due to the rigidity of the systems. In this study, we consider a composite material (epoxy/carbon fibre), both untreated and treated by oxygen and nitrogen plasmas, adhering to an epoxy gel. The latter was chosen as a compromise since it has chemical similarities with structural epoxy resins yet inherent flexibility, allowing peel tests to be performed. After studying effects due to variation of contact time during cure (total cure time remained constant to ensure comparable mechanical properties), it was found that plasma-treated composite gave better adhesion under similar test conditions. A model has been tentatively suggested to explain the improvement by the formation of chemical bonds at the composite–epoxy gel interface. It is concluded that even if only 1% of atomic sites develop chemical bonds, adhesion is considerably increased.

(Keywords: chemical bonds; composite; epoxy; interface; peel test; plasma treatment)

INTRODUCTION

When an adhesive joint is formed, clearly the type of interaction at the interface between the two phases is fundamental. The science of adhesion has largely been devoted to identification of the various mechanisms involved. Although early propositions date back to the 1920s[1], enormous progress in understanding has been made in the last 30 years or so. Recognition of the importance of adhesion has clearly played a dominant role, and in this regard credit is due to Keith Allen, together with David Alner, who instituted a series of annual conferences on adhesion, the first dating back to 1963, that is still continuing after more than 30 years! Keith Allen reviewed adhesion theories in the 1960s[2] and has continued to remain active in the field ever since, an example of a recent article appearing in this journal[3]. Of the various adhesion mechanisms, we mention the roles played by mechanical interlocking[1], electrostatic adhesion[4], adhesion due to the establishment of chemical bonds at the interface[5,6], diffusion of macromolecules[7,8] and adsorption or wetting[9,10] (weak, but long-range physical interactions of the van der Waals' type), which have been suggested over the years.

Although the type of interaction at the interface between the two phases in contact is of fundamental importance, it is well recognised these days that interfacial bonds are not the only characteristic to be taken into account. Indeed, the formation of an inter*phase* with properties intermediary between those of the two bulk materials may be of considerable importance[11]. In addition, the energy of adhesion measured, or at least apparent, from the failure of an adhesive assembly is often many times greater than that which would be predicted from a calculation allowing uniquely for interfacial bond energies. When an adhesive bond fails due to the application of mechanical forces, there is usually considerable local deformation of one or both phases near the fracture front and, if the materials are dissipative, considerable energy can be expended in the zone near failure by viscoelastic or plastic strain. Since failure energy corresponds to the sum of the energy required to break the interfacial bonds and that used irreversibly in deforming the solids, the effective adhesive energy corresponds to a 'magnification' of the intrinsic value[12–15].

When a relatively soft material adheres to a rigid substrate, there are a number of practical adhesion tests which may be used in order to ascertain the effective, or apparent, work of adhesion, including peel and the so-called Johnson, Kendall and Roberts[16] (JKR) technique in which two spherical surfaces are placed in contact and the radius of their circle of contact is measured. However, when dealing with relatively rigid substrates and adhesives, the latter including such materials as epoxy resins, the range of informative tests available is more limited. Certainly

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*To whom correspondence should be addressed the classic overlap joint is simple to make and test and can give very useful data both for adhesives under service conditions and for ranking the effectiveness of similar materials or the benefits of surface treatments, for example. Nevertheless, an overall strength is the datum usually obtained, even when allowing for the well-known complex stress distributions present in such geometries[17, 18]. Another geometry, presenting the advantage of a simple, well-defined stress distribution, is the so-called 'napkin ring[19, 20] and its variations[21, 22]. The use of fracture mechanics for adhesive strength assessment has gained favour in recent years[23, 24]. However, although the use of these various tests leads to a knowledge of the overall strength of adhesive joints, it is difficult with these techniques to obtain data concerning the fundamental interface (or interphase).

In this context, the present authors have aimed to gain a better understanding of improvements to adhesion obtained after the surface treatment of polymeric composite materials bonded with structural adhesives. Since the composite represents a rigid substrate and an epoxy resin is also usually rigid at ambient temperature, a compromise has been made. By replacing the adhesive by a rubbery epoxy material, we expect to have similarities as far as the chemistry is concerned. At the same time, the compliant nature of such an elastomer means that a peel test can be used in order to consider changes in adhesive performance brought about by surface treatment. Clearly we may not expect identical interfacial behaviour when replacing an epoxy resin by a rubbery epoxy, but the results should be informative.

EXPERIMENTAL

Materials and preparation

The composite substrate used for this study was epoxy resin 924 reinforced with carbon fibres, made by Ciba Composites, and supplied in sheets of thickness 3 mm. Test pieces of ~30 cm length and 4.5 cm width were cut. The rubbery epoxy was a two-component, clear, transparent epoxy gel, based on the reaction product of bisphenol A and epichlorhydrin (molecular weight $\leqslant 700$) and cured with a polyamine product, manufactured by W.R. Grace (electronic materials) and denoted Stycast 1265. A total curing time of 16 h at 65°C was employed, as advised by the manufacturers. As the adhesion force developed during peel could be quite high, a poly(ethylene terephthalate) (PET) film of 75 μm was used as a backing material to impede elongation of the rubbery epoxy separated from the substrate. Since early trials showed that contact between the substrate and the elastomer for the entirety of the 16 h cure cycle led to such a high degree of adhesion that peeling could not be effected satisfactorily, curing was done in two stages. Initially the epoxy gel was maintained at 65°C for $(16 - t)$ h, and then contact with the composite was made for the remainder of the cure time, t. This ensured that the epoxy gel was always fully cured and thus had essentially the same mechanical properties when tested, but with increasing t the number of potential interfacial interactions increased[25, 26].

A PET film of approximately the same dimensions as the composite test-pieces was placed on a rigid base followed by an elastomeric gasket of 2 mm thickness containing a rectangular hole of ~28 cm length and 3 cm width. A metallic mask with similar sized opening was then added and secured to keep the elastomer flat. The elastomeric mould was then filled with the premixed epoxy gel and curing for $(16 - t)$ h ensued. After removing the metallic mask, the elastomer/epoxy gel/PET assembly was inverted, applied to the composite and 'rolled on' to eliminate trapped air before securing a compression plate and curing for the remaining time t at 65°C. The elastomeric mask and excess PET were removed before testing.

Composite substrates were used both in their initial state as supplied (after removal of a protective film) and after plasma treatment. Two plasma treatments, carried out at the Institut de Recherche Appliquée sur les Polymères (IRAP–LeMans), were used, corresponding to atmospheres of 100% oxygen or 100% nitrogen and a power of 150 W at 13.56 MHz applied for 1 min in a cylindrical reactor of diameter 20 cm and length 50 cm (Branson IPC 4000).

Wetting experiments were conducted on a chemically similar composite material, 914, also from Ciba Composites since lack of available material precluded use of the 924.

Techniques

The bulk of peel experiments were conducted on an Instron tensile testing machine at ambient temperature. A peel geometry with a 180° peel angle was adopted and, in order to limit flexion of the peel band, use was made of a cylinder of radius $R = 6$ mm resting in the curved part of the detached epoxy gel/PET film (see *Figure 1*). Cylinder weight P was 1 N, but extra masses could be added symmetrically on either side of the rolling band if necessary. With this arrangement, the work of adhesion W is given by [27]:

$$W = \left(\frac{2F - P}{l}\right) \qquad (1)$$

where F is the measured force of separation and l is the peel front width (~3 cm). The peel rate (half the crosshead speed) range covered was from 2.5×10^{-2} to 25 mm min^{-1}.

At very low speeds, in some cases the peel load F became too small for reliable measurements to be made on the tensile testing machine with the load cells available. In addition, with low values of F, the weight of the peeled section of epoxy gel/PET may become significant. For these reasons a dead load peel test at 180° was sometimes used, which is shown schematically in *Figure 1*. Essentially, the only difference compared

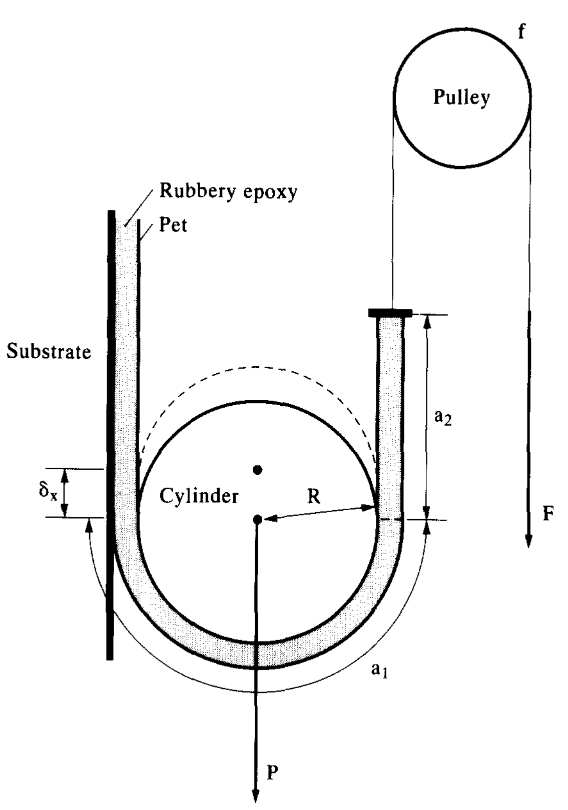

Figure 1 Schematic diagram of dead load 180° peel test

with the tensile tester geometry is the addition of a pulley over which passes a thread attached at one end to the extremity of the peeled section and at the other end to the applied load, F. It is, however, instructive to consider the force balance of this arrangement and derive the corresponding expression for the effective energy of adhesion, W.

Consider an infinitesimal distance of peel, δx, as shown in *Figure 1*. The work of detachment is given by $W\,l\,\delta x$. Energy has also been expended in raising the cylinder used for preventing excessive curvature of the peeled section near the separation front. This corresponds to $P\,\delta x$ (where conversion from weight to force is implicit — this also applies to the following weights). There are two further contributions to the work needed for peel over length δx. Any frictional force in the pulley, f, requires additional work equal to $2f\,\delta x$ and the band of peeled epoxy gel/PET film becomes longer and its centre of gravity ascends. (It is assumed that the thin thread is in extensible and virtually weightless, and that any dissipation associated with its curving over the pulley is negligible.) We denote as w the gravitational force (weight) per unit area at constant thickness of the epoxy gel/PET film assembly, and as $s(x)$ the total detached length ($s(0) = s_0$ is the initial detached length before the peel test commences). Length $s(x) = a_1 + a_2$, where a_1 corresponds to the semi-cylindrical part wrapped round the cylinder P of radius R and a_2 represents the remainder leading to the thread attachment point. During detachment δx, a_1 increases its potential energy by $\pi R\,w\,l\,\delta x$ whilst a_2, of effective weight $[s(x) - \pi R]\,lw$, has its centre of gravity rise by $3\delta x/2$ leading to work effected equal to $3[s(x) - \pi R]lw \cdot \delta x/2$. The sum of the contributions above corresponds to the work done by the dead load F descending a distance $2\delta x$. Thus we arrive at the energy balance

$$2F = Wl + P + 2f + \pi Rwl + \frac{3}{2}[s(x) - \pi R]lw \qquad (2)$$

leading to:

$$W = \frac{1}{l}[2(F - f) - P] - \frac{w}{2}[3(s_0 + x) - \pi R] \qquad (3)$$

Equation (3) reduces simply to equation (1) when pulley friction and peeled epoxy gel/PET film weight are negligible. Since under normal conditions W increases with peel rate, in principle at least, under dead load peel conditions, peel rate should decrease as the process continues. The effect is, however, small.

Wetting experiments were conducted using an optical bench arrangement, described elsewhere[28], enabling the advancing contact angles of small sessile drops of probe liquids, triple-distilled water and diiodomethane, to be measured.

RESULTS AND DISCUSSION

Wetting

Although the main part of this study is devoted to peel experiments and effective adhesion, use has been made of the thermodynamic or Dupré[29] energy of adhesion, W_0^ϕ, due to van der Waals' interactions. Although several interpretations of wetting experiments exist for estimating W_0^ϕ (depending on the school of thought adopted and the various components of surface free energy thought to be pertinent for a given system[30–34]), we have used a relatively simple interpretation based on the Fowkes equation[31], and the so-called (erroneously!) extended Fowkes equation[32] to allow for non-dispersive interactions. Although the strict validity of this method is open to debate, our primary concern here is to obtain approximate figures of W_0^ϕ for application to peel results. The main point to be retained is that wetting experiments did not suggest any vastly different values of the intrinsic Dupré work of adhesion due to physical or van der Waals' interfacial interactions.

When surface free energy γ is assumed to be dependent on dispersive and non-dispersive components, respectively γ^D and γ^{ND}, such that $\gamma = \gamma^D + \gamma^{ND}$, application of Young's equation for contact angle equilibrium[35], and Fowkes[31], and Owens and Wendt's[32] geometric mean relations for dispersive and non-dispersive interactions respectively, leads to the following expression for the contact angle θ of a drop of liquid L on a solid surface S in the presence of vapour V[36]:

$$\cos\theta = \frac{2}{\gamma_{LV}}\left[(\gamma_{SV}^{D}\gamma_{LV}^{D})^{1/2} + (\gamma_{SV}^{ND}\gamma_{LV}^{ND})^{1/2}\right] - 1 \qquad (4)$$

For low-energy surfaces such as polymers, the surface free energy in the presence of vapour γ_{SV} may be assumed to be very close to the intrinsic value γ_S.

Using the probe liquids previously mentioned, values of the surface free energy of both the epoxy composite and the (cured) epoxy gel were evaluated and used in conjunction with the Dupré equation[29] to obtain the physical, reversible work of adhesion, W_o^ϕ:

$$W_o^\phi = \gamma_1 + \gamma_2 - \gamma_{12} \tag{5}$$

where γ_1, γ_2 and γ_{12} represent respectively the surface free energy of solid 1 and solid 2 and their mutual interfacial interaction. The values of the energy of adhesion between the epoxy gel and untreated (reference), oxygen-plasma-treated and nitrogen-plasma-treated epoxy composites will be denoted respectively as W_{oR}^ϕ, W_{oO}^ϕ and W_{oN}^ϕ and were found to be 93, 95 and 100 mJ m^{-2}. Although plasma treatment apparently leads to a slight increase in physical adhesion, this is small and most probably the differences are within the margin of error related to the choice of a particular type of interpretation of wetting experiments. We shall nevertheless take these figures at their face value in the following.

Peel

Preliminary tests were carried out using the untreated composite and varying the contact cure time t. There was considerable scatter in the results but the trend, as expected, was that the energy of adhesion W increased both with increasing peel rate v and increasing t. The adhesion was extremely high for $t = 16$ h, and even at $t = 8$ h peel results were unusable since after peel was initiated at the composite–epoxy gel interface, the locus of failure rapidly and spontaneously transferred to the epoxy gel–PET interface once a crack had progressed across the epoxy gel: the backing film adhesion was insufficient for successful evaluation of the energy of adhesion of the interface of interest. By reducing contact time t, the epoxy gel–PET film interfacial bonding was weakened and at the other extreme, when $t = 0.25$ h, no measurable adhesion developed. (It was shown separately using viscoelasticimetry that after a curing time of ~12 h, the initially liquid epoxy gel mixture became a solid with mechanical characteristics very similar to the final product, indicating that crosslinking was already quite advanced.) Finally, three values of t were adopted: 4, 2 and 0.75 h, of which the last two gave the most consistent results. Failure was apparently interfacial leaving no traces of epoxy gel on the composite, as judged by the naked eye. *Figure 2* shows results of log W *versus* log v for peel effected at ambient temperature for the three values of t in question. Lines shown are regression fits of the form $\log W = a \log v + b$.

Since plasma treatment of the composite is likely to increase the strength of the adhesive bond to the epoxy gel, it is hardly surprising to note that for $t = 8$ h, no peel was possible both for oxygen and nitrogen plasma treatments, and for $t = 4$ h, separation of the PET film from the epoxy gel occurred. Even for $t = 1$ h, adhesion strength was high and comparable to that obtained with the untreated composite for $t = 4$ h. However, these peel experiments were found difficult to perform and the test-pieces presented many defects (bubbles and air films). For these reasons and given the relatively small number of treated composite test-pieces available, we opted for a fixed value of t equal to 0.5 h. With this value, it was found possible to test the composite–epoxy gel interface adequately without problems of change of locus of failure. *Figure 3* gives results of log W *versus* log v for the same test conditions as *Figure 2* together with regression lines for both oxygen and nitrogen plasma treatments. Although the nitrogen plasma treatment gave higher adhesion strengths than the oxygen, it can be seen that both represent an improvement compared with the untreated substrate at similar peel rates and value of t (note that $t = 0.75$ h for the untreated case, so the plasma treatments should — other things being equal — present lower values of W). Unfortunately, we were unable to compare directly treated and untreated peel energies for an identical value of t due to lack of

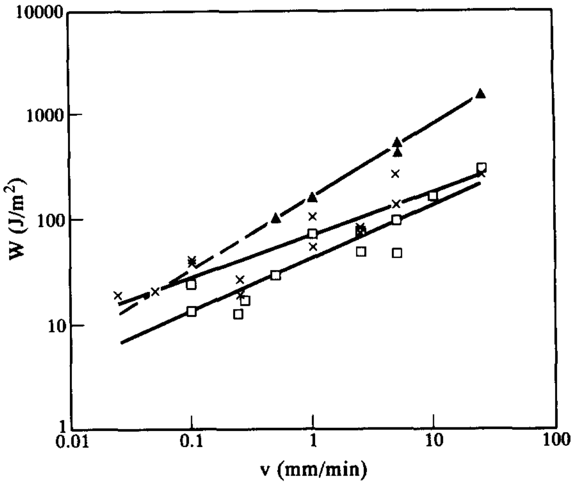

Figure 2 Peel energy W *versus* peel rate v (both on logarithmic scales) for the untreated composite/epoxy gel assembly for difference contact times, t: ▲, 4 h; ×, 2 h; □, 0.75 h

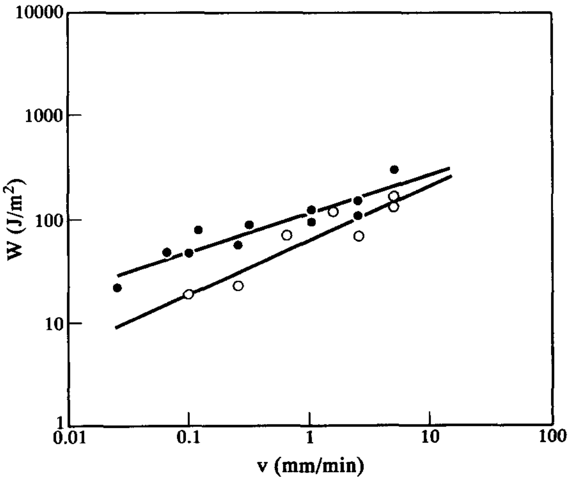

Figure 3 Peel energy W *versus* peel rate v (both on logarithmic scales) for the oxygen (○) and nitrogen (●) plasma-treated composite/epoxy gel assembly. Contact time $t = 0.5$ h

available composite. However, by plotting W *versus* contact time during cure t for a given peel rate v, we may reasonably extrapolate to find the expected value of W for $t = 0.5$ h for the untreated material. (Although it is true that linear extrapolation is a little risky, given that (as previously mentioned) adhesion was unmeasurably low for $t = 0.25$, this procedure can at worst only reasonably overestimate the value of W for the untreated composite.) The procedure is demonstrated in *Figure 4* where log W *versus* t is shown for $v = 0.1$, 1 and 10 mm min^{-1}, together with the values corresponding to the plasma-treated composites. As can be seen quite clearly, adhesion is improved after plasma treatment.

We shall now quantify this improvement and suggest a tentative explanation. Maugis and Barquins[15] have shown that the peel energy of elastomers W may often be successfully described by:

$$W = W_0\,[1 + \phi(a_T v)] \tag{6}$$

using the present nomenclature, where ϕ is a dimensionless function of crack (or peel) speed v and temperature, W_0 is the intrinsic interfacial adhesion energy, and a_T is the Williams–Landel–Ferry time–temperature shift factor[37]. It was shown that ϕ ($a_T v$) varies as $(a_T v)^n$ where n is a constant. Since we expect (and indeed find) that $W \gg W_0$, we may write:

$$W \approx W_0\,\phi(a_T v) \tag{7}$$

which is similar to a relation proposed by Gent and Schultz[13]. W_0 for the various systems has been estimated on the understanding that only physical interactions exist, as may be evaluated from wetting measurements, i.e. $W_0 = W_0^\phi$. Since the finally cured epoxy gel should have essentially the same mechanical properties in all cases, we may treat $\phi(a_T v)$ as a unique function, irrespective of the composite substrate surface preparation. We define W_R as the effective energy of adhesion, evaluated from peel experiments, for the reference (or untreated) composite (at a given peel rate v) and W_i as the equivalent for the plasma-treated material (i is either O or N, depending on whether oxygen or nitrogen plasma is in question). From equation (7), we may then expect that:

$$\frac{W_i}{W_R} = \frac{W_{0i}\,\phi(a_T v)}{W_{0R}\,\phi(a_T v)} = \frac{W_{0i}}{W_{0R}} \tag{8}$$

where W_{0i} and W_{0R} are intrinsic interfacial energies. However, experimentally we find that:

$$\frac{W_i}{W_R} = \frac{W_{0i}^\phi}{W_{0R}^\phi} + \varepsilon \tag{9}$$

where ε is a positive quantity. We shall simplify the problem by postulating that the intrinsic energy of adhesion of the untreated composite to the epoxy gel is due essentially only to physical interactions, i.e. $W_{0R} = W_{0R}^\phi$, but that W_{0i} consists of two (additive) components: W_{0i}^ϕ due to physical bonds and W_{0i}^χ due to chemical bonds (of the various theories of adhesion discussed earlier, this seems the most likely hypothesis due to the possibility of creation of activated species after plasma treatment).

We may then write:

$$\frac{W_i}{W_R} = \frac{W_{0i}}{W_{0R}} = \frac{W_{0i}^\phi + W_{0i}^\chi}{W_{0R}} \tag{10}$$

Equation (10) may be rearranged to give:

$$W_{0i}^\chi = W_{0R}\left[\frac{W_i}{W_R} - \frac{W_{0i}^\phi}{W_{0R}}\right] \tag{11}$$

Had the gradients obtained for the log W *versus* log v relationships of *Figures 2* and *3* been identical, equation (11) could have been used simply for determining W_{0i}^χ for each plasma treatment (neglecting any difficulties associated with evaluation of the values of W_{0R}^ϕ and W_{0i}^ϕ, discussed previously). However, experimental scatter (and maybe unrecognised factors) gave rise to differences in slope and therefore equation (11) was employed to evaluate W_{0i}^χ for the two plasma treatments using values of W_i and W_R appropriate to three peel speeds covering essentially the range of rates considered, viz. 0.1, 1, and 10 mm min^{-1}. Results are summarized in *Table 1*. Taking the average values of W_{0i}^χ obtained, corresponding closely to those near the 'centre of gravity' of the log v range considered (i.e. $v = 1$ mm min^{-1}) as representative, we obtain ~60 and ~180 mJ m^{-2} respectively for oxygen and nitrogen plasma treatments. Although the nitrogen treatment would seem superior, both lead to significant increases above the value of 93 mJ m^{-2} for W_{0R}.

We are unsure of the types of chemical bonds which may be created between plasma treated composite and epoxy gel, but there is a likelihood that these will be of the character C–N, C–O or C–C, having intrinsic energies[38] of the order of 250–350 kJ mol^{-1}. Let us assume that a mole of such bonds, representing 6×10^{23} units, is 'smeared out' to a monolayer. Taking a typical atomic cross-section to be $\sim 3 \times 10^{-20}$ m^2, a mole of bonds representing ~300 kJ will then occupy $\sim 1.8 \times 10^4$ m^2.

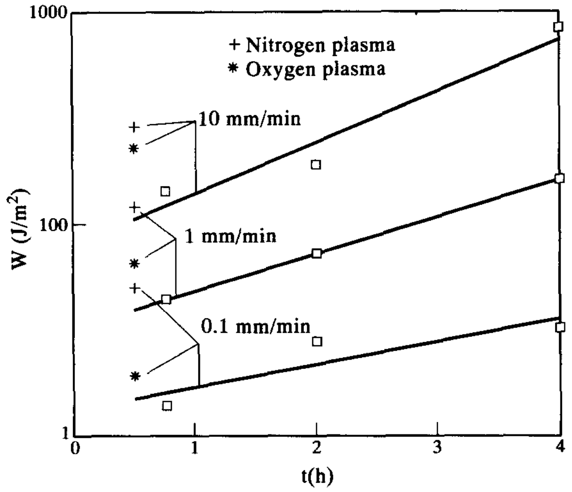

Figure 4 Peel energy W at peel rates v of 0.1, 1 and 10 mm min^{-1}, as a function of contact time t for the untreated composite, and values at $t = 0.5$ h for oxygen- and nitrogen-treated composites

Table 1 Values of W_{0i}^{χ} (in mJ m^{-2}), the (assumed) chemical bonding component of the intrinsic energy of adhesion of plasma-treated composite to epoxy gel, as calculated at various peel rates, together with the average

Plasma treatment	Peel rate (mm min^{-1})			Average
	0.1	1	10	
Oxygen	22	58	99	60 ± 39
Nitrogen	212	184	145	180 ± 34

Thus complete chemical bonding at the interface should give an intrinsic value of W_{0i}^{χ} of $\sim$17 J m^{-2}. Clearly this figure is very approximate and it is probably more correct to say that W_{0i}^{χ} for complete chemical interfacial bonding is of the order of tens of J m^{-2}.

Referring to our earlier calculated values of $\sim$60 and $\sim$180 mJ m^{-2} for W_{0i}^{χ} for the oxygen- and nitrogen-plasma-treated composite, we now estimate that chemical bonds occupy something of the order of 0.3–1% of the total number of possible sites*. We thus conclude that a fairly small surface fraction of chemical bonds created at the interface can lead to a substantial improvement in adhesive strength. Conversely, if all the sites available were to react chemically and allowing for a conversion factor from W_0 to W [equation (7)] of $\sim$500 (it can easily be more), we predict a value of W of $\sim$10 kJ m^{-2} which is extremely high. It was indeed noted earlier for contact cure times t in excess of 1 h when using plasma-treated composite, that satisfactory peel tests could not be performed since peel strength at the composite–epoxy gel interface was too high and therefore not the limiting factor: failure occurred elsewhere in the system. Although it is unlikely that all sites would lead to chemical bonds forming even for higher values of t, the approximate calculation above renders quite plausible the idea that prolonged contact during cure may cause significant interfacial strength by the creation of covalent bonding.

Finally, although the simple model proposed here gives a reasonable explanation of observed phenomena, refinements can no doubt be made. In particular, the estimation of the physical contribution to the intrinsic energy of adhesion, W_0^{ϕ}, can probably be improved by allowing for such contributions as those due to Lewis acid–base interactions[34], and also the variation of W_R with contact time t suggests that some degree of chemical bonding may well occur even when employing the untreated composite. However, this latter effect is likely to be limited for the short contact times t used in the model.

CONCLUSIONS

It is known that the plasma treatment of polymeric surfaces can lead to better adhesion. This can be of use when bonding composite materials with (rigid) structural adhesives. We have undertaken a model study in which an epoxy/carbon fibre composite was made to adhere to an epoxy gel, the latter component being a chosen as a compromise in that it has chemical similarities to an epoxy adhesive, yet the flexibility required in order to perform peel tests at ambient temperatures. Both untreated and oxygen- and nitrogen-plasma-treated composites were studied. Wetting experiments were performed to estimate the Dupré energy of adhesion between the composite and epoxy gel, but the major part of the study concerned peel tests at 180°. By varying the contact time t of the composite/epoxy gel assembly during cure (whilst maintaining constant the total cure time in order to have reproducible mechanical properties), suitable peel test-pieces were obtained with separation occurring at the composite–epoxy gel interface. Comparison of untreated and plasma-treated systems showed the latter to give significantly higher peel strengths after comparable cure cycles, more so, in fact, than could be expected from changes in the intrinsic work of adhesion of Dupré due to physical bonds, as assessed from wetting. A model has been tentatively suggested in which the increase in peel strength is due essentially to chemical bonding occurring between the (activated) treated composite and the epoxy gel. The model suggests that only about 1% of available sites have been occupied by chemical bonds and yet this leads to significant increases in mechanical strength.

ACKNOWLEDGEMENT

The authors thank Dr A. Carré for suggesting the epoxy gel used in this study.

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*The term 'possible' assumes that all molecular sites are potentially active chemically. This, of course, is unlikely to be the case and so the percentages should be somewhat higher. In the absence of further information, the percentage of *active* sites having reacted cannot be estimated

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