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Effect of water and ice on strength and fracture toughness of intermittently bonded boron-epoxy composites

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The effects of water and ice on the strength and fracture toughness of boron–epoxy composites with polyurethane intermittent bonding have been investigated. Neither simple soaking in water nor soaking followed by freezing and thawing have marked effects on the strength of the fully-coated composites, but they have disastrous effects on the uncoated composites. Toughness is affected only marginally, with some small reductions in the fully-coated samples, and with essentially no effect on the uncoated composites. An analysis is presented which explains adequately the experimental strength and toughness results obtained, and which is based on an argument that water absorption reduces the interfacial shear strength only of the uncoated areas and not those regions coated by the polyurethane varnish. The results indicate that the advantages of appropriate intermittent bonding (i.e. high strength combined with high toughness) are retained in wet conditions so that such composites may be favourably used in such adverse environmental conditions.

1. Introduction

Recent work [1–3] by one of us has shown that "intermittent bonding" with appropriate coatings (such as polyurethane varnish) allows high toughness to be obtained in brittle filament/brittle matrix composites without significant loss of tensile strength. Filaments are arranged to have alternate regions of high and low shear stress (and low and high toughness) by interrupted coating along the filaments. The strong uncoated regions ensure that the filament strength is picked up; randomly positioned weak-coated areas effectively blunt cracks by the Cook-Gordon mechanism [4], which in turn produces long pull-out lengths with an associated large contribution to toughness. Unidirectional boron–epoxy composites of fibre volume fraction $0.20 \simeq 0.25$ have been made in this way; they have fracture toughnesses of over $200\,\text{kJ m}^{-2}$, (as opposed to about $40\,\text{kJ m}^{-2}$ with no coating), and they retain rule of mixtures tensile strengths ($\simeq 650\,\text{MN m}^{-2}$).

In practical applications of intermittently bonded composites, the effects of rain, soaking by water, and possible freezing of that water must be assessed, particularly because it is known that many composites suffer loss of strength and reduction in fracture toughness when exposed to water environments [5–8]. Consequently, it was decided to perform an exploratory study upon the effects of water (both liquid and frozen) on the strength and toughness of these intermittently bonded boron–epoxy composites in order to

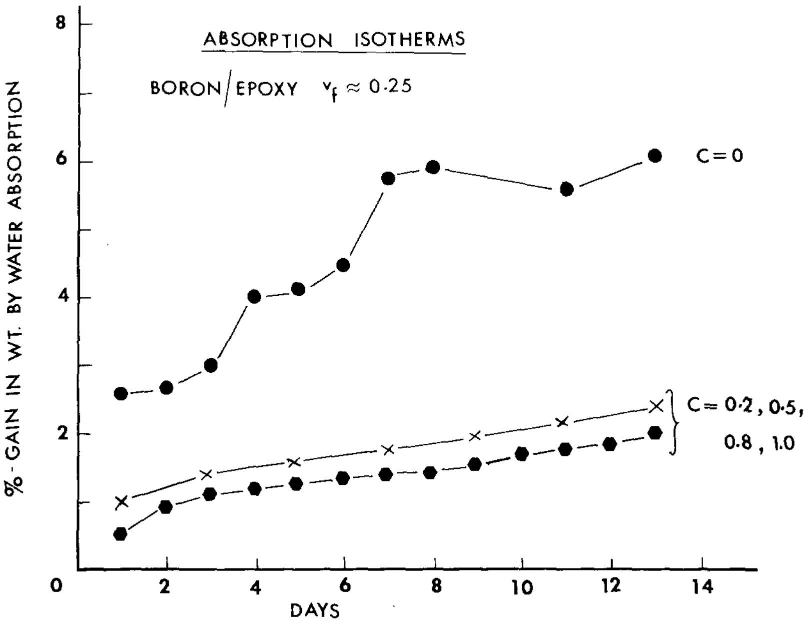

Figure 1 Water absorption isotherms (•: $C = 0$, ×: $C = 0.2$, hexagon: $C = 1.0$). Data for $C = 0.5$ and 0.8 which are positioned between the curves for $C = 0.2$ and 1.0 are not shown.

determine whether all the advantages of intermittent bonding would be retained when wet.

2. Testpieces and experiments

The same types of specimens as reported in [1–3] were used in this investigation, i.e. five-layer tensile bars, about 115 mm long by 10 mm wide by 2 mm thick, and seven-layer compact tension profile toughness specimens, 2.8 mm × 75 mm × 75 mm with a 54 mm starter crack (where the two outside layers of the testpiece parallel to the starter crack were intended to encourage the crack to propagate in a straight line). Both unidirectional laminates (five layers perpendicular to the pre-crack) and angle-ply laminates (layers at 0, −45, 0, +45, 0) were made for tensile and toughness measurements. All specimens were made from 0.20 ≃ 0.25 fibre volume fraction (v_f) tapes, intermittently bonded with polyurethane varnish to produce the following coated fractions: (a) zero, (b) $C = 0.2$, (c) $C = 0.5$, (d) $C = 0.8$, and (e) $C = 1.0$, where C is the ratio of the coated length to the pattern repeat distance along the filament.

All specimens were submerged in a tray of water and allowed to soak for many days. Every testpiece was removed from the water and weighed at the end of each day, excess water being lightly removed with blotting paper. The absorption isotherms thereby produced are shown in Fig. 1, where the ordinate represents the percentage gain in weight (measured in g/g) against number of days. It will be observed that the uncoated specimens took up considerably more water than the others, and in broadest terms, the absorption seems to vary inversely with the coated fraction, although the differences between the data for $C = 0.2, 0.5, 0.8$ and 1.0 are not marked.

Even though arguably the specimens were still absorbing water after a fortnight, and thus were not fully saturated, it was decided to test them in that wet condition. Also, a number of specimens were set aside, put into the freezing compartment of a refrigerator, and left overnight. Having thawed, they were included into the programme of tensile and toughness measurements. The experimental details followed previous practice (in particular, fracture toughness was determined by Gurney's irreversible work area method* [8–13]). Each experimental point on the tensile strength

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*Gurney's irreversible work area method for measurement of fracture toughness of various materials has been described in detail in [9–14]. Application of Gurney's method to R-measurements of boron–epoxy composites such as used in this investigation has already been discussed in an earlier paper [3] so that the same analysis will not be repeated here.

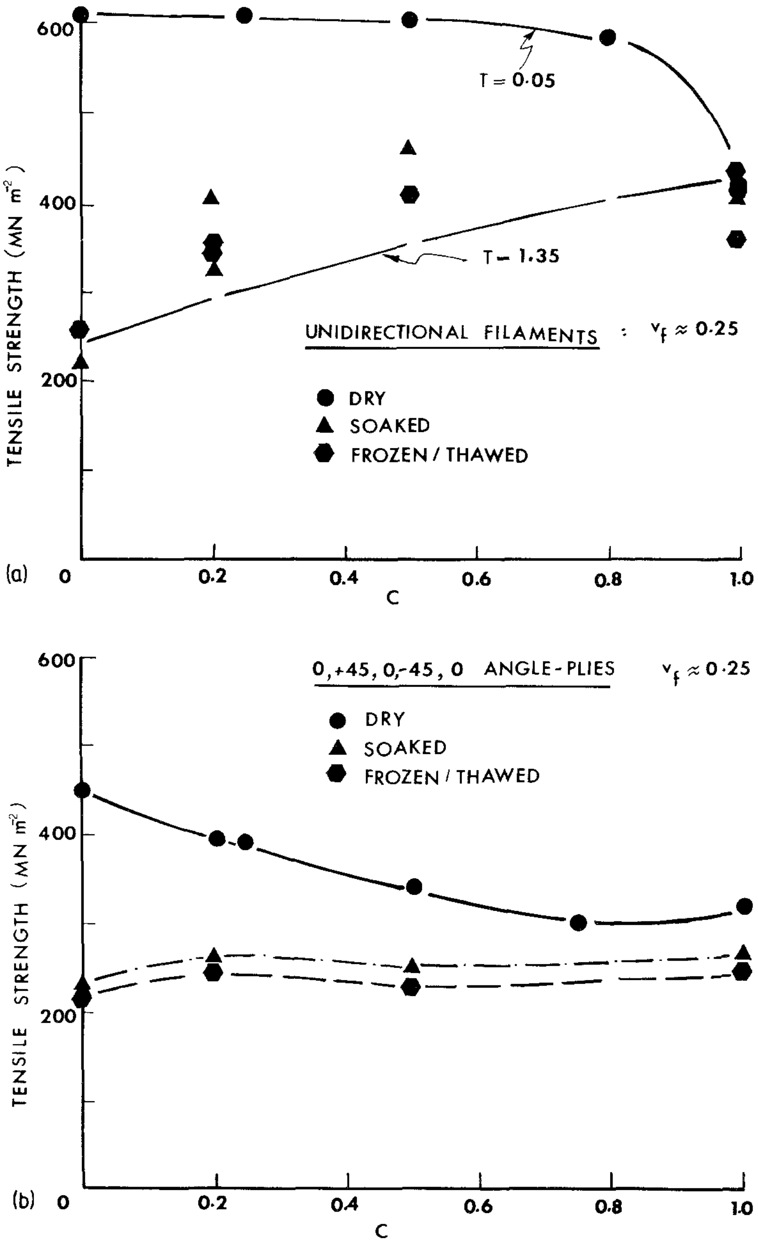

Figure 2 (a) Tensile strengths of wet and thawed unidirectional filament testpieces. (b) Tensile strengths of wet and thawed angle-ply testpieces.

and fracture toughness results shown later in Figs. 2 and 3 represents the average value of at least three similar tests.

3. Results

Fig. 2a shows the tensile strength results for both wet and thawed unidirectional filament testpieces, and Fig. 2b gives the corresponding data for angle-ply laminates. The results for identical dry specimens [3, 15] are also shown[†]. There is a marked reduction in the strength of wet uncoated samples ($C = 0$), when compared with the strength of dry uncoated testpieces. On the other hand, there is hardly any difference between the strength of wet and dry fully-coated samples ($C = 1$). At intermediate values of C, the data blend in between the

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[†] The fibre volume fractions of the dry samples are closer to 0.2 than 0.25, whereas the present results have v_f closer to 0.25 than 0.2. This affects one-to-one comparisons.

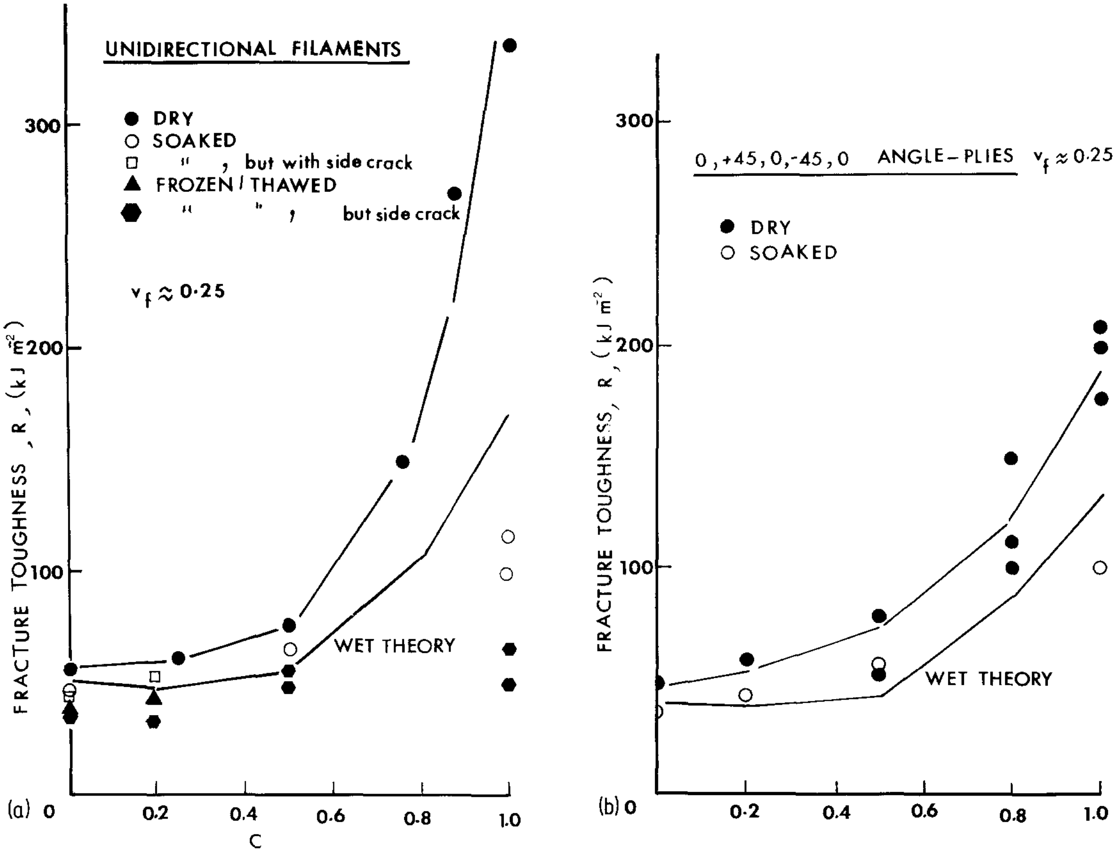

Figure 3 (a) Fracture toughness of wet and thawed unidirectional filament testpieces. (b) Fracture toughness of wet and thawed angle-ply testpieces.

$C = 0$ and $C = 1$ results, the dry specimens falling off in strength between $C = 0$ and $C = 1$, and the wet specimens increasing in strength as the fully-coated condition is approached.

The reduction in uncoated wet strength for the angle-ply specimens is not proportionately as great as that of the unidirectional specimens, (about 250 MN m^{-2} compared with 450 MN m^{-2}, as opposed to about 250 MN m^{-2} compared with 620 MN m^{-2}). This is presumably because the load carried by the 45° angle plies is a smaller proportion of the load carried by the unidirectional filaments, so that reductions in interfacial strength caused by the wet environment do not produce as big an effect. In the experiments, the uniaxial fibres broke first, then upon load transfer, the 45° filaments suffered normal fractures.

In general, the effect of freezing and thawing seems to deteriorate further the strength of the angle-ply specimens when compared with the dry results. But this effect is not obvious for the unidirectional specimens.

Fig. 3a and b show the toughness results for unidirectional and angle-ply laminates respectively. Again, data for corresponding dry samples are given, noting (as for the tensile results) that the fibre volume fractions may be somewhat different. The results suggest that toughness levels are not markedly different from the dry samples, except for the highest percentage coating, when the gain in toughness with increasing C is rather limited. The data are unfortunately restricted, since some of the unidirectional specimens failed by crack propagation perpendicular to the starter crack direction; this is discussed later. Nevertheless, it seems that respectable toughnesses are attainable in coated samples even when fully wet, and even after one freezing/thawing cycle.

As in the earlier studies [1–3], pull-out experiments (after the filaments had broken) were performed in order to establish the interfacial frictional stress, acting after complete debonding and filament fracture. Specimens were re-gripped above the remaining crack ligaments and pull-out work estimated from the area under the load/displacement plot on the tensile testing machine. As shown in Fig. 4, many filaments pulled out over long lengths, which made it very difficult to

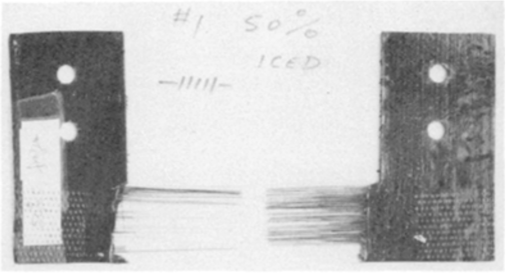

Figure 4 "Pull-out" filaments in wet and thawed CT fracture toughness specimens.

count individual filaments. To solve this problem, the number of filaments pulling out was estimated from the known fibre volume fraction of the specimens, and the size of the remaining crack ligament over which pull-out was taking place.

In this way, the following average values of the interfacial frictional stress (τ') during pull-out were established.

4. Analysis of results

4.1. Interfacial shear strengths

The tensile strength results seem to suggest that water (and ice) affected the uncoated regions along the filaments, but caused only minor effects in the polyurethane coated regions. It follows from the observation that the tensile data for wet and dry conditions are very different for $C = 0$, but are essentially the same for $C = 1$.

The behaviour may be modelled by saying that the wet uncoated interfacial shear strength, $(\tau_{uc})_{wet}$, is altered considerably, whereas in the coated regions, $(\tau_c)_{wet} \simeq (\tau_c)_{dry}$. The rule of mixtures for the wet tensile strengths of uncoated and fully-coated unidirectional fibre samples, i.e. $C = 0$ and $C = 1$, gives [3]:

$$250 = (1 - v_f)\sigma_m + v_f\sigma_f\left(1 - \frac{\psi}{2n}\right) \quad (1a)$$

and

$$420 = (1 - v_f)\sigma_m + v_f\sigma_f\left(1 - \frac{\psi}{2nT_{wet}}\right). \quad (1b)$$

TABLE I

C	Pull-out (τ') friction (MN m^{-2})	Condition
0	0.49	Water soaked
0.2	0.41	Water soaked
0.5	0.46	Water soaked
1.0	2.75	Water soaked
0	0.12	Frozen and thawed
0.5	1.54	Frozen and thawed

These values should be contrasted with $\tau' \simeq 2\,\text{MN m}^{-2}$ from earlier "dry" tests.

In Equation 1, σ_f and σ_m are the tensile strengths of the filament and matrix, respectively, ψ/n is equal to $\{(l_{crit})_{uc}/l_r \div L/l_r\}$ where $(l_{crit})_{uc}$ is the critical transfer length of the uncoated fibres (in this case the *wet* critical transfer length), l_r is the repeat distance of the intermittent bond, and L is the effective gauge length of the testpiece. Also in Equation 1b, $T_{wet} = (\tau_c/\tau_{uc})_{wet}$. Note that in the previous work [3] the parameter T was referenced with respect to the *dry* τ_{uc}, and $(l_{crit})_{uc}$ meant the *dry* critical transfer length. Equation 1a may be solved for $(\psi/n)_{wet}$, which, using $v_f = 0.25$, $\sigma_m = 81\,\text{MN m}^{-2}$, and $\sigma_f = 3.45\,\text{GN m}^{-2}$ gives:

$$(\psi/n)_{wet} = 1.56 = \{(l_{crit})_{uc}/L\}_{wet}. \quad (2)$$

Using this value in Equation 1b enables T_{wet} to be solved as $T_{wet} = 1.35$. The interfacial shear strength of the polyurethane coated interfacial bond is therefore *stronger* than the interfacial shear strength of the *wet* uncoated regions. Previous investigations [3] gave $T_{dry} = (\tau_c/\tau_{uc})_{dry} = 0.05$, so we have $(\tau_c/\tau_{uc})_{wet} = 1.35$ and $(\tau_c/\tau_{uc})_{dry} = 0.05$. Whence if, as postulated, the coated regions are unaffected by water, τ_c may be eliminated between the relationships to give:

$$(\tau_{uc})_{dry} = 27(\tau_{uc})_{wet}, \quad (3)$$

i.e. water has reduced the uncoated bond strength by a factor of 27.

It seems, therefore, that the opposite behaviours of the wet and dry data – the wet increasing in strength to the fully-coated value of circa 420 MN m^{-2} from the uncoated value of 250 MN m^{-2}, but the dry falling from 650 MN m^{-2} to about 450 MN m^{-2} – may be explained in terms of different Ts, with $T_{dry} < 1$ and $T_{wet} > 1$. T_{dry} is referenced to $(\tau_{uc})_{dry}$; T_{wet} is referenced to $(\tau_{uc})_{wet}$.

This may be checked by noting that $d\sigma/dC$ from the rule of mixtures equation is proportional to:

$$-(1 - C(1 - T))^2(1 - T) \quad (4)$$

so that $d\sigma/dC$ is positive for $T > 1$, and negative for $T < 1$ (cf. Fig. 2a).

Because the thawed specimens displayed slightly lower strengths, but showed the same trends as the simply wet samples, it follows that the freezing/thawing cycle must have further weakened the interfacial shear strength, or caused physical separation of filament and matrix, or some physical separation of the layered testpieces (i.e. delamination).

4.2. Wet critical lengths

The critical lengths of the filaments, in their various wet conditions, may be determined as follows: the critical length of the uncoated dry specimens is, from previous studies [3], about 3.5 mm; this comes from $l_{\text{crit}} = \sigma_f d/2\tau$ with $\sigma_f = 3.45\,\text{GN m}^{-2}$, $\tau = 69\,\text{MN m}^{-2}$ and filament diameter (d) of $140\,\mu\text{m}$. If: $(\tau_{\text{uc}})_{\text{wet}} = (1/27)(\tau_{\text{uc}})_{\text{dry}}$, it follows that $[(l_{\text{crit}})_{\text{uc}}]_{\text{wet}} = 27[(l_{\text{crit}})_{\text{uc}}]_{\text{dry}}$, i.e. about 95 mm. However, for the fully-coated wet and dry samples: $[(l_{\text{crit}})_{\text{c}}]_{\text{wet}} \simeq [(l_{\text{crit}})_{\text{c}}]_{\text{dry}}$ because their tensile strengths are similar ($\sim 420 \simeq 450\,\text{MN m}^{-2}$). The interfacial shear bond strengths of all fully-coated polyurethane samples (wet and dry) seem to be the same. From [3], $T_{\text{dry}} = (\tau_{\text{c}}/\tau_{\text{uc}})_{\text{dry}} = 0.05$, so that the fully-coated critical length is $[(l_{\text{crit}})_{\text{c}}]_{\text{dry}} = 3.5\,\text{mm}/0.05 = 70\,\text{mm}$. Or, equivalently in terms of T_{wet} we have $(\tau_{\text{c}}/\tau_{\text{uc}})_{\text{wet}} = 1.35$, so that:

$$[(l_{\text{crit}})_{\text{c}}]_{\text{wet}} = \frac{[(l_{\text{crit}})_{\text{uc}}]_{\text{wet}}}{1.35} = \frac{95}{1.35} = 70\,\text{mm}$$

again.

The critical length of a partly coated intermittently bonded specimen is given by:

$$(l_{\text{crit}}) = (l_{\text{crit}})_{\text{uc}}/[1 - C(1 - T)], \qquad (5)$$

where T may be T_{dry} or T_{wet} depending upon whether $(l_{\text{crit}})_{\text{uc}}$ is given for dry or wet conditions, respectively. Thus, for *dry* samples [3]:

$$(l_{\text{crit}}) = 3.5/(1 - 0.95\,C)\text{mm} \qquad (6)$$

because $T = 0.05$ references to *dry* uncoated interfaces, and equivalently:

$$(l_{\text{crit}}) = 95/(1 + 0.35\,C)\text{mm} \qquad (7)$$

because $T = 1.35$ referenced to *wet* uncoated interfaces. For $C = 1$, both expressions give the same l_{crit}.

All the foregoing is predicted on using $\sigma = 420\,\text{MN m}^{-2}$ at $C = 1$ for the wet samples. In fact, our (limited) experiments give a higher value of σ for $C = 0.5$. In order to give a better fit to the experimental data in Fig. 2a, calculations can be performed taking $\sigma = 420\,\text{MN m}^{-2}$ at $C = 0.5$ instead of at $C = 1$. Then, $T = (\tau_{\text{c}}/\tau_{\text{uc}})_{\text{wet}} = 1.7$ instead of 1.35, whence: $(\tau_{\text{uc}})_{\text{dry}} = 34(\tau_{\text{uc}})_{\text{wet}}$, and $(l_{\text{crit}}) = 95/(1 + 0.7\,C)\text{mm}$. This would make some difference to the critical lengths, the fully-coated value ($C = 1$) being 56 mm instead of 70 mm.

4.3. Effective length of tensile specimen (L)

We have from [3]:

$$\begin{aligned}\sigma &= (1 - v_f)\sigma_m + v_f\sigma_f\left\{1 - \frac{\psi}{2n[1 - C(1 - T)]}\right\}\\ &= (1 - v_f)\sigma_m + v_f\sigma_f\left\{1 - \frac{(l_{\text{crit}})_{\text{uc}}}{2L[1 - C(1 - T)]}\right\}\end{aligned} \qquad (8)$$

where $(l_{\text{crit}})_{\text{uc}}$ refers to wet or dry conditions depending on the way in which T is defined. Now, it was determined that $(\psi/n)_{\text{wet}} = [(l_{\text{crit}})_{\text{uc}}/L]_{\text{wet}} = 1.56$ from the $C = 0$ wet result. Thus, given: $[(l_{\text{crit}})_{\text{uc}}]_{\text{wet}} = 95\,\text{mm}$ it follows that $L_{\text{wet}} = 61\,\text{mm}$.

A comparable result follows from the dry data because $(\psi/n)_{\text{dry}} = [(l_{\text{crit}})_{\text{uc}}/L]_{\text{dry}} = 0.05$. Thus, $L_{\text{dry}} = 3.5/0.05 = 70\,\text{mm}$. The dry tensile specimens (manufactured and tested much earlier, see [3]) were roughly the same in size, i.e. with overall length of 100 mm including end tabs.

It must be pointed out that since the effective lengths of the wet tensile specimens (61 mm) is *less* than the critical length of the uncoated wet samples (95 mm), and only just about the critical length of the fully-coated wet samples (70 mm), the "simple" rule of mixtures:

$$\sigma = (1 - v_f)\sigma_m + v_f\sigma_f$$

would markedly over-estimate the observed strengths. Longer tensile specimens would give higher results, but all would show the same changes with C as in Fig. 2a and b.

4.4. Pull-out lengths

The changes in wet critical lengths are reflected in the filament pull-out lengths, both of the tensile specimens and also the toughness specimens (to be discussed later). As is well known, the longest pull-out length should be $(l_{\text{crit}})/2$, and the average pull-out length $(l_{\text{crit}})/4$, since the shortest pull-out length will be zero. Thus, the longest pull-out lengths should be $(95/2) = 48\,\text{mm}$ for the uncoated wet samples, and $(70/2) = 35\,\text{mm}$ for the fully-coated wet samples – other samples with C

between 0 and 1 taking intermediate values. Because $L < (l_{\text{crit}})$ for the wet samples, these full values for pull-out were not observed. Rather values of about 20 mm were seen for wet uncoated samples, with yet smaller values for samples that had C approaching unity.

A significant feature of the angle-ply laminates was that the 45° filaments broke off essentially in the main plane of fracture, displaying virtually no pull-out.

4.5. Toughness analysis

4.5.1. Unidirectional and angle-ply results

It was argued in [3] that the total toughness is given by:

$$R_{\text{total}} = R_{\text{surfaces}} + R_{\text{redist}} + R_{\text{pull-out}} \qquad (9)$$

where R_{surfaces} relates to debonding (mode II), R_{redist} relates to the Piggott/FitzRandolph stress redistribution (or relaxation) [16, 17], and $R_{\text{pull-out}}$ relates to the Cottrell/Kelly pull-out [18]. An additional component, $R_{\text{Cook/Gordon}}$, must be added to the above if tensile debonding (mode I) takes place ahead of the running crack. The Cook/Gordon mechanism itself is a small toughness sink, but the associated additional long debond lengths in the presence of Cook/Gordon debonding significantly increase the pull-out lengths and hence the total toughness. These aspects of toughness components were discussed in detail in [3].

The differences in dry toughness levels of the intermittently bonded angle-ply laminates compared with the unidirectional specimens (see Fig. 3a and b) may be explained principally in terms of loss of pull-out component of the 45° angle-plies (since, as described in Section 4.4, the 45° filaments break off in the plane of fracture with little or no pull-out).

With regard to an analysis of the toughnesses of the wet and thawed samples (both unidirectional and angle-ply), we are faced with the same difficulty as before [3], namely that interfacial toughnesses are important parameters, yet measurement of them is difficult (particularly in mode I fracture). Certainly, to infer interfacial toughnesses from interfacial shear strengths can lead to gross errors, as was demonstrated in the earlier studies [1–3] by the fact that silicone vacuum grease and polyurethane varnish coatings seemed to produce comparable interfacial shear strengths, yet displayed quite different toughness behaviours. In the earlier work [3], it was loosely argued that if any relationship at all existed between interfacial τ values and interfacial R values, it probably was predicated on the interfacial stress intensity factors (K). That is, since the interfacial debonding stress is proportional to some interfacial K, and if $K^2 = ER$ in the usual fashion, then $\tau \propto \sqrt{R}$.

This idea may be applied to the wet interfaces and wet interfacial toughnesses inferred from wet interfacial shear strengths. For example, if $(\tau_{\text{uc}})_{\text{wet}} \simeq (1/27)[(\tau_{\text{uc}})_{\text{dry}}]$, then

$$(R_{\text{uc}})_{\text{wet}} \simeq \frac{1}{27^2}\,[(R_{\text{uc}})_{\text{dry}}]$$

$$\simeq \frac{1}{730}\,[(R_{\text{uc}})_{\text{dry}}]. \qquad (10)$$

The interfacial toughnesses of wet intermittently bonded composites may then be worked out, and R_{surfaces}, R_{redist} and $R_{\text{pull-out}}$ evaluated. In this way, the anticipated variation of R_{total} with C may be determined – angle-ply predictions taking account of the loss of the pull-out contribution in the 45° layers. Details of these procedures are given in the Appendix. Pull-out is the greatest contributor to crack propagation resistance, on account of the long pull-out lengths. Curves following the anticipated R_{total} versus C relationship have been superimposed on Fig. 3a and b. The agreement is reasonable.

Attention must be brought to a significant fact that affects the data. The half-height of the compact tension profile toughness specimen was 38 mm. Because the low interfacial shear stresses cause long critical lengths (95 mm for uncoated wet samples and 70 mm for fully-coated wet samples), the theoretical longest pull-out lengths ($l_{\text{crit}}/2$) are longer than, or comparable to, the size of the specimen. The discrepancy is worse when Cook/Gordon debond lengths ($= Cl_{\text{r}}/2$) are added on. Thus, the potential contribution to toughness from pull-out is diminished and the formula for $R_{\text{pull-out}}$ in [3] should be modified. This is done in the Appendix on the assumption of a normal distribution of pull-out lengths between zero and $l_{\text{crit}}/2$, account being taken of the "missing" lengths (greater than 38 mm long) which do not contribute to the resistance to crack propagation. Similar thoughts apply to the Piggott/FitzRandolph contribution to toughness, which is also smaller than anticipated owing to the inadequate lengths over which irreversible interfacial slip can take place.

In the dry cases discussed in [3], the uncoated critical lengths (~ 3.5 mm) are much smaller than the size of the specimen, so these considerations do not apply. However, the fully-coated critical lengths are comparable with the fully-coated wet results given here. Comment was made in [3] upon the fact that the theoretical pull-out lengths of fully-coated samples were greater than the size of the specimen, but an analysis, such as presented here, was not given for the numerical effects on toughness contributions. Larger specimens would, of course, have allowed the full potential toughness to have been picked up.

5. Conclusions

Although the present specimen sizes are not large enough to display the full potential strength and toughness behaviour of the wet (and thawed) boron–epoxy unidirectional and angle-ply samples, it is clear that the extreme consequences of soaking with water are to:

(i) reduce markedly the tensile strength of the uncoated composites;

(ii) make hardly any difference in tensile strength to the composites fully-coated with polyurethane varnish;

(iii) make hardly any difference to the uncoated toughnesses;

(iv) cause only a comparatively small reduction in the toughnesses of the fully-coated samples.

The effect of one freezing/thawing cycle is to reduce all the strength values of the angle-ply samples and the toughness values of the unidirectional specimens by a further small amount below the water-soaked results. The effect of repeated freezing/thawing cycles is not known and will be the subject of future investigations.

It seems very important, given that respectable wet toughnesses are still attainable, that the tensile strengths of fully-coated polyurethane varnish specimens are the same whether wet or dry. Although there is a loss relative to the dry uncoated strength, that value (600 to 650 MN m^{-2}) is not of much use if, upon getting soaked, it is reduced to only some 250 MN m^{-2}.

Appendix

R_{surfaces}

The component of R_{surfaces} that concerns interfacial fractures is given by [3]:

$$v_{\mathrm{f}} \cdot \frac{l_{\text{crit}}}{d} \cdot R_{\text{interface}}. \tag{A1}$$

For the wet uncoated case, $l_{\text{crit}} = 95$ mm, i.e. $27 \times (l_{\text{crit}})_{\text{dry}}$, $d = 140\,\mu$m and $(R_{\text{uc}})_{\text{wet}} = (1/27^2)(R_{\text{uc}})_{\text{dry}}$ so that the toughness contribution from debonding the wet interface is:

$$\frac{(0.25)(27 \times 3.5)10^{-3}}{140 \times 10^{-6}} \frac{1}{27^2} (R_{\text{uc}})_{\text{dry}} = 0.23\,(R_{\text{uc}})_{\text{dry}}.$$

It was assumed in earlier work that $(R_{\text{uc}})_{\text{dry}} \simeq R_{\mathrm{m}} \simeq 2.6\,\mathrm{kJ\,m^2}$. so that in the *wet* uncoated case the debond surfaces contribution to R may only be about 0.6 kJ m^{-2}.

At intermediate values of C, R_{surfaces} is given by [3]:

$$v_{\mathrm{f}}\psi\lambda \left\{\frac{1 - C(1 - \rho_{\mathrm{II}})}{1 - C(1 - T)}\right\} (R_{\mathrm{II_{if}}})_{\text{uc}}. \tag{A2}$$

Referencing quantities with respect to the *wet* uncoated case, i.e. $T = 1.35$, $\rho_{\mathrm{II}} \propto T^2 = 1.8$, $\psi\lambda = \frac{[(l_{\text{crit}})_{\text{uc}}]_{\text{wet}}}{d} = \frac{95 \times 10^{-3}}{140 \times 10^{-3}} = 680$, so, for $v_{\mathrm{f}} = 0.25$:

$$R_{\text{surfaces}} = (0.25)(680)\left\{\frac{1 + 0.8C}{1 + 0.35C}\right\} \frac{2.6}{27^2} \mathrm{kJ\,m^{-2}},$$

which for $C = 1$, becomes 0.8 kJ m^{-2}. This is really quite small compared with the total measured values. In fact, the contribution is even less because the half-height of the toughness specimen (38 mm) is less than half the critical lengths, so that full "potential" debonding is never attained.

It seems, therefore, that of all the surfaces components, probably the most significant is that of the matrix itself, at $(1 - v_{\mathrm{f}})R_{\mathrm{m}} \simeq 2\,\mathrm{kJ\,m^{-2}}$.

R_{redist}

Regarding the Piggott/FitzRandolph redistribution contribution, we have [3]:

$$R_{\text{redist}} = \frac{v_{\mathrm{f}}\sigma_{\mathrm{f}}^2\,\psi\lambda d}{6E_{\mathrm{f}}[1 - C(1 - T)]} \tag{A3}$$

for Boron/epoxy systems, where the filament fracture strain is less than the matrix fracture strain. Referencing quantities to the wet uncoated condition, we have $(\psi\lambda d) = [(l_{\text{crit}})_{\text{uc}}]_{\text{wet}} = 95$ mm, $T = 1.35$, $\sigma_{\mathrm{f}} = 3.45\,\mathrm{GN\,m^{-2}}$, $E_{\mathrm{f}} = 380\,\mathrm{GN\,m^{-2}}$. Thus:

$$R_{\text{redist}} = \frac{(0.25)(3.45\times 10^{9})^{2}95\times 10^{-3}}{6\times 380\times 10^{9}(1+0.35C)}$$

$$= \frac{30.7}{1+0.35C}\ \text{kJ m}^{-2}$$

which for $C=0$, is $30.7\,\text{kJ m}^{-2}$ and for $C=1$ is $23\,\text{kJ m}^{-2}$.

Since the critical lengths of the filaments in their various wet intermittently bonded conditions are all greater than the specimen height, R_{redist} should be reduced below the foregoing values. Given that random filament fracture, on average, should occur at $\pm(l_{\text{crit}})/4$ above or below the main crack plane, it is clear that broken filaments have only $[38-(l_{\text{crit}})/4]$ mm and $[38+(l_{\text{crit}})/4]$ mm on which irreversible interfacial slip can take place. Given the fact that Piggot/FitzRandolph stress relaxation is predicated on irreversible slip over interfacial lengths $(l_{\text{crit}}/2)$ on either side of the filament fracture, it seems that one side of a broken filament can only produce a share $\{[38-(l_{\text{crit}})/4]/(l_{\text{crit}})/2\}$ towards $\frac{1}{2}R_{\text{redist}}$, and the other side $\{[38+(l_{\text{crit}})/4]/(l_{\text{crit}})/2\}$ towards $\frac{1}{2}R_{\text{redist}}$. Thus, the corrected R_{redist} is:

$$\left\{\frac{[38-(l_{\text{crit}})/4]}{(l_{\text{crit}})/2}\right\}\tfrac{1}{2}R_{\text{redist}} + \left\{\frac{[38+l_{\text{crit}})/4]}{(l_{\text{crit}})/2}\right\}\tfrac{1}{2}R_{\text{redist}} \qquad \text{(A4)}$$

for l_{crit} in mm. This becomes:

$$\{76/95\}(1+0.35C)R_{\text{redist}}$$

because (l_{crit}) at any C is $\{[(l_{\text{crit}})_{\text{uc}}]_{\text{wet}}/[1-C(1-T_{\text{wet}})]\}$. Now $R_{\text{redist}} \simeq \dfrac{30.7}{(1+0.35C)}\,\text{kJ m}^{-2}$, which gives, for the corrected result, the constant value of circa $25\,\text{kJ m}^{2}$, independent of C, for the particular size of specimens used.

$R_{\text{pull-out}}$

Pull-out toughness is given by [3]:

$$R_{\text{pull-out}} = v_{\text{f}}\tau'\lambda h\left(\frac{\psi}{(1-C(1-T))} + 2C\right) \qquad \text{(A5)}$$

where h is the crack opening displacement at the propagated crack length used in the Gurney segmental area method (say, 0.5 mm) [3, 9–14] and τ' is the interfacial frictional stress during pull-out (values of which have been given in Section 3, at various C). Thus, for the wet samples:

$$R_{\text{pull-out}} = (0.25)\tau'\left(\frac{25.4\times 10^{-3}}{140\times 10^{-6}}\right)0.5\times 10^{-3} \times \left[\frac{95\times 10^{-3}}{25.4\times 10^{-3}(1+0.35\,C)} + 2C\right]$$

$$= \tau'\left[\frac{8.5\times 10^{-5}}{(1+0.35C)} + 4.5\times 10^{-5}\,C\right]\ \text{kJ m}^{-2}.$$

For $C=0$, $\tau'=0.5\,\text{MN m}^{-2}$, so $R_{\text{pull-out}} = 42.5\,\text{kJ m}^{-2}$.

For $C=1$, $\tau'=2.75\,\text{MN m}^{-2}$, so $R_{\text{pull-out}} = (173+124) = 297\,\text{kJ m}^{-2}$, or, using $\tau'=2\,\text{MN m}^{-2}$ [3] for dry samples, $R_{\text{pull-out}} = (126+90) = 216\,\text{kJ m}^{-2}$.

Again, because the size of the specimens is comparable to, or less than, the critical lengths, and because the pull-out lengths with Cook/Gordon debonding are larger than the half-heights of the specimens, the full potential contribution to toughness from pull-out may not be achieved. In [3] it has been shown that:

$$R_{\text{pull-out}} \simeq 4v_{\text{f}}\tau' Dh/d. \qquad \text{(A6)}$$

where D, on average, was $l_{\text{crit}}/4$ in the absence of Cook/Gordon debonding, or was $(l_{\text{crit}}/4 + Cl_{\text{r}}/2)$ on average in its presence, where l_{r} is the repeat distance. Only when $D < 38$ mm (the half-heigh of the toughness specimen) would full pull-out be attained, otherwise it would be merely the frictional work over the finite 38 mm. For wet coated samples, $l_{\text{crit}} = 70$ mm, so $D = 70/4 + 25/2 = 30$ mm with $l_{\text{r}} = 25$ mm, or $D = 43$ mm with $l_{\text{r}} = 51$ mm.

Note that these calculations are based on averages, i.e. that some filaments break with zero pull-out (in the plane of gross fracture) and others break with the longest possible pull-out of $l_{\text{crit}}/2$ (all subsequently augmented by Cook/Gordon pull-out lengths). Therefore, the size of specimen does *not* allow the *longest* pull-out lengths ($70/2 + 25 = 60$ mm for $C=1$) to occur. This must skew the average distribution of pull-out lengths and reduce the potential toughness contribution. Assuming a Gaussian normal distribution between

0 mm pull-out lengths and 60 mm pull-out lengths for $C = 1$, the reduction is the (fractional) area under the distribution curve between zero pull-out and 38 mm pull-out in terms of the total area between zero and 60 mm pull-out. This is roughly 0.67, so that for $C = 1$, the effective pull-out contribution may be:

$$R_{\text{pull-out}} = (0.67)(216 \text{ or } 297) = \\ = 144 \text{ or } 198 \,\text{kJ m}^{-2}$$

where $216 \,\text{kJ m}^{-2}$ applies to dry samples and $297 \,\text{kJ m}^{-2}$ to water soaked samples.

R_{total}

Thus, for the total toughness of unidirectional wet composites we might expect, using the corrected values for $C = 1$, $R_{\text{total}} \simeq 2 + 25 + (144 \text{ or } 198) = 171 \text{ or } 225 \,\text{kJ m}^{-2}$.

For the total toughness of angle-ply composites, arguing that the two 45° layers give no pull-out contribution, we have for $C = 1$, $R_{\text{total}} \simeq 2 + 25 + (3/5)(144 \text{ or } 198) = 114 \text{ or } 147 \,\text{kJ m}^{-2}$.

Lines following these relations have been superimposed on Fig. 3a and b, and the agreement with experiment is not bad.

Again, reverting to the differences between unidirectional and angle-ply *dry* results (Section 4.5), it is likely that the pull-out value should have been corrected along the foregoing lines to recognize the fact that the specimen size was comparable to the critical length. That is, for $C = 1$, the unidirectional five-layer, $231 \,\text{kJ m}^{-2}$ pull-out work (see [3]) should be reduced to about $(0.67)(231) = 155 \,\text{kJ m}^{-2}$. Then it may be proportioned by the "active" three layers in five which display pull-out, the 45° plies breaking off with no pull-out contribution. Thus:

$$R_{\text{pull-out}} = (3/5)(155) = 93 \,\text{kJ m}^{-2}$$

which gives for the total toughness of the full-coated dry angle-ply composite (adding R_{surfaces}, R_{redist} and $R_{\text{pull-out}}$ from [3]:

$$R_{\text{total}} = 18 + 100 + 93 = 211 \,\text{kJ m}^{-2}$$

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References

1. T. U. MARSTON, A. G. ATKINS and D. K. FELBECK, *J. Mater. Sci.* **9** (1974) 447.
2. A. G. ATKINS, *Nature, Letters* **252** (1974) 116.
3. *Idem, J. Mater. Sci.* **10** (1975) 819.
4. J. COOK and J. E. GORDON, *Proc. Roy. Soc. (London)* **A282** (1964) 508.
5. P. W. R. BEAUMONT AND B. HARRIS, *J. Mater. Sci.* **7** (1972) 1265.
6. B. HARRIS, P. W. R. BEAUMONT and E. M. de FERRAN, *ibid* **6** (1971) 238.
7. H. T. SUMSION and D. P. WILLIAMS, in "Fatigue of Composite Materials", ASTM STP 569 (1975) pp. 226–247.
8. B. GERSHON and G. MAROM, *J. Mater. Sci.* **10** (1975) 1549.
9. C. GURNEY and J. HUNT, *Proc. Roy. Soc. (London)* **A299** (1967) 508.
10. C. GURNEY and Y. W. MAI, *Eng. Fract. Mech.* **4** (1972) 853.
11. C. GURNEY and K. M. NGAN, *Proc. Roy. Soc. (London)* **A325** (1971) 207.
12. C. GURNEY, Y. W. MAI and R. C. OWEN, *ibid* **A340** (1975) 213.
13. Y. W. MAI, *J. Adhesion* **7** (1975) 141.
14. Y. W. MAI, A. G. ATKINS and R. M. CADDELL, *Int. J. Fracture* **9** (1975) 939.
15. A. G. ATKINS, paper presented at AIAA/ASME/-SAE 16th Structures, Structural Dynamics, and Materials Conference, Denver, Colorado, 27–29 May, 1975. See also *Trans. AIAA (Journal of Aircraft)*, **12** (1976) 850.
16. M. R. PIGGOTT, *J. Mater. Sci.* **5** (1970) 669.
17. P. W. R. BEAUMONT, J. FITZRANDOLPH, D. C. PHILIPS and A. S. TETELMAN, *J. Com. Mater.* **5** (1971) 542. See also *J. Mater. Sci.* **7** (1972) 289.
18. A. KELLY, in "Strong Solids" (Oxford University Press, 1966).

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