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Fracture toughness of Kevlar–epoxy composites with controlled interfacial bonding

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The fracture toughness of Kevlar–epoxy resin composites with intermittent fibre bonding of a silicone vacuum fluid (SVF-200) and a polyurethane varnish (Estapol 7008) have been studied over the temperature range −60 to 40° C and strain rates 0.03 to 5000 min^{-1}. Whilst both coating materials give similar tensile strengths their effects on toughness are very different. As far as toughening is concerned Estapol 7008 is more effective than SVF-200. The toughening effect increases with increasing intermittent lengths of the Estapol-7008 coating, i.e. coating parameter C, increasing temperature and decreasing strain rate. At low strain rates and high temperatures, for $C = 1$, the toughness increase is some 200 to 300% compared to the uncoated composites. Some initial work has also been conducted for hygrothermally aged uncoated and coated fibre composites. The SVF-200 coated composites do not show any toughness degradation compared to the dry control samples. However, both the uncoated and Estapol-7008 coated composites suffer some toughness loss. Even so, the toughness of the fully coated aged specimens is as good as the uncoated dry controls. A fracture analysis is presented which gives reasonable agreement between predicted fracture toughness values and experimental measurements. It is shown that fibre pull-out toughness and fibre fracture work are the main contributors to the total fracture toughness of these fibre composites; their relative significance being dependent on the type of coating material, the temperature and strain rate of testing.

1. Introduction

Conventionally made, high strength and high modulus fibre composites are often disadvantaged by their low fracture toughness. To alleviate this problem several new methods have been recently developed in order to impart high toughness to these composites without introducing a significant loss of tensile and flexural strengths. These methods are summarized in Table I and they all rely on suitably modifying the mechanical properties of the interfaces between the fibre and matrix, e.g. methods 1 to 4, as well as between composite plies, e.g. methods 5 and 6. In Atkins' method [1, 2] the fibres are intermittently coated with an appropriate viscous fluid such as polyurethane varnish. The coated regions where the interfacial bonding is weak serve to blunt the propagating cracks by the Cook–Gordon debonding mechanism [3] and thereby increase the fibre pull-out length [2] so that the toughness can be greatly increased. The strong uncoated regions ensure that the full strength of the composite can be adequately developed. As shown in Table I the 80% coated unidirectionally boron–epoxy resin composites do not suffer any strength loss and there is a 400% improvement in fracture toughness. For the fully coated composites, although the toughness can be further increased to over 500% this is at the expense of a 25% loss of tensile strength. Based on the same idea,

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TABLE I Comparison of toughening methods for fibre composites

Toughening method	Composite system	% increase in toughness*	% decrease in strength*	Test method	Reference
1. Intermittent bonding	Boron–epoxy resin (100% polurethane coated fibres)	550	25	Compact tension and quasi-static crack propagation	[2]
	(80% polyurethane coated fibres)	400	nil	Compact tension and quasi-static crack propagation	[2]
2. Silicone rubber coatings	Carbon–epoxy (fibres fully coated)	110	nil	Izod impact	[4]
3. Rate sensitive viscous coatings	glass–polyester resin (fully coated fibres)	150	NA	Izod impact	[5]
4. Non-fracturing core/sheath elements	Brass sheets	Depends on crack length	NA	Double-cantilever-beam and quasi-static cracking	[7]
5. Delamination promotors	Carbon–epoxy resin (full nylon films intercalated between plies)	170	nil	Charpy impact	[9]
6. Intermittent interlaminar bonding	Boron–epoxy (Perforated Mylar films)	170	15	Compact tension and quasi-static cracking	[11]
	Carbon–epoxy resin (Perforated Mylar films)	250	25	Compact tension and quasi-static cracking	[10, 11]

*Comparison are made with control samples. NA = not available.

Hancox and Wells [4] are able to improve the toughness of their carbon–epoxy resin composites by some 100% with no sacrifice of flexural strength by fully coating the carbon fibres with approximately 1% silicone rubber. Further increase in coating fluid does not give any more rise in toughness but a significant drop in flexural strength. In these two methods a weaker bond strength is deliberately introduced at the fibre–matrix interface so that energy absorptions due to fracture mechanisms such as stress relaxation and fibre pull-out can be maximized [1, 2]. For fibre composites in which the main source of toughness is fibre pull-out it is not sufficient just to weaken the interfacial bond strength between fibre and matrix because this only increases the fibre pull-out length. It is also necessary to increase the friction between them so that after debonding and fibre fracture have occurred the frictional pull-out work can be enhanced. Sung *et al.* [5] are the first ones to investigate the use of strain rate sensitive coatings to improve the impact toughness of glass–polyester resin composites. The viscous shear work during fibre pull-out is maximized by a suitable selection of fluid viscosity and film thickness of the applied coating. They have shown in this way that the composite toughness can be improved by 150%. However, they have not determined the attendant reduction in strength which may prove to be a severe limitation for use with such composites. Another method of enhancing the pull-out toughness of composites is the so-called "duplex fibre" concept due to Morley and Millman [6]. The duplex fibre consists of core/sheath reinforcing elements. The sheath is to be strongly bonded to the matrix to provide good flexural and tensile strengths and the core element is frictionally bonded to the sheath and made to decouple progressively as the load it carries increases. The core element therefore never fractures and it bridges the crack faces as the matrix fails. In subsequent work on experimental sheet metal composite structures reinforced by an array of such sheath/core elements [6, 7] they have demonstrated that indeed the fracture propagation resistance is improved many times over the unreinforced metal. While this idea is attractive, in practice, it is difficult to see how such "duplex fibres" can be prepared and incorporated in a real composite material. Furthermore, the excessive pull-out length of the non-fracturing fibres is not usually allowed in practical engineering design and therefore the full toughness cannot be developed [8].

The energy absorption of a composite during fracture can also be increased by promoting interlaminar delamination or splitting such as by weakening the interlaminar bond strength. Modification of the fibre–matrix properties as discussed above does not lead to this form of toughness enhancement. Favre [9], Jea and Felbeck [10] as well as Mai *et al.* [11] have successfully increased the fracture toughness of graphite and boron–epoxy resin composites by inserting delamination promotors between the composite plies during fabrication (see also Table I). In Favre's work [9] the delamination promotors consists of full films of either metallic or organic materials; but in the work of Jea and Felbeck [10] and Mai *et al.* [11] both full and perforated plastic films are used. Experiments conducted so far seem to suggest that perforated films are preferred to full films [11]. This is because for the perforated inlays a weak interlaminar shear strength exists in regions of the film and a strong interlaminar shear strength, typical of regularly laid up composites, is developed in the perforated areas. In the weak regions interlaminar debonding takes place resulting in crack front bifurcation and subcrack propagation along the laminar interface; this greatly increases the fracture energy of the composite [10, 11]. In the strong regions delamination is discouraged and shear stress transfer is permitted; this enables the original interlaminar shear strength to be maintained. It may be noted that this "intermittent interlaminar bonding" concept has also been applied successfully to improve the toughness of cement mortars by using perforated papers as delamination promotors [12].

In summarizing the introduction it may be concluded that controlled interfacial bonding is an effective method to impart toughness to composites without any large loss of strength. As far as fibre–matrix interface control is concerned it seems from the experimental results given in Table I that the intermittent bonding concept is the most useful. It must, however, be cautioned that this comparison may not be strictly correct since the test methods are different. Impact tests give much higher strain rates than the quasi-static crack propagation experiments using either three-point notched bend or compact tension specimens [2, 11]. Since most fibre coating

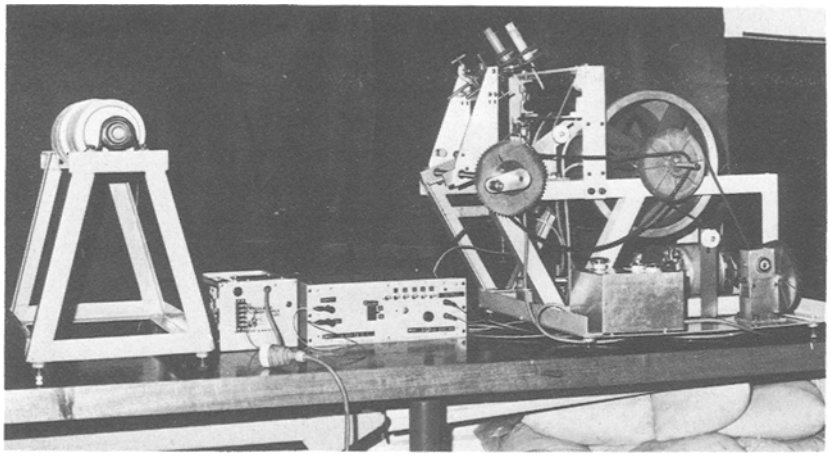

Figure 1 The composite tape making machine.

materials are temperature and strain-rate sensitive it is surprising that not many previous investigations have been devoted to the study of these effects on composite behaviour. In this work we have further investigated the usefulness of the intermittent bonding concept on Kevlar–epoxy resin composites. Two fibre coating materials, a silicone vacuum fluid (SVF-200) and a polyurethane varnish (Estapol-7008), were used. The effects of hygrothermal ageing, strain rate and temperature on the fracture toughness of these interface modified composites are reported.

2. Experimental work

2.1. Fabrication of composites

A composite tape making machine similar to that used by Atkins [2], Fig. 1, was constructed and employed to manufacture the Kevlar–epoxy resin tapes. The fibres were laid up on the periphery of the drum and the fibre volume fraction could be altered by varying the drum wrapping rate. The coating device consisted basically of a set of rubber rollers which could be opened and closed by an electronic control system. The coating fluid was gravity fed to the rollers through a set of hypodermic syringes mounted on a traversing carriage which moved the fibres across the width of the drum. The fibres became coated when the rollers were closed and uncoated when they opened. The coated/uncoated lengths could be varied by changing the frequency of operation.

In the present work the fibre used was Kevlar-49 obtained from E. I. du Pont de Nemours Company Inc. (USA) in the form of 380 denier yarns. Each strand contained approximately 267 individual continuous fibres with a fibre diameter of 11.7 μm. The matrix material was made from Shell (Australia) epoxy resin "Epikote 828" and curing agent "Epikure 113" in the ratio 100:33 by weight. For the intermittent bonding study here two principal coating materials, a silicone vacuum fluid and a polyurethane varnish, were used. The silicone vacuum fluid was supplied by Dow Corning (Australia) Ltd. and designated "SVF-200". It has a viscosity of 500 centistokes at 25° C. Initial work conducted by one of us [13] showed that it would not mix or chemically react with the epoxy resin and hardener during curing of the composite and remained fluidic at the fibre–matrix interface. The polyurethane varnish was originally prepared from mixing in stoichiometric proportions isocyanates with a polyester/polyether resin blend. This was found to be unsuitable as the resulting coating fluid became too viscous to be effectively applied to the fibres. It was decided then to use only the polyester/polyether resin, supplied by Wattyl Pty Ltd and designated "Estapol-7008", as the coating material. Unlike SVF-200 this coating material reacted to a certain degree chemically with the epoxy resin during curing [13, 14]. It was suggested that in the finished composites, the interface region between fibre and matrix could be considered chemically distinct and rubbery elastic in nature, with chemical covalent bonding to the epoxy resin and with only mechanical bonding to the fibre [13, 14].

A few other coating compounds were also used but they were found to be detrimental to the toughness of fully coated fibre composites. These included: (a) "Hypoy B90", a gear oil by Castrol

Pty Ltd, (b) "Swarfega", a lanolin based hand cleaner by Deb Chemical Pty Ltd, and (c) "Molykote 41", a graphite filled vacuum grease by Dow Corning (Australia) Ltd. No further work was conducted on composites having intermittent bonding using these coating compounds.

Kevlar–epoxy resin composite tapes with a fibre volume fraction (v_f) of approximately 5 to 6% were made in which the fibres were coated in varying proportions (C) over a repeated distance or length (l_r) of 30 mm. C can be defined as the ratio of coated length (l_c) to the repeat length (l_r), i.e. $C = l_c/l_r$. When $C = 0$, the fibres were uncoated and when $C = 1$ they were fully coated. Two other coating ratios, $C = 0.41$ and 0.63, were also studied for the SVF-200 and Estapol-7008 coating materials.

2.2. Test samples and test procedures

Both tensile and toughness specimens were prepared from stacking up layers of the composite tape and then cured in the vacuum oven for 3 h at 150° C and cooled down slowly to room temperature over several hours. Only unidirectional fibre composites were studied in this work. The dumb-bell shaped tensile specimens had 8 plies giving a nominal thickness of 2.25 mm, a test section width of 19 mm and length of 75 mm. Tests were conducted in an Instron testing machine with a crosshead rate of 5 mm min^{-1} and a controlled temperature of 20 ± 2° C. The strains were measured with an Instron extensometer over a gauge length of 25 mm. For the toughness specimens they were comprised of 16 layers of the composite tape with a nominal thickness of 4.50 mm, a beam depth (D) of 10 mm and a length (L) of 75 mm. Initially, notch depths (a) of varying ratios of the beam depth (D), 0.05 to 0.50, were made midway along the length of the specimen. It was later found that this was not necessary since the fracture toughness (R), was independent of a/D [13]. In all subsequent work all toughness specimens were made to have notch depths (a) approximately 2 to 3 mm. All impact tests were performed with a "Zwick" type 5102 model D-7900 Charpy impact tester for the temperature range −60 to 40° C. The specimens were supported 40 mm apart giving a beam depth to span (D/S) ratio of 4. The impact fracture energies absorbed were directly obtained from the calibrated scale of the machine. To investigate the effect of strain rate on the fracture toughness, three point bend tests were also conducted on these impact specimens at varying crosshead speeds ($\dot{\delta}$) of the Instron machine. $\dot{\delta}$ could be converted to equivalent strain rates ($\dot{e}$) as given in [13] i.e. $\dot{e} = 6(D-a)\dot{\delta}/S^2$. The fracture toughness was determined by dividing the work area under the load–displacement curve with the fractured ligament area. In addition some preliminary work on the impact toughness of hygrothermally aged specimens was also carried out in order to assess the usefulness of the intermittently and fully coated Kevlar–epoxy resin composites when subjected to such severe and adversed service conditions. Hygrothermal ageing was conducted by immersing the toughness specimens at 20 ± 2° C in water and measuring the water uptake with time. For the SVF-coated composites it was necessary to increase the ageing temperature to 100° C in a humidifier for a further 28 days, since after 14 days at the low temperature the water uptake was less than 1%. Saturation absorption was obtained by the Estapol-7008 coated composites after only 20 days at 20 ± 2° C [15]. These specimens were therefore not aged at the higher temperature in water.

3. Results

3.1. Tensile strength and elastic modulus

Figs. 2 and 3 show the tensile strength (σ_c) and elastic modulus (E_c) results for the Kevlar–epoxy resin composites. All test samples broke with a linear stress–strain curve up to failure. Each point represents a minimum of 5 separate results and the bars indicate one standard deviation from the mean value. Within experimental scatter, for both types of SVF-200 and Estapol-7008 coating materials, σ_c and E_c remain essentially constant with the same magnitudes as the uncoated composites for $C \leqslant 0.63$. For the fully coated composites, $C = 1.0$, there is an approximate 10 to 15% loss of strength and modulus but this is not considered as significant.

3.2. Effects of intermittent bonding and hygrothermal ageing on impact toughness

The impact fracture toughness (R) results at 20 ± 2° C are given in Fig. 4 for the SVF-200 coated composites and in Fig. 5 for the Estapol-7008 coated samples. Results for hygrothermally aged specimens are also shown in these figures. Again each point is obtained from at least 5 test

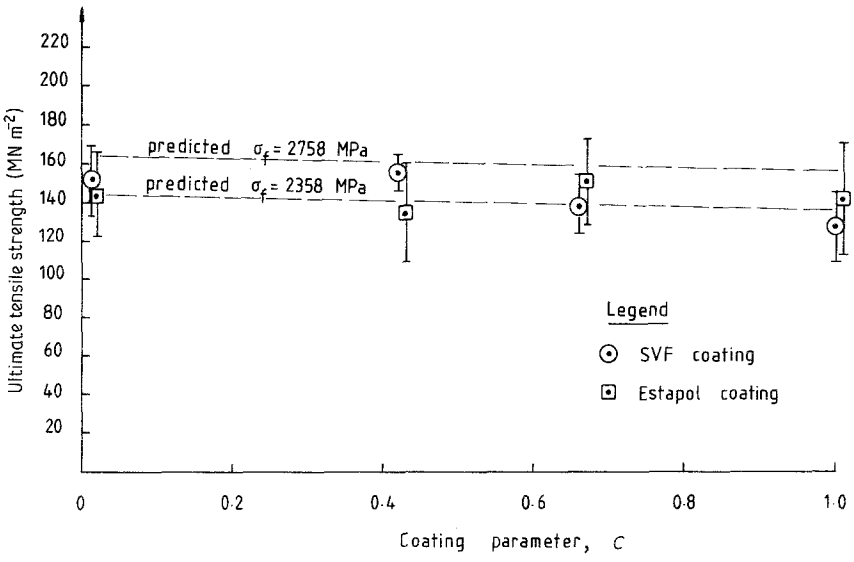

Figure 2 Variation of tensile strength (σ_c) with fibre coating parameter (C).

results and one standard deviation from the mean value is given. For the dry results, it it quite clear that the Estapol-7008 fully coated fibre composites only increases R by some 60% over the uncoated composites, Fig. 5. The increase is even less for the intermittently bonded composites with $C = 0.41$ and 0.63. Nevertheless, these results do indicate that a beneficial increase in composite toughness can be obtained with increasing intermittent lengths of Estapol-7008 coating with only small sacrifices in tensile strength and elastic modulus. It will be shown later in Section 3.3 that a much larger improvement in toughness can be achieved at lower strain rates and higher temperatures. As shown in Fig. 4, the other coating materials, including SVF-200, gear oil, "Swarfega" and "Molykote 41", all result in small decreases in R. These coating materials are therefore not useful for improving the toughness of Kevlar–epoxy resin composites. It is given in Section 4.2.2 the apparent different toughening effect produced by SVF-200 and Estapol-7008 coatings on this composite material is largely due to the different fibre pull-out lengths, Fig. 6, as measured from the fracture samples using a x 100 optical profilometer.

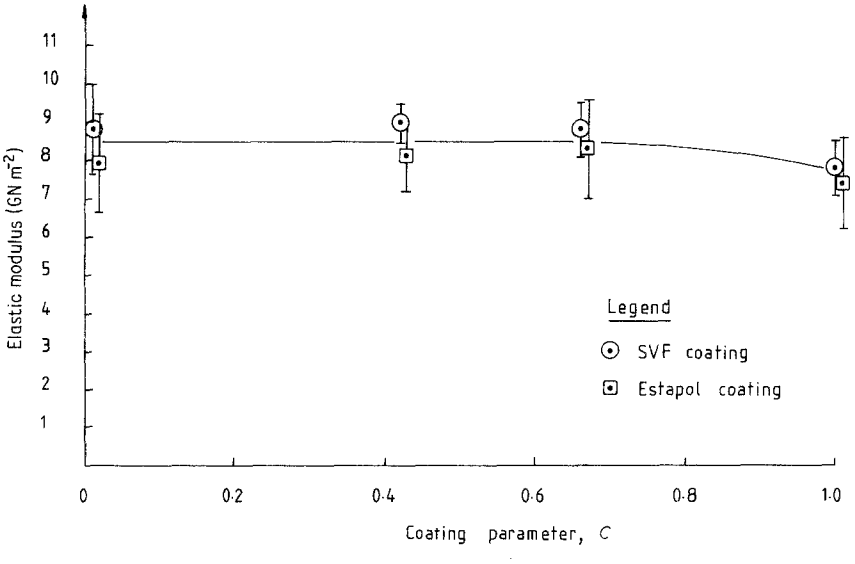

Figure 3 Variation of elastic modulus (E_c) with fibre coating parameter (C).

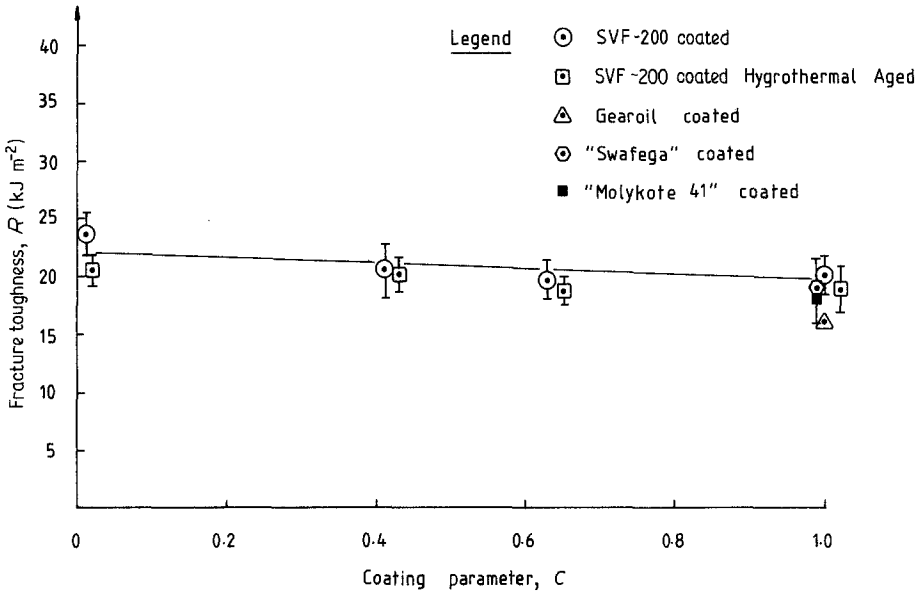

Figure 4 Variation of impact fracture toughness (R) with fibre coating parameter (C) for various coating fluids including the effect of hygrothermal ageing at 20 ± 2° C.

As can be seen from the results given in Fig. 4 there is no significant difference in impact fracture toughness values between uncoated, intermittently and fully coated SVF-200 specimens for the aged condition. When compared to the dry controls there is however a 13% decrease in toughness for the $C = 0$ specimens but no decrease is observed for the other $C = 0.41$, 0.63 and 1.0 specimens. A very different behaviour is displayed by the hygrothermally aged Estapol-7008 coated samples, Fig. 5. Here R is shown to increase with C for the aged condition and this implies that the beneficial toughening effect given by this coating material is retained. However, when compared to the dry controls for all C values water absorption has a considerable damaging effect on the impact

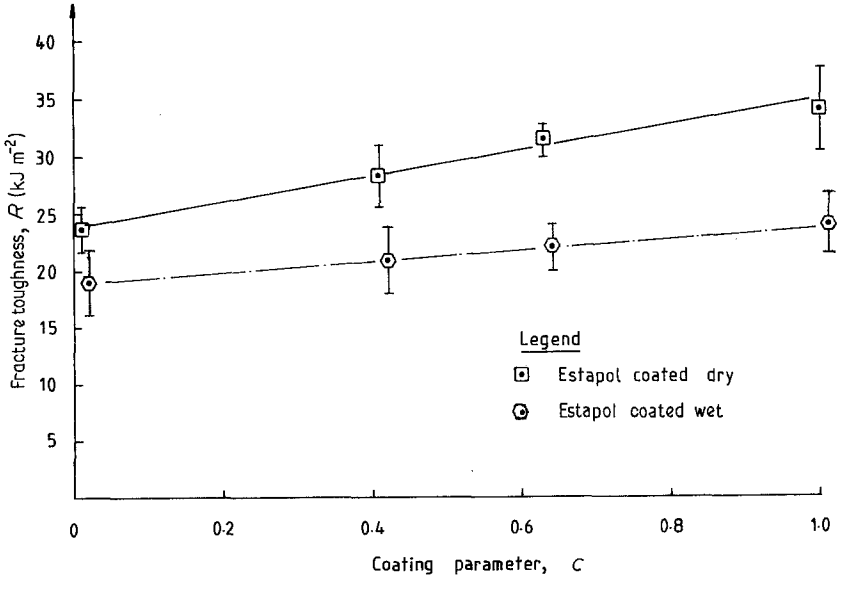

Figure 5 Variation of impact fracture toughness (R) with fibre coating parameter (C) for Estapol-7008 including the effect of hygrothermal ageing at 20 ± 2° C.

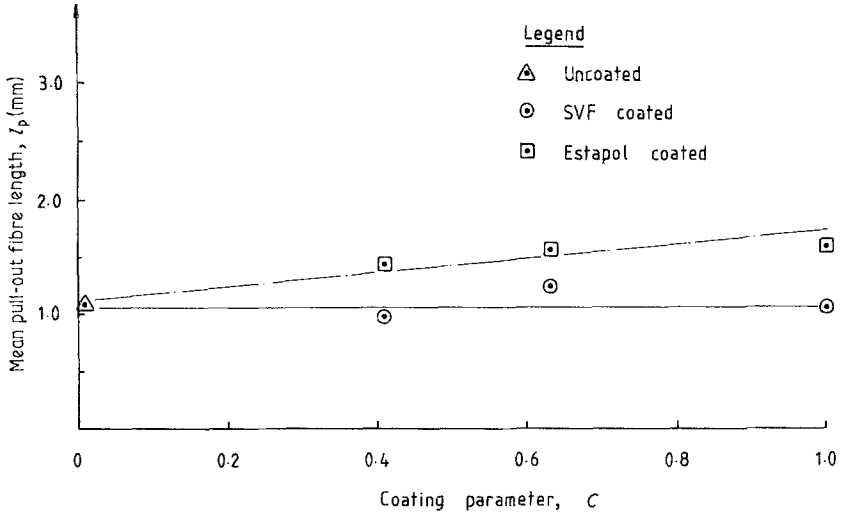

Figure 6 The average pull-out fibre length ($\bar{l}_p$) against coating parameter (C) for SVF-200 and Estapol-7008 coated composites after impact fracture at 20 ± 2° C.

toughness. Even so, the fully coated aged specimens have toughnesses as good as the unaged dry control samples. For the Estapol-7008 coated composites it was observed that after 20 days at 20 ± 2° C the water absorption was higher for larger C values. For example, the fully coated samples absorbed twice as much as the uncoated controls [15] and this was thought to be responsible for the relatively larger reduction in R. For the SVF-200 coated specimens water absorption was generally independent of C. Indeed for the fully coated samples the water uptake was only about 75% of the uncoated controls as shown in Fig. 7. These results indicate that SVF-200 has a much higher water repellancy than Estapol-7008.

3.3. Effects of strain rate and temperature on fracture toughness

Fig. 8 shows the fracture toughness variation with strain rate for uncoated and fully coated Kevlar–epoxy resin composites. The equivalent strain rate of the impact test is about 5000 min^{-1}. There is no difference in R between the uncoated and SVF-200 coated fibre composites for all strain rates. However, for the Estapol-7008 coated composite R rises quite significantly with decreasing strain rate. At $\dot{e} = 0.03\,min^{-1}$ R is some

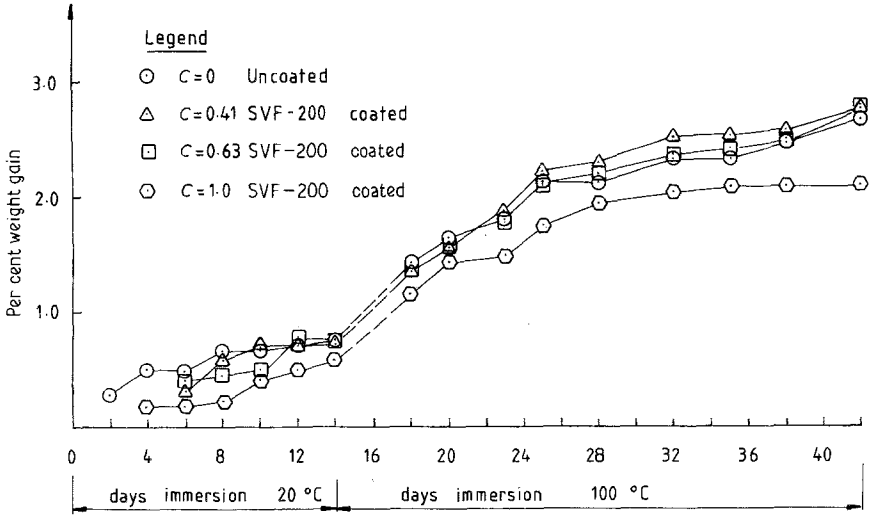

Figure 7 Water absorption isotherms for uncoated and SVF-200 coated fibre composites at 20° C and 100° C.

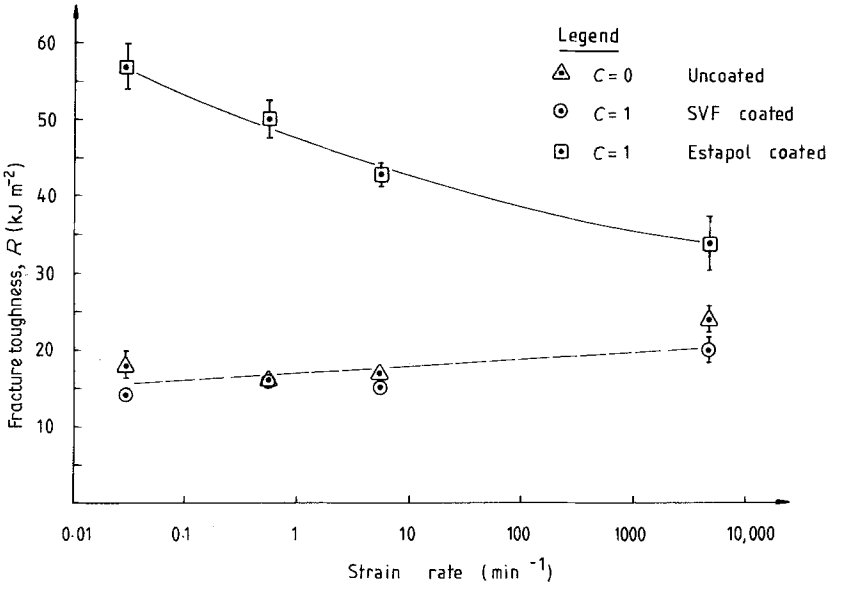

Figure 8 Variation of fracture toughness (R) with strain rate ($\dot{\epsilon}$) for Kevlar–epoxy resin composites at 20 ± 2° C.

57 kJ m^{-2} as opposed to the uncoated composite value of 14 kJ m^{-2}. This represents an over 300% increase in toughness and is much larger than the 60% improvement obtained at impact test conditions. Toughening effect is therefore strain rate dependent.

Temperature has also some significant effects on the impact toughness of these fibre composites. As shown in Figs. 9 and 10 the uncoated composite toughness increases steadily as temperature decreases; this is also true for the SVF-200 coated fibre composites whose toughess whilst temperature dependent is not C dependent, Fig. 10. Again a reverse trend is given by the composites with Estapol-7008 coatings, i.e. R increases with temperature for $C = 1.0$, but it remains more or less constant for other C values. Compared to the uncoated fibre composites there is a very small toughness improvement at $-60°$ C but an approximately 140% toughening at 40° C.

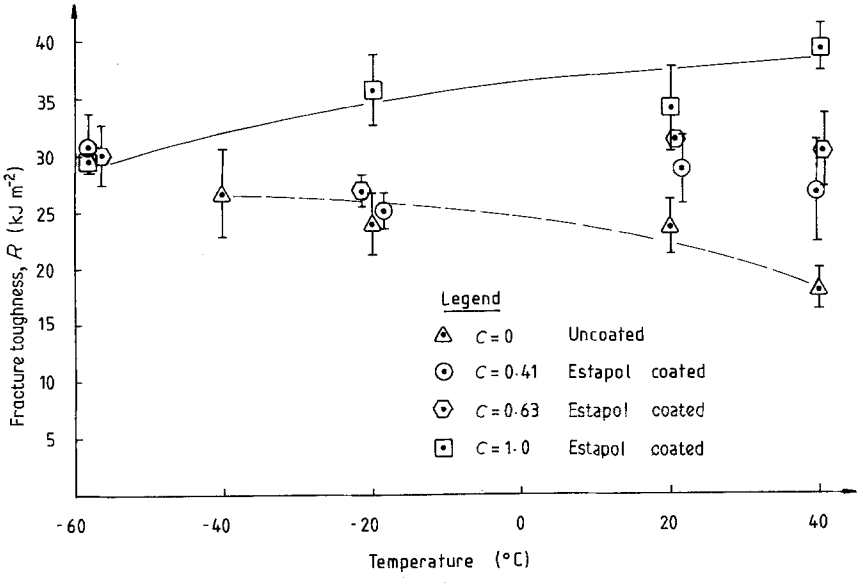

Figure 9 Variation of impact fracture toughness (R) with temperature for uncoated and Estapol-7008 coated fibre composites.

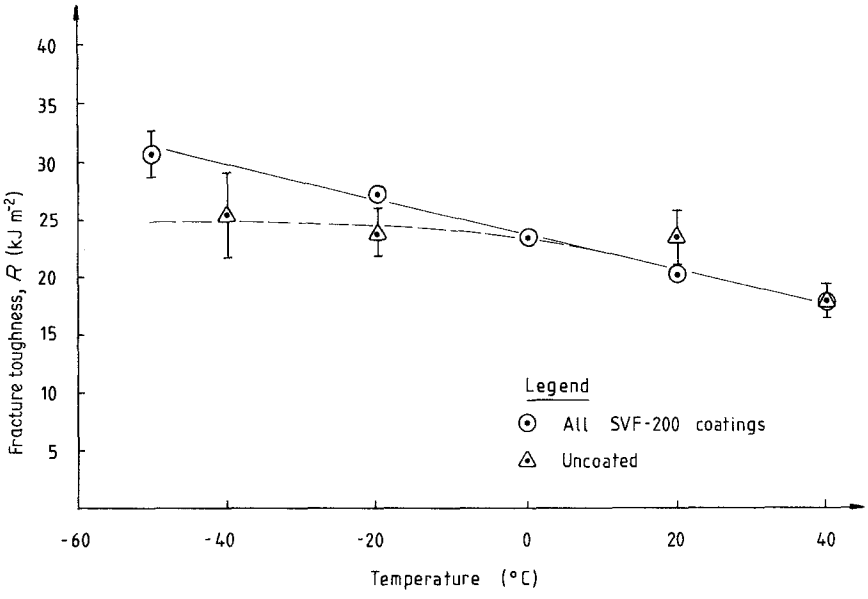

Figure 10 Variation of impact fracture toughness (R) with temperature for uncoated and SVF-200 coated fibre composite.

In order to explain these strain rate and temperature effects on toughness it is necessary to determine how the fibre pull-out lengths (l_p) and the interfacial shear strength (τ) and friction stress (τ^*) change with these two variables. In Figs. 11 and 12 the variations of $\bar{l}_p$ with strain rate and temperature are given and they are measured from the respective fracture samples from three-point bend tests. The trend of these data does correspond with the trend of the toughness results, i.e. longer fibre pull-out lengths give larger toughness. The fibre pull-out lengths for the SVF-200 and uncoated composites do not vary very much with $\dot{\epsilon}$ giving $\bar{l}_p \doteq 1.0$ mm.

Single filament pull-out tests were also conducted for uncoated and coated fibres embedded in the epoxy resin matrix. Details of these tests have already been given in [13]. For the present work these results are reproduced in Figs. 13 and 14. Strain rate ($\dot{\epsilon}$) is defined here as the fibre pull out rate ($\dot{u}$) divided by the fibre length embedded in the epoxy resin block. Note that in the three-point bend tests, where the cross-head rate of the Instron machine is $\dot{\delta}$, the fibres

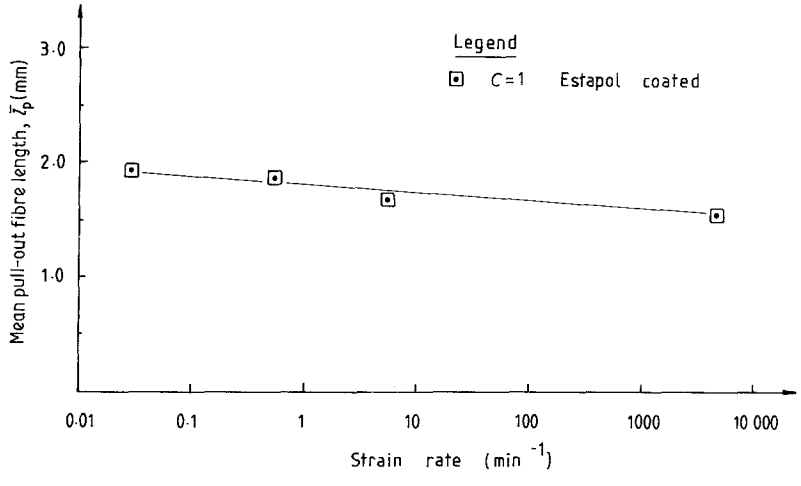

Figure 11 A plot of mean fibre pull-out length (l_p) against strain rate ($\dot{\epsilon}$) for fully Estapol-7008 coated composites after fracture at 20 ± 2° C.

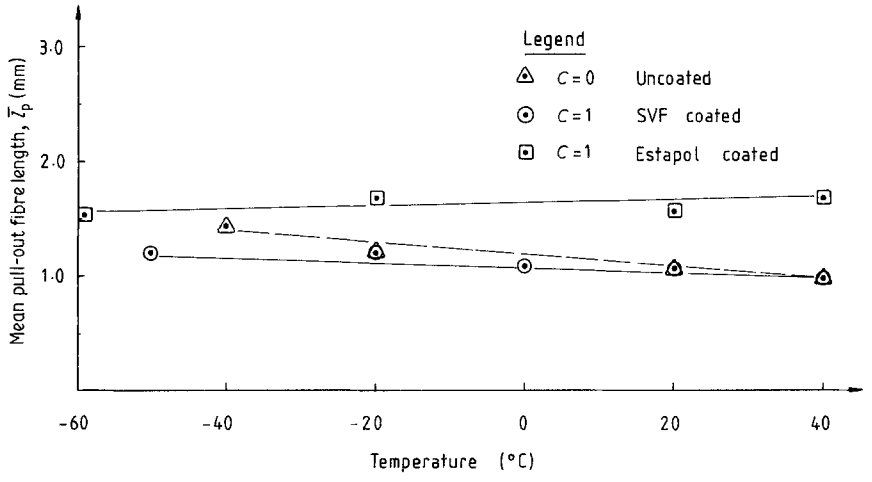

Figure 12 Plots of mean fibre pull-out lengths ($\bar{l}_p$) against temperature for uncoated and coated composites after impact fracture.

are being pulled out at an average rate ($\dot{u}$) approximately given by $\dot{\delta}/4$ from geometry considerations. It can be seen from these results for the Estapol-7008 coated fibres τ increases with $\dot{\epsilon}$ but decreases with temperature. The opposite trends are observed for τ^*. It may be noted that τ is rather low and this is indicative of the poor bonding between the coated Kevlar fibre and epoxy resin matrix. For the SVF-200 coated fibres only $\tau(= 2.10\,\text{MPa})$ for $\dot{\epsilon} = 0.17\,\text{min}^{-1}$ and $\tau^*(= 0.31$ MPa) for $\dot{u} = 0.5\,\text{mm min}^{-1}$ were measured at 20° C. Higher strain rate and fibre pull-out velocity tests were not conducted. But since $\bar{l}_p$ are approximately independent of $\dot{\epsilon}$ and $\dot{u}$ we have assumed in the following analysis that these interfacial stresses are constant. We will return to this point later. According to the theory given in [5] τ^* varies directly with the apparent viscosity for a given fibre pull-out velocity. From the manufacturer's temperature dependent viscosity data we have calculated τ^* at various other temperatures and they are given in Table II. Fibre pull-out tests were not successful for the uncoated fibre case since fibre breakage occurred before fibre pull-out. Only an upperbound $\tau(= 4.5\,\text{MPa})$ could be established. We have also estimated τ^*

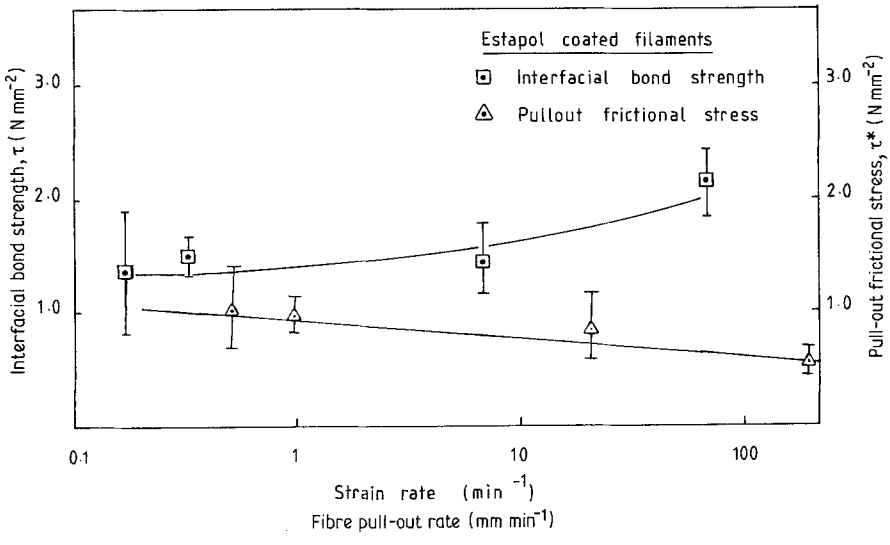

Figure 13 Variation of interfacial shear strength (τ) and friction stress (τ^*) with strain rate ($\dot{\epsilon}$) and fibre pull-out rate ($\dot{u}$) for Estapol-7008 coated ($C = 1$) composites at 20 ± 2° C.

TABLE II Comparison of predicted and experimental fracture toughness for fully coated composites as a function of strain rate ($\dot{\epsilon}$) and temperature (T)

Coating type	Strain rate $\dot{\epsilon}$ (min^{-1}) or temperature T(° C)	τ^* (MPa)	$R_{surfaces}$($kJ\,m^{-2}$)			R_{redist} ($kJ\,m^{-2}$)	$R_{pull\text{-}out}$ ($kJ\,m^{-2}$)	R(predicted) ($kJ\,m^{-2}$)	R(experimantal) ($kJ\,m^{-2}$)
			Filament	matrix	interface (mode I)				
SVF-200	0.03	0.31	4.0	0.5	12.3(1.8)*	2.8	3.5	23 (12.6)*	13.9 ± 0.9
	0.56	0.31	4.0	0.5	12.3 (1.8)	2.8	3.5	23 (12.6)	15.8 ± 1.7
	5.60	0.31	4.0	0.5	12.3 (1.8)	2.8	3.5	23 (12.6)	15.1 ± 0.6
	5000	0.31	4.0	0.5	12.3 (1.8)	2.8	3.5	23 (12.6)	20 ± 1.7
Estapol-7008	0.03	1.04	7.3	0.5	12.3 (3.3)	1.63	39.3	61.3 (52.3)	57 ± 3.8
	0.56	0.98	7.1	0.5	12.3 (3.1)	1.63	34.8	56.3 (47.1)	50 ± 3.2
	5.60	0.83	6.4	0.5	12.3 (2.8)	1.63	23.5	44.3 (35)	43 ± 1.7
	5000	0.50	6.1	0.5	12.3 (2.7)	1.63	13.1	33.5 (24)	34 ± 3.6
SVF-200	40	0.23	3.6	0.5	12.3 (1.6)	2.8	2.1	21.3 (11.5)	18 ± 1.2
	20	0.31	4.0	0.5	12.3 (1.8)	2.8	3.5	23 (12.6)	20 ± 1.7
	−20	0.56	4.9	0.5	12.3 (2.1)	2.8	9.3	29.8 (19.6)	25 ± 2.5
	−50	0.93	4.6	0.5	12.3 (2.1)	2.8	13.8	34 (24)	31 ± 2.4
Estapol-7008	40	0.50	6.4	0.5	12.3 (2.8)	1.63	14.2	35 (25.4)	39 ± 2.2
	20	0.50	6.1	0.5	12.3 (3.1)	1.63	13.1	33.5 (24.1)	34 ± 3.6
	−20	0.50	6.3	0.5	12.3 (2.6)	1.63	13.8	34.5 (22)	34 ± 3.8
	−60	0.50	5.8	0.5	12.3 (2.5)	1.63	11.7	32 (22.2)	30 ± 1.3

*Number in parenthese correspond to corrected $R_{Cook/Gordon}$.

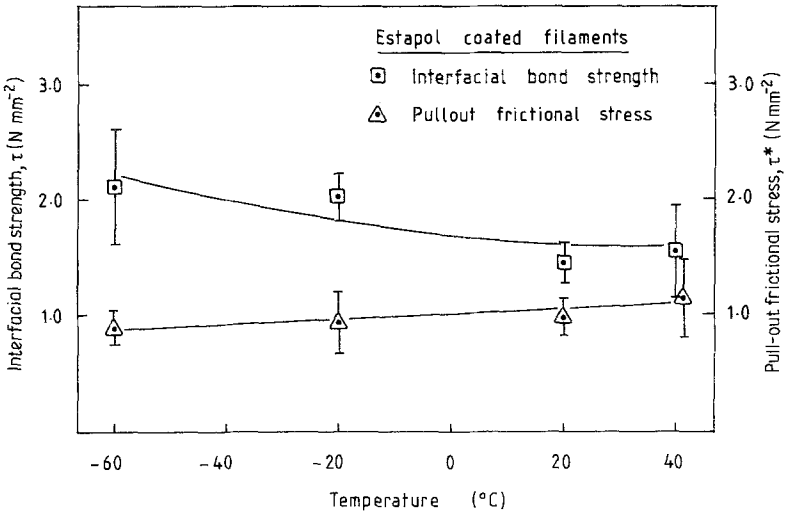

Figure 14 Variation of τ and τ^* with temperature for Estapol-7008 coated ($C = 1$) composites at $\dot{\epsilon} = 0.20\,\text{min}^{-1}$ and $\dot{u} = 0.5\,\text{mm min}^{-1}$.

to be approximately equal to 1 MPa. This is not an unreasonable magnitude for the friction stress of the uncoated fibre and as shown later it gives a good prediction for the total fracture toughness of the uncoated composites.

4. Analysis and discussion

4.1. Tensile results

Since the tensile strength and elastic modulus results for both SVF-200 and Estapol-7008 coated composites as shown in Figs. 2 and 3 are similar they are treated together in the following discussion. It was observed that both uncoated and coated tensile specimens failed at a strain of ~ 0.018 which was identical to the fracture strain obtained for the Kevlar strands [13]. This means that tensile fracture of the composite is controlled by fibre fracture. The composite tensile strength can be analysed according to Atkins [2] where:

$$\sigma_c = (1 - v_f)\sigma_m^* + v_f\sigma_f\left\{1 - \frac{\psi}{2n[1 - C(1 - T)]}\right\} \quad (1)$$

For uncoated ($C = 0$) and fully coated ($C = 1$) composites Equation 1 degenerates to the familiar expression given in [1], i.e.

$$\sigma_c = (1 - v_f)\sigma_m^* + v_f\sigma_f\left[1 - \frac{\sigma_f d}{4\tau L}\right] \quad (2)$$

where the interfacial shear bond strength $\tau = \tau_{uc}$ for $C = 0$ and $\tau = \tau_c$ for $C = 1.0$; the subscripts "uc" and "c" being for uncoated and coated fibres, respectively. The non-dimensional parameters n, ψ and T are defined as follows:–

$$\left.\begin{aligned} n &= L/l_r \\ T &= \tau_c/\tau_{uc} \\ \text{and} \\ \psi &= \frac{(l_{crit})_{uc}}{l_r} \end{aligned}\right\} \quad (3)$$

Here L is the finite length of the tensile specimen and l_{crit} is the critical transfer length for the fibre.

For the composites studied in this work we have $l_r = 30\,\text{mm}$, $L = 75\,\text{mm}$, $v_f = 0.048$, $\sigma_m^* = 36\,\text{MPa}$ (i.e. matrix tensile strength at approximately 1.8% strain), and $\sigma_f = 2358\,\text{MPa}$. The fibre tensile strength given by the manufacture is slightly larger at 2758 MPa corresponding to a fracture strain of about 2%. The interfacial shear strengths at the strain rate of the tensile experiments ($\dot{\epsilon} = 0.2\,\text{min}^{-1}$) were determined from filament pull-out tests. Thus, τ_c (Estapol-7008) = 1.35 MPa, τ_c(SVF-200) = 2.10 MPa and τ_{uc} = 4.5 MPa which in turn gives $(l_{crit})_{uc} = 3.0\,\text{mm}$. Equation 1 can now be used to predict σ_c for both coating materials and are shown in Fig. 2 for $\sigma_f = 2358\,\text{MPa}$ and 2758 MPa. The predicted results are relatively insensitive to varying C and T values, but they agree very well with experimental measurements.

The elastic modulus may also be predicted from

the rule of mixtures equation where:

$$E_c = v_f(E_f - E_m) + E_m \quad (4)$$

where $E_f = 131\,\text{GPa}$ for the Kevlar fibre and $E_m = 2.6\,\text{GPa}$ for the matrix. This gives $E_c = 8.7\,\text{GPa}$ for $v_f = 0.048$ and is independent of C. Compared to the average experimental value of about 8.3 GPa the agreement is considered excellent.

4.2. Fracture toughness results

4.2.1. Toughness analysis

A general analysis for the toughness of composites arising from various possible sources of fracture mechanisms has been given by Marston *et al.* [1] and Atkins and co-worker [2, 16]. The total toughness (R) is given by:–

$$R = R_{\text{surfaces}} + R_{\text{redist}} + R_{\text{pull-out}} \quad (5)$$

R_{surfaces} includes the fracture work involved in breaking the fibre and matrix as well as any mode II debonding work. For brittle fibre and brittle matrix their fracture energy absorptions are insignificant compared to the total R. However, for ductile fibres such as Kevlar, the fibre fracture work is quite important and this can be estimated as follows. Let σ_f and ϵ_f be the fracture stress and strain for the Kevlar fibre then the specific work done over an average debonded length equal to $4\bar{l}_p$, where $\bar{l}_p$ is the average pull-out length, is:–

$$R_f = 2\sigma_f\epsilon_f\bar{l}_p \quad (6)$$

From the work of Fuwa [17] as reported by Bunsell [18] only three-quarters of the total strain energy is converted into useful fibre fracture work so that Equation 6 has to be multiplied by this factor. Thus the contribution by fibre fracture to toughness is:

$$v_f R_f = 1.5\sigma_f\epsilon_f\bar{l}_p v_f = 3.82\bar{l}_p(\text{kJ m}^{-2}) \quad (7)$$

where $\sigma_f = 2358\,\text{MPa}$, $\epsilon_f = 0.018$, and $v_f = 0.06$ for the toughness specimens. In Kevlar–epoxy resin composites mode II debonding cannot occur because the fracture strain of the matrix is larger than that of the fibre [1]. If mode I debonding occurs due to the Cook–Gordon mechanism then an additional fracture energy term has to be included in R_{surfaces}. From [2] this is:

$$R_{\text{Cook/Gordon}} = 4v_f C^2\lambda\rho_I(R_i)_{uc} \quad (8)$$

where $\lambda = l_r/d$, $(R_i)_{uc}$ is the mode I interfacial toughness for the uncoated composite and ρ_I is the ratio of the coated to uncoated interfacial tensile stresses and consequently their mode I toughness. Atkins [2] gives two limiting values for ρ_I: One is 4×10^{-2} based on a tensile strength ratio of 1/5 according to Cook and Gordon [3] and the other is 4×10^{-4} based on a strength ratio of 1/50 considering the anistotropy of the composites [19]. In the analysis to follow we only consider the upper limit for ρ_I since the lower limit only makes the Cook–Gordon debonding toughness practically zero. There is also some doubt as to whether Equation 8 should be modified or not due to the measured fibre pull-out lengths much less than those predicted if Cook–Gordon debond has occurred. The question will be addressed again in Section 4.2.2.

The total fracture work due to creation of new surfaces now becomes:

$$R_{\text{surfaces}} = (1 - v_f)R_m + 3.82\bar{l}_p + 4v_f C^2\lambda R_m\rho_I \quad (9)$$

where $(R_i)_{uc}$ is assumed to be equal to the matrix toughness $R_m (= 0.5\,\text{kJ mol}^{-1})$. This is an upper bound assumption since microscopic examination of the Kevlar fibres at the fracture surface does not reveal any attached matrix material.

The toughness due to the Piggott/Fitz-Randolph stress redistribution [20, 21] is:

$$R_{\text{redist}} = \frac{1}{2}\left\{\frac{v_f\sigma_f^2\psi\lambda d}{3E_f[1 - C(1 - T)]}\right\} \quad (10)$$

The above equation represents only the contribution when the fibre breaks and retracts against the interface doing irreversible work; the "forward slip" term which is also given by Equation 10 is zero since the fibre fracture strain is less than the matrix failure strain. The Cottrell/Kelly [22, 23] pull-out toughness has been modified by Atkins [2] to take into account of the fact that "full" pull-out is not usually achieved. It is argued that the fibres are only pulled out a distance of the order of the crack opening displacement in most practical experiments. He has also provided $R_{\text{pull-out}}$ expressions when the pull-out length is augmented by the Cook/Gordon debonded length. It is, however, felt that the analysis is not relevant here. This is because complete fibre pull-out is involved in all the impact and three-point bend tests and also for the coated composites the average pull-out fibre length ($\bar{l}_p$) is much less than $[(l_{\text{crit}})_{av}/4 + Cl_r/2]$.

Following [2] a modified fibre pull-out toughness equation can be derived. This is given by:-

$$R_{\text{pull-out}} = \frac{2v_f\tau^*\bar{l}_p^2}{d} \qquad (11)$$

It may be assumed that τ^* varies according to $\tau^* = \tau^*_{uc}[1 - C(1 - T^*)]$ and $T^*(= \tau^*_c/\tau^*_{uc})$ is not necessarily equal to T.

The total toughness is thus given by the sum of Equations 9, 10 and 11.

4.2.2. Toughness predictions – effect of intermittent bonding

To predict the room temperature ($20 \pm 2^\circ$ C) impact toughness of the uncoated and coated fibre composites the following data were used for the calculations: $\bar{l}_p$ is measured from Fig. 6, $\sigma_f = 2358$ MPa, $v_f = 0.06$, $d = 11.7\,\mu$m; at the equivalent strain rate and fibre pull out rate of the impact tests, i.e. $\dot{\epsilon} = 5000\,\text{min}^{-1}$, $\dot{u} = 45\,\text{m min}^{-1}$, $\tau_{uc} = 4.5$ MPa, τ_c (SVF-200) = 2.1 MPa, τ_c(Estapol-7008) = 3.50 MPa, $\tau^*_{uc} = 1$ MPa, τ^*_c (SVF-200) = 0.31 MPa and τ^*_c (Estapol-7008) = 0.50 MPa. All interfacial bond strengths and frictional stresses for the Estapol-7008 coatings were obtained by extrapolation of single filament pull-out data shown in Fig. 13. Thus, we have T(SVF-200) = 0.46, T(Estapol-7008) = 0.78; T^*(SVF-200) = 0.31, T^*(Estapol-7008) = 0.50; $\lambda = 2564$ and $\psi = 0.1$. Table III shows the predicted and experimental impact toughness values. Since the tensile strength ratios between the interface and matrix are 1/6, 1/10 and 1/15, respectively, for the uncoated, Estapol-7008 and SVF-200 coated composites it is assumed here that mode I debonding does not take place in the uncoated samples but occurs in the coated specimens [3]. Implicit in the debonding toughness of Equation 8 is a debonded length Cl_r. However, the measured average pull out fibre lengths ($\bar{l}_p$) are always shorter than $Cl_r/4$ for all C values. Such discrepancies have also been observed by Atkins [2] but we cannot offer any explanations here. However, we may suggest that $R_{\text{Cook/Gordon}}$ in Equation 8 be modified by the factor $\bar{l}_p/l_r$. The corrected toughness values are given in Table III in parentheses for Cook–Gordon debonding and total fracture toughness. For $C \geqslant 0.63$, there is a lot of difference between the corrected and uncorrected mode I interface debonding term; this subsequently affects the total predicted R. From Table III, it can be seen that there is good agreement between predicted and experimental results for the composites with intermittent bonding if uncorrected mode I interface debonding work is used. There is only fair agreement if the predicted total R is based on the corrected $R_{\text{Cook/Gordon}}$ as shown in parentheses in Table III. However, for the SVF-200 coated fibres, the numbers given in the parentheses may have been underestimated because $\tau^* = 0.31$ MPa for $\dot{u} = 0.5\,\text{mm min}^{-1}$ is used in the impact fibre pull-out calculations. If $R_{\text{pull-out}}$ is increased due to higher impact τ^* the total R given in the parentheses may have given better agreement with experimental results. For the Estapol-7008 coated fibre composites, the pull-out toughness contribution is about 40 to 60% of the total R, the balance coming mainly from fibre fracture work and mode I interface debonding (if the uncorrected term is used). For the SVF-200 coated composites $R_{\text{pull-out}}$ and fibre fracture work are equally important contributors to the total toughness. It should however be noted that $R_{\text{pull-out}}$ for Estapol-7008 coated fibres are bigger than those for SVF-200 coated fibres (see Table III). This is because of their longer fibre pull-out lengths $\bar{l}_p$ as shown in Fig. 6 and their somewhat higher τ^* value (0.50 MPa as opposed to 0.31 MPa). The pull-out fibre lengths for SVF-200 coated and uncoated composites are identical, Fig. 6, but since τ^* is less than the uncoated fibre value (i.e. 1 MPa) $R_{\text{pull-out}}$ for SVF-200 coated composites are even less than uncoated composites (Table III). It is therefore not surprising that the SVF-200 coated composites studied here have impact toughness values less than the uncoated controls (if the loss in fibre pull-out work is not made up by the gain in the mode I interfacial debonding work). Although it is possible to increase τ^* for SVF-200 coated fibres by having a suitable combination of viscosity and film thickness so that $R_{\text{pull-out}}$ can be maximized [5] this has not been pursued in the present investigation. It may be noted that the amount of coatings put on the Kevlar fibres is about 10^{-3} g cm^{-1} of yarn. For the SVF-200 coating material this amount may be too much for its application to be effective [5].

There is not enough information to allow a toughness analysis to be conducted for the hygrothermally aged composites as is done previously in [16]. However, based on the results given in Figs. 4 and 5 it is logical to suggest that water has no effect on the interfacial frictional stress

TABLE III Comparison of predicted and experiment impact toughness

Coating fluid	Coating parameters (C)	$R_{surfaces}$ (kJ m^{-2})			R_{redist} (kJ m^{-2})	$R_{pull\text{-}out}$ (kJ m^{-2})	R(Predicted) (kJ m^{-2})	R(experimental) (kJ m^{-2})
		Fibre	Matrix	Interface (mode I)				
Uncoated	0	4.2	0.5	nil	1.3	12.2	18.2	23.7 ± 1.8
SVF-200	0.41	3.7	0.5	2.1 (0.8)*	1.6	7.0	15.3 (14.0)*	20.6 ± 2.5
	0.63	4.7	0.5	4.9 (1.3)	1.9	8.5	20.5 (16.8)	19.5 ± 1.8
	1.00	4.0	0.5	12.3 (1.8)	2.8	3.4	23.0 (12.6)	20 ± 1.7
Estapol-7008	0.41	5.4	0.5	2.1 (1)	1.4	16	25.4 (24.2)	26.1 ± 2.4
	0.63	5.9	0.5	4.9 (1.6)	1.5	17	29.8 (26.5)	31.4 ± 1.2
	1.0	6.1	0.5	12.3 (2.6)	1.6	13	33.5 (24)	34 ± 3.6

*Numbers in parentheses correspond to corrected $R_{Cook/Gordon}$.

for the SVF-200 coated fibre composites but has a more damaging effect on τ^* of the Estapol-7008 coated fibres.

4.2.3. Toughness predictions – effects of strain rate and temperature

In using Equations 9 and 10 to estimate R_{surfaces} and R_{redist} we have assumed that T, R_m, σ_f and ϵ_f are constant for the range of temperatures and strain rates studied and $\bar{l}_p$ are given in Figs. 11 and 12. To evaluate $R_{\text{pull-out}}$ from Equation 11 we need to know τ^*. For Estapol-7008 coated fibres, τ^* as a function of fibre pull out rate ($\dot{u}$) are given in Fig. 13. The variation of τ^* with temperature shown in Fig. 14 is not relevant here as these data were obtained for $\dot{u} = 0.5\,\text{mm}\,\text{min}^{-1}$. We need to have τ^* at impact conditions. As given in Section 4.2.2, τ^* is 0.5 MPa and is assumed to be independent of temperature here. Judging from the trend of the τ^* data in Fig. 14 this temperature independence assumption is not unreasonable. The dependence of τ^* (SVF-200) on fibre pull out rate and temperature have already been discussed in Section 3.3.

The predicted fracture toughness values for the fully coated ($C = 1.0$) composites are compared with the experimental measurements in Table II. Very good agreement is obtained for the Estapol-7008 coated composites for both strain rate and temperature effects if the uncorrected mode I interface debonding work term is considered. This is consistent with the analysis given in Section 4.2.2. Again, if the corrected $R_{\text{Cook/Gordon}}$ expression is used for the predicted R (shown in parentheses in Table II), there is only fair agreement with experimental R measurements. For the SVF-200 coated fibre composites the temperature effects are well predicted if the uncorrected $R_{\text{Cook/Gordon}}$ is used. Agreement with experimental toughness results for strain rate effects is however poor. Not only is there the uncertainty of whether the corrected or uncorrected $R_{\text{Cook/Gordon}}$ should be used but there is also the additional problem of whether τ^* is independent of $\dot{u}$. Although $\bar{l}_p$ is independent of $\dot{\epsilon}$ as obtained from experiments, the theory for strain rate sensitive coatings [5] predicts that τ^* should increase with $\dot{\epsilon}$ or alternatively $\dot{u}$. We believe that the corrected mode I interface work term and higher τ^* for larger $\dot{\epsilon}$ should be used in the total R calculations and that this will give better agreement with experimental R values.

It can be seen from Table II, for the Estapol-7008 coated fibre composites for both temperature and strain rate effects, the fibre pull-out toughness component contributes more than half of the total toughness, with the remaining half coming from mode I fibre–matrix interface debonding, fibre fracture and stress redistribution work. At low strain rates $R_{\text{pull-out}}$ is the single most important contribution to R. For SVF-200 coated composites, fibre pull-out work is about the same as fibre fracture work except at low temperatures where $R_{\text{pull-out}}$ again becomes the dominant source of toughness.

For all strain rates and temperatures investigated here the Estapol-7008 coating is superior to the SVF-200 coating with respect to enhancing the toughness of Kevlar–epoxy resin composites. However, close examination of Table II shows that at temperatures lower than -60° C the SVF-200 coated composites will have R values larger than the Estapol-7008 coated samples. This was confirmed by a few tests at -120° C where the impact toughnesses were respectively $40\,\text{kJ}\,\text{m}^{-2}$ and $25\,\text{kJ}\,\text{m}^{-2}$ for the two coating materials [13].

5. Conclusions

The fracture toughness of Kevlar–epoxy resin composites with intermittent bonding of SVF-200 and Estapol-7008 coating materials have been studied over a range of temperatures (-60 to 40° C) and strain rates (0.03 to $5000\,\text{min}^{-1}$). Estapol-7008 was found to be more effective than SVF-200 in enhancing the toughness of the composites. This toughening effect is shown to be a function of both temperature and strain rate. At low strain rates and high temperatures the increase can be as much as 300%. It is therefore reasonable to conclude that provided the appropriate coating fluid is selected, in this case Estapol-7008 as opposed to SVF-200, the intermittent fibre bonding concept to improve the toughness without introducing a significant drop of tensile strength can be successfully applied to Kevlar–epoxy resin composites. Maximum toughening effect is obtained for $C = 1.0$. Hygrothermal ageing has no effect on the impact toughness of the SVF-200 coated fibre composites but degrades considerably those for the Estapol-7008 coated samples when compared to the dry controls.

An analysis of the fracture mechanisms shows that the fibre fracture work and fibre pull-out

toughness are important contributors to the total fracture toughness of these intermittent bonded composites. Although there is some uncertainty about the magnitude of the mode I fibre–matrix interface debonding toughness, predicted fracture toughness values are in reasonable agreement with experimental measurements.

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