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Thermal degradation of the mode I interlaminar fracture properties of stitched glass fibre/vinyl ester composites

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Changes to the Mode I interlaminar fracture toughness, G_{Ic}, and fracture mechanisms of stitched and unstitched fibreglass/vinyl ester composites were investigated after exposure to elevated temperatures. The fibreglass was stitched through the thickness with Kevlar®-49 thread in two orientations with two stitch densities, and then resin transfer moulded with a cold-curing vinyl ester resin. After curing at room temperature ($\sim$20 °C) for several weeks, the composites were heated to between 100 and 300 °C for 1 h or at 175 °C for times ranging from 0.25–100 h. The G_{Ic} values, which were measured using the double cantilever beam method, of stitched composites in the cold-cured condition were between 1.5 and 2.3 times higher than the unstitched composite. It was observed with scanning electron microscopy that this toughening occurred by deflection of the crack tip at the stitches, by the ability of the stitches to remain intact for a short distance (7–15 mm) behind the crack front, and by partial pull-out of broken stitches. The interlaminar fracture toughness of the unstitched composite increased slightly following heating, despite a possible breakdown of the chemical structure of the vinyl ester between 150 and 300 °C. In contrast, the interlaminar toughness of the stitched composites was degraded significantly by heating, and this was probably caused by thermal deterioration of the Kevlar® stitches. This study reveals that the elevated-temperature post-curing of stitched composites will reduce the effectiveness of Kevlar® stitching in raising the Mode I interlaminar fracture toughness.

1. Introduction

Fibreglass composites are used in a wide variety of lightweight marine vessels, such as racing yachts, fast passenger ferries, coastal patrol boats, fishing trawlers, naval ships and small submersibles. Most marine composites are fabricated from E-glass and cold-curing polyester, epoxy, phenolic or vinyl ester resins. Polyesters are presently the most popular thermosetting resin because of their lower cost, although vinyl ester resins are often used in high-performance vessels because of their superior resistance to water ingress and chemical attack, better retention of strength and stiffness at elevated temperatures (up to 100–150 °C), and higher fracture toughness and elongation to failure [1]. Regnier and Mortaigne [2] suggest that the only obstacle impeding the wide-spread use of fibreglass/vinyl ester composites in ships is their poor fire properties. The high temperature generated by ship fires can ignite vinyl ester within a short time, and as the composite burns a large amount of smoke, toxic fumes and heat is released. As a result, over-heating and fire can severely reduce the in-plane mechanical properties and interlaminar fracture toughness properties. This deterioration of the interlaminar toughness of glass fibre-reinforced polymer (GFRP) composites is of concern to boat manufacturers and operators because, in their pristine condition, these materials already possess low Mode I interlaminar fracture toughness ($G_{Ic} = 0.2$–$1.2\ kJ\ m^{-2}$), and any further reduction caused by over-heating is likely to make the vessel even more susceptible to delamination cracking.

One novel approach to improving the interlaminar fracture toughness properties of fibre-reinforced

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polymer (FRP) composites, including GFRP, is by through-the-thickness stitching [3, 4]. This involves sewing a fabric preform or prepreg tape with a high strength thread, usually made from polyester, carbon, glass or Kevlar®, to provide reinforcement in the through-thickness direction. Studies of interlaminar fracture toughness have shown that the delamination resistance of stitched composites under Mode I [5–11] and, in some cases, Mode II [11–13] loading are much higher than the unstitched laminate.

While the Mode I interlaminar fracture toughness of stitched FRP composites has been extensively studied, the ability of stitching to retain high toughness after thermal degradation of the resin matrix has not been investigated. If stitching is capable of providing adequate toughness after GFRP has been degraded by over-heating or fire, then the use of vinyl esters in marine composites may be increased. Therefore, the aim of this work was to examine the influence of over-heating on the Mode I interlaminar fracture toughness and delamination crack growth mechanisms of a fibreglass/vinyl ester composite stitched with Kevlar®. The composites were initially cold-cured for several weeks, and then heated between 100 and 300 °C for 1 h or exposed to 175 °C for 0.25–100 h to study the effects of temperature and exposure time on interlaminar toughness, respectively.

2. Experimental procedure

2.1. Materials

GFRP composites were made from E-glass and a cold-curing vinyl ester resin, known commercially as Derakane® 411-45 which is produced by the Dow Chemical Company. The composites contained two types of fibreglass: a plain woven glass (with an areal density of 0.6 kg m^{-2}) and a chopped strand mat (0.3 kg m^{-2}). These glasses were layered in an alternating sequence to a total of 14 plies, and this layup sequence is commonly used for composite yachts and boats. The woven glass is used to provide in-plane strength and stiffness while the chopped fibreglass contributes to interlaminar fracture toughness by promoting fibre bridging between the plies.

The fibreglass preforms had dimensions of 0.5 m length, 0.3 m width and ~6 mm thickness, and were stitched with Kevlar®-49 yarn using a Toyota straight sewing machine. The Kevlar® was a 40 tex (i.e. 2 × 20 tex) spun thread with a diameter of 0.16 mm. Jain [11] reported the tensile strength of this thread to vary from 2.57–2.92 GPa, depending on the loading rate and fibre gauge length used in the tensile tests. The sewing was performed in straight parallel rows along the length or across the width of the preforms. The stitches were spaced 5 mm apart along these rows using a modified lock stitch (Fig. 1). The distance between the rows was set at 6 or 3 mm to produce a low (3 stitches per cm^2) or high (6 stitches per cm^2) stitch density, respectively. Around the edges of each preform, a 70 μm thick Teflon film was inserted between the middle plies to a distance of 50 mm, and this was used to initiate a delamination in the interlaminar fracture toughness specimens.

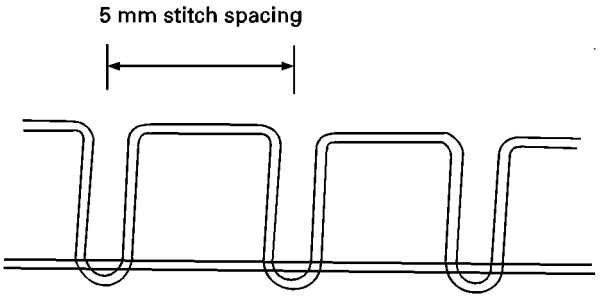

Figure 1 A diagram showing the sewing pattern along a row of modified lock stitches.

Stitched and unstitched preforms were then impregnated with the vinyl ester resin to a content of about 40% by weight using vacuum-assisted resin transfer moulding (RTM). The stitching and RTM was performed by the Cooperative Research Centre for Advanced Composite Structures Ltd (CRC-ACS). The resin contained about 1% methyl ethyl ketone peroxide (MEKP), 0.02% cobalt octoate and 0.05% 2,4-pentanedione. After RTM, the composite panels were cold-cured under ambient conditions within the mould for 24 h. The panels were then cut into rectangular coupons for fracture toughness testing, as illustrated in Fig. 2 for the stitched composites. The specimens were cured at room temperature (~20 °C) for several weeks, and after this time differential scanning calorimetry revealed that the cure polymerization reaction was about 85% complete.

Following the cold-curing process, the composites were post-cured between 100 and 300 °C for 1 h to examine the effect of temperature on interlaminar fracture toughness. The number of specimens exposed for 1 h at each temperature is shown in Table I. The influence of heat exposure time on interlaminar toughness was studied for the unstitched GFRP and the GFRP stitched in the parallel direction to a low density. Two specimens of each material were exposed to 175 °C for 0.25, 0.5, 1, 2, 10, 50 or 100 h.

2.2. Interlaminar fracture toughness testing

The G_{Ic} values were measured using the double cantilever beam (DCB) method in accordance with ASTM D5528-94a specifications [14]. An Instron testing machine (Model 4502) was used to apply load at a crosshead speed of 2 mm min^{-1} to end blocks attached to the DCB specimens. The interlaminar crack was grown for a distance of 4–6 mm from the edge of the Teflon insert, at which point the load, P, and crosshead displacement, δ, were recorded and the crack length, a, was measured using a travelling optical microscope. The load was then reduced before being reapplied to extend the crack for a further 4–6 mm. This incremental crack growth process was repeated 12 times over a single DCB test, and this produced a total crack extension, Σa, of 50–70 mm. The interlaminar fracture toughness was calculated using the modified beam equation derived

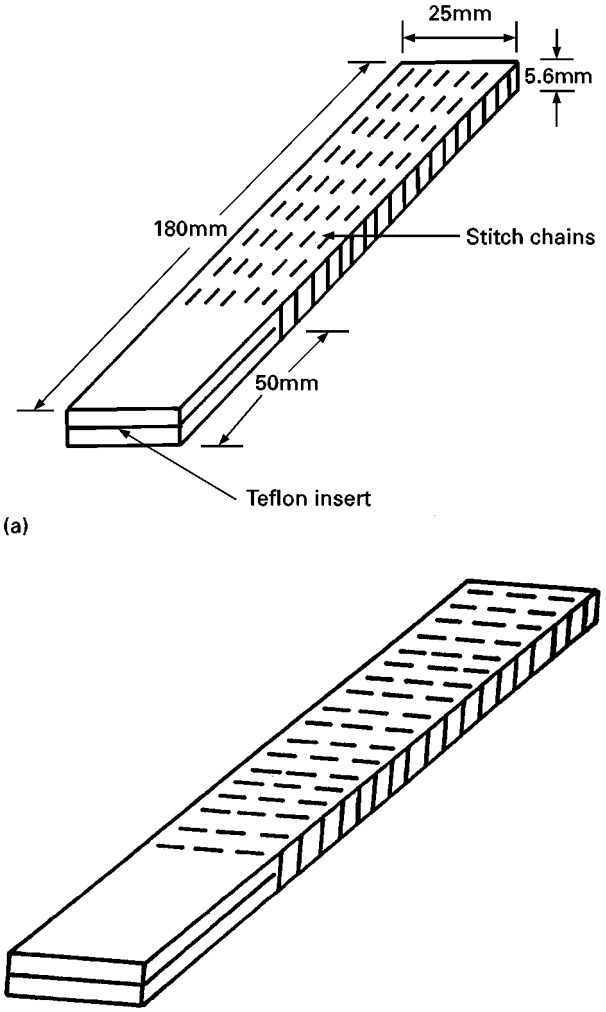

Figure 2 Diagrams showing the DCB specimens stitched in the (a) parallel and (b) normal directions.

TABLE I Number of DCB-specimens exposed to various temperatures for 1 h

Composite	Number of specimens				
	20 °C[a]	100 °C	175 °C	220 °C	300 °C
Unstitched GFRP	5	3	3	3	3
GFRP stitched in parallel direction to low density	5	3	3	3	3
GFRP stitched in normal direction to low density	5	3	3	3	3
GFRP stitched in parallel direction to high density	5	3	3	3	3
GFRP stitched in normal direction to high density	5	2	–	2	–

[a] These specimens were cold-cured at room temperature (~20 °C) for several weeks, and were not heat treated.

by Hashemi *et al.* [15]

$$G_{Ic} = \frac{3P\delta}{2b(a + \chi h)}\left(\frac{F}{N}\right) \quad (1)$$

where b is the crack width, h is the half-thickness of the specimen, F is a correction factor to account for shortening of the crack length due to large displacements, N is a factor to correct for the stiffening effects of the end blocks, and the term χh adjusts the measured crack length for compliance in the uncracked part of the DCB specimen. Expressions for calculating the values of F, N and χ are found in Hashemi *et al.* [15].

3. Results

3.1. Mode I interlaminar fracture toughness properties

A comparison of a typical delamination crack growth resistance, R, curve for the unstitched GFRP against R-curves for composites stitched in the (a) parallel and (b) normal directions, is presented in Fig. 3. In this example, the specimens were exposed to 100 °C for 1 h, and the parameter "crack length, Δa" is the distance the delamination has grown from the tip of the Teflon insert. The R-curve for the unstitched laminate is relatively smooth, indicating that stable interlaminar crack growth occurred over the course of the DCB test. In contrast, the G_I values of the stitched composites show slightly more scatter. During the tests it was observed that crack growth was often impeded by the stitches, but when these broke on further loading the delamination propagated rapidly to the next row of stitches and the process then repeated itself.

Fig. 4 shows examples of the effect of temperature on the R-curve behaviour for unstitched and stitched composites. In Fig. 4b the GFRP was stitched in the parallel direction to a high density, and both composites were held at each temperature for 1 h. It is important to note, however, that the data for 20 °C presented in this and other figures in the paper are for specimens cold-cured for several weeks at room temperature without subsequent heating prior to toughness testing. The R-curves for the unstitched laminate were reasonably similar for the various temperatures with the possible exception of 300 °C when most of the G_I values are slightly higher. There is, however, considerable scatter in the data. With the stitched composite, on the other hand, the magnitude of the R-curves decreased with increasing temperature.

The effect of temperature on interlaminar fracture toughness is revealed more clearly in Fig. 5, where G_{Ic} values are shown for the unstitched laminate and composites stitched in the (a) parallel and (b) normal directions. In a DCB test, twelve G_I measurements were taken, but only the last nine were used to calculate the G_{Ic} value. It was observed in the tests that the bridging zone in the wake of the interlaminar crack front was not fully formed in the stitched specimens within the first three measurements (which covered a total extension, Δa, of less than 25 mm or the equivalent of 4–8 stitch rows), and therefore these three G_I values were ignored when determining G_{Ic}. Fig. 5 shows the unstitched laminate experienced a slight increase in interlaminar toughness with increasing temperature, revealing that heating actually promoted a small improvement in delamination resistance. In

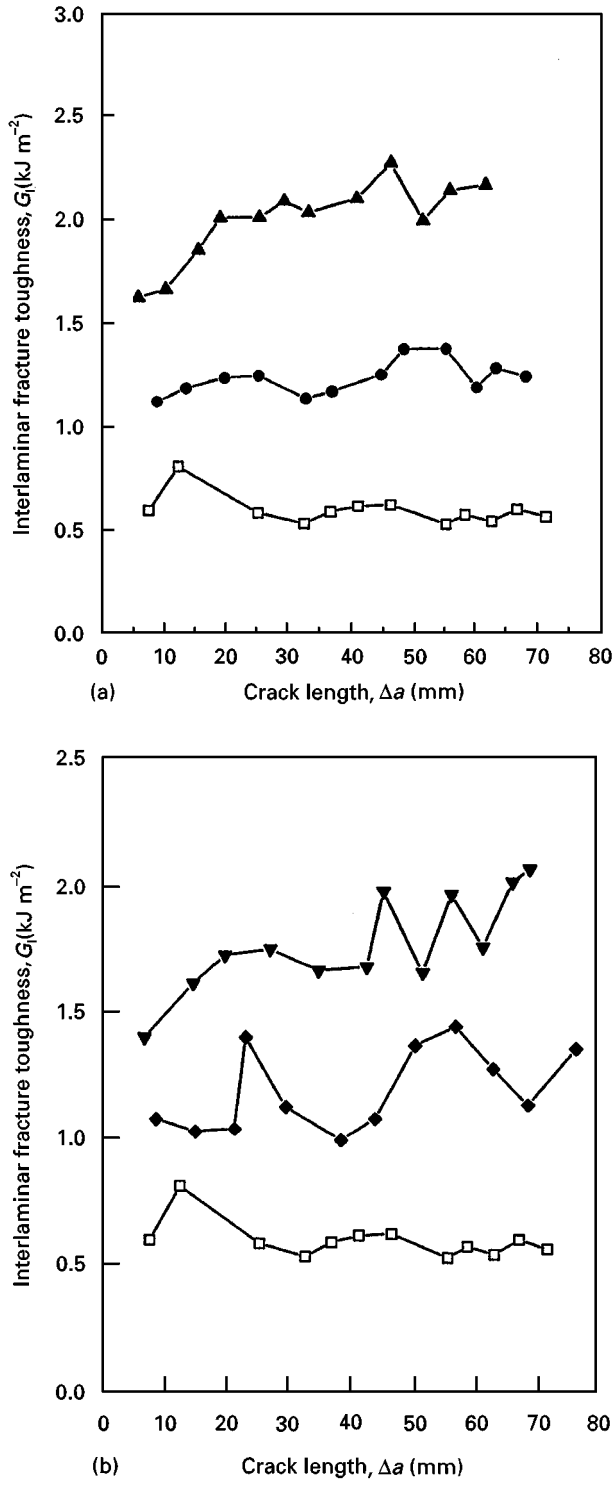

Figure 3 Examples of *R*-curves for the (a) (□) unstitched GFRP and the composites stitched in the parallel direction with (●) low and (▲) high stitch densities, and (b) (□) unstitched GFRP and the composites stitched in the normal direction with (◆) low and (▼) high stitch densities. These materials were exposed to 100 °C for 1 h prior to DCB testing.

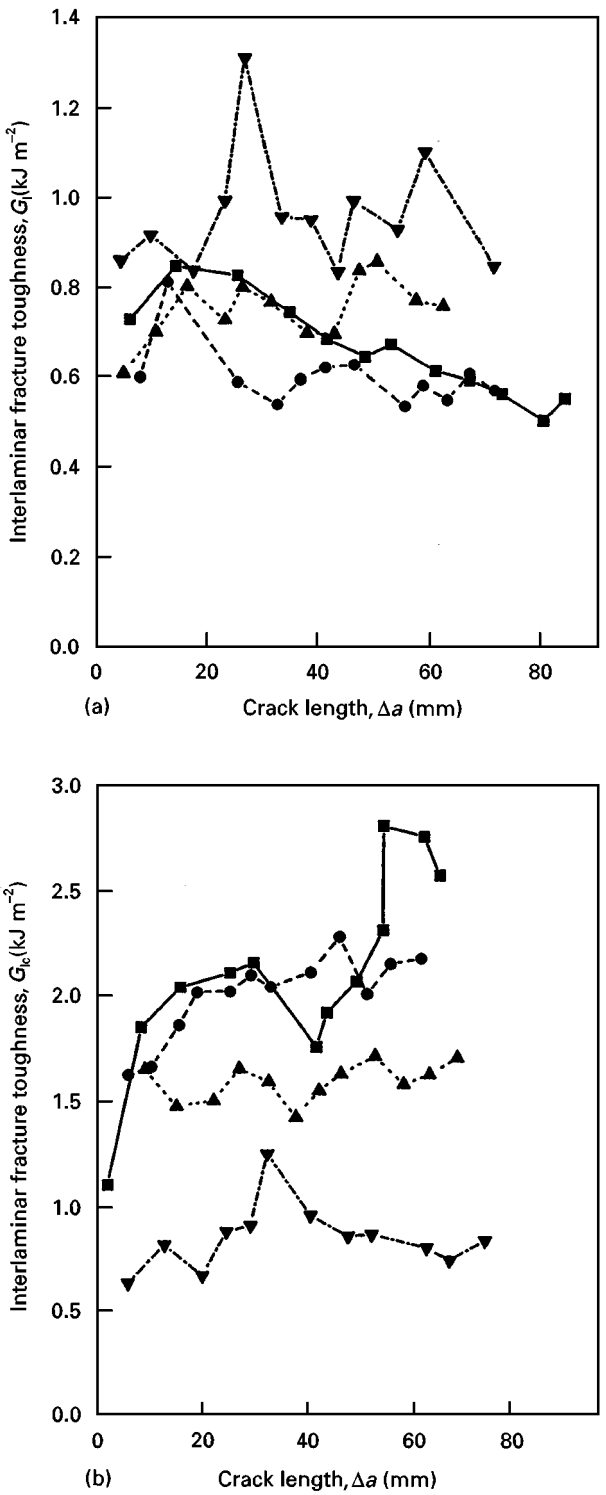

Figure 4 Examples of *R*-curves for the (a) unstitched GFRP and (b) composite stitched in the parallel direction with a high stitch density, after cold-curing at (■) 20 °C for several weeks, and after heating to (●) 100, (▲) 175 and (▼) 300 °C for 1 h.

comparison, the toughness of the stitched composites fell rapidly after exposure to higher temperatures, and by ~250–300 °C their fracture resistance was similar to or slightly lower than the unstitched laminate. It is interesting to note that below 220 °C the deterioration in toughness of composites stitched in the normal direction was not as severe as for those specimens stitched in the parallel direction. The reason for this anomaly is not clear, and further work is continuing.

The effect of heating at 175 °C for increasing times on interlaminar fracture toughness is shown in Fig. 6. The toughness of the unstitched laminate was not affected appreciably by increasing the heat exposure time while the stitched composite experienced a small, but statistically significant, reduction after heating for 100 h.

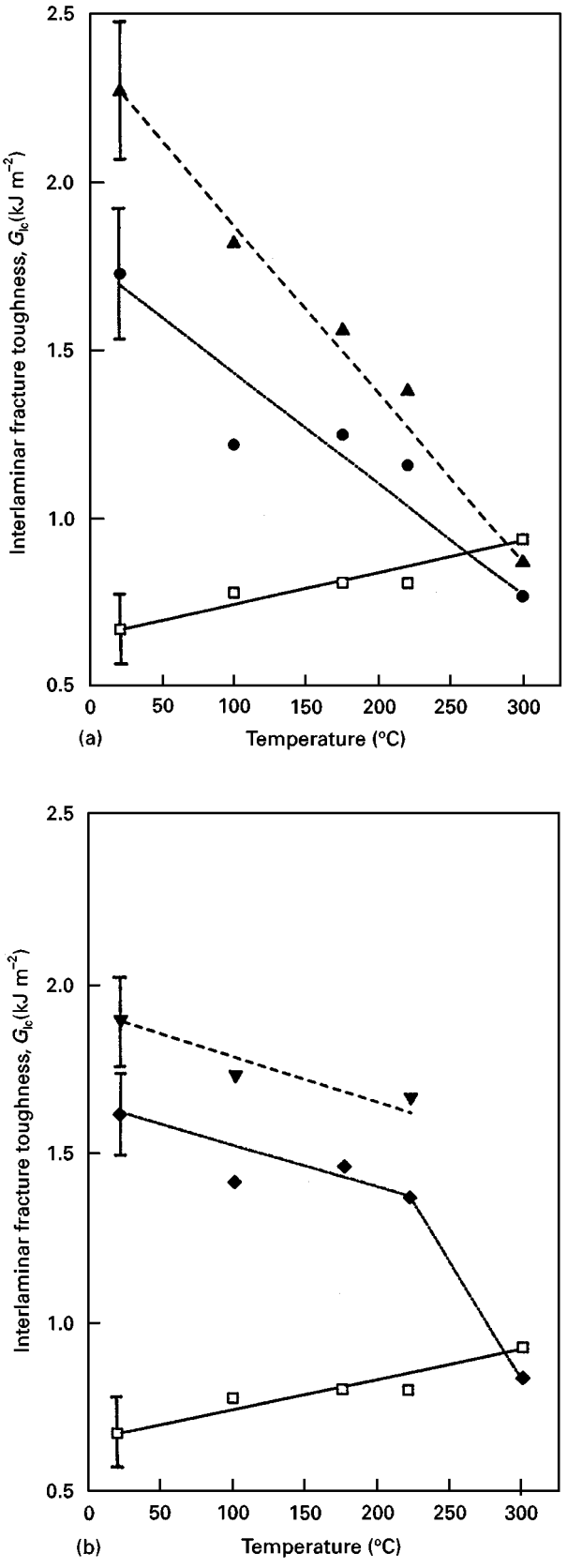

Figure 5 Plots of temperature against interlaminar fracture toughness, G_{Ic}, for the (□) unstitched GFRP and the (●, ◆) low stitch density and (▲, ▼) high stitch density composites stitched in the (a) parallel, and (b) normal direction. The specimens were heated for 1 h except for the 20 °C condition. The error bars represent the standard deviation calculated from 45 G_I measurements taken from five DCB tests.

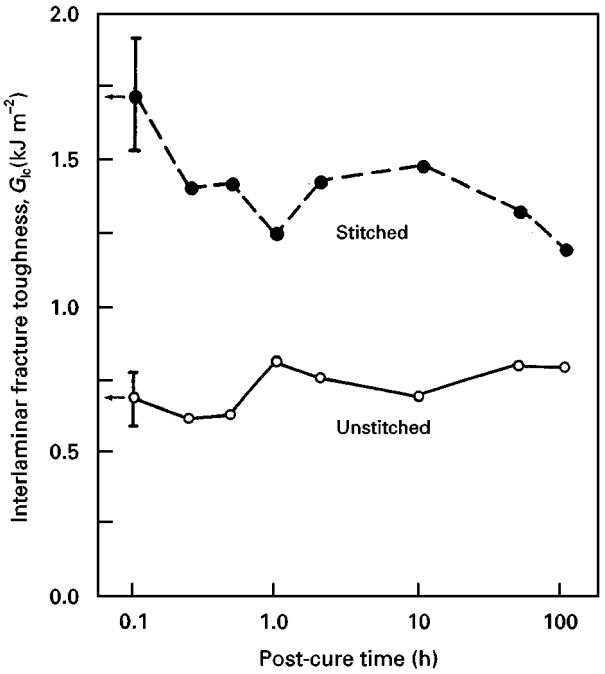

Figure 6 Plot of post-curing time against interlaminar fracture toughness, G_{Ic}, for the unstitched GFRP and the composite stitched in the parallel direction with a low density. These materials were heated at 175 °C. The data points with arrows represent the G_{Ic} values of the composites cold-cured at 20 °C for several weeks.

3.2. Mode I interlaminar fracture toughening mechanisms

The delamination crack growth mechanisms were studied through an SEM examination of the fracture surfaces on DCB specimens (Fig. 7). Fig. 7(a) shows glass fibres at a typical region on the fracture surface of a specimen cold-cured at 20 °C for several weeks without further heating. It is obvious that fibres remain partly coated with the vinyl ester resin, indicating reasonably good adhesion of the resin to the glass. Fig. 7 also shows fracture surfaces to composites exposed to elevated temperatures for 1 h. The amount of resin adhering to the fibres in these composites was reduced considerably, and by 220 °C (Fig. 7c) to 300 °C (Fig. 7d) virtually no resin remained on the glass.

Another feature on the fracture surfaces were broken Kevlar® stitches, as shown in Fig. 8. Broken filaments from the same stitches were found on opposing fracture surfaces, which suggests that the stitches did not fail at a single location but rather the individual Kevlar® fibres broke at different locations along the stitch and were then pulled out under a larger crack opening displacement.

The DCB specimens were examined by SEM in cross-section to study in detail the interactions between the delamination crack front and stitches, as well as to identify the failure mode of stitches. Fig. 9 presents a series of micrographs showing the different fracture processes observed in the stitched composites at increasing distances behind the crack front. The same fracture mechanisms were observed for all the stitched composites except when heated to 300 °C.

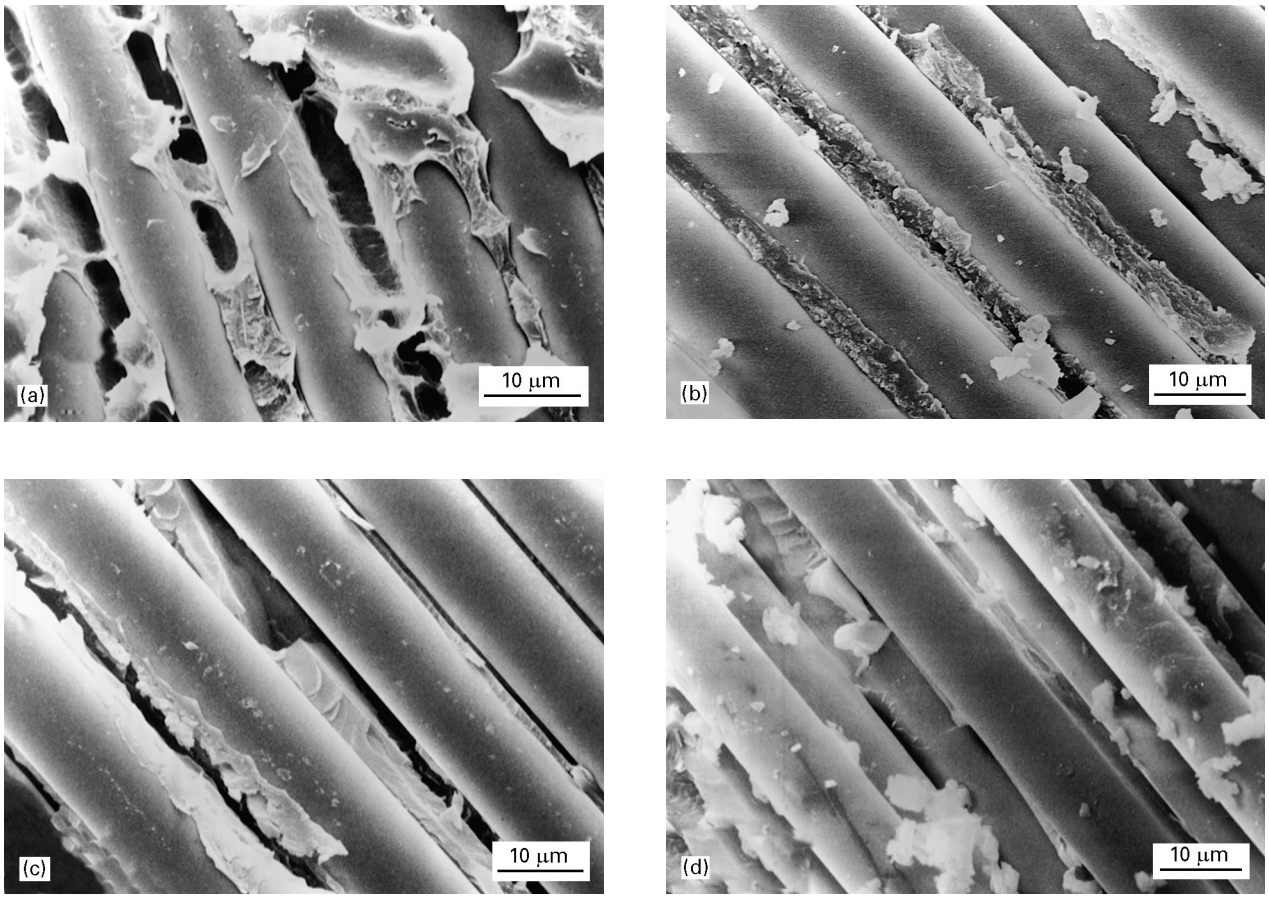

Figure 7 Scanning electron micrographs of DCB fracture surfaces from the GFRP composite (a) cold-cured at 20 °C for several weeks and after exposure to (b) 175 °C, (c) 220 °C and (d) 300 °C for 1 h.

Figure 8 Filaments from a broken Kevlar® thread protruding from a DCB fracture surface. (This photograph was taken with the surface inclined by 80°.)

A stitched composite during DCB testing is shown in Fig. 9a, with the position of the crack front together with the locations of the stitches presented in Fig. 9b–f being indicated. For those composites exposed to temperatures below 300 °C, a single delamination grew along the mid-plane of the DCB specimen. When the crack reached a stitch it was momentarily arrested (Fig. 9b) before being deflected by 90° along the interface between the stitch and surrounding GFRP for about 1 mm (Fig. 9c). These deflections have not been observed previously in stitched composites, and it is one toughening process by which the stitches impede crack growth. Under increasing load, the delamination eventually grows around the stitch and then continues along the mid-plane of the DCB specimen (Fig. 9d). Fig. 9b–d show that stitches close to the crack tip were not damaged, and in composites stitched to the low and high densities the stitch bridging zone extended for 5–7 mm and 10–15 mm, respectively. Beyond this region, Kevlar® filaments began to break at different locations along the stitch but within 0.5–1.0 mm of the fracture surface (Fig. 9e). Under a higher crack opening displacement the stitch then breaks (Fig. 9f).

When exposed to 300 °C for 1 h the fracture mechanisms of both the stitched and unstitched composites were different to those observed at lower temperatures. Multiple delaminations developed through the thickness of the specimens as shown in Fig. 10, rather than a single crack along the mid-plane. In most of these specimens, between four and six delaminations were created, and as a result identification of the exact position of the crack front proved difficult. Fig. 11 shows that, in the stitched composites, the threads were usually damaged at several locations before complete failure occurred.

4. Discussion

The recent interest shown in stitching has been due mainly to its ability to improve the delamination

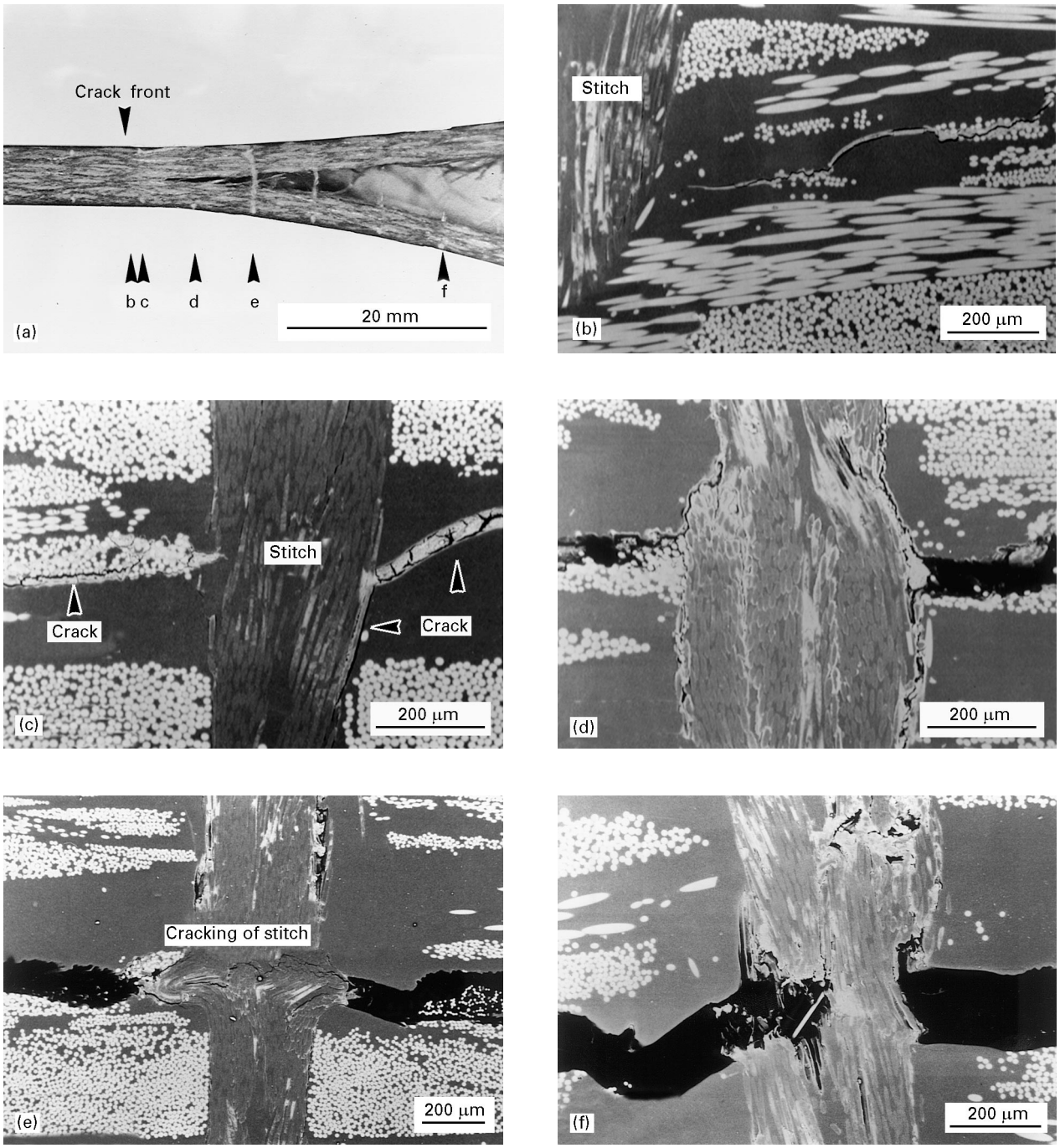

Figure 9 Photographs showing gradual failure of the stitches at increasing distances behind the crack front. (a) DCB specimen showing the position of the crack front and threads shown in (b–f). The threads were located at (b) the crack front and (c) 2.5 mm, (d) 5 mm, (e) 10 mm and (f) 25 mm behind the crack tip. The direction of crack growth is to the left.

resistance of FRP composites. For example, an interlaminar fracture study of carbon fibre-reinforced polymer (CFRP) laminates by Jain [11] found that stitching with Kevlar® or carbon thread caused the G_{Ic} value to increase by a factor of 1.6–15.7, depending on the density and type of stitch. In the light of studies such as this it is not surprising to find that the interlaminar fracture toughness of the fibreglass/vinyl ester composite was improved by stitching, particularly when cold-cured at room temperature for several weeks. In this condition, stitching increased the G_{Ic} value by a factor of between 2.5 and 3.4. Previous stitching studies [6–11] attribute the large improvement in interlaminar fracture toughness to the ability of the stitches to carry some of the load, although micromechanical modelling studies by Jain and Mai [7] have also considered the small contribution to toughening which can occur by the pull-out of stitches. The examination of the fibreglass/vinyl ester DCB specimens showed that an important toughening mechanism was the ability of the stitches to remain intact behind the crack front, and this observation is in agreement with other Mode I fracture studies on stitched composites. However, this study did find that only a relatively small number of stitches contributed to the toughening at any one time. The unbroken

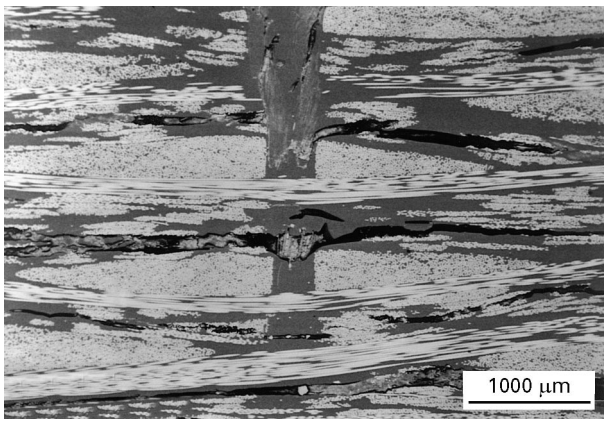

Figure 10 Multiple delamination cracking in a stitched composite heated at 300 °C for 1 h.

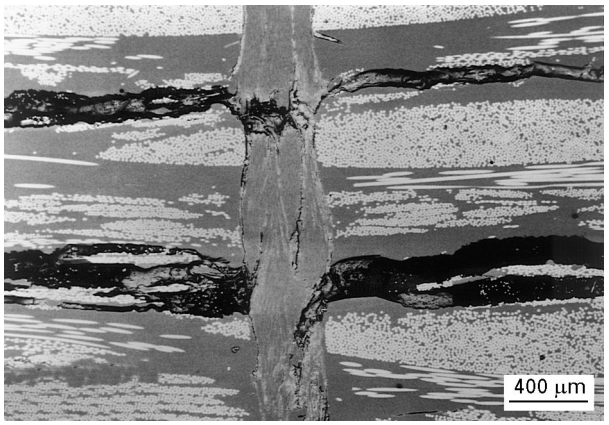

Figure 11 Multiple fractures of the Kevlar® thread in a composite heated at 300 °C for 1 h.

stitches extended for only 5–15 mm behind the crack front (Fig. 9), which means between 4 and 22 threads (depending on stitch density) contributed to the 2.5–3.4 times increase in fracture toughness of the GFRP cured at room temperature. The SEM examination also revealed that the stitches impeded the delamination by deflecting the crack along the stitch/GFRP interface (Fig. 9c). The crack grew along the interface for about 1 mm, which indicates that a shear stress is generated between the thread and surrounding GFRP in the DCB test. This shear stress probably arises from the difference in the tensile stiffness of the Kevlar thread (E = 54–80 GPa) [11] and the stiffness of the composite in the through-thickness direction (E = 3–5 GPa). This toughening mechanism has not been observed previously in stitched composites, and is believed to contribute to the increase in interlaminar fracture toughness. The third toughening mechanism was the pull-out of broken filaments from the stitches (Fig. 8).

The interlaminar fracture toughness of the unstitched laminate increased slightly after exposure to increasing temperature while the fracture toughness of the stitched composites were reduced, particularly at the higher temperatures (Fig. 5). Regnier and Mortaigne [2] investigated the influence of heating an unstitched GFRP laminate between 50 and 600 °C on the chemical stability of the Derakane® 411 vinyl ester resin matrix. This laminate contained the same resin as that used in the stitched fibreglass/vinyl ester composites. Regnier and Mortaigne found that post-curing between 90 and 120 °C improved the thermal stability of the resin by creating additional cross-linking between the polystyrene chains. However, increasing the temperature to 150–200 °C caused some polystyrene chains to degrade by statistical cleavage and by depolymerization. In addition, debonding of small molecules from the polystyrene chain ends occurred above 200 °C. Degradation of the resin by these processes became more prevalent as the temperature was increased to 300 °C, but rupture of the polystyrene chains did not occur until 350–400 °C, which is above the temperature range used for heating the stitched composites. From the study by Regnier and Mortaigne it appears that the resin in the fibreglass/vinyl ester composites was partially degraded by heating between 150 and 300 °C, and this may account for the poor adhesion between the resin and glass observed on the DCB specimen fracture surfaces (Fig. 7). Despite the possible degradation to the resin, the interlaminar fracture toughness of the unstitched composite was improved slightly after heating. This may have occurred because the reduced adhesion would make it easier for the fibres to be pulled from the resin and thereby bridge across the two fracture surfaces. This would increase the amount of fibre bridging, and consequently increase the interlaminar fracture toughness.

The large reduction in interlaminar fracture toughness of the stitched composites with increasing temperature may be due to thermal degradation of the Kevlar® threads. Deterioration of the chemical structure and mechanical properties of Kevlar®-49 threads when exposed to high temperatures (75–600 °C) has been extensively studied [18–22]. Brown and Browne [18] report that the high tensile strength of Kevlar® before heating is the result of two factors: (i) the high degree of molecular order within the poly(1,4-phenylene terephthalamide) molecules, which is the major chemical constituent of Kevlar®, and (ii) the high intermolecular (hydrogen) bonding forces between the polymer chains. Brown and Browne [18] found that when Kevlar® was heated above ~200 °C many of the hydrogen bonds were ruptured, and partial degradation of the polymer occurred by oxidation, chain fracture, cross-linking and disorientation. At ~300 °C, Brown and Ennis [19] found that Kevlar® enters a glass transition region, although Brown and Browne [18] and Brown and Hodgeman [22] report that complete breakdown of the polymer structure does not occur until 350–400 °C. As a result of these thermal degradation processes, the creep stress rupture, compressive and tensile properties of Kevlar® threads are reduced [18, 21, 22]. For example, Brown and Browne [18] measured large reductions in the tensile strength of Kevlar® with increasing temperature and heat exposure time, as shown in Fig. 12. Penn and Larsen [21] also measured a large deterioration in the tensile properties of Kevlar®, with the strength falling by 30% when heated to 200 °C. These studies indicate that the tensile strength of the Kevlar®

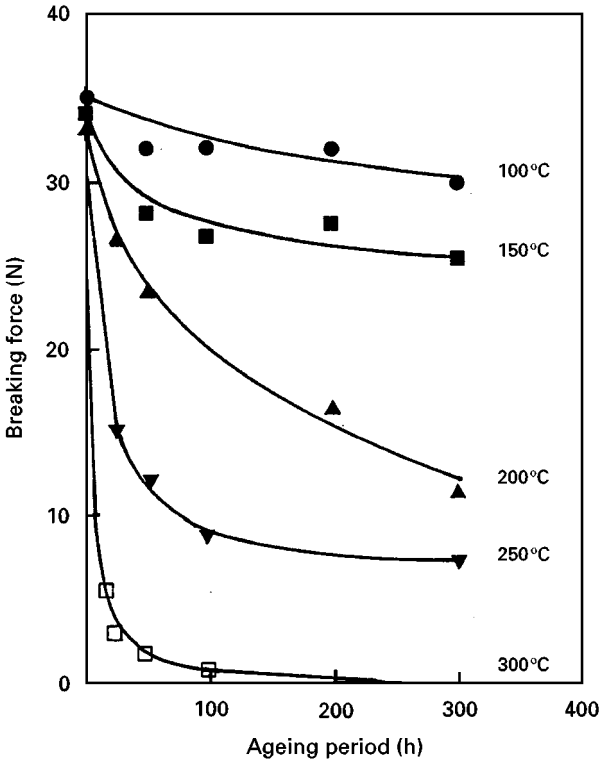

Figure 12 Effect of thermal ageing on the tensile breaking force of Kevlar® threads. After Brown and Browne [18].

threads in the stitched composites would have been reduced considerably by heating, and this would probably account for the large reductions in interlaminar fracture toughness.

It is interesting to note that Fig. 12 shows the tensile strength falling most rapidly within the first ~20–50 h of heating, and within even shorter times at extreme temperatures (above 250 °C). While tensile properties for Kevlar® heated to 175 °C have not been measured, based on the data presented in Fig. 12 it appears that at this temperature the strength would be reduced by 20%–30% when heated for 100 h. This reduction probably accounts for the slight deterioration in the interlaminar fracture toughness of the stitched composite after exposure to 175 °C for 100 h (Fig. 6).

After the fibreglass/vinyl ester composites were heated to 300 °C for 1 h, multiple delaminations were produced rather than one crack at the mid-plane of the DCB specimens (Fig. 10). This cracking indicates that the G_{Ic} values measured for 300 °C are an overestimation of the true interlaminar toughness. The G_{Ic} values were calculated using the beam equation derived by Hashemi *et al.* [15], which assumes that a single delamination grows along the mid-plane. As a result this equation cannot be used for the composites heated to 300 °C, and it is expected that the true G_{Ic} values are much lower than those shown in Fig. 5.

The main aim of this study was to assess the ability of Kevlar® stitching to retain high Mode I interlaminar fracture toughness in fibreglass/vinyl ester composites after the resin had been chemically degraded to some extent by over-heating. This assessment would then make it possible to determine whether stitching with Kevlar® is an effective technique for improving the delamination resistance of marine-grade fibreglass/vinyl ester composites at high temperatures. Obviously the fracture toughness tests show that Kevlar® is not an effective reinforcement after exposure to high temperatures. Polyester fibre has also been used to stitch FRP composites, but it is expected that this will also degrade over a similar or lower temperature range as Kevlar®. Carbon and glass threads, on the other hand, possess superior elevated temperature properties, and it is expected that stitching with these should provide fibreglass/vinyl ester composites with better high-temperature interlaminar fracture toughness properties than Kevlar®.

While stitching with Kevlar® does not appear to be a particularly useful through-thickness reinforcement for marine composites, it is currently being assessed in civil engineering composite structures such as "T"-, "I"- and "L"-shaped beams [23] and for automobile composite components such as bumper bars, floor panels and door members [24]. The aerospace industry is showing the greatest interest in stitching with Kevlar® to improve the interlaminar fracture toughness and impact damage tolerance of new-generation commercial aircraft wings [25, 26]. Many of these stitched composite structures have been fabricated using an epoxy resin rather than a cold-curing vinyl ester. The epoxy needs to be post-cured at about 150–180 °C for several hours to achieve optimal mechanical properties for the composite. It is interesting to note that the fracture toughness tests performed on the stitched fibreglass/vinyl ester composites showed that heating at 150–180 °C reduced the G_{Ic} values by ~15%–35% (Fig. 5). This indicates that during the post-curing of epoxy-based composites the Kevlar® stitches will be degraded, causing a loss in toughness. However, the fracture studies on the fibreglass/vinyl ester composites also showed that the reduction in toughness was influenced more by temperature (Fig. 5) than by heating time (Fig. 6). This suggests that the highest fracture toughness in stitched epoxy-based composites will be achieved by post-curing at the lowest possible temperature for a longer time. This finding is of importance in the processing of civil, automotive and aircraft structures made from Kevlar® stitched composites.

5. Conclusions

1. Stitching increases the delamination resistance of fibreglass/vinyl ester composites by three toughening mechanisms: (i) deflection of the crack tip at the stitches, (ii) partial pull-out of broken filaments from the stitches, and (iii) ability of the stitches to remain unbroken for a short distance behind the crack front, which reduces the opening of the crack and thereby lowers the tensile stress in the region of the crack tip.

2. The interlaminar fracture toughness of the unstitched fibreglass/vinyl ester composite improved slightly when exposed to increasing temperature up to 300 °C for 1 h. It is proposed that the resin may have

suffered some thermal degradation by the over-heating, which reduced the adhesion between the resin and fibres. This could have resulted in a higher amount of crack fibre bridging under Mode I interlaminar loading of the unstitched DCB specimens.

3. The stitched composites suffered a rapid deterioration in interlaminar fracture toughness when exposed to increasing temperature up to 300 °C. Excessive heating probably degraded to some extent the chemical structure and tensile strength of the Kevlar® stitching. This would have made it easier to break the stitches under Mode I interlaminar loading, thereby raising the stress level at the crack tip and, as a consequence, reducing the interlaminar fracture toughness. It is proposed that other types of stitching yarns with better thermal stability than Kevlar®, such as glass and carbon, may retain higher toughness properties at elevated temperatures.

4. High-temperature post-curing of stitched epoxy-based composites is expected to reduce the magnitude of the improvement in toughness. It is recommended that when post-curing civil, automotive and aircraft structures made from Kevlar® stitched composites, the lowest possible curing temperature should be used.

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