



Short communication

# Cure path dependency of mode I fracture toughness in thermoplastic particle interleaf toughened prepreg laminates



Chris Hunt, James Kratz\*, Ivana K. Partridge

Advanced Composite Centre for Innovation and Science (ACCIS), University of Bristol, Queen's Building, University Walk, Bristol BS8 1TR, UK

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## ABSTRACT

The effect of cure cycle on fracture behaviour of a commercial thermoplastic particle interleaved prepreg system was investigated. Laminates were manufactured at 700 kPa in an autoclave using eight different thermal cycles that included both raising the cure temperature above the standard 180 °C cure cycle and incorporating an intermediate dwell stage between 150 and 170 °C prior to reaching the 180 °C cure temperature. Double cantilever beam tests were conducted on specimens from the cured laminates. The stick-slip crack behaviour, observed in samples manufactured using the standard cure cycle, changed to stable crack growth when processing deviated by 10 °C. The mode I fracture toughness values were reduced by 11–22% when incorporating an intermediate dwell stage before the final cure temperature. Scanning electron microscopy inspection of the fracture surfaces showed differences between samples made by standard cure cycles and those made using process deviations.

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## 1. Introduction

Interleaving or interlayer toughening is a common technology used to improved delamination resistance of advanced composite materials. By creating a thick material interlayer between plies, interleaving may reduce limitations on plastic zone development ahead of the crack tip, allowing higher absorption of fracture energy [1–3]. One popular method for increasing interlayer thickness is the addition of thermoplastic particles [4]. As well as increasing the plastic zone ahead of the crack tip, this also may involve a number of supplementary toughening mechanisms including particle bridging, crack pinning, crack path deflection and microcracking [5,6]. The addition of an interlayer has been shown to increase the interlaminar fracture toughness of the parent laminate [2,7,8], and there are now a number of commercial material systems using thermoplastic particles in the interleaf region.

Curing reactions of thermosetting resins are exothermic, and when combined with the low through-thickness thermal conductivity of prepregs, thermal gradients and local temperature overshoots can arise within a part while curing [9]. This phenomenon is particularly prevalent in the manufacturing of thick composite parts, where high temperatures can lead to polymer degradation and the generation of residual stresses [10]. For composites con-

taining thermoplastic interleaf particles, temperature overshoots present the additional concern of potential particle melting. Paris [11] reports that increasing part temperatures above the melting temperature of polyamide based interleaf particles resulted in a change morphology of the interlayer, increasing the measured mode I fracture toughness by up to 50%.

To reduce thermal gradients and overshoots in thick parts, the common practice is to vary the manufacturing cure cycle to feature lower ramp rates and/or additional lower temperature dwell stages [12]. It is well understood that because of the heterogeneous nature of fibre reinforced composites, such variations in the manufacturing cure cycle can affect the generation of residual stresses in a part [13,14]. However, the effect of cure cycle modifications on the delamination resistance in particle interleaf systems with heterogeneous interlayers has yet to be fully addressed. Altering the cure path has been shown to influence phase separation of dissolved thermoplastics in a particle toughened epoxy [15], the resulting effects on mechanical properties were not investigated. A study by White and Kim [16] investigated the effect of staged curing on interlaminar properties, and they found that the cure path had a negligible effect on the fracture toughness in a non-particle toughened material. The influence of the manufacturing process on interlaminar properties of an interleaf particle toughened prepreg was investigated by Zhang and Fox [17]. They found that for laminates cured using the quickstep process, mode I fracture toughness was 2.6 times higher than those cured in an autoclave.

\* Corresponding author.

E-mail address: [james.kratz@bristol.ac.uk](mailto:james.kratz@bristol.ac.uk) (J. Kratz).

Any cure path influence on part properties where temperature gradients are present during the manufacturing process could result in different properties across the part. This study was undertaken to establish a link between cure path and the interlaminar performance of a thermoplastic particle interlayer toughened prepreg. Mode I opening tests were conducted on specimens manufactured using a variety of cure cycles. The cure cycles were chosen to investigate the effects of temperature overshoots and typical cure cycle modifications used to avoid temperature overshoots, including additional temperature dwell stages and lower ramp rates.

## 2. Laminate manufacturing

A commercially available prepreg, HexPly® M21 with IMA fibre, representative of the ‘interlayer toughened’ class of carbon fibre reinforced epoxy systems, was used to produce [0]<sub>18</sub> laminates with a nominal thickness of 3.4 mm. All laminates were cured in an autoclave using a vessel pressure of 700 kPa and a vented vacuum bag. The eight cure cycles chosen for the study are detailed in Table 1.

The standard cure cycle featured a 2 °C/min ramp to a typical 180 °C dwell temperature, denoted as cure cycle 5. In cure cycles 1–4, intermediate dwell stages were introduced to gel the resin prior to reaching the 180 °C final cure temperature. To investigate any effects of ramp rate, cure cycles 1 and 2 had identical dwell stages but had variations in temperature rise rate. The final three cure cycles (6–8) have raised curing temperatures of 185 °C, 190 °C and 200 °C, which were used to study the effect potential temperature overshoots in thicker parts or hotter sections of the autoclave.

A 20 µm thick Fluorinated Ethylene Propylene (FEP) fluoropolymer release film was inserted into the laminate mid-plane during lay-up to act as a crack initiator. After cure, piano hinges were bonded to the test specimens for load introduction using Araldite® 2014-1 epoxy paste adhesive.

During cure cycle 8, the target 200 °C autoclave set-point approached the upper limits of the bagging consumables. During the manufacturing process, the vacuum bag containing this laminate developed a leak just prior to reaching the 200 °C cure temperature. Specimens from this cure cycle had a similar total and interlaminar thickness as laminates from the other cycles (see Table 1).

## 3. Test procedure

Six specimens were cut from a single plate each cure cycle and tested for Mode I fracture toughness according to the ASTM D5528-13 test standard [18] using a displacement rate of 2 mm/min. The Modified Beam Theory (MBT) method, shown in Eq. (1), was used to calculate  $G_{IC}$  values [18]:

$$G_{IC} = \frac{3P\delta}{2b(a + |\Delta|)} \quad (1)$$

Some samples displayed stick–slip behaviour under loading. Where this occurred, propagation values of  $G_{IP}$  were recorded at the peak load values, using the analysis methods outlined by Hojo et al. [19].

## 4. Results and discussion

Stick–slip, stable crack growth, and a combination of the two were observed during the mode I testing of specimens processed by the various cure cycles. These responses are reported in Fig. 1, which shows DCB load vs load point displacement graphs for typical test specimens from each cure cycle. In Fig. 1a the samples from cure cycles 150 f and 150 s, which had the lowest temperature intermediate dwell stage, exhibited mostly stable crack propagation in the resin interlayer, with no fibre bridging. Increasing the intermediate dwell temperature to 160 °C and 170 °C (Fig. 1b) caused the specimens to show some stick–slip behaviour during testing. Fig. 1c shows the responses of samples from the 180 and 185 °C single stage cure cycles, both of which exhibited stick–slip behaviour throughout testing. Increasing the cure temperature to 190 and 200 °C (Fig. 1d) resulted in stick–slip behaviour at small crack lengths, but towards the end of the test, a transition to stable crack growth was observed. This phenomenon was common in all specimens from cycles 190 and 200 but was not observed in any other cycle. Upon visual inspection of the fracture surfaces it was found that this was caused by a transition of the crack from the particle toughened interlayer into the fibrous intralaminar region.

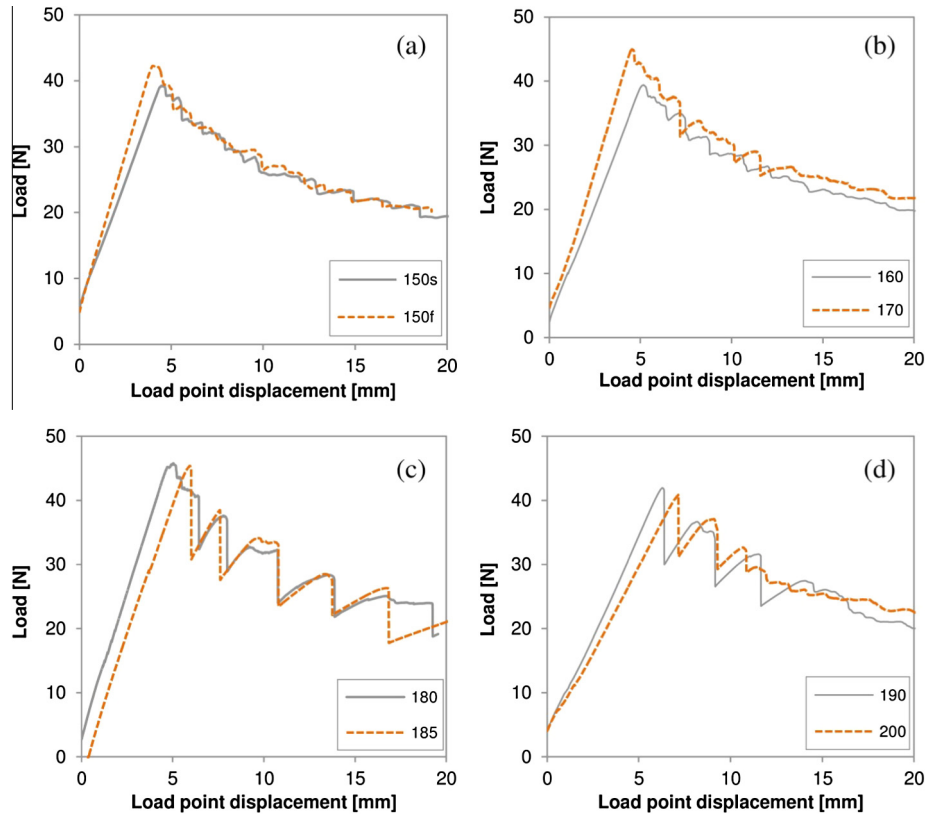
Delamination resistance curves (R-curves) for samples from cure cycles 150 f, 180, and 200 are displayed in Fig. 2. For cycles 150 f and 180, the  $G_{IP}$  values remain constant throughout the test. For cure cycle 200,  $G_{IP}$  is seen to start around 0.3 kJ/m<sup>2</sup> and then drops to 0.26 kJ/m<sup>2</sup>. This was observed in the 190 and 200 °C temperature cure cycles and was found to correspond with the crack transitioning from the interlayer into the interlaminar region; this phenomenon has also been observed by Zhang and Fox [17].

Average fracture propagation values for each of the cure cycles are displayed in Fig. 3. Increasing the intermediate dwell temperature has shown to increase the measured mode I fracture toughness of particle interleaf specimens. In addition, laminates manufactured with a single stage cure cycle have higher  $G_{IP}$  values than laminates manufactured with an intermediate dwell stage. For the raised temperature cure cycles at 190 and 200 °C, the mode I fracture toughness was calculated for both interlayer (solid bars) and intralaminar (dashed bars) crack growth; the fracture toughness was lower in the intralaminar region than in the interlaminar region.

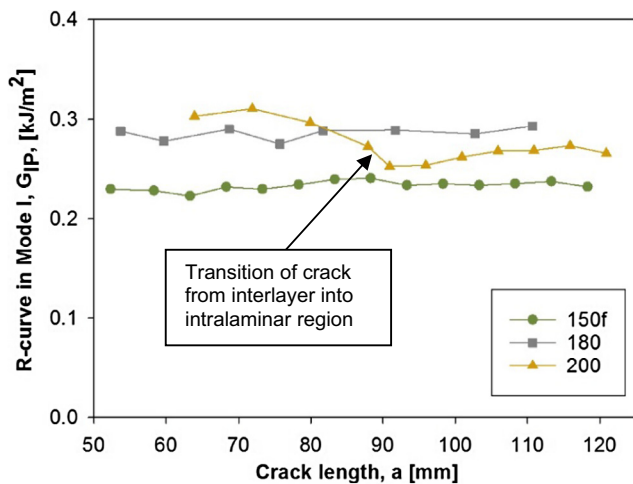
**Table 1**  
Cure cycles.

Cure cycle number	ID	Ramp rate (°C)	Initial dwell stage		Final stage		Average cured interleaf thickness ± one standard deviation (µm)
			Temperature (°C)	Time (min)	Temperature (°C)	Time (min)	
1	150 f	1	150	220	180	150	31.5 ± 4.3
2	150 s	0.5	150	220	180	150	31.7 ± 3.7
3	160	1	160	180	180	150	32.6 ± 9.9
4	170	1	170	150	180	150	32.3 ± 4.2
5 <sup>a</sup>	180	2	–	–	180	120	29.9 ± 6.1
6	185	2	–	–	185	160	31.3 ± 3.9
7	190	2	–	–	190	160	31.3 ± 6.0
8	200	2	–	–	200	160	31.4 ± 3.8

<sup>a</sup> Standard cure cycle.



**Fig. 1.** Load vs load point displacement plots for cycles: (a) 150 s and 150 f; (b) 160 and 170; (c) 180 and 185; (d) 190 and 200. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 2.** Delamination resistance curve for samples from cure cycle 150 f, 180 and 200. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

#### 4.1. Microstructure observations

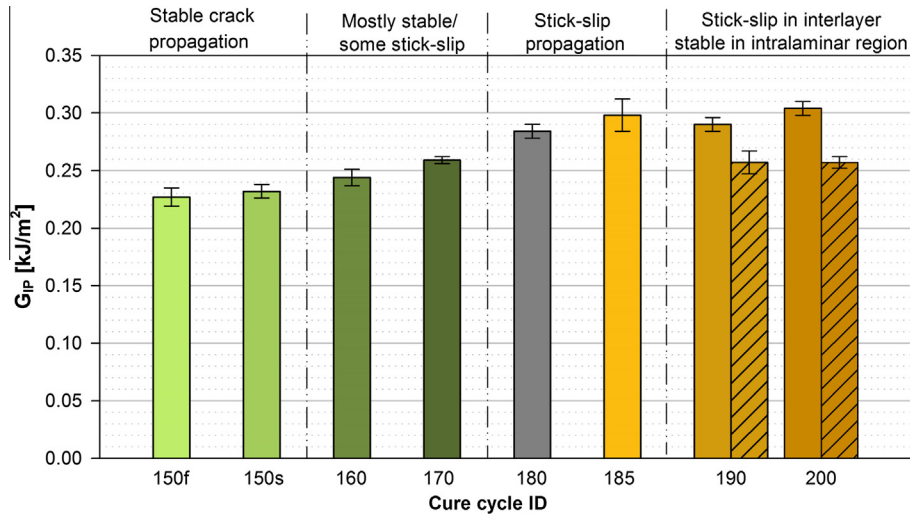
In-order to identify if the differences in mechanical responses observed during testing were visible on the fracture surface, a Zeiss Evo<sup>®</sup> MA 25 Scanning Electron Microscope (SEM) was used to inspect areas of interest. Samples were sputter coated with 10 nm of gold prior to scanning.

Four regions of interest were identified from the fracture surfaces, and are labelled in Fig. 4a and b. Fig. 4a shows the fracture surface of a cure cycle 150 s test specimen, which exhibited stable

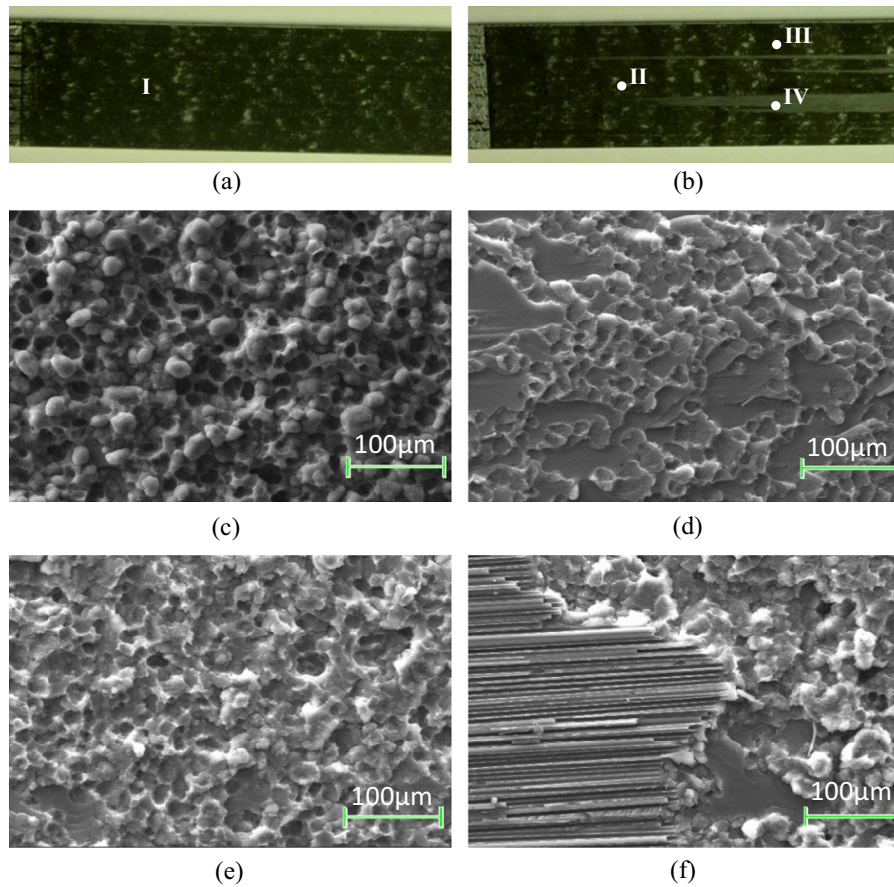
crack propagation in the interlaminar region during testing and had a consistent fracture surface; this was identified as region I. Fig. 4b shows the fracture surface of a cure cycle 185 test specimen. This specimen exhibited stick–slip behaviour during testing and its fracture surface has three distinct areas of interest. Banded light and dark regions perpendicular to the crack growth direction are visible on the fracture surface and have been identified as region II and III, respectively. The lighter, wider bands are believed to be regions where slow ‘stick’ crack growth occurred, and the darker, narrower bands are regions where sudden ‘slip’ crack growth occurred. The fracture surface where the crack was seen to propagate into the intralaminar fibre region (identified as region IV) was also investigated.

The SEM analysis of the fracture surfaces was seen to be consistent within each region and representative SEM images of the four regions are displayed in Fig. 4c–f. The interlayer fracture surface in region I, where stable crack propagation occurred, is shown in Fig. 4c. This region features easily identifiable thermoplastic particles and craters which would appear to be where particles were removed as the crack propagated during testing. Fig. 4d–e show the interlayer fracture surface in regions II, the faster ‘slip’ crack growth, and region III, the slower ‘stick’ crack growth, respectively. Here, the thermoplastic particles are less clearly visible than in Fig. 4c. An example of the transition of the crack from the particle interlayer region into the fibrous intralaminar region is shown in Fig. 4f.

Higher magnification SEM images of fracture surfaces are shown in Fig. 5. An example of a fracture surface from a specimen that exhibited stable crack behaviour (from a dual stage cure cycles) is shown in Fig. 5a, and a specimen that showed stick–slip behaviour (from a single stage cure cycle) is shown in Fig. 5b. The shear yielding mechanism, responsible for toughness enhancement



**Fig. 3.** Average mode I propagation fracture toughness,  $G_{IP}$ , (solid bars represent  $G_{IP}$  in interlayer region, dashed bars in the intralaminar region). Error bars equal to one standard deviation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

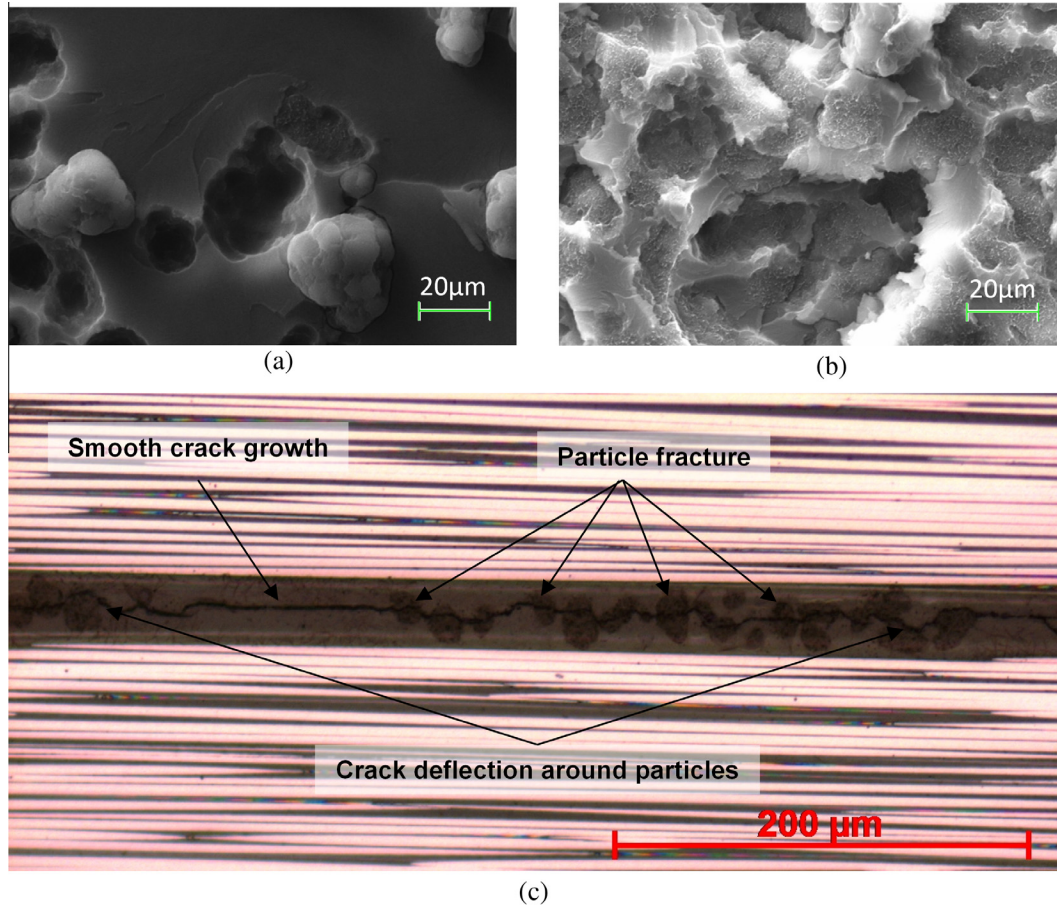


**Fig. 4.** Fracture surface images of DCB test specimens from cure cycles: (a) 150 s; (b) 185 (crack propagation from left to right). SEM images of the identified regions of interest: (c) I; (d) II; (e) III; (f) IV. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in the resin, appears to be more evident in the specimen processed by a single stage cure cycle. A side-view optical micrograph of a specimen from cure cycle 6 shows the complex crack pathways that are possible during DCB testing. The crack path was observed to deflect around interleaf particles, fracture the particles, and propagate in a smooth fashion in regions lacking the interleaf particles.

#### 4.2. Unconstrained plastic zone

Previous studies have shown that the interlayer thickness will influence the fracture behaviour in laminated composites [1,2]. Therefore the interlayer thickness was measured at nine locations for each cure cycle using an optical microscope to identify whether a change in interlayer thickness was responsible for the observed



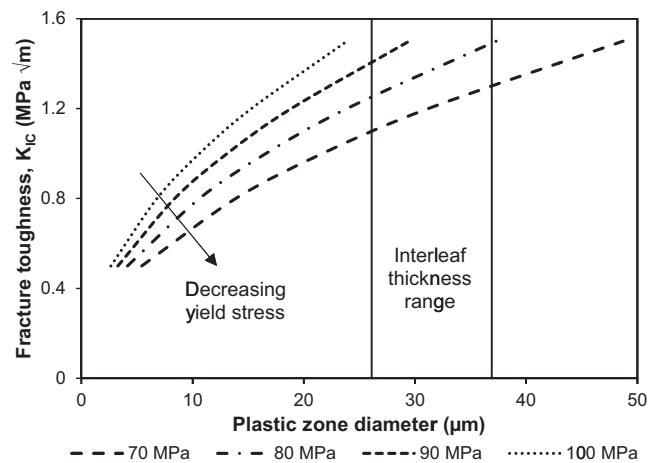
**Fig. 5.** SEM images of the fracture surface from DCB test specimens from regions exhibiting (a) stable crack propagation; and (b) stick-slip behaviour. A side view optical micrograph of a tested DCB specimen in (c) shows different crack paths in the interleaf region. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

changes in fracture toughness. The measurements for each cure cycle are reported in Table 1, and an average interleaf thickness of 31.5  $\mu\text{m}$ , with a 5.4  $\mu\text{m}$  standard deviation, was measured across all laminates.

If the crack is to remain in the interleaf region, the diameter of the plane strain unconstrained plastic zone,  $d_y$ , must be smaller than the interleaf region. The plastic zone ahead of the crack tip can be described by [20]:

$$d_y = \frac{1}{3\pi} \left( \frac{K_{IC}}{\sigma_y} \right)^2 \quad (2)$$

where  $K_{IC}$  is the stress intensity factor and  $\sigma_y$  is the yield stress. The values of  $K_{IC}$  and  $\sigma_y$  are unknown for this specific case, but are expected to be between 0.8 to 1.2  $\text{MPa}\sqrt{\text{m}}$ , and 70 to 100 MPa for toughened epoxies [20], respectively. These values are considered with the measured interleaf thickness range shown in Fig. 6. When the plastic zone diameter exceeds the interleaf thickness of the laminate, the crack may divert into the fibrous intralaminar region. Local reductions in interleaf thickness could cause the crack to divert into the fibre bed, as observed in Fig. 4b. The case of full crack front departure from the central interleaf region in the raised temperature cure cycles 7 and 8 could be due to a change in material properties  $K_{IC}$  or  $\sigma_y$ . While the former is unlikely, the latter is possible due to thermal degradation at elevated temperatures. This requires further investigation as both properties influence the measured strain fracture toughness and the mechanisms by which cracks propagate in interleaf toughened laminates.



**Fig. 6.** Predicted plastic zone diameter as a function of fracture toughness and yield stress using Eq. (2). The interleaf thickness range is the average  $\pm$  one standard deviation measured across all laminates.

## 5. Conclusion

Mode I delamination fracture toughness of an interleaf toughened prepreg was investigated in laminates manufactured with a variety of cure cycles, some of which were outside the manufacturers' recommended 180  $^{\circ}\text{C}$  cure cycle. The cure path was found to

have some influence on the qualitative observations in response to loading, as well as the measured fracture toughness values.

Samples cured with a single stage cure cycle generally exhibited stick–slip behaviour, whereas samples cured with an intermediate dwell stage showed stable crack propagation, and as a result, a lower mode I fracture toughness with up to a 22% reduction in  $G_{IIP}$ . The effect of temperature overshoots was investigated by exceeding the standard 180 °C cure temperature by 10 °C and 20 °C. The propagating crack tended to move from the laminate interleaf region into the fibrous intralaminar region during DCB testing of these specimens. This may be due to an increased unconstrained plastic zone ahead of the crack tip, the cause of which has yet to be determined.

These results indicate that a cure path dependency of some mechanical properties might need to be considered when designing particle interleaf laminated composites. Variable thickness composite structures will likely have spatial variations in temperature during processing, and will require special attention to avoid a local reduction in the mechanical properties of the finished article.

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Access to supporting data may be requested from Prof. I.K. Partridge, which due to commercial contracts in place, will be subject to consent being granted from the original project participants.

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