CURE PATH DEPENDENCY OF MODE I FRACTURE TOUGHNESS OF RECYCLED AEROSPACE-GRADE PREPREGS

Marrone, L.[1,2], Hubert, P.[1,2*]
[1] Mechanical Engineering, McGill University, Montreal, Canada
[2] Research Centre for High Performance Polymer and Composite Systems (CREPEC), Montreal, Canada
* pascal.hubert@mcgill.ca

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ABSTRACT

It has been demonstrated that new parts can be made from aerospace manufacturers' discarded composite prepreg materials via compression moulding. The key is partially curing them beforehand to make the resin within them more viscous, a process known as "staging." Though this has been shown to improve the surface finish and integrity of geometrically complex parts made with these materials, its effect on their mechanical properties is still relatively unknown. In this work, the effect of modifying this pre-cure cycle on the toughness of the material was investigated. Flat panels were manufactured from a commercially-available carbon fibre prepreg, CYCOM 5320-EO, and their Mode I fracture toughness was measured. It was found that there was a significant decline in the fracture toughness of the panels made from prepregs that had been subjected to the most severe degree of staging when compared to parts made without staging. However, samples made with lighter degrees of staging did not exhibit a significant decline in toughness. These results suggest that there may exist an optimal amount of staging, in which most of the benefits of improved part quality and manufacturability are achieved without reducing fracture toughness.

1 INTRODUCTION

In the pursuit of ever-increasing fuel efficiency, the aerospace industry has turned to extensive use of carbon fibre parts in aircraft production. They typically use carbon fibre weaves pre-impregnated with resin, so-called 'prepregs', to accelerate the manufacturing process. However, significant amounts of these materials must be thrown out due to various inefficiencies in the manufacturing process; trimmings left over from cutting processes as well as rolls that whose resins have expired are environmental hazards and must be disposed of in ways that are often expensive.

Recent studies have proposed reusing these materials in a compression moulding process to produce lower-value components; though the materials no longer meet the requirements of the most critical parts of the aircraft, they are still capable of satisfying the requirements of other parts that are currently made from plastic or aluminum. To produce acceptable parts, however, the viscosity of the resins must be increased, as these materials are typically designed to be used either in autoclave or out-of-autoclave (OOA) processes where consolidation pressures are orders of magnitude lower. Smith et al. [1] demonstrated that putting the untreated OOA resin in a compression moulding process results in low-quality parts; the low viscosity of these resins causes them to flow under compression without taking any fibre reinforcement with it, resulting in excessive resin bleed, incomplete feature filling, and resin-rich regions in the part. That study found that increasing the viscosity of the resin in the prepreg, by way of a partial curing process called "staging", eliminated virtually all the manufacturing defects present in the demonstrator parts produced. There is, however, an upper limit to how much the material can be staged before the material gels, which would cause it to fail to consolidate during cure. Thus, the existence of an optimal window of processing conditions, within which good parts can be made, is implied.

While it has been conclusively demonstrated that staging improves the quality of the final part made by compression moulding, it remains to be seen what effect it has on the mechanical properties of said part. In particular, the effect of the cure path on the fracture toughness of the cured material, which is heavily dependent on the chemical properties of the resin, has seen little to no investigation for this particular class of thermoset resin. This study will thus seek to determine the relationship between the initial degree of cure of a part made from CYCOM 5320-EO (Solvay) and its Mode I fracture toughness.

1.1 Background

The flow behaviour of the resin is of critical importance in compression moulding processes. In general, there are two competing modes for resin flow during this process: percolation flow and shear flow. In the former the resin flows independently of the fibres, whereas they flow together in the latter [2]. The property that governs which flow mode will be favoured during compression is the viscosity of the resin used; a low resin viscosity will tend to encourage percolation flow, while shear flow tends to become dominant at high viscosities. Promoting shear flow is generally desirable in compression moulding to ensure that the mould fills completely with both resin and reinforcement.

Several studies have been done to develop recycling and remanufacturing techniques to resolve the problem of wasted uncured prepreg. The aforementioned staging study completed by Smith, in which the viscosity of the resin from a CYCOM 5276-1 prepreg was increased to make it a suitable precursor for compression moulding, found that a staging program that raised the moulding viscosity (i.e. the viscosity of the resin under the conditions of compression moulding) to the range of 202-290 Pa-s created a material capable of producing geometrically complex parts with good surface quality and excellent specific stiffness [1].

Measuring the degree of cure (DoC) of a received prepreg roll without having to extract the resin is possible by using dynamic scanning calorimetry (DSC). Kratz et al. developed a model to correlate the glass transition temperature (T_g) of a Cycom 5320 prepreg's resin, as measured by a DSC or by dynamic mechanical analysis (DMA), to its current degree of cure, α [3]. They used a DMA to test pre-cured laminates and then fit the data to a model developed by DiBenedetto[4], as shown in Equation 1.

$$\frac{T_g + 8.4}{212 + 8.4} = \frac{0.66\alpha}{1 - 0.34\alpha} \tag{1}$$

The effect of modifying the cure cycle of OOA prepregs has been examined in several studies. Hyun et al. investigated whether there was a difference in quality and tensile strength in parts made from Cycom 5320-1, an OOA prepreg. They modified the manufacturer-recommended cure cycle, which includes a room-temperature debulk step, a temperature dwell step at 121°C for two hours, and a final cure set at 177°C for two more hours. By removing the room-temperature debulk and lowering the dwell temperature to 55°C, the authors were able to improve the tensile strength of the material by 2.4% when compared to specimens made by following the manufacturer's recommended cure cycle [5]. This suggests that the mechanical properties of this class of material can be affected by the cure path, though the exact nature of this effect on the fracture toughness was not studied.

Hunt et al. [6] found that the cure path did have some effect on the measured fracture toughness values of thermoplastic-particle-interleaf-toughened prepreg laminates. They compared the toughness of laminates cured in a single stage to those whose cure programs included an intermediate dwell stage, roughly analogous to the staging procedure used by Smith. They found that laminates cured with an intermediate dwell stage suffered a 22% reduction in Mode I fracture toughness compared to those cured with a single stage cycle. Additionally, they observed that adding a dwell stage to the cure cycle changed the fracture behaviour of the laminate; the typical "stick slip" behaviour, in which the crack grows in small, sudden jumps, was replaced by a smooth, stable crack propagation. They proposed that this might be caused by a change in the yield strength of the interlayer matrix, causing the crack to deflect out of the interleaf region of the laminates that have been cured in a single stage, high temperature cure cycles.

2 METHODOLOGY

2.1 Panel Manufacturing

Five panels were produced from CYCOM 5320-EO PW prepreg, which is a toughened carbon fibre reinforced polymer prepreg system with a plain-weave fibre architecture designed for use in OOA manufacturing. It is a version of the commercially available CYCOM 5320 prepreg modified to extend its out-life. Plies were cut from the roll to dimensions of 30 cm by 30 cm with the aid of a 3D-printed guide. The plies were then staged in stacks of four in a pre-heated Blue-M industrial oven (Thermal Product Solutions Inc., New Columbia, PA, USA), following the parameters shown in Table 1. Small, single ply "witness parts" were placed in the oven with the test material for later analysis by DSC to verify the DoC of the material. After staging, the plies were laid up in stacks of 26 with a [0°/90°] ply orientation and a 54-micron thick piece of Teflon film placed in the midplane as a crack initiator.

Table 1. Staging parameters

Panel ID	Staging Temperature (°C)	Staging Time (min)	DoC After Staging
Baseline	0	0	0.02
S1	95	171	0.08
S2	95	330	0.24
S3	95	345	0.26
S4	130	48	0.28

For the staging procedure, two flat aluminum plates were pre-heated in a PPMH 250 press (Macrodyne Technologies inc., Concord, ON, Canada) to the manufacturer's recommended curing temperature of 120°C. Once they were laid-up, the stacks were placed on the aluminum plates on the press and compressed at a closing speed of 3 cm per second with 27 short tons of force for two hours. This value was selected for convenience, as it was near the minimum limit of the capabilities of the press. Afterwards, the panels were returned to the oven for a two-hour post-cure at 180°C. Dual-cantilever-beam (DCB) specimens were then cut from each panel with either a diamond cut-off saw or a CNC machine, depending on availability. The contact surfaces of the specimens were then cleaned with acetone, abraded with 80-grit sandpaper, and then cleaned with acetone again. Aluminum hinges meeting the MS20001-6 standard were then bonded to the top and bottom of each specimen using 3M 2216 two-part epoxy (3M Company, Maplewood, MN, USA) with the aid of another 3D printed guide to ensure conformity. Finally, the sides of the specimens were painted white with Bic correction fluid (Société Bic S.A., Clichy, France) so that the crack growth could be more easily seen.

2.2 Test Procedure

Five specimens were tested from each panel and their fracture toughness was tested according to the ASTM D5528-1 (2007) standard [7], using a displacement rate of 5 mm/min [7]. Testing was carried out on an MTS Insight 5kN

Extended Length Universal Testing Machine (MTS Systems Corporation, Eden Prairie, MN, USA), as shown in Figure 1. The tests were recorded with a Nikon D5300 DSLR (Nikon Corporation, Minato, Tokyo, Japan) equipped with a Sigma 105 mm 1:2.8 macro lens (Sigma Corporation, Kawasaki, Kawanaga, Japan). The opening Mode I fracture toughness, G_{IC}, was calculated using the Modified Beam Theory method, shown in Equation 2. The G_{IC} value used for each specimen was taken at the point where the load-displacement curve deviates from linearity.

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

where *P* is the applied load, *b* is the width of the DCB specimen, *a* is the delamination length, and **Δ** is a correction factor to account for the rotation of the arms of the DCB specimen during testing. The standard defines **Δ** as the x-axis intercept of the least squares plot of the cube root of the specimen's compliance as a function of delamination length.

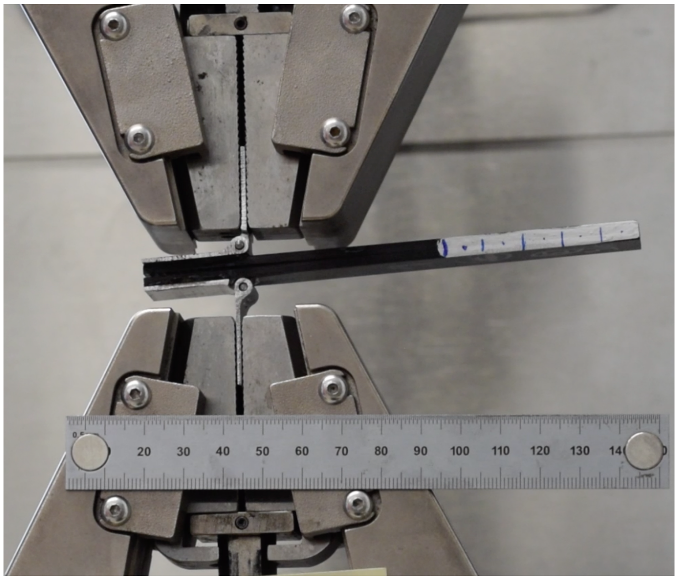

Figure 1 Testing setup for Mode I fracture toughness

3 RESULTS AND DISCUSSION

The average recorded Mode I opening fracture toughness, including 95% confidence interval, is summarized in Figure 2. These calculated values were plotted against the DSC-measured DoC of the witness parts from each panel's staging cycle. Up to a DoC of 0.24, there appears to be a very slight increase of the opening fracture toughness of the laminate, though the difference falls within the 95% confidence interval of the data. After this point, however, there is a clear drop in fracture toughness. Thus, it appears that this is a limit to staging using these parameters, after which the toughness is significantly compromised.

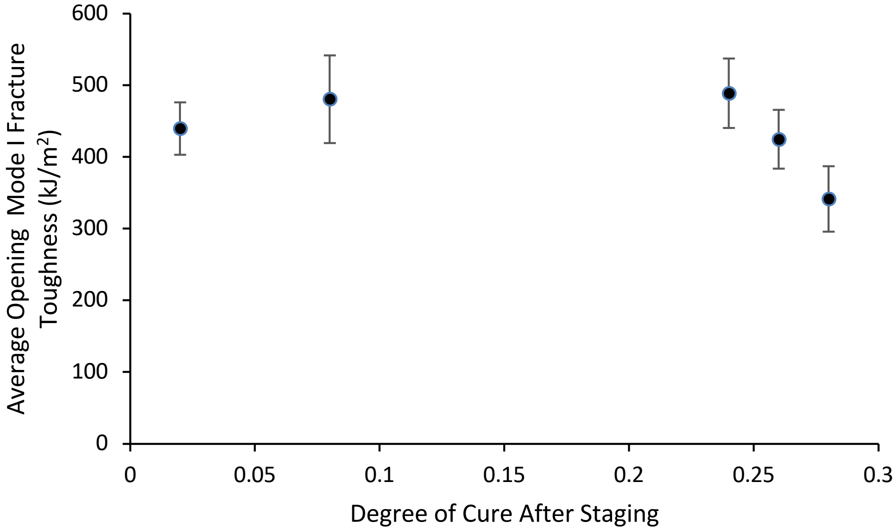

Figure 2 Average Mode I fracture toughness as a function of the prepreg's DoC after the staging cycle.

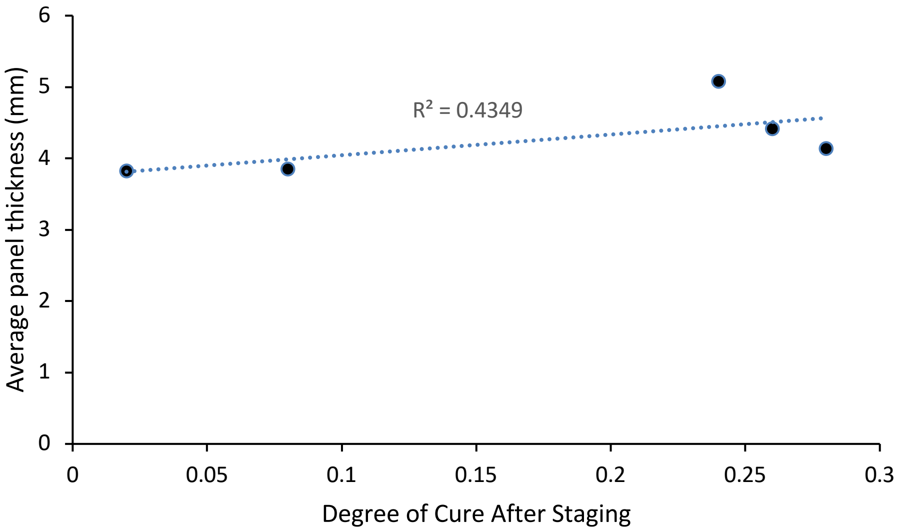

Figure 3 Effect of degree of cure after staging on panel thickness.

In his study, Smith [1] targeted a moulding viscosity of 250 Pa-s to manufacture quality demonstrator parts from CYCOM 5276-1 prepreg, which contains a similar toughened thermoset prepreg to that of the CYCOM 5320-EO used in the current study. In the current study, the moulding viscosity of the resin was not directly measured; instead, it was estimated using numerical methods. By using the CYCOM 5320-1 model contained in the RAVEN3 software (Convergent Manufacturing Technologies Inc., Vancouver, BC, Canada), it was estimated that the moulding viscosity of the resin at a staged DoC of 0.24 was 455 Pa-s, well above the target. This suggests that the optimal staging parameters for the processability of this material are safely below the onset of toughness degradation.

The effect of the degree of cure after staging on panel thickness is shown in Figure 3. As only one panel was manufactured for each condition, and variance in the panels' thicknesses were virtually non-existent, the 95% confidence interval is too narrow to be visible. While the thickness is affected by several factors, there is a clear, if slight, upward trend with respect to the degree of staging, as demonstrated by the dotted trendline added to the figure. The most likely explanation is that the laminates that had a higher degree of staging had, in turn, a higher moulding viscosity. Thus, following the theory presented in Section 1, the flow behaviour of the resin of laminates that had less (or no) staging tended towards percolation, wherein the resin leaves the fibre weave and flows out of the laminate. There was a visible outflow of resin from laminates with lower staging levels during the compression moulding step, suggesting that this was the case. The implications this would have for the fracture toughness are two-fold: first, the loss of resin in the laminate would change its fibre volume fraction slightly; and second, the distance between plies in the laminate (i.e. the interlaminar distance) would be decreased.

The effect of increasing the fibre volume fraction (as is the case when resin is removed) of a laminate was studied by Feret, who found that an increased fibre volume fraction can decrease the Mode I fracture toughness of a composite manufactured by resin transfer moulding (RTM) [8]. In that study, it was found that increasing fibre volume fraction from 57% to 66% lead to an average 16.2% decline in Mode I fracture toughness. Thus, as it is the low-staging laminates in the current study that had the highest resin loss, while still having higher toughness values than the high-staging laminates, it suggests that effect due to staging is more significant to the toughness than the effect of fibre volume fraction. It is worth noting, however, that neither the measuring the thickness of the panel nor the resin outflow during moulding are adequate to estimate the final fibre volume fraction of the laminate, as these measurements would not be able to exclude the possibility of changes in void content within the panel. Bubbles within the resin outflow would artificially increase the appearance of resin leaving the laminate, while voids within the panel would increase its thickness, and therefore the apparent amount of resin contained, without this really being the case. Optical micrographs taken of the panels qualitatively confirm an apparently higher incidence of porosity in panels that had no staging than those that did. Two typical images are shown in Figure 4 for comparison. As such, while some resin loss is clearly occurring at low levels of staging, no comment can be currently made on the exact void content of the test specimens.

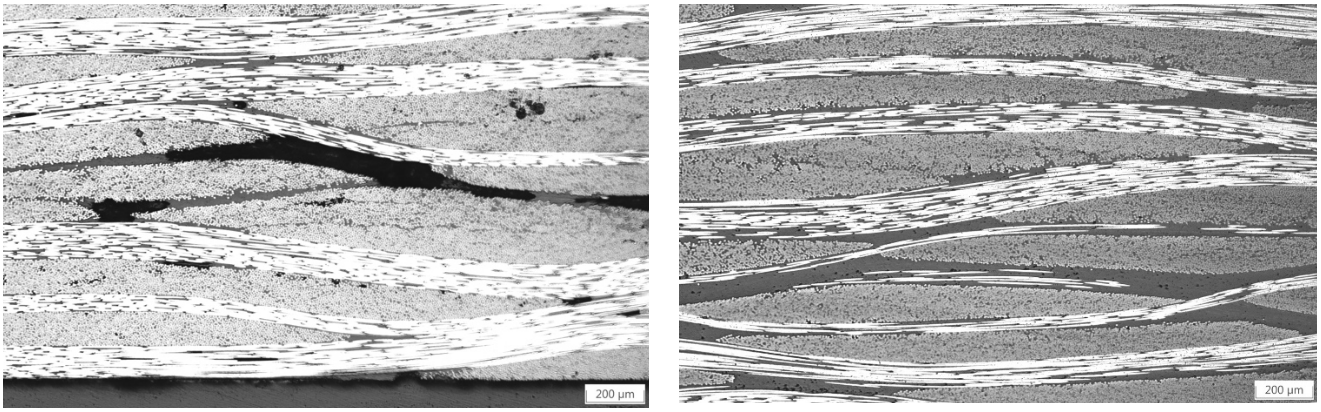

Figure 4 Typical micrograph taken at 5x magnification. Left: baseline sample. Right: high stage sample (S2).

Several studies have investigated the effect of changing the thickness of the interlayer zone on the fracture toughness of a CFRP laminate. Singh and Partridge [9] increased this interlaminar zone in their CFRP laminates by adding films of resin around the midplane, creating a central resin-rich zone, and investigated the effect on its fracture toughness. They found increasing the interlaminar thickness increased the mode I fracture toughness and explained it by using classic fracture mechanics. They posited that a thicker interleaf region on the crack plane allows for a taller unconstrained plastic zone, thus relieving the stress at the crack tip during propagation. Once again, however, this runs counter to the findings of the current study, in which the thicker laminates tended to be less tough. The differences in thicknesses between panels were relatively small, however, and so this effect was likely not significant in these results. Hunt et al. [6] also considered the effect of the size of the plastic zone ahead of the crack tip, theorizing that a change in the resin's yield stress could change the size of this zone and cause the crack to deflect out of the interleaf resin-rich zone and to the fibre bed, where it could propagate more easily. They did not speculate as to the causes of this change, however.

Classic fracture mechanics appear to be insufficient to explain the fracture behaviour of these panels; the high moulding pressure used by the compaction process reduces the size of the interlaminar zone considerably, and thus some key assumptions of these theories cannot be applied. Critically, classic fracture mechanics assume a homogeneous material, which isn't applicable if the plastic zone contains fibres from neighbouring plies. Ultimately, as the recycling and remanufacturing process this study is attempting to serve produces highly heterogeneous parts, the properties of the resin itself are more important than the fracture mechanics of these laminates. As the effects of these classic fracture mechanical considerations appear to be limited, it can be assumed that the changes in fracture toughness observed in this study are most likely the result of changes within the resin itself.

4 CONCLUSIONS AND FUTURE WORK

In summary, five laminates were made from CYCOM 5320-EO were subjected to different staging cycles, pressed via compression moulding with a 2-hour, 120°C cure cycle, and their Mode I opening fracture toughness was measured. It was ultimately found that increasing the degree of staging up to 0.24 may slightly increase the Mode I fracture toughness of the laminates, staging them beyond this point lead to a significant decrease in this material property. This decline could not be explained by other manufacturing factors or classic fracture theory.

Ultimately, these results prove that the cure path used to prepare discarded prepreg material for recycling does have an effect on the fracture toughness of the final part. While designing processes for these materials, attention must be paid to how the desired resin viscosity is achieved. This effect may be different for each material; for this material, however, the optimal moulding viscosity appears to be achievable without significantly damaging the toughness. Future work will attempt to isolate the effects of varying temperature and time, rather than the generalized degree of staging, on the toughness of a laminate.

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6 REFERENCES

[1] A. W. Smith, “Development of a Recycled Compression Moulding Compound,” McGill University, Montreal, QC, Canada, 2021.

[2] P. Hubert, “Aspects of flow and compaction of laminated composite shapes during cure,” Text, 1996. [Online]. Available: https://open.library.ubc.ca/collections/831/items/1.0078499

[3] J. Kratz, K. Hsiao, G. Fernlund, and P. Hubert, “Thermal models for MTM45-1 and Cycom 5320 out-of-autoclave prepreg resins,” *J. Compos. Mater.*, vol. 47, no. 3, pp. 341–352, Mar. 2012, doi: 10.1177/0021998312440131.

[4] A. T. DiBenedetto, “Prediction of the glass transition temperature of polymers: A model based on the principle of corresponding states,” *J. Polym. Sci. Part B Polym. Phys.*, vol. 25, no. 9, pp. 1949–1969, Sep. 1987, doi: 10.1002/polb.1987.090250914.

[5] D.-K. Hyun, D. Kim, J. Hwan Shin, B.-E. Lee, D.-H. Shin, and J. Hoon Kim, “Cure cycle modification for efficient vacuum bag only prepreg process,” *J. Compos. Mater.*, vol. 55, no. 8, pp. 1039–1051, 2021.

[6] C. Hunt, J. Kratz, and I. K. Partridge, “Cure path dependency of mode I fracture toughness in thermoplastic particle interleaf toughened prepreg laminates,” *Compos. Part Appl. Sci. Manuf.*, vol. 87, pp. 109–114, Aug. 2016, doi: 10.1016/j.compositesa.2016.04.016.

[7] ASTM D5528-01, “Standard Test Method for Mode I Interlaminar Fracture Toughness of Unidirectional Fiber-Reinforced Polymer Matrix Composites.” 2007.

[8] V. Feret, “Development of a mixed-mode fracture criterion for a five harness satin carbon/epoxy manufactured by resin transfer moulding,” M.Eng Thesis, McGill University, Montreal, QC, Canada, 2009.

[9] S. Singh and I. K. Partridge, “Mixed-mode fracture in an interleaved carbon-fibre/epoxy composite,” *Compos. Sci. Technol.*, vol. 55, no. 4, pp. 319–327, Jan. 1995, doi: 10.1016/0266-3538(95)00062-3.