MECHANICAL BEHAVIOUR OF PATTERNED MULTI-MATRIX COMPOSITES WITH GRADIENT PROPERTIES

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Abstract

This study explores the feasibility of improving damage resilience around structural features in composite components through varying (a) the internal geometry of the reinforcement and (b) matrix properties. The gradients in fibre architecture are realised through varying the braiding angle in triaxial braided sleeve. Introducing matrix gradients is implemented through a novel Liquid Resin Print technique which is applied through precise point-wise injections of dissimilar brittle and tough polymers into dry textile preforms prior to infusion. Open hole tensile tests are used to assess the damage development in reference and modified materials.

1. Introduction

The concept of gradient properties is widely used in a wide range of materials and material systems: functional multi-material coatings [1], interphases between dissimilar materials [2], graded adhesives [3, 4], *etc.* The primary purpose of grading material properties is to decrease the stress concentration at edges and interfaces, decrease residual/thermal stresses, and, as a result, improve important material properties such as toughness, hardness and damage resilience. In some cases, as was shown for adhesive joints [4], grading allows achieving synergistic effects where the strength of a two-element system (*e.g.* adhesive with varying glass transition temperature and related stiffness from high to low) exceeds the properties achieved by using each of its components separately.

Despite the advantages widely documented for ceramics, metals, polymers and natural materials, there was a limited effort in implementing grading in the domain of composites with continuous reinforcement. The primary reason for that was that the technology used for grading homogeneous engineering materials, *e.g.* powder stacking, laser sintering, slurry dipping, 3D printing, *etc.* [1, 5], appear to be incompatible with conventional composite manufacturing.

The mainstream approach to the local modification of composite properties is achieved through fibre steering through automatic fibre deposition and varying the internal architecture of textile preforms through the component length [6]. These techniques prove to be very useful for redistributing stress and optimizing the load flow. However, grading matrix properties appears to be more challenging for

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implementation. Only few available technologies allow combining various matrices in one component such as co-injection RTM [7, 8] where the plies are separated by an impermeable layer.

This study takes an advantage of a novel method of integrating resin: 3D print of liquid co-reactive resins into continuous textile preforms [9, 10]. This approach enables the creation of patterned multi-matrix composite systems with internal interfaces. This way of combining matrices offers new instruments for manipulating damage accumulation mechanisms. As shown recently [10], these fibre-bridged interfaces can both trigger delamination and arrest it. The relation between ability to accumulate damage and composite strength is complicated. Wisnom and Hallett provided an important insight into this phenomenon [11]. Consdering an open hole tensile test they demonstrated that more extensive damage in the vicinity of a feature can sometimes have a strong positive effect on composite strength.

The print process allows to play with a wide range of parameters and internal properties allowing to apply tough or stiff and brittle systems around the feature. The properties and geometry of internal interfaces can also be manipulated. The transition in properties can be abrupt or smooth depending on preform architecture and the constraints of preform during injection procedure. A smooth gradient transition in local matrix properties can be achieved either by the process of filtering of particles carried by the injected resin or by non-uniform flow of the resin within preform. Alternatively, a series of neighbouring patches with graded properties can create smoothely evolving properties.

This study is set to conduct trials towards achieveing the goal of creating a more resilient material through combination of matrices. In the first trials relied on the natural mechanisms of grading through particle filtering around the injection site and smeared interface between the infused and injected matrices due to the unconstrained capillary flow. Two material systems were tested as candidates for changing the properties around the stress concentrator: a high T_g cyanate ester resin [12] and a low T_g epoxy resin toughened with the core shell rubber additives. Open hole tests are used to make an initial assessment of grading potential.

2. Experimental study

2.1 Print process

The concept of liquid resin print can be briefly summarized as follows. Resin is injected through a steel needle (21 G, 0.5 mm inner diameter) at a predefined depth using a recently developed printing concept [9, 10]. Each injection impregrnates a thin layer of preform around the injection site. A series of these injections through preform thickness creates an an impregnated area which, upon pressure/heat assisted consolidation, transforms into a solid patch. In a subsequent liquid moulding process the fibre-bridged interfaces between the injected and infused resins are formed. Any reactive resin can be injected as long as it maintains sufficiently low viscosity at the time scales and temperatures of injection. The resins can also be functionalized, reinforced and/or toughened with dispersed micro- or nanoparticles.

2.2 Bradied preforms

A triaxially braided, glass preform, manufactured in the University of Manchester, was used as the reinforcement. The preforms were braided in a regular pattern with braiding angle of ±60° (±0.5° is the variation of the braiding angle), 20% weight fraction of inlays, and 97-99% coverage of the surface (no significant yarn free space within the ply). The measured areal density of the preform is 618 g/m^2 with 600 tex for braiding and inlay yarns (roving type Hybon 2001). The braiding yarn width is about 1.9 mm, the width of inlay yarn constituting 2.2 mm, spacing between inlay yarns is 4.9 mm.

In addition to the baseline preform, a fibre steered braided preform was manufactured. This steering was implemented through varying the speed of braiding. In the steered (angle graded) configuration the braiding angle was varied from ±60° (at both ends of the sample) to ±45° (towards the centre of the sample). The angle of ±45° was set constant at the span of approximately 100 mm with the

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transition area length of about 30-60 mm at each side. The areal density of ±45° zone and transition area was estimated to be around 525 g/m^2 with 95% surface coverage. Four ply laminates were constructed for the both steered and non-steered configurations which produced composites of 2.2 mm thickness for the reference configuration and 1.8 mm in the location of ±45° steering.

2.2 Matrix systems for infusion and injection

As a hosting matrix the low viscosity epoxy (Prime^{TM} 20LV) with a slow hardener (manufactured by Gurit) was selected. The cured resin has low glass transition temperature (83°C) and good mechanical properties (stiffness 3.5 GPa, tensile strength 73 MPa, and strain to failure 3.5%). Two material systems were tried in this study as the candidates for matrix grading:

(a) LECy (1,1-bis(4-cyanatophenyl)ethane) cyanate ester (CE) from Lonza AG (Visp, Switzerland). This is system with a high glass transition temperature, dry T_g (258°C) and mechanical properties similar to the epoxy (tensile modulus: 3.2 GPa, tensile strength: 88 MPa, strain to failure: 3.2%, G_{IC} in neat resin = 190 J/m^2 [12]). Owing to its higher glass transition temperature the system as a composite matrix is likely to be more brittle and exhibit higher level of thermal stress compared to the host matrix.

(b) The second injected system is toughened: Prime^{TM} 20 is mixed with cross-linked core-shell silicon particles GENIOPERL® P52 (manufactured by Wacker AG) which constist of a polymeric acrylic shell enveloping a siloxane core. This material has been recently examined with some success in the context of polybenzoxazines to modify stress-strain behaviour [13]. The particles are dispersed in the injected resin at a weight fraction of 6%. An average agglomerate size of the powder is 30 - 100 μm with primary particle size of approximately 200 nm [14].

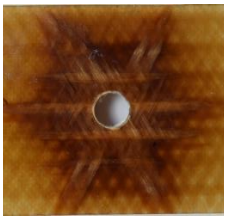
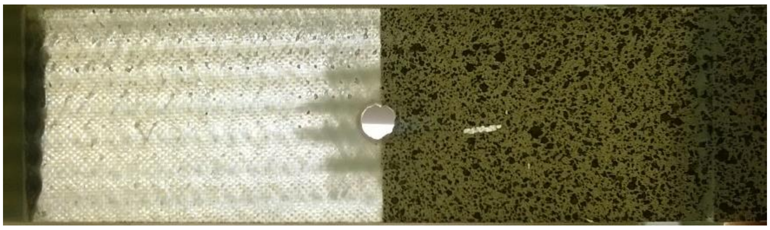
a)  b) 

Figure 1. a) CE patch in the sample with hole (the hole diameter is 6 mm), b) The sample patched with core-shell rubber toughened epoxy (the right side of the samples shows DIC speckling).

Upon the injection the resin was cured under press according to the recommended schedule: for the CE resin: for one hour at 150°C, then ramped to 200°C and dwelled at this temperature for three hours, then post-cured at 260°C for an hour in the oven, for Prime 20 curing at 70°C for 6 hours. The creation of patches was followed by the conventional liquid resin infusion with the flexible tooling. The infused resin was cured at 70°C for 6 hours. The hole was drilled in the centre of the patch of fully infused samples.

2.4. Open hole tests

The sample dimensions for the open hole were defined using the guidelines of ASTM D5766/D5766M – 11 standard [15]: a width of 36 mm, a hole size of 6 mm, a gauge length 100 mm for the reference braid configuration and 200 mm for the steered braid with the variation in braiding angle. The glass-epoxy woven end tabs of 2 mm thickness were used on the span of 50 mm. One half of each sample (down from the centre of the hole) was speckled in black and white pattern to facilitate strain recognition – Figure 1b. 3D Digital Image Correlation (DIC) measurements were conducted using a commercially available DIC Dantec system. The top side of the samples were used to observe damage growth through the transmitted light. At least three (mostly four) samples of each configuration were tested. The sample strength was calculated by normalising the load at failure with respect to the cross-sectional area of the sample remaining after the hole cut in the narrowest location (*i.e.* 30 mm).

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3. Results

The testing revealed clear differences in the mechanical properties of the modified graded and reference samples. Whereas the strength of the samples with CE patches did not show a statistically significant improvement, the material with toughened patches showed 15% increase in strength compared to the non-patched configuration of the same architecture – Figure 1. The fibre steered samples showed apparent improvement in strength both for the toughened and non-toughned configurations. However, this effect is only due to the smaller thickness, and hence cross-sectional area, of the 0°/±45°braid compared to 0°/±60° (1.8 mm vs 2.2 mm). The load at failure for fibre steered and non-steered configuration was approximately the same for the compared matrix/patch system.

Table 1. Strength of graded and reference samples: average, minimum and maximum values (MPa) are shown.

		No patch	**Toughened patch**	**CE patch**
Triaxial ±0//60° braided composite	Average	131.4	151.4	143.8
	Min-max	124.0 – 143.4	140.4 – 163.6	134.1 – 150.2
Triaxial steered 0°/(±60°-±45-±60°) braided composite	Average	164.7	188.7	N/A
	Min-max	163.0 – 166.6	178.9 – 196.0	N/A

The characteristic stress-strain diagrams for the reference and CE-patched materials are shown in Figure 2. The curves show a non-linearity beyond 0.5-0.6% typical for textile glass-epoxy composites and associated with matrix cracking in the off-axis (braiding) yarns. The stiffness of patched and non-patched composites are practically the same. However, the tangent modulus of the patched composites (with both CE and toughened resins) at the damage accumulation stage is slightly higher.

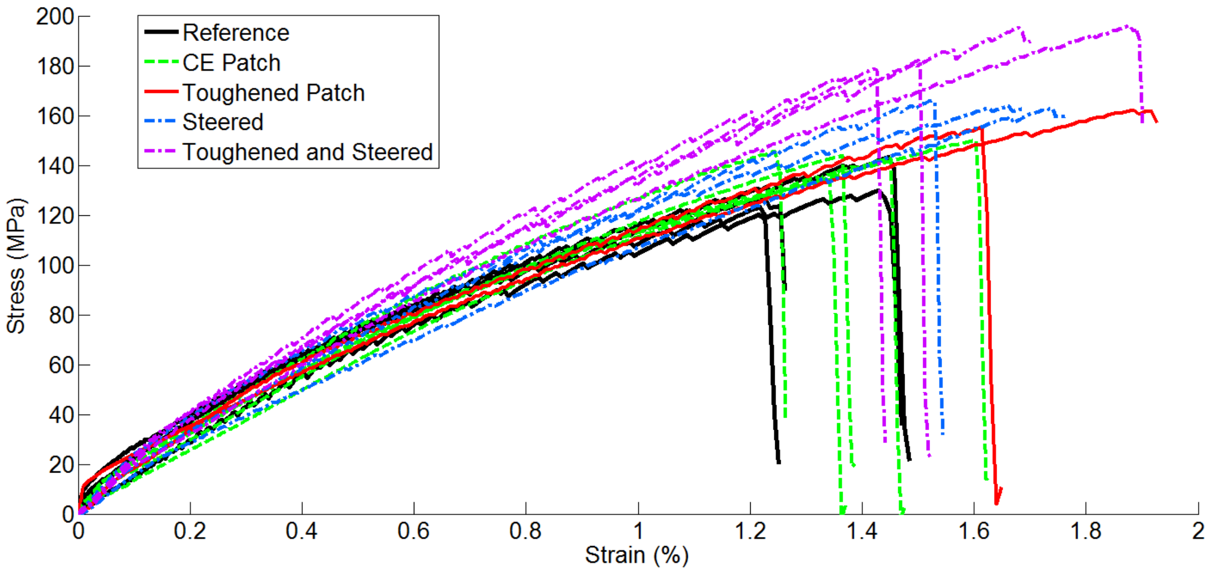

Figure 2. Stress-strain diagrams for all the samples discussed in the study.

3. Discussion

Preliminary testing of patched/graded materials show promising results for two different fibrous architectures: in both the composite strength increased distinctly compared to the reference material. The deformation and damage accumulation mechanisms need to be studied further. However, few observations can be highlighted:

1) The presence of the patches did not cause any noticable damage associated with the interface between the injected and the infused resins.
2) The presence of rubber particles did not reveal itself in a stiffness reduction, but had a clear positive effect on prolonging the bearing capacity of the material and led to an increase in both the strength and the strain to failure.
3) No difference in fracture zone size and type between patched and non-patched samples can be immediately revealed.
4) The load bearing capacity of the fibre steered samples did not drop down even though (a) the areal density of preform around the hole and hence, the thickness were 18 % lower than in the reference sample and roughly comparable to the thickness of one ply, (b) the thickness variation along the sample length should have caused an additional bending stress in the inlay yarns.
5) The fibre steering appeared to have a significant effect on composite damage accumulation mechanism. Local steering of the yarns led to much higher crack density away from the hole than in the hole vicinity – Figure 3.

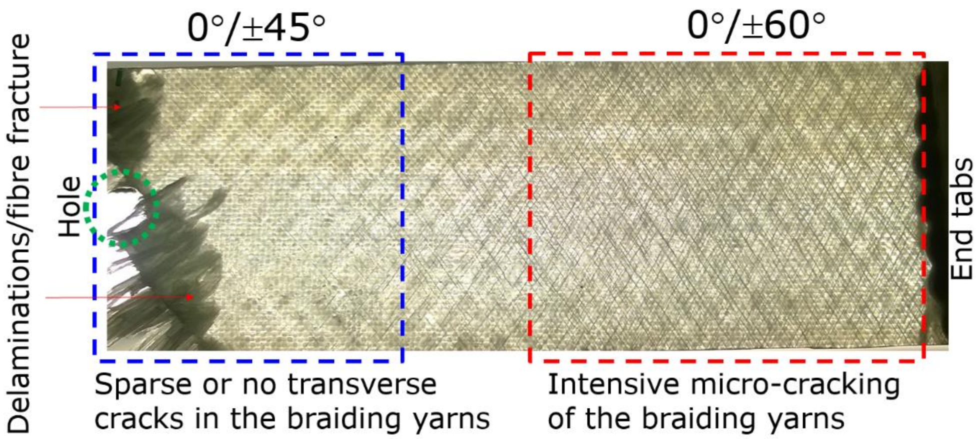

Figure 3. Fractured steered braided composite in transmitted light showing variation in transverse matrix cracking over the sample length and failure zone

3. Conclusions

The study showed a number of promising results. It proved that combining resins in one composite system may have a clear positive effect on composite properties, even for those dominated by fibres. More needs to be done in understanding the exact mechanism of redistributing the load and failure around matrix graded zones. However, it is clear that matrix grading has perspectives in achieving tougher and more resilient composites. The key concept enabling matrix grading is the new 3D Liquid Resin Print, which proved to be an efficient method of incorporating large fraction of additives. The presence of toughener around the stress concentrator, for instance, appeared to have a pronounced effect on composite performance. The filtration mechanism around the injection zone provided a natural mechanisms of grading and smooth transition between dissimilar matrices. Steering of fibre through braiding grants another effective tool in redistributing the load flow and dictating the damage accumulation mechanisms. It was shown that with an effective mechanisms of load transfer a reduction in thickness and areal density of the composite did not compromise the composite strength

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and left ~20% of laminate vacant for further addition of reinforcing plies and strength increase without impacting on laminate thickness.

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