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Toughening and self-healing of epoxy matrix laminates using mendable polymer stitching

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ABSTRACT

This paper presents an experimental study into a new type of stitched fibre–polymer laminate that combines high interlaminar toughness with self-healing repair of delamination damage. Poly(ethylene-*co*-methacrylic acid) (EMAA) filaments were stitched into carbon fibre/epoxy laminate to create a three-dimensional self-healing fibre system that also provides high fracture toughness. Double cantilever beam testing revealed that the stitched EMAA fibres increased the mode I interlaminar fracture toughness (by ∼120%) of the laminate, and this reduced the amount of delamination damage that must subsequently be repaired by the self-healing stitches. The 3D stitched network was effective in delivering self-healing EMAA material extracted from the stitches into the damaged region, and this resulted in high recovery in the delamination fracture toughness (∼150% compared to the original material). The new self-healing stitching method provides high toughness which resists delamination growth while also having the functionality to repeatedly repair multiple layers of damage in epoxy matrix laminates.

1. Introduction

A long-standing problem with fibre reinforced polymer laminates is their susceptibility to delamination damage and matrix cracking, which are usually repaired by removing the damaged material and replacing with new laminate, e.g. [1]. Self-healing offers the possibility of repairing in-service damage to composite materials at lower cost, within shorter time, and with higher mechanical properties than conventional repair methods, e.g. [2,3]. Here the term "repair" refers to the process of recovering the mechanical properties of damaged composites. There are many types of self-healing composite materials, which can self-repair either autonomously or under external intervention (such as thermally activated self-healing that is triggered by heating). Self-healing can be achieved using capsules [4,5] or microvascular network [6–9] to deliver the necessary healing agent. A promising alternative to the above two self-healing concepts are mendable polymers [10–19], which refer to a class of polymeric systems that can revert to either their monomeric, oligomeric or non-cross-linked state [20]. Self-healing by mendable polymers is achieved by reversible covalent and/or non-covalent bonds [20], under the action of external stimulus.

Poly(ethylene-*co*-methacrylic acid) (EMAA) is a mendable thermoplastic that has recently been used to heal cracks in epoxy resin and delamination and ballistic impact damage to epoxy matrix laminates when activated by heat [13–16,19]. The EMAA is used in the form of dispersed particles in epoxy resin or as particles or fibre mesh in epoxy matrix laminates [14,15,18,19]. Self-healing is triggered by heating which activates an acid–hydroxyl condensation reaction between the EMAA and epoxy phases [21]. The reaction produces water vapour, which forms small high-pressure bubbles that force the EMAA melt into the damaged region, where it solidifies and heals upon cooling. The EMAA adheres strongly (via covalent and hydrogen bonding) with the epoxy resin, resulting in high recovery to the fracture toughness of the healed material [14,15,18,19]. EMAA is not consumed during the condensation reaction process, and therefore it can be reused for repeated self-healing operations.

A limitation of the current approach to repair of laminates using EMAA (and other thermoplastic additives) is that healing can only occur close to where the thermoplastic particles or fibres are located. Damage to laminates often involves interply and intraply cracking in multiple ply layers and therefore it is necessary to locate the self-healing agent at every ply interface, although this has the adverse effects of reducing the in-plane mechanical properties and lowering the average fibre volume content. An alternate approach, which has not been previously investigated, is to insert EMAA filaments in the through-thickness direction using stitching

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to create a three-dimensional self-healing fibre network that can repair multiple layers of damage.

In this paper a new type of self-healing composite material containing a three-dimensional thermoplastic (EMAA) fibre system created by stitching is evaluated. The use of stitching to insert the self-healing fibres provides a simple and practical means of achieving the synergistic combination of interlaminar toughening and self-healing of epoxy matrix composites. The interlaminar toughness, self-healing efficiency, and repeatability of the self-healing process were experimentally determined.

2. Experimental

2.1. Preparation of laminates with and without self-healing stitched networks

Carbon fibre/epoxy composite prepreg (VTM 264, Advanced Composites Group) with a $[0°/90°]_{3s}$ ply stacking sequence was stitched in the through-thickness direction to create a 3D self-healing network of EMAA fibres. The design of the stitched network is illustrated in Fig. 1. The stitched network was designed to provide a synergistic combination of interlaminar toughening (via crack bridging) and self-healing of damage at any location in the through-thickness direction. The EMAA stitches supplied self-healing material through each row of stitches, as well as the interconnected stitched fibres, which were able to draw upon additional self-healing agent to the damaged region.

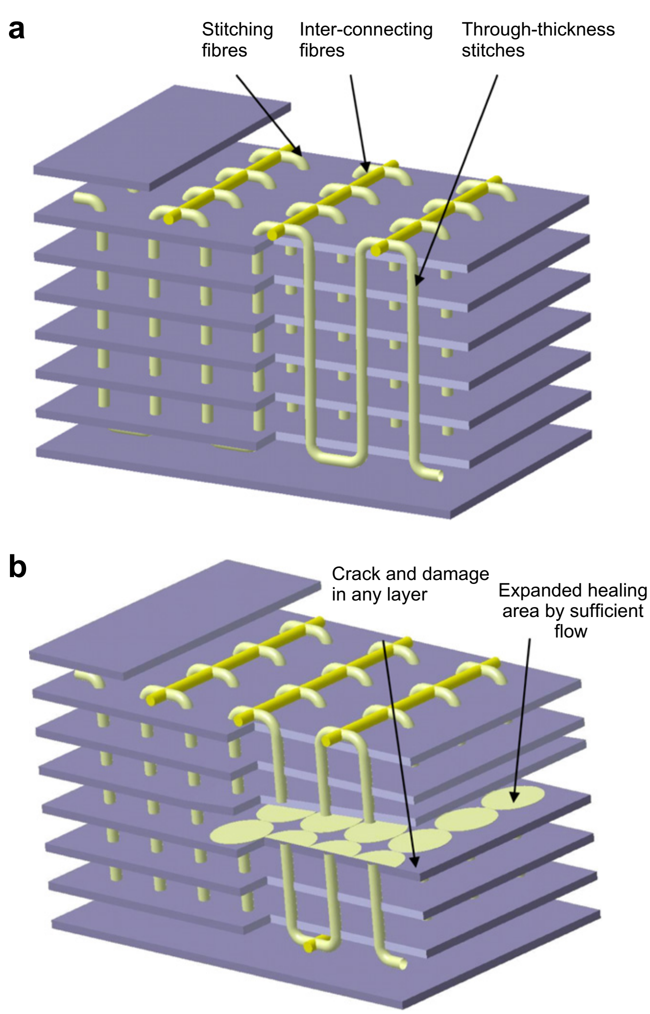

Fig. 1. Schematic representations of the 3D stitched network (a) before healing and (b) after healing in the carbon fibre/epoxy laminate.

The stitching fibre used in the self-healing network was 1.5 mm diameter EMAA filament (Aldrich Chemical Company), and it was sewn manually into the uncured carbon fibre/epoxy prepreg. The areal density of EMAA stitches at the mid-plane of the laminate (which was where delamination crack growth occurred) was 1 stitch/cm^2, and this was equivalent to an areal fraction of 1.8%.

After stitching, two prepreg plies were placed over the stitched network to prevent the potential loss of EMAA from the laminate during high temperature curing and subsequent thermal self-healing. A carbon fibre/epoxy laminate without stitches but with the same ply stacking sequence to the EMAA-stitched laminate was produced as the control (bench-mark) material. The unstitched and stitched laminates were cured inside an autoclave at 120 °C and 620 kPa for 1 h. The melting temperature of EMAA is 83 °C, and therefore the stitches melted during curing. However, microstructural examination of the laminate after curing revealed that the physical integrity of the stitched network was not changed during curing.

2.2. Interlaminar fracture toughness testing and self-healing treatment

The mode I interlaminar fracture toughness properties of the unstitched and stitched laminates were determined using the double cantilever beam (DCB) test in accordance with ASTM D5528-01. The dimensions of the DCB specimens and the EMAA stitch pattern are shown in Fig. 2. Teflon film was inserted between the mid-thickness plies of the DCB specimens before curing to create a 50 mm long pre-crack. The pre-cracked end of the DCB specimens were loaded at a crosshead (crack opening) displacement rate of 2 mm/min. The delamination crack grew along the specimen mid-plane in short increments (5–10 mm), and the applied load, crack opening displacement and crack length values were recorded at each increment to determine the mode I strain energy release rate (G_I). The DCB tests were terminated when the crack had propagated ~60 mm, and this distance was sufficient to fully develop a stitch bridging traction zone along the delamination in the self-healing laminate as well as to assess the efficiency of the stitched network to heal long cracks.

After fracture testing, the DCB specimens were heated to 150 °C for 1 h to activate self-healing of the EMAA stitches. After healing, the DCB stitched specimens were consolidated under low-pressure compression (20 kPa for 10 min) at room temperature. The specimens were then retested using the DCB method to measure the repair efficiency of the stitched laminate, as indicated by the level of restoration of the interlaminar fracture toughness. This process was repeated twice to assess whether the stitches can heal damage and restore toughness for multiple self-healing cycles.

From the recorded load versus crack opening displacement data, values of the mode I strain energy release rates were computed using the corrected beam theory derived by Hashemi et al. [22]:

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

where P is the applied load, δ is the crack opening displacement (COD), b is the specimen width, a is the crack length and $|\Delta|$ is the crack length correction factor which is determined to be the X-axis intercept of the plot of the cube root of compliance C (=δ/P) versus the crack length a. The effects of large displacements and the stiffening caused by the metal block are accounted for by the correction factors F and N [22].