THERMOPLASTIC COATING ON CARBON FIBER FOR THE DESIGN OF SUSTAINABLE COMPOSITE MATERIALS

Mónica Peñas Caballero[a], Enrico Chemello[b], Antonio Mattia Grande[b], Marianella Hernández Santana[a], Raquel Verdejo[a], Miguel Ángel López-Manchado[a]

[a]: Institute of Polymer Science and Technology (ICTP-CSIC) (Madrid, Spain) – mpcaballero@ictp.csic.es
[b]: Department of Aerospace Science and Technology, Politecnico di Milano, (Milan, Italy)

Abstract:

Self-healing carbon fiber reinforced plastics have been developed through the deposition of poly(ethylene-co-methacrylic acid) (EMAA) nanoparticles on the fiber surface, by aerography. EMAA nanoparticles are homogeneously distributed, showing a strong adhesion to the fiber. EMAA coating improves the fracture toughness, G_{IC} and provides self-healing capacity to the material. The healing efficiency decreases gradually with the number cycles, but retains more than 40% after a third cycle.

Keywords: Self-healing; Thermoset; Thermoplastic; Coating.

1. Introduction

Fiber reinforced plastics (FRP) have excellent properties, such as high fatigue and corrosion resistance, good dimensional stability and light weight, as well as an excellent strength-to-weight ratio. As a result, they have found widespread use in different sectors. In 2020, the FRP market was valued at €60 billion and is expected to grow to €96 billion in 2026 [1]. However, this growth implies an increase in the waste generated at the end-of-life of the products derived from these materials. In order to overcome this situation, research lines are emerging focusing on the design of sustainable FRPs. Different strategies are being considered, such as the use of thermoplastic matrices that can be easily recycled; the substitution of synthetic fibers by natural fibers (as flax, hemp or jute); or conferring self-healing capability to the FRP, among others.

Currently, there are different possibilities to address the self-healing strategy, such as the incorporation of capsules, vascular systems, or thermoplastics into epoxy matrices; being the latter the most industrially scalable. Poly (ethylene-co-methacrylic acid) (EMAA) is one of the prefer thermoplastic that has shown high healing efficiency due to its high coefficient of thermal expansion and its covalent cross-linking with the epoxy resin. Its healing mechanism has been ascribed to a pressure-delivery mechanism [2]. As the temperature increases, the EMAA melts and flows, driven by high-pressure gas-filled bubbles, produced by the reaction of the acid group of the thermoplastic with the hydroxyl group of the resin [3]. EMAA has been introduced into FRPs as discrete particles in the epoxy resin, and as sheets between the carbon fiber plies or as filaments that stitch carbon fiber yarns together. In this work, we will incorporate EMAA into the fiber by using a spray coating method, a versatile and easily scalable technique. The self-healing capability will be studied through the recovery of the interlaminar fracture toughness.

  doi:10.5075/epfl-298799_978-2-9701614-0-0

2. Materials and Methods

2.1 Materials

The used carbon fiber was unidirectional UD 12k, 340 g/m^2 and 45 µm supplied by *INP96*. The matrix was an epoxy resin Resoltech 1050/1053s, from Resoltech consisting of diglycidyl ether of bisphenol F (DGEBF 50-80 %), diglycidyl ether of bisphenol A (DGEBA, 10-40 %) and 1,6 hexanediol diglycidyl ether, with a hardener of polioxialcalinoamine/n-aminoetilpiperacine/dietiletriamine, at specific resin:hardener ratio of 100:35 in parts by weight. According to the supplier specifications, the curing reaction is carried out at 60 ° for 16 h. As healing agent, we used pellets of poly (ethylene-co-methacrylic acid) (EMAA) from Sigma-Aldrich.

2.2 Sample preparation

The coatings were prepared following three steps: 1) dissolution of the thermoplastic, 2) cooling, and 3) spraying and drying. In step 1, EMAA was dissolved in THF at a concentration of 0.012 g/ml; the solution was heated at 60 °C (below the boiling point of the THF) with stirring and assisted by an ultrasonic bath. Once the EMAA is completely dissolved, it is cooled in an ice bath and the solution turns milky white as a result of the formation of nano-sized particles [4]. Finally, the solution was sprayed onto the fiber surface to the required concentration (10 wt.%) and dried at 65 °C in the oven to remove the solvent, until the weight remained unchanged.

The coated fibers were placed unidirectionally and 14-layer laminates were prepared by vacuum-assisted resin infusion (VARI). The laminates were heated up to 60 °C and kept for 16 h for curing. The laminates were post-cured (150 °C/2 h) in the press to promote the compaction of the layers. The samples were cut on a Neurtek Brillant 220 precision cutting machine.

2.3 Characterization

The uncoated and EMAA-coated carbon fibers were observed with a Scanning Electron Microscope (SEM), Phillips, model XL30 with a tungsten filament and an accelerating voltage of 25 kV, after sputter-coating with gold. The healing fracture surface of the laminates was observed with an Optical Microscope Olympus, model DSCX1000.

The interlaminar fracture toughness properties under mode I static and fatigue loading were measured using the double cantilever beam (DCB), ASTM D55S8. The specimen's dimensions were 100 x 20 mm with a pre-crack of 40 mm. Two metallic tabs were bonded to the outer surface of the DCB specimen using a two-component epoxy adhesive (3M Scotch-Weld DP110). The composite was measured by applying a monotonically increasing crack opening displacement speed of 1 mm/min to the pre-cracked end of the DCB specimen using MTS 858 mini Bionix. Mode I interlaminar fracture toughness (G_{IC}) was calculated by the modified beam theory (MBT) method, using Load (N), displacement (mm), crack length (mm), specimen width (mm) and specimen thickness (mm). After testing, the DCB specimens were healed by heating them at 150 °C for 120 min. The healing efficiency was improved by applying pressure to the delaminated composite to minimize the volume of open crack that will be infiltrated by the thermoplastic. The cured samples were then cooled to room temperature and retested under the same conditions. The self-healing efficiency was calculated by:

η (%) = ($f^{repaired}/f^{virgin}$) x 100, where f is the studied property, peak load or G_{IC}.

  doi:10.5075/epfl-298799_978-2-9701614-0-0

3. Results and discussion

3.1 Coating

The SEM micrographs in Figure 1 show the uncoated and EMAA-coated carbon fibers. The EMAA nanoparticles uniformly and homogeneously coat the fiber, due to their large surface area. In addition, it was possible to manipulate the coated fibers without damaging the coating evidencing the good adhesion to the fiber surface. Thus, spray coating increases the roughness of the fiber and provides a scalable procedure to introduce the EMAA nanoparticles.

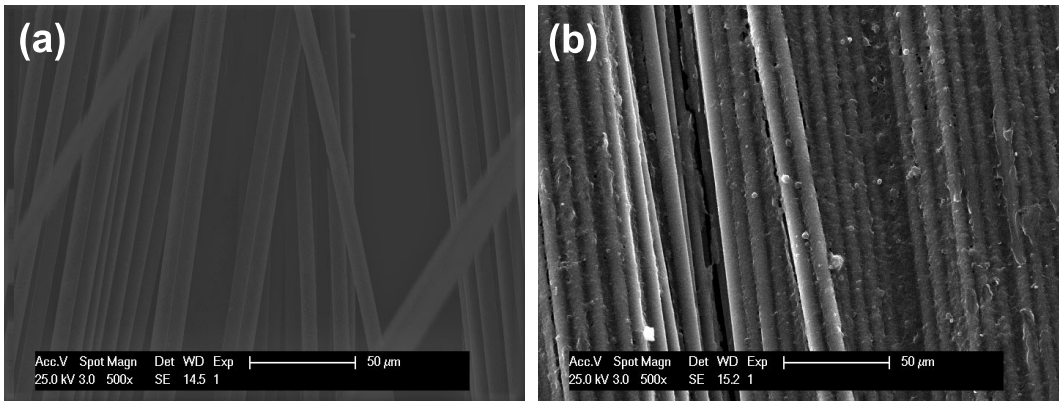

Figure 1. (a) Uncoated carbon fibers; (b) EMAA-coated carbon fibers.

3.2 Mode I Double Cantilever Beam testing

The effect of EMAA coating on the mode I interlaminar fracture toughness of the composite material is shown in Table 1. The peak load and G_{IC} values follow an opposite trend to that observed in the flexural tests, as the incorporation of EMAA leads to an increase in the properties. This effect may be due to the enhanced interfacial adhesion between the fiber and the matrix, thanks to the presence of the thermoplastic on the surface of the fiber. This behavior has been previously reported in the literature for mode I and mode II interlaminar fracture toughness [5,6].

Table 1. Peak load and interlaminar strength toughness of laminates with uncoated and EMAA-coated fibers.

Sample	Peak Load (kN)	G_{IC} (J/m^2)
Uncoated	104 ± 6	1070 ± 80
EMAA-coated	150 ± 30	2300 ± 300

The samples were re-measured after healing at 150 °C for 2 h under pressure. Figure 2 shows the repair efficiency based on the recovery of peak load and mode I interlaminar fracture toughness, after several healing cycles. Specimens achieved a mean peak load healing efficiency of 63 % in the first cycle, 54 % in the second and 43 % in the third one. The decrease in self-healing efficiency with the number of cycles is caused by the fact that the EMAA reactive compound is depleted in the reaction cycles and the crack surfaces become more irregular. However, this is quite significant as some studies in the literature only report values for a first

  doi:10.5075/epfl-298799_978-2-9701614-0-0

healing cycle [7]. The fracture toughness efficiency (44 %, 24 % and 18 %) was lower if compared to that reported in the literature [8]. This reduction and discrepancy with the peak load efficiency could be explained by the fact that the G_{IC} calculations assume a linear elastic behaviour in rigid materials, but the EMAA is ductile [9]. Nevertheless, these values are significant and decrease by only 20 % between the first and second cycle.

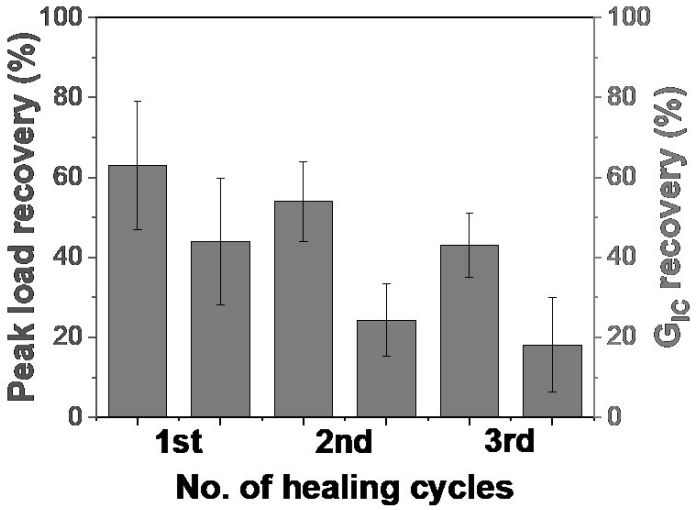

Figure 2. Peak load recovery (left) and GIC recovery (right) of EMAA-coated FRP after several healing cycles.

3.3 Fracture surface morphology

Optical microscopy was used for visual characterization of the healing process. Figure 3(a) shows a FRP with a crack width of approximately 50 µm, resulting after flexural testing. After heating his sample in the press at 150 °C for 2 h, the thermoplastic flows to the outside and appears to protrude from the crack (Figure 3(b)). Thus, the EMAA is capable of filling and sealing the crack. Previous studies have shown that EMAA remains strongly adhered to the matrix, and after cooling, it forms bridging stitches between the two crack surfaces [6,10].

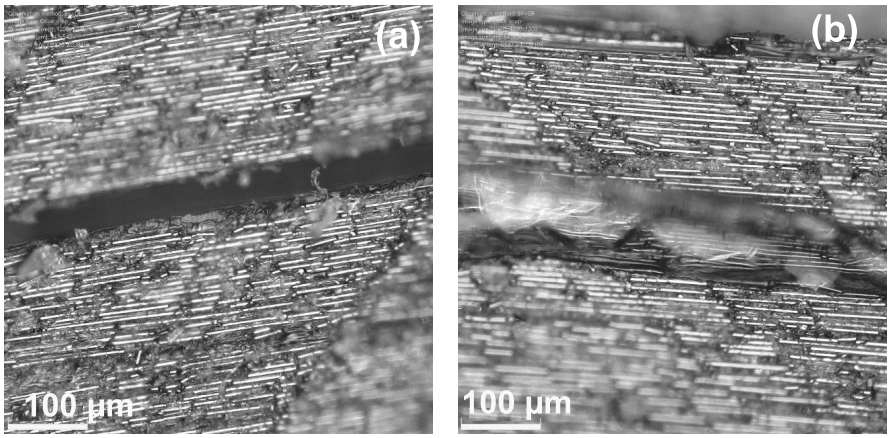

Figure 3. Micrographs of the (a) initial and (b) healed crack in an EMAA-coated FRP.

  doi:10.5075/epfl-298799_978-2-9701614-0-0

4. Conclusions

In this work, self-healing FRP composites were developed by coating carbon fibers with EMAA at 10 wt.%. The materials showed an improved interlaminar fracture toughness, and a good healing capability. After three healing cycles, the material kept a repair efficiency of more than 40%. These results are promising to consider that the deposition of EMAA on carbon fiber surface by aerography is a simple and easily scalable method, that enables the incorporation of high quantities of thermoplastic healing agent.

Acknowledgements

This research was funded by the Agencia Estatal de Investigación (AEI) through grants PID2019-107501RB-I00, RYC-2017-22837 and MAT2016-81138-R. Mónica Peñas-Caballero thanks for a Predoctoral contract (BES-2017-079899).

5. References

1. Fiber-Reinforced Plastic Market Research Report by Material, by Application, by Industry, by Region - Global Forecast to 2027 - Cumulative Impact of COVID-19 [cited 2022 Feb 21]. Available from: https://www.reportlinker.com/p06160105/Fiber-Reinforced-Plastic-Market-Research-Report-by-Material-by-Application-by-Industry-by-Region-Global-Forecast-to-Cumulative-Impact-of-COVID-19.html?

2. Meure S, Varley RJ, Wu DY, Mayo S, Nairn K, Furman S. Confirmation of the healing mechanism in a mendable EMAA-epoxy resin. European Polymer Journal 2012; 48(3):524–31.

3. Pingkarawat K, Wang CH, Varley RJ, Mouritz AP. Self-healing of delamination cracks in mendable epoxy matrix laminates using poly [ethylene-co-(methacrylic acid)] thermoplastic. Composites Part A: Applied Science and Manufacturing 2012; 43(8):1301–7.

4. Huang HC, Zacharia NS. Layer-by-layer rose petal mimic surface with oleophilicity and underwater oleophobicity. Langmuir 2015; 31(2):714–20.

5. Ladani RB, Nguyen ATTT, Wang CH, Mouritz AP. Mode II interlaminar delamination resistance and healing performance of 3D composites with hybrid z-fibre reinforcement. Composites Part A: Applied Science and Manufacturing 2019; 120:21–32.

6. Pingkarawat K, Wang CH, Varley RJ, Mouritz AP. Healing of fatigue delamination cracks in carbon-epoxy composite using mendable polymer stitching. Journal of Intelligent Material Systems and Structures 2014; 25(1):75–86.

7. Azevedo A, Fernandez F, Fábio S, Ferreira EPC, Daniel J, Melo D, et al. Addition of poly (ethylene-co-methacrylic acid) (EMAA) as self-healing agent to carbon-epoxy composites. Composite Part A 2020; 137:106016.

8. Shanmugam L, Naebe M, Kim J, Varley RJ, Yang J. Recovery of Mode I self-healing interlaminar fracture toughness of fiber metal laminate by modified double cantilever beam test. Composites Communications 2019; 16:25–9.

  doi:10.5075/epfl-298799_978-2-9701614-0-0 published under CC BY-NC 4.0 license

9. Meure S, Furman S, Khor S. Poly [ethylene-co-(methacrylic acid)] healing agents for mendable carbon fiber laminates. Macromolecular Materials and Engineering 2010; 295(5):420–4.

10. Pingkarawat K, Bhat T, Craze DA, Wang CH, Varley RJ, Mouritz AP. Healing of carbon fibre-epoxy composites using thermoplastic additives. Polymer Chemistry 2013; 4(18):5007–15.

  doi:10.5075/epfl-298799_978-2-9701614-0-0