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R.J. da Silva

T.H. Panzera



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## Effect of addition of thermoplastic self-healing agent on fracture toughness of epoxy

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**Keywords:** self-healing, epoxy, thermoplastic, fracture

**Abstract:** Self-healing agents have the potential to restore mechanical properties and extend service life of composite materials. Thermoplastic healing agents have been extensively investigated for this purpose in epoxy matrix composites due to their strong adhesion to epoxy and their ability to fill in microcracks. One of the most investigated thermoplastic additives for this purpose is poly(ethylene-co-methacrylic acid) (EMAA). Despite the ability of thermoplastic healing agents to restore mechanical properties, it is important to assess how the addition of thermoplastic healing agents affect properties of the original epoxy material. In this work, EMAA was added to epoxy resin and the effect of the additive on fracture toughness of epoxy was evaluated. Results indicate that although added in low concentrations, EMAA can affect fracture toughness.

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### 1. Introduction

Polymer matrix composites have limitations related to matrix cracks and delamination due to low ductility and strength of thermoset polymer matrices [1,2]. Additionally, environmental aging [3] due to exposure to various environmental factors such as humidity, UV radiation and temperature cycles, as well as exposure to continuous fatigue may affect composite properties and impair their safety and reliability as structural components. Repair alternatives of laminates may include removal of damaged area and patches, taper sanding or scarf repair [4], which are however not effective for repairing microcracks. As an attempt to heal microcracks, one promising approach investigated in the last years is the development of materials capable of self-healing.

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The addition of thermoplastics as healing agents is an intrinsic self-healing technique that allows multiple healing events. Mechanical properties of the composite may be partially recovered, when heat is employed to increase mobility of the thermoplastic additive, which fills in microcracks in the matrix. Poly(ethylene-co-methacrylic acid) (EMAA) has been one of the most studied thermoplastic healing agents. Several reports in the literature demonstrate the potential of EMAA as a healing agent in epoxy and epoxy composites due to observed healing efficiencies [e.g. 5-8].

Although thermoplastics have been employed as toughening agents in epoxy resins and many studies show promising results for their use as healing agents, further understanding related to the influence of the healing additive on original properties of the epoxy material is necessary. A thermoplastic healing agent (poly-bisphenol-A-co-epichloridrine) dissolved in epoxy showed reduction in  $K_{IC}$  and  $G_{IC}$  in compact tension tests as compared to the neat resin when 20 wt.% of the healing agent was added to epoxy, although the system proved capable of recovering between 50% and 70% of its pre-fracture strength after healing [9]. Another study shows that mode I interlaminar fracture toughness ( $G_{IC}$ ) of carbon-epoxy laminates containing EMAA was about the same or lower than the toughness of the control material, revealing there was no beneficial toughening effect when the EMAA is in the original condition (as either fibres or particles) in the material [6]. In the same study, it was also observed that EMAA promoted unstable delamination crack growth [6].

In this context, understanding the effects of the addition of thermoplastic on the original material properties is necessary to evaluate its use as a self-healing agent. In this work, fracture toughness of neat epoxy and epoxy modified with the thermoplastic healing agent EMAA is investigated.

## 2. Methodology

Plates of 25 cm x 25 cm x 5 mm of neat epoxy and epoxy modified with addition of thermoplastic were manufactured using epoxy resin EPIKOTE RIMR 135 and hardener RIMH 137 from Hexion at stoichiometry ratio 100:30. Poly (ethylene-co-methacrylic acid) (EMAA) from Sigma-Aldrich, a random copolymer with 14.5% – 15.5% of methacrylic acid, was used as thermoplastic to produce the modified epoxy plate.

Thermoplastic pellets were cryogenically ground and the particles were sieved with mesh size between 150  $\mu\text{m}$  and 315  $\mu\text{m}$ . Two different contents of thermoplastic particles in epoxy were investigated: 2 g of EMAA per 100 g of resin (1.96 wt.%) and 5g of EMAA per 100 g of resin (4.75 wt.%). Considering the density values provided by the manufacturers, the equivalent percentage by volume (vol.%) was also calculated. The two components used have density values of 1.15  $\text{g}/\text{cm}^3$  and 0.91  $\text{g}/\text{cm}^3$ , for epoxy and EMAA respectively, so the percentages by volume are 2.39 vol.% and 5.76 vol.%.

Epoxy plates with EMAA particles were produced by mixing particles into epoxy resin prior to addition of the hardener. Resin and particles were manually mixed for 15 min and, after this first mixing, hardener was added and mixed for additional 15 min. Then, the mixture was held at room temperature for 2 h and, after that, gently mixed before molding. The hold step was added in order to minimize particles flotation during the cure process, since the viscosity of the mixture increases with time due to crosslinking. A vacuum oven was used for degasification after every mixing step. Two epoxy-EMAA plates were produced with different concentrations of thermoplastic, as

shown in Table . Samples were named according to EMAA content and particle size and a neat epoxy plate was manufactured using the same processing parameters to provide a basis for comparison.

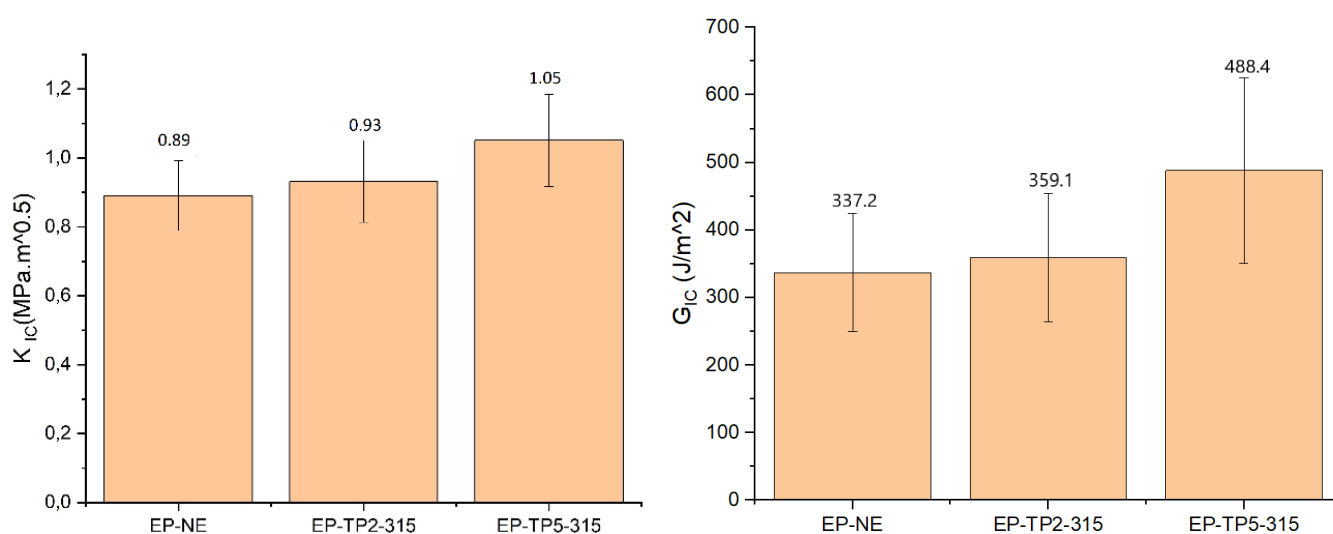
**Table 1.** Overview of samples produced.

Sample	EMAA content	EMAA particles size ( $\mu\text{m}$ )
EP-NE	-	-
EP-TP2-315	2 g per 100 g epoxy	150 to 315 $\mu\text{m}$
EP-TP5-315	5 g per 100 g epoxy	150 to 315 $\mu\text{m}$

All plates were pre-cured for 48 h at room temperature and cured for 15 h at 80 °C in a 5 mm thickness stainless-steel mold. Compact tensile (CT) samples were cut using a diamond saw and machined using a computerized controlled (CNC) drilling machine for final dimensions, according to ISO 13586:2000 for evaluation of fracture toughness. For modified epoxy plates, a 3D X-ray Computed Tomography (XCT) was used to investigate EMAA content and particle sizes. Samples taken from the produced plates were scanned using a commercial ZEISS Xradia 620 Versa X-ray microscope.

### 3. Results and Discussions

Results for fracture toughness ( $K_{IC}$  and  $G_{IC}$ ) are shown in Figure 1:



**Fig. 1.** Results for fracture toughness tests for neat epoxy (EP-NE) and epoxy modified with thermoplastic particles (EP-TP2-315 and EP-TP5-315). (a)  $K_{IC}$  and (b)  $G_{IC}$ .

Results suggest that both critical stress intensity factor and critical energy release rate are increased when thermoplastic material is added, with the increase mostly within the scatter band. Thus, for the conditions investigated in this study, the addition of thermoplastic was successful in increasing fracture toughness.

XCT results suggest that a flotation of particles occurred during the cure process, resulting in a gradient in concentration of particles along the length of the plate, which may have contributed to scattering of results.

#### 4. Conclusions

Due to the high crosslink density of epoxy resin, the material is very brittle and modification of resins with thermoplastic healing agents for the development of self-healing materials should be investigated regarding alteration in fracture toughness. In this work, results suggest that the addition of EMAA thermoplastic may increase  $K_{IC}$  and  $G_{IC}$  in compact tensile tests, with potential also as a toughening agent to epoxy. Further investigations will be focused on crack growth studies.

#### Declaration of Competing Interest

The authors declare no conflict of interest.

#### CRediT author statement

**AP Cysne Barbosa:** Conceptualisation; Methodology; Formal Analysis; Writing – original draft. **A Azevedo do Nascimento:** Methodology; Formal analysis. **L Pavasaryte:** Methodology, Formal analysis. **V Trappe:** Resources; Supervision, Writing - review. **JD Diniz Melo:** Resources, Writing – review.

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