EXPERIMENTAL INVESTIGATION ON SELF-HEALING EFFICIENCY OF DOPED FIBER REINFORCED PLASTICS WITH PET MICRO-PARTICLES

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In the current investigation, an established resin was modified with Polyethylene terephthalate (PET) micro-particles and used for the fabrication of Carbon Fibre Reinforced Plastic laminas (CFRPs). The materials were tested in interlaminar fracture and compared to the reference one. Restoration of the fracture properties of the mendable composites following healing of delamination damage was also assessed. Additionally DMA tests were conducted in order to identify the post curing effect as well as the better adhesion of the thermoplastic particles with the matrix. Finally the cross section was examined using optical microscopy.

Keywords: CFRPs, PET micro-particles, fracture mechanics, damage tolerance, self-healing efficiency.

1. Introduction

During the last decades, the use of composites in aeronautics, wind energy, automotive, and other mechanical engineering applications has been significantly increased. However, composites are prone to in-service induced matrix cracks and delamination, which both regardless their size lead to rapid degradation of the material performance. Conventional repair techniques of composites are – among their other weak points – not appropriate for the repair of micro-defects deep

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inside the material. Thus, the widespread utilization of composites in primary components is blocked. An alternative approach that aims to face the problems of conventional repair methods is self-healing materials [1, 2]. This technology although, has not been integrated yet to high performance composites, promises to reduce the operational and maintenance cost and to increase the damage tolerance of composite structures.

A self-repaired structural composite consists of a matrix which is modified with an agent (healing agent) which takes the responsibility to implement the healing functionality to the parent (non-healable) material. Based on existing literature, a promising way to implement the healing functionality into a composite material is via modification of its thermoset matrix with thermoplastics. A wide range of thermoplastics have been utilized as healing agents into FRPs [3-8]. Zako and Takano [3] achieved to restore part of the stiffness and the fatigue performance, using a particle-type thermosetting epoxy adhesive as additive into GFRPs. Hayes et al. [4] modified epoxy resin with the linear chain polymer PBE and achieved impact performance restoration in composites. A variety of studies has been conducted about the modification of FRPs with the co-polymer EMAA [5, 6]. This semi-crystalline thermoplastic was proven to be able to recover a great amount of the mode I interlaminar fracture toughness in CFRPs. In addition, the potential self-healing ability of some other thermoplastics, reactive or not with the epoxy matrix, such as PEGMA, EVA and ABS [7] has been examined. Very recently Selver et al. [8] investigated the healing potential of composites consisting of glass/polypropylene hybrid yarns and epoxy resin.

All these studies cultivate an interest for exploring the healing potential of some non-studied thermoplastics. The scope of the present work is the use of Polyethylene terephthalate (PET) micro-particle additives into conventional woven CFRPs in order to investigate their healing capability. This study is presenting an overview of the role of the PET particles in the fracture behaviour and the ability to heal the cracks in CFRPs. The reference as well as the modified composites was subjected to mode I and mode II interlaminar fracture toughness tests. After the interlaminar fracture tests, the modified samples were subjected to heating under loading in order the cracks to be healed. DMA tests were conducted for the reference and the PET modified composites before and after the application of the healing process. Finally optical microscopy examination led to qualitative conclusions regarding the involved failure mechanisms.

2. Materials and methods

2.1. Materials and specimens preparation

The epoxy system that was utilized in this investigation was the L/ EPH 161 (resin/hardener) and was supplied by R&G, Germany. The Polyethylene terephthalate (PET) was supplied in the form of small pellets by NGP, Greece. Using a powdering machine the small pellets were placed into Nitrogen and converted into micro-particles with average size of 80-140 μm according to SEM examinations (Fig. 1b). Specimens of 16 plies, of woven carbon fiber laminas were manufactured for this investigation, using the polymeric system mentioned earlier. Woven carbon fabric was supplied by Sigma Aldrich, Germany having a specific weight of 280 gr/m^2.

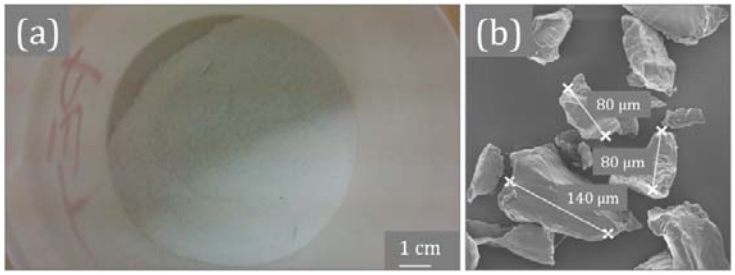
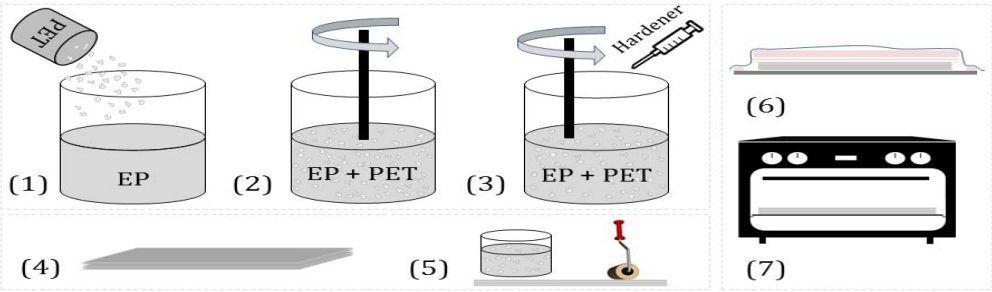


Fig. 1. The PET thermoplastic healing agent utilized in the current study (a) in powder form and (b) zoom in micro-scale

The matrix modification, for the selected material system has been made by the dispersion of the PET particles at a quantity of 7% wt. into the matrix material. The dispersion was carried out by mechanical shear mixing at room temperature. Modified and unmodified matrices were used to manufacture carbon reinforced laminated plates. A polytetrafluoroethylene (PTFE) film of 12 μm thickness was used as a crack initiator at the mid-thickness plane of both types of plates. The preparation process of CFRP plates was that of liquid impregnation technique. Following lay-up, the laminates were vacuum bagged and cured for 24 h at ambient temperature, followed by a post-cure regime of 60 °C for 10 h, as suggested by the resin manufacturer. The manufacturing process is schematically presented in Fig. 2.



(1) Addition of PET particles into the epoxy. (2) Mixing by hand for 30 min. (3) Addition of the curing agent and mixing. (4) Cutting of the CF reinforcing layers. (5) Fabrication of the baseline and modified CFRPs via the wet hand lay-up method. (6) Vacuum bagging of the wet laminates. (7) Curing (at room temperature for 24 h and at 60 °C for 10 h).

Fig. 2. The step-by-step manufacturing process for the preparation of the laminates

2.2. Characterization techniques

Interlaminar fracture toughness tests were performed at a 25 KN Instron Universal testing machine (Instron, High Wycombe, UK). The mode I interlaminar fracture toughness was measured using the double cantilever beam (DCB) method according to the AITM 1.0005 standard. The specimens' dimensions were approximately 25 mm wide by 250 mm long. The PTFE starter film was 25 mm long place at the edge of the samples, where the loading blocks were glued for the application of the opening load. A typical DCB specimen is presented in Fig. 3a. The pre-cracked end of the DCB specimens was tested in tension at a cross head velocity of 10 mm/min until the crack was propagated to approximately 75 mm. Five coupons were tested for each fracture toughness assessment. The mode I fracture toughness energy of the CFRPs was calculated using the areas method that is:

$$G_{IC} = \frac{A}{aw} 10^6 \left(\frac{J}{m^2} \right) \tag{1}$$

where, A is the required energy to achieve the total propagated crack length, a is the propagated crack length (final crack length minus initial crack length) and w is the specimen's width. The mode II interlaminar fracture toughness was measured using the 3-point end-notched flexure method. The pre-cracked specimen was subjected to flexural loading that generates a shear crack driving force at the crack tip region. The test specimens were longer than 110 mm and 25 mm wide (Fig. 3b). The initial crack length was approximately 40 mm that results from the application of mode I loading in order to achieve a natural starter crack. The distance between the supports (i.e. the span length) was 100 mm. The cross-head velocity was 1 mm/min. Five samples were tested for each material group. The

fracture toughness energy II (G_{IIC}) was determining using the areas method and calculated using the Eq. (2):

$$G_{IIC} = \frac{9Pa^2d1000}{2w\left(\frac{1}{4L^3}+3a^3\right)}\left(\frac{J}{m^2}\right) \tag{2}$$

where, d is the crosshead displacement at crack delamination onset, P is the critical load to start the crack to propagate, a is the initial crack length (from the support point to the end of the crack), w is the width of the specimen and L is the span length.

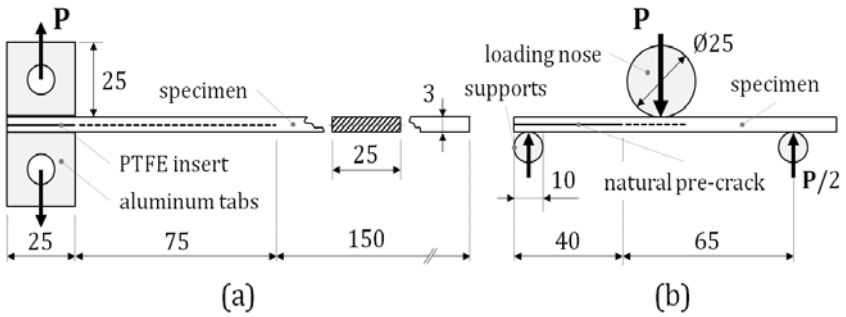


Fig. 3. Schematic representation of the (a) DCB and (b) 3ENF test set-up. All dimensions in mm

Dynamic mechanical analysis (DMA) tests were performed for the reference and the PET modified composites before and after the application of the heating process. These experiments were conducted in order to investigate the effect of the PET particles into the matrix as well as the effect of the healing process (i.e. healing temperature) on thermomechanical properties of the composites. Three rectangular samples of 50 mm x 10 mm x 3 mm were tested for each category separately. The after healing used samples, are PET modified samples that pass through the same conditions as the ones used for the healing of the tested samples. A DuPont 983 Dynamic Mechanical Analysis (DMA) was used in the resonant-frequency mode from room temperature to 150 °C at a heating rate of 5 °C/min. The T_g values were determined from the peak in the tanδ spectra. Finally optical microscopy examinations were conducted for the cross-section surfaces of the unmodified and remediate composites.

2.3. Healing process and healing efficiency calculations

After the testing process, the composites were subjected to a simple healing cycle of 130 °C for 5 h under a gentle loading of 15 N using an oven. The applied temperature was chosen to be 50 °C higher than the T_g value (approx. 80 °C) for a long time (5 h) in order to achieve the healing effect because the melting

point of the PET is very high (approx. 234 °C) according to DSC experiments. Temperatures higher than 200 °C would damage the composites. The loading value was chosen as the minimum necessary to ensure that the adjacent fracture flanks were kept in intimate contact during the healing procedure. Then, the samples were left to cool at room temperature. After the healing process, the samples were tested again using the same configurations. The calculations of the healing efficiency of the estimated system were based on Eq. (3).

$$\eta = \frac{a_{\text{healed}}}{a_{\text{modified}}} x100\% \tag{3}$$

where, a is the property under examination, a_{healed} refers to the value of the property after healing and $a_{modified}$ refers to the property before healing.

3. Results and discussion

Fig. 4a shows the load-displacement curves for the reference as well as for the modified samples in mode I fracture tests. It is observed that the modified sample starts to break earlier (at approx. 1 mm crack opening displacement (COD)) compare to the modified one (at approx. 2 mm COD) and there was no change in failure modes. For both the unmodified and modified composite DCB specimens, the applied load initially increased linearly, followed by load drop as the crack propagated. It is shown that by the incorporation of the PET particles into the matrix of the laminates, a slight increase for P_{max} close to 4% was observed, while the G_{IC} value was decreased of about 20% (Table 1). The decrease of G_{IC} is attributed to the presence of PET particles at the interface that due to their size act as stress concentration sites. Furthermore, the presence of PET particles results to an increase of the volume fraction polymer phase and reduction in carbon fibre content (Fig. 5a & b).

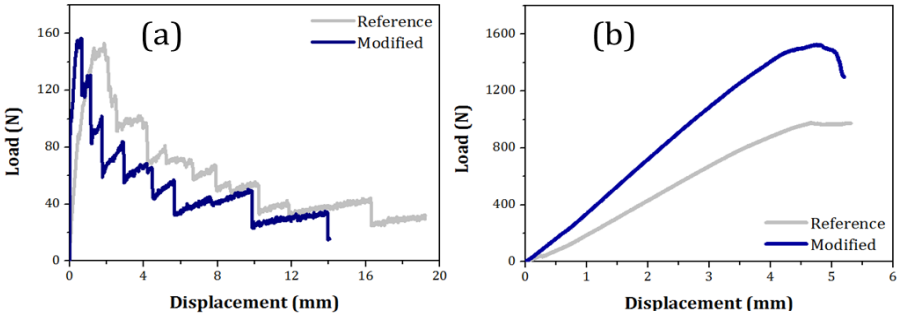


Fig. 4. Resistance of baseline and modified composites to delamination. (a) Mode I. (b) Mode II

Fig. 4b shows a typical load-displacement relation for the reference and the modified samples in the case of mode II fracture tests. It was observed that during the tests both 3ENF specimens continued to carry load after initial crack extension, while the crack became unstable at the peak load, followed by load drop as the crack propagated. It was shown that by the addiction of the PET particles into the matrix P_{max} was increased of approximately 55% while G_{IIC} also increased of approximately 37%. The inclusion of the thermoplastic particles into the matrix resulted in increasing of the interplay region thickness promotes more tortuous paths through the layers in an effective way to suppress propagating mode II delamination cracks and thus increases G_{IIC} of the CFRP laminates. This is attributed to the weak adhesion properties between the PET particle and the thermoset matrix.

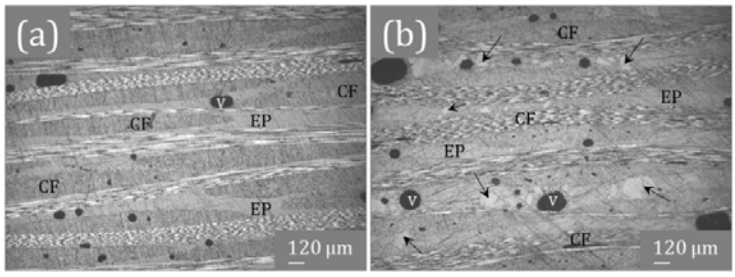


Fig. 5. Optical microscopy micrographs of the (a) reference and (b) modified CFRP where the resin-rich regions (EP) and the reinforcement-rich regions (CF) are observed. Also, in the same figures, the manufacturing-induced porosity (V) and the PET (darts) are marked

Fig. 6a and 6b show the load displacement fracture curves concluded under mode I and mode II experiments respectively in the case of tested samples that follow the interlaminar fracture tests and then they pass through the application of the healing process described earlier. The healing efficiency values achieved are given in Table 3. In the case of mode I tested samples healing caused a modest recovery in mode I fracture toughness properties. Recovery of 5% and 12% was monitored for the P_{max} and G_{IC} respectively. The partial recovery of the aforementioned properties is attributed to the change in fracture behavior, following healing (Fig. 5a). The healing process was activated by the thermoplastic particles that partially fill the delamination, by a bridging type bonding between the crack flanks, although regions with unrepaired damage remained at the mid-plane of the composite specimen. Additionally this modest recovery of the mode I interlaminar fracture toughness is attributed to the weak bonding between the epoxy matrix and the thermoplastic particles. On the other hand, healing application in the case of mode II experiments results to much higher recovery of the fracture properties. It was shown that the healing efficiency

for the P_{max}, was about 82% and 71% after the first and the second healing cycle respectively.

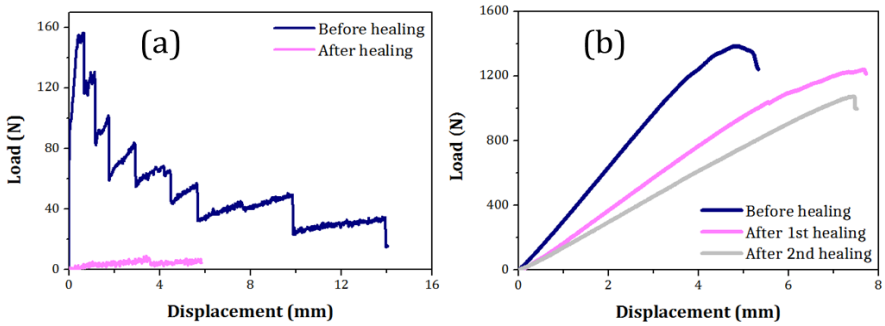


Fig. 6. Recovery ability of modified composites after healing. (a) Mode I. (b) Mode II

For G_{IIC}, the healing efficiency was measured at the level of 140% and 118% after the first and the second healing cycle respectively. As mentioned above, healing caused by the thermoplastic particles results to partially bridge the delamination, although regions of unrepaired damage remained on the mid-plane of the composite sample. The small reduction of the P_{max} after the application of the healing process is attributed to this effect as well as to the fact that the thermoplastic particles degrade during the heating process, which results to the reduction of their healing capability. Also it was shown that after the second healing cycle the samples break under three point bending loading. Additionally after the application of the healing cycles, it was observed that the load – displacement curves are transferred to the right as a result the increase of the displacement value at the point that the peak load appears. The increase of the displacement value leads to an increase of the G_{IIC} value according to Eq. (2) after the healing process. This behavior is attributed to the partial load transfer between the two sections of the healed composite through the PET particles. This effect confirms the more compliant behavior of the modified and healed composites, which further increases with the increase of the number of the healing cycles.

Table 1

Interlaminar fracture toughness under mode I (G_{IC}) and peak load (P_{max}) average values and standard deviations of the mode I test

Material type	G_{IC} (KJ/m^2)	Changing (%)	P_{max} (N)	Changing (%)
Reference	0.42 (0.03)	-	148.8 (10.1)	-
Modified	0.35 (0.02)	-20	154.7 (12.5)	4

Table 2

Interlaminar fracture toughness under mode II (G_{IIC}) and peak load (P_{max}) average values and standard deviations of the mode II test

Material type	G_{IIC} (KJ/m^2)	Changing (%)	P_{max} (N)	Changing (%)
Reference	2.53 (0.08)	-	974.4 (29.1)	-
Modified	4.04 (0.11)	37.3	1521.5 (78.2)	56.1

Table 3

Average healing efficiency values (%) achieved during the fracture toughness tests in terms of the fracture toughness energy and the maximum load

		G_{IC} or G_{IIC} (KJ/m^2)	P_{max} (N)
Mode I	After healing	12.3 (1.9)	5 (0.8)
Mode II	After 1st healing	139.5 (12.7)	81.7 (8.8)
	After 2nd healing	117.7 (9.8)	70.8 (12.4)

In order to identify the post curing effect and the better adhesion of the particles with the epoxy matrix, DMA experiments where conducted. Fig. 7 summarizes the T_g measurements for both the reference and the PET modified samples before and after the application of the healing process. It was shown that by the incorporation of the PET particles into the epoxy matrix, a slight decrease of the T_g value occurs of about 3.5% (from 116 °C to 112 °C). This behaviour is attributed to the softening of the material after the incorporation of the PET particles. Comparing the T_g values of the reference material before and after the heating was observed an increase of T_g approximately 8% (from 115 °C to 125 °C). This increase is attributed to the post curing effect that occurs during the heating while cross-linking reactions occurred between functional groups into the matrix. Finally, when comparing the T_g values of the modified samples before and after the application of the healing process, it is observed an increase of T_g approximately 22% (from 112 °C to 137 °C). This increase occurs because of the melting of the particles during the heating together with the post curing of the epoxy matrix.

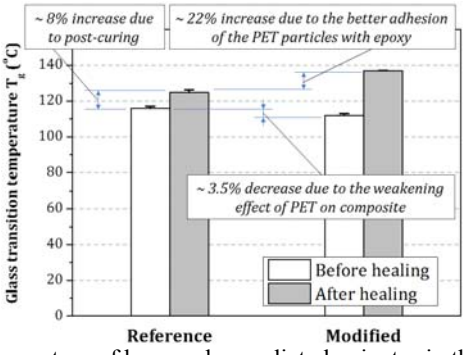


Fig. 7. Glass transition temperature of base and remediate laminates in the before and after healing situation

4. Conclusions

The present work reveals that mode I fracture toughness properties of PET modified composites are reduced by the incorporation of the PET particles. On the other hand mode II fracture toughness characteristics increase by the incorporation of them. Additionally the introduction of the PET particles results to slight reduction of the carbon fibre volume fraction. PET modified composites have the capacity of healing. The application of the healing process in the case of delamination damaged samples using the thermal activation of thermoplastic particles partially restores the mode I fracture properties, while recovery of the fracture properties was significant in the case mode II tests. Finally DMA tests were conducted and shown that the application of the healing process slightly increases the glass transition temperature of the composites.

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