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Strategies on implementing a potential self-healing functionality in a composite structure

X. Tsilimigkra[a], A. Baltopoulos[a], S. Tsantzalis[a], A. Kotrotsos[a], N. Siakavellas[b], V. Kostopoulos[a,*], S. Flórez[c]

[a]*Applied Mechanics Laboratory, Department of Mechanical Engineering & Aeronautics, University of Patras, Patras University Campus, GR 265 00 Patras, Greece*
[b]*Nuclear Technology Laboratory, Department of Mechanical Engineering & Aeronautics, University of Patras, Patras University Campus, GR 265 00 Patras, Greece*
[c]*Industry and Transport Unit, Tecnalia, Parque Tecnológico de San Sebastián, Paseo Mikeletegi,2, E-20009 San Sebastian, Spain*

Abstract

Deteriorations generated in service can cause catastrophic failure at the specific properties of the polymer composite materials. In view of this, scientists have drawn inspirations by natural biological systems and their unique ability to heal an external wound, to develop a similar repair system within a material. Carbon and glass fiber reinforced polymers were manufactured following the wet lay up or the prepreg process. Microcapsules at contents, 5% or 10% by weight, vascular networks from wax and steel wires and finally reversible polymers were implemented within a composite as a potential self-healing system. Inspection techniques, including Ultrasonic C-Scan and Infrared Thermography, were applied, where possible. Optical microscopy revealed the disruption of the composite structural integrity, regarding the observed ply waviness and the resin reach zones around the vascular structures. Three point bending experiments determined the knock down factor, expressed as a decrease on flexural strength and modulus values, for each case, compared to the reference material. The reduction ranged from 12%-64% depending mainly not only to the selected manufacturing method but also to the different implemented healing system.

Keywords: Composites; self-healing functionality; implementation strategies; knock down factor.

1. Introduction

The use of composite materials has grown rapidly since their introduction in a variety of application fields, one of which is the aerospace industry. However, besides their exponential growth, polymer composites are susceptible to damage in the form of micro cracking and delamination generated mostly during their service. Regardless of the application, once cracks are developed, the overall mechanical performance of the composite structure is compromised and the damage evolution can be fatal. Riefsnider et al. [1] predicted the degradation in tensile strength and fatigue life of fiber reinforced composites due to the redistribution of loads caused by matrix damage. Chamis et al. [2] and Wilson et al. [3] worked in the same direction for defining how the matrix cracking affects the compressive strength of the composite structure. Jang et al. [4] and more extensively Morton et al. [5] studied the behavior of polymer composites and concluded that matrix cracking is responsible for the delamination and subsequent the fiber fracture. It is conceivable that degradation, damage and finally failure of the materials are natural consequences due to their exposure to harsh operation conditions. In light of the aforementioned issues, scientists developed several conventional techniques like welding [6], patching [7], and in situ curing of new resins [8], which were adopted by industries in order to repair visible or detectable damages in polymer matrix composite structures. However, these methods are applied once

* Corresponding author.

E-mail address: kostopoulos@mech.upatras.gr (V. Kostopoulos)

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the damage has been detected either by the naked eye or other non-destructive techniques which are time consuming and quite costly processes. Additionally invisible micro cracks developed during service life are not taken into account as they are barely detected.

In view of this, researchers were inspired by the biological systems in nature, which are able to repair themselves and recover their functionality using their inherently available resources. This idea triggered an entire new field of research. Different techniques were developed according to the mechanism in which the healing system is implemented. In the case of extrinsic self-healing the healing agent is stored and incorporated within the material in advance. On the contrary, the intrinsic self-healing polymers are based on the specific molecular structures which under certain stimulation (mostly heating and pressure) enable crack healing. From the early 1990s Dry et al. [9] investigated the development of a smart polymer composite, which had the ability to self-repair internal micro cracks by a vascular type healing system. C.J Norris et al. [10] described very detailed the design considerations for a successful vascular network implementation in a carbon fiber reinforced laminate. Ideally this process could be achieved with the minimal disruption in the material structural integrity. Later, White et al. [11] further promoted the concept of extrinsic self-healing by introducing an autonomic healing in polymer composites. The study proposed a system in which the healing agent was encapsulated and incorporated within the material. Upon crack intrusion, the healing agent was released, triggered by the contact with an embedded catalyst, polymerized and finally healed the damaged area. Jud et al. [12] studied the copolymerization degree on the crack healing behavior of PolyMethylmethacrylate (PMMA). The healing time, temperature and the clamping pressure were investigated for better properties recovery.

The scope of the present work is the investigation of the handling and processing difficulties arising from the incorporation of the different self-healing technologies, during FRPs manufacturing (Table 1). Capsules and vascular network approached the extrinsic self-healing strategy. In case 1, PMMA microcapsules were used as potential self-healing carriers (Fig. 1a). Two different wire materials (wax and steel) were tested in case 2 (Fig. 1b), for their suitability for the vascular formation. Finally, the intrinsic self-healing technology was approached via the incorporation of reversible thermoplastic particles (Figure 1c). The current case was also investigated by combining modified Nylon with Multiwall Carbon Nanotubes (MWCNTs). The composite geometric distortion caused by the potential self-healing materials incorporation was considered. Furthermore, the knock down factor as a result of the healing system implementation was determined under three point bending loading conditions

2. Manufacturing

2.1. Materials selection

The primary materials used for the present study were SIGRAFIL unidirectional carbon fiber prepreg ($150 g/m^2$), purchased from SGL group, Germany, and woven glass and carbon fabric ($280 g/m^2$) supplied by R&G, Germany. Table 1 presents in details the manufacturing method for each case study (Fig. 1).

In wet layup technique, the matrix material was a two part epoxy system supplied by R&G consisting of an epoxy resin (L) and a hardener (EPH 161).

Empty microcapsules with an approximately diameter of 50 μm, provided by TECNALIA, Spain, were incorporated within the matrix material for case study 1 in contents of 5% and 10% by weight.

Vascular network in case 2 were formed from wax wires having diameters of 0.9 and 1.4 mm, supplied by Chryssotechniki, Greece and steel wires commercially available at 0.9 mm diameter size.

Two different thermoplastic materials were used for providing intrinsic healing functionality to the epoxy composites. Polyethylene Terephthalate (PET) was supplied by NGP, Greece, in pellet form. It was transformed to sub-micro-particles using a powdering machine into Nitrogen.

Doped nylon (Copolyamide) Griltex D 1330A, with 10% wt. Multi Walled Carbon Nanotubes (MWCNTs), was supplied by Nanocyl, Belgium, in the form of powder of sub-micron size.

2.2. Composite manufacture

Unidirectional carbon fiber composite plates (CFRP) $[0]_{22}$ were manufactured by prepreg process for case study 1.

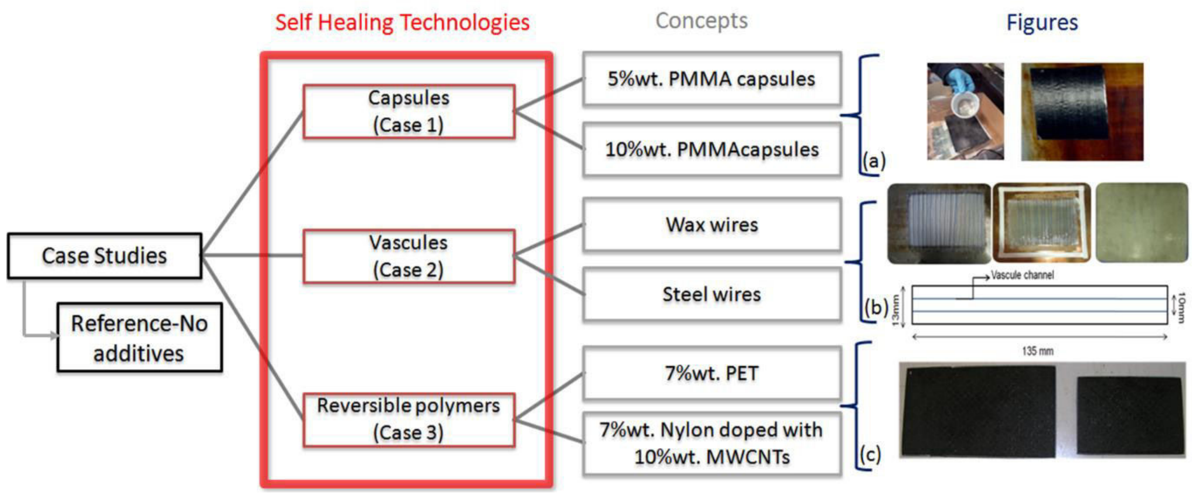


Fig. 1. Self-healing technologies a) capsules sieving process, b) GFRP with vascular network made by wax and steel wires, vascular specimen configuration c) CFRP with 7%wt. PET, CFRP with 7%wt. Nylon doped with 10%wt. MWCNTs.

Microcapsules were homogenously dispersed in each layer through sieving (Fig. 1a) in two different contents, 5% and 10% wt. Curing was undertaken according to the manufacturer recommendations at 130 ºC, 6 bar pressure, for 2 hours in a controlled oven. Fiber volume fraction was calculated to be approximately at 60%.

Furthermore, under the investigation of case 2, laminates consisting of sixteen woven glass fabric layers (GFRP) were manufactured, using wet layup technique. The matrix system (resin and hardener) was manually mixed at a ratio of 100:25 by weight as manufacturer recommended. The vascular network was integrated in the mid layer of the composite plate, formed by wax wires of 0.9 mm and 1.4 mm diameter and steel wires 0.9 mm diameter (Fig. 1b). Steel wires prior of their use were coated with polytetrafluoroethylene (PTFE) release agent. The glass fabric in this case was selected due to its transparency, which enables the optical observation of the network. Cure process was performed according to the manufacturer at room temperature for 24h followed by a post curing phase for 15h at 60ºC. Steel wires were manually pulled out from the final composite, while wax wires were melt and removed by heating at 105 ºC after the cure process was completed. Fiber volume fraction was lower in this case, as expected due to the selected technique, and calculated to be around 35%.

Thermoplastic particles (size of 80-120 μm) were introduced into the matrix as healing agents, in order to simulate the intrinsic reversible strategy in case 3. Pure PET at content of 7%wt. was manually mixed in the epoxy system for 30 minutes. Sixteen layers of the woven carbon fabric were impregnated with the mixture, through wet layup technique. Furthermore, a second thermoplastic root was used for exploiting its healing efficiency. The epoxy system was modified with Nylon micro particles of the same size, at a content of 7%wt., which were doped with 10%wt. of MWCNTs in order to mitigate the detrimental effect in the mechanical properties due to the particles implementation. Cure cycle was performed for 24h followed by post curing for 15h at 60ºC.

All composite plates, with the different self-healing approaches (capsules, vascular net, reversible polymers) were tested under three point bending (3PB) loading. The aforementioned modified composites were compared for their mechanical properties to the reference material with no healing modification.

3. Experimental

3.1. Demonstration tools and test procedure

C-scan technique was used for the quality control of the manufactured composite plates. The equipment consists of a MISTRAS Group AD-IPR 1210-PCI card and a VUB2000 tank. The transducer was a Krautkramer single element probe at 5 MHz, non-focal.

Optical microscopy (OM) revealed, where possible, the geometrical disruption caused by the incorporation of the capsules or the vascular net or the thermoplastic micro-particles.

Additionally, an Infrared Thermography (IR) FLIR system (SC660) with a 640x480 IR pixel detector and thermal sensitivity <45mK(IR) imprinted the exact formation of each vascule along the plate and captured the distribution of a fluid inside the network.

An Instron 8872 test machine was used for three point bending tests following the ASTM D7264M-07. Table 1 summarizes the healing concepts tested and their differentiations. Specimens, from composite plates of each technology were cut according to the ASTM D7264M-07 for three point bending tests. In case 2, specimens were slightly different as they contained two longitudinal channels, aligned with the fibers direction and placed symmetrically along the mid plane (Fig. 1b). Resin and hardener were separately and manually injected, through a syringe, within the vascular net. Commercial ink was used, mixed with the filling material, for visualization reasons. Specimens were taped before testing to avoid the loss of the injected system. At least five specimens per concept were tested. Flexural strength and modulus was measured in each case as shown in Figures 8, 9 and 10. The modified composites contain additives (capsules or reversible particles) or vascular net, which disrupt the material internal structure. It is assumed that the neat material with no additives and no vanes has the highest value of each property without any inherent distortions (capsules, vanes, reversible particles). This is the benchmark from which the reduction percentage is defined.

Table 1. Summary of the studied healing concepts.

Composite Plate	Manufacturing Method	Plies	Material Incorporation	Demonstration Tools
CFRP	Prepreg	22	Capsules	C-Scan, 3PB
GFRP	Wet layup	16	Vascular net	OM, IR, 3PB
CFRP	Wet layup	16	Pure PET	OM, 3PB
CFRP	Wet layup	16	Nylon/MWCNTs	OM, 3PB

3.1.1. C-scan

In case study 1, capsules were successfully incorporated within the composite through sieving. C-scan results (Fig. 2) indicated a satisfactory quality for the composite and a good dispersion of the capsules through the layers in order to continue the experimental campaign. The color bar presents the signal response from the weakest (green) to the strongest (red). In particular, as it is observed in Fig. 2, modified plates include an additional phase, which absorbs part of the ultrasonic signal. Capsules are detected as possible defects within the material and for that reason the signal reflection is weaker as the capsules content increase.

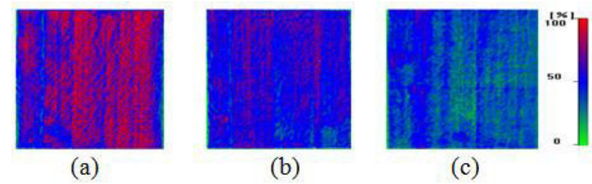
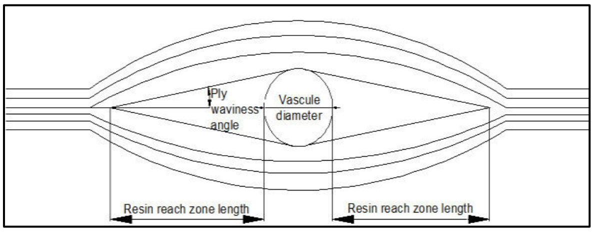


Fig. 2. C-scan figures from case study 1 a) Reference composite plate, b) composite with 5 %wt. capsules and c) 10 %wt. capsules.

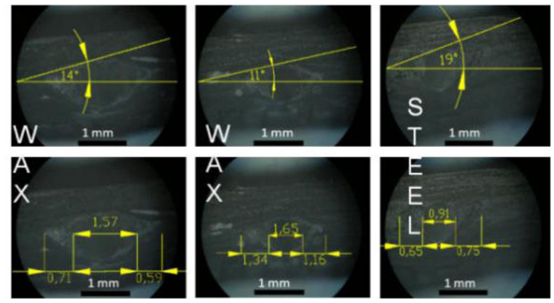
3.1.2. Optical microscopy

In case study 2, the vascular networks resulted in geometric distortion of the surrounding fibers due to the uneven distribution of the resin close to the channels (resin reach zones) and due to the plies which are forced to pass around the channels (ply waviness) (Fig. 3a and 3b). As it was expected, increasing the diameter of the vanes, both resin reach zones and ply waviness were increased. Comparing the diameter of 0.9 mm for the different vascular net material (wax over steel) it is observed that wax wires disrupts slightly less the structural integrity of the composite regarding the ply waviness and the resin reach zones. This is probably attributable to the technique applied for removing the wires, which is harsher in the case of steel wires, compared to the wax melting process. On the contrary, the final calculated diameter of the vanes formed from steel wires remained closer to the reference embedded diameter (Fig. 4c.)

In case 3 thermoplastic particles dispersed between the layers of GFRP can be observed (Fig. 5) at the cross section of the laminate along with the voids and the resin reach zones caused by the selected manufacturing technique.

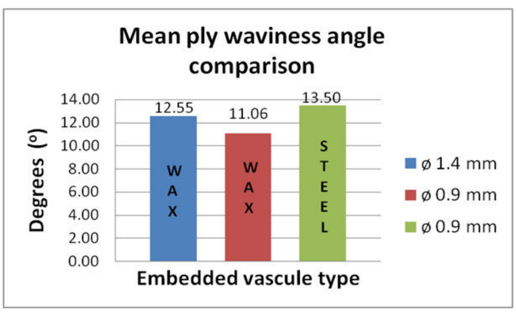


(a)



(b)

Fig. 3. Case study 2 a) distortion parameters schematic b) cross section figures observation through OM.



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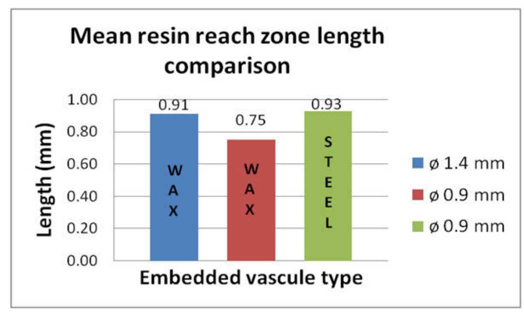

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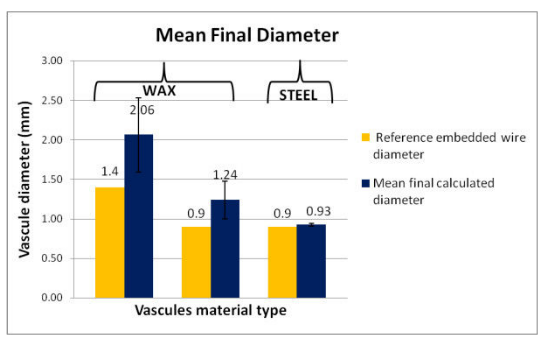
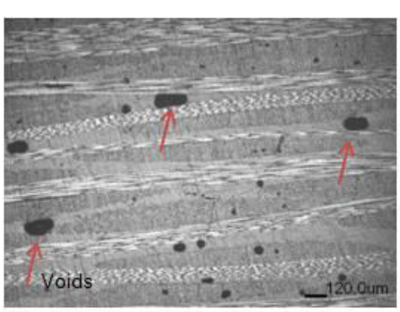


(c)

Fig, 4. Case study 2 a) mean ply waviness value for all tested specimens b) mean resin rich zone value for all tested specimens c) vanes final mean calculated diameter compared to the embedded size.



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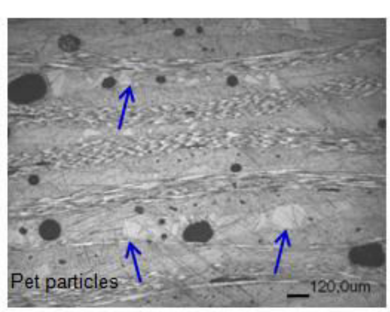

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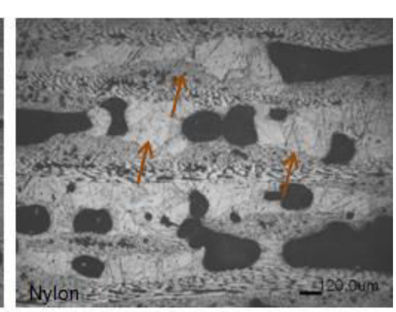
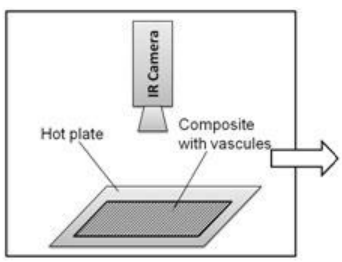


(c)

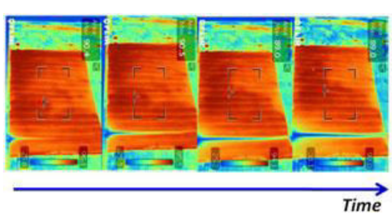
Fig. 5. Cross sections of composite plates with polymer micro-particles under case study 3 a) reference with no additives b) doped with 7%wt. particles c) doped with 7%wt. Nylon with 10%wt. MWCNT.

3.1.3. Infrared thermography

Infrared (IR) Thermography was used to visualize the vascular network formed along the composite plate. For this reason the manufactured plate was placed on a hot plate. FLIR thermal camera monitored the complete heating process (Fig. 6a), while at the same time water was manually injected, using a syringe, in the hollow channels as shown in Fig. 6b. With the channels being hollow, the activation fluid can easily and smoothly pass through the net without any obstructions. IR Thermography technique managed to depict the heat distribution of the fluid through the channels within the material. This indicates the presence of a working vascular net, which has the ability to provide a path for the distribution of a fluid inside the material and create a potential self-healing functionality.



(a)



(b)

Fig. 6. Thermal imaging visualization a) set up, b) heat distribution while water was manually injected.

3.2. Mechanical experiments

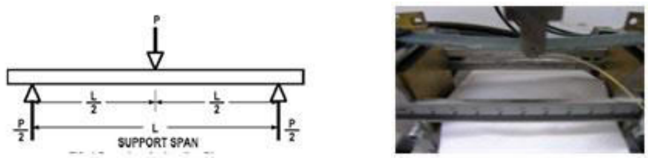
3.2.1. Extrinsic approach

The mechanical properties were considerably affected by the capsules integration in case study 1. The flexural modulus was reduced up to 28% when 5%wt. capsules were integrated and up to 43% in the case of 10%wt. capsules (Fig. 8a). Flexural strength is also affected. However, the strength reduction was smaller. More precisely a decrease was observed up to 12% in the case of 5%wt. capsules and 13% in the case of 10%wt. capsules (Fig. 8b).

Three point bending tests determined the flexural strength and modulus reduction for specimens with empty and filled vascular net compared to the reference ones for case study 2. Flexural strength and modulus are strongly affected in both cases, empty or filled vascular net (Fig. 9 a & b). The percentage reduction is equal at 30% for both flexural modulus and strength for the empty vanes. On the other hand the filled vascular net results to a bit smaller reduction in flexural modulus of about 26%, while the decrease is almost 29% for flexural strength. Although vascular network is implemented in the neutral zone, along the mid plane, their existence has definitely detrimental effect on the composite mechanical properties. This is due to the vascular net diameter (0.9 & 1.4 mm), which are considered large and caused extensive fiber distortion between the plies. A suggested solution to this problem is the decrease of the embedded vanes diameter and further investigation for the knock down effect.

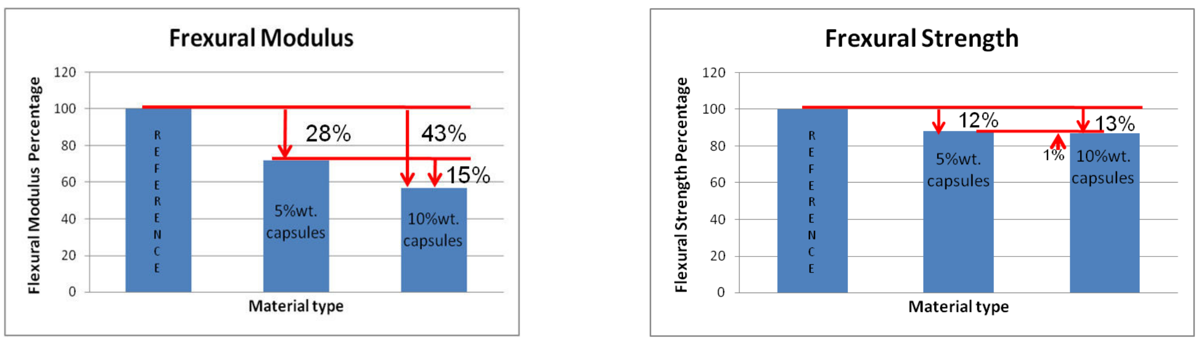
3.2.2. Intrinsic approach

As the content of micro-particles increases, voids become denser. In this direction, a severe mechanical knock down factor is noticed among the different tested composites. The doped composite which includes MWCNTs reinforced Nylon micro-particles, is observed to appear higher knock down factor. More precisely flexural modulus is reduced of about 48% in the case of pure PET micro-particles and up to 62% for the composite with MWCNTs reinforced Nylon (Fig. 10a). Following the same reduction trend, flexural strength for pure PET is reduced of about 51%, while MWCNTs reinforced Nylon decrease the flexural strength of about 64% (Fig. 10b). This occurs due to the extensive void content, along with the resin reach zones formed around micro-particles as shown in Fig. 5. Furthermore, the presence of the thermoplastic micro-particles also contributes to the observed knock down factor. The slightly better behavior of the composite with PET micro-particles is associated to the higher mechanical properties of PET compared to Nylon. Finally, it is obvious that wet layup technique cannot succeed a satisfactory particles dispersion, which results to higher degradation of mechanical properties.



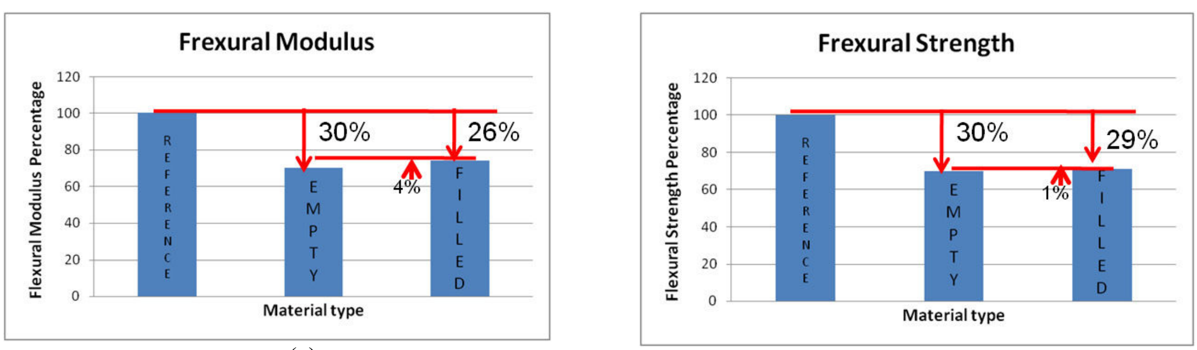
(a) (b)

Fig. 7. Three point bending a) schematic b) actual loading conditions.



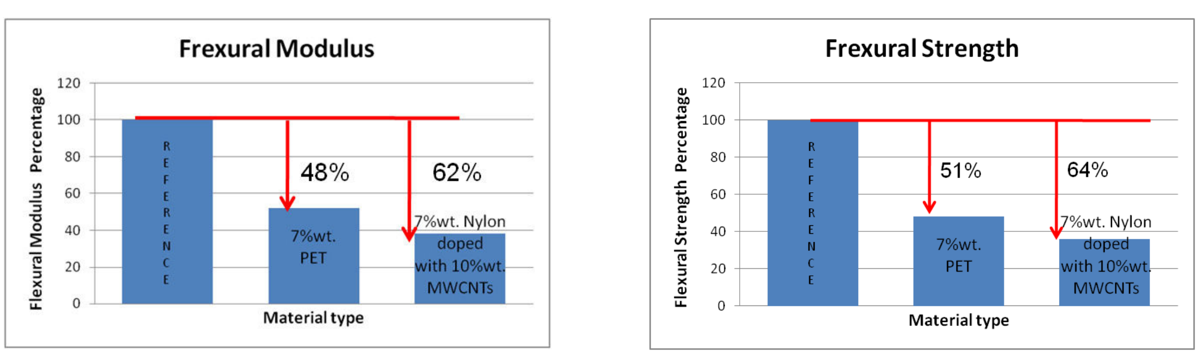
(a) (b)

Fig. 8. Knock down factor comparative results for case study 1 a) flexural modulus, b) flexural strength.



(a) (b)

Fig. 9. Knock down factor comparative results for case study 2 a) flexural modulus, b) flexural strength.



(a) (b)

Fig. 10. Knock down factor comparative results for case study 3 a) flexural modulus, b) flexural strength.

4. Conclusions

The present study focused on the strategies for the implementation of a potential self-healing functionality within a composite structure. Three different technologies of possible self-healing systems were tested for their feasibility to be incorporated in a repeatable manner in composites. Using micro-capsules and vascular net the extrinsic technique was approached, while intrinsic strategy was implemented by reversible polymers and more specifically by thermoplastic micro-particles. Where possible, the geometric distortion caused by the integrated material was visualized. The knock down factor for each study case was also determined. It is conceivable that according to the selected self-healing technology there are significant differences.

Regarding the 1st case, capsules can easily be incorporated within the composite as an additive during manufacturing. The mechanical properties of the material are slightly affected. The main limitation of this method is the single healing cycle once the capsule breaks along with the remaining debris.

The distribution of a healing agent through a vascular network, as described in the 2nd case study, is closer to biological systems. Vascular composites are advanced towards multiple healing cycles. Moreover, according to the application, the network architecture can be varied. On the other hand, vascular net formation is quite complicated process and several parameters should be examined. Moreover, there is a notable knock down factor due to the vascular net implementation, which is considered as large voids.

Both aforementioned strategies, initiate the healing process automatically once damage occurs which is argued as one of their main advantages.

Reversible polymers were studied in case 3, as a potential self-healing technology. The current method enables multiple healing cycles as the integrated healing system upon heating and pressure can be triggered and be functional at every damage event. Nevertheless, there is a severe knock down to the composite material mechanical properties, as particles where observed as potential voids within the structure. Their dispersion is a major issue for their successful incorporation. Moreover, reversible polymers main drawback is that their non-autonomously nature requires an external mechanism for triggering the healing process.

The final composite is differently affected in each case study and this should be taken into serious consideration when designing a self-healing material, in order to mitigate the deleterious effects. It is suggested, the manufacturing of a composite structure with a self-healing functionality in a targeted area where damage is more likely to occur according to the application and the loading conditions.

Acknowledgements

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