The flexural properties of self healing fiber reinforced polymer composites

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Abstract: Fiber reinforced polymer composites have a complex damage prediction and repair mechanism. Such complexities made the researchers to implement new techniques like self healing. Amendments in the existing material can modify its properties. So, it is necessary to study the change in property due to inclusion of self healing in fiber reinforced composite materials. This work aims to investigate the self recovery response of composites prepared by reinforcing glass fibers and carbon fibers in epoxy matrix. The healing was achieved by inclusion of dual microcapsules made of epoxy and hardener encased in separate capsules. To investigate the recovery activity of the composite laminate, a 5mm diameter indentation was produced at the centre of specimen and the healing was monitored by measuring the diameter of indentation after 12 hrs and 24 hrs. To notice the influence of micro-inclusions on flexural strength, flexural test was conducted on neat, indented and healed specimens. It was observed that inclusion of microcapsules did not majorly alter flexural strength of glass fiber reinforced and carbon fiber reinforced polymer composites. Results also indicated complete healing of both carbon fiber reinforced polymer and glass fiber reinforced polymer composite specimens with healing efficiency of 103.4% and 101.8% respectively.

1. Introduction
Self healing materials have innate capacity to recuperate its properties. There are two kinds of such materials i.e. autonomous and non-autonomous. Autonomous materials can attain healing without any surplus help like force and temperature. These materials carry healing agents and curing agents in tiny closed vessels like microcapsules, hollow fibers and hollow tubes. Whenever any damage such as crack arises in the material due to any kind of load, the load will rupture the closed vessel making the healing agents and the curing agents to come out of the capsule thereby activating the healing process. The healing action will be propagated and finished by movement of the agents followed by polymerization reaction at the area where damage exists. Non autonomous healing cannot be accomplished without any auxiliary help. It requires additional pressure or temperature to trigger healing. Non-autonomous systems contain such polymers which can rebuild their polymer chains in the presence of external stimulus [1,2]. Fiber reinforced polymer (FRP) composite materials have high demand in various industries like civil, transportation and sports. They are favored over metals and alloys in applications like automobile and airplane structures due to their capability to give superior properties with less weight. The FRP’s have anisotropic nature due to alignment of reinforcements/fibers in disparate directions. This enables them to carry multidirectional loads. These loads are transferred to fibers by polymer matrix. Polymer matrix possesses low toughness, so generally whenever the material gets damaged, matrix is primarily affected and micro cracks appear in it [3,4]. Further the damage increases in size and leads to failure of complete FRP composite material.
Discovering the damage and its repair execution is complicated, time consuming and a costly affair. In order to find the solution to these problems, various researchers got allured by self healing techniques.

Bleay et.al [5] fabricated hollow glass fiber (HGF)/epoxy composites by including healing agent in hollow glass fiber (HGF) having inner and outer diameter of 5 µm and 15 µm respectively. Compression after impact test was conducted on the laminate by impacting it at 80 J followed by compression. Only 5% of healing efficiency was achieved due to heavy damage which broke the fibers themselves. As the self healing system mainly focuses on healing of matrix phase fiber damage was not recovered. Pang and Bond [6,7] prepared HGF/Solid E-glass fiber epoxy composite by using solid glass fibers and hollow glass fibers filled with healing agent of 60 µm external diameter and 50% hollowness. Low energy impact was created by the indentation process and a four point bend test was conducted. Healing efficiency of 73% was achieved. Trask and Bond [8] used solid and hollow glass fibers for creation of fiber reinforced polymer composites. The test samples were heated at 100°C for 2 hours before four point bend test for acquiring better healing. 87% of recuperation of flexural strength was acquired. William et al [9] manufactured carbon fiber reinforced polymer (CFRP) laminate and healing agents were incorporated in it through hollow glass fibers (HGF) which were included in interfaces. Indentations were produced by applying 1.7 KN, 2 KN loads and flexural tests were conducted to ascertain the achievement of healing. CFRP did not provide much evidence of healing for indentation produced at peak load of 1.7 KN whereas indentation due to peak load of 2 KN showed 83% recovery. It was also found that higher density of hollow glass fibers boosted the degradation of flexural strength. Kling et al [10] concocted HGF/epoxy laminates through hand lay-up and vacuum assisted resin transfer molding techniques. Hollow glass fibers with 50% hollowness and diameter of 10-13 µm were used for manufacturing of laminates. Three point bending test was conducted twice, i.e. before and after the introduction of impact damage, healing at 60°C for 12 hours. Test results proved better healing can be achieved by preparation of laminates with hand lay-up process. Healing efficiency obtained was 35%, fiber volume fraction was not mentioned. Zhu et al [11] prepared E-glass epoxy composite laminate and included a heal ply in it. The heal ply was made up of epoxy/mercaptan filled hollow polypropylene tubes. The laminate was prepared by hand lay-up process and heated in the range of 25°C to 40°C for storage of healing agent in the hollow fibers. The impact simulation was formulated by indentation damage in the specimens. Four point bend test was conducted in order to determine healing efficiency. The healing efficiency of 62% was achieved by heating the laminate at 70°C after damage production. Internal pressure formation due to gas raised the supply of healing agent at damage site which resulted in repair of damaged area and recovery of flexural strength.

Lee et al [12] found the compression and tensile properties of a self-healed fiber reinforced epoxy composites developed by microencapsulating DGEBA and DETA. The healing efficiency was calculated to be 119% when the strength ratio of the virgin and healed composite was considered. Yuan et al [13] fabricated glass fiber/epoxy composite by enfolding Diglycidyl Ether of Bisphenol A (DGEBA) and Benzyl Dimethyl Amine in microcapsules. The low velocity impact tests were done at various energy levels like 1.5 J, 2.5 J, 3.5 J and 5.5 J. It was also noted that the composite was completely healed within 12 hours when impacted at 1.5 J as the energy was absorbed by microcapsules but the healing efficiency was observed to be 52% when impacted at 3.5 J. Ghazali et al. [14] incorporated the dual microcapsules filled with DGEBA and amine hardener into the resin system of carbon fiber epoxy composite laminates. The mode II interlaminar fracture toughness of composite laminate was investigated by using end notch flexure specimen. It was observed that the fracture toughness was improved and healing efficiency was found to be 63%.

In past years, most of the research was focused on bulk polymers and limited research was done on fiber reinforced polymer composites. This work focus on experimental investigation on variation in flexural strength with addition of healing agent and curing agent stuffed microcapsules. Minor indentation damage was created at the center of each specimen and healing of the indentation damage was checked by observing the change in diameter of indentation and property restoration. Flexural tests were then conducted on pristine, damaged and healed specimens.
The mechanism of self healing and the effect of various entities on the self healing behavior are represented in figure 1.

2. Materials and Methodology

2.1. Microcapsule formation
Microcapsules were synthesized by in situ polymerization. The method of synthesis was similar to the method described in [15]. Melamine, formaldehyde, ammonium chloride, resorcinol, styrene and ethylene maleic anhydride were used in adequate amount to form microcapsules. The LY556, HY951 and benzyl dimethyl amine was used as healing agent, curing and catalyst respectively. Microcapsule creation was attained in three major steps (1) formation of melamine formaldehyde (2) formation of epoxy solution (3) blending of melamine formaldehyde and epoxy solution. The continuous blending was done with mechanical stirrer at 850 rpm for one hour. Formed microcapsules were filtered, rinsed and dried. Both epoxy and hardener filled microcapsules were prepared by following the same
method. For encasing the catalyst, dried hardener filled microcapsules were immersed in the catalyst for 5-6 hours. Catalyst filled microcapsules were then filtered, cleaned and dried. The step by step procedure for creation of epoxy filled microcapsules is shown in figure 2 and formed microcapsules are shown in figure 3.

![Figure 2. Procedure for creation of epoxy filled microcapsules.](image)

![Figure 3. Formed Microcapsules.](image)

2.2. Formation of resin and hardener filled microcapsules

Bidirectional (0/90) fabrics of Toray T300 carbon fibers and E-glass fibers were used as reinforcements. LY556 epoxy resin and HY951 amine hardener were mixed in ratio of 10:1 for creation of laminates. Hand layup technique was implemented for fabrication of the laminate. The granite table was used as mold to create flat plates. The fabrication was started by placing a cleaned and waxed mylar sheet on the table. The resin / hardener mixture was poured and evenly spread over the surface followed by placing of fabric reinforcements over it. Similarly seven alternate layers of fabric and resin / hardener mixture were stacked over each other to achieve thickness of 2.5mm.

For creation of fiber reinforced epoxy composite with microcapsules, the prepared microcapsules were mixed in LY556 resin with mechanical stirring equipment. Both resin filled and hardener filled capsules were added in 50:50 ratio. The total quantity of the capsules added was 2.5% by weight of the resin. The same steps were followed for fabrication as used in creation of fiber reinforced epoxy composite without capsules.
Four different laminates of dimension 300 mm * 300 mm were prepared i.e. (i) carbon fiber reinforced epoxy composite without capsules (CFE) (ii) carbon fiber reinforced epoxy composite with capsules (CFEC) (iii) glass fiber reinforced epoxy composite without capsules (GFE) (iv) carbon fiber reinforced epoxy composite with capsules (GFEC). The composite fabrication process and fabricated laminate is shown in figure 4.

![Composite fabrication process and fabricated laminate](image)

**Figure 4.** (a) Composite fabrication process (b) Fabricated laminate.

Abrasive water jet cutting was used to cut the specimens in the dimensions of 12.7 mm width and 125 mm length. Three samples each were cut from GFE and CFE laminates and nine samples each were cut from GFEC and CFEC laminates. Six samples from both CFEC and GFEC categories were indented by using ball indenter which left indentation of 5 mm on the center of the specimen.

The damaged samples were marked as damaged carbon fiber epoxy composite with capsule (CFECD) and damaged glass fiber epoxy composite with capsule (GFECD) while the samples kept aside for healing were marked as repaired carbon fiber epoxy composite with capsule (CFECR) and repaired glass fiber epoxy composite with capsule (GFECR). The water jet cutting set-up is shown in figure 5 and the prepared pristine and damaged samples are shown in figure 6.

![Water jet cutting set-up](image)

**Figure 5.** Water jet cutting set-up.
3. Experimental Investigations

Flexural tests were carried out on all CFRP and GFRP samples by using universal testing machine. The specimen dimensions were maintained according to ASTM D 790 standard. Tests were initiated by fixing the specimen on the supporting pins such that the gauge length was 80 mm. The bending load was applied on the specimen through loading pin until the specimen ruptured. All tests were accomplished in ambient conditions. The test set-up is displayed in figure 7.

4. Results and Discussion

After scrutinizing the flexural test results for three similar samples each of GFE, GFEC, CFE and CFEC categories respectively, it was discerned that the insertion of healing liquid and curing liquid filled microcapsules did not significantly amend the flexural strength of fiber reinforced epoxy composites. It was also discovered that presence of indentation damage reduced the flexural strength, but as the damage was minor the variation of flexural strength was also not so great and the damage samples started healing after 2 hours and took 24 hours to heal completely. Figure 8 indicates the average flexural strength of GFE, GFEC, GFECRD, and GFECR samples. Figure 9 shows the average flexural strength of CFE, CFEC, CFECRD, CFECR samples.
According to Figure 8, the samples consisting of microcapsules (GFEC) had 278.3 MPa flexural strength and the samples not consisting of microcapsules (GFE) had 282.3 MPa flexural strength. After indenting the GFEC samples, the left over flexural strength was 172.5 MPa. This indicated that due to damage the flexural strength was mitigated by 38%. Recuperated flexural strength of GFECR samples was 283.3 MPa. This means the samples were able to regain their complete flexural strength and have 101.8 % of healing efficiency. Based on Figure 9, the samples with microcapsules (CFEC) had flexural strength of 537.6 MPa and pristine samples without microcapsules (CFE) had flexural strength of 542 MPa. Damaged samples (CFECD) showed 349.5 MPa flexural strength. This indicated that the damage diminished flexural strength of samples by 35%. After recovery the samples (CFECR) attained flexural strength of 556.3 MPa. The samples have more flexural strength as compared to their initial flexural strength. The healing efficiency of these samples was 103.4%.

5. Conclusion
In this research, the auto-regaining ability of glass fiber epoxy composites and carbon fiber epoxy composites was discovered. The samples with inclusion of microcapsules (having core of healing agents and curing agent) and without inclusion of microcapsules were prepared and tested at ambient
conditions by applying flexural load. It was clearly visible from the test results that there was insignificant variation in flexural strength upon inclusion of microcapsules in glass fiber epoxy composites and carbon fiber epoxy composites. Introduction of an indentation flaw diminished the flexural strength of CFECD samples and GFECD samples by 35% and 38%. It was also noticed that the damaged samples were able to heal completely and attained higher strength than undamaged specimens. The healing efficiency was found to be 103.4% for CFRCR and 101.8% for GFRCR samples.

6. References
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