Response of adhesively bonded single lap joint doped with MWCNT and Fullerene $C_{60}$ in the adhesive to the tensile strength of the joints

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Abstract: The basis for this research is to create joints that have greater joint strength and capability of carrying greater damage load. The structural damage behaviour of adhesively bonded single lap joints (ABSLJ’s) was investigated. Laminates formed by carbon fibre woven in plane weave pattern and bonded by epoxy were used as adherend. Since a variety of nano materials are currently in use and are said to improve the damage strength of the composite when dispersed in them during the fabrication, two such nano materials namely multi walled carbon nano tube (MWCNT) and Fullerene $C_{60}$ in different weight percentages of 0%, 1%, 3%, 5% and 7% were introduced by the method of ultrasonication to disperse them in the adhesive. A two part epoxy ROTEX EP - 416 resin and ROTEX EH – 153 hardener mixtures were used as adhesive for creating the joints. Results stipulate that the addition of MWCNT nanofillers in 1 wt % and 3 wt % in the adhesive has lead to a considerable increase in the tensile damage load of the ABSLJ’s by about 93% and 199% respectively. While the addition of 1 wt % Fullerene $C_{60}$ in the adhesive increased the failure load but there was not much significant improvement when compared with the same percent of MWCNT.

Keywords: MWCNT, Fullerene $C_{60}$, ABSLJ, Ultrasonication.

1. Introduction

The employment of nano materials have shown an increase in recent years due to their ability to generate better material properties like increased strength and assistance in creating a tougher and stiffer component. These nano composites are known to be multiphase solid in nature that have one of the phase dimension of the material structure less than 100 nm and the nanoscale fillers are suppose to be zero-dimensional (embedded particles), one-dimensional (nanotubes and nanorods), two-dimensional (nanocrystalline multilayers), nanostructured materials [1]. Implementation of adhesive bonding technique along with reinforced nano particles for fastening composites is advantageous in terms of cost, mechanical properties, environmental condition resistance and greater strength [2, 3].

Mechanical stirring with the use of automatic speed controlled stirrer can be used to disperse the nanofillers in the resin. For proper dispersion a suitable rpm (speed of motor) and mixing time is required to be maintained so that there are no lumps formed during the dispersion process and the nanofillers gets completely dispersed. Care should be taken to avoid usage of stirrer having sharp edges as the sharp edges may sometime damage the nanofillers if the rpm is too high [4]. Adding nanofillers such as fullerene in the adhesive increases the adhesive strength by a greater percentage. Involvement of temperature during hardening cannot be undone when considering the adhesive strength. At lower temperature, the strength
decreases when compared to the material hardened at higher temperature regime [5]. Further there are joints which find various applications in sectors of automobiles, aerospace, marine etc. These joints are basically single lap joint created by different techniques like by using rivets, nuts and bolts, adhesives etc. Among these adhesive bonded joints are noteworthy and are swiftly in use. Along with the use of conventional nano particles, carbon based particles have gained importance in improving the joint strength when mixed with adhesives to create the joint. Flexural strength increase of 20.7 % was observed with the addition of nanofillers like MWCNT at 1% by weight in the epoxy to blend a glass fibre composite thereby showing an improvement in the damping properties [6]. Also an increment of 47% and 86% was observed in the bonding strength of the single lap joints created with the use of 0.1 wt % and 0.3 wt % of MWCNT respectively [7].

Likewise a growth of 26.4% and 24% respectively in the flexural strength, fracture toughness in case of a quasi isotropic laminate was observed when alumina nano particles were added to the epoxy. While for a unidirectional laminate, the addition of alumina showed negligible improvement in flexural properties [8]. When Al2O3, SiC and MWCNT particles were added to Epocast 50 – Al946 epoxy to be used as an adhesive to create an adhesive bonded joint, the dispersion of Al2O3, SiC nano particles was simple due to their lower aspect ratio for greater weight percentage of nano particles. The MWCNT is slightly different due to its high aspect ratio and dispersion gets burdensome even with lower weight percentage of nano particles. The advancement attained in the tensile strength and shear strength for the bonded joints having 0.5 wt % MWCNT, 1.5 wt % SiC and 1.5wt % Al2O3 are 7.5%, 4%, 0.5 % and 5.5%, 4.9%, 6.3% respectively [9].

The use of different nano fillers at different weight percentages help in determining the properties of the joints but as the weight percentage keeps on increasing, a subsequent decrease in properties is observed and the dispersion becomes difficult [10, 11]. The ability of CNT’s to show resistance towards water showed that the epoxy specimen with CNT added to it showed greater water resistance compared to a normal epoxy specimen [11]. Mixing MWCNT along with the adhesive improves the bonding strength and resists the propagation of crack due to strong interfacial bond strength [12]. Addition of graphene nano particles in the adhesive with 10 layers of carbon fibre as an adherend leads to an increase in the peak load of approximately 21 % at 1 wt. % and 57 % at 2 wt. % [13]. Incorporating CNT’s in the adhesives improved the adhesion efficiency and provided a tailored galvanic behaviour of nano composites [14]. The addition of 1 Vol % of Zirconia nano particles lead to an increase in shear strength of about 60%. Additionally the joints containing Zirconia showed decreased contact angle with water [15]. Two different failure modes are considered in the adhesive bonded joints, one is adhesive failure where failure materializes at the interface between the adhesive and adherend due to weak adhesion of the boundary layer while other is cohesive failure where due to fracture in the adherend, the adherend fails first before the adhesive does [16].

2. Experimental Work

2.1 Materials

A plain weave carbon fibre fabric as shown in Figure 1a, T300 of 200 gsm manufactured by Toray Composite Materials, was used to create a laminate to be used as the adherend. The required thickness was obtained by using 11 layers of the carbon fibre. For preparation of the laminate, bonding of each layer of carbon fibre fabric was done by using a two-part epoxy resin namely ROTEX EP – 306 and hardener ROTEX EH – 758. For joint creation a separate bonding material was used which is also a two-part epoxy adhesive ROTEX EP- 416 and the hardener was ROTEX EH-153 as the epoxy adhesives are considered as the strongest adhesives.
Table 1. Properties of Carbon/Epoxy Laminate

| Properties                        | Values   |
|-----------------------------------|----------|
| Longitudinal Young’s Modulus ($E_1$) | 70 GPa   |
| Transverse Young’s Modulus ($E_2$)  | 70 GPa   |
| In-Plane Shear Modulus ($G_{12}$)  | 5 GPa    |
| Major Poisson Ratio ($\nu_{12}$)   | 0.10     |

MWCNT of 99% purity, 10 – 15 nm average diameter, 5μm average length and 400 m²/g and Fullerene C60 of 99% purity with 1600g/cm³ of relative density was used as the filler material to be added in the adhesive for creating the joints. Properties of the adherend and adhesives (one for creating the laminate and other for creating joint) are mentioned in Table 1 and 2.

Table 2. Properties of Adhesive System

| Properties  | Values       |
|-------------|--------------|
| FOR RESIN   |              |
| Viscosity   | 30000-50000  |
| Specific Gravity | 1.15-1.20     |
| FOR HARDENER|              |
| Viscosity   | 25000-40000  |
| Specific Gravity | 0.90-0.99     |

2.2 Laminate Preparation

CFRP laminate shown in Figure 1b was prepared by using hand layup technique. Carbon fibre fabrics of dimensions 500 mm * 500 mm were used for preparing the laminate. A mylar sheet of required dimensions were cut and cleaned by using thinner and then wax was applied for easy removal of the laminate and also for removal of air bubbles. ROTEX EP – 306 resin along with ROTEX EH – 758 hardener was mixed in the ratio of 10:1 by weight and applied over the mylar sheet. A layer of carbon fibre fabric was laid over the resin hardener mixture and a roller was used to remove the excess resin and the air bubbles. The same process was repeated for the next 11 layers.

Finally a cleaned and waxed mylar sheet was laid over the final layer of carbon fibre and then required amount of weight was put in order to apply pressure. The prepared laminate was then cured at room temperature for 24 hours following which curing was carried out in an oven for 2 hours at 60˚ C. Two such laminates were prepared.
2.3. Specimen Preparation

2.3.1 Preparation of Specimen and Preparation of Specimen Surface
The laminate was cut by using abrasive water jet cutting technique to produce the required specimen. The dimension of the specimens are 101.6 mm * 25.4 mm as per ASTM D-5868-01 standard as mentioned in Figure 2. This method of cutting was chosen over the other methods due to its advantage of producing smooth edges and avoids delamination at the edges. A high speed jet of water mixed with sand particles which act as abrasive was used as a medium for cutting the specimens. The average thickness of the cut specimens was measured to be 2.98 mm. Further the surface of specimens was prepared for making the joints. The surface preparation was necessary in order to create a strong and long lasting bond between the adhesive and adherend. Thus a part of the specimen was rubbed with 40 grit sand papers to make the surface rough where joint was supposed to be made. The specimens were then cleaned with acetone to remove any dust or loose particles formed after rubbing with sand paper.

2.3.2 Preparation of Adhesive System
This process is of prime importance, as it requires proper and homogeneous dispersion of nanofillers in the adhesive. Dispersion of nanofillers done mechanically provides even distribution thereby enhancing its properties, while the dispersion done by high speed mixing creates bubbles that cannot be easily removable, though both the methods can be used for dispersion [17]. Thus in the current study, mechanical/ultrasonication was carried out to disperse MWCNT and Fullerene C_{60} into ROTEX EP - 416 resin as shown in Figure 3. During the process, firstly 15 g of resin was taken and then 1 wt %, 3 wt %, 5 wt % and 7 wt % of MWCNT and Fullerene C_{60} was added respectively and kept in ultrasonicator at a frequency of 30 Hz for 45 minutes to obtain proper dispersion. During the process the temperature was maintained at 60 °C. Further to the mixture, an equal amount of ROTEX EH – 153 hardener was added.
During the sonication process, it was observed that epoxy containing 1 wt % and 3 wt % of MWCNT and Fullerene C₆₀ respectively got easily and completely dispersed but as the nanofiller percentage was increased to 5 wt % and then to 7 wt %, the nanofillers even though partially dispersed, began to coagulate resulting in uneven and dense dispersion. An unreinforced mixture of adhesive was also prepared by hand stirring of resin and hardener.

![Ultrasonication of nanofillers (MWCNT and Fullerene C₆₀) in the Adhesive](image)

**Figure 3.** Ultrasonication of nanofillers (MWCNT and Fullerene C₆₀) in the Adhesive

2.3.3 Preparation of Joints

To prepare the sample of ABSLJs unreinforced adhesive and adhesive reinforced with nanofillers were applied to one of the rough and cleaned surface of the adherend covering the overlap distance. Metal shims were placed to provide a uniform thickness to the adhesive. On top of the adhesive layer, the rough surface of another adherend was placed covering the overlap and making a complete single lap joint. The joint was then cured by clamping for 8 hours at room temperature. The metal shims were then removed and further the empty space on the sides was filled up with the respective adhesive mixture. Care was taken during removal of the metal shims so as to not disturb the alignment and bonding. Once the joint was filled with adhesive after removal of the shims, they were clamped again and left to cure for 24 hours at room temperature and further curing was done by placing the ABSLJs in oven at 60 °C for 6 hours. 3 samples were made for each joint type taking the total to 27 sets. Once the curing was completed, ABSLJs were obtained as shown in Figure 4 and the average thickness of the joint was found to be 3.23 mm.

![ABSLJ’s](image)

**Figure 4.** ABSLJ’s
2.4 Testing Procedure

The single lap joint test was carried out using a computer controlled universal testing machine at a temperature of 32 °C. Specimens were categorised into 5 main groups with each group containing 3 joint samples each as given in Table 3. Specimens with different configuration of joints were subjected to tensile loading as shown in Figure 5 at a rate of 1 mm/min. Overall thickness of adhesive layer was measured for all the joint configuration before the test and the average thickness was found to be 0.25 mm. Once the test was concluded, the joints were visualised for adhesive and cohesive failure.

Table 3. Designation and Configuration of various samples

| Joint Designation | Adhesive/Reinforcement |
|-------------------|------------------------|
| C/EP416+EH153     | C/EP416+EH153/Non reinforced |
| C/EP416+EH153/CNT/I | C/EP416+EH153/MWCNT/1% |
| C/EP416+EH153/F/I   | C/EP416+EH153/Fullerene/1% |
| C/EP416+EH153/CNT/II | C/EP416+EH153/MWCNT/3% |
| C/EP416+EH153/F/II   | C/EP416+EH153/Fullerene/3% |
| C/EP416+EH153/CNT/III | C/EP416+EH153/MWCNT/5% |
| C/EP416+EH153/F/III   | C/EP416+EH153/Fullerene/5% |
| C/EP416+EH153/CNT/IV   | C/EP416+EH153/MWCNT/7% |
| C/EP416+EH153/F/IV    | C/EP416+EH153/Fullerene/7% |

3. Results and Discussions

Three samples each from the above mentioned configuration given in Table 3 were tested to determine the maximum load at which the joints failed. The average value was taken to determine the average failure load given in Table 4 and Figure 6. The addition of nanofillers to the adhesive increases the failure/damage load but only till certain weight percentage of nanofillers. With addition of 1 wt % of CNT as a reinforcement to the adhesive in comparison with unreinforced adhesive, the average damage load increases by 93%. This indicates that the addition of MWCNT nanofillers substantially improves the bonding strength when compared to the bonds formed by the unreinforced adhesive. Increasing the weight percentage of MWCNT to 3% further increases the damage load to 199%. This increase in the damage load is due to homogeneous dispersion of MWCNT nanofillers in the adhesive. Also the failure load had increase because of better bonding between the adhesive and adherend. However the addition of Fullerene
C$_{60}$ to the adhesive in 1 wt % and 3 wt %, the average damage failure load increased by 56% and 35% but the increase in considerably lower by 37% and 164% when compared with the similar weight percentage of MWCNT.

Further when the percentage of MWCNT was increased to 5 wt % and 7 wt % respectively, the average load decreased by 14% and further by 32% respectively when taken in comparison with the peak damage load obtained by using 3 wt % of MWCNT. Also providing an increase in the percentage of Fullerene C$_{60}$ by 5 wt % and 7 wt % resulted in decrease in the average damage load in comparison with similar weight percent of MWCNT.

This decrease is observed due to the increase in amount of MWCNT and Fullerene C$_{60}$ added to the adhesive which lead to improper dispersion thereby making it impossible to create a proper bond between the former and the later.

| Joint Designation          | Failure Load (N) | Average Failure Load (N) |
|----------------------------|-----------------|--------------------------|
| C/EP416+EH153              | 1875            | 1877                     |
|                            | 1842            |                          |
|                            | 1914            |                          |
|                            | 3548            |                          |
| C/EP416+EH153/CNT/I        | 3641            | 3625                     |
|                            | 3684            |                          |
|                            | 2967            |                          |
| C/EP416+EH153/F/I          | 2892            | 2931                     |
|                            | 2934            |                          |
|                            | 5679            |                          |
| C/EP416+EH153/CNT/II       | 5583            | 5626                     |
|                            | 5618            |                          |
|                            | 2542            |                          |
| C/EP416+EH153/F/II         | 2586            | 2541                     |
|                            | 2495            |                          |
|                            | 4684            |                          |
| C/EP416+EH153/CNT/III      | 4819            | 4825                     |
|                            | 4972            |                          |
|                            | 1872            |                          |
| C/EP416+EH153/F/III        | 1951            | 1907                     |
|                            | 1898            |                          |
|                            | 3890            |                          |
| C/EP416+EH153/CNT/IV       | 3762            | 3833                     |
|                            | 3847            |                          |
|                            | 1539            |                          |
| C/EP416+EH153/F/IV         | 1598            | 1570                     |
|                            | 1573            |                          |
When we consider the load v/s displacement curve as shown in Figure 7 and Figure 8, it is evident that the addition of MWCNT and Fullerene C$_{60}$ nanofillers to the adhesive improves the displacement capacity of the joints which gives an indication that the adhesively bonded joints doped with nanofillers are capable of taking more failure load. Similarly the load v/s displacement curve also saw a decreasing trend wherein the displacement capacity decreased with increase in MWCNT and Fullerene C$_{60}$ percent but the displacement obtained by doping the adhesive with MWCNT is higher for all categories of joints when compared with the joints created by addition of Fullerene C$_{60}$.

It was also noted that, majority of the ABSLJ’s suffered adhesive failure, where the failure initiated at edges and moved to the center, even though the adhesive thickness was maintained the same throughout, due to the weak bonding between the adhesive and the adherend.
4. Conclusion
The current work involved finding the effect of addition of various wt % of MWCNT and Fullerene C$_{60}$ to the adhesive used to create ABSLJ’s on the tensile failure load. From the results it is concluded that:

- The epoxy adhesive used here was capable of producing strong bond there and thereby can be classified as a rigid type of adhesive.
- The tensile damage load depends on dispersion of various percentages of nanofillers in the adhesive. Homogenous dispersion was obtained when the nanofillers were added in optimum weight percent thereby increasing the strength at the interface. While with the increase in percent of nanofillers, complete dispersion was not obtained resulting in decrease in the damage load.
- Addition of MWCNT nanofillers to the adhesive in 1 wt % and 3 wt % increases the average failure load by 93% and 199 % respectively but with further increase in percentage of MWCNT to 5% and 7%, the average failure load decreased. This is because of limit in the dispersion of nanofillers and also due to inadequate bonding between the adhesive and adherend.
- Adding Fullerene C$_{60}$ to the adhesive in 1 wt % and 3 wt % led to increase in the average failure load but with further increase in percent of Fullerene C$_{60}$, the average failure loads decreased. It can be said that with the addition of Fullerene in the adhesive, there was no significant increment or decrement in the load carrying capacity of the joints.
- The displacement capacity of the joints with MWCNT was found to be greater when compared with non reinforced joints and joints with Fullerene C$_{60}$ added in the adhesive.
- Adhesive failure was observed in the ABSLJ’s due to insufficient adhesion between the adhesive and the adherend.

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