ECCM17 - 17th European Conference on Composite Materials
Munich, Germany, 26-30th June 2016

ADHESIVE PROPERTY MODIFICATION THROUGH ADDITION OF MWCNTS FOR DISSIMILAR MATERIAL JOINT APPLICATIONS

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Keywords: Multi-walled Carbon Nanotubes (MWCNTs), Joint Strength, Overlap Length, Adhesively Bonded Joints

Abstract

The influence on the bond strength of metal to composite joints through the modification of the adhesive properties by the addition of Multi-walled Carbon Nanotubes (MWCNTs) has been investigated. MWCNT/epoxy resin mixtures of different weight fractions, i.e. 0.1%, 0.3%, 0.5% and 1% were prepared and used for the bonding of dissimilar material joints. Pure epoxy resin was also used in order to obtain the properties of the reference material. Co-cured CFRP/Steel and GFRP/Aluminium single lap joints with three different overlap lengths i.e. 25, 40 and 60 mm were manufactured in order to determine how the joint strength is influenced by the increase of the overlap length and whether the MWCNT additives alter the failure mechanisms involved.

The lap shear strength of both CFRP/Steel and GFRP/Aluminium single lap joints decreased with the increase of the overlap length for all MWCNT weight fractions. However, the incorporation of MWCNTs to the epoxy resin increased the lap shear strength of the joints when the overlap length was 25mm. For the case of CFRP/Steel joints, joint strength increased by 41% for 0.3 wt. % CNT and for 0.5 wt. % CNT, the lap shear strength of GFRP/Aluminium joints increased by 27%.

1. Introduction

Depending on the structural requirements a wide variety of adhesively bonded joints exists, e.g. single lap joints, double lap joints, scarf joints, step joints etc. The single lap joint is one of the most widely used joint configurations because of its design simplicity, low-cost manufacture and simple testing procedure. Many geometrical factors such as the overlap length and adhesive and adherend thickness are parameters that can influence the lap shear strength. In the literature, the effect of these parameters on the joint performance has been extensively investigated [1-8], however, more emphasis will be given to the overlap length and the possibility of reinforcing the adhesive with various micro- and nano-fillers.

In [1], joints with three different adhesives (i.e. ductile, intermediate and brittle), three types of steel adherends (i.e. low, intermediate and high strength steel) and three overlap lengths (12.5mm, 25mm and 50mm) were examined. It was found that when the overlap length increased and provided that the adhesive was sufficiently ductile and the adherends did not yield, joint lap shear strength increased almost linearly. For substrates that yielded, lap shear strength reached a plateau with the increase of the overlap length and this plateau was defined by the yielding of the adherend. The increase of the failure load with the increase of the overlap length for flexible adhesives was also reported in [9]. In another study [2], an increase by 45.5% of the lap shear strength of joints with steel adherends was also shown,

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when the overlap length increased from 12.5mm up to 50mm. Song et al. [3] investigated how various overlap lengths (i.e. 12.7mm, 19.05mm, 25.4mm, 38.1mm and 50.8mm) influenced the lap shear strength of the corresponding joint configurations. The results suggested that by increasing the overlap length, the failure load obtained was higher, because the overall stress level including the peak stresses at the end areas decreased. However, the reduction rate in shear and peak stresses was not linearly proportional to the overlap length. The increase of the overlap length was therefore effective up to a threshold. Similar findings were reported in [4], where the overlap length varied from 15mm to 60mm. The maximum shear strength of aluminium single lap joints was obtained for 40mm overlap length with further increase of the overlap length leading to a decrease in joint strength. Seong et al. [10] studied how the variation of the overlap length (15mm, 20mm, 25mm, 30mm, 35mm, and 40mm) of adhesively bonded CFRP to aluminium single lap joints affects the joint strength. The failure load increased with the increase of the overlap length. However, when the overlap length was greater than 25mm or when the overlap length-to-width ratio was greater than 1, the failure load did not increase substantially. It was therefore concluded that when the overlap length-to-width ratio of single lap bonded joints is much greater than 1, further increase of the overlap is not beneficial.

Most of the structural adhesives [11], such as epoxies, exhibit lower toughness than that of the adherends resulting in failure in the bondline. Therefore, reinforcement of the adhesive is often considered as an alternative approach. In many studies it has been reported that the incorporation of various nanofillers within the adhesive can improve not only the mechanical properties of the bulk adhesive, but also increase the joint strength. Micro-fillers, such as glass and alumina powder are often used as reinforcement to enhance the properties of polymeric materials. Carbon nanotubes are also found amongst the most widely used nanofillers due to their exceptional mechanical properties; Young's modulus=1.2TPa and Tensile strength=50-200GPa [12]. Some of the studies in which a reinforced adhesive was used for the manufacturing of the joints are mentioned below.

Gude et al. [13] assessed the strength and toughness of CFRP composite joints after the incorporation of carbon nanotubes (0.25 wt. %) and carbon nanofibres (0.5 wt. %) to the epoxy resin adhesive. It was found that both nano-reinforcements increased the fracture energy, G_{IC}, of the joints without however, affecting the lap shear strength. Carbon nanotubes also improved the interfacial shear strength between the adherend and the adhesive and prevented the crack from propagating along the adhesive layer by changing the failure mode from fully adhesive to partly cohesive. Srivastava [14] examined the use of epoxy resin containing 3 wt. % of MWCNTs in order to bond carbon/carbon (C/C) and carbon/carbon-silicon carbide (C/C-SiC) composites. It was found that MWCNTs increased the strength and toughness of the bulk adhesive also resulting to the increase of the strength in lap joints bonded with the MWCNT reinforced epoxy adhesive. Hsiao et al. [15] investigated the effect of the incorporation of multi-walled carbon nanotubes (i.e. 1 wt. % and 5 wt. %) in epoxy resin, which was used to bond graphite fibre/epoxy composite adherends. After the addition of 5 wt. % of MWCNTs into the adhesive, lap shear strength increased by 45.6% compared to the values obtained for the case of pure epoxy resin adhesive. Another interesting finding was that the failure mode shifted from adhesive (along the bonding interface) for the epoxy adhesive to cohesive for the MWCNT reinforced adhesive where the graphite fibres of the adherends were fractured and exposed.

The MWCNT reinforced adhesive has also been used to bond metal to composite joints. Kang et al.[16] incorporated 2 wt. % of CNTs into epoxy resin in order to use it as adhesive for CFRP/aluminium single lap joints. Lap shear strength decreased by 36.62%, whereas fatigue strength increased by 12.8% compared to the joints without carbon nanotubes. The addition of 1 wt. % MWCNTs increased the Mode II critical strain energy release rate by approximately 20% in steel/CFRP joints [17]. An interesting observation was that for the samples with higher G_{IIC} values, failure occurred mainly through the steel/adhesive interface, while for the samples with lower G_{IIC} values failure was apparent at the composite/adhesive interface. Finally, Meguid and Sun [18] studied the tensile and shear properties of composite interfaces reinforced with two types of nanofillers, i.e. carbon nanotubes and alumina nanopowder (up to 15 wt. %). CFRP substrates were bonded to aluminium alloy substrates using the reinforced epoxy adhesive. Both shear and tensile properties (strength and modulus) increased with the

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increase of the weight percentage of the nanofillers. However, a further increase of nanofillers above 10 wt. % degraded the properties
In the current study, co-cured CFRP/Steel and GFRP/Aluminium single lap joints with three different overlap lengths, i.e. 25, 40 and 60 mm are bonded using a MWCNT/epoxy resin mix of various weight fractions, i.e. 0.1%, 0.3%, 0.5% and 1%. Lap shear tests are conducted to quantify the effect of the incorporation of MWCNTs on the joint strength.

2. Experimental Methods

2.1 Materials

A standard two-part epoxy resin supplied by PRF Composites was used as matrix. The thermosetting epoxy resin (RS-L135) was mixed with an amine based hardener (RS-H136) at a weight ratio of 100:35. The viscosity of the epoxy system is 500-1000mPa s at 25ºC and the pot life varies from 90 to 120min. Industrial grade (90% purity) thin multi-walled CNTs, NC7000™, supplied by Nanocyl were used as reinforcement. NC7000™ CNTs, which are produced via Catalysed Chemical Vapour Deposition (CVD) method, have a diameter in the range of 9.5nm, their average tube length is 1.5μm and the surface area is around 250-300m^2/g. Some of their properties are shown in Table 1.

Table 1: Mechanical Properties of MWCNTs.

E (TPa)	1	**Strain at Break (%)**	10
Strength (GPa)	10-60	**Specific Density**	1.3-2

The metal substrates were cut from either a 5061 aluminium alloy or a mild steel plate. Woven glass and carbon fabric (290 gsm plain weave) supplied by Easycomposites was used for the manufacturing of the composite substrates. The mechanical properties of both metal and composite substrates obtained from mechanical tests are shown in Table 2.

Table 2: Mechanical properties of substrates.

Substrates	Young’s Modulus (GPa)	Tensile Strength (MPa)
Steel	222.724	356.54
Aluminium	69.73	308.44
CFRP	52.05	329.85
GFRP	20.02	-

2.2 Reinforced Adhesive with MWCNTs

Prior to joint manufacturing, the MWCNT reinforced epoxy resin adhesive of weight fraction ranging from 0.1% to 1% was prepared. The manufacturing process involved mechanical stirring and ultrasonic excitation (or sonication) method to achieve uniform dispersion of the MWCNTs in the matrix. More specifically, the epoxy resin and MWCNTs were mechanically stirred for 5min at 10,000rpm, followed

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by sonication (amplitude=65% and cycle=0.6) for 30min. The mixture was then placed in a vacuum chamber for 20min in order to remove the air trapped during mixing (degassing). The hardener was then added and after 5min of hand stirring, the mixture (resin+CNTs+hardener) was degassed again for 20min.

2.3 Dissimilar Material Bonded Joints

Substrate surface preparation is vital for the successful implementation of the adhesive bonding technology. Therefore, all metal substrates were thoroughly prepared via gritblasting of the bonding area which created an average surface roughness of 7.5μm. Gritblasting was then followed by acetone degreasing of the surface prior to the application of the adhesive. Following the adhesive and metal surface preparation, co-cured CFRP/Steel and GFRP/Aluminium joints were manufactured.

The manufacturing process was a combination of hand lay-up (HLU) and vacuum bagging process. The MWCNT reinforced epoxy resin, which was prepared as described above, was applied onto the bonding area of the metal substrate. A layer of either woven glass or carbon cloth of 0.23mm and 0.27mm ply thickness respectively was laid on top. Then, the subsequent layers were added. Sixteen layers of glass cloth and twelve layers of carbon cloth impregnated with pure epoxy resin by simple HLU were laid in total to achieve a laminate thickness of approximately 4mm and 3mm respectively (Figure 1).

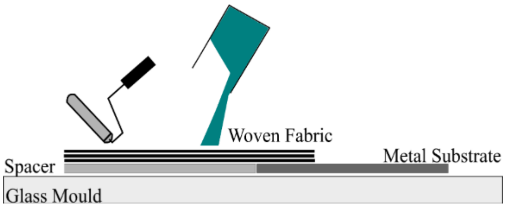

Figure 1: HLU process.

Vacuum bagging process was then used to remove the excess air introduced through the HLU and achieve uniform thickness of the composite laminate. The resin curing process involved 24h at room temperature followed by a post-curing process of 15h at 50°C. Due to the fact that the bonding and curing of the composite substrate occur at the same conditions, i.e. time and temperature, co-curing method is simplifying not only the manufacturing process, but also the analysis of the joint [19].

2.4 Mechanical Testing

Lap shear tests [20] were conducted at constant crosshead speed (1mm/min). The single lap joint configuration is shown in **Error! Reference source not found.**a. The bonding area was 25mm x 25mm, 25mm x 40mm and 25mm x 60mm for 25mm, 40mm and 60mm overlap length respectively.

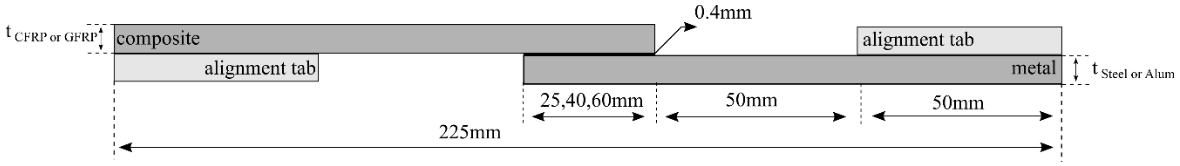

Figure 2: Single lap joint configuration.

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3. Results and Discussion

The tensile stress-strain curves [21] for the adhesives with various MWCNT weight fractions are shown in Figure 3. The addition of MWCNTs in the epoxy affects the mechanical behaviour of the adhesive by decreasing both tensile strength and strain to failure.

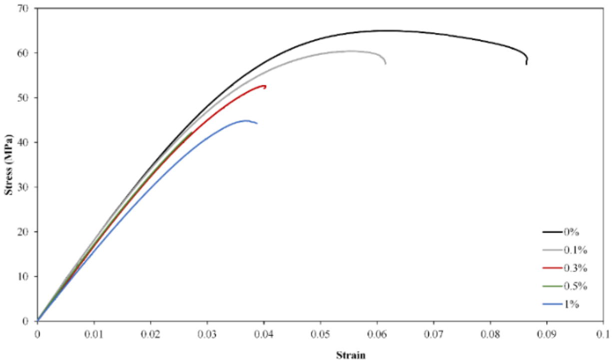

Figure 3: Tensile stress-strain curves of the various adhesives used [21].

In Figure 4 and Figure 5 the lap shear strengths of CFRP/Steel and GFRP/Aluminim joints respectively are plotted against the CNT weight fraction of the adhesive for all three overlap lengths tested.

The lap shear strength of CFRP/Steel single lap joints decreases with the increase of the overlap length for all MWCNT weight fractions. This result suggest that an optimized joint design can be achieved with overlap length-to-width ratio of 1, i.e. for the case of 25mm overlap length (25mm: 25mm). Similar findings were also reported in [10].

In addition, the incorporation of MWCNTs in the epoxy resin seems to affect the joint strength values only when the overlap length equals to 25 mm. The highest loading capacity is obtained for 0.1 wt. % CNT and 0.3 wt. % CNT, where the lap shear strength increases by 29% and 41% respectively. A further increase of the CNT content to 0.5 wt. % leads to joint strength almost equal to that achieved when pure epoxy is used for bonding. However, when the CNT content reaches 1%, a significant decrease of the strength is observed, which might be attributed to the poor dispersion of the MWCNTs in the epoxy resin adhesive. For greater overlap lengths (40mm and 60mm), the bonding strength remains almost constant for all MWCNT contents.

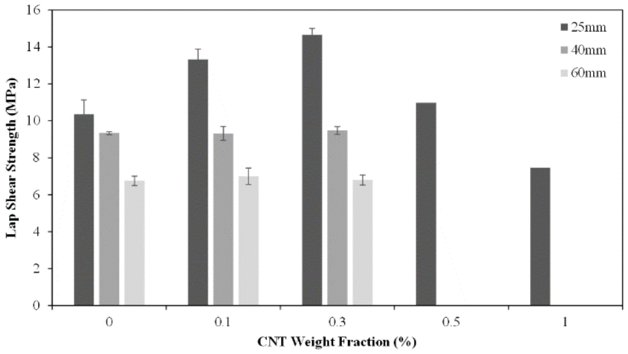

Figure 4: Lap shear strength versus CNT weight fraction of CFRP/Steel joints for three overlap lengths.

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Similar observations can be made for the case of GFRP/Aluminium single lap joints (Figure 5). The joint strength also decreases with the increase of the overlap length. For the case of 25mm overlap length, the lap shear strength increases by approximately 17% and 27% for 0.1 and 0.5 wt. % CNT respectively. However, when the overlap length equals to 40mm or 60mm, the joint strength shows almost no variation with the MWCNT content.

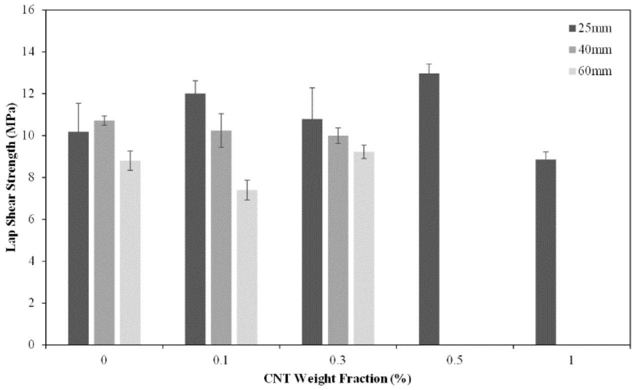

Figure 5: Lap shear strength versus CNT weight fraction of GFRP/Aluminium joints for three overlap lengths.

The fracture surfaces of CFRP/Steel and GFRP/Aluminium joints are shown in Figure 6. The addition of MWCNTs in the epoxy resin used for bonding affects the failure mode of the joints. As the MWCNT content increases, the failure mode shifts from cohesive to adhesive.

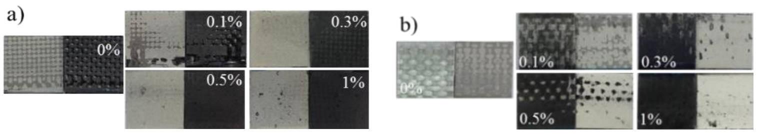

Figure 6: Bonding area of: a) CFRP/Steel and b) GFRP/aluminium single lap joints bonded with pure epoxy resin, 0.1 wt. % CNT, 0.3 wt. % CNT, 0.5 wt. % CNT and 1 wt. % CNT.

Finite element analysis was employed in order to determine the stress field along the overlap length at the middle of the adhesive layer. A 2-D single lap joint was modelled and plane strain was assumed. The metal adherend was assumed to deform plastically, while the adhesive behaves linearly. Quadrilateral-shaped elements were used with the mesh density being refined at the wedges (Figure 7).

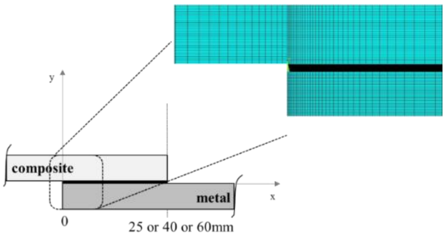

Figure 7: Mesh density at the wedges.

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Shear stress distribution normally exhibits the same values at the overlap ends, however a significant variation of the shear stress values between the two ends is observed for both CFRP/Steel and GFRP/Aluminium joints in Figure 8. The asymmetry in shear stress distribution along the overlap length is because the single lap joints consist of two different material adherends.

For both types of joints shear stress values at the side of the composite are much higher than those at the side of the metal due to the lower Young's modulus of the composite material which results to higher shear deformations in the adhesive and hence, to higher shear stresses.

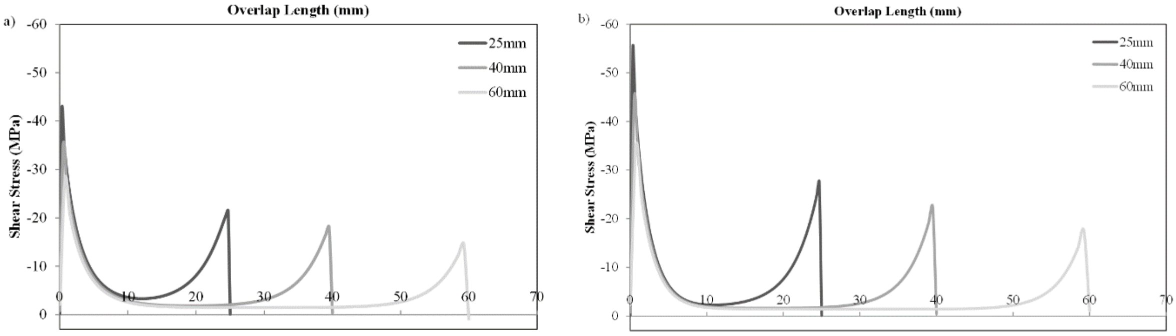

Figure 8: Shear Stress along the overlap length of: a) CFRP/Steel and b) GFRP/Aluminium joints at the middle of the adhesive layer (for a tensile load of 6000N).

However, GFRP/Aluminium joints exhibit higher peak stresses than CFRP/Steel joints. This might be attributed to the fact that CFRP and steel adherends are stiffer that the GFRP and aluminium ones. The stiffer the adherends, the more uniform shear stress distribution within the adhesive resulting to higher lap shear strength.

In Figure 9, peel stresses for both dissimilar material joints are plotted along the overlap length.

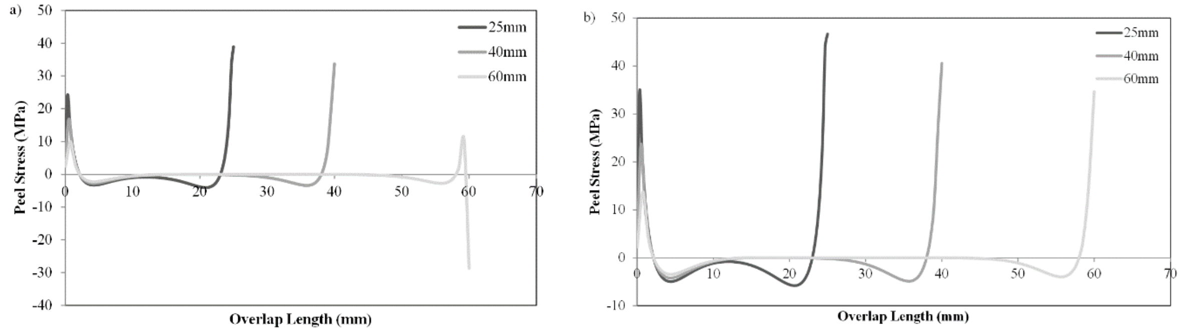

Figure 9: Peel Stress along the overlap length of: a) CFRP/Steel and b) GFRP/Aluminium joints at the middle of the adhesive layer (for a tensile load of 6000N).

As the overlap length increases, the overall stress level, including the peak stress at the overlap ends decreases [3, 22].

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The reduction of the peak stresses results to the increase of the failure load with the increase of the overlap length (Figure 10). Typical load-displacement curves of: a) CFRP/Steel and b) GFRP/Aluminium joints are shown below.

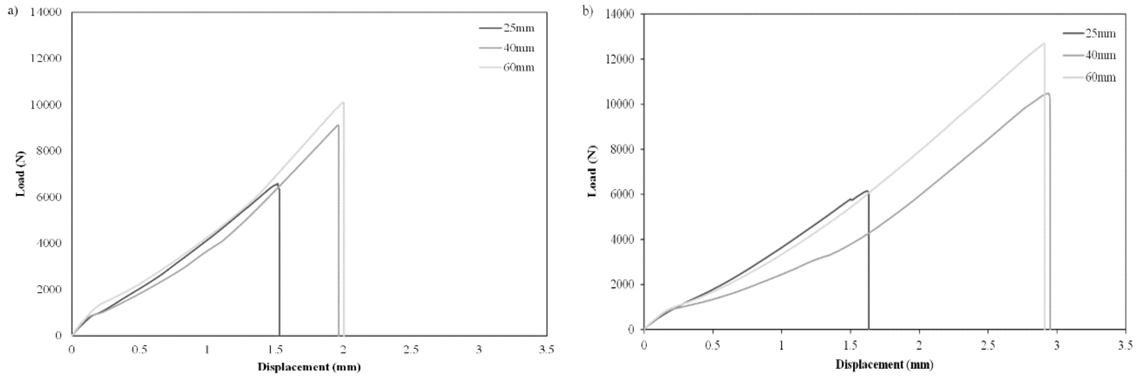

Figure 10: Load–displacement curves of: a) CFRP/Steel and b) GFRP/Aluminium joints obtained during testing for three overlap lengths.

4. Conclusions

The lap shear strength of both CFRP/Steel and GFRP/Aluminium single lap joints decreases with the increase of the overlap length for all MWCNT weight fractions. The increase of the joint load bearing capacity is not proportional to the increase of the overlap length, thus an optimized joint design can be attained with overlap length-to-width ratio of 1.

In addition, the incorporation of MWCNTs to the epoxy resin seems to affect the joint strength values only when the overlap length equals to 25 mm. For the case of CFRP/Steel joints, the highest loading capacity is obtained for 0.1 wt. % CNT and 0.3 wt. % CNT, where the lap shear strength increases by 29% and 41% respectively. For the GFRP/Aluminium joints, the lap shear strength increases by approximately 17% and 27% for 0.1 and 0.5 wt. % CNT respectively. However, when the overlap length equals to 40mm or 60mm, the joint strength shows almost no variation with the MWCNT content.

Shear stress distribution along the overlap length at the middle of the adhesive determined through FEA was found to be asymmetric at the overlap ends due to the different material adherends used with the shear stress values at the side of the composite being much higher than those at the side of the metal.

Acknowledgements

The authors acknowledge the EU FP7 “SAFEJOINT” project for financial support.

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