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The Use of Nano-modified Epoxy Adhesive in Metallic Bonded Joints: Experimental Analysis

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Abstract. *This paper addresses the performance study on, high viscosity, nano-modified epoxy adhesive by addition of carbon-based nanostructure (multiwall carbon nanotubes and multi-layered graphene). To disperse more efficiently the carbon based nanostructure, two different surfactants were employed, i.e. Sodium dodecyl benzenesulfonate (SDBS) and Polyoxyethylene nonylphenyl ether (IGEPAL CO890). The apparent shear stress test for single-lap joints showed that the dispersion of 0.15%wt and 0.3%wt of MWNT-SDBS lead to increase the average of peak shear strength in 99.91% and 124.34%, respectively, when compared with the control group. The hybrid nanostructures (MWNT+G) were able to improve the stiffness of the bonded joint in around 27.4%. It was possible to notice a change in the failure mechanism from adhesive to cohesive failure mode in some of the groups tested. AFM analysis proves the interaction between the epoxy system and the nanostructures.*

Keywords: *nanocomposite, graphene nanosheets, single-lap joint, nano-modified adhesives, carbon nanotubes*

1. INTRODUCTION

In many practical applications, the use of joints allows the manufacturing of complex structures that could not be created in a single piece due to the high costs involved and geometrical limitations (Avila and Bueno, 2003). According to Tong and Steven (1999), bonded joints present the interesting solution to assembly components due to the more uniform distribution of stress. The efficiency of bonded process is highly dependent of bonded area, adhesive strength and the quality of the adherent's surfaces. As commented by Cruz *et al.* (2013) and Banea and da Silva (2009), bonded joints are frequently expected to sustain static load or cyclic load for considerable periods of time without any adverse effect on the load-bearing capacity of the structure. They must hold a high stability towards a variety of mechanical, chemical and physical changes under service conditions.

Adhesives have been used for so long, but, as discussed by Croccombie and Ashcroft (2008), it was only in 1940´s that the progress in the polymer science allowed the development of new adhesives and consequently an increase on load-bearing capacity. Among the polymeric resins, epoxies are the most used system as high-performance structural adhesive. As commented by Kahraman *et al.* (2008), epoxy resins are attractive for metal-bonding adhesive systems because of their ability to cure without producing volatile by-product and their low shrinkage upon cure. Also they have a good affinity for aluminum alloy surfaces and the oxide layers produced during surface preparation. In recent studies, the polymeric adhesive systems are often modified by adding fillers or nanofillers. Thostenson *et al.* (2005) called this modified resins of nanocomposite or nano-modified polymeric composite, which, in general, possesses much higher mechanical properties when compared with net polymeric resin. This new approach based on nanotechnology shows great potential in the industrial applications.

The discovery of CNTs has opened vast areas of research in the nanoscale reinforcements for composites, in order to improve their mechanical, thermal and electrical properties. According Gouda *et al.* (2013), the multi-walled carbon nanotubes with diametrical range of 5-40 nm are known for their exceptional mechanical properties. Their modulus are compared to that of diamond (around 1.2 TPa), they have strength 10-100 times higher than the strongest steel, and possesses 500 more surface area per gram (if compared with a typical carbon fiber).

Many works showed the positives effects of fill polymer resins with carbon nanotubes. Godara *et al.* (2009) observed an increase in crack initiation energy (GI_c) by 75% of MWCNT-epoxy system with a compatibilizer if compared to the benchmark carbon epoxy system. Davis *et al.* (2010) tested carbon fiber reinforced epoxy composite with different amounts of fluorine functionalized CNTs. Their results showed that sample with 0.5wt. % f-CNT presented an average increase of 18% in strength and 24% in stiffness, compared with neat material. Ashrafi *et al.* (2011) performed impact and compression-after-impact (CAI) tests, Mode I Interlaminar fracture toughness and Mode II Interlaminar fracture toughness tests in modified epoxy resin filled with different quantities of functionalized single-wall nanotubes. They found that incorporation of 0.1 wt. % of SWCNT resulted in a 5% reduction of the area of impact damage, a 3.5% increase in CAI strength, a 13% increase in Mode I and 28% in Mode II of fracture toughness.

Graphene, another carbon nanostructure, has been attracted great attention of scientific community since of its discovery. Gein and Novoselev (2007) defined graphene as a single layer of carbon atoms tightly packed into a two-dimensional honeycomb lattice. Notice that graphene can be described as the basic layer components of graphite. According Avila *et al.* (2014), one of the pioneers on graphite research is Yasmin, they stated that graphene based nanocomposite can be an alternative option for engineering applications due to their outstanding specific strength and stiffness. However, the different routes to obtain grapheme nanosheets and their dispersion processes can lead a large variety of mechanical properties. Wang *et al.* (2012) employed functionalized graphene nanosheets (f-GNSs) in epoxy resin, and they found that adding 1 wt. % f-GNSs is capable to increase the tensile strength and elongation to failure of epoxy resins by 45% and 133%, respectively. Kuilla *et al.* (2009) in their work, showed that the adding of 1 wt. % GO to the epoxy resins had a similar effect on improving the thermal conductivity to that of filling the resin with 1wt. % of SWNT. A 5 wt. % GO-filled epoxy resin showed a thermal of 1 W/mK, which is 4 times higher than that of the neat epoxy resin.

Cai *et al.* (2008) was one of the pioneers to report the use of a hybrid nano-filler reinforcement composed by CNTs and graphene/graphite oxide. Their work analyzed the influence of filler containing GO nanosheets obtained by Hummer method and commercial MWCNTs with OH groups on electrical properties of thin films. Following this same idea Avila *et al.* (2014) tested the influence of adding a functionalized hybrid CNT-MLG on mechanical properties of Carbon/Epoxy laminate. They found a peak stress increase from 542.76 MPa to 667.51 MPa for tensile and an increase from 369.40 MPa to 584.15 MPa in bending peak stress. This new group of materials derived from hybridization of CNTs and graphene or graphite oxide has been showed better performances than their corresponding CNTs and G/GO isolated.

As pointed by Li *et al.* (2008) a key of challenge in the synthesis and processing of bulk-quantity of graphene, carbon nanotubes and many others nanomaterials is aggregation. For example, graphene, due to their high specific surface area, unless well separated from each other's, tend to form irreversible agglomerates or even restack to form graphite through van der Walls interactions. To avoid graphene/CNT clusters/agglomerates Tkalya *et al.* (2012) suggested the use of surfactants. According to them, during the dispersion process by sonication (by bath or horn) carbon based nanostructures are exfoliated into individual nanostructures. The exfoliation process is due to the mechanical energy provided by sonication which overcomes the Van der Waals interactions between CNTs bundles and graphene platelets. If this energy is removed, the individual nanostructures have the tendency to agglomerate. The usage of surfactants during the sonication promotes the surfactants molecules adsorption onto individual exfoliated nanostructures and consequently avoiding agglomeration.

In parallel, new designs also contributed to increase the bonded joint efficiency. Many designs have been proposed by several authors, between then, Zeng and Sun (2001) and Avila and Bueno (2003), which proposed a single wavy lap joint. This new design avoids the load eccentricity common to the single lap joints and allows the development of compressive stress at the end of the overlap section. According Tong and Steven (1999), the presence of a peel stress at the end of overlap region can be highly destructive for the adhesive. However, the homologation process of these new design joints takes a long time and the costs associated with the development and tests are in the most cases impracticable for industrial purposes

This work has the objective of development a new nano modified adhesive by adding functionalized carbon based nanostructures.

2. MATERIAL AND EXPERIMENTAL PROCEDURES

The single-Lap joints were made of aluminum 2024-T3 with thickness of 3.2 mm and width of 25.4 mm. The single-lap joints geometry followed the ASTM D1002-10 standard. Figure 1 describes the single-lap dimensions. Adhesive was modified by multi-layered graphene and multi-wall carbon nanotubes dispersion fallowing the concentrations described in Table 1. The MWNT were grown by CVD as described by Lacerda *et al.* (2004), while the multi-layered graphene (MLG) were produced from expandable graphite using the technique developed by Avila *et al.* (2012). As discussed by Carley *et al.* (2013), the optimum concentration for MWNT dispersion into epoxy system seems to be 0.3 wt. %. Neto *et al.* (2013) argues that multi-layered graphene dispersion into epoxy systems has a saturation limit close to 2 wt. %. Therefore, the amount of MLG employed in this research will be 0.3 wt. % the same quantity of carbon nanotubes.

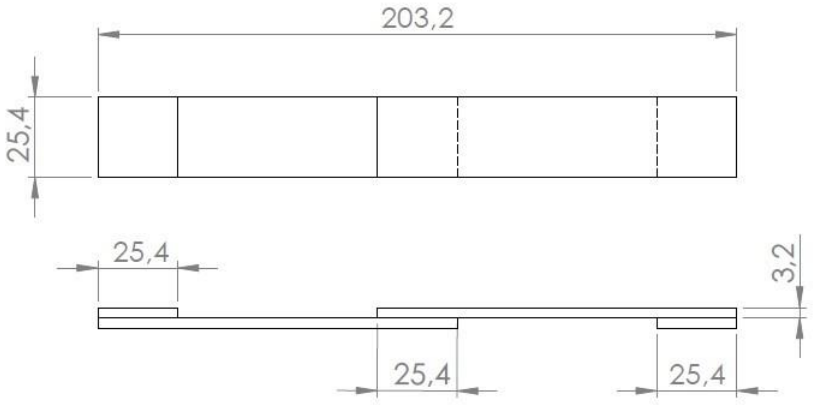


Figure 1. Dimensions of Sample

Table 1. Concentration of nanofillers in each sample

Sample Group	MWNT-SDBS concentration	MLG-CO890 concentration (wt.%)
1	-	-
2	0.15	-
3	0.3	-
4	-	0.15
5	-	0.3
6	0.15	0.15
7	0.15	0.30
8	0.3	0.15
9	0.3	0.3

Based on Tkalya *et al.* (2012) and Pu *et al.* (2012) results, two surfactants were selected, i.e. nonylphenylether (CO890) and Sodium dodecyl benzenesulfonate (SDBS). The graphene aqueous solutions were prepared at 300 ppm of CO890 and MWNT solution were prepared with 200 ppm of SDBS. A bath sonication system at 42 KHz was employed for at least 30 minutes. After the carbon nano-fillers were completely dispersed, the aqueous solution was dried in a vacuum oven for 24hours.

The epoxy system used in this study was the AH345, a two-part epoxy adhesive supplied by Barracuda Advanced Composite. Due to its high viscosity (106.000 cps), in this first study with this adhesive, the dispersion of the nano-fillers was conducted manually over 30 min. The epoxy system has a gel time of 65 minutes and average viscosity (resin+hardner) of 61.000 cps. The SLJ was cure on air for 24 hours. The tests were performed in accordance with ASTM D1002-10 standard.

3. RESULTS AND DISCUSSION

Figure 2 shows a typical force-displacement curve for all groups studied. As it can be noticed in Figure 2, the addition of carbon based nanostructures led to an increase on stiffness in all cases. For group ID-1 the average stiffness was around 2945 N/mm, while for groups ID-2 and ID-4 the average value was close to 3513 N/mm (an increase of 19.3%). Another two groups with the same stiffness (slope) were ID-3 and ID-5. Again an increase on stiffness (3660 N/mm) when compared against group ID-1 was noticed. This change on stiffness (an increase close to 24.3%) can be linked, as well as the previous case, to the addition of the carbon based nanostructures. Noticed that these nanostructures, MWNT or MLG, have stiffness close to 1.0 TPa as described by Avila *et al.* (2014). Therefore, an increase on stiffness was expected. Finally, the addition of Mixed nanostructures (ID-6, ID-7, ID-8, ID-9) also provided an increase on stiffness (3752 N/mm), in this case around 27.4%.

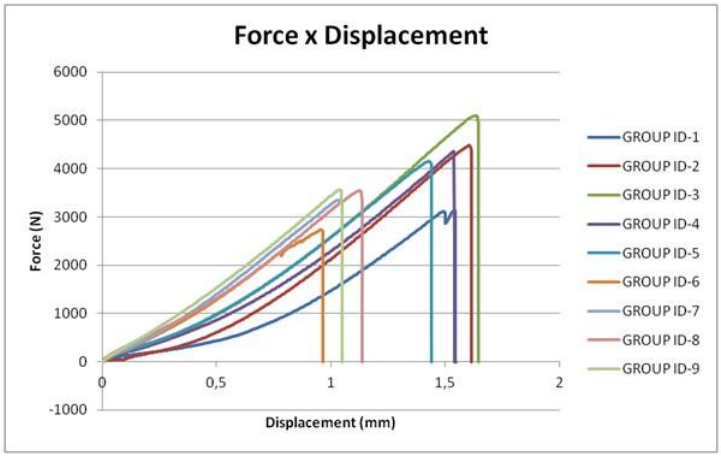


Figure 2. Typical force-displacement curves for single-lap joints tested

Figure 3 shows the results of shear stress found in the sample groups, to be able to have a comparison basis, the shear stress were normalized by the adhesive thickness. After performing a t-test using the software origin, it is possible to observe that all data are statically different at the level of 0.05 with relation to the blank specimen (group ID-1). The addition of 0.15 wt. % and 0.3 wt. % of MWNT-SDBS shows the best results of all groups ID, the increase in the mean value of normalized peak shear strength was, respectively 99.91% and 124. 34%.

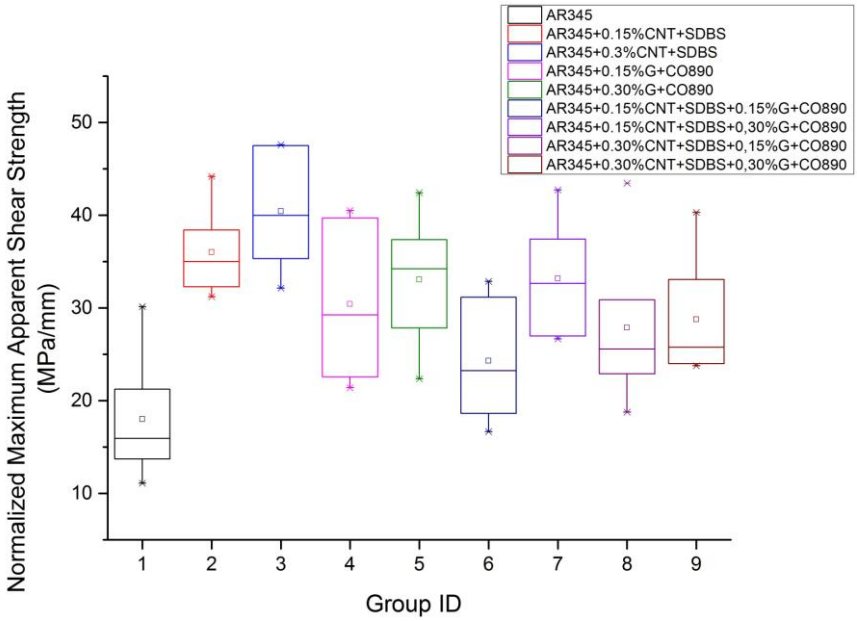
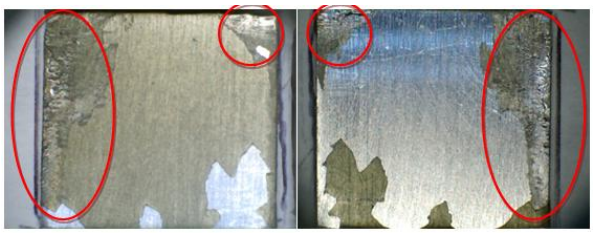


Figure 3. Normalized maximum shear stress (τ/t), where τ is the maximum shear stress and t is the thickness of the bond line

The main failure mode found in the samples is the adhesive type, but in these two nano-modified groups (ID-2 and ID-3) are possible to observe the presence of large areas of cohesive failure. The figure 4 shows cohesive failures observed in some specimens of these groups. The cohesive areas correspond 23.1% of failure region to group ID-2 and 31.25% to group ID-3, approximately. This increase in the cohesive failure mode area could explain the increase in the peak shear strength presented by these two groups. The explanation for these changes can be attributed to the nano-structures inside the adhesive and the interface adhesive/adherents. These nanostructures possibly promoted a redistribution of stress around the bonded area.

(a)



(b)

Figure 4. Representative images of failure modes. In all figures, in the first failure region the free edge is pointing up and pointing down in the second failure region. (a) 0.15 wt.% MWNT-SDBS; (b) 0.3 wt.% MWNT-SDBS

The t-tests showed that groups ID4, ID-5, ID-6, ID-7, ID-8, ID-9 have a average peak shear strength that are not statistically different between then. Presence of the same failure mode (adhesive) for these groups could explain the "average" effect similar. Figure 5 shows the adhesive failures in these groups.

(a)

(b)

(c)

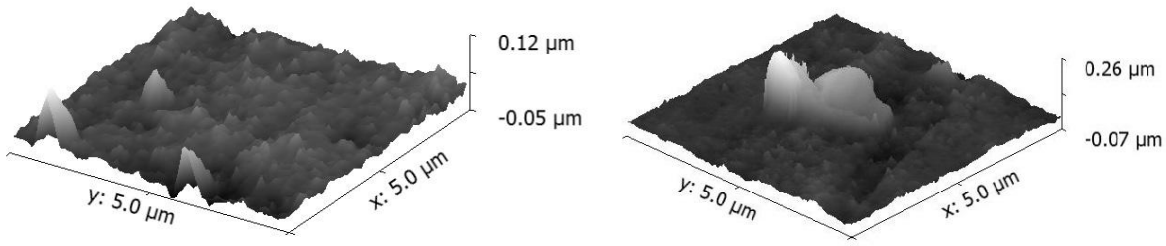
(d)

(e)

(f)

Figure 5. The adhesive failure region. In all figures the free edge is pointing down. (a) ID-4; (b) ID-5; (c) ID-6; (d)ID-7; (e) ID-8; (f) ID-9.

To be able to understand the mechanism behind the nanostructure addition to the adhesive an AFM analysis was performed. As an illustrative example, the group ID-3 and ID-5 were analyzed. Figure 6 shows the AFM representations for these groups. AFM analysis showed a height peak close to 120 nm for the sample with 0.3 wt.% of MWNT-SDBS (ID-3) and around 260 nm for the group with 0.3 wt.% of G-CO890 (ID-5).



(a) (b)

Figure 6. AFM 3-D representation. (a) ID-3; (b) ID-5

4. CONCLUSION

An investigation on carbon based nanostructures on commercial high viscosity adhesive shows promising results. The addition of the nanostructures led a significant increase on stiffness and strength for all groups tested. The dispersion of mixed nanostructures (MWNT-SDBS and G-CO890) was able to improve the stiffness of samples in around 27.4%. The best results for apparent shear strength was found in the groups with 0.15 wt.% of MWNT-SDBS (ID-2) and 0.30 wt.% of MWNT-SDBS (ID-3). These samples showed an improvement in average peak of shear strength around 99.91% and 124.34%, respectively. Failure region of the same groups also showed an increase on cohesive failure area of 23.1% and 31.25%, if compared against blank group. AFM analysis confirms the presence of dispersed nanostructures in the epoxy system, which corroborates with the hypothesis that nanostructures possibly promoted a redistribution of stress around the bonded area.

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