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GRAPHENE-BASED NANO REINFORCEMENT OF ADHESIVES: THE SINGLE LAP JOINT STUDY

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Abstract. *For years the adhesive industry is introducing different types of adhesive composition for increasing the bonded joints performance. However, due to the large variety of adherents and joint designs, the search for a better performance is still a working in progress. The enhancement of bonded joints can be pursued by adhesives new chemical formulations or by changing the stress field distribution on lap joints. Another possible solution for increasing the bonded joints load capacity is the addition of nano particles to the adhesives. The main objective here is to carry out a performance study on nano-modified adhesives. The dispersion of graphene nano sheets into adhesive epoxy based lead to a better mechanical performance to single lap bonded joints. The average increase on load capacity is around 19% with the addition of small amounts of graphene nano sheets, i.e. 1wt%, when compared against the conventional structural adhesive. By performing SEM and TEM observations, the graphene cluster formations were detected and their presence correlated to the mechanical properties.*

Keywords*: Adhesive, Graphene, Nanocomposites, Nanotechnology, Single-lap joint.*

1. INTRODUCTION

The manufacture of a single piece structure is usually impracticable due to the high costs involved or geometrical limitations. Now-a-days, in large majority of cases, the manufacturing process is made of an assembly of small parts that together perform a particular function. The assembly process typically uses the concept of bolted or bonded joints. Their duty is to transfer the load from one part to another of the structure allowing it to achieve the required stiffness. Tong and Steven (1999) used the joint manufacturing process as key point to classify the joints in many ways. They were divided into welded, bolted/riveted and bonded. The last one is more commonly used on composite structures due to induction of stress concentrations by holes (Benatar et al., 1997). In his study, Jones (1999) pointed out that a uniform circumferential stress distribution around the hole can lead to a possible failure. Li et al. (2001) pointed out that the key advantage of adhesive bonded joints is that it enables the development of large, cost-effective, and highly integrated structures. Tsai and Morton (1994) stated that the most commonly used adhesive bonded design is the single-lap joint due to its combined simplicity and efficiency.

The adhesive industry quest for new solutions introduced different type of adhesive composition for increasing the bonded joints performance. One idea is to change the design of the joints to increase adhesive load capacity. Zeng and Sun (2001), Ávila and Bueno (2004) are one of those who proposed new joint designs (wavy-lap) for replacing single-lap joints. However the paradigm shift from manufacturing and the costs associated to the homologation process of such new designs, which now-a-days is very time demanding and almost impracticable for industry. Therefore, the only option left is to increase the load capacity of the adhesives. To achieve such goal there are two options: (i) changing the adhesive chemistry, which is expensive and time consuming; (ii) somehow modify existing adhesives. Nanotechnology may be a good approach to this problem. As described in Thostenson et al. (2005), the so called nanocomposites or nano modified polymeric composites have, in general, much higher mechanical properties when compared to the net polymeric matrices. Furthermore, their manufacturing process is attractive to industry due to their cost-effectiveness and huge market appeal.

The main objective here is to do a performance study on nano modified adhesives and a comparison study between a well-established product on market and a viable alternative. To be able to achieve this goal, conventional single-lap joints following ASTM D5868 (2001) were manufactured and used as case studies.

2. EXPERIMENTAL PROCEDURES

2.1. Materials and Methods

The single lap joint specimens are prepared according to standard test method ASTM D5868 (2001). The 16 layers fiberglass-epoxy laminate used as adherent is cut within the dimensions showed in Fig. 1. They are all made by hand layup and cured on air and room temperature for 24 hours. A post-cure at 70 ℃ for 6 hours is also performed. The laminates have a fiber volume fraction equals to 65%. The epoxy system used is made of *bisphenol A* resin (i.e. RemLam M BR) and amine hardener (i.e. HY956) from Huntsman Inc. The fibers have aerial density of 200 g/m^2 with a plain weave configuration.

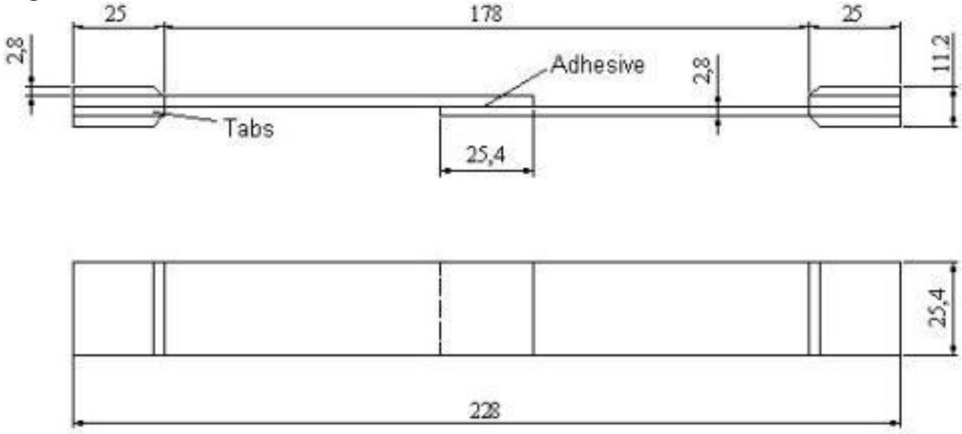
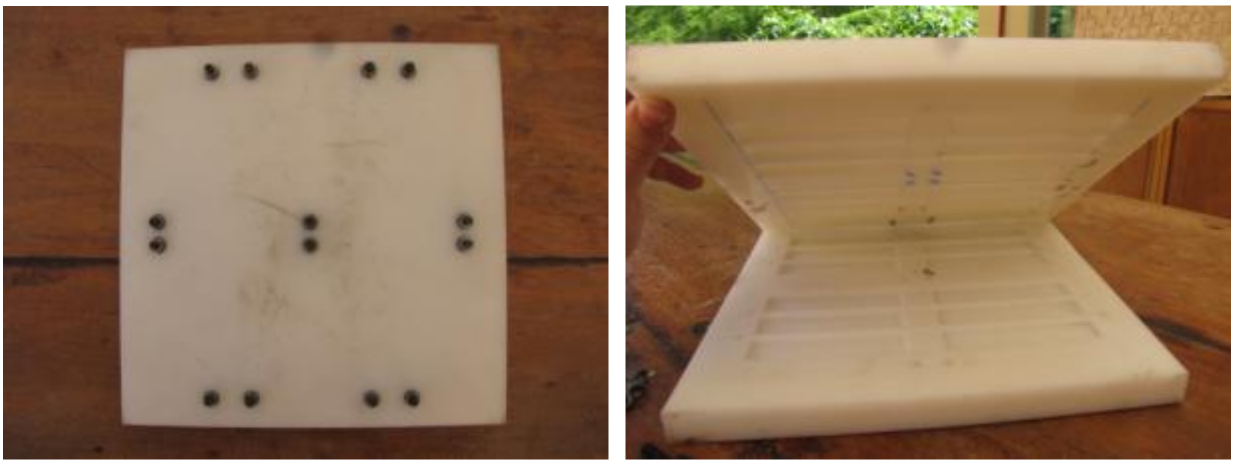


Figure 1. Single lap joint dimensions in millimeters

The bonding regions are prepared according to ASTM D2093 (2003). They are wiped with acetone, abraded with 320 grid silicon carbide abrasive paper until no evidence of surface gloss is visible, any particles from sanding are cleaned with a dry cloth and then acetone wipe is repeated. After specimen's cut and clean processes they are placed in a polyethylene mold (Fig. 2) to guide the parts and to apply pressure the bonding areas. There were made five specimens for each set.

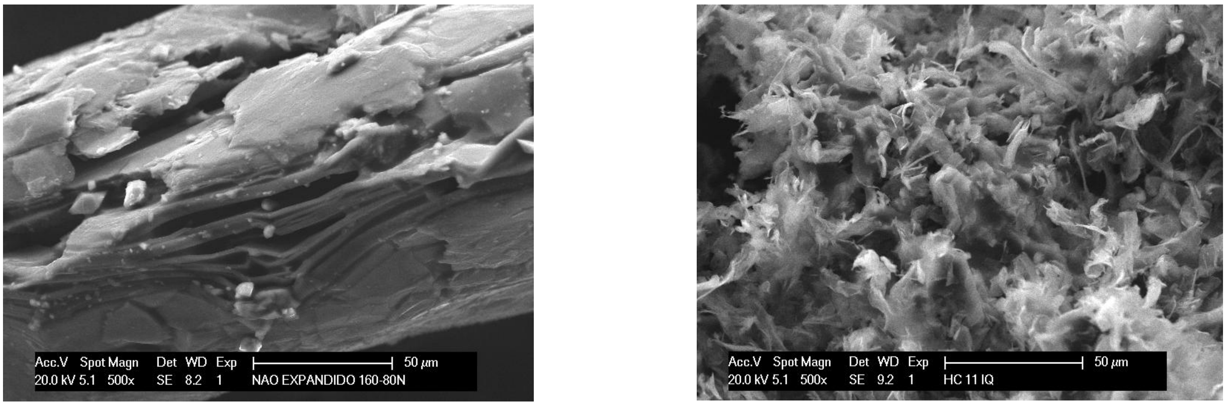


(a) (b)

Figure 2. Polyethylene guiding mold. (a) Top view; (b) open mold.

The adhesives employed in this investigation are: (i) bi-component structural adhesive AW106 and HV953U by Huntsman Inc., considered the golden standard; (ii) epoxy system AR300 with hardener AH30-150 supplied by Barracuda Advanced Composites. For the AR300/AH30-150 system the cure process is modified to include a co-cure at 70 ℃.The nano structured adhesives are prepared by adding 1wt% graphene and mixing it mechanically for two hours until complete dispersion. This concentration was defined based on the epoxy system saturation limit observed by Ávila et al. (2008). Control samples are prepared with no graphene to each adhesive leading to four sets and 20 specimens.

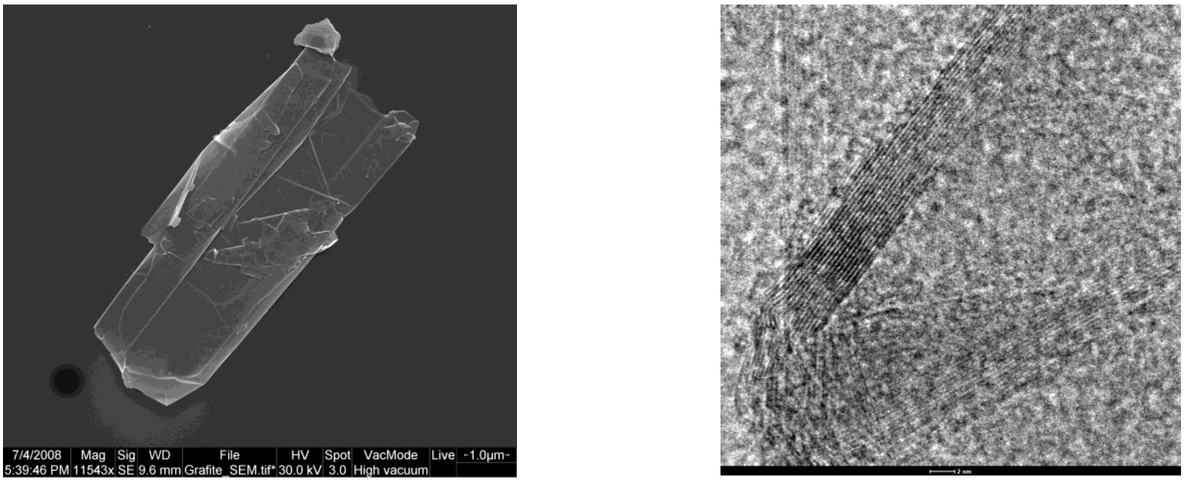
The nano particles used in this research were supplied by Nacional Grafite Incorporated. The graphene used has its origin from expandable graphite. When the HC 11-IQ graphite is submitted to a 900 ℃ thermal gradient in a 30 second period or less, the polymeric layers between the graphite plies volatilizes. This sudden reaction leads to the graphite speedy expansion. As the volume must remain constant, the graphite thickness approaches nano scale. The graphite nano sheets are later on functionalized using a mix of sulfuric and nitric acid. Figure 3a shows the expanded graphite before the thermal shock. As it can be noticed, the structure is multilayer, where the polymeric matrix is located between graphite layers. The flake like structure is formed after the thermal expansion as shown in Fig. 3b.



(a) (b)

Figure 3. Expandable graphite. (a) Before thermal expansion; (b) after thermal expansion

From previous results of Ávila´s research group, it is possible to demonstrate that a large amount of graphene was presented into the nano graphite (Ávila et al., 2010). Figure 4a shows a scanning electronic microscope (SEM) observation of a single nano graphite sheet. By using a transmission electronic microscope (TEM), Ávila et al. (2010) were able to observe clusters of graphene nano sheets piled up as described in Figure 4b.



(a) (b)

Figure 4. Single nano graphite sheet observation. (a) SEM analysis; (b) TEM analysis

The lap shear adhesion tests were performed at 2 mm/min. For each set of specimens, the mean maximum load, shear stress and displacement at maximum load were defined by applying this constant displacement rate. The failure modes are then classified according to ASTM D5573 (2005).

2.2. Results and Discussions

Before discuss the mechanical tests results, a key issue must be addressed. One possible option for characterizing adhesives is by tensile tests. However, a real performance test of an adhesive can only be done considering the interactions between adhesive and adherents. Therefore, our mechanical tests will focus exclusively into the single lap joint test. By applying this approach, it will be easy to extend our results to real life applications, e.g. oil pipes connections. The load capacity performance tests results are summarized in Tab. 1. The force-displacement behavior of representative samples for each group is shown in Fig. 5.

Table 1. Load capacity, maximum stress and displacement at maximum load for different materials and graphene concentrations

Material	Concentration	Load (kN)		Average Stress (MPa)	Average Displacement (mm)
		Peak	Average		
AW106 HV953U	0%	6.132	4.655 ± 0.968	7.014 ± 1.438	2.12 ± 0.38
	1%	5.568	4.810 ± 0.648	7.190 ± 0.810	2.15 ± 0.39
AR300 AH30-150	0%	6.315	5.347 ± 0.732	8.887 ± 1.247	3.09 ± 0.47
	1%	5.945	5.748 ± 0.399	9.374 ± 0.553	3.16 ± 0.06

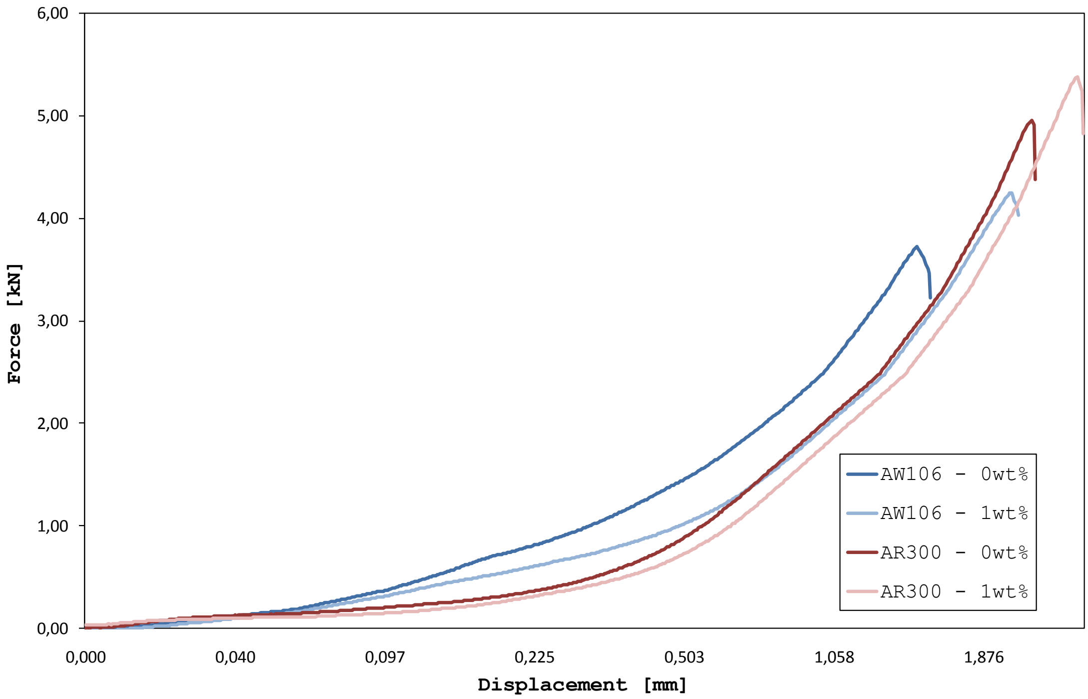
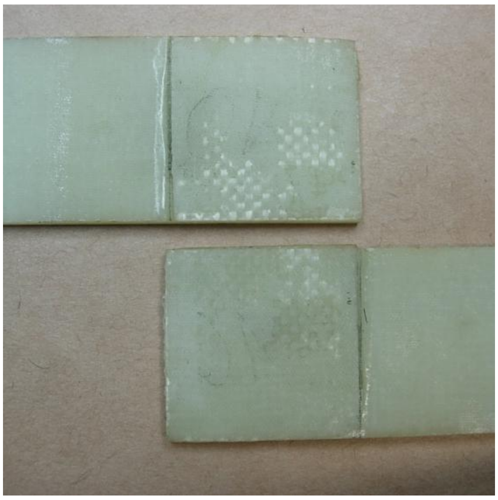


Figure 5. Force-Displacement behavior of representative samples of each set

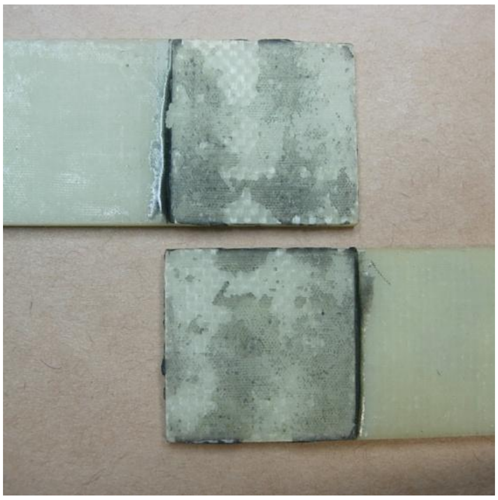
As shown in Tab. 1, there is an increase on average load capacity and ultimate stress when the graphene is dispersed into the adhesive matrix. Remarkably, this gain is even greater to the AR300 resin (3.20% against 6.97% of increase). This can be due to a better chemical affinity between the epoxy system and graphene. This phenomenon can be explained by the AR300 system lower viscosity (0.35 against 37.5 $s \cdot Pa$ for AW106), which leads to the graphene better dispersion. The failure modes are described in Tab. 2, where the ratio in parentheses is the approximate area percentage for each failure mode. Another important issue is the apparent more flexibility of the nano modified AR300 system. This system presented the largest displacement. This large displacement could lead to a better stress distribution into the laminate/adhesive, and consequently larger load capacity. The failure modes representative for each set of samples are shown in Figs. 6a-6d.

Table 2. Failure modes of each specimen according to ASTM D5573 (2005)

Adhesive	Concentration (wt%)	Specimens Id				
		1	2	3	4	5
AW106 HV953U	0%	ADH-LFT (90-10)	LFT	LFT	LFT-ADH (66-33)	ADH-LFT (93-07)
	1%	LTF-ADH (75-25)	LTF-ADH (95-05)	ADH-LTF (65-35)	LTF	LTF-ADH (90-10)
AR300 AH30-150	0%	LFT	LFT	LFT-ADH (90-10)	LFT- TLC (60-40)	LFT
	1%	LFT	LFT	LFT	LFT-ADH (95-05)	LFT



(a)



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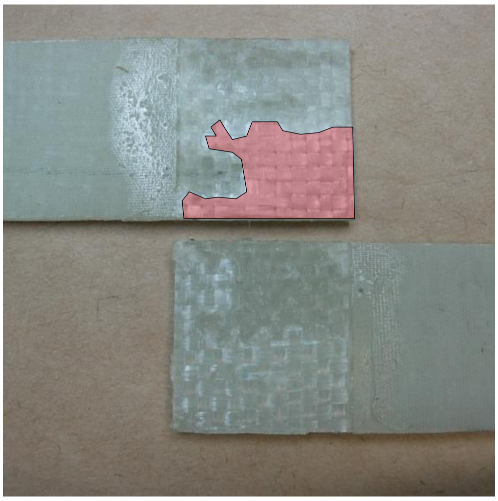
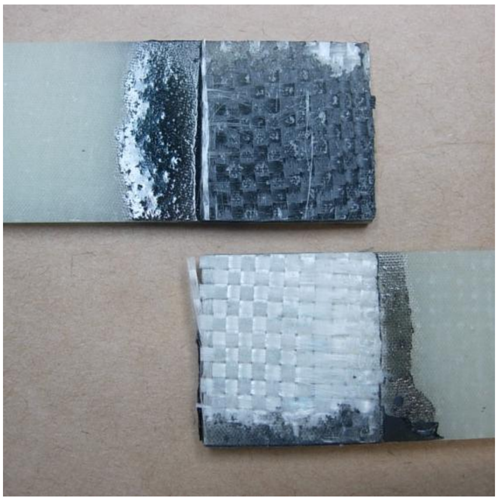


(c)



(d)

Figure 6. Representative samples of each set. (a) AW106 0wt% #1; (b) AW106 1wt% #5; (c) AR300 0wt% #4; (d) AR300 1wt% #4

As can be seen, in all cases the Light Fiber Tear Failure – LFT occurred in at least part of the de-bonded area. The AR300 failure modes are more uniform then AW106. AR300-1wt% graphene is a typical example of this behavior. Notice that for this case, all samples are predominantly LFT. This indicates an excellent bonding between adhesive and adherent's resin getting to the limit of fiberglass reinforced composite. This assumption can be confirmed by the low values of standard deviation for AR300 with 1wt% graphene addition. The Fig. 6a shows predominantly Adhesive Failure – ADH on specimen #1 of AW106 with no graphene. It can also be noticed that in 10% of the area the LFT failure mode occurred. A complete different trend was noticed in Fig 6b, where specimen #5 of AW106 with 1wt% graphene had 90% of its area with LFT failure mode. Figures 6c and 6d represent the specimens #4 of AR300 without and with graphene addition, respectively. The red region on Fig. 6c indicates the area in which Thin-Layer Cohesive Failure – TLC was observed.

2.3. Conclusions

The dispersion of graphene nano sheets into adhesive epoxy based brought as consequence a better mechanical performance to single lap bonded joints. Different adhesives showed different improvements with the addition of graphene nano sheets. The AR300 system presented a better performance with an average increase of load capacity around 6.97%, while the traditional structural adhesive AW106 system experienced an average enhancement close to 3.20%. The failure modes seem to be unaffected by the graphene dispersion as the light fiber tear failure mode was observed in all cases. Another important issue is the cost/effectiveness of the two systems studied. Epoxy system

AR300 experiences the largest displacement, which can be an indication of stress redistribution around the bonding area. When the cost variable is added to the equation, again the AR300 is the best choice, as its cost is only one third of the AW106. The average increase on load capacity is around 19% with the addition of small amounts of graphene nano sheets, i.e. 1wt%, when compared against the conventional structural adhesive with no graphene.

3. ACKNOWLEDGEMENTS

The authors would like to recognize the financial support provided by Brazilian Research Council (CNPq). We would like to express our gratitude to the Nacional Grafite for providing the HC 11-IQ nano graphite and the Center for Electronic Microscopy Analysis of Universidade Federal de Minas Gerais. And finally, we would also like to express our gratitude to REA Indústria e Comércio Ltda for manufacturing the devices used in this study.

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