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COBEM-2017-0570 IMPROVING COMPOSITES SINGLE-LAP JOINT PERFORMANCE BY CARBON NANOTUBES

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Abstract.*This study investigates the influence of the adhesive (epoxy) thickness and the dispersions of non-functionalized carbon based nanostructures (carbon nanotubes – CNT) on mechanical properties of single-lap bonded joints. To achieve this goal, three CNT concentrations (0.5%, 1.0% and 2.0% wt./wt.); and three different thicknesses (0.05 mm, 0.15 mm and 0.40 mm) were evaluated. The mechanical properties were measured using the apparent shear tensile test, based on ASTM D5868. The results showed that the addition of 1.0 wt% CNTs improved the interface strength, leading to an increase on delaminated areas in failure region up to 55.36% and also improving the peak force up to 13.85%. Decrease in adhesive thickness from 0.40 mm to 0.05 mm improved the peak force up to 13.91% and increased delaminated area in 45.96%.*

Keywords: *composites, nanocomposites, polymer, carbon nanotubes, bonded joints*

1. INTRODUCTION

In recent years, the application of composite materials has been growing in many industries: civil engineering, aerospace, naval and automotive. Its main advantages are low density, high mechanical and corrosion resistance, the low cost of manufacture process and maintenance (Gouda *et al.*, 2013). In many of these practical applications, it is virtually impossible to create structures made of a single piece due to the high costs involved and geometrical limitations. The solution is the manufacturing of small parts that can be assembled together later (Avila and Bueno, 2003). The assembly process requires the use of joints. Joints are responsible to transfer load from one part to another, allowing the structure to achieve the require stiffness. In most cases, traditional fastening methods (screws and rivets) may not be suitable for fiber reinforced composites due to the stress concentration generated into the fibers/layers when holes are created for passing these fasteners. According Lucic *et al.* (2005) the use of bonded joints in load-bearing structures has been atracted great interest to aerospace, automotive and to machine module development. Time and cost savings, corrosion and fatigue resistence, crack retardance and good damping chacteristics are the major advances of these joints.

As commented by Neto *et al.* (2013) and Banea and da Silva (2009), bonded joints are frequently expected to sustain static 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. Many studies are developed in order to predicting possible failures in bonded joints. However, this is a difficult task due to the variations in joint's properties caused by the different manufacturing procedures.According Lucic *et al.* (2005), bonded joints are very susceptible to the geometric paremeters. Altering the geometry changes stress and strain distribution. These differences can also have a profound effect on stress concentration and consequently the load-capacity and long-term performance of the joint.

The effect of adhesive layer thickness on the performance of various types of joints has been reported by several researchers over the years. According to Grant *et al.* (2008) single-lap joints under tensile stress are very sensitive to the thickness of the adhesive layer. As the adhesive layer increases, there is an increase in momentum under the overlap region due to eccentricity of the forces. Consequently the joint's strength decreases. Tamblin *et al.* (2001) studied several thicknesses varying from 0.4 mm to 3 mm, using three types of adherents: Aluminum Alloy (2024-T3), carbon fabrics and glass fiber fabrics. They observed a decrease in the values of the peak shear stress with the increase of the adhesive thickness. Kahraman *et al.* (2008) investigated the influence of thickness on the single-lap joints properties. In their study, the thickness of the adhesive ranged from 0.03 mm to 1.3 mm, the adherents was made from aluminum and the adhesive was filled with aluminum powder. The results showed a decrease of 35-40% in joints shear strength, when thickness increased from 0.03 mm to 1.3 mm. According Davies *et al.* (2009), the decrease of the joint strength with the increase of adhesive layer thickness may be difficult to analyze due to the several factors: the natures of internal defects; the adhesive structure may change as adhesive layer increase; the energy dissipation mechanism (plasticity, damage propagation, etc.) can be modified by change the distance between adharents, etc.

Adhesives has 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. Epoxies, also are able to bond well to a variety of treated or untreated metal surface. In recent application, like aeronautic and aerospace industries, polymeric adhesives are often modified by adding fillers to enhance physical properties. Among the fillers, one of the most promising is the Carbon nanotubes or simply called CNT's.

The discovery of carbon nanotubes (CNT's) has opened vast areas of research in the nano-scale reinforcements for composites, in order to improve their mechanical, thermal and electrical properties. The CNTs was first reported in 1991 by Iijima (1991) but reports of the existence of "worm-like" carbon structures date back to the 1950's, when Russian researchers observed the formation of long filaments of carbonic crystals with a diameter of approximately 50 nm in soot resulting from the decomposition of CO on iron particles at 600 $^{\circ}C$. Morphologically CNT can be compared to a graphene sheet rolled up, having at the end a hemispherical structure derived from a fullerene (C_{60}) (Pereira, 2013). 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 is 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. Gojny *et al.* (2004) tested the behavior of epoxidized resins reinforced with functionalized and non-functionalized nanotubes. According to their results, a 43% increase in the fracture strength of the resin was observed with the addition of 0.5% of functionalized nanotubes (MWCNTs). Godara *et al.* (2009) observed an increase in crack initiation energy (G_{I_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.

This study investigates the influence of the adhesive thickness and the dispersions of carbon based nanostructures (carbon nanotubes - CNT) on mechanical properties of single-lap bonded joints. The final goal is to increase the single lap joint load capacity

2. EXPERIMENTAL PROCEDURES

The adherents were manufactured using a plain weave glass fiber fabric (300 g/m^2) and an epoxy system supplied by Huntsman Inc (RenLam M and HY956). The mixing ratio was 100 parts resin to 20 parts hardener and the gel time is 30 minutes at 25 $^{\circ}C$. The final resin has a density of 1.1 g /cm^3. The cure was performed for 24 hours at room temperature and post cure for 6 hours at 60 $^{\circ}C$. The adherents were made using the ratio of 60% fiber and 40% resin. The composite plates were made in 250 mm x 250 mm, all of them consisting of 9 layers of fibers, leading to an avarage thickness of 2.37 mm. To obtain the final dimensions of the adherents and tabs (in accordance with ASTM-D5868), the plates were cut and sanded (using sandpaper grit 50 and 300).

The adhesive employed was an epoxy system AR300-AH30 / 150, supplied by Barracuda Advanced Composites. The hardener is composed of 90% AH-30 and 10% AH-150, providing a gel time of 60 minutes at 25 $^{\circ}C$. The ratio resin / hardener used was 100:33, with an approximate viscosity between 0.8 and 0.9 Pa.s 25. The curing process was performed at room temperature followed by post cure at 80 $^{\circ}C$ for 6 hours. MWCNT samples, grown by CVD, were supplied by the Department of Physics of the Universidade Federal de Minas Gerais (Ferlauto *et al.*, 2006).

The mass ratios of the carbon nanotubes to the adhesive were set to 0%, 0.5%, 1.0%, 2.0%, Table 1 lists the test groups developed. An ultrasonic bath Norking at 42 kHz was used to disperse the CNTs into the adhesive. Mixture Adhesive/CNT was sonicate for 80 min. The adherents were sanded with 200 grit sandpaper (overlap region only) to increase surface roughness, and then, cleaned with acetone. The hardener was mixed in the solution of resin and MWCNT. The specimens were bonded using a device developed to maintain the alignment of joints. In order to ensure a uniform pressure (7.45 mPa) on the overlap region. The adhesive was cured for 24 hours at room temperature and post cure was performed for 6 hours at 80 $^{\circ}C$.

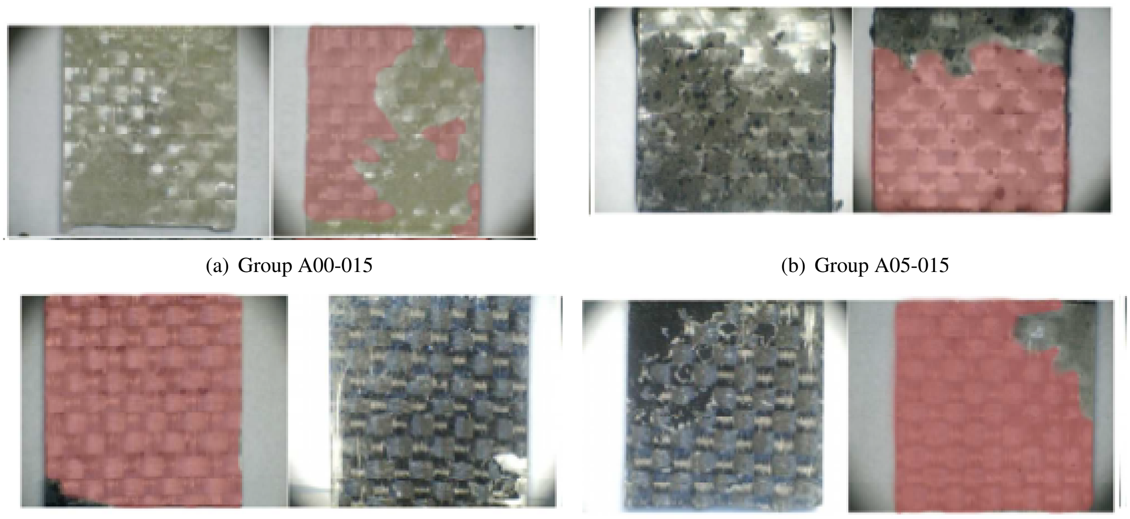
The tests were performed according to the specifications of Standard ASTM-D5868 in Load Frame Testing. The displacement velocity of the head was set at 13 mm /min. The load cell has a maximum capacity of 100 kN. The obtained data were exported to other software for the accomplishment of calculations, generation of the graphs and data analysis.

Table 1. Test Groups

Nanoparticle Concentration	Adhesive Thickness	Group Name
0% CNT	0.05	A00-005
	0.15	A00-015
	0.4	A00-040
0.5% CNT	0.05	A05-005
	0.15	A05-015
	0.4	A05-040
1.0 % CNT	0.05	A10-005
	0.15	A10-015
	0.4	A10-040
2.0% CNT	0.05	A20-005
	0.15	A20-015
	0.4	A20-040

3. RESULTS AND DISCUSSIONS

Analyzing the influence of CNT addition on joint mechanical behavior, the best results were observed in samples with 1,0% of CNT. This behavior was observed for all adhesives thickiness observed. In these groups a significant change occurred in failure mode due to the increase of CNT concentration. The highest improvement in mechanical properties was observed in samples with 0.15 mm of adhesive thickness. In this group the addition of CNT promoted an increase in delaminated areas, called light fiber tear (LFT) during failure process, as could be observed in Fig. 1. Samples with 0.0 wt% of CNT (group A00-015) showed an average delaminated area corresponding of 61.72%. This value was increased up to 77.89% for samples with 0.5 wt% CNT (group A05-015), 95.89% for samples with 1.0 wt% CNT (group A10-015) and 92.23% for samples with 2.0 wt.% CNT (group A20-015). It was observed an increase in load capacity up to 13.85 % for group with 1.0 wt. % CNT (group A10-015), compared against group with pure epoxy adhesive. Increases of 5.1% and 4.3% also was observed in groups with 0.5 wt.% CNT and 2.0 wt.% CNT (see Fig. 2).



(a) Group A00-015

(b) Group A05-015

(c) Group A10-015

(d) Group A20-015

Figure 1. Failure modes for groups with 0.15 mm of thickness

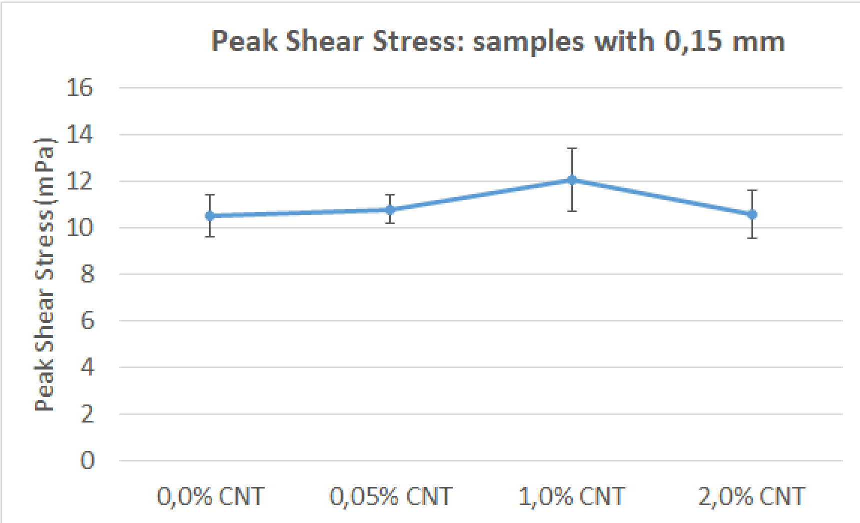
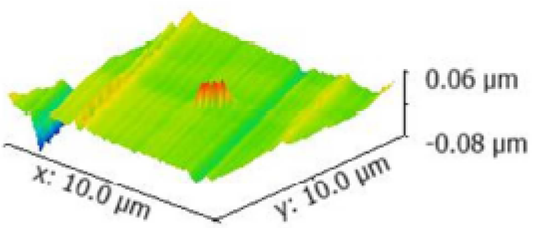
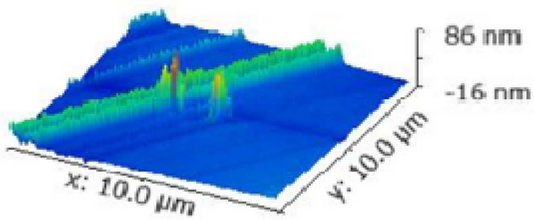


Figure 2. Peak Shear Stress. Groups with 0.15 mm

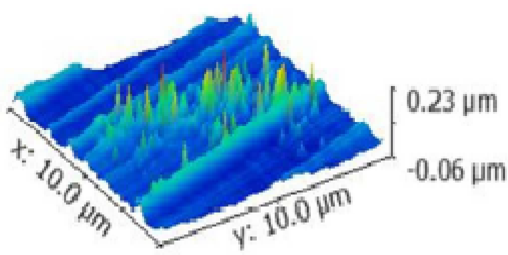
These changes in failure modes and also load capacity, could be related to the stress redistribution caused by the dispersion of CNT. The CNT may have interacted with the polymer chains creating a mechanical barrier, reducing the nucleation and propagation of cracks. This interaction could be provide a better surface adhesion between adhesive and adherent, creating a stronger interface. Sydlik *et al.* (2013) also hypothesized that improvement promoted by CNT is linked to its ability to deflect the crack as it propagates through adhesive. The AFM analyses in Fig. 3 showed the CNT distribution inside the adhesive for all three concentration. As could be observed, with increase of CNT amount dispersed in epoxy adhesive, agglomerates begin to form.



(a) Epoxy+0.5 wt% CNT



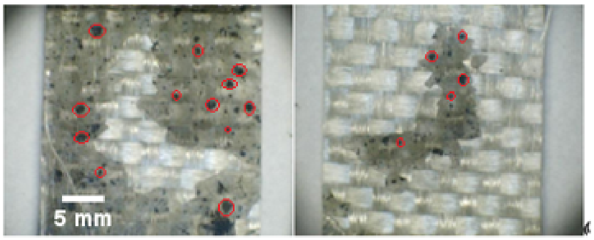
(b) Epoxy+1.0 wt% CNT



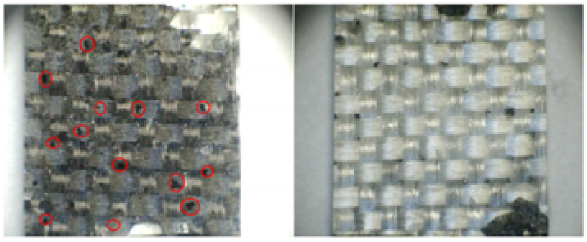
(c) Epoxy+2.0 wt% CNT

Figure 3. AFM Analysis

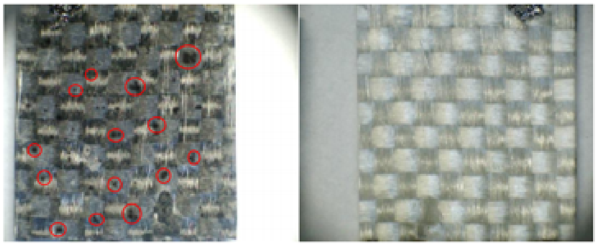
The tendency to form CNT agglomerates due increase in concentration dispersed was also reported by Munhoz (2016). This phenomenon can be observed macroscopically in Fig. 4, where black dots in failure area seems to be CNT agglomerates. These black dots seems to be randomly dispersed and their size increases with CNT concentration. For 0.5 wt. % CNT concentration (group A05-015) the average diameter for these agglomerates was 0.24 mm, this value increased to 0.29 mm and 0.32 mm for groups with 1.0 wt.% CNT (A10-015) and 2.0 wt. % CNT (A20-015), respectively. Agglomerates usually act as stress concentrators, reducing the overall capacity of CNT to improve mechanical properties.



(a) Epoxy+0.5 wt% CNT



(b) Epoxy+1.0 wt% CNT



(c) Epoxy+2.0 wt% CNT

Figure 4. Failure regions: samples with 0.15 mm. Adapted from Monteiro (2016)

Similar effect was found by Wernik and Meguid (2014). They analysed the influence of carbon nanotubes in several mechanical properties of cabon nanotubes reinforced epoxy adhesives. Their experimental investigation indicated a critical carbon nanotube concentration around 1.5 wt% that resulted in the largest improvements in the measured properties. At concentrations beyond this value, properties began to degrade, in some cases to values below to that of pure epoxy resin. The STEM analisys showed that size and number of agglomerates increased signicantly when concentration reached values beyond 1.0 wt.%.

Analyzing the effects of adhesive thickness layer onto mechanical properties of single-lap joints tested, it is possible to observe that decrease in joints adhesive thickness changes the failure modes and affects the joint load capacity, as consequence. Figure 5 shows the the peak shear stress for samples with 0.0% CNT as function of thickness. Compared against group with 0.40 mm of thickness (A00-040), groups with 0.15 mm (A00-015) and 0.05 mm (A00-005) showed an increase in peak force of 11.23% and 13.91%, respectively. A comparison of failure modes between these groups also showed a decrease on delaminated areas (LFT), with increase in adhesive thickness. The average delaminated area, shown in red at Fig. 6, increases from 55.22% in group A00-040 to 63.73% in group A00-015 and 70.99% in group A00-005. According Budhe *et al.* (2017), this behavior could be related to two main factors: redistribution of stress inside the adhesive layer and the number of internal deffects, such voids, which increases with the adhesive layer.

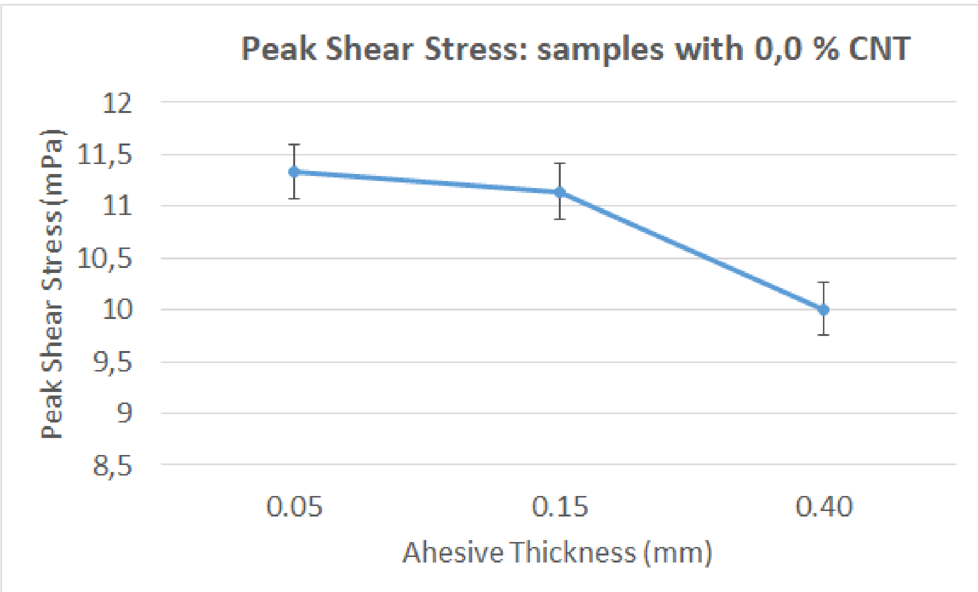
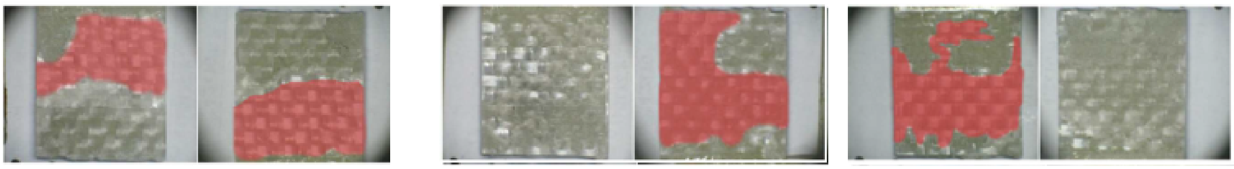


Figure 5. Peak Shear Stress. Groups with 0.0 % CNT

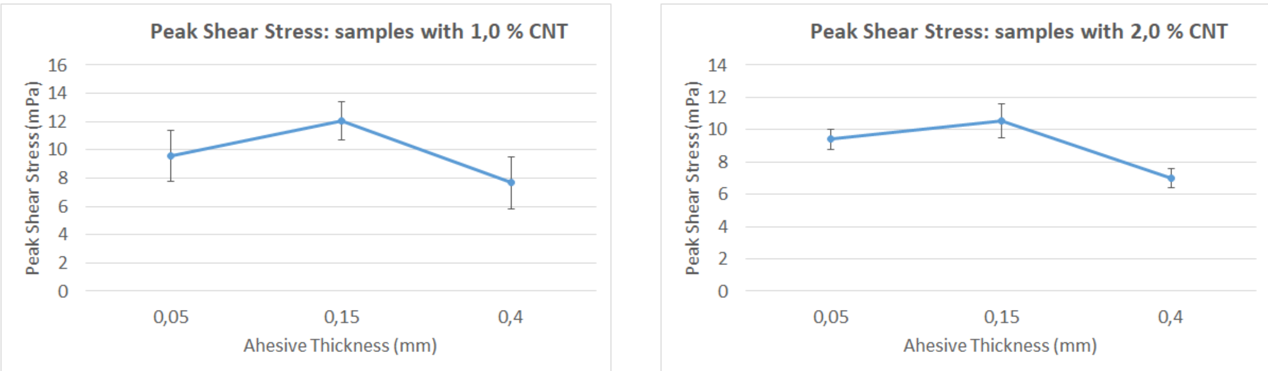


(a) Group A00-005 (b) Group A00-015 (c) Group A00-040

Figure 6. Failure region fo groups with 0.0% of CNT. Adapted from Monteiro (2016)

The thickness analysis conducted in all concentrations of dispersed CNT had similar tendency. However, groups with 1.0% and 2.0% showed best results in thickness of 0.15 mm instead 0.05 mm, as can be seen in Fig. 7. Samples with 1.0% CNT and 0.15 mm of adhesive layer (A10-015) showed failure regions constituted by 95.86% of delamination areas (LFT) and a peak shear stress 57.12% higher than samples with 0.40 mm (A10-040).

This behavior could be linked to an increase in number of agglomerates observed in samples with 0.05 mm, as CNT concentration increases (see Fig. 8). The CNT agglomerates seems randonly dispersed and their average diameter increases from 0.26 mm in group A05-005 to 0.32 mm in group A10-005 and 0.38 mm in group A20-005. This fact indicates that decreases in adhesive layer thickness to very low values coould influence the formation of CNT agglomerates.



(a) Epoxy+1.0% CNT (b) Epoxy+2.0% CNT

Figure 7. Peak Shear Stress. Groups with 1.0% and 2.0% CNT

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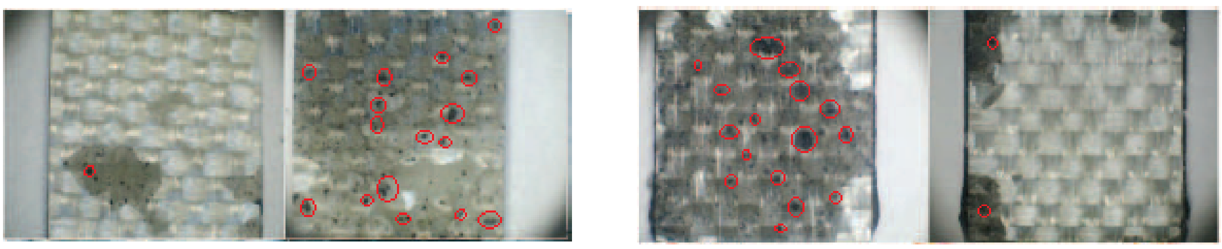

(a) Group A05-005 (b) Group A10-005

(c) Group A20-005

Figure 8. Failure region fo groups with 0.05 mm. Adapted from Monteiro (2016)

4. CONCLUSION

The CNT effects into single-lap joint performance was investigated. The results showed that CNT dispersion seems to improved the interface strength leading to an increase in delaminated areas. Groups with thickness of 0.15 mm, showed a relative increase of 55.36%, when delaminated areas changed from 61.72% of failure region in group A00-015 (pure adhesive) to 95.89% in group A10-015 (adhesive + 1.0% CNT). Also an improvement of 13.85% in peak force was reported in group with 1.0 wt% CNT. These effects could be associated to interactions between CNT and polymeric chains leading to formation of a mechanical barrier, reducing the nucleation and propagation of cracks and improving the adhesion between adhesive and adherent.

Decrease in thickness showed influence in peak force and also in failure modes. Improvements in peak force over 13.91% was observed when thickness was reduced from 0.40 mm to 0.05 mm. For the same case increases in delaminated areas up to 45.96 % also was observed. This effect could be related to the redistribution of stress inside overlap region due to the decrease in thickness. Also was observed that increase in CNT concentration associated with thinner adhesive layer propitiate the formation of agglomerates.

5. ACKNOWLEGMENTS

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