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Mechanical Characterization of Nano-Modified Single Lap Bonded Joints: The Aging Effect Investigation

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ABSTRACT

This paper addresses the effect of graphene dispersion into epoxy adhesives into the aging process by UVA light exposure. To achieve such goal two approaches were employed. The first one was direct exposure of the nano-modified AR300/AH1 epoxy system, with 0wt%, 1wt% and 2wt% graphene concentration, to UVA light. The samples were exposure to UVA light for two hundred hours. After the aging process, nano-indentation tests were performed. The second approach was to prepare single lap joints (SLJ) using the same concentration of graphene and them exposure the SLJ to UVA light for 200 hours. The ASTM D5868 were used obtain the bearing-load capacity of each SLJ group. The graphene nanostructures formed inside the AR300/AH30-150 nano-modified adhesive seems to block the aging process, as none of the specimens presented a decrease on stiffness. Furthermore, the force-displacement curves obtained by nano-indentation seem to indicate a good dispersion process, as the large majority of the curves laid down at the same path. When the single lap joints were tested after 100 hours of aging, the results also indicated an average increase on bearing-load capacity of 24.76% and 28.36% for 1 wt. % and 2 wt. %, respectively. When the aging reached two hundred hours, there is a decrease on load capacity when compared against the 100 hours results. Even though, the average load capacity was 12.48% and 18.04% higher than the not aged nano-modified AR300/AH30-150 single lap joints. The graphene dispersion into the epoxy adhesives seems to have a double folded effect, in one hand it is increase the bonded joint capacity and on the other hand block the aging effect of UVA light.

Keywords: Graphene, single-lap bonded joints, mechanical properties, nanocomposites

1 INTRODUCTION

Adhesives have been used since the early ages of mankind, but until a century ago, the vast majority was obtained from natural products such as bones, skins, fish, milk, and plants. It was only in the beginning of the XX century that adhesives based on synthetic polymers have been introduced, but their usages were limited due to their high cost and poor mechanical properties. As discussed by Crocombe and Ashcroft [1], it was only in 1940's that a more scientific approach has employed to understand the adhesion phenomenon. The progresses into polymer sciences lead to the development of new adhesives and consequently an increase on load-bearing capacity. Furthermore, new designs [2-6] also contributed to the increase on

bonded joints efficiency. A comprehensive study on single lap joints was performed by Hart-Smith [2]. The designs created by Zeng and Sun [3], and Ávila and Bueno [4] employed the concept of changing the peel stress distribution by employing the wavy shape configuration to the bonded area. A similar idea was employed by Ashrafi et al [5] in which the wavy shape was applied at the adherent adhesive interface. An analytical study on damage tolerance of bonded joints was described by Romilly and Clark [6]. They were able to develop a close form solution for cracked bonded structures. However, no environmental conditions were considered.

As commented by Banea and da Silva [7], bonded joints are frequently expected to sustain static or cyclic loads for considerable periods of time without any adverse effect on the load-bearing capacity of the structure. Even more important, as described by Petrova and Lukina [8], adhesive joints used in aerospace industry, e.g. airplane and helicopter structures operate in the loaded state. Therefore, they must hold a high stability toward a variety of mechanical and chemical and physical changes under service conditions. These changes are, in most cases, triggered by environmental conditions. According to Kablov et al [9], the climate changes can be represented by hygrothermal cycling. Although moisture diffusion and temperature changes are important factors to understand the adhesive mechanical and physical chemical changes, another issue must be considered, i.e. UV.

The polymeric matrices photo-degradation singularity by UV light was addressed by various researchers [10-15] using different approaches. Woo et al [10] investigated the residual properties of epoxy/nanoclay nanocomposites exposed to UV light and moisture. As expected, the flexural modulus decreased due to plasticization effect of moisture. Another well-known effect of UV light, the loss of ductility, was also detected by Woo and collaborators. However, Woo was not able to clear identify the nanoclay effect into the nanocomposites' aging process. Another investigation into the nanostructures effect into polymeric composite aging was performed by Allaoui et al [11], where carbon nanotubes (CNTs) were dispersed into epoxy systems. They were not able to assess clearly the influence of CNTs into the aging process. Their conclusions were mostly over clouded by the mechanical improvements provided by the CNTs. The work done by Mailhot et al [12] focused on how the nanoparticle/nanostructures morphology affected the aging process. Again, the conclusions seem to be obvious, the nanoparticles/nanostructures' morphology did not affect the aging process. Chemical changes are driven by photo-degradation and not by the nano fillers. The work done by Larché et al [13] addressed this issue for the phenoxy resin. The mechanism proposed by Larché et al [13] proposed a correlation between the molecular cross-linked caused by UV radiation and micro-cracks formed into the composite's surface. The same analogy was proposed by Dao et al [14] for epoxy based composites, in their case 8552/IM7, a year early. As discussed by Dao, the thermal-oxidation phenomenon leads to molecular stiffening, shrinking and micro-cracking. Furthermore, the chemical degradation of 8552/IM7 fibre composite indicates that degradation phenomenon is multifaceted, temperature and humidity dependent. Their conclusions were that modelling of real life degradation by thermally accelerated aging and Arrhenius extrapolations of the results are not able to produce very accurate predictions. The work done by Chang and Chow [15] went further, as they were able to correlate the UV exposure with interface debonding for glass/epoxy/organoclay hybrid composites. Although no information about the debonding mechanism was provided by the authors, a possible explanation for this phenomenon could be the mismatch on thermal expansion coefficient between the glass fibres and the nano- modified epoxy/MMT system.

Although the literature on polymeric matrices aging by hygrothermal and UV radiation addressed different aspects of mechanical properties degradation, bonded joints have special characteristics and are treated using a different approach. Higgins [16] discussed the durability of adhesive bonds as a function of weathering conditions. As Higgins pointed

out that subsonic airplanes, bonded joints have been applied for primary structures and one of the most important issues is their shear lap strength after exposition to temperature variations (typically an airplane has to operates in temperatures from -55C to +80 C), humidity and most of the fluids used during the plane's operation. Sugiman et al [17] focused their attention to the humidity diffusion process through the bonded joints, in their case single lap joints, and the correspondent loss of strength. In their work, the single lap joints made of aluminium 2024- T3 adherents and FM73 adhesives were immerse into deionized water at 50 C for one and two years respectively. They noticed that after a year, the FM73 reached its saturation limit. Furthermore, they also observed and decrease on bearing-load capacity of 22.1% after one year of water immersion and 24.2% after the second year. By analyzing Sugiman's results, it is possible to conclude that water diffusion is an important issue. However, for real life airplane operations (passing thought clouds, rain, de-icing, etc.) the water diffusion effect plays a secondary role, as there is no enough time for water diffusion into the bonded joints. More specifically, there is no enough time for moisture damage the adhesive/adherent interface region. As commented by Datla et al [18], the loss of bearing-load capacity in bonded joints is, in general, attributed to weaknesses into this region. It is possible, however, to have damage inside the adhesive itself. The work done by Knoght et al [19] concluded that under hydrothermal conditions (moisture diffusion associated to temperature variations) lead to changes on failure mode from cohesive zone (within adhesive layer) to fibre tear (within the top layers of the adherent). These facts can be attributed to the adhesive layer porosity and the voids formation during the laminate consolidation. Baldan [20], however, pointed out another important issue, the adhesive and adherent degradation by UV radiation.

This paper focuses on single lap joint performance after UV radiation exposure. To be able to decrease the bearing-load capacity loss, the epoxy system employed as adhesive was nano-modified by dispersing graphene nano-structures.

2 MATERIALS AND EXPERIMENTAL PROCEDURES

The single lap joints (SLJ) were made of aluminium 2024-T3 with thickness of 2.8 mm, width of 25.4 mm. The single lap joints geometry followed the ASTM D 5868-10 [21] standard. Figure 1 describes the single-lap dimensions. The adhesive employed in this research is an epoxy system AR300/AH30-150 supplied by Barracuda Composites. The adhesive was nano-modified by graphene dispersion. The graphene nanostructures dispersion process into the epoxy system followed the methodology described by Ávila et al [22], i.e. ultra-sonication at 20 KHz for 60 minutes followed by high shear mixing at 17400 RPM for 60 minutes. The graphene concentrations dispersed into the adhesives were 1 wt. % and 2wt% with respect to the adhesive weight.

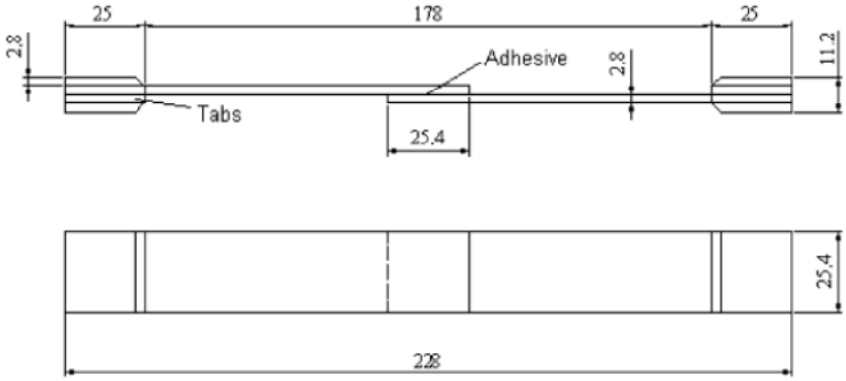


Figure 1: Single lap joint dimensions in millimetres

The ASTM standard G154-12 [23] recommendations were followed, and to be able to reproduce the day light a UVA light with wavelength of 340 nm was employed. Each set of single lap joints (5 specimens) were exposed to the UVA lights in a sealed chamber. Once the single lap joints were aged, the tensile tests following the ASTM D 5868-10 [21] standard were performed. The nano-indentation tests were carried out by Asylum Research's Atomic Force Microscope; model MFP-3D, with a diamond Berkovich tip.

3 DATA ANALYSIS AND DISCUSSION

3.1 Nano-indentation: Stiffness versus Aging

To understand how UVA light affects the nano-modified AR300/AH30-150 adhesive, a set of nano-indentation tests were performed. The nano-indentation tests were done in different locations to be able to check if the graphene nanostructures were even distributed. As suggested by Mailhot et al [24], the elastic moduli of aged polymeric matrices were kept unchanged for layers deeper than 40 µm from the exposed surface. Therefore, all nano-indentation tests were done at same distance from the surface, i.e. 300 *nm*. Figures 2A-F show the nano-indentation load-displacement curves for the specimens with 1% and 2%, at time equals to 0, 100 and 200 hours, respectively.

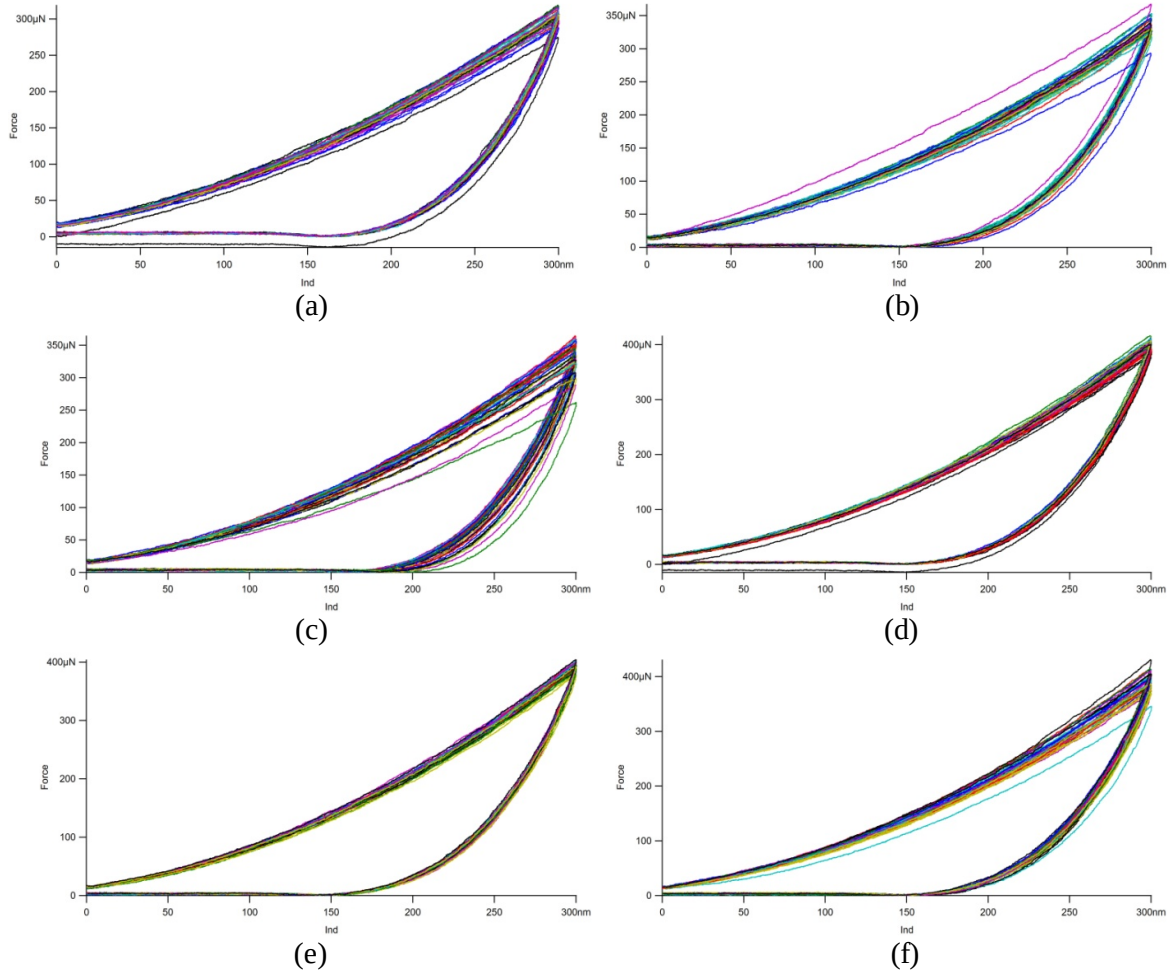


Figure 2: Nano-indentation load-displacement curves; (a) 1 wt.%, no aging; (b) 1 wt.%, 100 hours; (c) 1 wt.%, 200 hours; (d) 2 wt. %, no aging; (e) 2 wt. %, 100 hours; (f) 2wt%, 200 hours.

Although some variations seem to be spotted, the curves laid down in the same path. By observing these graphs, two conclusions can be done: *(i)* the graphene nanostructures seem to be uniformly distributed; *(ii)* the UVA radiation is also uniformly spread through the entire sample area. By observing Figure 3, it is possible to formulate a hypothesis. It seems that graphene nanostructures somehow shielded the epoxy adhesive from the UVA radiation. Both sets, 1 wt. % and 2 wt. % of graphene, had not decrease on stiffness due to UVA light.

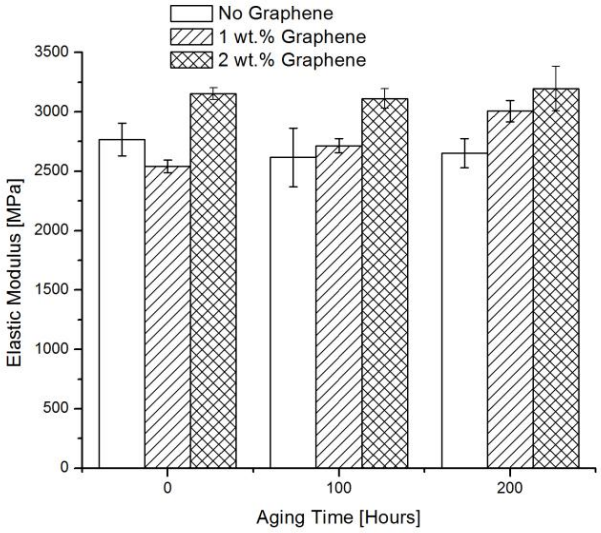


Figure 3: Stiffness versus aging

The nano-indentation results seem to indicate that graphene nanostructures dispersed into the AR300/AH30-150 epoxy system not only increase the stiffness but it also blocked the polymer degradation due to UVA radiation. This shielding effect can be explained by the two dimensional shape of graphene blocks dispersed into the polymeric matrix as it can be observed in Figure 4.

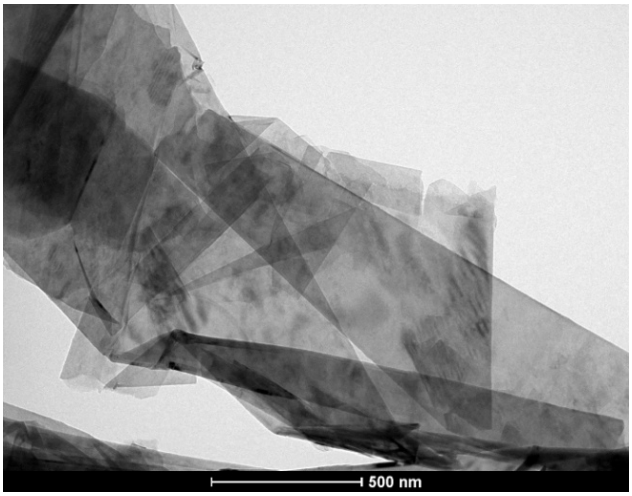


Figure 4: Graphene two-dimensional dispersion

3.2 Aluminium 2024-T3 single lap joint performance

By analyzing Figures 5A-C, it is possible to conclude that graphene dispersion lead to an

increase on single lap joint load capacity up to one hundred hours of aging. The two hundred hours aging reflected a decrease on load capacity. As commented by Woo et al [10], previous studies on epoxy systems photo-degradation suggested formation of carbonyl and hydroxyl groups through chain scission and hydrogen abstraction from the polymer backbone. The graphene blocks nanostructures seem to delay the oxygen and free radical penetration and the degradation described by Woo et al [10]. However, as the number of hours of UVA exposure increases, another factor takes place, i.e. the formation of small micro-cracks, which could be the reason for this decrease on SLJ load capacity. However, a possible explanation for the increase on strain (large displacement) at same time that stress (load capacity) is increased, is the competing process between the carbonyl and hydroxyl groups formation and recombination of hydrogen and carbon in the surrounded areas of graphene nanostructures. This theory, however, is still a working in progress.

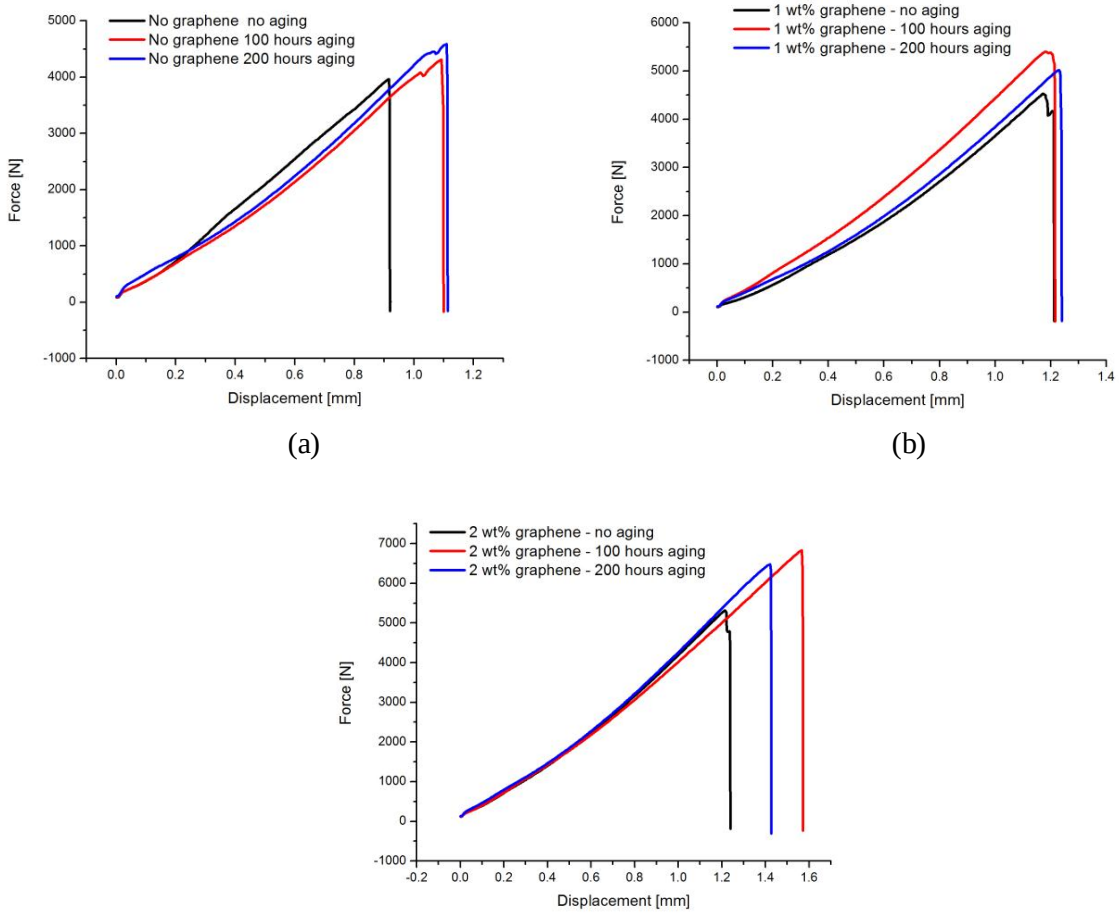
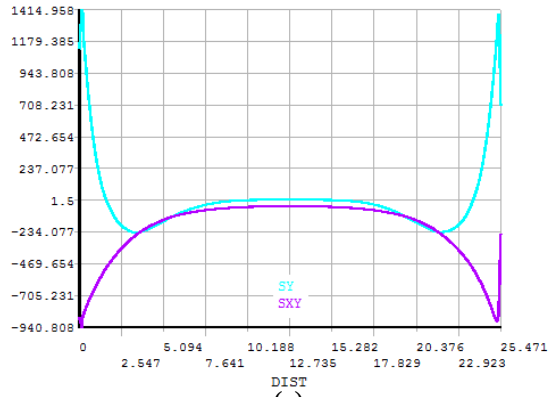


Figure 5: Load-displacement representative curves versus aging; (a) No graphene; (b) 1 wt. % graphene; (c) 1 wt. % graphene

To understand how the graphene dispersion and UVA light aging affected the peel and shear distribution inside the single lap joints a finite element simulation was performed. Notice that as discussed by Kumar et al [25], the two most important stresses into single lap joints are the σ_{yy} (peel) and the τ_{xy} (shear).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943.808
708.231
472.654
237.077
1.5
-234.077
-469.654
-705.231
-940.808
SY
SXY
0
5.094
10.188
15.282
20.376
25.471
2.547
7.641
12.735
17.829
22.923
DIST

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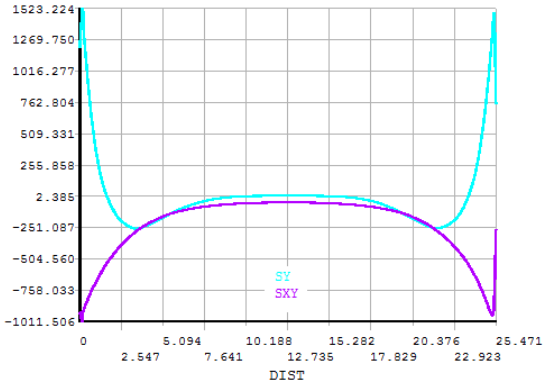
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SY
SXY
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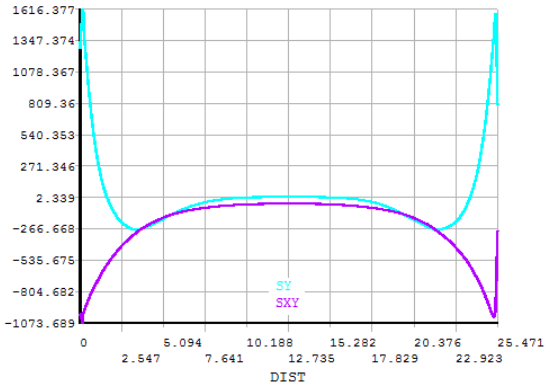
(b)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2.339
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SY
SXY
0
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12.735
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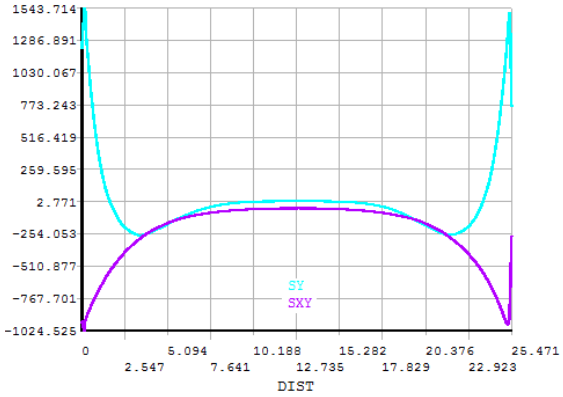
DIST

(c)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SY
SXY
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25.471
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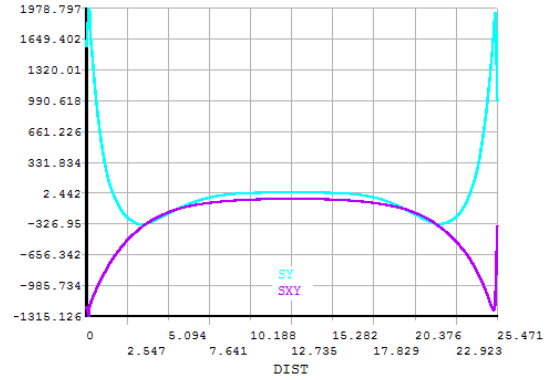
17.829
22.923
DIST

(d)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SY
SXY
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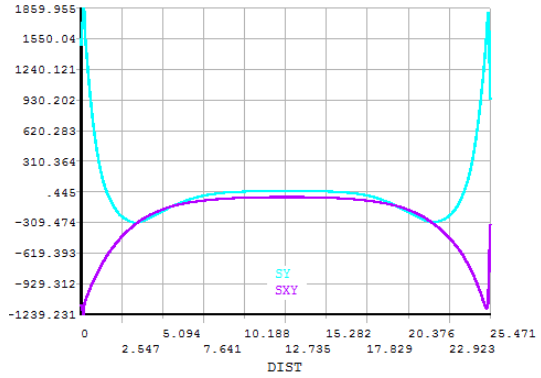
17.829
22.923
DIST

(e)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SY
SXY
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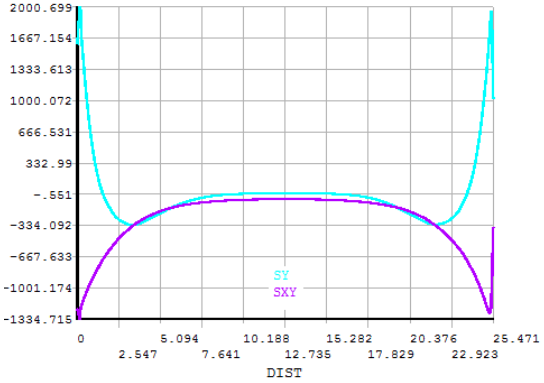
DIST

(f)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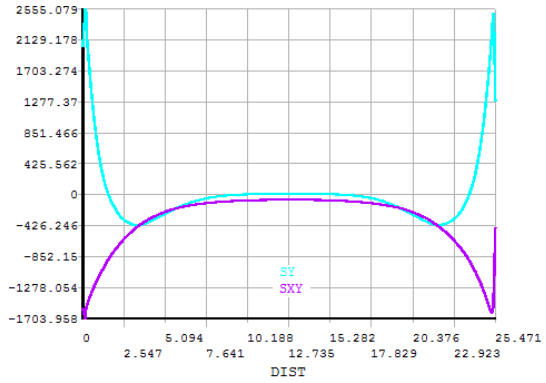
DIST

(g)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SXY
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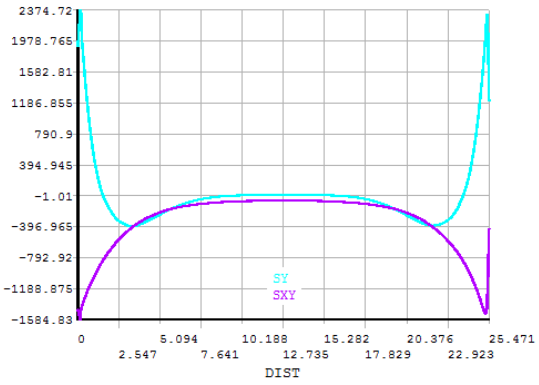
DIST

(h)



(i)

Figure 6: Peel and shear stress distribution. (a) No graphene, no aging; (b) No graphene, 100 hours aging; (c) No graphene, 200 hours aging; (d) 1 wt. % graphene, no aging; (e) 1 wt. % graphene, 100 hours aging; (f) 1 wt. % graphene, 200 hours aging; (g) 2 wt. % graphene, no aging; (h) 2 wt. % graphene, 100 hours aging; (i) 2 wt. % graphene, 200 hours aging.

The initial UVA exposure seems to allow the creation of more cross-linked among the molecular chain, and consequently an increase on peel and shear stresses at 100 hours aging. For the 200 hours aging, however, a decreased on these stress fields can be explained by the molecular chains breakage.

4 CONCLUSION

The graphene dispersion effects into epoxy adhesives under UVA light exposure were investigated. Two approaches were employed to understand this phenomenon. The first one was direct exposure of the nano-modified AR300/AH30-150 epoxy system, with 0 wt. %, 1 wt. % and 2 wt. % graphene concentrations, to UVA light. The samples were exposure to UVA light for two hundred hours. After the aging process, nano-indentation tests were performed. The second approach was to prepare single lap joints (SLJ) using the same concentration of graphene and them exposure the SLJ to UVA light for 200 hours. The ASTM D5868 were used obtain the bearing-load capacity of each SLJ group. The graphene nanostructures formed inside the AR300/AH30-150 nano- modified adhesive seems to block the aging process, as none of the specimens presented a decrease on stiffness. Furthermore, the force-displacement curves obtained by nano-indentation seem to indicate a good dispersion process, as the large majority of the curves laid down at the same path. When the single lap joints were tested, the results also indicated an average increase on bearing-load capacity of 24.76% and 28.36% for 1 wt. % and 2 wt. %, respectively for one hundred hours aging. When the aging reached two hundred hours, there is a decrease on load capacity when compared against the 100 hours results. Even though, the average load capacity was 12.48% and 18.04% higher than the not aged nano-modified AR300/AH30-150 single lap joints. The graphene dispersion into the epoxy adhesives seems to have a double folded effect, in one hand it is increase the bonded joint capacity and on the other hand block the aging effect of UVA light

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