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INFLUENCE OF SURFACE TREATMENT ON THE MECHANICAL AND VISCOELASTIC PROPERTIES OF ADHESIVE JOINTS APPLIED TO THE OIL AND GAS INDUSTRY.

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ABSTRACT

Structural adhesives emerge as an alternative technique for joining materials used in tertiary structures in the oil and gas industry instead of welding, for example, in order to mitigate risks caused by the use of sparks on offshore platforms. Therefore, the present work aims to contribute to the evaluation of the influence of different surface treatments of the bonded material, in this case, carbon fiber/epoxy composite, on the mechanical response of the adhesive joint through the Lap Shear test. Furthermore, the viscoelastic properties of the epoxy-based structural adhesive will be studied via dynamic-mechanical analysis (DMA). With this, it is intended to obtain a better understanding of the influence of the different methods of surface preparation and, consequently, the adhesion mechanisms of each one as well as their interaction with the viscoelastic properties of the polymeric adhesive.

Keywords: *Structural adhesives, Adhesive joints, Surface treatments, Viscoelastic properties.*

INTRODUCTION

The use of structural adhesives as a technique for joining materials in the oil and gas industry has as its main strategy the increase in the strength/weight ratio, through a significant reduction in structural weight, in addition to an increase in resistance through the better distribution of mechanical stresses by the entire area of the joint and greater corrosion resistance compared to conventional joining techniques, such as welds, screws and rivets [(1)].
In this sector, structural adhesives are used especially as an alternative to welds, due to some advantages, such as: reduction of operations involving hot work, corrosion protection and time savings [(2)]. Currently, the use of structural adhesives as a substitute for welds in the oil and gas sector comprises three main situations, namely: (i) composite/composite joints (composite duct connections, saddle supports for non-metallic tubes); (ii) composite/metal joints (repairs of metal pipeline, naval structure and storage tank); (iii) metal/metal joints (saddle supports for metal tubes) [(2)]. In the literature, several studies are still found [(3,4,5)] indicating the feasibility of using adhesive repairs in composites for two of the most common damages found in floating offshore units: fracture by fatigue and loss of thickness by corrosion [(2)].

In addition to the examples already mentioned, adhesive joints can also be present in secondary and tertiary structures of offshore installations (water ducts, railings, handrails, stairs, vessels, tanks and light fixtures), this being another universe for the application of this material, for which the same advantages of increased safety, reduced operating time and the possibility of extending the service life are extremely attractive [6].

As the term implies, adhesives work through the adhesion process, where two factors are fundamental for it to be effective, wettability and the method of adhesion. Wettability is defined as the tendency of a fluid to adhere or spread preferentially on a solid surface in the presence of another immiscible phase [7], that is, it is the ability of an adhesive to maintain close contact with the surfaces to be joined, and good wettability is a key factor in achieving maximum adhesion. As the adhesion process is characterized by the union between two distinct components through their surfaces, the greater the contact area between the adhesive and the adherent, the greater the effectiveness of the union, being necessary that the adhesive presents the greatest possible wettability on the adherent surface [7].

The adhesion method is the way in which the adhesive will interact with the surface, and can occur in three different ways: chemical, where the adhesive and the substrate form chemical bonds with each other; mechanical, where the adhesive fills the imperfections (void spaces, pores, surface irregularities, among others) on the surface of the substrate, promoting a mechanical anchorage between the components; and diffusion or adsorption, where the adhesive diffuses into the substrate at the molecular level [7].

For the cases of adhesive joints of fiber-reinforced polymeric materials, the failure mechanisms are defined through the ASTM D5573 (2012) standard. The possible failure modes of this type of material are: (i) Thin layer cohesive failure represents a failure similar to cohesive failure, but in this case the failure occurs very close to the adhesive-substrate interface, characterized by a thin layer of adhesive on a one of the substrate surfaces and another thicker layer of adhesive on the other substrate surface; (ii) Fiber breakage failure, characterized by the breakage of the reinforcing fibers of the material; (iii) Matrix failure, characterized by the failure of the substrate, but close to the region of union between the adhesive and the substrate; and (iv) Light fiber breakage failure, characterized by fiber breakage occurring very close to the adhesive-substrate interface, forming a thin layer of reinforcing fibers on the surface of the adhesive. It is worth mentioning that there are also failures resulting from the combination of two or more of the six classes of failure modes represented [7,8].

In this study, bonded joints of carbon fiber/epoxy composites with epoxy-based structural adhesive were evaluated using the Lap Shear test. The influences on such mechanical property caused by three types of surface preparation were evaluated, being them, surface cleaned with isopropyl alcohol, surface sanded and cleaned with isopropyl alcohol, and surface with peel ply (Fuseply) application. Also, the influence of the thickness of the adhesive layer were evaluated, with two different thicknesses, 0.5 mm and 1.0 mm. The viscoelastic properties of the adhesive were also evaluated through dynamic mechanical analysis (DMA) and the influences of the post curing process on such properties.

MATERIALS AND METHODS

In preparing the specimens for the Lap Shear test, the carbon fiber/epoxy laminates supplied by the Embraer company were marked and then cutted. In the bonding process of the specimens, the adherent surfaces were initially cleaned with neutral detergent and, later, the specific procedures of each surface preparation were performed. In order to guarantee the different thicknesses analyzed, supports made in a 3D printer were applied in the disposal areas of the laminates. After this procedure, the adhesive AeroPaste X1003 from Solvay was firstly mixed in a proportion of 2 parts of epoxy resin and 1 part of hardener, and then it was applied to the

surface delimited by the non-adherent film and pressure was applied with the clamps for 24 hours for the curing process to be carried out.
After the bonding process, some specimens were placed in an oven at 80ºC for 1 hour, for the post-curing process. The Lap Shear test was performed on a Shimadzu machine, model AG-X, with a load cell of 50 kN, with a test speed of 13 mm/min, in accordance with ASTM D5868 and ASTM D1002 standards. For each surface condition and adhesive layer thickness, five specimens were tested out.

Dynamic Mechanical Analysis (DMA)

For the DMA analysis, the adhesive bulk specimens were manufactured in a silicone mold, with dimensions specified in Figure 1. The analyzes were carried out in the equipment SII Exstar 6000, model DMS 6100, according to the following parameters: temperature range of 25 ºC to 300 ºC, dual cantilever mode, heating rate of 3 ºC/min, frequency of 1 Hz, and amplitude of 10 µm.

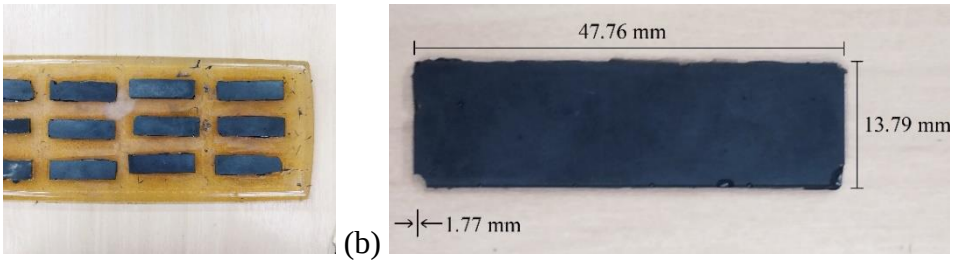

Figure 1: (a) DMA specimens; (b) dimensions of the specimens.

RESULTS AND DISCUSSION

After carrying out the procedures described in the methods section, Figure 2 illustrates the maximum shear strength obtained for each situation: fuseply (surface with peel ply) with thickness 0.5 mm of the adhesive; fuseply with 1.0 mm of the adhesive; sanding + solvent (surface treatment) with 0.5 mm and 1.0 mm of the adhesive, and only solvent surface treatment with 0.5 mm and 1.0 mm of adhesive.

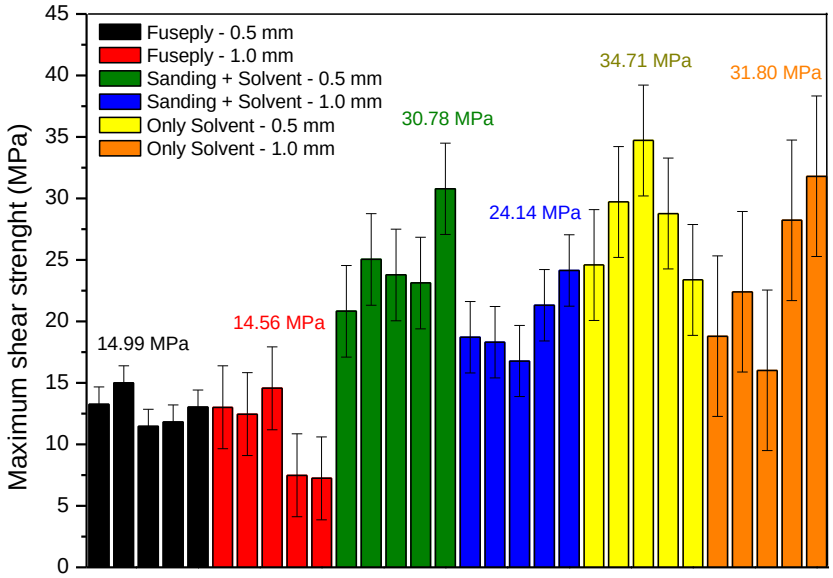

Figure 2: Shear strength behavior of the specimens with different surfaces conditions and adhesive layer thickness.

In order to better observe the results, Table 1 shows the maximum shear strength obtained for each specimen with their respective conditions. In addition, the average values of the rupture stress for each situation are indicated, in order to obtain a better way of comparison between the analyzed groups.

Table 1: Maximum failure strength for each condition analyzed.

	Fuseply 0.5 mm	**Fuseply 1.0 mm**	**Sanding + Solvent 0.5 mm**	**Sanding + Solvent 1.0 mm**	**Only Solvent 0.5 mm**	**Only Solvent 1.0 mm**
Sample	**Maximum shear strength (MPa)**					
1	13.27	13.01	20.83	18.71	24.59	18.80
2	14.99	12.46	25.04	18.31	29.72	22.41
3	11.46	14.56	23.78	16.78	34.71	16.02
4	11.82	7.48	23.12	21.32	28.77	28.22
5	13.03	7.24	30.78	24.14	23.38	31.80
Average	**12.91 ± 1.39**	**10.95 ± 3.37**	**24.71 ± 3.72**	**19.85 ± 2.90**	**28.23 ± 4.51**	**23.45 ± 6.53**
Failure mode	**Adhesive**	**Adhesive**	**Cohesive**	**Cohesive**	**Cohesive**	**Cohesive**

First, when analyzing the results within each tested condition, it can verify that there is a variation in the maximum shear strength, especially in the condition in which the Fuseply with an adhesive layer thickness of 1.0 mm was used. In which two specimens presented load much lower than the others, indicating that there were inconsistencies both in the cutting process of the laminates, causing dimensional variations in the specimens, and in the bonding process, where there were probably tension concentrators that affected the mechanical behavior of the sample.

However, it can verify that there is a consistency in the variation of the rupture tension between the analyzed groups, where the best condition evaluated was the cleaning of the laminate using only isopropyl alcohol (solvent), with an adhesive layer thickness of 0.5 mm, which showed an average maximum shear strength of (28.23 ± 4.51) MPa. This result indicates that the adhesion mechanism between the adhesive and the substrate is not only mechanical, but probably a mixture of mechanical and chemical adhesion, originated by the interaction between the solvent and the epoxy resin of the laminate.

This hypothesis is reinforced by the result obtained in the sanded specimen, removing a thin layer of resin from the laminate, reducing the interaction between solvent and resin and, therefore, reducing the chemical adhesion. Another point is the condition in which Fuseply was applied, which would be the best surface condition to increase mechanical adhesion. However, it was the condition that presented the lowest shear strengths, reinforcing the argument that the mechanical adhesion mechanism has less influence than the set of mechanical and chemical adhesion mechanisms. Another point is the thickness of the adhesive layer. The results indicate that a lower thickness of the adhesive layer is better for the shear strength, and an increase in thickness generates greater mobility of the adhesive bond and, therefore, lower shear strength and premature failure [2,7]. Also, an increase in thickness can generate a greater formation of voids and defects in the adhesive area, therefore reducing the resistance.

For DMA analyzes, Figure 3 illustrates the viscoelastic behavior of the adhesive after curing for 24 hours at room temperature. A partial T_g (glass transition temperature) can be observed at

60 °C indicated by the first peak in tan delta. It is verified that the storage modulus (E') curve, at temperatures close to 45 ºC, presents a drop related to the partial T_g of the adhesive. As the temperature increases, it is noted that at approximately 80 ºC, the storage modulus begins to increase, which is an indicative that there is a residual curing process to be done at this temperature, as expected because pasty adhesives cured at room temperature do not reach complete cure. In this way, it was verified that it would be necessary to carry out a post-curing step on the adhesives to guarantee their complete curing, consequently increasing their T_g value. This post-cure was carried out at 80 °C for 1 hour.

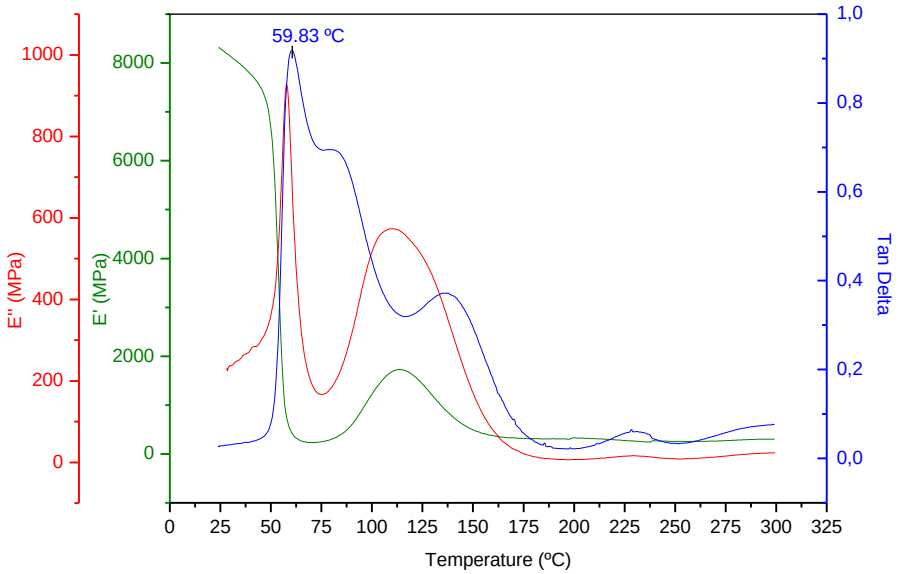

Figure 3: DMA curves of the adhesive after curing process at room temperature.

After the post curing process at a temperature of 80 ºC for 1 hour, as illustrated in Figure 4, it is verified that the T_g of the adhesive presents a value of 115.48 ºC. It can be observed in the E', E'' (loss modulus), and tan delta curves that no other thermal event was evidenced, confirming that that there is no more residual curing and, therefore, the post curing process at the chosen temperature and time was ideal to achieve complete curing of the adhesive.

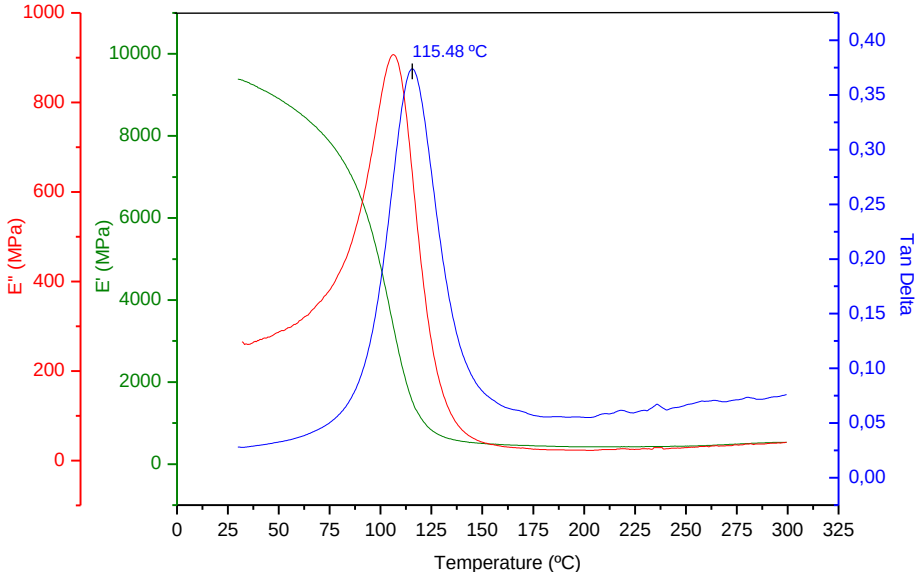

Figure 4: DMA curves of the adhesive after post curing process at 80 ºC for 1 hour.

CONCLUSIONS

From the analysis of the results, the following conclusions can be drawn:

- Among the three conditions of preparation of the adherent surface, the one that supported the highest shear strength was the cleaning condition only with solvent and the worst condition was with the application of Fuseply;
- There is an indication that a possible interaction between the isopropyl alcohol and the epoxy resin of the laminate generated a chemical adhesion mechanism that, combined with the mechanical adhesion mechanism of the adhesive and the surface, contributed to the increase in shear strength through the Lap Shear Test;
- The increase in thickness contributes negatively to the shear strength, making the adhesive bond more flexible and therefore less resistant and more prone to premature failure of the adhesive bond;
- The DMA analyzes indicate that the adhesive cured at room temperature does not reach complete cure and a post cure process at 80 ºC contributes to the increase of the glass transition temperature of the adhesive, making the adhesive bond more resistant in the thermal scope.

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REFERENCES

1. MONSEF, A. S. et al. Effect of environmental conditioning on pure mode I fracture behavior of adhesively bonded joints. Theoretical and Applied Fracture Mechanics, Amsterdam, v.110, n.102826, p.1-11, 2020.
2. SILVA, L. F. M.; ÖCHSNER, A.; ADAMS, R. D. Handbook of adhesion technology. 2nd ed. Berlin: Springer. 2008. v.1, 1805 p.
3. MALLY, T. S. et al. Performance of a carbon-fiber/epoxy composite for the underwater repair of pressure equipment. Composite Structures, v. 100, p. 542–547, 2013.
4. OSNES, H.; MCGEORGE, D. Experimental and analytical strength analysis of double-lap joints for marine applications. Composites Part B: Engineering, v. 40, n. 1, p. 29–40, 2009.
5. DA COSTA MATTOS, H. S. et al. Analysis of a glass fiber reinforced polyurethane composite repair system for corroded pipelines at elevated temperatures. Composite Structures, v. 114, n. 1, p. 117–123, 2014.
6. SETVATI, M. R. et al. A review on composite materials for offshore structures. In: PROCEEDINGS OF THE ASME 2014 33RD INTERNATIONAL CONFERENCE ON OCEAN, OFFSHORE AND ARCTIC ENGINEERING, 2014, San Francisco. San Francisco: 2014.
7. COGNARD, P. Handbook of adhesives and sealants. Versailles: Elsevier, 2006. v. 2.
8. OLIVA, H. N. P. Estudo de adesivo epóxi reforçado com nanotubo de carbono e comparação para juntas coladas, rebitadas e híbridas. 2016. 136 f. Tese (Mestrado em Engenharia Mecânicas) – Universidade Federal de Minas Gerais, Belo Horizonte, 2016.