ADHESIVENESS STUDY OF POLIMERYC MATRIX COMPOSITE MATERIAL FOR PIPELINES REPAIR

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Abstract. *The use of fiber reinforced polymer composites in the repair and rehabilitation of pipelines is a new concept that has the potential to improve the way we repair pipelines. The purpose of this paper is to discuss the adhesion of a glass fiber reinforced polymer matrix composite material used in pipeline repair on a steel substrate and some factors that could influence the metal/composite interface behavior, as the adhesive layer thickness, the cleaning of the surface and the adherent's surface treatment, as well as the study of the influence of humidity on the mechanical properties of the joints. The research was conducted in two stages. Firstly, selected surface treatments for the steel adherent were evaluated by single lap shear tests. For these tests, metal-composite adhesive joints were manufactured with different mechanical surface treatments with the dimensions recommended by the ASTM D 5868-01 standard, with different adhesive thickness. Specimens with the best surface treatments were subjected to hygrothermal ageing to evaluate the influence of the water on the mechanical properties of the joints. The fracture failure modes of the adhesive system were associated with the mechanical properties obtained in the adhesion tests. Surface treatment by shot penning resulted in joints with good environmental durability.*

Keywords*: polymeric matrix composites, joints, adhesion.*

1. Introduction

The rehabilitation of pipelines due to damage caused by environmental factors with fast and low cost methods has been a challenge, mainly because corrosion is a type of defect almost inevitable in pipes. As a consequence, knowing a technology of pipe repair is very important to reduce costs of hidrocarbonates transportation. Many techniques are being developed, amongst them, the repair with composite materials that consists in involving the damaged pipe with the composite material. The characterization of the adhesion and the study of techniques to maximize it are of great scientific and technologic interest, because the efficiency of the repair will depend on the good adhesion of the composite material of the repair on the steel.

The factors affecting durability of a composite/metal bond are: the nature of the surface treatments, the adhesive film and the adherend material. For example, a bond that has not been exposed to a harsh environment may show initial high strengths, the durability of this same bond when exposed to hot/humid conditions may be very poor (Molitor *et al*, 2001). The main area of environmental attack on a metallic/composite bond is that close to the adhesive, thus resulting in adhesive failure (Molitor *et al*, 2002). To prevent adhesive failure, it is desirable to transfer the locus of failure from the adhesive/adherend interface to within the adhesive, thus resulting in cohesive failure. A good surface treatment is achieved when one or a combination of the following factors occurs: the production of a surface free from contaminants; the production of a macro/microscopically rough surface and the production of a fresh stable oxide layer (Kinloch, 1980).

Surface treatments often involve chemicals reactions, which produce surfaces modifications on adherends, or mechanical procedures, which improve adhesion by increasing mechanical interlocking of the adhesive to the adherend. By this way, the primary objective of a surface treatment is to increase the surface energy of the adherend as much as possible and/or improve the contact between the adhesive/adherend by increasing the contact area.

Roughness or an increase in the surface area has been shown good results in improving adhesion. Subsequently, a relationship exists between good adhesion and bond durability (Kinloch, 1980).

2. Materials and Methods

The aim of this work is to study the adhesiveness of a composite material used in pipeline repair on a steel substrate. Hence, metal-composite single-lap adhesive joints were manufactured with different surface treatments with the dimensions recommended by the ASTM D 5868-01 standard, and five different adhesive thicknesses. The two surface treatments investigated were sand blasting and shot penning, both commonly used in the industry.

The best performing surface treatment and adhesive thickness were then evaluated following exposure to a humid environment. In this test, which investigated the environmental durability of the metal/composite bonding, the parameter that varied was the time of exposure at 60º C. After exposure, the fracture surfaces were analyzed by optical microscopy and classified according to the ASTM D 5573-94 standard. The fracture failure modes of the adhesive system were associated with the mechanical properties obtained in the adhesion tests.

2.1. Materials

Single lap joints were manufactured in accordance with ASTM D 5868-1 Standard test method for lap shear adhesion for fiber reinforced plastic bonding. The specimens' configurations are shown on Fig.1

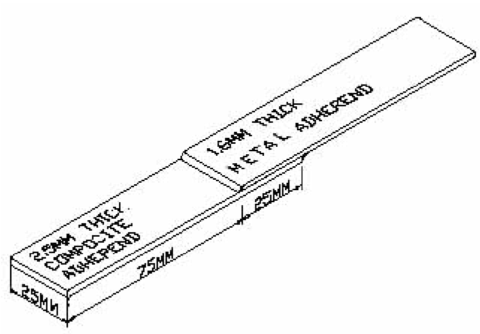


Figure 1 - Single lap joint configuration

2.1.1. Composite Adherend

The composite used as one of the adherends was developed for pipelines repairs in the Laboratory of Composites Materials of UFRJ by Souza, 2002. The material was a fiberglass polymeric matrix reinforced composite, manufactured by the hand-lay-up method, in the proportion of 65% of fibers and 35% of matrix. As the matrix, it was used a thermosetting epoxy resin, called Diglicil Éter of Bisfenol A (DGEBA), belonging to the family of resins from Dow Química® with an flexible agent, DY104, produced by Ciba Geisy®. The reinforcement constituted of fiberglass (type E), in the fabric form with 120g/m^2, manufactured by Texiglass®. The composite presents about 3 mm of thickness constituted by 25 layers of the fiberglass fabric alternated with 27 layers of 5 grams each of resin. Four plates in the dimensions 150 x 500 mm were laminated for subsequent cut in the normalized adherends dimensions. The final aspect of the laminated plate can be seen in Fig.2, after cure for 24 hours at room temperature.

Figure 2 - Composite plate after cure for 24 hours at room temperature.

2.1.2. Adhesive

As adhesive, it was used a polymeric matrix composite reinforced by dispersed small particles of quartz, developed by Souza, 2002, whose polymeric matrix is constituted of epoxy resin (DGEBA), D.E.R 331, belonging to the family of resins from Dow Química® with a cure called DY 12, manufactured by Ciba Geisy®. The disperse phase is constituted by particles of quartz in 5% in weight. Figure 3 shows a micrography of the adhesive developed to glue the composite/metal joints.

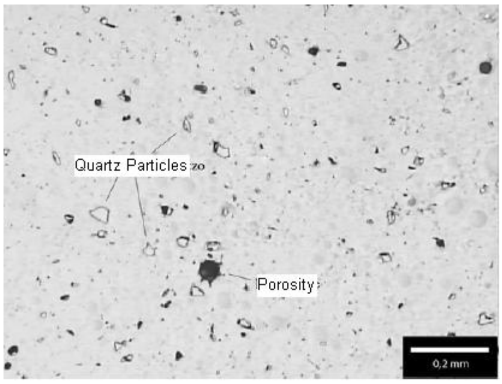


Figure 3 - Adhesive Sample, 200X.

2.1.3. Metal Adherend

The adherend used to simulate what would be the pipe’s outer surface was a plate of carbon steel ABNT 1010. The plates were cut in the dimensions of the standard mentioned previously.

2.2.Surface Treatments

A variety of surface treatments have been used with various degrees of sucess to increase surface tension, surface roughness and increase bond strength and durability of polymer composite adhesive joints (Fourche, 1998).

Prior to adhesive bonding the metal adherends had been degreased in solvent for 10 minutes, rinsed in alcohol and dried. A group of 25 metal adherends were abraded using 80mesh alumina and then wiped clean with alcohol and dried again. The other group of 25 samples was shot peened using alumina grit blast with one pass at a distance of 20-25 cm, and then they were also cleaned with alcohol and dried.

Some researchers (Yoshino, 1997; Bergeret, 1995) have found a relation between surface roughness and bond strengh for thermoset polymer composites. However, the abrasion to increase the termoplastic polymer composite roughness did not reveal any significant increase neither in bond strength nor in bond durability, due to the fact that some of these composites have low surface energy (Molitor, 2002).

All the 50 composite adherends were degreased in alcolhol, rinsed and dried, then smoothly blasted with a 60 mesh alumina and cleaned with alcool and dried again.

Such mechanical treatments have as objective increasing the superficial area of contact promoting mechanical anchorage optimizing, consequently, the adhesion. The metal surface roughnesses were characterized by roughness tests.

2.3. Methodolgy

For the adhesion experiments, five samples of each adhesive thickness were used for each surface treatment. The combination of two surface treatments and five adhesive thicknesses with each thickness comprising five specimens resulted in ten experiments. The resulting test is given in Tab.1.

Table 1 - Test matrix for investigation of surface treatment and optimum adhesive thickness.

Surface Treatment	Adhesive Thickness	Number of specimens
Sand Blasting	0,2	5
	0,3	5
	0,6	5
	0,9	5
	1,4	5

Surface Treatment	Adhesive Thickness	Number of specimens
Shot Penning	0,2	5
	0,3	5
	0,6	5
	0,9	5
	1,4	5

In order to obtain good alignment of specimens and the control of the adhesive thickness it was necessary a collage device. This jig was made of acrylic in the form of a step with 1,5 mm height; the same metal adherend thickness, so that, in the upper part of the step, plaques with known thickness could be put between the composite and the metal in order to guarantee the control of the adhesive thickness. The dimensions of this collage device can be seen in the Fig. 4. Using this device, the adhesive thicknesses were varied from 0,2 to 1,4 mm.

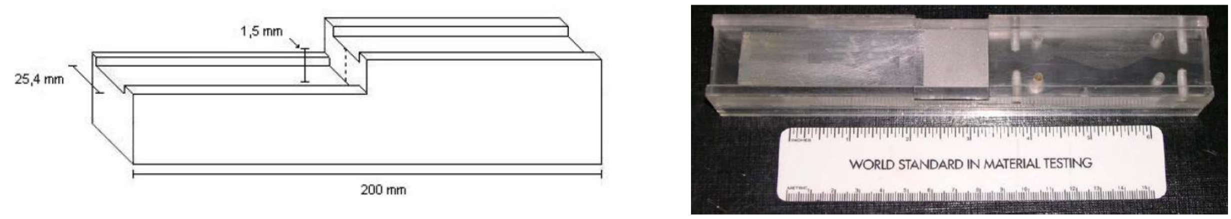


Figure 4 – Gig used for specimen glueing

Single lap shear testing was performed in an Instron testing machine at a loading rate of 1 mm/min, a smaller rate than of 13 mm/min recommended by the ASTM D 5868. This recommended rate was unviable for the material of this study, because it was very high, and consequently not allowing data acquisition in an appropriate way for subsequent construction of the tension versus displacement graphs. To guarantee a precision displacement measure an extensometer system was coupled. The extensometer was positioned in a centralized way. This configuration can be seen in Fig 5.

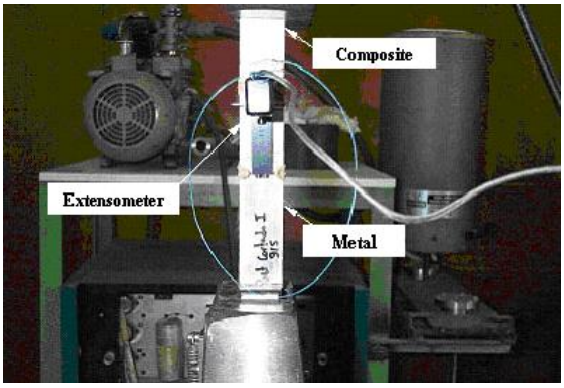


Figure 5 – Test Machine

In the second stage of the experiments, the joints optimized in thickness and superficial mechanical treatment were submitted to aging in water at 60 º C at different intervals of time. The aging tests followed the ASTM D 5229 standard. Besides, to study the effect of the humidity absorption in the mechanical properties of the adhesive, coupons were made in molds of silicon, with five coupons used for each interval of time. All samples were aged in distilled water in a stainless steel climatization camera at 60 º C at intervals of 24, 72, 120, 240 and 720 hours. Such intervals were chosen in agreement with previous works on aging of composites (Fujiyamna, 2002)

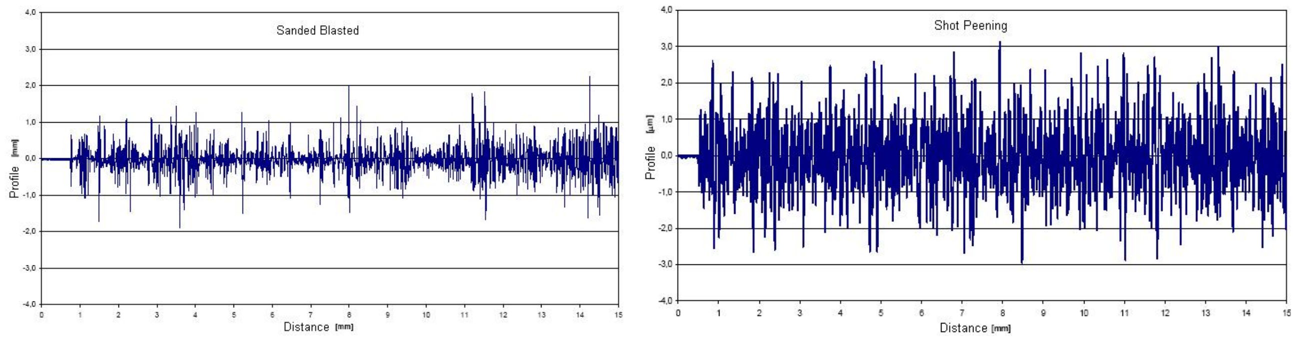
3. Results

The result of surface roughness analyzed by a rougness gauge is show in Tab 2. The roughness curves and the amplitude distribution curves showed that the metal plates treated with shot peening process presented better results, as can be seen in Tab.2

Table 2 – Roughness measures.

Sand Blasted	**R_a (µm)**	**R_q (µm)**	**R_{valley} (µm)**	**R_{peak} (µm)**	**R_{total} (µm)**	**R_{sk} (µm)**
Average	0,340	0,482	2,398	2,759	5,155	0,212
Stand. Dev	0,052	0,066	0,422	0,397	0,753	0,133
Shot Peened	**R_a (µm)**	**R_q (µm)**	**R_{valley} (µm)**	**R_{peak} (µm)**	**R_{total} (µm)**	**R_{sk} (µm)**
Average	0,919	1,198	4,142	5,019	9,161	0,119
Stand. Dev	0,177	0,233	1,020	1,266	2,217	0,106

It is observed in Fig.6 and Tab.2 that the metallic adherends with shot peening superficial finish presented higher roughness values of Ra and R_q parameters, more concentrated and homogeneous roughness, and a larger predominance of picks in both surfaces treated mechanically when comparing the parameter R_{sk} obtained for both superficial treatments. Although studies had shown (Sampaio, 1998; Kinloch, 1982) that roughness is associated to mechanical anchorage and also allow a more intimate contact between the adhesive and adherends, the literature also shows that the increase of the superficial area cannot be considered the only condition to guarantee optimum adhesion (Taylor *et al*, 1998).



(a) (b)

Figure 6 - Examples of shot peening and sanded blasted joints roughness profile

The data obtained in shear tests allowed the construction of graphs tension versus displacement for each of the joints with variable thickness and different surface treatment. In the abscissa of these graphs the displacement was plotted, because the measure supplied by the extensômetro is actually a relative displacement, proportional to the deformation of adhesive. This proportionality can be admitted assuming that the adherends behave as inexistensible materials in comparison to the adhesive. Figure 7 shows the shear tests results.

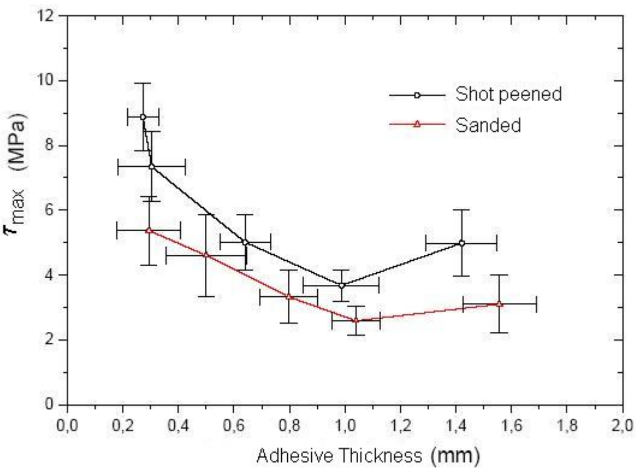


Figure 7 – Shear Tests Results

The maximum shear stress of the adhesive joints is affected by the adhesive thickness layer and the best surface treatment was shot peening, whose joints showed higher shear stress values and cohesive failure mode.

The joints with 0,2 mm adhesive thickness and the metal adherend treated by shot peening process were submitted to hygrotermal ageing at intervals of 24, 72, 120, 240 and 720 hours. Figure 8 shows the adhesives' coupons water absorption. No microstructural change on the adhesives was observed.

It is observed in Fig.7 that the amount of absorbed humidity increases with time of immersion. In this experiment, although the graph can suggest, the saturation point was not reached and the diffusion type was not modeled, as well as the coefficient of diffusion of the adhesive material. To obtain such data it would be necessary to follow the procedure A of the standard ASTM D 5229.

The aged joints were submitted to shear tests for subsequent comparison with the results of the reference samples that were not aged. The joints mechanical properties decrease with time as shown by Fig.9 and all of them failed by adhesive mode.

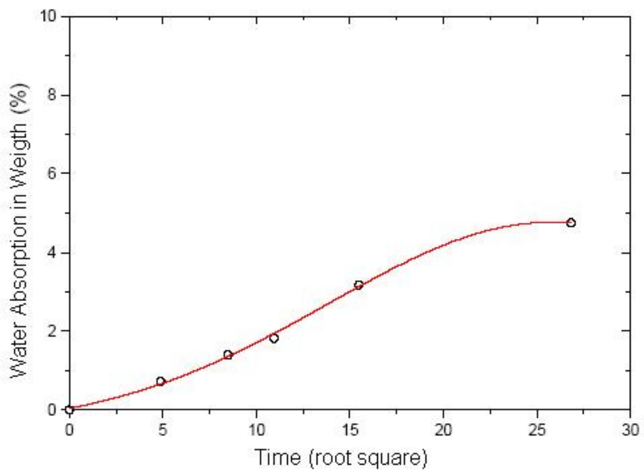


Figure 8 – Water Absorption.

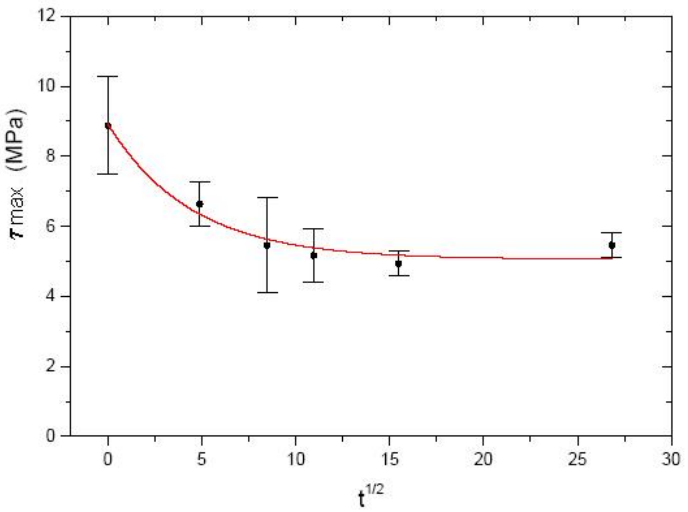
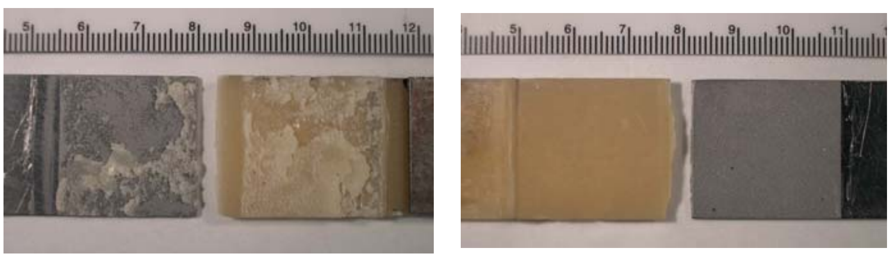


Figure 9 – Shear Strength Decrease for Aged Joints.

Although changes in the adhesive joints failure mode were observed, as shown on Fig.10, no significant change was observed in the microstructural analyzes. In the same way, the metallic surface of the collage area did not show oxidation.



(a) **(b)**

Figure 10 – Failure modes of shot peening adhesive joints: (a) cohesive failure in joints without ageing and (b) adhesive failure in aged joint.

4. Conclusions

It is possible to conclude that:

- The maximum shear stress of the adhesive joint is affected by the adhesive thickness layer: as the thickness increases the maximum shear stress decreases no matter what was the mechanical surface treatment employed.
- The best mechanical surface treatment was shot peening, whose joints showed higher shear stress values, higher values of R_a and R_q roughness and cohesive failure mode, which is also an important criteria for the selection of surface treatments.
- It was not possible to quantify the contribution of the theories of adhesion, but it can stand out the contribution of the mechanical interlocking in the adhesion due to better adhesion found in the joints with more pronounced roughness.
- The adhesive joints failure mode suffers influence of the steel adherends surface treatment and of the adhesive thicknesses. For sanded joints the adhesive fracture was observed for all sanded blasted joints with different thickness. In the shot peened joints, it was also observed the influence of the thickness. In joints with nominal 1,4 mm thickness adhesive fracture happened in 100% of the five tested samples and for the ones with smaller nominal thickness the failured mode varied from fracture by tearing for the smallest thickness to cohesive fracture for intermediate thickness.
- Moisture absorption harms the mechanical properties of the adhesive joints. The maximum shear strength decreases with time of exposure.
- Aging influences the failure mode of the adhesive joints. The optimized joints in the no aged condition presented fracture by tearing and after aging presented adhesive failure in all the samples tested in the different intervals of time of immersion in water. Such fact can represent a degradation of the joint when exposed to moisture without protection.
- In the aged joints oxidation was not observed in the metallic adherend after fracture. Although the lateral faces of the aged adhesive joints have been attacked by the humidity, the metal adherend didn't suffer corrosion, even for the largest time of immersion in water
- Microstructural changes were not observed in the adhesive after aging.

For continuation of this study, there are some suggestions:

- To take measurements of contact angle between adhesive and adherent surfaces.
- To study top joints, using the same methodology adopted for the shear tests
- To verify the moisture absorption model of the polymeric composite adherend and also of the adhesive using samples with appropriate dimensions.
- To verify the influence of moisture absorption in the glass transition temperature of the polymers that constitutes the composite adherend and the adhesive.
- To make the aging tests at room temperature to verify the possible influence of the thermal dilation of the materials used in the adhesive joints.
- To verify the contribution of the chemical bond in the adhesion through the characterization of the surface of the steel and of the epoxy through ray-X (XPS)

5. Acknowledgements

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