Evaluation of the Effects of Fluids Upon the Flexural and Parallel-plate Loading Behavior of Glass Fiber Reinforced-vinyl Ester Resin Matrix Composite Pipes

Ademi Nobeto da Silvaa, Guilherme Sampaio Moria, Jose Roberto Moraes d’Almeidaa,b*

aMechanical Engineering Department, Universidade do Estado do Rio de Janeiro, Rua São Francisco Xavier, 524, Maracanã, CEP 20550-090, Rio de Janeiro, RJ, Brazil
bMaterials Engineering Department, Pontifícia Universidade Católica do Rio de Janeiro, Rua Marquês de São Vicente, 225, Gávea, CEP 22453-900, Rio de Janeiro, RJ, Brazil

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Commercial glass fiber reinforced-vinyl ester resin composite pipes used in onshore and offshore utilities were exposed to the action of fluids that could normally come into contact with them during their service life, namely: salt water, biodiesel and a mixture of water and oil. The influence of these fluids upon the flexural properties and parallel-plate loading behavior of the composites was evaluated. The results of the mechanical tests point out that physical aging was the main phenomenon, and that it causes a reduction of stiffness of around 20-30% – at the parallel-plate test – and a decrease of toughness of up to 40% – at the flexural test. The results of the flexural tests were very dependent of the inhomogeneous microstructure of the commercial composite analyzed.

Keywords: glass fibers composites, environmental aging, mechanical properties, parallel-plate test

1. Introduction

The use of polymer composites at onshore and offshore facilities increased over the last years due to the several advantages of these materials in respect to more traditional materials, such as steel alloys. These advantages include a high specific strength - i.e., a high tensile strength to density ratio - what implies weight savings on a volume basis1. For many industrial applications, in fact, weight saving can be a major factor to choose or not a material, and polymer matrix composite pipes have as one of their advantages low weight when compared to their steel counterparts. The ease and speed of assembling a light pipe is also fundamental in, for example, offshore facilities where any material or personnel to be transported to or allocated at the offshore plant has a substantially high cost. Polymers and polymer composites can, however, degrade when exposed to several common environments that they can be brought into contact during their service life. Ultraviolet radiation2-4 and humidity5 are the most common of the service environments that one could expect a resin matrix composite pipe to be exposed to. Their effects and prevention are well discussed in the literature6. However, several other environments can be expected to cause degradation to polymers and polymer composites; these include salt water7,8, and other common fluids, like diesel and petrol9-11. Although many works had already treated the problem of the interaction of several fluids with polymers and their composites5-12, generalization of the observed behavior is not, in many instances, a simple task. This is due to the fact that very particular interactions can occur between a specific composite and also the specific fluid under analysis; this aspect is especially true when the performance of a commercial material is being analyzed. When a commercial composite is being tested, and even when tight manufacturing parameters are used, local variations on the amount of cure, on the fiber distribution and fiber volume fraction, or on the volume fraction of voids can occur and can be a source of deviations of the expected composite behavior13. Therefore, in this work, a study was undertaken to analyze the effect caused by fluids that can be ordinarily in contact with composite pipes - namely salt water, biodiesel and a mixture of water and oil - upon the flexural and parallel-plate loading behavior of a commercial glass fiber reinforced-vinyl ester resin matrix composite pipe.

2. Material and Experimental Methods

A commercial glass fiber-vinyl ester matrix reinforced composite pipe with proprietary specifications and manufactured by filament winding was used in this work. The as received 2000 mm long pipe had nominal external diameter of 115 mm and thickness of 7.3 mm. Flexural specimens 125 mm long and 25.5 mm large were machined along the longitudinal direction of the pipe. These specimens were machined 30 mm apart from each other, along the pipes’ length, in order to encompass possible variations on the fiber volume fraction and spatial distribution along the pipes’ length. This procedure has the objective to give average values for the properties being evaluated. The three point bending tests were performed following the ASTM D 79014 standard. The test span used

*e-mail: dalmeida@puc-rio.br
The test specimens were immersed into these prepared following the recommendations of ASTM standard has 87.7% of water and pH of 6.89. The salt water was reduce the diameter of the parallel-plate loading specimens as stress raisers and serve as points for fluid accumulation. Resin rich areas are regions with low strength inside de composites. The voids can act as sources of weakness for this composite. The voids can act as points for fluid accumulation. The microstructure of the composite was analyzed by optical microscopy. Samples were prepared following the usual mounting, grinding and polishing procedures. After being mounted on an epoxy base, the samples were ground from sandpaper # 220 to 1200, and the polishing procedure used diamond paste from 6 µm to 1 µm. Each grinding/polishing step lasted for about 3 minutes.

Three different aging fluids were used, namely: a) salt water; b) biodiesel; and c) oily water. The specific characteristics of the biodiesel were: pH 5.9; acidic index: 0.08 mg/kg; specific gravity: 882 kg/m³. The oily water has 87.7% of water and pH of 6.89. The salt water was prepared following the recommendations of ASTM standard D 1141. The test specimens were immersed into these fluids at ambient temperature, 23 ± 2 °C, during 6 months. Six specimens were tested per composite condition and test performed.

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3. Experimental Results and Discussion

Figure 2 shows the common aspects of the composite’s microstructure. One can see that a heterogeneous fiber distribution exists along the thickness of the composite’s wall. Resin rich areas and voids are observed, and these areas are sources of weakness for this composite. The voids can act as stress raisers and serve as points for fluid accumulation. Resin rich areas are regions with low strength inside de composite serving as crack initiation points.

Figure 3 shows the compressive loads necessary to reduce the diameter of the parallel-plate loading specimens by 10% before and after aging. One can see that all aging media affected the behavior of the composite, and a load bearing capacity reduction varying between 20-30% was noted. Using the t-Student test with a significance level of 0.05 the average values of the aged composites are not significantly different among each other, but they are significantly different in respect to the as-received composite.

Although the load bearing capacity of the aged composites in respect to the as received one was reduced, the macroscopic inspection by naked eye did not reveal the presence of cracks or delamination at the tensile side of all specimens, Figure 4a, regardless the composites being or not aged. This simple visual inspection is the standard practice, as recommended by ASTM D 2412 standard15, to determine if a material fails or not in respect to the parallel-plate loading test. At the compressive inner side, there were some whitening effects accompanying the fiber winding angle, Figure 4b. Whitened zones are associated to the development of debonding at the fiber-matrix interface17. At the compressive side of the test specimen, the presence of these marks could indicate that fiber buckling can be a failure mode of relevance. However, from the standard point of view all specimens were approved.

The results, however, point to a decrease of the specimens’ stiffness. This same behavior was also observed for another glass fiber reinforced pipe after its exposure to tap water18, and can be attributed to the diffusion of the fluids to the interior of the matrix resin, and to the accompanying plasticization effect1. The diffusion of a liquid into a polymer usually produces, at least at the first stages of the diffusion process, physical aging of the polymer, with the fluid diffusing into the free volume of the macromolecular structure. The uniform decrease of the load capacity observed at Figure 3, seems to indicate that, for the aging time of this work, the effect of the fluids was, indeed, very similar, and one could expect that only physical aging is occurring.

The stiffness reduction of the parallel plate test can be evaluated using the following expression19:

\[
\Delta L = 0.1488 \frac{Pr^3}{EI}
\]

where \(\Delta L\) is diameter reduction due to \(P\), \(P\) is the load, \(r\) is the ring’s radius, and \(E\) is the flexural modulus. The moment of inertia, \(I\), for the ring configuration is given by:

\[
I = \frac{bt^3}{12}
\]

where \(b\) and \(t\) are, respectively, the width and the thickness of the ring specimen. From Equation (1) it is clear that the value of \(E\) decreased for the aged specimens, since the load \(P\) decreased, as shown in Figure 3, and the other variables at Equation (1) are geometrical constant parameters \((I\) and \(r))\), and \(\Delta L\) was an experimental constant parameter – all the rings were loaded to produce a 10% reduction of their original diameter. The calculated values of \(E\) for the
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Figure 2. Uneven distribution of fibers along the composite pipe wall. a) Fiber rich region, and b) Resin rich areas and large voids can be observed.

Figure 3. Load necessary to reduce the specimen’s diameter by 10% of its original value.

Figure 4. a) Macroscopic view of the tensile side (90° position, see Figure 1) of the tested specimens; and b) the inner surface, showing some whitening following the fiber winding directions.
as-received and for the aged specimens were, respectively, 8.9 GPa and 6.9 GPa.

The results of the three-point bending flexure test, Figure 5, were not so straightforward. One can observe that the average flexural strength of the aged composites showed higher values than the average flexural strength of the as-received composite. The statistical analysis using the t-Student test with a significance level of 0.05, however, showed that the values of the as-received and the composite immersed in oily water are not significantly different. The values for both salt water and biodiesel aged composites are statistically equal between each other, and are statistically different from the value of the as-received composite.

These results do reveal, however, the combined effects caused by plasticization, the very inhomogeneous microstructure observed for this composite, and also the stress state imposed by the flexure test. Plasticization enhances the toughness of the polymer matrix, and therefore can delay the propagation of a crack, favoring the attainment of a higher stress before the collapse of the composite. At the first stages of fluid absorption this could, therefore, increase the load bearing capacity of the material. For example, the interlaminar shear stress of carbon and glass fiber composites increased for the first stages of water absorption, and the fracture toughness parameter, \( G_{Ic} \), also increased due to moisture for glass fiber composites with several different polymeric matrices, namely: ortho-polyester, vinylster and epoxy.

However, inhomogeneity of fiber distribution is, maybe, the leading factor behind the results presented at Figure 5. If a resin rich area, such as the one showed at Figure 2, is close to the outer layers of the composite, failure will be greatly favored when a three point bending test is performed, since the maximum stress is attained only at the outer layer, and occurs just at the single point under the central support. Therefore, any local variation of the fiber volume fraction or the presence of a high void content or resin rich areas can have a significant effect on the result obtained. It is important to highlight here that the tubes from where the specimens were machined are 2 m long, and after the microstructural analysis performed, large variation of the fiber distribution is likely to be found along the tube’s length. This spatial variation of fiber and resin on a real commercial product was, indeed, observed for other composites, even those that have a much more homogeneous microstructure.

Figure 6 shows a tested specimen, where one can see that the failure begins at the surface of the composite, at the outermost layer at the tensile side of the test specimen, as it should be. One can also observe (Figure 6b) delamination across the specimen’s thickness. Delamination was predominant at the tensile side of the specimen, decreasing as the neutral axis was approached.

Table 1 shows the variation of the flexural mechanical behavior of the composites before and after aging in terms of the flexural modulus, \( E \), and also the initiation energy, \( U_i \), defined as the area under the stress-strain curve until the maximum stress. The increase of the flexural modulus for the aged specimens in relation to the value of the as-received composite corroborates the hypothesis that the large variation of the fiber volume fraction and of the fiber spatial distribution is the most influential parameter governing the mechanical behavior of this composite. However, is worth saying that moduli increase after aging is also reported in the literature. Mouzakis and coworkers attributed the relative stiffening effect observed to a post-curing effect of the polyester matrix due to the effect of aging at a humid environment of the polyester/glass fiber reinforced composite they analyzed.

In respect to the energy absorbed one can see that the energy needed to begin the macroscopic crack propagation \( (U_i) \) of the aged specimens decreased in respect to that of the as-received composite, indicating that aging is affecting the structural integrity of the composite and decreasing its toughness. There is not, however, a statistical difference between the results of the aged samples – using the t-Student test with a significance level of 0.05. This result confirms the hypothesis that, under the aging conditions used in this work, the effect of the aging media was similar, and that physical aging is expected to be playing the major role.

Table 1. Flexural modulus (E), and the energy consumed to initiate the macroscopic crack propagation (U_i).

|          | E, GPa    | \( U_i \times 10^6 \) J/m² |
|----------|-----------|-----------------------------|
| As-received | 2.89 ± 0.47 | 3.58 ± 0.42                |
| Oily water   | 4.58 ± 0.51 | 1.82 ± 1.30                |
| Seawater     | 5.13 ± 0.62 | 1.43 ± 1.11                |
| Biodiesel    | 5.41 ± 1.61 | 1.69 ± 1.15                |
both the uneven microstructural characteristics and the particular stress state imposed by the three-point bending test, where the tensile stress varies along the specimens' thickness and the maximum bending moment is attained only at a single cross section.

4. Conclusions

Aging of a commercial glass fiber reinforced-vinyl ester resin composite pipe used in onshore and offshore utilities in salt water, biodiesel and oily water showed:

- Stiffness reduction of the aged composites in relationship to the as-received one under the stress state imposed by the parallel-plate loading test.
- The statistically equal values of the load necessary to compress the aged composites between each other indicate that under the aging time used in this work, physical aging was the main phenomenon causing the reduction of stiffness.
- The same behavior was observed in respect to the decrease of the energy necessary to initiate macroscopic crack propagation at the flexural test. The results of the aged samples are not statistically different between each other, indicating a similar effect of the fluids upon the composite.
- The results of the flexural mechanical properties, i.e. the strength and modulus of the composites, were influenced by the inhomogeneous microstructure of the commercial composite analyzed and by the particular stress state imposed by a three point-bending test. Plasticization was identified as the phenomenon governing the variation of the flexural properties.
- The macroscopic failure of the composites submitted to the flexural test was initiated by tensile cracks and was followed by delamination across the thickness of the composites.

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