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Prolonged Real Marine Environment Exposure of Composite Marine Structures

Abstract

As fiber reinforced polymer (FRP) composites become ever more established construction materials in the marine industry sector the influence of the harsh environmental operational conditions and its consequence on failure prediction of such structures is an imperative. Coupons of epoxy/glass and polyester/glass with various fiber layout configurations have been submerged under the sea for prolonged periods (6 and 12 months) in order to assess the impact on mechanical behavior of the material exposed to real marine environment as opposed to the more commonly adopted artificially produced laboratory sea environment and accelerated testing. Changes in mass, marine microbiology growth, tensile strength and morphological structures were analyzed after submersion and compared with samples exposed to room environment. All coupons have shown mass increase due to seawater absorption and microorganism growth in the organic resins matrices. The dynamic and level of change in tensile strength proved to be dependent on the fiber layout configuration. Optical and scanning electron microscopical investigation performed showed significant matrix morphological changes primarily due to salt crystal formation and the impact of sea microorganisms embedding in the resin. The collected experimental data will be used to develop a more realistic environmental input parameters for structural modeling of marine structures.

Keywords: FRP composites, marine environment, marine structures durability

1. Introduction

Fiber reinforced polymer (FRP) composites are used in the engineering constructions, whether as an exclusive option for construction [1] or as a combination with traditional materials, such as steel concrete [2] or rock [3]. In the last couple of decades, significant effort was made to combine the experimental and scientific knowledge obtained so far in these field of research to enable prediction models that can be safely used to achieve sustainable and safe design of engineering structures [4–7].

Mechanical properties of composite materials can be customized accordingly to specific applications demands by defining layup sequences, number of plies, and fiber orientation in the load direction [8,9], which makes them appealing for design of marine structures with complex shapes. As the application field for marine composites widens, the request for mechanical and environmental resilience rises. Adequate knowledge of limit stress states, durability and life span, failure modes, fracture toughness, fire resistance, and environment influence parameters is crucial for an efficient and sustainable design process for structures in this demanding industry sector [10,11].

The micromechanical aspect of composite materials design is often considered too complex and time-consuming for marine structural designers to deal with. The scientific research in this field of study should be aimed at simplifying the complex micromechanical level analysis and transform it into simple-to-use and time-saving engineering tools. The current practice for obtaining data for composites failure is based on experiments. As experiments can be relatively expensive and microscale data are usually unavailable to shipbuilders, they often turn to data and models prescribed by rules and procedures, thus leading to empirical based design process of marine structures. All of this yields rules that are very conservative in formulating design requests, which in turn hinders optimal design of marine structures concerning failure mechanisms.

One of the most important parameters influencing the mechanical properties of composite materials in marine applications is the absorption of seawater [12]. Previous research on this matter is based on immersing test samples, called coupons, in laboratory conditions using accelerated procedures [13] to simulate 20+ years of expected lifespan of typical marine structures [14,15]. The ageing of composites is usually carried out in climatic chambers in laboratory conditions to reduce the time of the test [16–19].

In addition, water absorption tests are often done with tap water, demineralized water, or artificial seawater [20,21]. This approach yields a lack of long-term data pertaining to degradation of mechanical properties exposed to the marine environment. Furthermore, the effects of the moving seawater (waves, sea level variations due to tides) and radically variant environmental effects that a typical marine vessel or structure are exposed to during their life cycle [22] are not considered in accelerated ageing laboratory methods.

The absorption process of moisture and water of a composite exhibits complex behavior and dependence on various factors [23], such as resin type and curing characteristics, void content, resin/fiber volume fractions [24], the manufacturing technique, etc., [25–27].

All this served as motivation to concentrate the research presented here on the influence of absorbed water on marine composites in real-life conditions, not laboratory, by submerging the coupons in the sea for prolonged periods of 6 and 12 months.

The dominant choice of composite materials in the civil sector of the marine vessels industries is glass fiber reinforced plastics (GRP), both for commercial and leisure vessels hulls [28], resulting in a more cost-effective product. Classification societies can be somewhat restrictive when it comes to allowing composites as structural material. The choice of fibers is restricted to E-glass or carbon fibers, whilst resins are limited to epoxy, polyester, or vinyl-ester.

2. Materials and methods

2.1. Materials

The ISO 527 standard series prescribe the testing procedures for the determination of tensile properties of fiber-reinforced plastic composites. In this research, standardized tensile testing coupons were produced as various combinations of continuous glass fibers layout with epoxy (Sicomin SR 8200 and SD 720 series hardener) and polyester resin (Reichhold POLYLITE 507-574) used as matrices. The resins mechanical properties are shown in Table 1, as provided by the manufacturers of each component.

Table 1. Resin systems properties.

Property	**Epoxy**	**Polyester**
Tensile strength [MPa]	47	42
Elasticity modulus [MPa]	3,240	2,700
Glass transition temperature [°C]	50	55

UD stitched E-glass fiber matt fabric (Sicomin UDV600), with 594 g/m^2 ply specific area weight, was used. Four different layup configurations were chosen for both matrix/fiber combinations to evaluate mechanical properties deterioration in the marine environment. The layup schematics are unidirectional with longitudinal fiber orientation (UD0) and two multidirectional (0/90 and 0/45/90 symmetrical), all according to standard notation for composite layup [29].

Rectangular plates (300×450 mm) with the mentioned different layup schemes were produced for each of the material combinations using 8 plies of the UD fabric per plate. The epoxy/glass plates were produced by vacuum assisted infusion process, resulting in 3 + 0.2 mm thick plates. The infusion process proved problematic for the polyester resin as it was resulting in dry fibers on the tool surfaces, so the polyester/glass plates were finally produced by hand layup process, resulting in 5±0.5 mm thick plates.

2.2. Coupons and exposure to marine environment

Coupons measuring 250 mm in length and 25 mm in width [30] were then cut out of the plates on a waterjet cutting machine (OMAX Maxiem series). The cutting pressure was between 1,400 and 3,400 bar, with the average cutting speed of 1,187 mm/min.

Waterjet cutting takes advantage of the brittleness of composite materials as localized damage points on the locations of first contact of the cutting high-pressure waterjet with the material can be introduced precisely. The intent here is to introduce a point on the coupon in order to simulate real damage on marine structures. This damage point theoretically represents a facilitated entry point of seawater in a real marine structure on eventual damage spots that would occur during exploitation. Composite marine vessels and structures are usually protected by a final layer of gel coat that protects them from water penetration. When this protective layer is damaged during application, a more significant sea water intake rate in the structure material is expected.

All the coupons were weighed dry and measured with a ±0.1 mm accuracy. The coupons were divided in groups of 5 pieces according fiber-matrix combinations (epoxy/glass, polyester/glass) and subdivided into 3 groups according the time of exposure to real marine environment (dry, 6 months, 12 months).The “dry” groups were control ones, while the other two subgroups were exposed to real-life sea environment, i.e., submerged into the sea on a depth of 10 m, at northern Adriatic in front of the city of Rijeka in Croatia for a duration of 6 and 12 months, respectively. The sea temperature at the location of experiment varies between 10–14 °C annually, salinity changes between 37.8–38.3 PPT, while the pH value is between 8.22–8.29 [31]. The coupons were mounted on special stainless-steel frames (AISI 316L).

2.3. Testing procedures

Each coupon was weighed with the same digital scale (200 g measuring range and 0.01 g resolution) as dry and after the submerging time-period to determine the mass gain of the absorbed seawater. Wet coupons were taken out of the sea, cleaned from sea organisms accumulated during submersion with a soft brush, still submerged in seawater. Special care was taken not to damage the coupon. After cleaning, the coupons were left to drain, dried superficially with a cloth, and weighed all in a period under one minute to assure maximal possible measuring of the absorbed water amount.

The coupon ends were reinforced using end tabs before the tensile test to minimize the influence of the grips pressure on the test results [32]. The size of the tabs was chosen based on ISO 527-4 recommendations.

Uniaxial tensile tests used for the determination of the material properties were performed on a Zwick 400 kN universal testing machine. A macro extensometer was used to measure the specimens’ elongation. The displacement rate of the testing machine crosshead during testing was 2 mm/min.

Tensile testing was conducted in accordance with ISO 527 series standards recommendations.

Microscopical investigation was performed on all fractured coupons. Surface and cross-sectional images were taken of all coupons, with special attention given to the grips areas and locations with observed damage after the tensile test

Optical microscopy systems (Olympus SZX10 stereo optical microscope and Olympus BX51 SM optical microscope analysis system, both produced by Olympus corporation, Japan) and scanning electron microscope (SEM, FEI QUANTA 250 FEG, FEI Company, USA) with the OXFORD INSTRUMENTS PENTAFET, UK, Energy Dispersive Spectroscopy (EDS) analysis module were used to investigate the state of the coupon's surfaces exposed to real sea environment and to identify changes in surface morphology caused by the exposure to seawater. Photographs were taken before and after the tensile tests.

3. Results

The results of the experimental investigation of epoxy/glass and polyester/glass coupons exposed to marine environment are presented in the form of diagrams, images, and tables. Experimental testing results shown here are comprised of coupon weight change (seawater absorption, algae growth) analysis, tensile strength determination, and surface morphology changes observations.

3.1. Mass gain - algae and marine organisms' growth and water intake

The average aggregate mass gain due to the coupled algae/marine organisms' growth and water absorption and only water absorption for the two matrix resins is given in Figure 1, where the denotations E and PE stand for epoxy and polyester resin respectively, while the numbers 6 and 12 indicate the period of submersion in months.

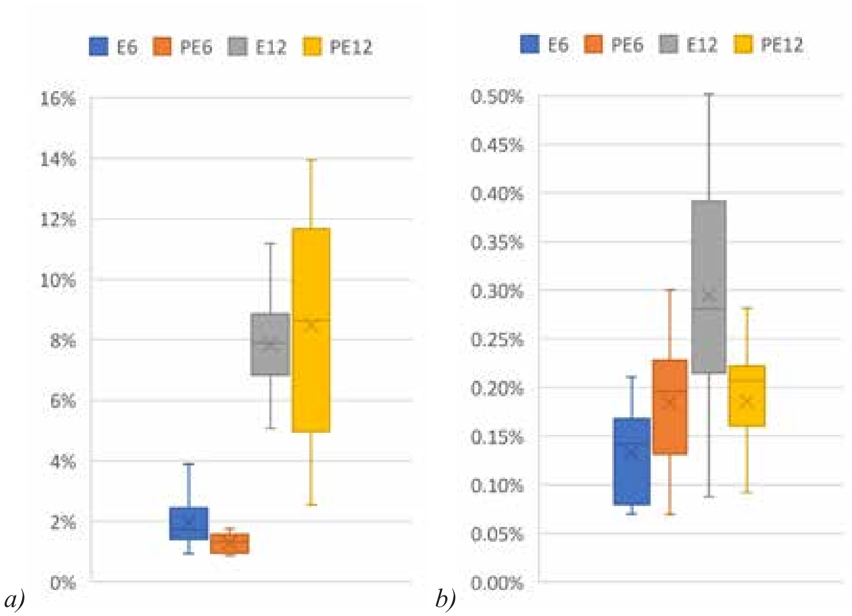

Figure 1: Mass gain due (a) bio growth and water absorption; (b) only water absorption.

3.2. Tensile test results

Engineering stress-strain diagrams were obtained from performed uniaxial tensile strength on dry coupons and wet coupons that were submerged in the sea for 6 and 12 months. The change in tensile strength due to the prolonged submersion in seawater is shown in Figures 2 and 3.

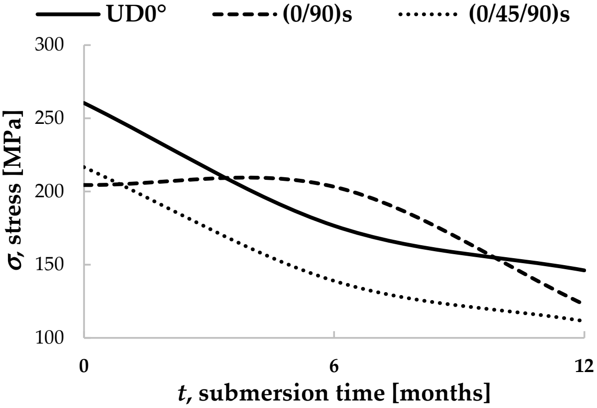

Figure 2: Average tensile strength degradation of epoxy resin coupons

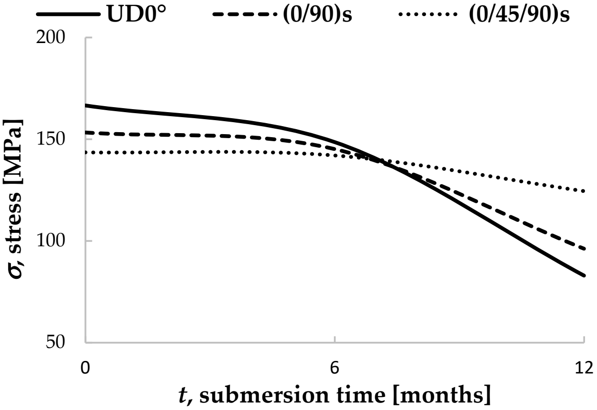

Figure 3: Average tensile strength degradation of polyester resin coupons.

3.3 Microscopical investigation

Surface and cross-sectional images obtained by optical microscopy are not presented here but are available in a publicly accessible repository to save paper space and keep the readers focus on the more detailed and more illustrative SEM results.

The images obtained by SEM investigation are presented in Figures 4 to 6. Only some representative images were chosen as a portrayal of the performed research to limit the length of the paper, whilst the complete set of all obtained images is posted on an online repository as supplementary material to this article.

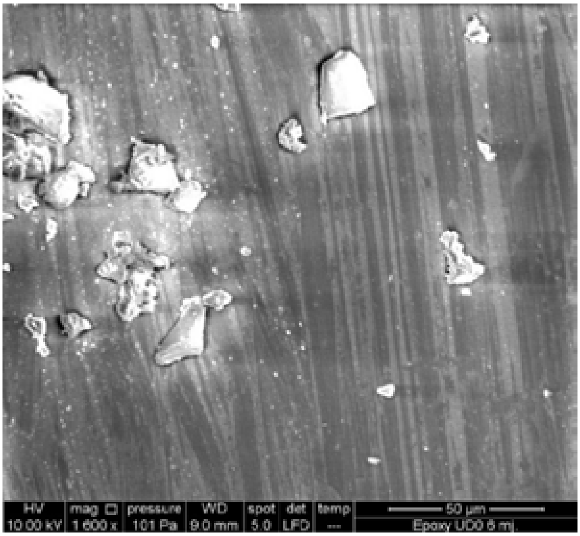

Figure 4: Epoxy coupons, salt crystals

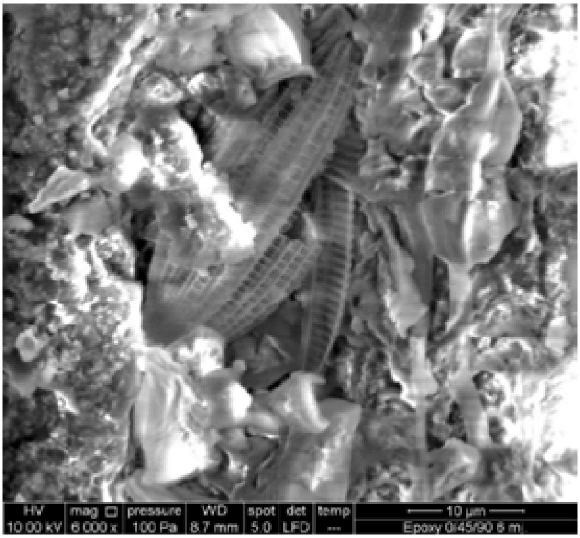

Figure 5: Epoxy coupons embeded microbes.

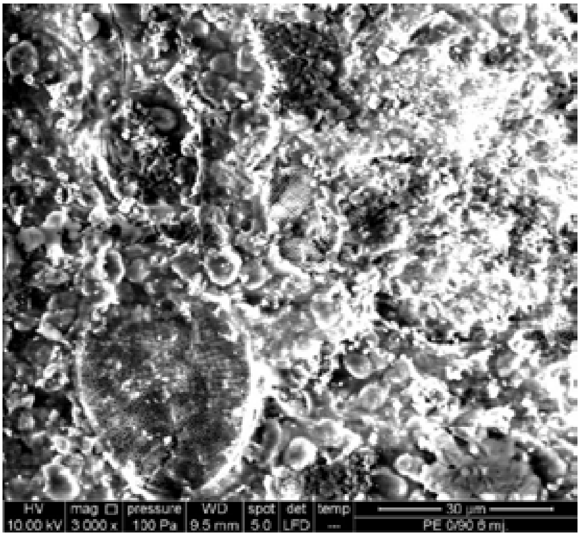

Figure 6: Polyester coupons - embeded microbes

4. Conclusions

The real sea environment has considerable effects on composite materials in the form of reduced mechanical strength for the tested coupons submerged in the sea. The submerged UD0, 0/90, and 0/45/90 epoxy/glass coupons exhibited tensile strength reduction of 32%, 14%, and 36% after 6 months of submersion (with the exception of one inadequately manufactured 0/90 coupon), whilst 44%, 40%, and 49% after 12 months of submersion, respectively. The polyester/glass UD0, 0/90, and 0/45/90 coupons have lost 11%, 5%, and 1% after 6 months of submersion, and 50%, 37%, and 13% after 12 months in the sea. The 0/45/90 layout configuration for the polyester/glass combination showed the greatest resilience to the marine environment. The research indicated that further study is needed here because the polyester coupons were made by hand-layup process, which can significantly affect mechanical characteristics of the composite. This issue will be examined more in detail during future research.

The growth of microorganisms embedded in the resin and invertebrate (Nematoda) organism attached to the surface of the coupons effectively created voids in the matrix resin and produced a direct effect on mechanical properties. The mechanism of this effects needs deeper analysis and research. The findings of the research indicate the importance of biofouling in environmental degradation of mechanical properties of composite materials in the marine environment. The main goal of this research remains the development of a reliable predictive numerical model of the mechanical behavior of composite materials exposed to real sea environment, which would represent a basic tool to assess the durability of composite marine structures during their exploitation. Research findings can be useful in design process of composite marine structures or in use of composite for repair of already damaged structures [33,34]. In order to fully understand the effect of exposure effect on the composites, additional coupons are already submerged in the sea and data should be presented in the continuation of this paper. This additional set of data will help in building a predictive numerical model that could successfully replace the time and resource consuming experiments which is a next step of this research However, the stochastic nature of the environmental loading must be incorporated in that model [35]. For that reason, placing coupons in different types of marine environment (regarding the temperature, salinity, pH value, etc.) would bring even better accuracy of the numerical model.

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