

Seawater absorption properties and equilibrium for carbon fiber reinforced epoxy autonomous underwater vehicle hull at 1000m depth

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Abstract—The hull of an Autonomous Underwater Vehicle (AUV) is one of the main factors that determine its overall compressibility and drag. The hull as well, acting as a pressure vessel, is the most essential part that will allow the vehicle to accomplish deep diving. In order to minimize the total weight and volume of the vehicle, many modern vehicles benefit from composite materials rather than conventional materials. Moisture absorption, known as the hygral effect, has a significant impact on the mechanical properties of the material. Not to mention it also has an effect on the buoyancy of the vehicle, since the overall weight changes. This paper characterizes the seawater absorption and diffusivity of Carbon Fiber Reinforced Epoxy (CFRE) pressure hull samples in ambient conditions at sea level and at 1000m depth. The tests were performed using seawater taken from Oslo fjord in Norway and using a pressure vessel. Twelve specimens, all manufactured from CFRE using filament winding technique, were tested in both conditions, and the moisture absorption curve is compared. Periodic gravimetric measurements were taken, where the equilibrium state was reached after approximately 65 days at sea level and after 35 days at 1000m depth. The results showed that moisture diffusivity for composites used in underwater applications should be defined by both pressure and temperature since it changes with respect to submersion depth.

Keywords—Carbon fiber reinforced epoxy; Hygral effect; Time-dependent moisture diffusion; Seawater aging; Environmental degradation.

I. INTRODUCTION

The hull of an Autonomous Underwater Vehicle (AUV) is one of the main factors that determine the overall compressibility and drag. Since these characteristics have a great impact on the endurance and the cost of the vehicle, the detailed design of the hull is of paramount importance to the good performance of the vehicle. The hull, acting as a pressure vessel, is the most essential part that will allow the vehicle to operate at high depth. In order to minimize the total weight and volume of the AUV, its hull should be as light as possible. Fiber-reinforced composites offer a greater strength-to-weight ratio in comparison with conventional materials, such as metals. CFRE (Carbon Fiber-Reinforced Epoxy) in particular, is commonly used in many applications, including marine ones, because of its outstanding performance throughout its design life.

A critical aspect of the performance of composites is their moisture content and their ability to absorb humidity. Hygral effect has a substantial impact, particularly in the long-term use of the component, on the chemical and physical

characteristics of the composite. Water absorbed by the epoxy matrix of the composite can be categorized into two types based on their bonding with the matrix [1]. The first type forms a single hydrogen bond with the resin; hence it can be removed easily by increasing the temperature of the material, unlike the second type which forms multiple hydrogen bonds with the matrix, which requires even higher temperatures to be removed from the material [2]. The first type, however, has a higher effect on the material due to the fact that it diffuses more easily in the resin, breaking the initial Van der Waal bonds resulting in swelling of the material [2]. It contributes highly to the plasticization of the resin, unlike the second type which does not contribute much to the plasticization rather than creating secondary crosslinking between chain segments of the resin, resulting in what is known as pseudo crosslinking, as shown in Figure 1 [2]. This type is harder to form in the material since it requires a long exposure time as well as high temperatures for the inter-chemical bonds to form. Although a hull of a submersible vehicle is exposed to water for a very long time, the temperature gradient of the ambient environment is not high enough to form the second type.

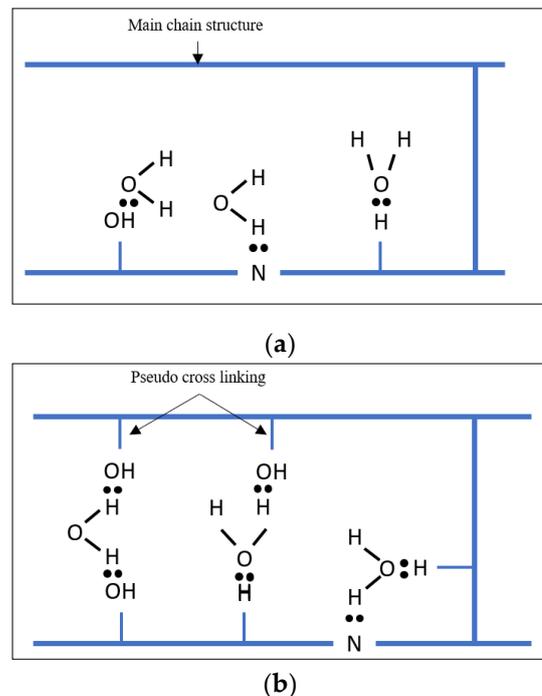


Fig. 1. Water bonding with the matrix of the composite. (a) Hydrogen primary bonding; (b) Pseudo secondary bonding

One important impact of the moisture content is that it decreases the glass transition temperature of the matrix (T_g) which reduces the bonding between the reinforcement and the matrix affecting the mechanical behavior of the composites and their durability. [3] found that the modulus of epoxy resin decreased from 2GPa to only 0.02GPa as its T_g decreased from 215°C to 127°C.

The hygral effect, also, causes the composite material to swell, resulting in a dimensional change and dilatational strain which induce residual stresses in the laminate [1]. If not counted for in the design, these residual stresses along with the thermal residual stresses resulting from the curing process of the material can cause the material to fail prematurely. For example, the inter-laminar shear strength of a carbon fiber/epoxy was reduced by 10% due to a moisture content of 1.2% according to [4] and reduced by 25% due to the moisture content of 1.5% according to [5]. Reference [6] concluded that the fracture toughness of stitched glass fibers reinforced epoxy was significantly affected after being immersed in seawater for 24 days. It was reduced to 70% of its value after 24 days, and to 45% of its value after 35 days. The samples also gained 5.2% and 7.9% extra weight after 24 and 35 days of immersion.

As for CFRP, much of the previous literature has worked on obtaining the mechanical properties of the material after immersion, whether in seawater or freshwater, at different temperatures. Reference [7] studied the effect of hygrothermal on the failure mechanism of the material after bending long and short beam samples. They also established a Finite Element Analysis (FEA) to model the diffusion of the moisture in the material. the study showed that the longitudinal diffusivity has a higher value than the through-the-surface diffusivity. It represented 60% of the total diffusion. Another important finding was that the hygral stresses occur even at the beginning of the immersion, and they occur mainly at the edges. Reference [8] studied also the effect of hygrothermal aging, but on the static properties of the material. The tests were performed at room temperature and at high temperature at 70°C. The hygrothermal tested specimens showed higher moisture absorption than the hygral tested specimens. The compressive strength of the material showed a major deterioration higher than the tensile strength did. Reference [9] studied the moisture diffusion in CFRP with different sodium chloride concentrations and at different temperatures. They concluded that the concentration of the salt has a negligible effect on the diffusivity, unlike the temperature. The study showed that the glass transition temperature of the matrix T_g has dropped to 75% of its original value after saturation.

Other literature worked on providing analytical formulae that predict the hygrothermal effects on the material properties. Reference [10] proposed an equation for predicting these effects on the mechanical properties of the matrix. These empirical formulae, equation (1-2), can be used only with epoxy composites, but still need further experimental validation to be used on other types of matrices.

$$\frac{P_{wT}}{P_0} = \sqrt{\frac{(T_{gw}-T)}{(T_{gd}-T_0)}} \quad (1)$$

$$T_{gw} = (0.005M^2 - 0.1M + 1)T_{gd} \quad (M \leq 10\%) \quad (2)$$

Where P_{wT} is the property of the matrix at a given temperature T and a given moisture content M , T_{gw} is the new glass transition temperature at the given moisture content M , P_0 is the reference matrix property at the reference temperature T_0 , and T_{gd} is the glass transition temperature in the dry state.

In practice, the material is rarely used in a humidity-free environment. Hence, the swelling of the material is negligible, as long as it is below a certain threshold. The permissible percentage of moisture concentration for different epoxy resins was found to be within 0.3-0.7% [11].

The longitudinal ϵ_{mL} and transverse dilation strain ϵ_{mT} in a unidirectional laminate, according to [4], is:

$$\epsilon_{mL} = 0 \quad (3)$$

$$\epsilon_{mT} = [(1 + \nu_m)(\beta_m \times \rho_m / \rho_c)] \times [M - (Vv \times \rho_w / \rho_c)] \quad (4)$$

$$\beta_m = \frac{\rho_m}{3\rho_w} \quad (5)$$

Where ρ_m is the density of the matrix, ρ_c is the density of composite, ρ_w is the density of the water, β_m swelling coefficient, ν_m Poisson's ratio of the matrix, M is the moisture content, and Vv is the micro-voids volume fraction. After calculating these parameters, it is possible to know the residual stresses in the material and count for them in the design process of the material.

II. METHODOLOGY

This test mainly focuses on the measurement of the moisture content in the "across layers" direction, through the thickness of the lamina, over time. For this reason, the edges of the samples were covered with metal foils bonded to the edge of each sample, as insurance that any absorption of moisture through the edges of the samples is excluded. The material tested, CFRE, has constant absorption properties through the thickness. It is treated as a single-phase material, with a single-phase Fickian diffusion model [4]. A Fickian diffusion is a model that describes the absorption and desorption of substances that will flow through the material, in this case, seawater, during the time [12]. In other words, it describes the change of substance concentration with respect to time, following the second law of Fick in one dimension described in equation (6).

$$\frac{\partial c}{\partial t} = D_z \frac{\partial^2 c}{\partial z^2} \quad (6)$$

Where c is the fluid concentration per unit volume, t is time, D_z is the diffusivity constant in the Z -direction (through the thickness), and z is the position. According to [13], in order to classify the diffusivity of a material as a Fickian, there are three conditions to satisfy. The first one is that the absorption and desorption rates must be mainly linear up to 60% of saturation. Secondly, in the non-linear region, the absorption and desorption rate curves must be concaved to the X -axis. Finally, for the same environmental testing, the absorption curve should be identical for specimens with different thicknesses. A fiber-reinforced polymer matrix below its T_g satisfies these conditions [14].

The diffusivity constant D_z in composites is anisotropic property, hence the sub notation z , and is influenced by temperature [14]. However, treating the material as Fickian material means that this property is not related to and independent of the exposure level [14].

The absorption equilibrium, which is the state where there is no further change in the sample weight, can be either definite or effective. The effective value permits a minor change in the average content with respect to time. The effective value is reached when the mass change is less than 0.02% between two different readings across the reference time [14]. This property, unlike the diffusivity constant, is independent of temperature.

The test is a gravimetric one that keeps track of the moisture content in the material by measuring the total mass change of the specimens over time. The test follows the recommendations of ASTM D5229 standard [14]. The term “moisture” is not limited to vapor or condensate of a liquid but also includes water, seawater, fuel, or any other liquid that the specimen is immersed in. The objective of the tests is to identify the diffusivity of the material, and to plot its moisture absorption curve for seawater at room temperature at sea level and at 1000m depth.

A. Specimen sizing

The specimen should have a weight greater than 5g, and the thickness of the specimen should be within $\pm 5\%$ of the surface of the material. Reference [14] recommended using a rectangular plate with minimum dimensions of 100x100mm. This is hard to produce using the “filament winding” technique. It can be produced using filament material by the “hot press” technique. However, doing so will affect the results, because filament winding technique is known to produce more micro-voids in the composite material than “hot press”. The existence of voids increases the susceptibility of the material to absorb moisture [15]. Hence the results will not be realistic. Instead, smaller tubes were cut that were filament wound and had metal foil bonded firmly to their side edges to avoid in-plane diffusion, as explained earlier. The cutting of the material is done using diamond-tipped tooling, to prevent delamination of the material, and uneven, or rough edges. The samples were cut from two filament-wound tubes that had ply angles of $[12_3 / 85_2]_s$. This particular sequence was used because a similar stacking sequence will be used in the design of the vehicle’s hull. The composite used in this work consists of Torray® T-700 Standard Modulus Carbon Fibers, and the matrix used is epoxy Hexion® EPIKOTE 828 as a resin mixed with EPIKURE 866 curing agent and EPIKURE 101 catalyst with the ratio of 100:80:1.5 by weight, respectively. The wounded tube was cured at 90°C for 1.5 hours, then at 150°C for 2.5 hours. A thermo-shrinkable folio tape that is designed to be used with epoxy resins, is wrapped in direct contact with the external lamina and compresses the tube over the mandrel when it is put in the oven for curing.

Two different thicknesses were tested, one has a thickness of 2.25mm, and the other has 3.25mm. The thin samples are required for calculating the moisture diffusivity for the material, which is going to be explained in detail later. Six samples were tested in each thickness. The bigger length and width of the sample, the higher the accuracy of the tests. However, low-weight samples can be used, at the expense of increasing the accuracy of the used scale. The minimum sample mass can be calculated using equation (7). The accuracy criterion should be 0.05% or lower [14].

$$\text{Min. specimen mass} = \frac{10 \times \text{balance accuracy}}{\text{accuracy criterion}} \quad (7)$$

B. Pre-conditioning of samples

The samples are marked, and their weight is measured and recorded as the “as-received” mass. The specimens are put in a temperature-controlled drying oven at a temperature of 115°C for 24 hours and then inserted in a desiccator with silica gel to cool down. The specimens are then weighed to the nearest 0.01g, and their weight is recorded as the “oven dry” mass. The specimens are then stored back in the desiccator for the tests.

Care should be taken not to overheat the samples because any excessive heat might cause mass loss, and thermal stresses, which in return will cause micro-cracks or a combination of both. It is also important not to increase the temperature high enough to reach the glass temperature (T_g) of the matrix. A temperature ranging between 110-120°C should be enough to help the material desorb any moisture content in it, and at the same time not damage the test samples.

C. Testing procedures

The default conditioning temperature for water immersion according to [14] is 70°C. However, this temperature is not of interest in this specific application, since the temperature should be ambient. Testing at 70°C will produce excess hygrothermal strain and unrealistic results since the moisture diffusion is thermo-dependent as explained earlier. Two sets of tests were performed on the same samples. One set is measured in ambient condition at room temperature, which represents the submersion at sea level, and the other in a pressure testing vessel, shown in Figure 2, at a pressure of 100bar which represents the submersion at 1000m.



Fig. 2. Pressure testing rig with digital pressure gauge, that is used to perform high pressure tests.

As mentioned earlier, to provide the most accurate results, actual seawater was used in the test procedures. The salinity of the seawater, taken from Oslo Fjord, was measured before the start of the tests and using a conductivity sensor and the conductivity was found to be 32213.8 $\mu\text{S}/\text{cm}$ ($\pm 2\%$ accuracy).

The samples are then immersed until the effective value of the equilibrium is reached (less than 0.02% of mass change). Recordings of mass and thickness are taken periodically. At the beginning of the tests, recordings were taken every 12h, then the frequency of the readings decrease to every 48-72h, and then to once a week. The samples are removed from the bath, wiped carefully with lint-free absorbent cloths to remove any moisture or droplets, their weight is measured to the nearest 0.01g, and then re-immersed within 3 minutes from the time they were removed from it.

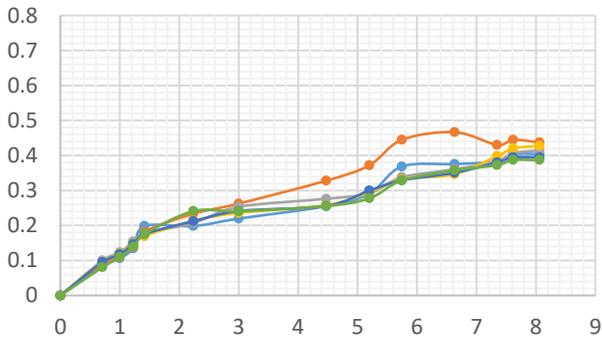
The diffusivity D_z is then defined after the effective equilibrium is reached for the thin samples and after 70% of the effective equilibrium is reached for the thick values. It can be defined using equation (8).

$$D_z = \pi \left(\frac{h}{4M_m} \right)^2 \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2 \quad (8)$$

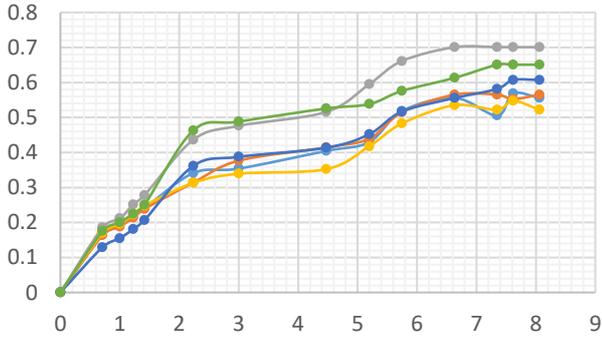
Where h is the thickness of the specimen, M_i and t_i terms represent the slope of the linear part of the graph, and finally, M_m is the last value of mass change in the thin specimens. One of the study's aims was to find if the D_z is pressure dependent. Hence it is calculated two times, once at 0bar and another at 100bar.

III. RESULTS AND DISCUSSION

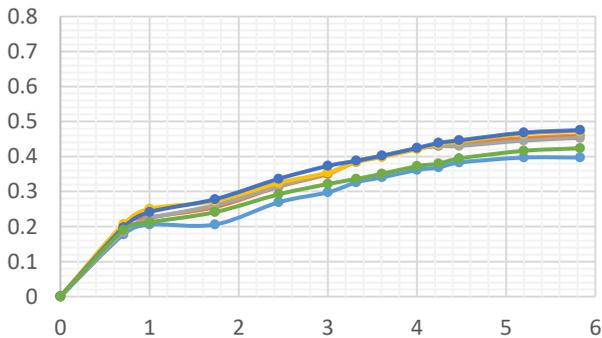
The thick samples tested at atmospheric conditions reached effective equilibrium after 44 days, while the thin ones reached it after 58 days. The samples were tested for a total of 65 days. On the other hand, the pressurized thick samples reached the effective equilibrium after only 16 days, and the thin ones did after 18 days. The results of the 12 samples are shown in Figure 3.



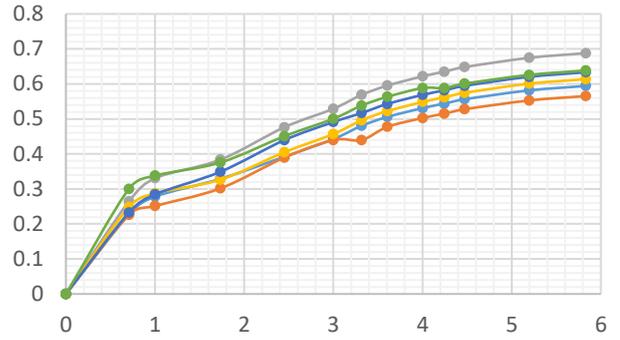
(a)



(b)



(c)



(d)

Fig. 3. Samples moisture absorption content, where the X-axis is the square root of number days of immersion and the Y-axis is the percentage of moisture content to dry sample weight; (a) Thick samples at sea level, (b) Thin samples at sea level, (c) Thick samples at 1000m depth, and (d) Thin samples at 1000m depth.

The moisture diffusivity was then calculated from the data obtained from the tests. The diffusivity for seawater at sea level was $D_z = 7.175 \times 10^{-7} \text{ mm}^2/\text{sec}$, while the diffusivity of seawater at the pressure of 100bar was $D_z = 8.415 \times 10^{-7} \text{ mm}^2/\text{sec}$. An average of the moisture content of the samples is taken at each measuring point and the curve in Figure 4 is drawn.

The results have shown that the pressure directly affects the diffusivity of the fluid through the material and that the term D_z is not only thermo-dependent but also pressure-dependent. Once the D_z is calculated, an anticipation of the moisture content can be made for the material depending on the surface area subject to seawater and the immersion time. However, if the edge of the material is subject to the water as well, the graph shown in Figure 5 can be used to estimate D_1 [14]. The moisture concentration at any instance can be calculated using equation (6).

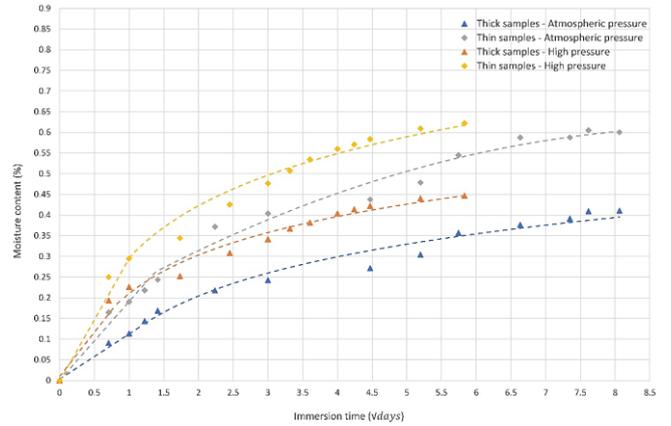


Fig. 4. Samples moisture absorption content, where the X-axis is the square root of number days of immersion and the Y-axis is the percentage of moisture content to dry sample weight; (a) Thick samples at sea level, (b) Thin samples at sea level, (c) Thick samples at 1000m depth, and (d) Thin samples at 1000m depth.

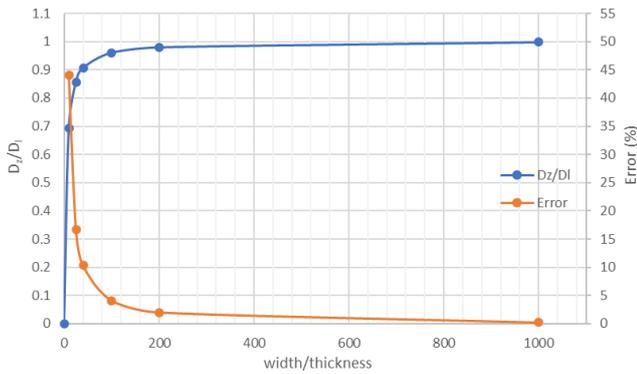


Fig. 5. Ratio of “through-the-surface” to “through-the-thickness” diffusivities based on the dimensions of the surface subject to the moisture.

IV. CONCLUSIONS

Moisture absorption is one of the drawbacks of composites. It has a great impact on the mechanical properties of the material. A realistic design considers the existence of moisture in the composite because the material is seldom used in a moisture-free environment.

This study aimed at measuring the moisture diffusivity and moisture content of carbon fiber reinforced epoxy to seawater, as well as studying the effect of pressure on the diffusivity of the material, to examine whether the diffusivity is dependent on the depth of the submerging fluid. The results are going to be used in the design of the hull of a deep underwater autonomous vehicle. The results are important to calculate the hygral stresses acting on the hull, as well calculating the amount of change in the vehicle’s buoyancy due to the absorption.

Twelve filament wound specimens were tested, at room temperature, in atmospheric pressure, representing immersion at sea level, and 100bar, representing immersion at 1000m. The results showed that the pressure has a direct effect on the absorption of the material, same as the thermal effect and that the diffusivity coefficient for composites used in underwater applications should not only be defined by temperature, but also pressure. The diffusivity of seawater at sea level is $D_z = 62 \times 10^{-3} \text{ mm}^2/\text{day}$, and the one at 1000m depth is $D_z = 72.7 \times 10^{-3} \text{ mm}^2/\text{day}$.

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