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CURING AND SEAWATER AGING EFFECTS ON MECHANICAL, THERMAL, AND PHYSICAL PROPERTIES OF GLASS/EPOXY FILAMENT WOUND COMPOSITE CYLINDERS

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Abstract

Polymer composites in marine structures that operate under seawater environment may be seriously affected, reducing durability estimates. This work aims at evaluating the effect of seawater exposure at 80 °C for 7 to 28 days on filament-wound glass fiber/epoxy composite cylinders partially cured by passing saturated steam through them just after winding seeking a faster curing route. The winding angle is varied (±55, ±65 and ±75) and some of the cylinders are later post-cured for comparison. The unaged partially cured specimens do not reach complete curing, with a glass transition temperature (T_g) of 132 °C, below the T_g for the other samples (154-159 °C). Fully cured cylinders present mechanical properties slightly higher than partially cured ones. Moreover, aging in seawater for 7 days enhances the cross-linking degree of epoxy, with a positive effect on both hoop tensile strength and stiffness. Aging is, however, not critical for the radial compressive properties.

Keywords: *Composite cylinder; GFRP composites; Aging; Filament winding.*

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1. Introduction

Fiber-reinforced polymer composites are largely used in aerospace, aeronautic, energy, automotive and marine sectors [1], [2]. However, glass fiber-reinforced polymer (GFRP) based on epoxy may be attacked when in prolonged contact with water [3], leading to matrix plasticization and a decrease in glass transition temperature (T_g), which may affect both strength and stiffness [4], [5].

Many reports in the literature focus on hygrothermal conditioning of flat composite laminates, but only a few on curved/cylindrical laminates. Merah et al. [6] studied GFRP cylinders and concluded that their stiffness was not significantly affected after 300 h of seawater conditioning, whereas hoop tensile strength was reduced. Deniz et al. [7] evaluated filament wound $[\pm 55]_3$ composite cylinders under low velocity impact and axial compression and a reduction in performance was noticed. Azevedo et al. [8] investigated the effect of the mosaic winding pattern on the response of filament wound CFRP cylinders aged in seawater and distilled water and concluded that the cylinders were slightly and similarly impacted by both conditionings. Deniz and Karakuzu [7] investigated GFRP cylinders under seawater and concluded that moisture uptake, salt concentration, cylinder diameter and residual stresses from the manufacturing process affected their impact characteristics.

In an industrial environment, the curing process is time-consuming and energy-consuming, increasing the cost of the product. Therefore, strategies to decrease the curing time for composite systems are of great interest. Considering that GFRP filament wound cylindrical composites are currently largely used in pipelines given their potential to reduce installation costs and improve reliability for gas and liquid transportation, alternatives to decrease production costs are of great industrial interest [9]. The decrease in production costs is a continuous industrial target and the behavior of these structures under seawater is yet to be fully understood, and both motivated the current investigation.

Thus, this work proposes a practical methodology to promote curing in filament wound cylinders and evaluates its effect on the mechanical, thermal and physical properties of the composites, along with the effect of seawater conditioning (0 to 28 days). The role of the winding angle ($[\pm 55]_3$, $[\pm 65]_3$ or $[\pm 75]_3$) on the properties after conditioning is also investigated since fiber orientation is a key design parameter.

2. Experimental details

2.1. Manufacturing and aging

The composite cylinders were produced with continuous rovings of E-glass fiber (type ECR, 1100 tex) from Owens Corning and a DGEBA epoxy resin (bisphenol A diglycidyl ester) system from Aralsul with an aromatic amine hardener. The cylinders were manufactured using a two-axis industrial filament winding machine from CNC Techniques with Siemens 804D CNC command. Winding of the cylinders was programmed through CadFil software (from Crescent Consultants Ltd, Derby, England). The fibers were placed side-by-side, and all cylinders had the same winding pattern, 1/1. Each layer is composed of a single angle-ply layer and three lay-up sequences are studied, $[\pm 55]_3$, $[\pm 65]_3$ and $[\pm 75]_3$. All cylinders were manufactured with inner diameter of 59 mm and average thickness of 1 mm. The filaments passed through a bath of epoxy resin+ hardener and wound onto a mandrel, which is heated by continuously passing saturated steam inside it.

In a way to speed up the overall production of the cylinders a key factor in the industry, a non-oven curing system was adopted. For that, saturated steam at 140 °C passed through the steel-based mandrel for 13 min after winding. The system was subsequently cooled down to room temperature (25 °C) by passing water through the mandrel for ≈5 min. The cylinder produced in such a way is herein referred to as "partial curing" (PC). Some cylinders underwent a post-curing stage by placing the PC cylinders in an oven for 3 h at 80 °C followed by 4 h at 160 °C, as per the supplier recommendation, being referred to as "complete curing" (CC).

The produced PC and CC cylinders were aged in simulated seawater prepared according to ASTM D1141 standard. For that, the samples were immersed in seawater bath and placed in an oven at 80 °C for 28 days (672 h).

2.2 Characterization

Water uptake of the cylinders was monitored by measuring the weight of three samples from each curing strategy (PC and CC), at 0, 7, 14, and 28 days. The nomenclature adopted for the samples is: $[\pm\alpha]\_PC/CC\_i$, where $[\pm\alpha]$ is the winding angle, PC or CC is the curing strategy, and i is the aging period. A differential scanning calorimeter (DSC) model DSC 60 was used to analyze the glass transition temperature (T_g) of the samples. Neat resin was analyzed along with the samples after 0, 7, 14 or 28 days of aging. Each sample, ≈15 mg, was heated at 20 °C/min up to 210 °C, using constant nitrogen flowrate of 50 ml/min.

Fiber volume fraction (V_f) of the samples was performed through burn-off tests using a furnace with oxidizing atmosphere at 600 °C for 4 h; The final winding angle of the cylinders was verified by cutting-off samples perpendicularly to their longitudinal axis and analyzing the fiber cross-sections in a Carl Zeiss optical microscope. All results related to physical and thermal evaluation is shown as supplementary material.

Apparent hoop tensile strength of the cylinders is determined following the procedure A of ASTM D2290, for thermoset composite cylinders. The samples have two reduced areas at the ring width, separated by 180°, and the notches have radii of 10 mm. The specimen gauge length is 20 mm and hoop tensile strength X_{hoop} is defined as the ratio between maximum load and cross-section gauge area. Even though not covered by ASTM D2290, the apparent hoop tensile stiffness S_{hoop} is calculated from the secant modulus using two points close to a strain level of 0.2% in each stress *vs* strain curve.

Parallel plate loading compression tests (radial compression) were carried out following the recommendations of ASTM D2412. The specimens were 100 mm long and positioned between two compression platens [10], [11]. The compressive stiffness was determined as $S_c = {}^{F}/_{\Delta y}$, where F is the force applied to produce an internal diameter variation (Δy) of 30%. A Shimadzu universal testing machine model AG-IS with load cell of 100 kN was used to perform both mechanical tests, and mechanical extensometers were used to obtain displacement measurements.

3. Results and discussion

Figure 1(a) depicts the hoop tensile strength of all composite cylinders, which expectedly increases with the winding angle since the cylinder behaves better under circumferential loading for winding angles closer to 90° (the loading axis). In addition, the samples are not significantly affected by the curing condition. Failure is characterized by a long off-axis crack along the fiber direction. Similar results have been found by Perillo et al. [12], and Eggers et al. [13].

The highest strength is found for the specimens aged for 7 days under seawater, being even higher than for the unaged cylinders, suggesting that limited aging is beneficial to hoop strength. This is a clear effect of the epoxy matrix plasticization triggered by the temperature in which the samples are submitted during aging (i.e. 80 °C), promoting further cross-linking of the epoxy chains. This result can be correlated with the low T_g of unaged epoxy, whose chains have not yet reached full cross-linking. A similar scenario is reported by Mourad et al. [14], who investigated glass/epoxy composites aged in seawater at 65 °C and reported initial relaxation of residual stresses and enhancement of tensile strength.

Nonetheless, prolonged aging (14-28 days) is harmful to the tensile strength of the cylinders for all winding angles. This is likely to be an effect of the weakening of the fiber/matrix interface attributed to both water uptake and the salt ions effects, which break the cross-linked epoxy matrix, especially at longer aging periods in seawater at high temperature (higher water uptake) (see supplementary material). In addition, the longer the exposure period and therefore the hygrothermal swelling, the greater the expected damage to the fiber/matrix interface, reducing interfacial strength and the load transfer ability. The longer aging periods also generate non-homogeneous distribution of water within the structure, which could yield localized stress concentrations, weakening the laminate. Besides, the decrease in strength at 14 and 28 days of aging is due to both damage on the fibers [15] and hot water diffusion, which can convert covalent chemical bonds in physical interactions (hydrogen bonds) among glass fibers, water molecules and salt ions [4], [14].

<< Insert Figure 1 >>

Figure 1(b) presents the hoop tensile stiffness of the cylinders. Similarly, the higher the winding angle, the higher the stiffness. The same effect is also seen with aging, i.e. conditioning at 80 °C has an initial post-curing effect, improving stiffness. Longer aging period decreases stiffness, partially due to the high moisture uptake. Epoxy resin has polar groups which makes it hydrophilic, and, as shown in the supplementary material, the final composite contains voids that can facilitate water diffusion [6].

In order to further understand the effects reported, a post-mortem analysis is performed on the failed specimens, as shown in Figure 2. In all samples, failure initiates in the inner layers between the notches and propagates along the off-axis winding angle directions and towards the outer layers. The failure mechanisms are summarized as:

- $[\pm 75]_3$: fiber/matrix debonding parallel to the applied load followed by catastrophic failure dominated by fiber fracture. After initial failure, some less pronounced delaminations are observed. These mechanisms are expected for off-axis specimens loaded in tension [13].
- $[\pm 65]_3$: failure mechanism is similar to ±75°samples, but with more evidence of fiber/matrix debonding rather than delamination. Their outer layers are more damaged than for ±75° samples, with a greater contribution of the matrix, generating several minor transverse cracks. Similar mechanisms are also found by Kaynak et al. [16] and Gemi et al. [17].
- $[\pm 55]_3$: fiber/matrix debonding dominates failure followed by delaminations. Ultimate failure is associated with major cracks along the layers. A similar failure mechanism is found by Misri et al. [18]. For lower winding angles, voids and heterogeneous areas are more likely to occur since the glass tow may twist during winding.

In general, the type of curing does not significantly change the failure mechanisms of the specimens in hoop tension. The same occurred regarding aging, even though it strongly affects both stiffness and apparent strength of the rings, and it also causes slight changes in color, i.e. the samples become darker. Furthermore, the formation of a salt layer can be observed on the outer surface of the specimens for longer aging periods.

<< Insert Figure 2 >>

Figure 3(a) presents stiffness results for the cylinders under radial compression and, as expected, the higher the angle, the stiffer the cylinder. Furthermore, the curing condition and aging do not show significant influence on radial compressive stiffness (all results are within the deviations), which was confirmed with ANOVA one-way statistical analysis, at a 95% reliability level.

<< Insert Figure 3 >>

The compressive strength of the cylinders is shown in Figure 3(b). Based on the mean results, they may be sub-divided into two groups:

- $[\pm 55]_3$_PC and $[\pm 75]_3$_PC: the longer the aging period, the lower the compressive strength. For these specimens, aging is detrimental in all periods.
- $[\pm 55]_3$_CC, $[\pm 65]_3$_PC, $[\pm 65]_3$_CC and $[\pm 75]_3$_CC: the highest strength for these families are achieved after 7 days aging, which perhaps indicates epoxy plasticization and therefore makes the cylinders stronger. Similar findings are reported by Komorek et al. [30].

Still regarding Figure 3(b), the cylinders wound at ±55°, independently of the curing cycle, have the highest compressive strength. Considering the greater deviations, post-hoc Tukey procedure with one-way ANOVA analysis is carried out and presented as a box chart (Figure 4). Differently from compressive stiffness, compressive strength results present significant differences. In general, aging up to 14 days does not significantly affect compressive strength and the lowest strengths are found for 28-day aging. Furthermore, the cylinders wound at ±55° are the strongest, whereas strength of the ±65° and ±75° cylinders is similar.

<< Insert Figure 4 >>

Figure 5 depicts macrographs of the specimens after radial compression testing. In general, the cylinders present two longitudinal cracks (highlighted with arrows in Figure 5), i.e. each crack parallel in relation to the compression platens. Again, neither aging nor curing strategy modify the failure mechanisms. They present large delaminations that started laterally and propagated at the contact with the compressive platens. Also, the delaminations start later for higher winding angles [10], [11].

<< Insert Figure 5 >>

4. Conclusions

This study presents a comprehensive experimental work focusing on the mechanical characteristics of filament wound GFRP composite cylinders using different curing strategies and after aging in seawater at 80 °C. Partially cured cylinders are obtained by passing a saturated steam flow inside the mandrel, which can significantly decrease overall time and costs related to the production of pipelines. Unaged partially cured composite cylinders have a low T_g attributed to the low degree of cross-linking of the epoxy resin. The T_g increases after aging and seven days is enough to stabilize this value. The exposure of the composite cylinders to seawater at 80 °C for seven days positively affects hoop tensile strength and stiffness, which increases compared to unaged specimens. Exposure for longer periods (14-28 days), however, leads to a decrease in these properties, probably due to a degraded fiber/matrix interface associated to the great increase in water uptake. For both properties, the curing strategy does not show significant influence. Finally, the higher the winding angle, the higher the radial compressive stiffness, as expected, but neither the curing strategy nor the exposure time influence this property. In addition, the cylinders wound at ±55° show higher compressive strength, and all composites significantly lose strength after 28-day aging.

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FIGURE CAPTIONS

Figure 1. (a) Hoop tensile strength (b) and stiffness of the cylinders.

Figure 2. Failure analysis of representative rings after split-disk testing.

Figure 3. a) Stiffness and b) strength for all cylinders under radial compression.

Figure 4. Box chart for compressive strength using ANOVA one-way approach.

Figure 5. Failure analysis of representative cylinders after radial compression tests.

Figure SM1. Optical micrographs and histograms for: (a) $[\pm55]_3$, (b) $[\pm65]_3$ and (c) $[\pm75]_3$ samples.

SUPPLEMENTARY MATERIAL

3.1 Physical properties

Table 1 presents water uptake for specimens of different curing and aging characteristics (mean values of three samples in each case). The winding angle is not included in this evaluation since water uptake is not expected to vary, i.e. the type of winding is the same (helical winding), as well as the material system and cylinder geometry.

Table 1. Water uptake for specimens of distinct curing and aging characteristics.

Sample	**PC_7**	**CC_7**	**PC_14**	**CC_14**	**PC_28**	**CC_28**
Water uptake (%)	1.695 ± 0.028	1.673 ± 0.143	2.213 ± 0.095	2.173 ± 0.020	2.322 ± 0.155	2.292 ± 0.009

Regardless of the aging period, the CC (complete curing) specimens absorb slightly less water than the partially cured ones, but the difference is not statistically significant. Both samples present high initial water uptake (i.e. 7 days), characterizing instantaneous water penetration, mainly through voids and fiber/matrix interfaces [19]. For the water uptake at 14 and 28 days, there is an indication that the curve is flattening, suggesting that saturation would be reached soon after 28 days. In all, two kinetically distinct phenomena are identified: a short period of sorption of water molecules that leads to weight increase. The water uptake results suggest that they follow a Fickian behavior, since the water uptake for all samples tend to stabilize after a rapid uptake before reaching the equilibrium weight change, indicating saturation, therefore a Fickian behavior can be assumed, regardless of curing condition and fiber orientation. Both partially cured and fully cured specimens gain weight in similar diffusion rates in both early and saturation stages, suggesting that the curing level herein used does not affect the weight gain of the composites.

Moisture absorption in GFRP composites is characterized by the migration of molecules down the concentration gradient, occurring through diffusion. The glass fibers are susceptible to leaching in seawater, and the water can diffuse between fibers and matrix, weakening the fiber/matrix interface. In general, the penetration of oxygenated seawater into the fiber/matrix interface may cause severe damage to the fiber/matrix interfacial binding. Another fact that can negatively influence the mechanical and thermal properties of the composites is that fact that epoxy matrix is hydrophilic given their affinity between their polar groups and water, and due to the existence of molecule-size holes within their polymeric structure. The impact of initial water uptake rates is related with the water penetration into the voids and fiber-matrix interface, therefore the type of curing should not, indeed, affect the water uptake. Water penetration can also initially reach the fiber-matrix interface, in which micro-cracks on the cylinder surface can generate residual stress after the curing process, creating hot spot areas [20].

To determine the fiber volume fraction (V_f), the density of the cylinders is required, in which they are on average of 1.84 kg/m^3. The obtained V_f of the samples varies slightly with the winding angle, being 68.8 ± 0.5%, 71.1 ± 0.5% and 68.7 ± 0.4% for the $[\pm55]_3$, $[\pm65]_3$ and $[\pm75]_3$ samples, respectively. This variation is expected since the specimens are produced via wet filament winding, in which the dry rovings enter a resin bath and are subsequently wound onto the mandrel, in a procedure that is not able to guarantee the exact same amount of resin in the rovings. Also, the amount of resin in the tray varies as the winding process progresses since the flow of resin to the bath is not continuous. Nevertheless, the variation in V_f was lower than 3%, which means that resin impregnation was very consistent.

Optical micrographs (Figure SM1) have been taken to estimate the winding angles and a histogram of angle distribution. Observation of the micrographs reveals some resin-rich areas and voids, typical of such filament-wound composites. The mean winding angles are very consistent with the programmed angles, being 55.6 ± 1.9°, 64.5 ± 3.2° and 74.8 ± 1.7° for the $[\pm55]_3$, $[\pm65]_3$ and $[\pm75]_3$ samples, respectively, again suggesting good control of the process. An image processing is used to calculate the void content of the cylinders through the optical micrographs presented in Figure SM1, which are as follows: 5.5%, 5.4%, and 5.1% for the $[\pm55]_3$, $[\pm65]_3$ and $[\pm75]_3$ samples, respectively. This is expected, since usually the higher the angle (towards hoop windings), the better the precision on the fiber placement, which generates less voids on the structure.

<< Insert Figure SM1 >>

3.2 Thermal behavior

The variation in winding angle does not influence the thermal response of the composites given the small size of the sample (≈10 mg). Nevertheless, it is still important to check if curing and aging conditions affect their thermal behavior, especially the glass transition temperature (T_g). The DSC thermograms for all specimens (first run) aims at erasing the thermal history of epoxy and evaluate curing of the polymer, being suitable to obtain the T_g. The second run is attached as supplementary material, since it is only useful to examine whether further curing can occur. In general, an exothermic peak is identified in the first run due to residual curing, and the second run presents an inflection that indicates the T_g. Among all T_g values, compiled in Table 2, only the PC_0 sample is considerably lower (132 °C), which suggests that the strategy to flow saturated steam inside the mandrel is not enough to fully cure the epoxy resin. The T_g values for the other partially cured samples vary between 154-157 °C, indicating that, for those samples, full curing is reached during exposition of the samples to aging at 60 °C for at least 7 days. Regarding the CC samples, no significant variation in T_g values is found, i.e. they are all within 154-159 °C. This suggests that post-curing promotes complete cross-linking of the epoxy and that aging does not significantly affect the samples due to plasticization or softening of the polymer matrix [21].

Table 2. Compilation of T_g values for all samples taken from DSC thermograms (from 1st run).

Sample	PC_0	PC_7	PC_14	PC_28	CC_0	CC_7	CC_14	CC_28
T_g (°C)	132 ± 1	156 ± 1	157 ± 1	154 ± 1	154 ± 1	155 ± 1	159 ± 1	156 ± 1