

The effect of matrix type on ageing of thick vinyl ester glass-fibre-reinforced laminates

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ABSTRACT

In this research, glass fibre reinforced composite laminate samples were manufactured with filament winding technique using four different vinyl ester resin systems to study ageing. The manufactured laminate samples were conditioned in an environmental cabinet (70 °C, 95 RH%), water immersion (95 °C), and in sulphuric acid solution immersion under pressure (5% H₂SO₄, 95 °C, 15 bar). After 6 and 12 months of conditioning, the samples were tensile tested and the results were compared with the initial values. Regardless of the matrix type, conditioning in the environmental cabinet resulted in the lowest weight gain and least decrease in tensile properties: the decrease in the tensile strength values was 10-25% after 12 months' conditioning depending on the vinyl ester used. The water immersion was more detrimental to the samples than the 5% H₂SO₄ immersion causing the highest weight gain and the greatest decrease in tensile strength (up to 65%). However, when comparing the tensile performance, it was noted that the highest weight gain did not inevitably correlate with the strongest ageing effect. In water immersion, the ultimate strength deteriorates faster than the proof stress level leading to a decreasing damage tolerance of the vinyl-ester composite laminates.

Keywords: GFRP, vinyl ester, ageing, tensile properties

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1. Introduction

Fibre-reinforced plastic (FRP) composites are often the only possible economical material for the process industry in the case when the operating environment is extremely aggressive. The use of FRP composites in such applications is favoured due to their light weight combined with excellent stiffness, strength, corrosion resistance and lower price compared to highly alloyed metals. FRP materials are successfully used in marine vessels, piping, corrosion equipment, and underground storage tanks that are constantly in contact with moisture and different aqueous solutions [1, 2]. These structures should have operational lifetime of several years or even decades and, therefore, their long-term properties have as much practical importance as their short-term response. During their operation, the material properties can be affected by several environmental factors, such as moisture, temperature, pressure, and chemicals. These factors may act individually or their combination may cause synergistic effects [3].

Vinyl esters are, in general, the choice of materials in applications where good corrosion resistance is required. The main body of the molecule remains unaffected when subjected to solvents due to low number of vulnerable reactive ester groups in the polymer chain [4]. The bisphenol-A based vinyl esters have two ester groups per molecule and their use in FRP structures in corrosive environments has become the industry standard. However, the incorporation of the novolac chemistry in the 1970s allowed higher service temperatures, better adhesion to fibres, and enhanced resistance to organic solvents due to higher crosslink density [4]. However, the number of ester groups in novolac based vinyl esters is higher.

The analysis of aging in the FRP materials is challenging since they are complex material systems with three distinctive components: the matrix, the fibre, and the interface region. Water molecules are very reactive since they dissolve readily giving a proton and a hydroxyl ion and can cause reversible and irreversible physical and/or chemical modifications in the FRP composite. These include plasticization and hydrolysis of the matrix, molecular degradation by polymer chain breakage, internal stresses caused by the swelling, as well as the cracking and crazing due to osmosis and the change of the water state [1]. Moisture can also diffuse into the fibre-matrix interface and cause debonding, leaching of fibre and reduction in fibre strength [1] as well as provide pathways for faster moisture absorption [5]. Thus FRPs are typically more prone to the detrimental effects of water compared to the bulk polymer of the same resin. The absorbed moisture generally decreases the glass transition temperature T_g of the composite, and softens the material causing a loss in the stiffness and strength, especially at elevated temperatures. In vinyl esters, the water uptake causes plasticization over a short-term conditioning and hydrolysis over a long term conditioning through the breakage of the ester linkages [6].

The long-term mechanical performance of different FRP materials has been extensively investigated. Vinyl ester based FRP [7-12] has gained significant interest in research, yet polyester [13-17], and [18]

based materials have also been studied. Generally, a decrease in tensile [9, 10, 13, 18], flexural [9-11, 15, 16, 18], shear [8, 11, 17], and impact [11] properties is observable after environmental conditioning. For example, Cabral-Fonseca et al. [10] have measured up to 40% decrease in the tensile strength values of pultruded vinyl ester profiles after a long-term water immersion at elevated temperatures. The decrease was more pronounced as the conditioning temperature was increased. In addition to temperature, the immersion medium has a significant effect on the long-term properties. Demineralized water, for example, has shown to have more aggressive effect compared to salt water due to osmotic effects [10].

The changing of the neutral ageing environment into an acidic or alkaline environment has shown to have varied effects: Hammami et al. [11] have noticed a clear decrease in the flexural properties of glass fibre reinforced vinyl ester composites when exposed to nitric acid solution. In that case, the decrease in properties was more pronounced as the concentration was increased from 2% to 5% or when the immersion time was extended. In a seawater immersion, the resulting decrease in stiffness was less than for nitric acid solution. When considering sulphuric acid media, it has been concluded that a polymer matrix cannot be regarded as a good barrier against water but it resists well the penetration of SO_4^{2-} ions [19]. Therefore, pure water immersion may be more detrimental to the FRP materials than dilute acid solutions. In fact, in our earlier study, water immersion was shown to have stronger effect on the FRP composite during a three-day test in 95 °C than a 5% H_2SO_4 solution: The samples tested in water showed significantly higher weight gain and increased erosion wear rate [20]. Similarly, Agarwal et al. [13] have measured a tensile strength decrease of 20% after water immersion, while the decrease was only 10% after 10% H_2SO_4 solution conditioning. However, a direct relation between the decrease in tensile strength and the solution concentration could not be drawn.

In this study, the performance of FRP materials is examined after a long-term conditioning. Four different commercial vinyl ester resins were used and the composite samples were exposed to one of three different environmental conditions: environmental cabinet (relative humidity 95% and temperature 70 °C), water immersion (temperature 95 °C), and pressurized 5% H_2SO_4 solution immersion (temperature 95 °C and pressure 15 bar). The weight gain and the changes in the glass transition temperature (T_g) values of the composites were monitored along with the tensile response of the composites.

2. Experimental details

2.1 Materials

In this study, four different vinyl ester resins were used as the matrix material in the composites: Derakane 441-400 (supplied by Momentum), Atlac E-Nova FW 1045 (supplied by DSM), Dion 9400 (supplied by Reichhold), and Derakane 455-400 (supplied by Momentum). The main goal of this study was to evaluate how the innate resin properties correlate with the long-term properties of the composite

laminates. This study includes both bisphenol-A based vinyl esters (Derakane 441 and Atlac E-Nova FW 1045) and novolac based vinyl esters (Dion 9400 and Derakane 455). In addition, Atlac E-Nova is a flexibilized bisphenol-A based vinyl ester urethane resin. Vinyl ester urethane modified resins generally show higher T_g than that of corresponding unmodified, solely styrene crosslinked resins [21]. The main properties of the applied resins are presented in Table 1. Based on the resin suppliers' data, the heat distortion temperature (HDT) is clearly lower in the bisphenol-A based resins than in the novolac based resins. However, all the resins should tolerate high service temperatures (up to 95 °C) without a significant deterioration.

Table 1: The properties of the used vinyl ester resins given by the manufacturers [22-25].

Resin	ID	HDT (°C)	Barcol hardness	Tensile strength (MPa)	Tensile modulus (GPa)	Tensile elongation (%)
Derakane 441-400	FRP-441	120	35	90	3.4	5-6*
Atlac E-Nova FW 1045	FRP-Atlac	125	45	85	3.3	5-6
Dion 9400	FRP-Dion	135	45	72	3.7	2.5-3
Derakane 455-400	FRP-455	145	45	88	3.5	4

* elongation at yield

In the vessels for aggressive chemicals, the FRP wall typically contains two distinctive layers: a structural layer, which has the main function in providing load bearing capacity for the structure, and a resin rich corrosion barrier layer (resin content roughly 75%), which protects the structural layer from chemical attack [26]. In this study, glass fibre reinforced vinyl ester pipe samples (Fig. 1a) were manufactured using a filament winding technique. All the pipe samples had a lay-up with structural and corrosive layers (Fig. 1b-c). The structural layers contained 20 layers of woven roving (3B-fiberglass R25HX14, 480 g/m²) and 16 layers of axial roving (Ahlstrom 9690-19-300, 256 g/m²). The axial roving was applied parallel to the symmetry axis of the pipe one after another with the woven roving. The total thickness of the structural layer was roughly 13 mm. A thick corrosion layer was manufactured on the other side of the samples using nine layers of chopped strand mat (Owens Corning M723A, 300 g/m²) and one layer of ECR-glass surface mat (Owens Corning M524-ECR30S, 30 g/m²) on the top. The total thickness of the corrosion layer was roughly 7 mm. The darker, resin-rich corrosion layer was placed on the inner or outer side of the sample (Fig. 1b-c). The nominal overall thickness of the pipe wall was 20 mm. All the pipe samples were post-cured according to the resin suppliers' instructions: FRP-441 for 10 hours at 80 °C, FRP-Atlac 5 hours at 90 °C, FRP-Dion 8 hours at 80 °C, and FRP-455 10 hours at 100 °C. For conditioning, the filament-wound pipe was cut in laminate segments of 400 x 400 mm².

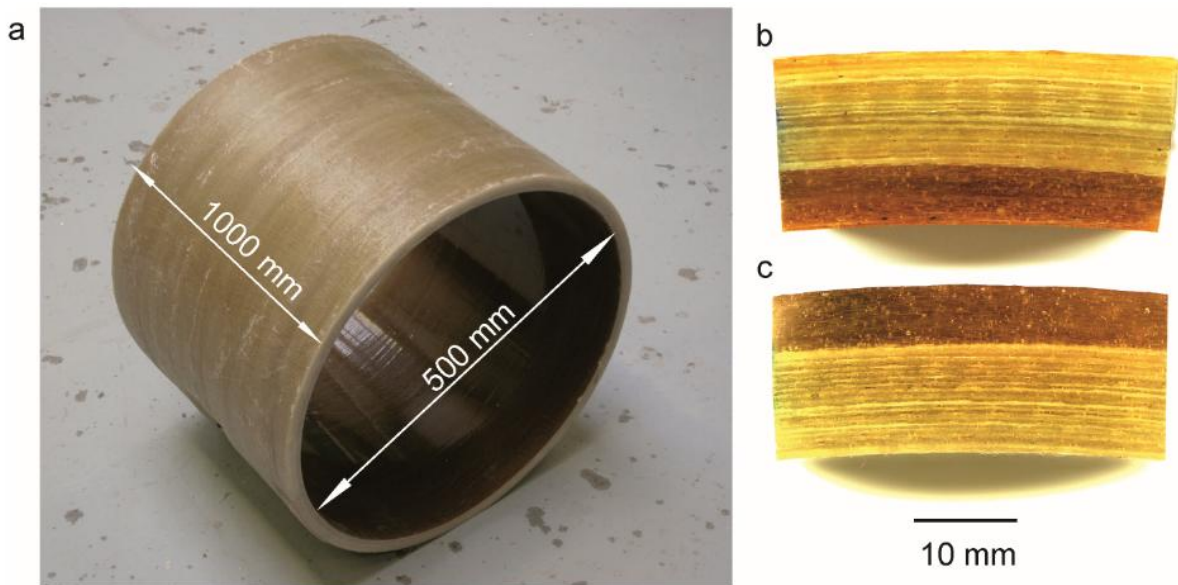


Figure 1: (a) Filament wound pipe sample and the lay-up for (b) environmental cabinet conditioning and water immersion and (c) 5% H_2SO_4 immersion. The dark layer in the laminate structure represents the corrosion layer and the light layer the structural layer.

2.2 Exposure conditions

In this study, three conditions were used to investigate the ageing of the laminates: a humid condition, a water immersion and an acidic immersion. While the hot acidic immersion is close to the actual industrial environment, the change between the water and acidic immersion reveals the effect of the acid and the change between the water immersion and the humid condition the effect of high mass uptake. The laminate segments were exposed to one of the three different environmental conditions for a maximum of 12 months. The segment properties were tested after 6 and 12 months of conditioning. Prior to conditioning, the laminate edges were sealed with a gelcoat (supplied by Ashland) to prevent excess water absorption via the free cut surfaces. The humidity conditioning was conducted by Weiss SB22 environmental chamber at a temperature of 70 °C and relative humidity of 95%. The water immersion was conducted by a water bath at a temperature of 95 °C. For the acidic conditions, a pressurized reactor was filled with 5% H_2SO_4 solution. Also 0.5 g/l of $Fe_2(SO_4)_3$ was added to act as a corrosion inhibitor for the metallic parts of the reactor. A total of four pressurized reactors were used, so that the segment samples manufactured with a specific resin were conditioned in individual reactors, separated from the other segment samples. The temperature of the solution was 95 °C and the pressure inside the reactor 15 bar. The temperature and pressure were monitored continuously. The reactors are presented in Fig. 2.

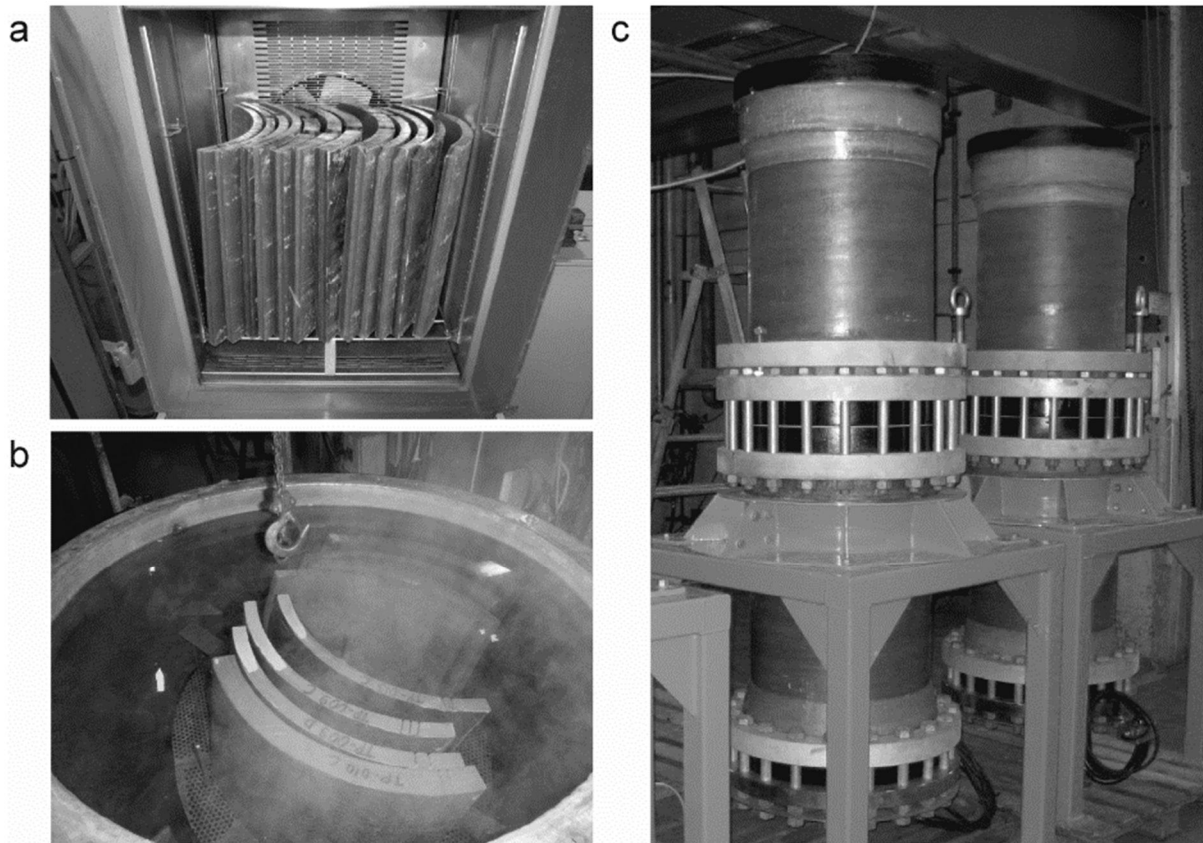


Figure 2: (a) Environmental chamber, (b) water immersion, and (c) two pressurized reactors with 5% H_2SO_4 and four segment samples inside.

2.3 Sample characterization

After the conditioning, the segment samples were weighed and immediately wrapped in plastic film so that they would not dry before further testing. The plastic film was removed only during sample cutting and the cut samples were sealed again by the plastic film until they were tested. All the segment samples were tested within two weeks after their removal from the exposure conditions.

The fibre fraction for the structural and corrosion layers were analysed with a residual ash determination test. In this test, a small sample (weight of approximately 1 g) was cut off the segment and its temperature was raised gradually to 600 °C in an oven. After all the resin had burned away, the remaining ash was weighed and compared to the original weight. The densities of the composite layers were measured with a Wallace electronic densimeter with three parallel measurements.

The glass transition temperatures (T_g), based on the $\tan \delta$ peak, were analysed with a dynamic mechanical thermal analysis (DMA, model Perkin Elmer Pyris Diamond). The DMA sample size was $2 \times 4 \times 40 \text{ mm}^3$ and one sample was measured per segment sample. The tests were conducted in a single cantilever mode at a frequency of 1 Hz and a heating rate of 2 °C/min from 25 °C to 270 °C. For a comparison, through-the-thickness values of T_g were studied with a differential scanning calorimeter (DSC, model Netzsch DSC 204) under a nitrogen flow (50 ml/min) over a temperature range of 25–200

°C. The T_g values were measured at six measuring points so that two of the measurements were taken from the corrosion layer and four from the structural layer.

Rectangular axial tensile specimens (Fig. 3a) were prepared of the structural layer of the exposed segments. The specimens had a nominal thickness of 14 mm, width of 25 mm, and a length of 250 mm; no end-tabs were used. The tensile tests were carried out according to a standard ISO 527-4 using a tensile test machine (Dartec 100 kN servo-hydraulic testing system) at a displacement rate of 2 mm/min (Fig. 3a). The elongation of the samples was measured using an extensometer with a gauge length of 50 mm. Five specimens were tested for each segment sample. The stress-strain curves for all the FRP specimens were observed to be bilinear in shape (Fig. 3b). Therefore, Young's modulus, tensile strength, and proof stress according to a 0.05% offset strain were determined. Finally, the fracture surfaces were characterized with a scanning electron microscope (SEM, model Jeol 6490LV).

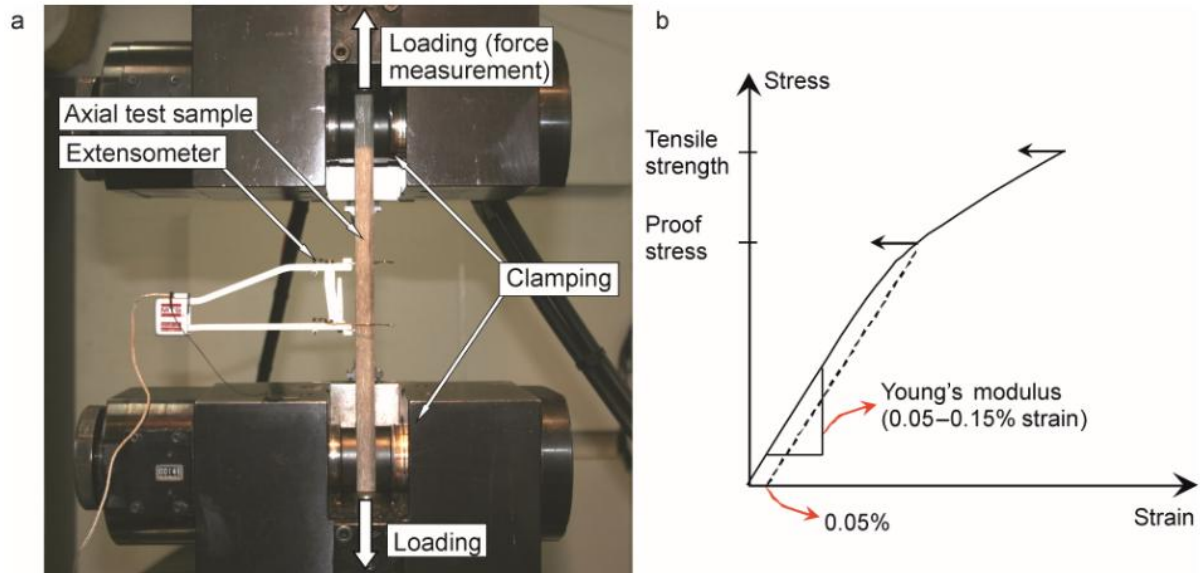


Figure 3: (a) The axial tensile test arrangement and (b) the schematics of the tensile stress-strain curve and the parameters obtained from the results.

3. Results

3.1 Properties of FRP composites prior long-term conditioning

The densities, fibre fractions, and T_g values for unconditioned samples are presented in Table 2. It can be seen that the fibre fractions and densities of the structural and corrosion layers were essentially similar in all of the samples. The fibre fraction of the structural layer was 71-74 wt%, while the corrosion layer obtained a fibre fraction of roughly 29-31 wt%. The T_g values, measured with DMA, were slightly higher in the structural layer than in the corrosion layer for all the composites. The binders of the chopped strand mats in the corrosion layer are assumed to decrease the T_g .

Table 2: Fibre fraction, density, and the $\tan \delta$ -peak (T_g) values for structural and corrosion layers in unconditioned segment samples.

Sample	Fibre fraction (wt%)		Density (g/cm ³)		T_g (°C)	
	Structural layer	Corrosion layer	Structural layer	Corrosion layer	Structural layer	Corrosion layer
FRP-441	71.8 ± 0.6	30.1 ± 0.4	1.88 ± 0.02	1.36 ± 0.01	129	125
FRP-Atlac	73.2 ± 0.5	30.4 ± 1.0	1.89 ± 0.01	1.37 ± 0.01	147	144
FRP-Dion	71.0 ± 1.0	29.4 ± 0.4	1.89 ± 0.02	1.40 ± 0.00	150	148
FRP-455	71.7 ± 0.4	30.1 ± 0.7	1.89 ± 0.00	1.39 ± 0.00	136	131

Axial tensile test results for the structural layer of the unconditioned specimens (Table 3) showed that the FRP-455 specimens had the highest performance regarding tensile strength and Young's modulus. FRP-Dion, on the other hand, obtained the poorest behaviour, even though the stiffness of the Dion matrix was the highest according to the data given by the suppliers. This may be due to weaker adhesion between the glass fibre and the Dion resin. The FRP-441 and FRP-455 specimens have the highest proof stress values while the FRP-Dion the lowest.

Table 3: Axial tensile test results for unconditioned FRP specimens.

Sample	Axial tensile strength (MPa)	Axial Young's modulus (GPa)	0.05% Axial proof stress (MPa)
FRP-441	148 ± 10	20.1 ± 1.2	63 ± 8
FRP-Atlac	167 ± 8	18.4 ± 0.9	59 ± 2
FRP-Dion	143 ± 5	18.4 ± 0.7	55 ± 2
FRP-455	166 ± 5	20.4 ± 1.2	62 ± 1

3.2 Weight gain and visual changes during the conditioning

The weight gain was measured during the conditioning in the environmental cabinet every 7 days until 6 months and after that once a month. The comparison between the samples (Fig. 4) shows that for the environmental chamber, the weight gain was the highest with the novolac based samples (FRP-455 and FRP-Dion), while bisphenol-A based samples FRP-Atlac and FRP-441 showed slightly lower increase in weight. The overall weight gain was in general low, less than 0.8 wt% during the 12 months' conditioning period. The higher weight gain of the novolac based vinyl ester FRPs was not expected, since novolac based vinyl esters are more resistant to moisture and chemicals than bisphenol-A based ones [4]. According to the weight gain curves, it seemed that only the FRP-Atlac reached the saturation moisture content in the environmental chamber during the conditioning.

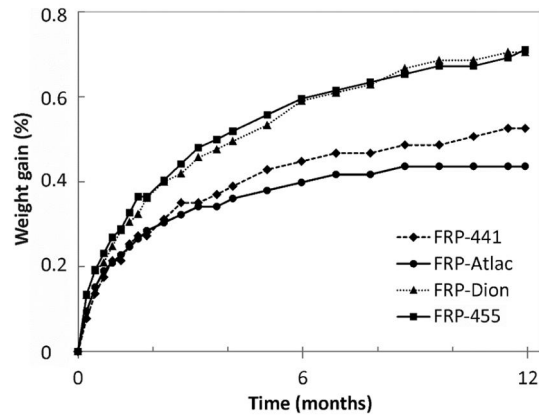


Figure 4: Weight gain of the segment samples during a 12 months' conditioning period in an environmental chamber.

Water immersed and 5% H₂SO₄ immersed samples were weighed only after 6 and 12 months due to the more difficult access to samples in the reactors. A comparison (Fig. 5) between the samples shows that the weight gain was at the highest for the water immersion while the environmental cabinet resulted in the lowest weight gain. When comparing the water and 5% H₂SO₄ immersions, the weight gain due to the 5% H₂SO₄ exposure was roughly a half of the weight gain in the water immersion. The measured weight gain is a sum of molecule absorption and the removal of other substituents from the structure such as removal of oligomers and monomers from the matrix and alkali and alkaline earth ingredients of the glass. Therefore, a low weight gain might also represent high leaching rates (weight removal).

When comparing the different resins, only in the environmental chamber a clear trend could be seen between the bisphenol-A and novolac based vinyl ester FRPs. The FRP-Atlac samples experienced the lowest weight for all the environments after 12 months' immersion: 0.4, 1.6, and 0.6 wt% in environmental chamber, water immersion, and 5% H₂SO₄ immersion, respectively. On the other hand, FRP-Atlac, having a bisphenol-A basis and more ester groups per molecule, may be more prone to monomer/oligomer leaching, which can decrease the total weight gain. The highest weight gain was observed for the novolac based FRP-455: 0.7, 3.0, and 1.5 wt% in environmental chamber, water immersion, and 5% H₂SO₄ immersion, respectively.

Visually the FRP-441 samples after the 12 months' conditioning in the environmental cabinet showed a clear difference in the appearance when compared to the water-immersed samples (Fig. 6): In water immersion the resin rich corrosion layer has turned from dark brown to light brown whereas in the environmental cabinet there are no visible changes. The colour change indicates hydrolysis and/or molecule leaching in the matrix [7]. In addition to the water molecule concentration at the FRP surface, the temperature difference between the environmental chamber conditioning and water immersion must be considered: Water occupies the free volume in the polymer matrix and binds to hydrophilic sites. Since the free volume is temperature dependent, higher water absorption can be expected at higher temperatures.

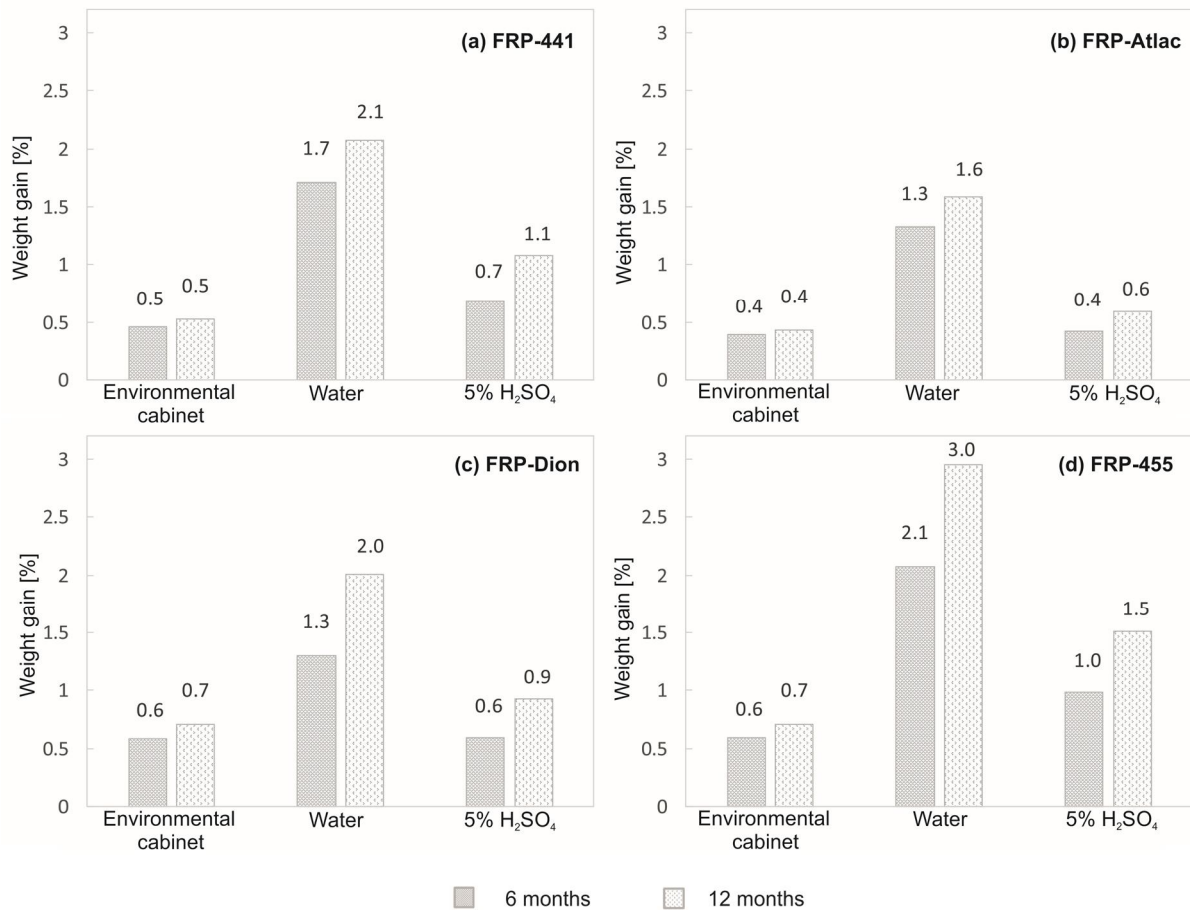


Figure 5: Weight gain of the exposed (a) FRP-441, (b) FRP-Atlac, (c) FRP-Dion, and (d) FRP-455 samples after 6 and 12 months of conditioning in environmental chamber, water, and 5% H₂SO₄ solution.

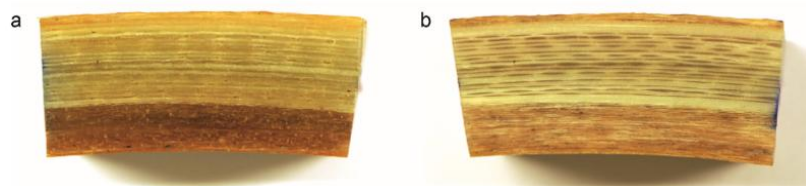


Figure 6: Visual FRP-441 sample appearance after 12 months in (a) environmental cabinet (70 °C) and (b) water immersion (95 °C).

A comparable colour change can be seen in the FRP-441 samples (Fig. 7) after 6 and 12 months conditioning in 5% H₂SO₄ solution. The effect of the acidic medium can be clearly seen as a lighter colour. The colour of the corrosive layer turns into reddish after 6 months of conditioning. After the conditioning of 12 months, the colour has turned into light brown and the distinctive boundary between the corrosive and structural layer has disappeared. When comparing the colour of the structural layer after the 12 months' conditioning in water and 5% H₂SO₄ solution, the water immersed samples show clearly whiter structure. This supports the weight gain measurements, where water seemed to penetrate the matrix more efficiently than the used acidic solution.



Figure 7: FRP-441 sample appearance (a) prior conditioning and after (b) 6 and (c) 12 months in 5% H_2SO_4 solution.

3.3 The glass transition temperatures of the conditioned FRPs

Hydrolysis and molecule leaching decrease the T_g value whereas further crosslinking due to high temperature conditioning or the loss of low molar mass plasticizers increases the T_g [5]. All aforementioned reactions are irreversible and thus affect the measured T_g values of conditioned samples. In addition, reversible reactions, such as plasticization, affect the T_g values [5], but since the T_g measurements were done for dried samples, plasticization is not assumed to affect the results of this study. Only one sample per position was tested.

In the environmental cabinet, the temperature was lower (70 °C) than the post-curing temperature and presumably no marked crosslinking took place during the conditioning. Therefore, the observed decrease in the measured T_g values (Table 4) is caused by degradation. In the water and 5% H_2SO_4 immersions, the temperature was high (95 °C) and crosslinking was more probable to occur. In this case, however, the total effect was still dominated by degradation causing a drop in the T_g values. While the difference between the effects of the water and 5% H_2SO_4 immersions were rather similar to the bisphenol-A based FRPs, the novolac based vinyl ester FRPs showed most significant decrease in T_g in 5% H_2SO_4 immersion reflecting their lower resistance to acidic environments. In general, clear differences between the weight gain results of the water and 5% H_2SO_4 immersion tests did not correlate with the T_g measurements which indicates that water immersion causes more reversible effects than acidic immersion.

Table 4: The $\tan \delta$ -peak (T_g) values of the structural layer of the tested laminates.

Time (months)	No conditioning	Environmental cabinet		Water immersion		5% H_2SO_4 immersion	
	0	6	12	6	12	6	12
FRP-441	129	122	124	126	128	128	125
FRP-Atlac	147	-	148	-	135	-	137
FRP-Dion	150	145	146	144	145	138	138
FRP-455	136	-	137	-	138	-	127

To estimate the progress of the FRP degradation through the laminate thickness, T_g values were measured from six points using a DSC. Two samples were taken from the outer surface and from the

middle of the 7 mm thick corrosion layer. From the structural layer, one sample was taken from the surface, one close to the interface between the layers and the other two from regular intervals between these. The results (Table 5) show only small variations in the T_g values as a function of the thickness. Generally, the accuracy of a T_g measurement of a FRP by DSC can be estimated to be 1-2 °C.

Table 5: Through-the-thickness T_g values (°C), measured with DSC, of the FRP-441 samples.

	Corrosion layer (°C)		Structural layer (°C)			
No conditioning	126	123	127	129	129	128
12 months in environmental cabinet	120	125	130	129	127	124
12 months in water immersion	132	132	133	132	133	134
12 months in 5% H ₂ SO ₄ immersion	127	133	130	131	128	129

3.4 The tensile properties of the conditioned FRPs

The tensile strength of all the FRP specimens was significantly lower after the long-term conditioning (Fig. 8a-d): the highest decrease resulted from water immersion followed by 5% H₂SO₄ immersion. The conditioning in the environmental cabinet affected the mechanical properties least. Even though the FRP-455 showed by far the highest weight gain during all the exposure conditions, the decrease in tensile strength was of a same magnitude or even lower than in the other FRP specimens. Thus, the weight gain and tensile properties did not correlate when the different resin types were compared. The tensile strength of the FRP-455 decreased 9, 52, and 30% after the 12 months' conditioning in the environmental cabinet, water immersion, and 5% H₂SO₄ immersion, respectively. The most significant decrease in tensile strength was obtained for the FRP-Atlac, which experienced a decrease in strength of 16, 63, and 52%. The effect of the environmental cabinet varied from 9 to 25% decrease compared to unconditioned values, while the corresponding effect was 46 to 63% in the water immersion, and 30 to 52% in the 5% H₂SO₄ immersion. In the current literature, the decrease in tensile strength is considered to depend highly on the raw materials and the quality of the manufacturing (e.g. the presence of voids). For example, Cabral-Fonseca et al. [10] have measured for glass reinforced vinyl ester composites 40% decrease in tensile strength values after 12 months in 40 °C water. Due to varying environments and sample materials, the results give only a rough estimate on their behaviour in different environments.

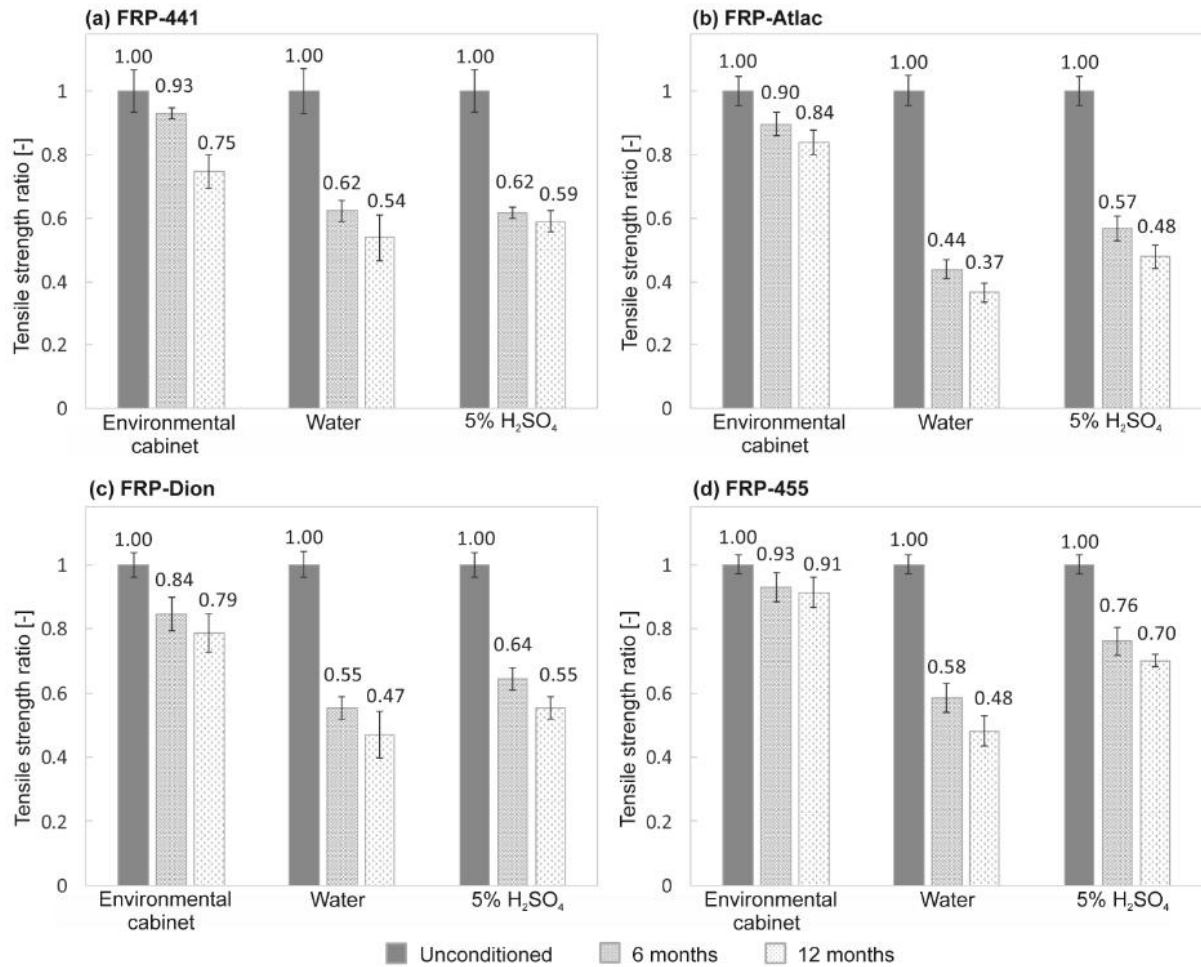


Figure 8: Decrease of axial tensile strength for (a) FRP-441, (b) FRP-Atlac, (c) FRP-Dion, and (d) FRP-455 compared to pristine specimens after 6 and 12 months of conditioning. The error bars represent the standard deviations per series of five specimens.

In general, the decrease of the Young's modulus values due to the conditioning procedures was of the order of 10% (Fig. 9a-d). The changes were not as significant and the results not as consistent as they were for the tensile strength results. Strength is determined by local weaknesses in the specimen and conditioning may have an effect on these imperfections. Consequently, strength is supposed to have higher sensitivity to conditioning than stiffness. The most significant stiffness decrease was experienced by the FRP-455 for which also the most significant mass gain values were measured. Among the tested materials, the FRP-Dion samples maintained their stiffness best and its stiffness was even increased in 6 months' water immersion. This is supposed to result from post-curing during the high temperature immersions and has been also reported elsewhere [11].

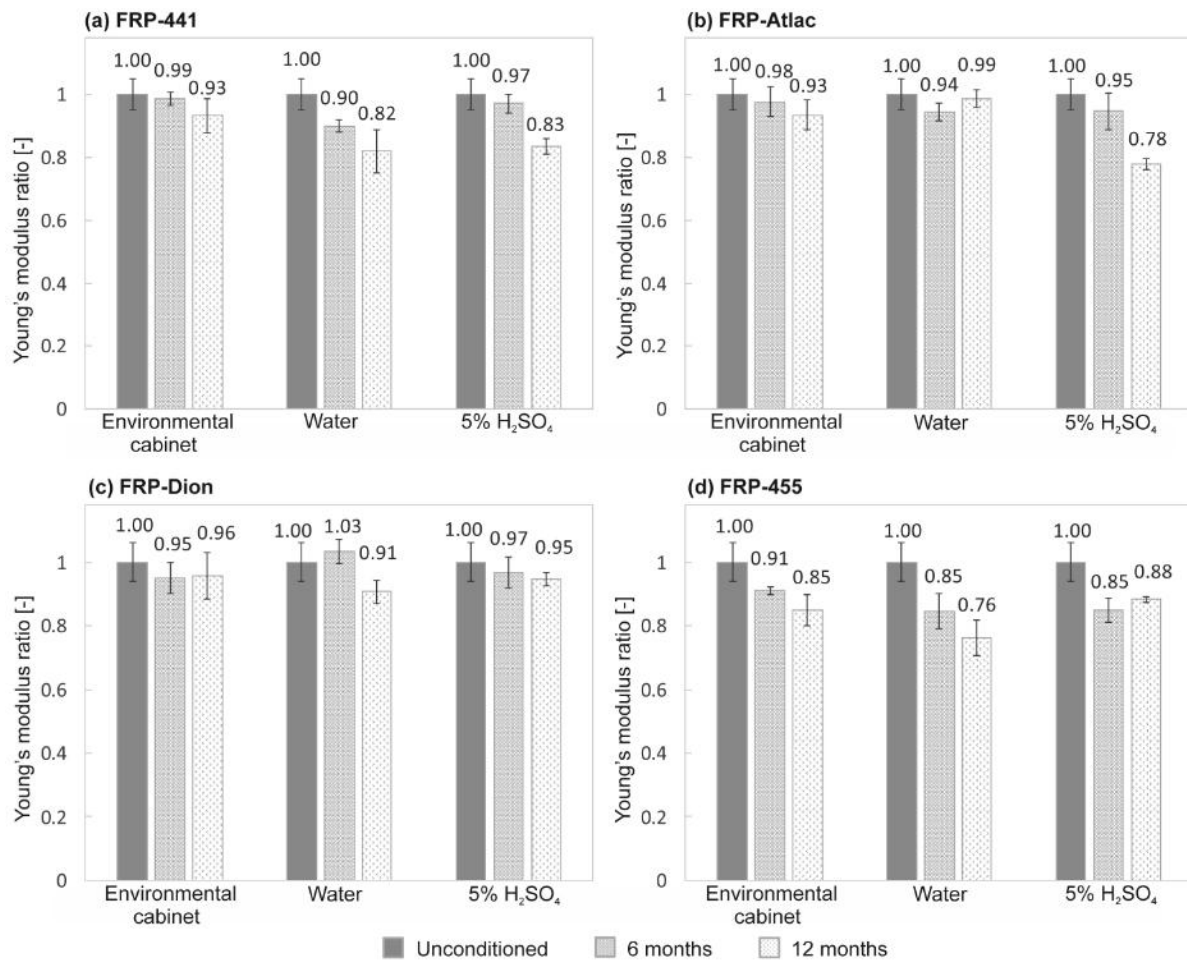


Figure 9: Change in axial Young's modulus for (a) FRP-441, (b) FRP-Atlac, (c) FRP-Dion, and (d) FRP-455 compared to pristine specimens after 6 and 12 months of conditioning. The error bars represent the standard deviations per series of five specimens.

The proof stress values (Fig. 10a-d) were not that susceptible to aging as the tensile stress values (Fig. 8a-d). The least decrease was determined after the environmental conditioning while the water and 5% H₂SO₄ immersions generated more significant deterioration. The FRP-Dion showed the least decrease in the proof stress values in all the conditions after 12 months' conditioning.

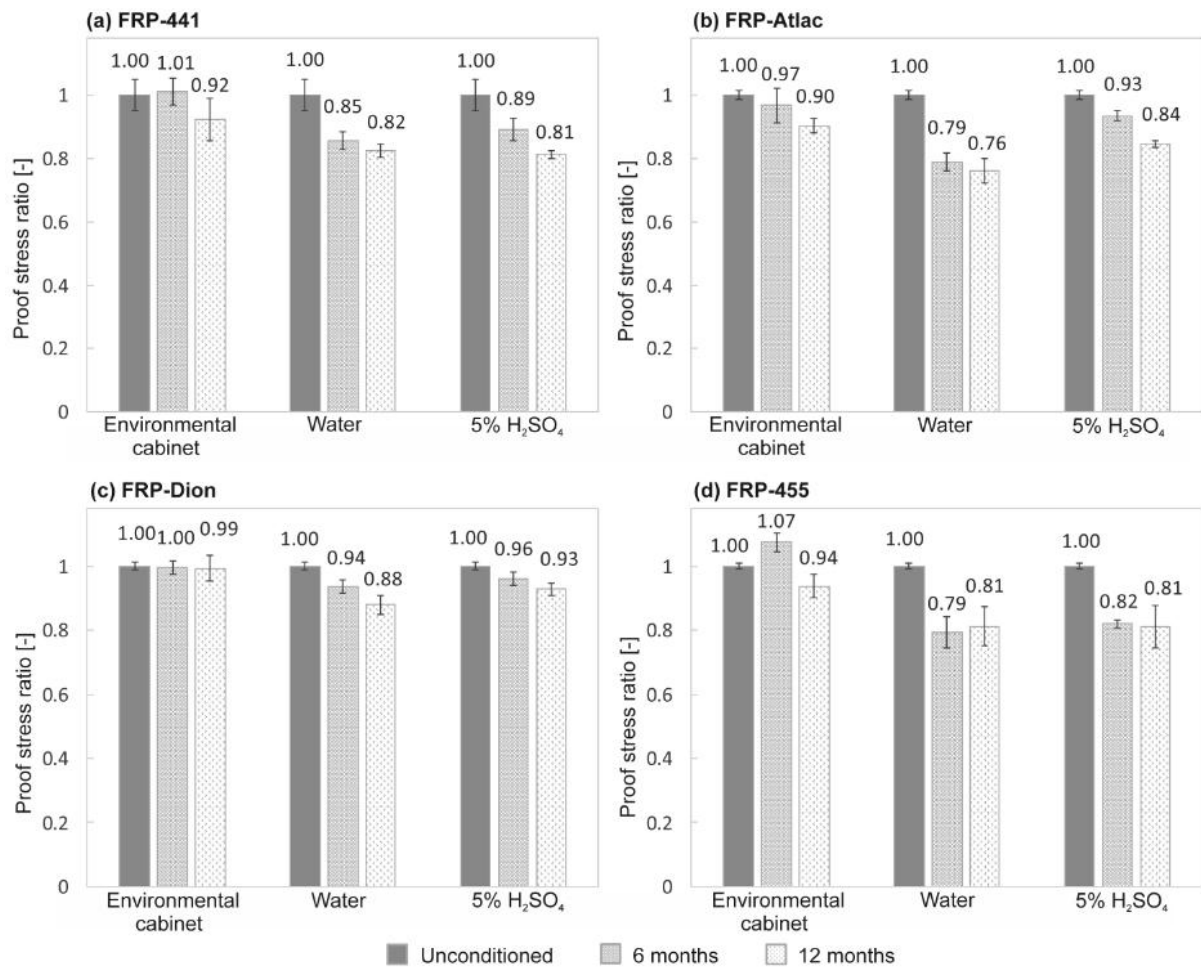


Figure 10: Loss of 0.05% proof stress in (a) FRP-441, (b) FRP-Atlac, (c) FRP-Dion, and (d) FRP-455 compared to pristine specimens after 6 and 12 months of conditioning. The error bars represent the standard deviations per series of five specimens.

3.5 The fracture surfaces of the tensile test specimens

The fracture surfaces of the tensile test specimens were studied with SEM. The revealed fibre surfaces were smooth and no visible cracks or dints could be seen in the unconditioned samples (Fig. 11a). Some fibres and fibre bundles were detached from the matrix during the fracture and matrix residues were visible on the fibre surfaces indicating good initial adhesion. No distinctive voids could be observed in the matrix, only some minor cavities were observed around the fibres due to the non-uniform wetting of the fibre bundles. The conditioning did not cause visible changes to the sample appearances (Fig. 11b).

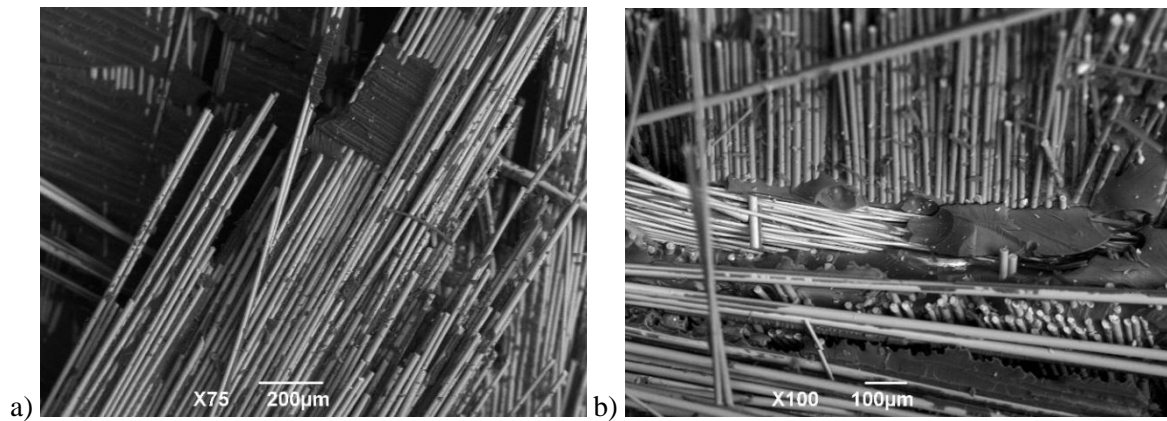


Figure 11. SEM images of tensile tested (a) unconditioned and (b) 6 months in water immersion conditioned FRP-411 composites.

4. Discussion

The effect of the type of the vinyl-ester matrix was shown to be significant on the deterioration of proof stress and tensile strength. The deterioration of Young’s modulus was relatively low and the effect of the matrix selection within the experimental scatter, as is typical for GFRP laminates [27, 28]. It is interesting to compare the remaining proof stress with the remaining tensile strength since they are expected to change differently as a function of time. In Fig. 12, it can be seen that the deterioration in the ultimate tensile strength is higher than that of the proof stress, i.e., all the columns are positive, irrespective of the conditioning time. It means that the damage onset during the tensile testing was less affected by the conditioning than the ultimate failure. This conclusion is also independent of the immersion medium.

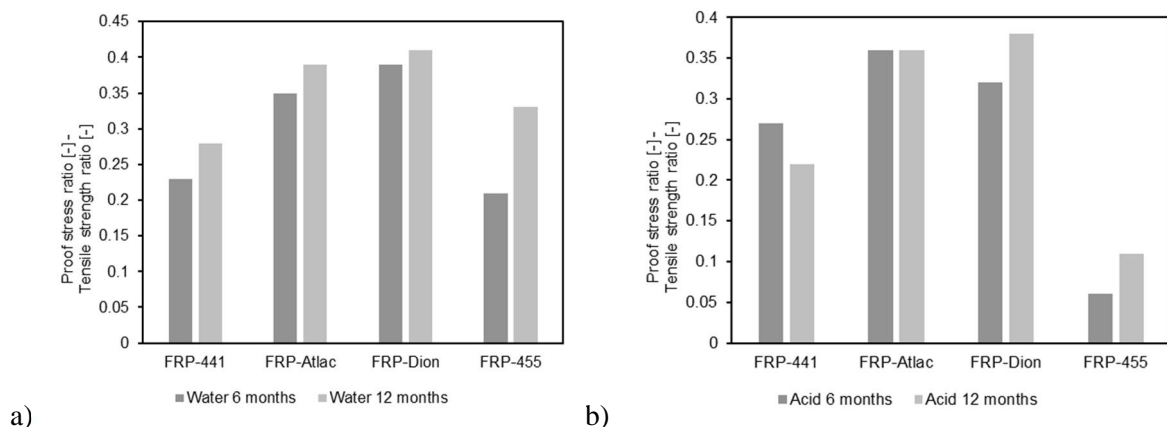


Figure 12: Comparison of the proof stress ratio with the tensile strength ratio (subtraction proof stress ratio – tensile strength ratio) when the laminates were conditioned 6 and 12 months in a) water immersion or b) acid immersion.

The damage onset, being often due to the first fibre breakage or crack in a resin-rich region or flaw, is typically expected to occur on the test specimen’s free surface. Therefore, the comparison in Fig. 12

indicates that the aging process of the composite results in even degradation over the entire laminate volume rather than attacking local details or flaws near the laminate surfaces. Subsequently, it is intuitively clear that the difference (proof stress ratio – tensile strength ratio) increases as a function of conditioning time when the diffusion and related chemical deterioration progress into the material. Indeed, the difference increases for the water immersion. However, the time-wise progress is not straightforward for the acid immersion (Fig. 12 b). Recent studies [29] have shown that glass-fibres go through significant degradation due to sulphuric acid immersion. It is hypothesized that the aging process of the laminates due to the H_2SO_4 immersion involves deterioration of the glass fibre reinforcement, which naturally affects greatly the ultimate strength of any continuous fibre reinforced plastic.

The discussion above raises the question whether it is advised to size FRP structures based on ultimate stress or proof stress. Due to the more pronounced effect of aging, ultimate stress would basically give a more conservative design – presuming a proper margin of safety between the proof stress level and a service loading. For the thick laminates studied here, the progression of any failure in the conditioned composite is significantly affected by aging and, thus, the proof stress (or strain) is a considerable design allowable for the sizing of structures. In other words, the damage tolerance after the onset of damage is a long-term conditioning-sensitive design parameter and is recommended to be accounted for when designing FRP structures with thick vinyl-ester laminates and a long service life.

5. Conclusions

This work studied the long-term performance of four different vinyl ester samples after different environmental conditioning. Based on the results, small water molecules can easily penetrate into the polymer matrix and actually be more harmful to the material than the corrosive substance. Water can degrade the FRP material by hydrolytic reactions and leaching of small molecules from the structure. It can also attack the interface region and/or cause ion exchange reaction in glass fibres. In this study, these changes in the material were shown to be more pronounced as the temperature was increased and the amount of humidity (the amount of H_2O molecules) was increased to full soak. The following conclusions can be made according to our analysis:

In all four vinyl ester composites, water immersion was more detrimental to the FRP samples than 5% H_2SO_4 at the same temperature causing the highest weight gain and the greatest decrease in tensile strength (up to 65%). The effect of environmental cabinet is small.

Reduction in the strength values does not automatically mean loss in stiffness: While water immersion caused the highest tensile strength decrease in FRP-Atlac, its stiffness properties were hardly affected. Proof stress decrease was the lowest in the FRP-Dion specimen, which had the most brittle base resin. Other FRP specimens showed higher reductions.

When comparing the different vinyl ester resins, the best long-term tensile strength values were obtained with Derakane 455, while the composite made of Atlac E-Nova FW 1045 showed the lowest values.

In water immersion, the ultimate strength deteriorates faster than the proof stress level leading to a decreasing damage tolerance of the thick vinyl-ester composite laminates.

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