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The influence of different glass fiber/epoxy matrix combinations on the durability under severe moisture impact

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Abstract. The growing success of fiber reinforced polymers (FRP) as material for the construction of high-performance lightweight structures used under maritime environmental conditions, requires foremost the knowledge about their long term durability. As the supplier market is still growing fast, methods which allow manufacturers to distinguish between suitable and less suitable composites are needed. In this study, the effects of moisture on the mechanical properties of glass fiber reinforced polymers (GFRP) using different glass fiber fabrics are investigated under several ageing and testing conditions. Focusing on the fabrics and introducing an ageing method prior to composite manufacturing, allows to describe the proportions of fiber, matrix, sizing and interphase damage to the composites durability in more detail. Absorption quantity related testing after ageing at temperatures between $8\,°C$ and $50\,°C$ highlights the resulting effects on the tensile strength of mostly unidirectional GFRPs. The strength of composites based on fabrics with high resistance to moisture degradation decreases steady but moderate during absorption. This effect is mainly associated with changes of matrix properties. However, less durable composites show a two-stage behavior. In this case, severe interphase damage and cracking leads to an additional drastic strength decrease when exceeding a defined amount of water absorption.

1. Introduction
The use of FRP in increasingly large, load-bearing structures like rotor blades of wind energy or tidal turbines requires detailed knowledge of their short and long-term properties to ensure safe use. Especially, years of exposure to high humidity and water, e.g. in terms of condensation or rain, can affect the material properties due to absorption related ageing [1]. Although the impact of moisture on mechanical properties of composites has been investigated for a long time, still to date, the interactions have not yet been fully described. In the past, various studies have been published reaching from short term up to 10 or 15-years in- and outdoor conditioning [2–6]. Therefore, it is known, that diffusion of water within composites affects the matrix [7], the fibers [8] and the interphase region [9–11] in different manners. But even for alike GFRPs, e.g. Starkova et al. [6] found recently that the effects of extreme long term ageing might result in entirely different material behavior and durability. In this particular example, the interlaminar shear strength of GFRP bars, which is strongly dependent on interphase properties, either did not decrease at all or decreased significantly. For amine-hardened epoxy resins used as matrix materials, absorption related effects like plasticization and swelling often weaken

the polymer and increase its ductility to some extent [7]. In this context, glass fibres are often associated with stress corrosion cracking [8], whereas these are usually protected from direct contact with water in the composite. However, as most often, authors concentrate on one specific material or extreme conditions like full saturation at elevated temperatures, it is hard to find general valid conclusions. Moreover, a comparison of different studies often fails due to different conditioning circumstances. Until today methodologies to investigate the durability of new material combinations within a reasonable amount of time are not standardized. Most recommended accelerated procedures are carried out under high temperature and raise the question of whether this causes additional damage. Therefore, this study aims to improve the understanding of how different glass fiber reinforced polymers perform under harsh environmental conditions by concentrating on accelerated ageing methods in combination with the choice of fiber systems. To avoid the need to carry out time-consuming studies for each possible combination in the future, the objective is to identify generally valid correlations. In particular, this study analyzes the effects of the ageing temperature, duration and amount of absorbed water on the tensile performance in detail.

The presented study is generally based on two different parts. One presents an accelerated ageing method for fiber fabrics that allows a specific manipulation of the composites fiber-matrix interphase. The results enable to identify the impact of a moisture degraded interphase on the composites tensile properties in and transverse to the fiber direction without changing the matrix properties. The second part focuses on conventionally produced and wet-aged unidirectional composites. It aims to enhance the knowledge about correlations between mechanical performance and various ageing or environmental conditions. The key issue in this part is the incremental influence of ageing temperature, duration and amount of absorbed water on tensile properties.

2. Materials and methods

2.1. Design of experiments
As it is difficult to distinguish between the proportions of fiber, matrix and interphase damage after ageing when performing one single mechanical test, the effects have to be separated somehow. The designed ageing method for pure glass fiber fabrics by humidity and temperature provides a possibility to concentrate on interphase effects. It uses the advantage that the humidity has direct contact with the fiber surface and sizing, thus, no diffusion through the matrix is necessary. So, the method provides fast results independently of the sample dimensions. Fabrics where stored at 50 °C and 80 % rel. humidity for 35 days in a climate chamber for ageing prior to resin infusion. A pre-investigation confirmed, that the duration of 5 weeks at 50 °C is sufficient for ageing as longer time was not decreasing the composites interphase performance further. Tensile fiber bundle tests and longitudinal tensile test of pre-aged composites were used to check that there is no essential damage that decreases glass fiber strength itself. Finally, a comparison of transverse tensile tests using the new method and classical accelerated ageing by immersion in 50 °C distilled water allows conclusions about the durability of individual composite systems. The test procedure is schematically presented in figure 1.

2.2. Materials, manufacturing and specimen preparation
All GFRP composites were manufactured using a resin transfer moulding (RTM) process at 50 °C for 16 h and an additional post-curing process at 80 °C according to the manufacturers' recommendation. Three glass fiber fabrics of different manufacturers were chosen for the study. The fabrics are used in wind energy application. Their denotation and most important properties are shown in table 1. While two of them contain backing fibres in each fabric layer, the SE 2020 fabric by Saertex consists only of aligned fibres stitched together by polyester yarn. In case of
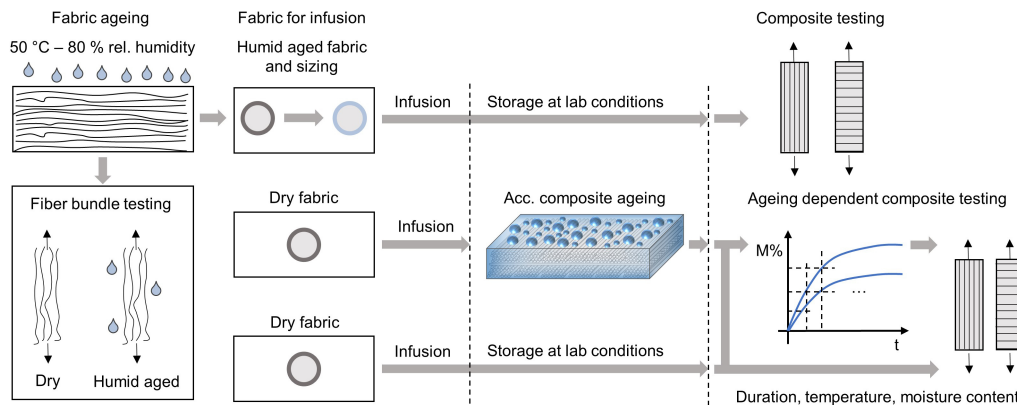
Figure 1. Methodology and test scheme for fabric and composite ageing.

the Hacotech G300U fabric, the backing fibers account for 15 % while the proportion is 10 % for the R&G 600 UD fabric. For reasons of a better comparison, results of the transverse tensile strength are presented in two ways. First, in terms of relative changes with regard to the measured strength at the knee point of the stress-strain diagram and second in absolute strength normalized to the proportion of backing fibers. This is done through micromechanics by the calculation of the stress acting in the 90-layers of the global stress acting on the total specimen cross-section. Furthermore, the thickness of the laminates is either 1 mm, 2 mm or 3 mm. The variations in thickness result from the targeted fiber volume content of 50 %, the fabric weight and the RTM frame availability. Results based on the duration are therefore normalized to the thickness. Focusing on the effects of fiber system selection, the two-component epoxy resin system consisting of Hexion EPIKOTE^{TM} Resin MGS^{TM} RIMR 135 and the amine hardener EPIKURE^{TM} Curing Agent MGS^{TM} RIMH 137 was used as matrix resin for every composite. GFRP specimen were prepared using an automatic saw with water-cooled aluminium oxide blades and subsequently checked for uniform quality. The fiber volume content φ_f was determined by burn of testing.

Table 1. Overview of the E-glass fiber fabrics structure and properties. All fabrics are sized with epoxy compatible sizes.

Supplier	Fabric	Fiber	Areal weight	0°	90°	Paper denotation
Saertex	UVE 977	SE 2020	977 g/m^2	99 %	1 %	SE 2020 UD
R&G	600 UD	—	600 g/m^2	90 %	10 %	R&G 600 UD
Hacotech	G300U	PPG 2002	373 g/m^2	85 %	15 %	PPG 2002 UD

2.3. Conditioning

In order to obtain data depending on ageing temperature, duration and water absorption, the chosen GFRP samples were aged immersed in distilled water at 8 °C, 30 °C and 50 °C, the fabrics in an environmental chamber (CTC256 from Memmert) at 50 °C at 80 % rel. humidity. Specimen were removed from conditioning for testing at defined points in time or respectively concerning the absorbed amount of moisture. This results in a crosswise comparable experimental scheme as shown exemplarily in figure 1. The presented results refer to ageing periods of up to 4000 h. Cutting edges were not coated to be able to evaluate the weight increase of single specimens.

2.4. Mechanical testing
Tensile tests in and transverse to the main fiber direction were performed with reference to DIN EN ISO 527-4 standard. Rectangular specimen of 250 mm length, 15 mm width for longitudinal and 25 mm width for transverse tests and their respective thickness were tested using a universal testing machine (Z100 from ZwickRoell) with 100 kN load cell and a mechanical extensometer. Fiber bundle tests were performed with reference to DIN EN 1007-5 standard, using a universal testing machine (Z2.5 from ZwickRoell) with 2.5 kN load cell and strain measurement via contactless video extensometer. The fiber bundles were glued to sandpaper at their gripping edges. This allowed a uniform load introduction.

3. Results and discussion

3.1. Water absorption characteristics
Diffusion characteristics of FRP are mainly determined by the absorption behavior of the matrix and the fiber-matrix interphase region [12–14]. In particular physical and chemical properties such as the polymer networks' polarity are the cause for water attraction and absorption [15]. Because all composites within this study are based on the same matrix resin, the water absorption can be analyzed in relation to the fabric used. Furthermore, the fiber volume, as well as pore and defect contents, have a direct influence on diffusion properties. Therefore, the characteristic water absorption at 50 °C is shown for the composites normalized to the fiber volume content and laminate thickness in comparison to the pure resin in figure 2(a). While the water absorption rate is almost identical, there are clear differences in the maximum content at the apparent saturation level. With about 3.57 m% (PPG), 3.12 m% (SE 2020) and 3.05 m% (R&G) the composites absorb more water in relation to the matrix proportion than the pure epoxy resin with 2.95 m%. The additional water absorption is a consequence of the absorbance due to the interphase areas, stitching yarns, as well as of pores and defects. Especially, for the PPG and the R&G composites extensive fiber-matrix debondings occurred beyond 2.40 m% weight gain and provided space for additional water uptake. In the case of the SE 2020 composite sporadic pores around the stitching yarns were found and can explain the additional uptake. These findings can be seen in section 3.4.

In figure 2(b) the water absorption at three different temperatures is exemplarily represented for the PPG 2002 composite. Elevated temperatures increase the absorption rate as well as the maximum moisture content significantly. During 170 days of ageing at 50 °C and 30 °C saturation was reached at 3.57 m% and 2.91 m% respectively. The further weight increases after reaching apparent saturation are supposed to be the result of arising space due to continued cracking and fiber-matrix separations. At 8 °C the saturation level is expected to be about 2.50 m% whereof already 2.25 m% were reached. So far, no debondings were identified.

3.2. Mechanical properties of dry, pre-aged and saturated composites
In figure 3 the bundle, longitudinal and transverse tensile strength of the fabric bundles and composites in dry condition are compared. Interestingly, only the transverse tensile strength differs significantly. While the SE 2020 and PPG composites have a sufficiently high transverse strength, this is already significantly lower for the RG composite. Thus, it can be seen that the interphase strength depends strongly on the compatibility of sizing and matrix. It should be mentioned that the given values have been mathematically corrected in the case of the fabrics with a cross-weft component in order to ensure better comparability.

Figures 4 and 5 show the effects of the fabric pre-ageing and the accelerated immersed ageing on tensile strength properties. By combining the tests, it can be demonstrated that the sizing of the fabrics degrades due to humid ageing in all cases. But as long as the matrix is dry and unaltered, this does not affect tensile strength in fiber direction. Furthermore, the pre-ageing
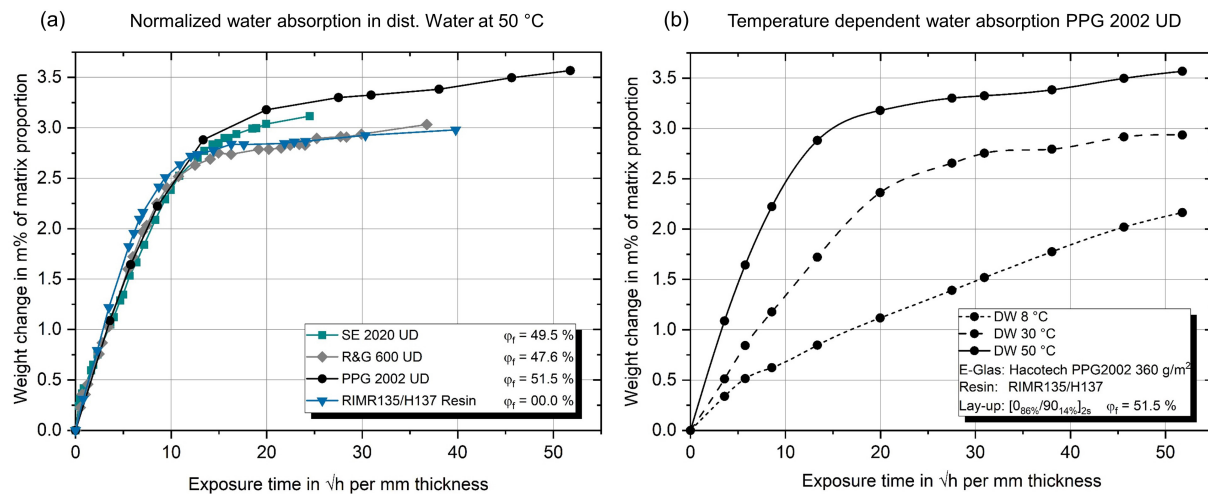
Figure 2. Water absorption characteristics of the composites and pure resin normalized to the fiber volume content immersed at $50\,^{\circ}$C (a). Exemplary temperature dependent water absorption of Hacotech PPG 2002 fabric based GFRP immersed at $8\,^{\circ}$C, $30\,^{\circ}$C and $50\,^{\circ}$C (b).
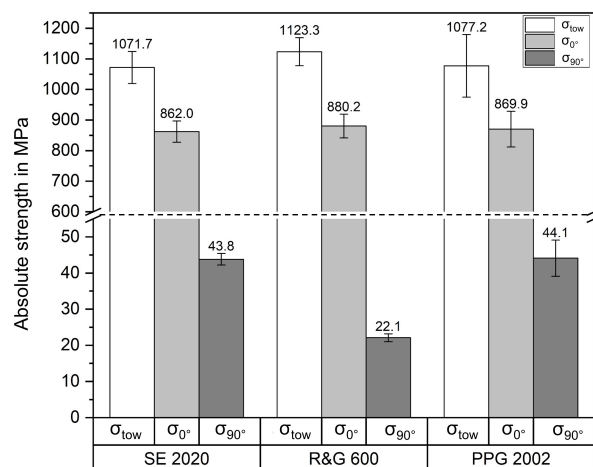

Figure 3. Absolute tow, longitudinal and transverse tensile strength of the studied fabrics and composites in dry reference condition.

indicates differences regarding the durability of the sizings, as the residual transverse strength in relation to the dry strength was found to be between 70 % in the best case and only 44 % in the worst. The wet ageing in comparison decreased the transverse strength just slightly stronger, which is likely mainly a result of a decrease in matrix properties and the additional weakening of the interphase. The differences in wet longitudinal tensile strength are also significant. Again, the SE 2020 composite performs best. Since the effects of the wet matrix should affect all systems equally, the results provide a clear indication that two overlying processes reduce the tensile strength in fiber direction. Classical ageing in a water bath not only causes plasticizing of the matrix, but also degradation within the interphase and perhaps of the fiber strength itself. Therefore, the extensive decrease of both, tensile strength in and transverse to the fiber direction, of the PPG and R&G composites is assumed to be a consequence of the more susceptible fabric sizes.
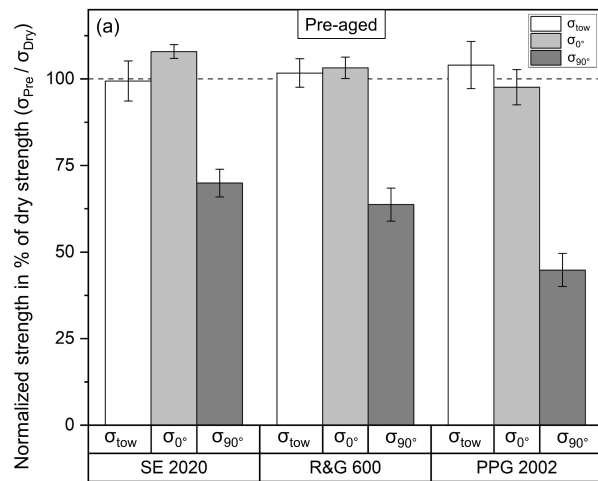
Figure 4. Normalized tow, longitudinal and transverse tensile strength of the studied fabrics and composites in pre-aged condition.
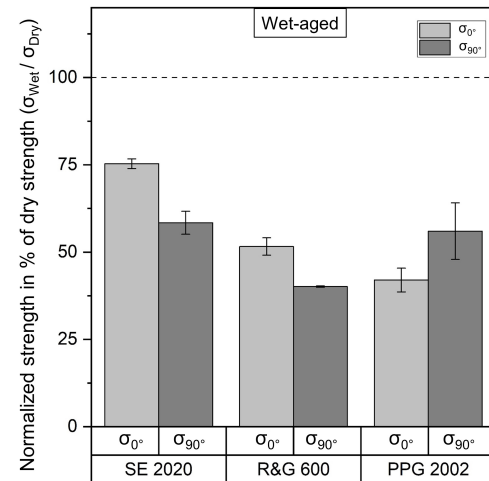
Figure 5. Normalized longitudinal and transverse tensile strength of the studied fabrics and composites in wet-aged condition.

3.3. Absorption and duration related strength properties

To improve understanding of the differences described above, the second part of the study does not only consider dry and saturated samples. In figure 6, the tensile strength in fiber direction is presented in relation to the amount of absorbed water for a total of 215 individual specimens. All specimen are categorised by their laminate type and ageing temperature. It becomes evident that there is a correlation between the increase in water content and strength. This correlation moreover shows a two-stage behavior. Up to a certain weight gain of about $2\,\mathrm{m\%}$, a moderate strength decrease by about $50\,\frac{MPa}{m\%}$ results almost independently of the specific composite type and ageing temperature. Above this level, the strength decrease becomes more drastic. Only in this region, significant differences between the single composites can be found. In the case of the PPG 2002 and R&G 600 based specimen, the additional strength decrease proceeds with about $200\,\frac{MPa}{m\%}$. At the same time, it was found by regular visual inspection, that local fiber-matrix debonding and cracking starts to occur within both composites as water absorption continues to increase. Finally, this results in a total strength reduction of about $50\,\%$. The SE 2020 composite on the other hand, shows no extensive debondings or cracking. Consequently, the strength reduction rate remains moderate and leads to a total strength decrease of $25\,\%$.

3.4. Absorption related damage behaviour

Microscopy of polished specimen cross-sections after ageing allowed to uncover the extent of damage which was introduced by water absorption. In figure 7 the damage pattern is shown representative for the R&G FRP. The defects, which can be seen in terms of opaque areas within the transparent laminate even by eye, are found to be massive cracks and delaminations. Typically, these defects arise within the densely packed areas of single fibre bundles and can reach all through a bundle. The details in figure 7 (b) and (c) show also, that fibres within the delaminated areas suffer from direct water contact. Since these kinds of defects have not been found for composites as long as the water absorption was explicitly lower than $2.4\,\mathrm{m\%}$ extensive absorption should be avoided. Damages like this are not reversible by drying and are expected to decrease the fiber strength.
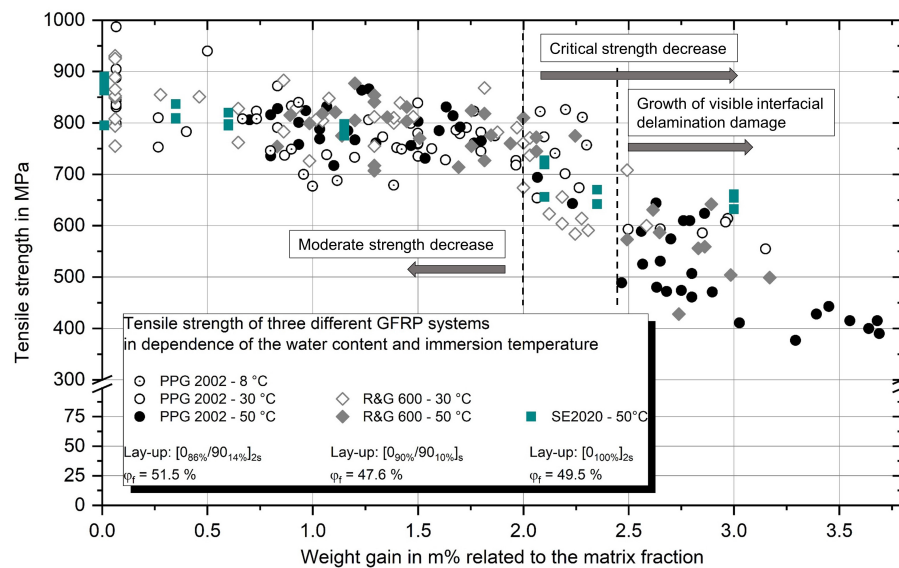
Figure 6. Interrelation between longitudinal tensile strength and amount of absorbed water in terms of matrix related mass increase. All fabrics are manufactured using the same epoxy resin.
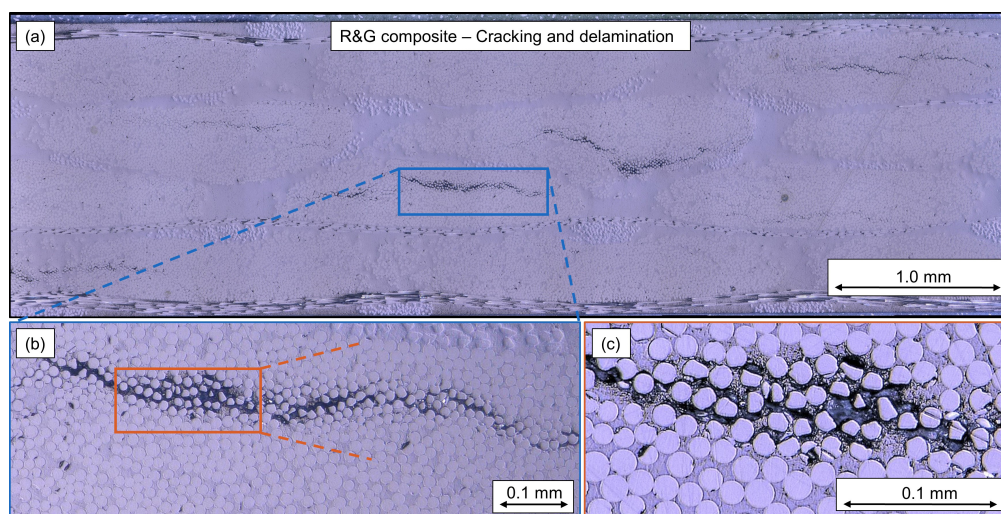

Figure 7. Exemplary microscopy of cracking and delamination damage due to water absorption for R&G composites after 4000 h in 50 °C distilled water.

4. Conlusions

In summary, the main conclusions of the presented study are:

- The introduced method of fabric conditioning allows producing composites of reduced interphase strength. But in contrast to wet-ageing methods, the matrix properties remain unchanged in this case. By combining both methods, ageing effects can now be separated. Thus, it could be demonstrated that the tensile strength in fiber direction does not change at all by weakening the interphase strength only. However, water absorption reduces the tensile strength due to plasticization and swelling stresses within the matrix and interphase. As far as the interphase damage leads to fiber-matrix debondings, the effects on the tensile strength become severe.

- A comparison of the different GFRPs investigated gives reasons to suppose that two superimposing effects characterise the durability of the composites tensile strength under marine conditions. Up to a certain level of water uptake, the strength decrease is mainly determined by the wet matrix resins characteristics. During this stage, the strength decrease is moderate and mostly independent of the specific fabric and sizing used. However, with increasing water absorption composites with sensitive fiber-matrix interphases tend to lose their integrity, which results in a drastic loss of strength. This is the main difference between marine suitable and unsuitable systems.

- The incremental study of unidirectional GFRP composites' tensile strength in fiber direction in terms of duration, temperature and amount of absorbed water led furthermore to three decisive conclusions. First, the amount of absorbed water or humidity is the main characteristic which affects the maximum tensile strength of unidirectional GFRP composites. Secondly, the ageing duration beyond saturation is less crucial, as strength was not further decreased when the apparent saturation level was reached. And thirdly, it has been shown that the only effect of elevated ageing temperatures (below T_g) seems to be, that they allow additional water to be absorbed.

- To find suitable fiber-matrix combination in terms of interfacial strength and to compare the durability of fabrics and their sizes under severe humid conditions the use of transverse tensile tests in combination with the fast fabric ageing method was found to be an efficient process.

Acknowledgments

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