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Marine Coolant Fluids' Effect on the Mechanical Properties of Glass Fiber-Reinforced Composites

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ABSTRACT

This study examines the effect of coolant and antifreeze solutions such as distilled water, ethylene glycol-based antifreeze with organic acid technology (OAT), and ethylene glycol-based antifreeze with inorganic inhibitors and glycerol (IAT/HOAT) on the tensile strength of glass fiber-reinforced polyester (GFRP-P) and vinyl ester (GFRP-VE) composites. Standardized specimens were produced and immersed in these solutions for three months at room temperature. Following exposure, tensile tests were conducted using the universal testing machine, supported by microscopic analysis to evaluate surface damage and internal structural changes such as composite layer delamination. The tensile test results show the highest decrease in tensile strength for GFRP-P specimens immersed in HOAT antifreeze (16.3%), whereas GFRP-VE specimens exhibit only a minimal reduction (3.4%). This difference is attributed to the higher chemical aggressiveness and alkalinity of the HOAT antifreeze. Furthermore, the decrease in the tensile strength of GFR-P exposed to OAT antifreeze is 6.1%, whereas GFRP-VE demonstrates a significantly smaller reduction of 1%, which can be attributed to the less aggressive chemical composition of the OAT formulation compared to HOAT. In contrast, the influence of distilled water on GFRP-P specimens is manifested as a tensile strength decrease of 12.7%, whereas GFRP-VE specimens show a reduction of 11%, attributed to the fluid's density and the rate of hydrolytic degradation. These results contribute to a deeper understanding of the effects of various coolant media on the performance of GFRP in marine cooling systems, highlighting GFRP-VE as a more suitable matrix for prolonged exposure to coolant environments.

1 Introduction

Fiber-reinforced polymer composites are widely used in the marine industry due to their excellent strength-to-weight ratio, corrosion resistance, and ability to form complex geometries. Glass fiber-reinforced composites (GFRP) materials are commonly employed in the construction of small vessel hulls, decks, tanks, pipelines, and equipment exposed to marine environments [1]. Structurally, GFRP consists of glass fibers (typically E-glass or S-glass) that carry the mechanical load, and a polymer matrix (most often unsaturated polyester, vinyl ester, or epoxy resin) that provides shape. Stress transfer and resistance to environmental effects were explained in [2] and [3].

Vinyl ester resins (VER) exhibit superior chemical resistance and lower moisture permeability compared to polyester resins (PR), making them a more favorable choice for aggressive environments such as fuel storage, various chemicals, and coolant media [4]. Exposure of GFRP materials to seawater, coolants, and hydrothermal conditions can significantly affect their mechanical properties; such influences include matrix degradation, weakened adhesion between fibers and resin, and the formation of microcracks [5]. GFRP-VE composites demonstrate higher resistance to moisture absorption and corrosion compared to GFRP-P composites [6].

Previous research confirmed that exposure of unsaturated polyester (UPR) and vinyl ester (VER) composites to aqueous environments and similar media is a

key factor in the degradation of their mechanical properties. Lee et al. [6] investigated the interaction of water with UPR, VER and acrylic resin, concluding that water causes hydrolysis of ester bonds and reduction in mechanical strength, with VER showing lower water absorption and greater resistance to degradation compared to UPR. Paczkowski et al. [7] analyzed the chemical resistance of composites based on UPR and VER resins and found that GFRP-VE exhibited significantly higher stability against hydrolytic processes, while GFPR-P showed susceptibility and marked decreases in strength after exposure to more aggressive liquids. Visco et al. [4] compared seawater absorption in different resins and confirmed that VER absorbs less water and better retains its mechanical properties compared to isophthalic polyester, while Ramakrishnan et al. [8] indicated that VER contains a lower proportion of ester groups in its chemical structure, making it more resistant to moisture and chemical media than PR.

The degradation of GFRP in marine environments occurs through several mechanisms, including water diffusion into the matrix, plasticization, hydrolysis of ester bonds, the formation of microcracks, and fiber matrix delamination [5], [9]. The extent of damage depends on temperature, exposure duration, salinity, and the pH value of the environment [1]. In addition to seawater, coolants (antifreezes) also play a key role in marine systems, as their chemical composition can affect the long-term stability of GFRP materials.

Antifreezes are categorized according to their corrosion inhibitor technology, such as IAT (Inorganic Additive Technology), OAT (Organic Acid Technology), and HOAT (Hybrid Organic Acid Technology) [10].

- IAT fluids contain silicate and phosphate inhibitors that form a protective layer but have a shorter service life.
- OAT antifreezes use organic carboxylate inhibitors that do not form a film but passivate metal surfaces and provide longer-lasting protection.
- HOAT variants combine carboxylates with smaller amounts of inorganic additives (e.g., silicates) to provide faster protection of aluminum components and compatibility with varied materials [11].

Coolants containing ethylene glycol and/or glycerol, along with specific additives, can cause changes in the matrix and interlaminar regions of GFRP during prolonged exposure due to chemical diffusion, plasticizer extraction, and alterations in surface energy [12].

A smaller number of studies have been specifically focused on the impact of coolant fluid use in marine environments, particularly in the context of larger ship systems and the specific applications of antifreeze. This research was motivated by the practical need to evaluate the effects of different coolants on GFRP materials commonly used in marine engineering. The aim of this study is to determine the effects of distilled water and ethylene glycol-based antifreeze with glycerol (Fricofin S; Inorganic Additive Technology, IAT – Hybrid Organic Acid Technology, HOAT), on the tensile strength and surface properties of GFRP-P and GFRP-VE composites after three months of exposure at room temperature. Through mechanical properties testing and microstructural analysis, this study seeks to provide key data on the compatibility of coolants and composites, and to recommend material selection for improved durability, reliability, and reduced maintenance costs in cooling systems where the tested antifreezes are applied.

2 Materials and methods

The materials used for specimens' fabrication were randomly chopped glass fibers, Easy Composites M705 (chopped strand mat) 450 g/m^2 in four layers, combined with an interlayer of woven roving 290 g/m^2, with dimensions of 50 x 50 cm [13]. For the matrix, UPR (POLIPOL 3401) was used for the first laminate plate, and VER (POLIVES 701) for the second laminate plate [14,15]. The curing reaction was initiated by adding MEKP catalyst (component B) at 2 % (m/m) of the resin, with mixing of the resin and hardener performed according to the manufacturer's recommendations [14,15] to ensure complete homogeneity of the mixture and optimal curing reaction. According to the technical datasheet, the catalyst composition includes 33-37% methyl ethyl ketone peroxide and 40 – 63% dimethyl phthalate [16]. The tensile strength and modulus of elasticity of the applied resins and glass fibers, as specified in the manufacturers' datasheets [13 – 15], are presented in Table 1.

The laminates were manufactured using a hand lay-up technique, chosen for their simplicity, low equipment requirements, and the ability to produce small-scale specimens with controlled fiber orientation, which makes it appropriate for laboratory investigations of GFRP materials [17]. This technique was applied since it is commonly used for building small boats and yachts [18]. The specimens were fabricated on a flat glass surface at room temperature. Twenty-four (24) specimens were produced: 12 polyester (P) and 12 vinyl ester (VE), in accordance with the ISO 527-4 standard. A three-month period was chosen as a preliminary test to establish the initial hypothesis. To confirm the hypothesis and obtain more relevant data, it will be necessary to continue the research for a longer period, spanning 6, 9, 12, 18 months, and 2 years.

After curing and drying in accordance with the manufacturer's instructions, the specimens were cut using the waterjet cutting machine Plesio 2515 at a cutting speed of 200 mm/min and an operating pressure of 3800 bar, ensuring dimensional precision and minimal thermal effects. Testing was performed in three fluids, i.e., solutions of different concentrations:

- Distilled water,
- TQ Antifreeze Long Life (ethylene glycol-based with organic acid technology inhibitors, OAT) – blue color, Fig. 1,
- Fricofin S (ethylene glycol-based with the addition of glycerol and sodium 2-ethylhexanoate, HOAT) – red color, Fig. 1.

These three fluids were selected because they are most commonly used as coolants in the cooling systems of internal combustion engines, as well as in other systems that require freeze protection and corrosion resistance. Specimens were manually immersed in sealed polypropylene containers to prevent evaporation and contamination. For each type of coolant and resin system, three specimens were tested (three specimens in one group).

The specimens were weighed before and after the testing, but since no differences in weight were observed, the weighing results are not presented.

To determine the effect of coolant water and antifreeze on the mechanical properties of the composite materials, a tensile strength test was performed using the universal testing machine Hegewald & Peschke Inspekt 20-1, which has a maximum load capacity of 20 kN. The tests were conducted in displacement-controlled mode at a crosshead speed of 3 mm/min to ensure uniform and controlled deformation of the specimen until the fracture occurred.

Microscope analysis was conducted using a Nikon SMZ745/745T optical microscope, Figure 3, which offers a magnification range of 3.35x to 300x (7.5x zoom) and a working distance of 115 mm, allowing for precise visualization of microstructural changes.

Table 1 Specifications of the materials used [8 – 10]

Materials	Tensile strength (MPa)	Modulus of elasticity (GPa)
POLIPOL 3401 (Polyester)	60	3.2
POLIVES 701 (Vinyl ester)	80	3.4
M705 CMS 450 g/m^2 (E-glass)	2000	73
Woven roving 300 g/m^2 (E-glass)	2100	74

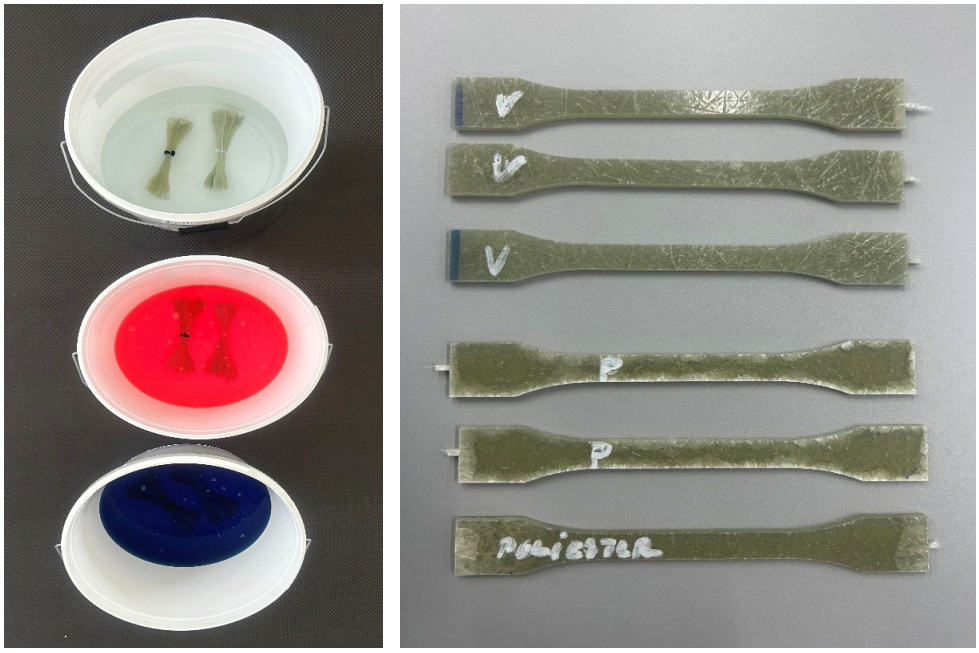

Figure 1 Examples of immersed and cut specimens

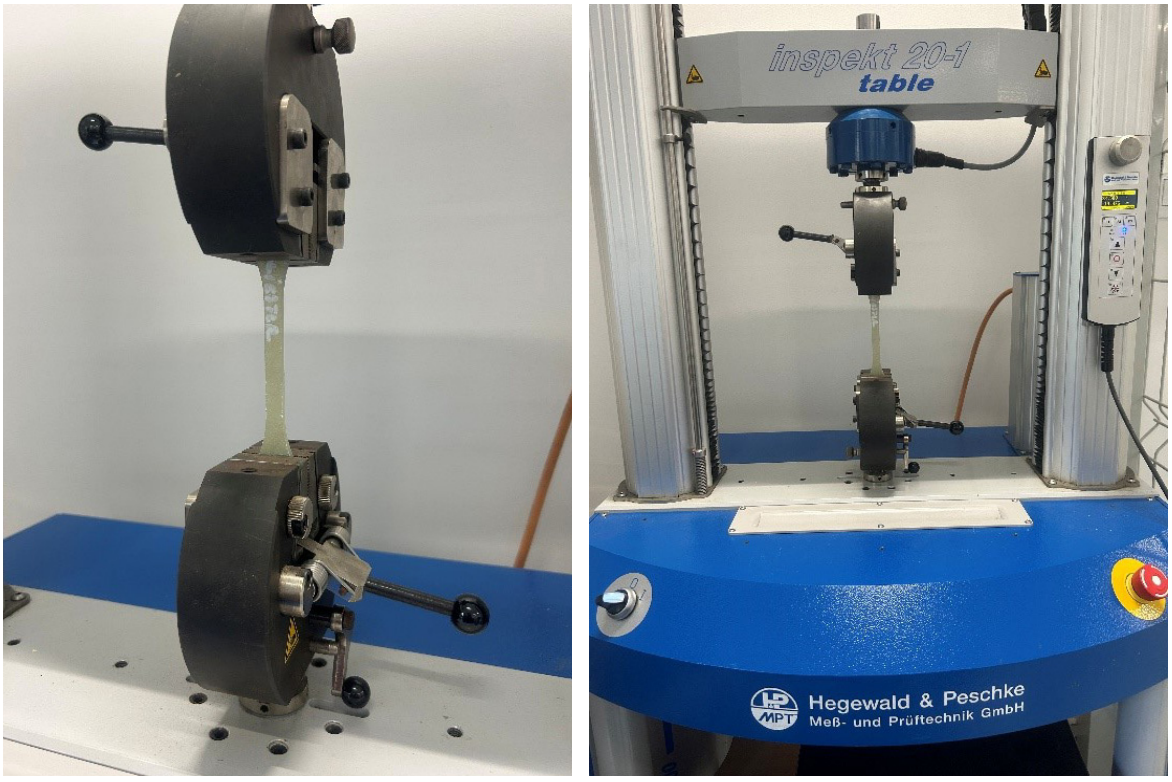

Figure 2 Testing setup

Figure 3 Nikon SMZ745/745T optical microscope

3 Results

The test results are presented in the form of the engineering stress-strain curves. This section also includes microscopic images of specimens' surfaces, providing a visual analysis of specimens.

Furthermore, calculations of arithmetic mean value ($\tilde{x}$), standard deviation (SD), coefficient of variation (CV), and specimens' tensile strength percentage reduction (TSR) are presented, in order to allow a comparison of reliability and consistency of the test results between polyester and vinyl ester specimens:

$$\tilde{x} = \frac{1}{n}\sum_{i=1}^{n} x_i \quad (1)$$

$$\mathrm{SD} = \sqrt{\frac{1}{n-1}}\sum_{i=1}^{n}(x_i - \tilde{x})^2 \quad (2)$$

$$\mathrm{CV}\,(\%) = \frac{\mathrm{SD}}{\tilde{x}} \times 100 \quad (3)$$

$$\mathrm{TSR}\,(\%) = \frac{\tilde{x}_s - \tilde{x}_{dv}}{\tilde{x}_s} \times 100 \quad (4)$$

where: $\tilde{x}$ – arithmetic mean, SD – standard deviation, CV – coefficient of variation (%), TSR – Tensile Strength Reduction (%), n = 3.

3.1 Dry specimens results

The diagram in Figure 4 presents the mean values of tensile test results of GFRP-P (MV P) and GFRP-VE (MV VE) specimens. The curves illustrate the behavior of GFRP under tensile loading. As stress increases, the curves initially rise linearly, gradually increasing the material deformation until the point of fracture (Ultimate Tensile Strength, UTS). The UTS mean value for the GFRP-P specimens is 147.2MPa, while the value for the GFRP-VE specimens is 151.3 MPa. Results indicate that both types of GFRP achieved comparable mechanical properties in a dry state.

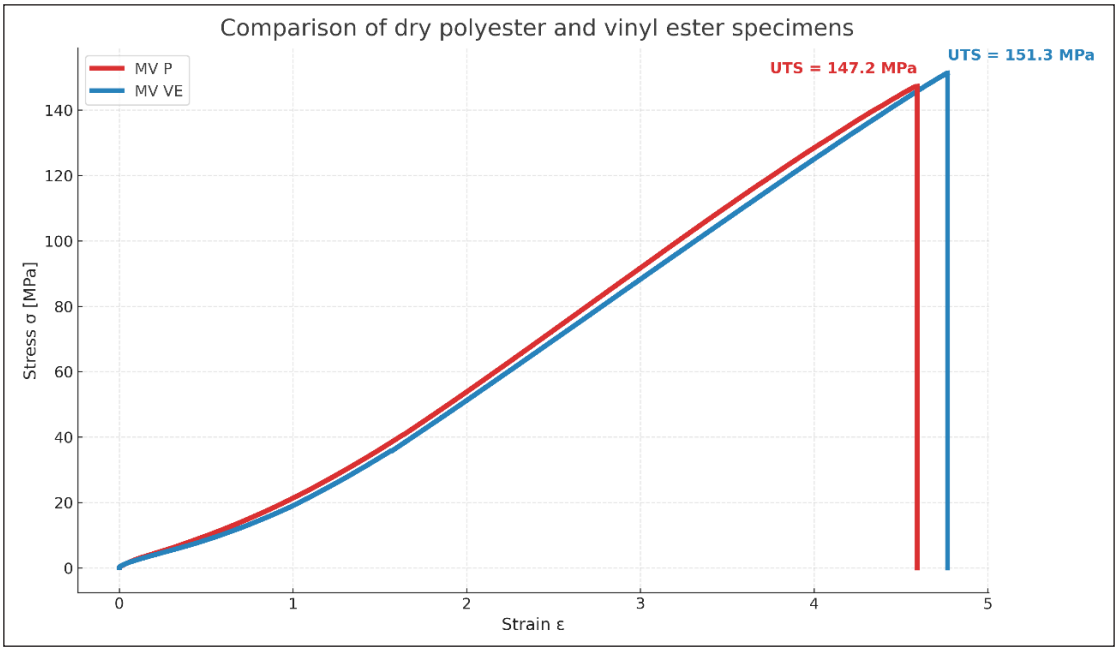

Figure 4 Stress-strain diagrams of dry specimens tested.

Table 2 UTS, x̃, SD and CV of stress values for GFRP-P and GFRP-VE dry specimens

Materials	UTS (MPa)	$\tilde{x}$ ± SD	CV (%)
Polyester (P)	141.2, 151.6, 148.9	147.2 ± 5.4	3.7
Vinyl ester (V)	146.1, 153.6, 154.1	151.3 ± 4.5	3.0

* Values are presented as mean ± standard deviation; CV indicates relative variability (a lower CV corresponds to more consistent results).

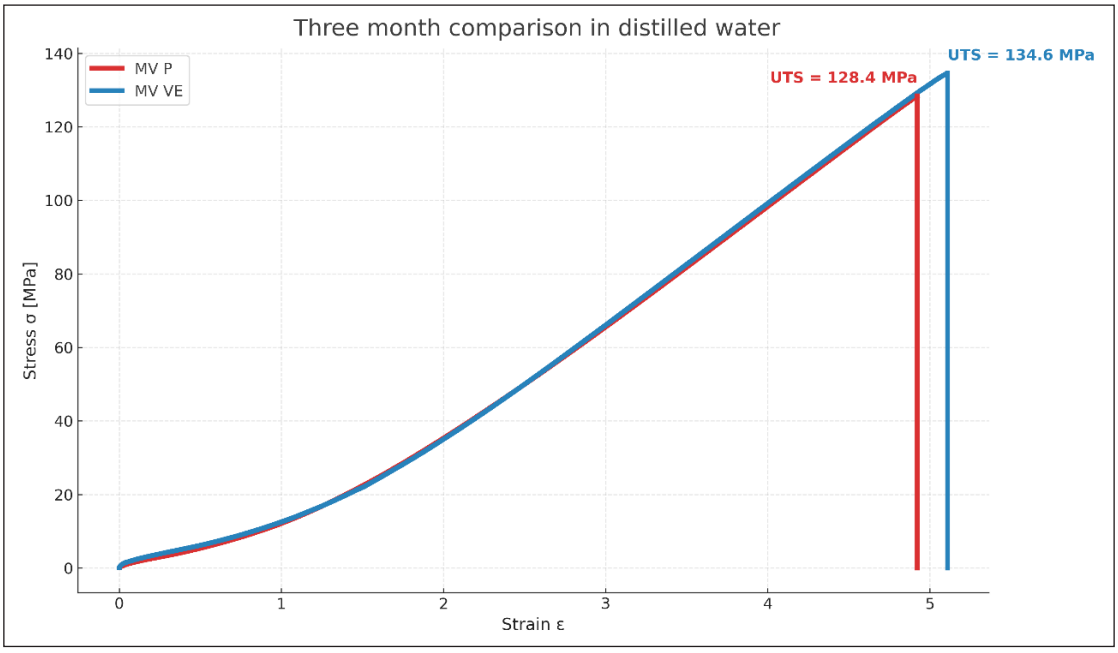

Figure 5 Stress-strain diagram of specimens immersed in distilled water

Table 3 UTS, x̃, SD, CV of stress values and TSR for GFRP-P and GFRP-VE specimens exposed to distilled water

Materials	UTS (MPa)	$\tilde{x}$ + SD	CV (%)	TSR (%)
Polyester (P)	113.9 128.4, 142.7	128.4 ± 14.4	11.2	12.7
Vinyl ester (V)	123.2, 140.4, 140.2	134.6 ± 9.9	7.33	11

3.2 Distilled water exposure results

The diagram in Figure 5 displays the mean values of the tensile strength of GFRP-P and GFRP-VE specimens exposed to distilled water for three months at room temperature. The results indicate a reduction in UTS compared to the dry specimens. The GFRP-P specimens achieved the mean value UTS of 128.4 MPa, while the GFRP-VE specimen reached a comparable mean value of 134.6 MPa. After three months in distilled water, GFRP-P tensile strength reduction of 12.7 % was noticed, while GFRP-VE specimens showed a decrease of 11 % compared to the dry specimens. These results highlight the sensitivity of both matrices to prolonged exposure to distilled water.

3.3 OAT antifreeze exposure results

The diagram in Figure 6 presents the mean tensile strength values of GFRP-P and GFRP-VE specimens after three months of exposure to OAT antifreeze at room temperature. The UTS mean value for GFRP-P is 138.2 MPa, and for GFRP-VE is 149.7 MPa. The results show a more pronounced reduction in tensile strength for GFRP-P, amounting to 6.1%, whereas GFRP-VE exhibited a significantly smaller average decrease of 1%, indicating that GFRP-VE has greater chemical resistance to degradation compared to polyester.

3.4 HOAT antifreeze exposure results

The diagram in Figure 7 shows the mean values of tensile strength for GFRP-P and GFRP-VE specimens after three months of exposure to HOAT antifreeze at room temperature. The results indicate a significant reduction in tensile strength for GFRP-P specimens, with a UTS mean value of 123.2 MPa, while the GFRP-VE specimens achieved a mean value of 146.1 MPa. The results confirmed superior mechanical and chemical properties of GFRP-VE, with a 3.4 % decrease in tensile strength, compared to a 16.3 % reduction for GFRP-P, indicating that GFRP-VE is a more suitable composite for long-term exposure to HOAT antifreeze.

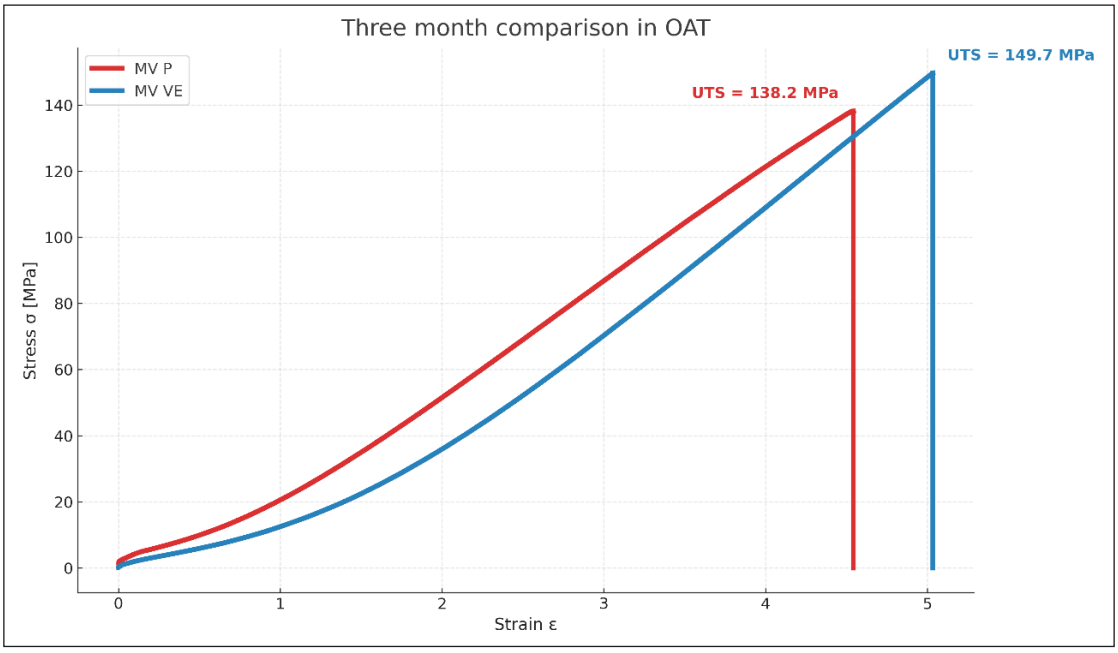

Figure 6 Stress-strain diagram of specimens immersed in OAT antifreeze

Table 4 UTS, x̃, SD, CV of stress values and TSR for GFRP-P and GFRP-VE specimens after 3 months exposure to OAT antifreeze

Materials	UTS (MPa)	$\tilde{x}$ + SD	CV (%)	TSR (%)
Polyester (P)	135.4, 138.5, 140.8	138.2 ± 2.7	2.0	6.1
Vinyl ester (V)	144, 151.6, 153.6	149.7 ± 5.1	3.4	1

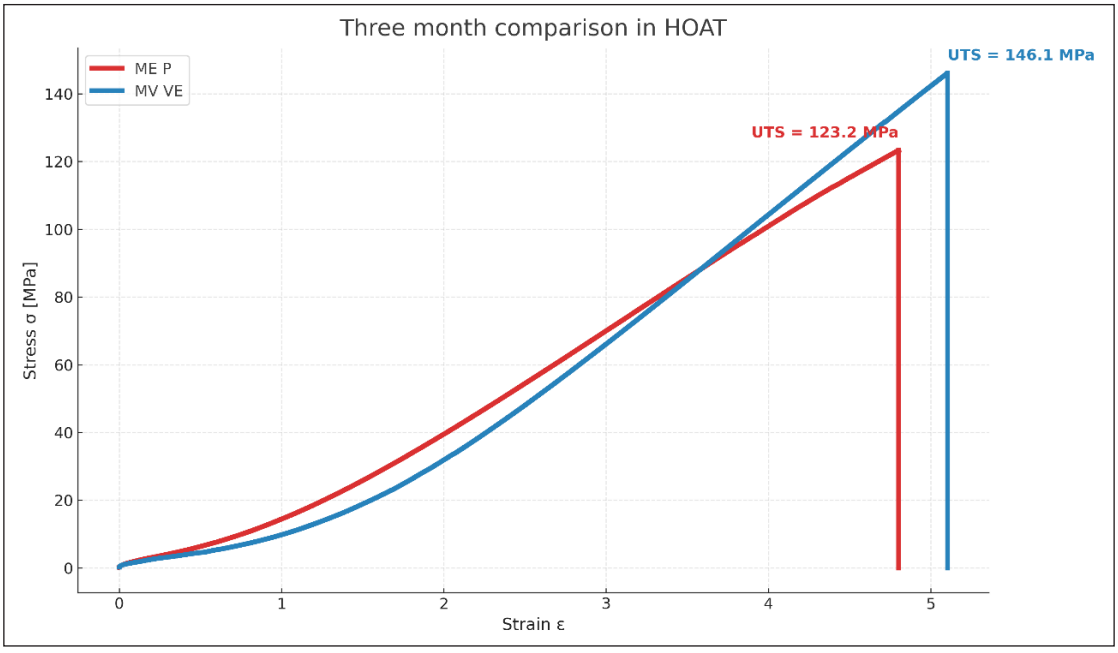

Figure 7 Stress-strain diagram of specimens immersed in HOAT antifreeze

Table 5 UTS, x̃, SD, CV of stress values and TSR for GFRP-P and GFRP-VE specimens after exposure to HOAT antifreeze

Materials	UTS (MPa)	$\tilde{x}$ + SD	CV (%)	TSR (%)
Polyester (P)	116.6, 121.5, 131.5,	123.2 ± 7.6	6.2	16.3
Vinyl ester (V)	133.7, 152.1, 152.6	146.1 ± 10.8	7.4	3.4

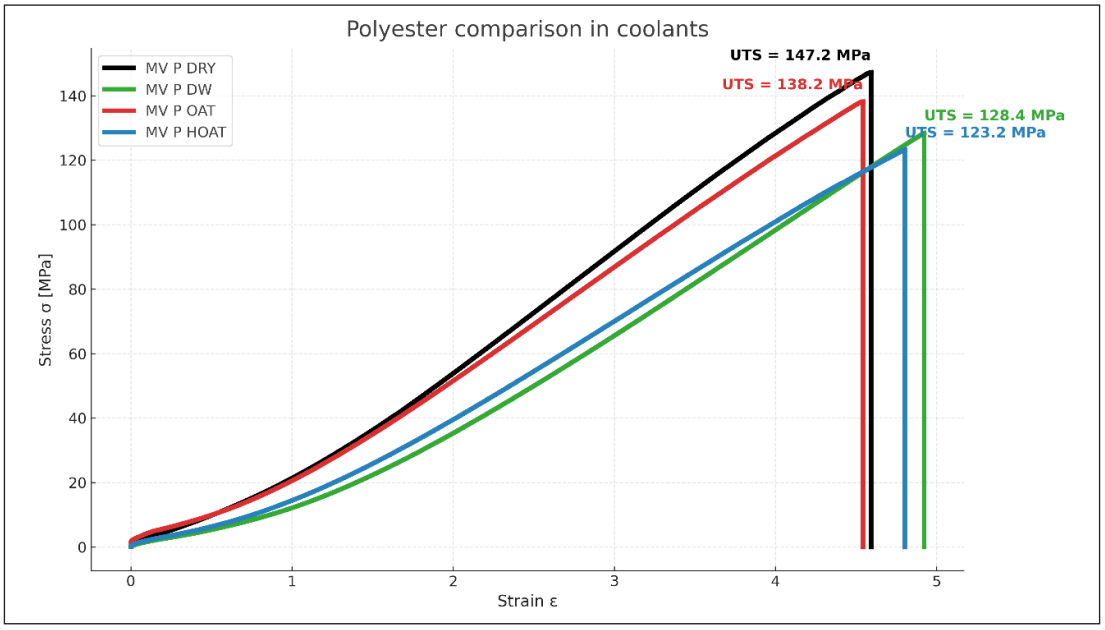

Figure 8 Stress-strain diagram of GFRP-P exposed to coolants

3.5 Polyester in coolants

The diagram in Figure 8 shows a comparison of the mean tensile strength values for GFRP-P specimens after three months of exposure in different coolants, relative to the dry state. The reference dry specimens reached a UTS of 147.2 MPa, in OAT of 138.2 MPa, in distilled water of 128.4 MPa, and in HOAT antifreeze of 123.2 MPa. The results indicate that OAT antifreeze has the mildest effect on the reduction of stress, whereas HOAT antifreeze has the most pronounced impact on the mechanical properties of GFRP-P.

3.6 Vinyl ester in coolants

The diagram in Figure 9 shows a comparison of the mean tensile strength values for GFRP-VE specimens after three months of exposure to different coolants, relative to the dry state. The reference dry specimens yield a UTS mean value of 151.3 MPa, 134.6 MPa in distilled water, 149.7 MPa in OAT antifreeze, and 146.1 MPa in HOAT antifreeze. The results indicate that OAT antifreeze has the mildest effect on the specimen's stress, while the specimens immersed and exposed to distilled water show a reduction in tensile stress.

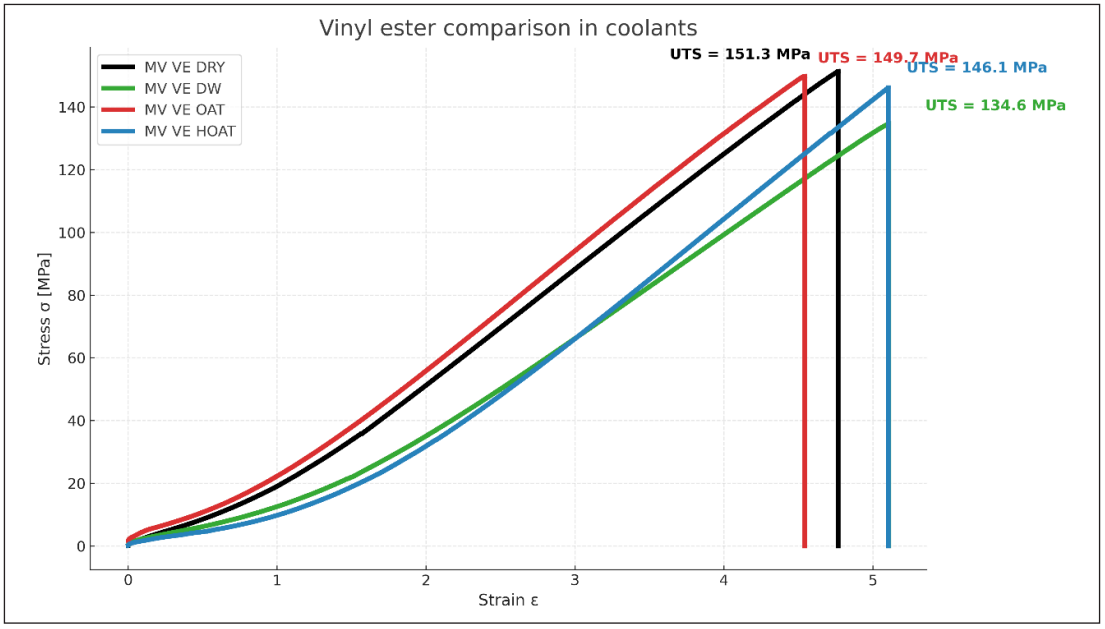

Figure 9 Stress-strain diagram of GFRP-VE exposed to coolants

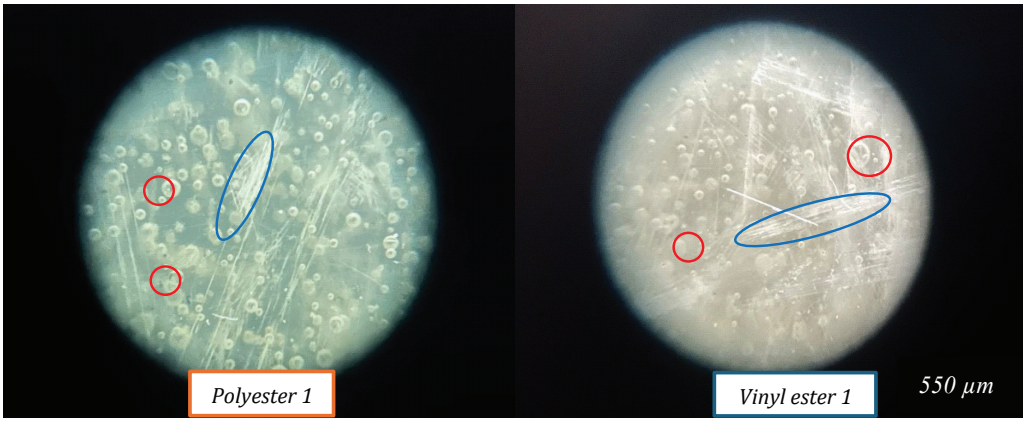

Figure 10 Surface microstructure of dry specimens

3.7 Microscopic analysis of specimens

Microscopic analysis was conducted using a Nikon SMZ745T stereo microscope to assess fabrication defects, including porosity, microcracks, and air voids. A cross-sectional microscopic analysis of the specimens was also conducted, revealing no signs of matrix delamination. Probably due to the short exposure period, the delamination process had not yet begun, or the changes were so small that they could not be observed with the microscope used. Since no delamination was identified between the dry and exposed specimens, images are not presented. Figure 10 shows GFRP-P and GFRP-VE specimens in dry conditions, where air voids and surface defects are visible.

The results of the microscopic analysis reveal the presence of air voids and surface defects in all specimens, which are attributed to the fabrication process. Air bubbles are a typical consequence of the hand lay-up lamination technique, and it is essential to note that an acceptable void content is typically up to 2-3% of the volume [19]. In this paper, the precise air void content was not quantified; however, microscopic analysis revealed no significant visual differences among the specimens, apart from those noted in Figure 10, which are unlikely to have influenced the mechanical test results.

4 Discussion

The analysis of tensile test results indicates that GFRP-P is more sensitive to the effects of the coolant compared to GFRP-VE. In the dry state, both matrices exhibited higher tensile strengths. However, after exposure to distilled water, OAT, and HOAT antifreeze, a reduction in mechanical strength and deformation was observed, indicating an increase in brittleness of the polymers. The greatest decrease in tensile strength was recorded in GFRP-P specimens exposed to HOAT antifreeze, with an average reduction of 16.3%, while GFRP-VE under the same conditions showed a decrease of only 3.4 %. The effect of OAT antifreeze was also more pronounced in GFRP-P specimens, with tensile strength reduction of 6.1 %, compared to TSR of 1 % in GFRP-VE specimens.

Microscopic analysis of GFRP-VE specimen 1 (Figure 10) revealed a higher presence of air voids in the matrix, compared to the other two in the same group, which is probably the reason for a greater decrease in tensile strength (5,2 %). The GFRP-P specimen 1 also had higher voids and production defects compared to the other two specimens, with a TSR of 6.9%. The results indicate that processing-related factors, such as residual air during hand lay-up, can influence mechanical properties and, under certain conditions, outweigh the chemical properties of the resin. Since hand lay-up involves manual resin application without vacuum, the formation of a higher number of air bubbles and increased porosity is characteristic compared to industrial methods such a vacuum infusion. Such porosity may partially reduce the absolute values of tensile strength; however.

For OAT antifreeze, a smaller reduction in tensile strength was observed compared to distilled water, which can be attributed to the difference in density between the coolant water and OAT antifreeze. The presence of organic inhibitors and ethylene glycol, due to their higher density, partially slows down diffusion and the rate of hydrolytic impact on the matrix. In contrast, distilled water more easily penetrates the matrix and accelerates the hydrolysis of ester bonds, leading to fiber-matrix debonding and increased brittleness [6].

The greatest reduction in mechanical properties was observed in specimens exposed to the HOAT concentrate, which can be attributed to its chemical composition. Ethylene glycol, combined with glycerol, increases the aggressiveness of the solution by facilitating diffusion through the polymer matrix. Meanwhile, sodium 2-ethylhexanoate creates a more alkaline environment, which chemically accelerates the degradation of ester

bonds in polymer matrices, particularly in polyester resins. Such hydrolytic and chemical degradation leads to fiber-matrix debonding, the formation of microcracks, and a marked decrease in tensile strength; however, this is not observed in this study. It can be assumed that it exists even though it was not visible with the microscope used. GFRP-VE specimens proved to be more resistant, as confirmed by Thomason et al. [3], since they contain a lower proportion of ester groups and possess a denser cross-linked network than GFRP-P, which slows down fluid diffusion and reduces hydrolytic degradation, resulting in a significantly milder reduction of mechanical properties.

5 Conclusion

The research confirmed that GFRP-P and GFRP-VE respond differently after three months of exposure to distilled water, OAT and HOAT antifreezes. Tensile strength analyses demonstrated that GFRP-P is more sensitive, while GFRP-VE retained greater mechanical resistance across all groups. In the dry state, both resins exhibited the highest tensile strength, whereas after exposure to distilled water, OAT, and HOAT antifreeze, a decrease in strength and increased brittleness were observed.

The greatest reduction in tensile strength was recorded in GFRP-P exposed to HOAT antifreeze. In distilled water, a greater reduction was noted compared to OAT antifreeze.

Microscopic cross-section analysis revealed no matrix delamination or significant porosity; however, the capabilities of the microscope used should be taken into account, as the authors were unable to utilize an electronic microscope. The defects resulting from the hand lay-up process are considered typical; yet, they confirm that technological factors can play a significant role in determining mechanical properties. GFRP-VE specimens proved more resistant due to their denser cross-linked network and lower proportion of ester groups, which reduces hydrolytic degradation and provides better chemical performance for long-term exposure to fluids used in cooling systems.

Further research should focus on more precise microstructural analysis using electronic microscopy (SEM/EDM) to gain better insight into porosity and early degradation mechanisms, combined with extended samples exposure interval (6, 9, 12, 18 months, and 2 years), to capture long-term effects, as well as increasing the number of specimens to improve statistical reliability and sensitivity to different cooling media.

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