TENSILE BEHAVIOR OF PULTRUDED COMPOSITE RODS EXPOSED TO DIFFERENT ENVIRONMENTAL CONDITIONS

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Abstract

This work presents an experimental study on the residual tensile strength (ASTM D3916/ASTM D7205) of four types of pultruded rods made of carbon and glass fibers reinforcing epoxy and vinyl-ester polymer matrices subjected to accelerated degradation in sea water (ASTM D1141) and hot water (ASTM D570), with an exposure time of 744 h for each aging treatment. The thermal stability of the aged rods was analyzed by thermogravimetry (TGA) and differential scanning calorimetry (DSC). It has been concluded that, the rods with vinyl-ester matrix and carbon fiber reinforcement showed higher residual strength after hot water aging, with loss less than 5% in mechanical properties.

1. Introduction

In recent years, the limited durability of civil engineering structures using traditional materials such as steel and concrete, coupled with increasing maintenance costs, has allowed for the use of innovative materials, including fiber-reinforced polymers (FRP) [1,2]. In this sector, the use of pultruded composites has been particularly prominent, fulfilling an important role in the development of more advanced civil construction technologies. FRP pultruded rods have been used in an increasing number of applications because of their low density, high strength and stiffness, relatively low maintenance costs and non-corrosive behavior as compared to traditional materials.

There are already several examples of bridges and buildings that have rods as structural elements [3-4]. These structural applications were initially driven under pilot projects or research, but are now finding their own way in terms of perspective to other sectors such as deep-water platforms [5-6].

The aging and degradation mechanisms of FRP pultruded rods still need to be completely understood, particularly the damage mechanisms under in-service conditions typically found in offshore and deep-water environments. Humidity, temperature, UV radiation, among others aging effects must always be considered in the design stage of composites parts, components and structures [7-8]. For instance, moisture penetrates in the polymeric matrix by diffusion process until the equilibrium concentration is reached, and this mechanism is accelerated by temperature increase (thermal activated). Indeed, the hygrothermal conditioning is one of the most deleterious treatments for FRPs. The effects of hygrothermal aging (in distilled water or saline solution) on the properties of rods with different types of polymer matrices and reinforcing fibers is of extreme importance for deep-water applications as in oil field platforms [9].

In this work, pultruded rods of carbon and glass fibers-reinforcing epoxy and vinyl-ester polymer matrices were subjected, respectively, to immersion in distilled water at 60 °C (hot water) and in sea water also at 60°C, during a time period of 744 hours in each case. The resistance to hygrothermal degradation was measured in terms of residual tensile strength and after-aging thermal stability of the FRP rods.

2. Materials and Methods

Data of four types of pultruded FRP cylindrical rods supplied by a Brazilian company are presented in Table 1 (manufacturer's data).

Sample Code	Fiber	Matrix	Diameter (mm)
CE30	Carbon	Epoxy	3.0
CV30	Carbon	Vinyl-ester	3.0
VE30	Glass	Epoxy	3.0
VV30	Glass	Vinyl-ester	3.0

Table 1. Rods' specifications as supplied by the manufacturer.

Accelerated aging tests in hot water were carried out based on ASTM D570 standard. The rods were immersed in distilled water and kept at 60 °C for 744 h in a heating chamber. The saline solution simulating sea water was prepared according to ASTM D1141 standard. Three types of solutions were formulated with the substances listed in ASTM D1141 standard, anhydrous sodium chloride ($NaSO_4$), in 20 L of distilled water. The rods were immersed in the solutions and kept at 60°C for 744 h in a heating chamber.

The main microstructural aspects of the pultruded composite rods were revealed with the aid of an optical reflected light Carl Zeiss microscope. The volume fraction of carbon fibers in composite rods was determined by acid digestion with sulfuric acid according to ASTM D3171 standard. In glass fiber composite rods, the volume fraction of the reinforcing phase was estimated via calcinations according to ASTM D2584 standard. Density measurements of rods in pristine and aged conditions were performed in triplicate by pycnometry according to ASTM D792.

Thermogravimetry (TGA) was conducted to evaluated thermal stability of the composites after aging of all rods, employing a Shimadzu Instruments Model TGA-50, the temperature range from 20 to 900°C, with a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) was utilized to evaluate the curing behavior of resins before and after the aging treatments. Measurements were carried out in a TA Instruments Model Q20 V24.2 in the temperature range from 20 to 330°C, with a heating rate of 10 °C/min.

Tensile residual strength was evaluated with a combination of ASTM D-3916 and ASTM D-205 standards. Tests were performed at ambient temperature in an MTS machine (model MTS Landmark Servohydraulic Test System with 370.10 Load Frame and FlexTest 40) with a 100 kN load cell, applying a crosshead rate of 5 mm/min. Typically, five test coupons were tested for each evaluated condition.

3. Results and discussion

3.1 Microstructural characterization

As shown in Figure 1, the rods have a typical pultruded structure with few voids and a high fraction of fiber-reinforcement, as listed in Table 3. The fibers are all aligned, homogeneously distributed in the resin and well compacted, revealing good resin infiltration during the manufacturing process, which can be better appreciated in Figure1a referring to the glass fiber / vinyl-ester composite (VV30). These characteristics are much desired because they are directly related to improved mechanical and physical properties of processed materials. The values of diameter, density and fiber volume fraction of the rods in the as-received condition are presented in Table 2.

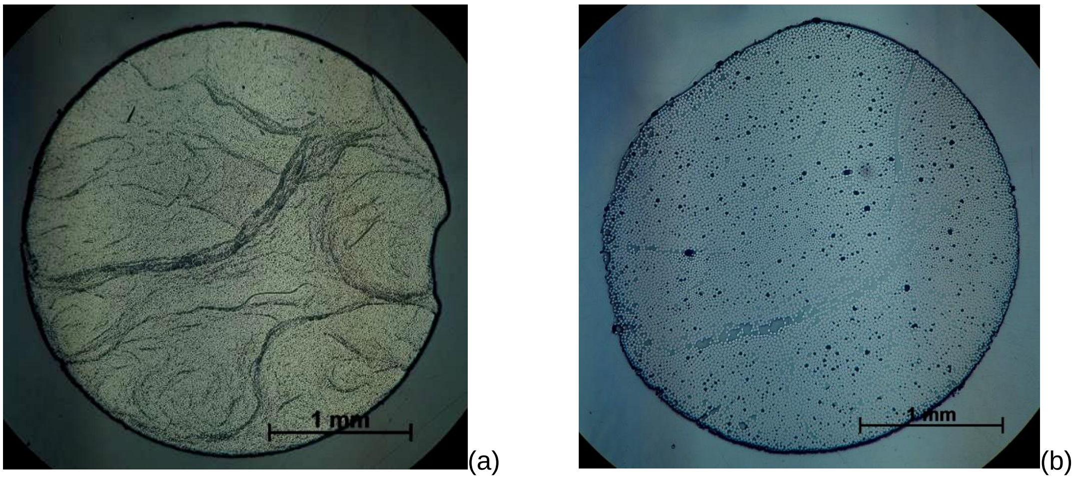

Figure 1. Micrographs of the cross section of the rods: (a) CV30, and (b) VV30.

Samples	Diameter (mm)	ρ (g/cm^3)	V_f (%)	Method
CE30	3.00±0.02	1.50±0.04	69.31±0.62	Digestion
CV30	3.02±0.02	1.51±0.07	67.59±0.47	Digestion
VE30	2.96±0.05	1.97±0.10	74.38±0.29	Calcinations
VV30	3.08±0.03	1.98±0.13	71.71±0.13	Calcinations

Table 2. Values of diameter, density and volume fraction of the pristine rods.

With respect to the visual aspects of the aged rods, only a change in the VE30 glass rods after seawater aging was noticed, as shown in Figure 2. Damages known as osmotic bubbles [10], typically displayed by composite laminated structures presenting a resin-rich surface when immersed in aqueous solutions, are indicated by an arrow. This resin-rich layer acts as a protective barrier to the moisture ingress, protecting the fibers from degradation. The observed phenomenon is explained by the osmotic effect, where the moisture (water) is constantly expelled from the composite, causing the bubbles to form in its surface.

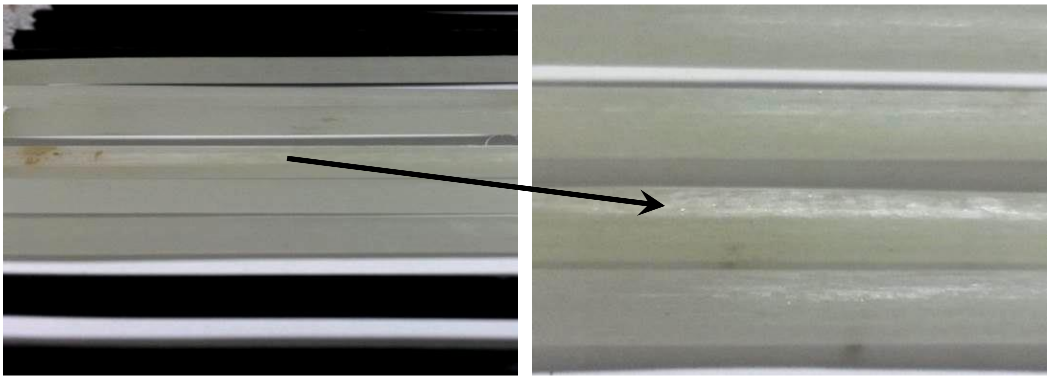

Figure 2. Visual aspects of the damage generated by seawater aging in VE30 rods.

Previous studies [11] reported that the presence of salts such as NaCl in aqueous solutions results in a reduction of saturation, and this trend is clearly observed in the current study. According to [12], the cross-linked matrix acts as a membrane permeable to water, but impassable to large inorganic sites. As a result, these ions can function as osmotic centers. In this case, the water with salts and the increase of the temperature of the water cannot be correlated with the increase in density and consequent increase in water absorbed by the composite as observed in Table 3. There were weight loss, in function of the density, probably these loss were caused by extraction of low molecular weight components through an immersion effect, as reported in previous studies [9].

Samples	ρ (g/cm³) AS-RECEIVED	ρ (g/cm³) SEA	ρ (g/cm³) HOT
CE30	1.50 ± 0.04	1.43 ± 0.02	1.42 ± 0.03
CV30	1.51 ± 0.07	1.47 ± 0.01	1.44 ± 0.03
VE30	1.97 ± 0.10	1.97 ± 0.03	1.95 ± 0.03
VV30	1.98 ± 0.13	1.92 ± 0.06	1.88 ± 0.02

Table 3. Density values of the rods after aging in, respectively, sea and distilled hot waters.

3.2 Thermal analysis

The rods did not show large thermal variations as a result of hygrothermal aging as can be seen in Figures 3 and 4. In carbon FRP rods (Figure 3) two drops in the remaining mass curve are present in the temperature range investigated.

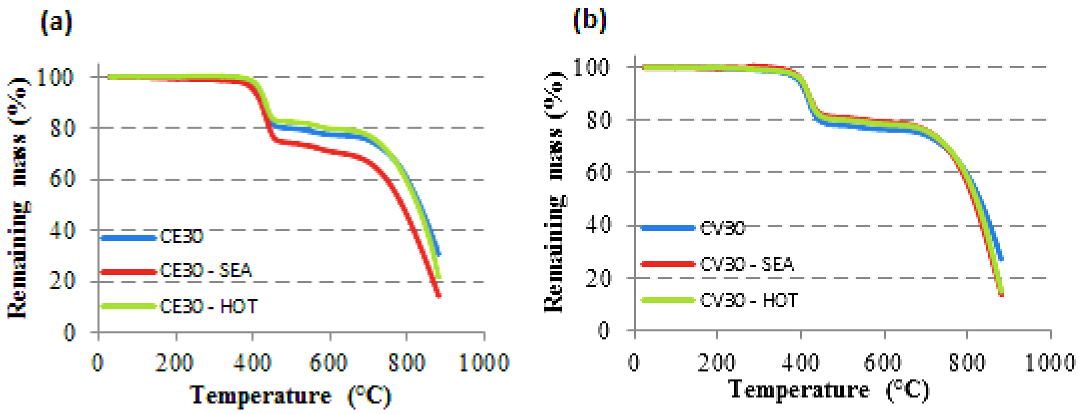

Figure 3. TGA thermograms of carbon fiber rods before and after different aging treatments: (a) CE30, and (b) CV30.

The first drop is linked to the polymer matrix degradation and the second one to oxidation and decomposition of carbon, releasing carbon dioxide (CO_2), exactly when there is an exchange of nitrogen to synthetic air (600 °C). Only the CE30-SEA composite rod showed a more pronounced mass loss, indicating a higher salt-attack of carbon fibers.

None of the rods had their thermal stability affected by the presence of aging salts or as a result of temperature increase. The calorimetric analysis of carbon fibers rods immersed, respectively, in distilled water at 60 °C and in simulated sea water at 60 °C showed different behaviors depending on the polymer matrices studied. The epoxy rods (CE30-SEA and CE30-HOT) showed practically the same behavior, as seen in Figure 5a. The first drop in the curve refers to T_g and is well defined for the as-received CE30 rod (123 °C). The second drop at approximately 190 °C may be related to the crosslinking of the resin chains. After both the aging treatments this drop seems to disappear, indicating that the aged rods were post-cured during the hygrothermal conditionings.

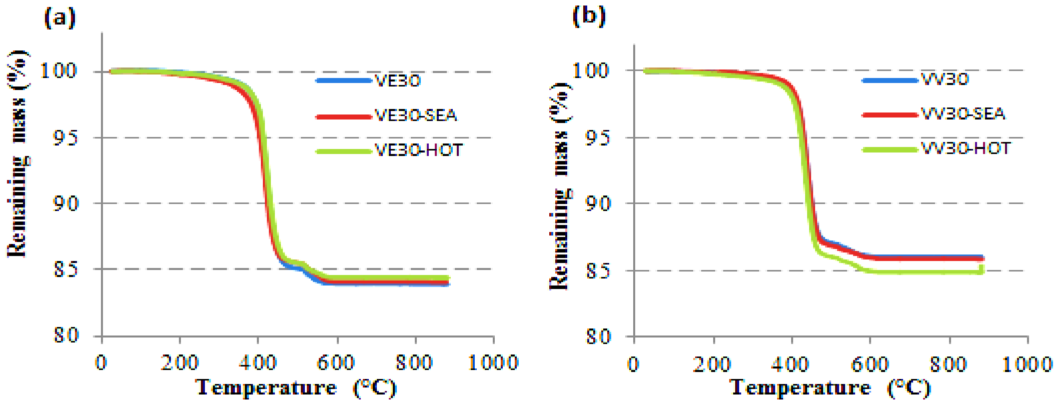

Figure 4. TGA thermograms of glass fiber rods before and after different aging treatments: (a) VE30, and (b) VV30 (b).

The rods manufactured with carbon fibers / vinyl-ester matrix composite also exhibited signs of post-curing during both aging treatments, as seen in Figure 5b. The T_g of the pristine CV30 rod is about 73 °C, as can be seen in the scarcely visible first drop of heat flow curve, and the second drop at 164 °C indicates crosslinking of the resin chains.

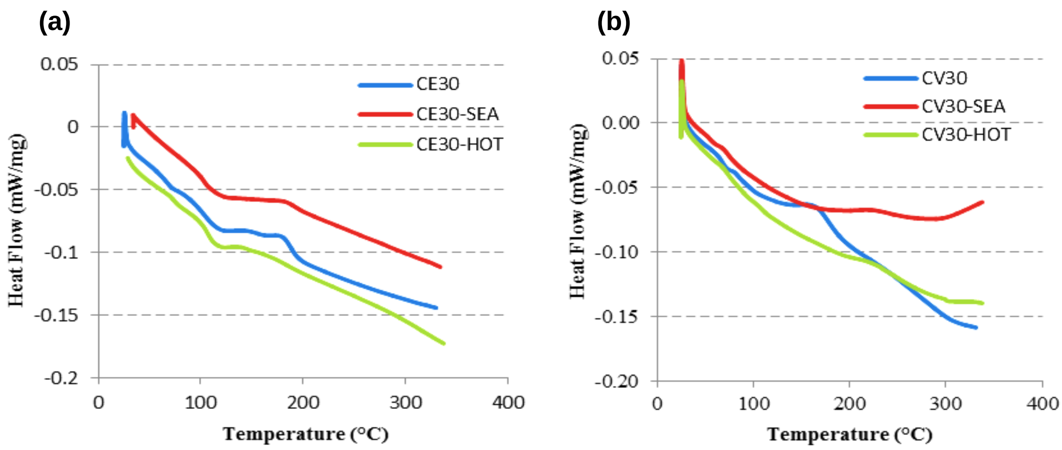

Figure 5. DSC thermograms of carbon fiber rods before and after different aging treatments: CE30 (a), and CV30 (b).

The same thermal behavior is observed for the calorimetric curves of glass fiber rods in Figure 6. The values of T_g of rods VE30 and VV30 are indicated by the first slope of the curve at 95 and 104°C, respectively. After aging, for both kinds of rods, the second slope of the curve disappears, indicating post-curing during the hygrothermal conditionings.

This post-curing is connected to curing of residual resin that usually remains in the composite after the manufacturing process. The different thermal behavior presented by the polymer matrices (epoxy and vinyl-ester, respectively) processed with the same fiber type is related to the distinct fiber sizing chemical interaction with them [9].

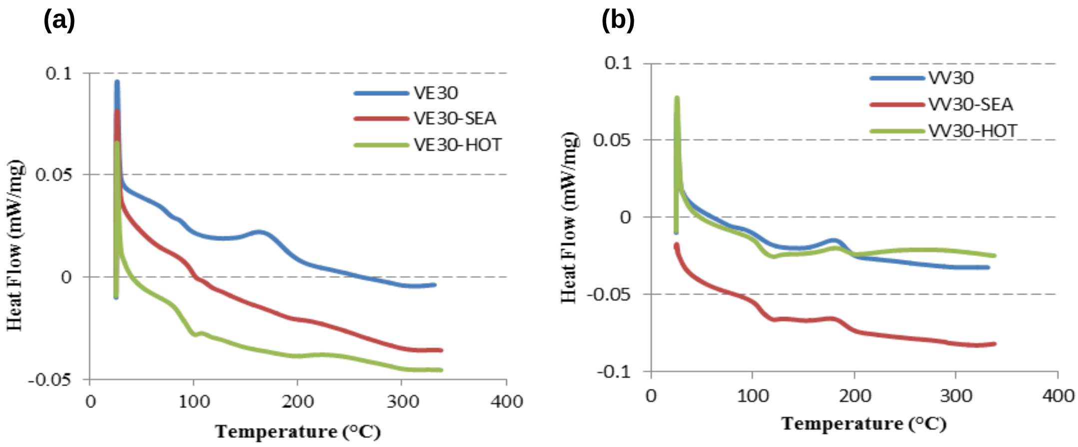

Figure 6. DSC thermograms of carbon fiber rods before and after different aging treatments: (a) VE30, and (b) VV30.

3.3 Quasi-static tensile testing

Figure 7 shows the curves of load × elongation obtained from pristine rods. All test coupons exhibit a typically linear elastic behavior up to the catastrophic failure. The images of the catastrophic failure of the pristine rods are shown in Figure 8, indicating the low damage tolerance of this type of structural material.

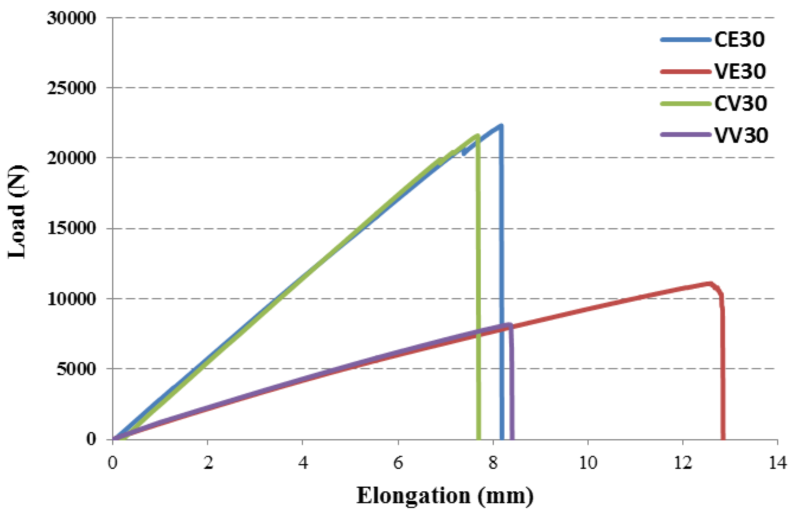

Figure 7. Typical curves of the tensile behavior of all the test rods in pristine state.

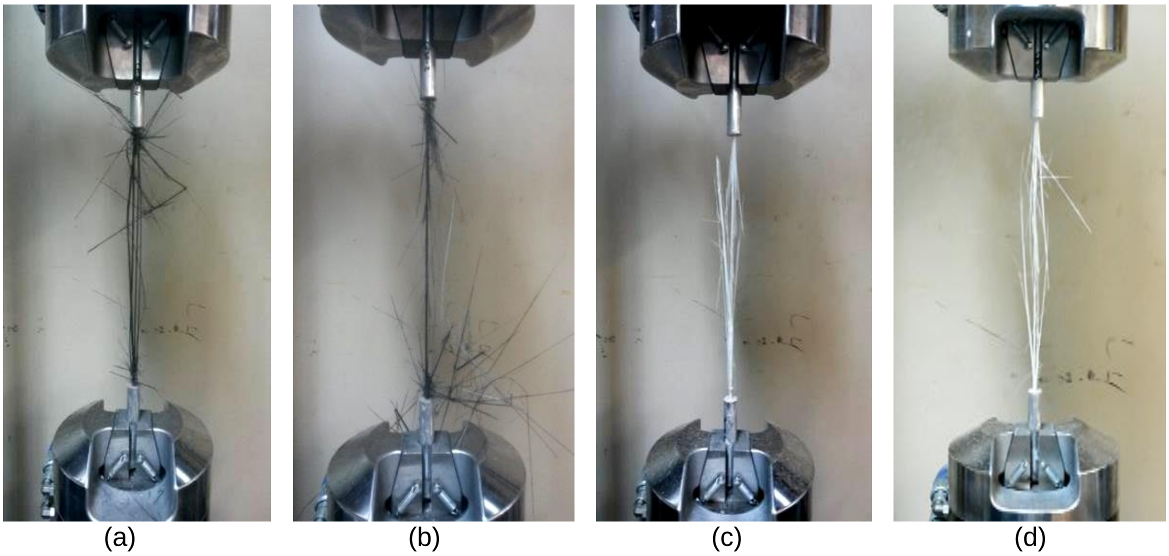

Figure 8. Typical failure aspects under tensile loading for each type of pultruded fibrous composite rod: (a) CE30, (b) CV30, (c) VE30, (d) VV30.

Figure 9 plots the ultimate tensile strength of the pultruded rods before and after aging treatments (sea hot water and distilled hot water, respectively). Carbon fiber rods present much higher ultimate tensile strength than glass fiber ones in both the pristine condition as well as after hygrothermal conditioning. Vinyl-ester resin was significantly more chemically resistant than epoxy resin in the studied environments. Glass fiber rods with epoxy resin is superior to those employing vinyl-ester resin, although after any kind of hygrothermal aging the residual ultimate strength is reduced to a same level in all these cases. In general distilled hot water was more aggressive than the hot saline solution for all the composite systems tested, probably due to osmotic effects. It can be inferred that as distilled water is free of solute ions, molecular diffusion through the rod is facilitated and so the extraction of low molecular weight compounds, thus corroborating results from previous studies [8].

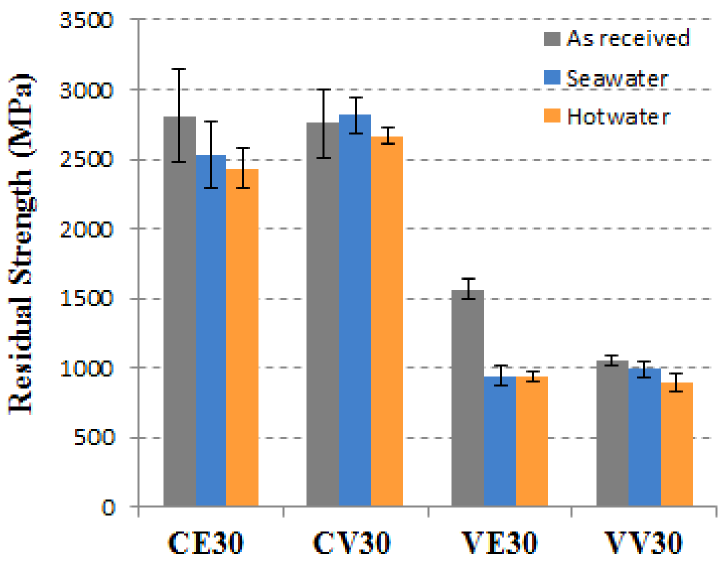

Figure 9. Ultimate tensile strength of pultruded composite rods subjected to different environmental conditions.

4. Conclusions

- In regard to the physical properties of the pultruded composite rods, it is possible to infer the deteriorative effect of hot water, especially distilled water which extracts low molecular weight compounds.
- With respect to thermal analysis, TGA and DSC studies confirmed that the thermal stability of the rods was not affected by exposure to hygrothermal environments. Both the epoxy and vinyl-ester matrices suffered post-curing during the two aging treatments applied.
- Concerning the results of quasi-static tensile tests, it was possible to conclude that immersion in hot distilled water was the most pernicious aging treatment.
- Regarding the rods' matrices, vinyl-ester resin was shown to be considerably more chemically resistant than epoxy resin in the studied environments.

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