Effect of Glass Fibres and Environments on Long-Term Durability of GFRP Composites.

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Abstract

Durability is a key feature that defines the value of composite materials. It is essential for the development of applications requiring good long-term performance to improve the understanding of long-term behavior of composites in various corrosive environments and to provide a basis for their structural design in specific environmental conditions.

To evaluate GFRP material durability, stress-corrosion tests have been conducted on pultruded rods under constant tensile stress in a few representative environments such as strong acids, cement extract, salt water, tap water and deionized water. In addition to testing at room temperature, some of the tests have been conducted at 60°C to assess the accelerating effect of temperature. Comparison with long-term rupture tests under constant load in air was completed to assess the effect of environments.

All these environmental stress-corrosion tests to failure were conducted with two sets of pultruded rods made with the same isophtalic polyester resin: one set reinforced with traditional boro-silicate E-glass and the other one reinforced with a boron-free, environmentally friendly, E-type of glass fiber (Advantex® glass).

These test results show a significant effect of the environmental conditions on the long-term performance of the GFRP composites and allow the determination of various reduction factors related to the effects of each parameter: stress, environments, and type of glass for the projected lifetime of the composite material.
For each studied environment, stress reduction factors are given for a projected lifetime of 50 years.

The test results indicate that the type of glass fiber has a strong effect on corrosion resistance and on composite durability: the boron-free E-glass considerably increases the resistance of GFRP composite rods to stress-corrosion in all aqueous environments, thereby significantly improving the long-term partial reduction factors.
This boron-free Advantex® glass is particularly suitable to all applications where environmental exposure may occur.

Introduction

In comparison with the traditional materials, Glass Fibre Reinforced Polymer (“GFRP”) composites have several features, which make them the materials of choice in many applications. Attributes are well demonstrated such as high strength-to-weight ratio, flexibility, easy assembly and installation, electrical and thermal insulation, corrosion resistance, low maintenance if any, and very low overall lifetime costs. This knowledge is the result of decades of testing, evaluation, and experience, with various thermoset and thermoplastic matrices, reinforced with traditional E-glass. With its high strength, superior hydrolysis resistance (e.g. to A-glass), and its excellent electrical properties, E-glass had become the industry’s glass standard.

As an initial step to make the manufacturing of glass fiber reinforcements more environmentally friendly, Owens Corning began producing ECRGlas® in the 1970’s. This boron-free glass was classified as an E-CR glass[1] as a result of its enhanced long-term corrosion resistance to acidic environments compared to traditional boro-silicate E-glass.

(Note: Advantex® and ECRGlas® are registered trademarks of Owens Corning)

In the late 1990's, Owens Corning developed and began producing a new formulation of boron-free E-type of glass i.e. a true E-CR glass, called Advantex® glass, combining the electrical and mechanical properties of E-glass with the superior corrosion resistance of E-CR glass. Advantex® glass has become the top quality standard, available worldwide, and constituting a new glass platform for producing the full range of fiber products.

After a short explanation of the difference between Advantex® glass and traditional E-glass, this paper will focus on the effects of some representative environments on the long-term performance of GFRP laminates reinforced with these glasses.

The objective is to provide a more comprehensive understanding of the performance of composite materials produced with the subject reinforcements, and to generate data quantifying the performance limits of these materials. Evaluation of the included test results supports the conclusion that Advantex® glass possesses properties that allow cost savings in existing GFRP applications while expanding global market opportunities for composites where corrosion-resistance under stress is a key performance requirement.

Glass types tested in the present study

Various glass types exist in the market and are described in standards.
In addition to glass definitions, ASTM D578-00 and DIN 1259/Part 1(2001) provide further composition details applying to the E-type glasses used in composite applications. (See Appendix 1)

According to these standards, the boron-free Advantex® glass is an E-type of glass "for use in general applications" (following the 2nd composition given by ASTM D578), and is at the same time a true E-CR glass exhibiting a particularly high resistance to corrosion by acids.
An assessment of the corrosion resistance of virgin glass fibers to two acids through a weight loss test method is reported in Appendix 2.

In this paper, Advantex® glass is compared to a traditional E-glass through stress-corrosion aging tests in various types of environments. In all cases, the glass sizing that chemically binds the fiber surface to the resin matrix is identical.

A comparison of the basic properties of the two glasses is reported Appendix 3.

Environments

The focus of this study was to assess the stress-rupture behavior with chemical exposure of composite rods exposed to various conditions that may be encountered in many different applications. To cover a relatively wide palette of applications, several environments were selected:

- 1Normal Sulfuric Acid (i.e. 5% H_2SO_4), pH 0.3 and 1Normal Hydrochloric Acid (i.e. 10% HCl), pH 0.1
- A Cement Extract solution, to simulate a standard concrete environment. This cement extract solution was obtained by mixing one part of Portland Cement Type 1 with two parts or tap water in a high shear mixer. The slurry was then allowed to react for 24 hours, at which point the liquid was decanted and filtered to obtain a solution having a pH of 12.6
- Salt water that was prepared by dissolving 5% of road salt (from Ohio DOT) in tap water.
- Tap water
- Pure, deionized water.
- Air exposure was included to define a stress-rupture baseline to allow the calculation of partial retention factors corresponding to the various environments.

The majority of the stress-rupture aging tests have been conducted at 23° C. To assess the accelerating effect of higher temperature, tests were conducted at 60° C. To assure consistent behavior, the elevated temperature was held to no more than 20° C below the glass transition temperature of the resin used.
Air at elevated temperature was simulated using silicone oil as a heat transfer agent.

Providing the failure mechanisms are comparable between the high temperature and the room temperature exposures, an extrapolation based on the "time shift" principle[2] could be made to predict the room temperature life time of the rods from high temperature accelerated data. Using this principle, long service life approximations could be extrapolated using relatively short-term data.

Tensile Stress-Corrosion Test Method

a) Principle of the method

The following test protocol has been designed to produce reliable comparisons of the combined influences of the glass types and of the environments on the long-term performance of composite rods. The use of pultruded rods was indicated as the fabrication method since it provides consistent specimens and requires only one type of reinforcement (rovings).

The principle of the test method is to expose a series of GFRP pultruded rods to a chemical environment at a defined temperature, while submitted to a constant tensile load, expressed as a percentage of ultimate initial tensile strength, until failure occurs. Several tests must be conducted at various levels of tensile stress to develop the behavior with time. Plotting the log of time-to-failure versus the log of tensile stress, or percent ultimate stress, yields a regression line showing time to failure in the specific corrosive environment and under the test temperature.

b) Sample preparation

For this study, cylindrical rods of 6.35 mm diameter were produced by pultrusion with both Advantex® glass and traditional E-glass fibers. The fiber sizing was the same for both glasses, the resin system, AOC F701 isophthalic unsaturated polyester, was the same, and so were all the production parameters and curing conditions. The average glass content was 75% by weight i.e. 58% by volume.
The samples were cut into specimen lengths of 610 mm. End tabs were bonded with epoxy resin to the rods for uniform load transfer from the tensile clamps to the specimen.

To evaluate the potential effect of preconditioning which could have had an influence on the initial results through a secondary effect of environmental absorption, a series of test coupons were exposed for 90 days at 60°C to an environment identical to that used in the stress-corrosion exposure. In this preconditioning time the samples achieved near-saturated condition. Preconditioning was found to not appreciably affect the stress-corrosion test results and had no significant influence on the slope of the regression lines.

c) Test protocol

Once prepared and preconditioned, the rods were mounted in specially designed loading frames. These loading frames (Figure 1) were built to safely induce constant loads up to 4 tons into the test coupons through a cantilever system having a 20:1 load ratio. The loads or stress levels were specifically calibrated for each test with a load cell placed in the frame. The load cell was removed and replaced with the test coupon while the load at the end of the frame was maintained.

Figure 1 - Tensile loading frames

Figure 2 - Test sample in its environmental chamber

The environmental exposure is accomplished by placing a glass tube over the test coupon in the gage length with the environment sealed into the container with rubber stoppers. (Figure 2)

For the samples tested at elevated temperature, the environment containers were equipped with a heating element and insulation jacket. For other samples, the room temperature was maintained at 23°C ± 2°C.

After the proper load has been applied to the frame and the environment has been added to the chamber, load is slowly applied to the test coupon and the timer is started. The sample is held under constant load until failure occurs and automatically stops a timer, recording the time to failure.

A range of loads was applied to a series of test coupons to allow data to be recorded for failure times ranging from less than one hour to over a year. Experience has indicated that data collected in 6 to 9 months is typically sufficient for accurately predicting long-term performance. The correlation coefficient for the least-squares data fit is a reasonable gage for assessing the accuracy of the data fit and of the predicted long-term performance. In the regression analysis, time was used as the dependent variable (failure time depends on the applied stress level), even though all plots show time on the x-axis to comply with the traditional presentation format.

Evaluation and interpretation of data are based on the extrapolation of the failure regression lines to 50 years. The comparison of such failure stress levels at 50 years in various environments with the corresponding failure stress level in air provides the basis for determining partial reduction coefficients corresponding to the specific environment and the specific type of reinforcement.

Test Results

a) Initial Tensile Strength of Pultruded Rods

To obtain a base line for evaluation of the aging behavior of the composite rods, the initial ultimate tensile strengths have been measured and reported in Table 1

Glass type	Tensile Strength (MPa)	Std. Dev.	Tensile Strain (%)	Std. Dev.	Tensile Modulus (GPa)	Std. Dev.	Glass Content (%)
Traditional E-glass	1124	13,1	3,77	0,08	47,8	1,4	77.2
Advantex® glass	1069	27,6	3,71	0,12	45,6	0,7	73.2

Table 1– Initial Tensile Strength, Strain, and Modulus of Pultruded Rods with UP resin

When normalized to 75% in weight of glass fiber reinforcement, the strengths and moduli are nearly identical for the samples, indicating that the samples were properly made and property variation is only related to variation in glass content. The pooled standard deviation of strength and modulus values provide a coefficient of variation of less than 5% indicating that all the products can be considered as statistically equivalent.
To provide a basic reference for further comparison, we may reasonably assume that these rods made with AOC F701 polyester resin and reinforced with 75% by weight of glass have an average initial tensile strength of approximately 1100 MPa. In the following aging stress-corrosion tests, all stresses will be expressed as a percentage of this ultimate initial tensile strength.

b) Stress-Rupture Tests in Air

Testing was first conducted in Air on traditional E-glass and Advantex® glass fiber reinforced rods to provide a baseline for the assessment of the effect of the environments and to assess the creep-rupture behavior of GFRP materials. The results of this tensile stress-rupture testing in Air are shown in Figure 3.

In these test results, half of each of the two populations (Advantex® glass and traditional E-glass) was tested at room temperature (23°C) and the other half was tested at 60°C. For both glass products taken separately, the results obtained at 60°C and those obtained at 23°C were found to be statistically no different after a “t” test was performed for the slopes and intercepts.

Each of the two glass products in Figure 3, the data from both temperatures have been combined, providing a baseline for the comparative performance of Advantex® versus E-glass in “dry creep-rupture” tensile test conditions. Extrapolation of the results to 50 years gives failure stress levels of 44.0% and 45.9% respectively for traditional E-glass and Advantex® glass composite materials.

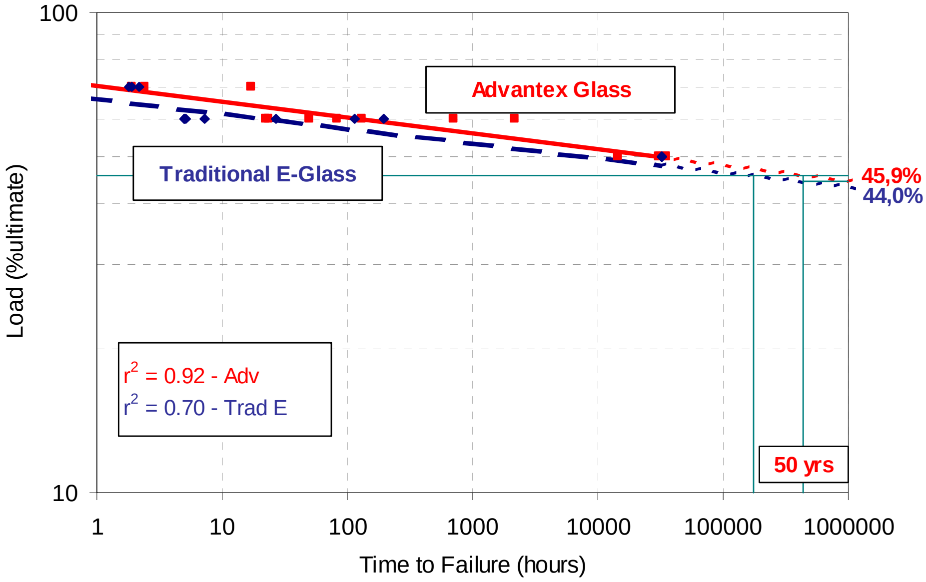

Figure 3 – Stress-rupture of GFRP rods in Air

c) <u>Stress-Rupture Tests in Cement Extract</u>

To simulate the behavior of GFRP rods used as concrete reinforcements in infrastructure applications, stress-rupture tests in a representative alkaline environment were conducted. These tests were conducted in a Cement Extract, pH of 12.6, both at 23° C and 60° C. The results at both temperatures are given in Figure 4a for traditional E-glass and in Figure 4b for Advantex® glass composite rods.

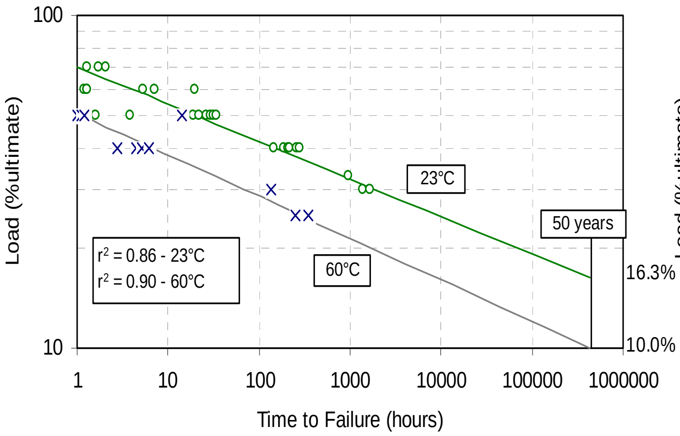

Figure 4a – Stress-rupture of traditional E-glass GFRP rods in Cement Extract at 23°C and 60°C

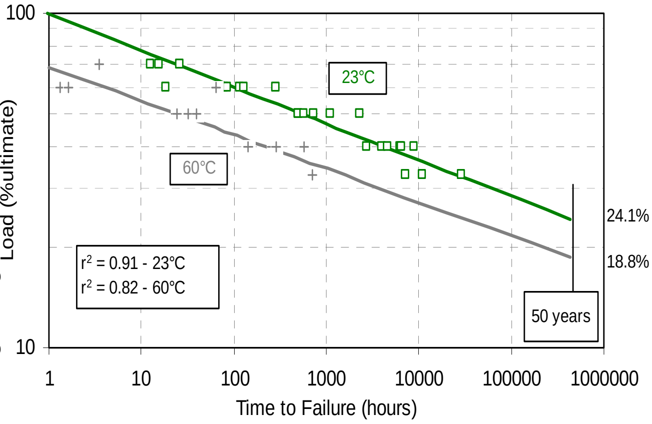

Figure 4b – Stress-rupture of Advantex® glass GFRP rods in Cement Extract at 23°C and 60°C

When examining the stress-rupture regression lines with both glass types at 23° C and 60° C in cement extract, the following observations can be made:

- The slopes of the regression lines are similar, as proven by a statistical “t” test, which implies that the mechanisms of degradation are similar and stress-time-temperature shifting is appropriate.

- The effect of aging acceleration due to an increase in temperature from 23°C to 60°C is a simple time shift of the regression lines. The amplitudes of this shift are 1.51 decade and 1.31 decade respectively for traditional E-glass and Advantex® glass composite rods in cement extract.

After shifting the 60°C data towards the 23°C data by these shift amplitudes, the data at both temperatures can be pooled as shown on Figures 5a and 5b. The correlation coefficients for the regression lines of the combined data are respectively 0.88 and 0.87, implying reasonable agreement.

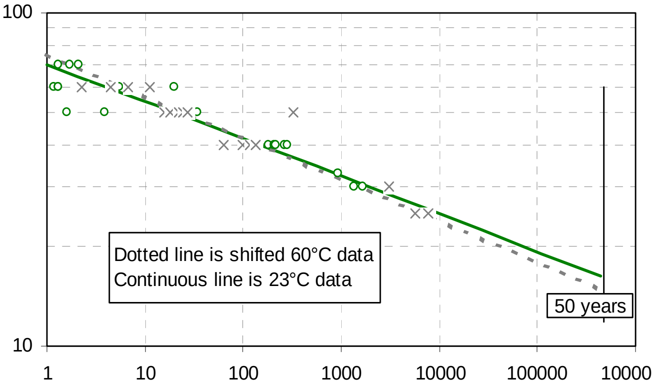

Figure 5a – Stress-rupture of traditional E-glass GFRP rods in Cement Extract at 23°C and shifted 60°C data

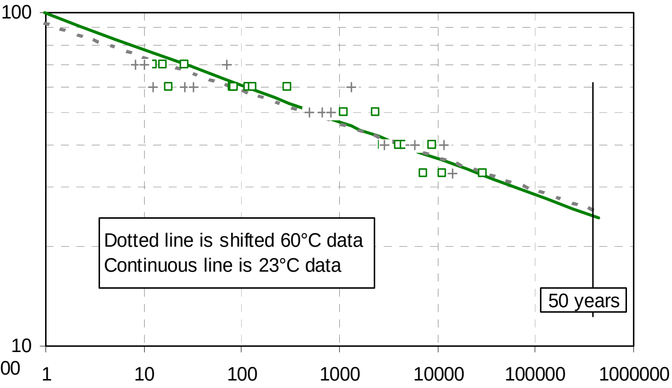

Figure 5b – Stress-rupture of Advantex® glass GFRP rods in Cement Extract at 23°C and shifted 60°C data

Regression analysis of the combined data is used to compare the performances of Advantex® and traditional E-glass reinforced rods in cement extract at 23°C. (Figure 6)

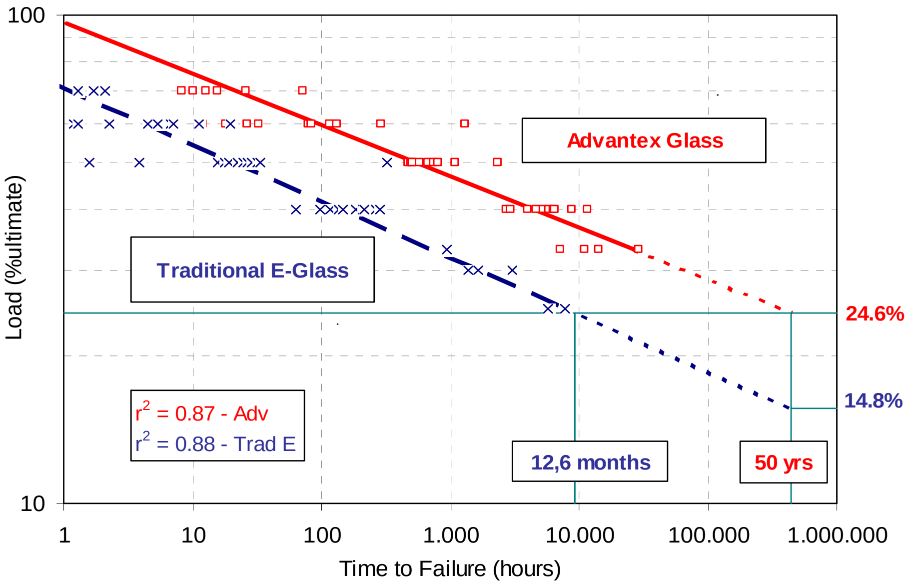

Figure 6 – Stress-rupture of GFRP rods in Cement Extract (pH12.6) at 23° C

Extrapolation of the results to 438300 hrs leads to 50-year failure stresses of 14.8% and 24.6% ultimate strength respectively for traditional E-glass and Advantex® glass composite rods. Expressed in a different way, this means that at the stress level of 24.6% ultimate, a rod made with Advantex® glass and submitted to constant load in a cement extract at room temperature would last for 50 years, while its counterpart made with traditional E-glass would last for about one year.

d) Stress-Rupture Tests in Acids, pH < 0.5

Creep-rupture testing was also conducted in 1 Normal Hydrochloric Acid and Sulfuric Acid aqueous solutions, i.e. in 10% HCl with pH of 0.1 and in 5% H_2SO_4 with pH of 0.3. The observed effects of these acids on the stress-rupture behavior of the GFRP rods under constant tension were statistically equivalent with equal slopes and intercepts of the regression lines with a 95% CL.

The accelerating effect of temperature over the stress-rupture performance of the rods in 1N HCl is shown for traditional E-glass and for Advantex® glass respectively in Figures 7a and 7b. The regression lines at 60°C and at 23°C for the Advantex® GFRP rods (Figure 7b) show that the rod degradations proceed from a similar mechanism, the difference being a time shift of 1.04 decade of hours. The data from both temperatures may be pooled after shifting the 60°C data by 1.04 decade towards those obtained from testing at 23°C. This combined Advantex® GFRP data provides a statistically sound regression line (Figure 8) having a correlation coefficient of 0.97

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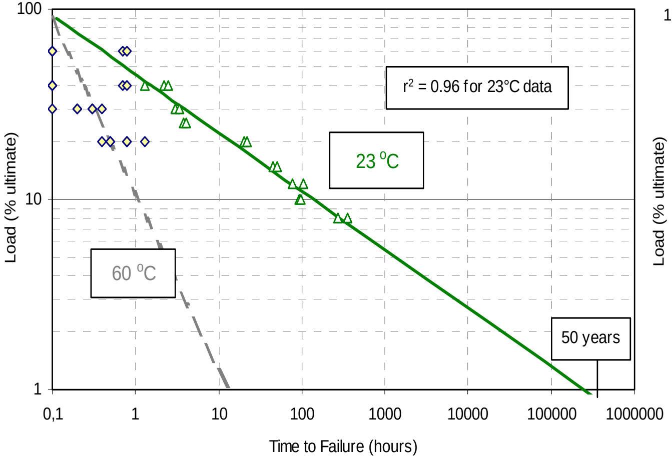

Figure 7a – Stress-rupture of traditional E-glass GFRP rods in 1N HCl at 23°C and 60°C

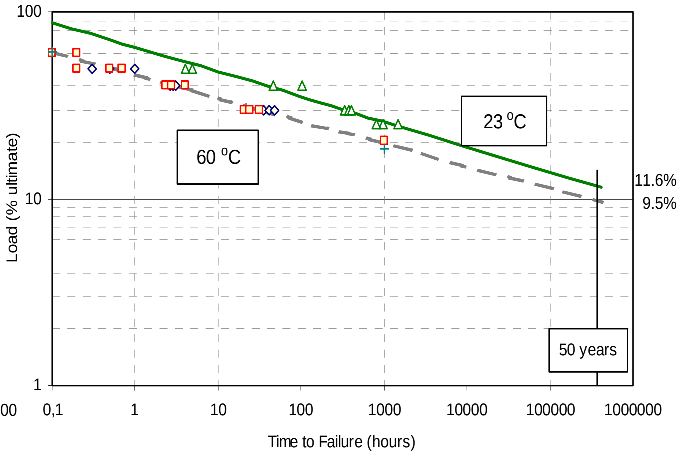

Figure 7b – Stress-rupture of Advantex® glass GFRP rods in 1N HCl at 23°C and 60°C

The regression lines obtained for traditional E-glass FRP rods at 60°C and at 23°C (Figure 7a) are significantly different, indicating that the degradation processes at the two temperatures are not identical. The temperature acceleration effect could not be determined since the data for the 60°C exposure could not be reasonably regressed. The explanation of the erratic data generated by the E-glass rods at 60°C is likely that the material limits were exceeded with the combination of temperature and stress. The 60°C data for E-glass could not be properly used to predict with a simple time shift the performance of the rods at 23°C.
Hence only the test data obtained at 23°C for E-glass GFRP rods have been plotted in Figure 8 to obtain the comparison between traditional E-glass and Advantex® results.

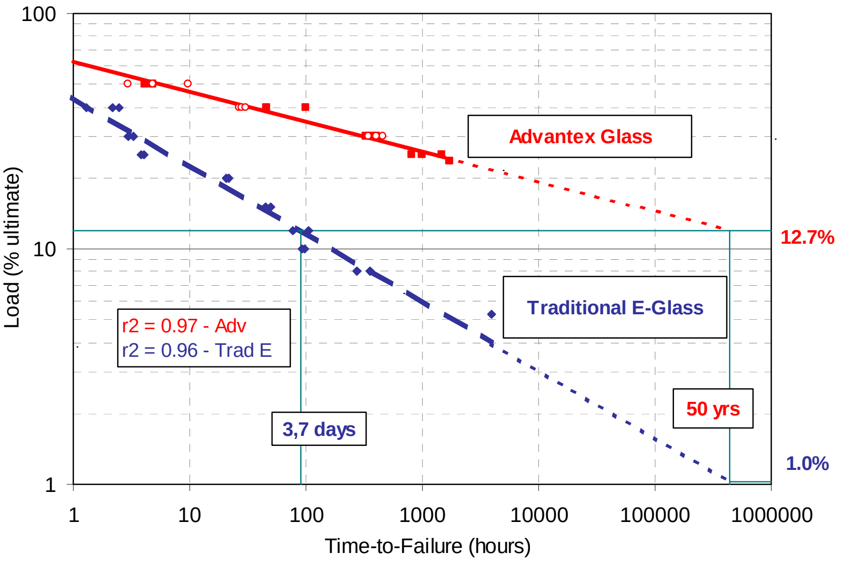

Figure 8 – Stress-rupture of GFRP rods in 1N HCl at RT

Regression lines reflecting the general stress-rupture behaviors of both E-glass and Advantex® GFRP rods under constant tensile stress in a 1N HCl environment at room temperature are drawn in Figure 8, with correlation coefficients of 0.96 and 0.97 respectively. Their extrapolation to 50 years gives stress values of 12,7% ultimate stress for Advantex® glass and 1% ultimate stress for E-glass. At a stress level of 12.7% ultimate strength, the traditional E-glass reinforced rods would have had a lifetime to failure of 3.7 days.

These results appear particularly severe, Relative to historic performance of corrosion-resistant equipment made with isophthalic polyester reinforced and traditional E-glass. These tests have been conducted on pultruded rods having a glass content of 75% by weight. Typically, laminates designed to hold acids incorporate a liner or chemical barrier that would delay the adverse effects of such acid corrosion.
The trend in behavior is consistent with strain-corrosion testing[3] of GFRP pipe with liners tested in 1N H_2SO_4 by demonstrating a significant difference in time to failure between pipes reinforced with Advantex® glass and identical pipes reinforced with traditional E-glass.

e) <u>Stress-Rupture Tests in Salt Water</u>

To evaluate the aging behavior of GFRP composites used in various industrial or infrastructure applications, other comparative stress-rupture tests have been conducted in an environment made from 5% road salt in tap water at 23°C. The test results with the corresponding regression lines are given in Figure 9.

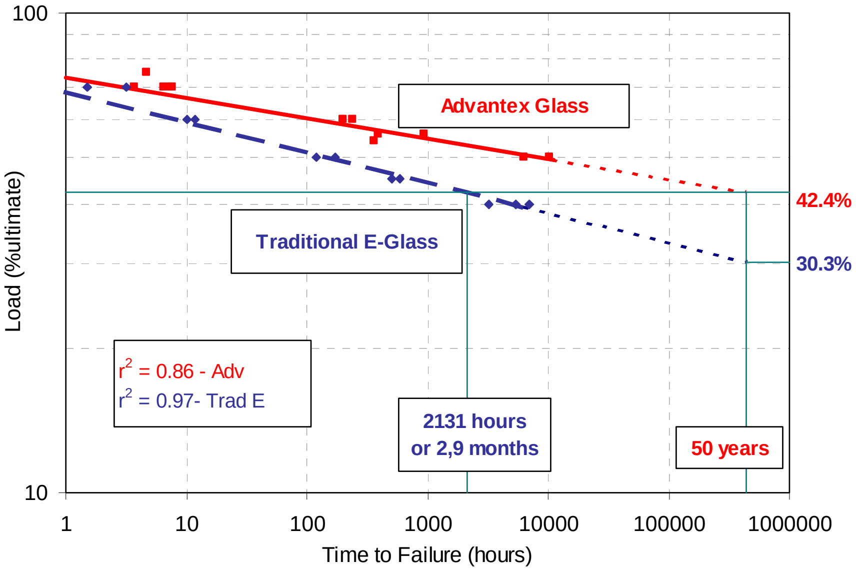

Figure 9 – Stress-rupture of GFRP rods in Saltwater at RT

Extrapolation of the regression lines to 50 years yields failure stress levels of 42,4 % for Advantex® glass versus 30.3 % for traditional E-glass FRP rods. From a different perspective, at the stress level of 42.4% of ultimate strength, the lifetime would be 50 yrs for Advantex® glass versus about 3 months for traditional E-glass. This difference may appear exaggerated in light of the usual lifetime of applications such as boats that have historically been long-lasting. The example demonstrates that in the above testing procedure, the rods are subjected to a constant stress, and exaggerates the severity of degradation effects. The data does indicate that Advantex® glass may have improved performance over traditional E-glass in applications where the composites may be exposed to saltwater corrosion and stress. Many applications may benefit from such improved performance, such as offshore and on-shore infrastructure applications, marine applications, bridges, water treatment equipment, brine and effluents treatment, pipes and tanks, and etc.

f) <u>Stress-Rupture Tests in Tap Water</u>

Tap water is certainly one of the most common environments. Thousands of kilometers of GFRP pipes are installed to transport and distribute tap water, to provide cooling water, fire extinguisher loops, and etc. … Stress-rupture evaluation has therefore also been conducted on the GFRP rods in Tap Water. The corresponding results are represented in Figure 10.

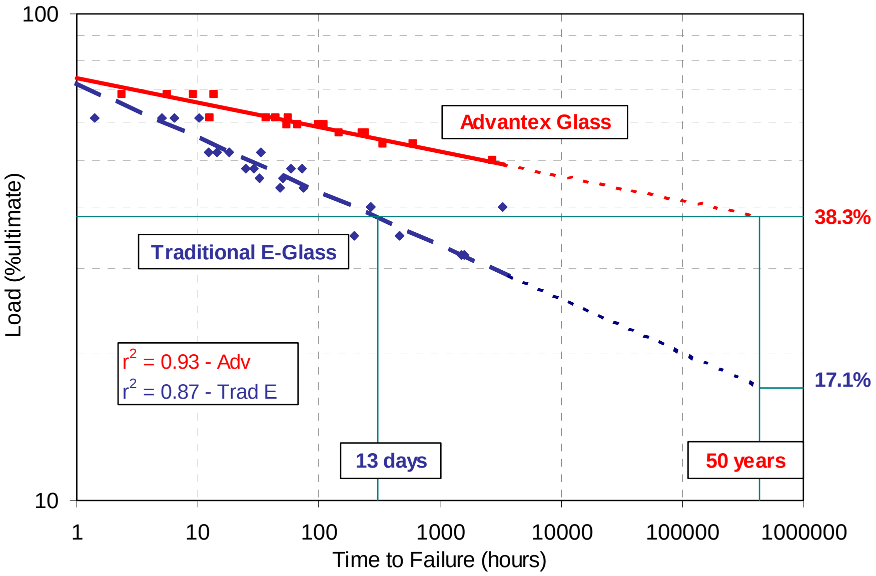

Figure 10 – Stress-rupture of GFRP rods in Tap Water at 23°C

Even though additional data is needed to make conclusive extrapolations to 50 years, this data provides results of interest by showing a consistent trend in performance to the other water environments. Extrapolations of the regression lines yield 50-year stress-rupture levels of 38.3% of ultimate strength for Advantex® GFRP rods and 17.1% for traditional E-glass, respectively. Under a constant stress level of 38.3% of ultimate strength, Advantex® GFRP rods would have a lifetime of 50 years, versus 13 days for the traditional E-glass reinforced rods.

g) Stress-Rupture Tests in Deionized Water

Since Tap Water data appeared to show more severe degradation than saltwater, Tests have been launched to assess the effect of deionized water on the long-term stress-rupture behavior of GFRP rods. The results are collected in Figure 11.

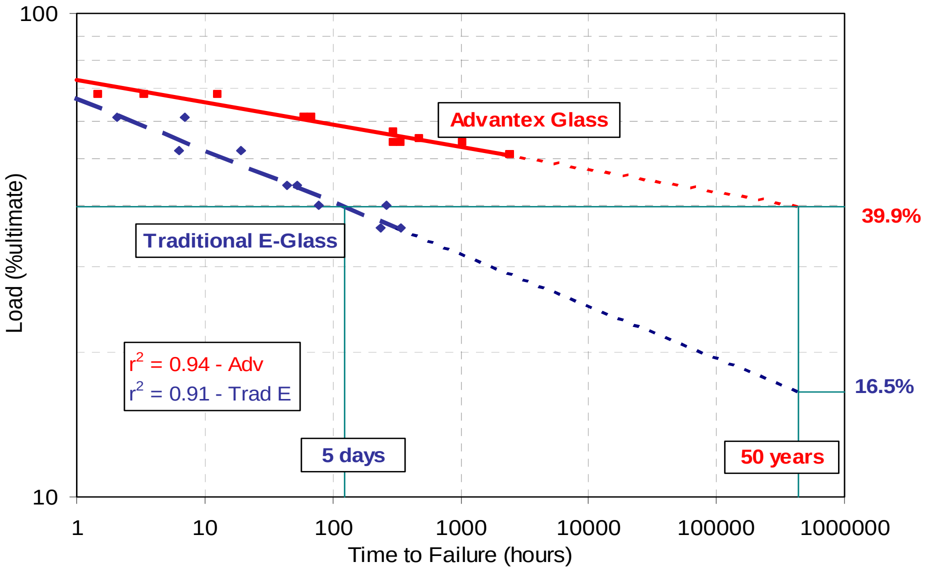

Figure 11 – Stress-rupture of GFRP rods in Deionized Water at 23°C

This data is of limited duration and extrapolations must be tempered with additional data. However, the data does indicate trends that are similar to the preceding evaluations in saltwater and tap water. The regression lines obtained from these limited failure data have similar 50-year stress limits to those obtained in a Tap Water environment.

Summary of results and partial reduction factors

To facilitate the comparison of long-term the effects of the environments and stress on the tensile stress-rupture behavior of the GFRP rods, Table 2 is provided. Table 2 tabulates the 50-year extrapolated stress limits, expressed as percentage of initial ultimate tensile strength (1100 MPa for these samples), for each combination of environment and glass type.

Environments	Traditional E-glass	Advantex® glass
Air at 23°C	44 %	46 %
Salt water at 23°C	30 %	42 %
Tap water at 23°C	17 %	38 %
Deionized water at 23°C	16 %	40 %
Cement extract (pH 12.6) at 23°C	15 %	25 %
1N Hydrochloric acid at 23°C	1 %	13 %

Table 2 – 50-year extrapolated stress limits for pultruded rods under constant tension
(expressed as % of ultimate tensile strength)

To distinguish between the various components of an aging process, a table of partial retention factors can be calculated as shown in Table 3, as suggested in proposed design guides [4,5]. These partial retention factors are defined as the incremental portion caused by each individual aging component in the combined process of identifying long-term stress retention factors for creep-rupture and environment.

Partial retention factors at 50 yrs (for 23°C)	Traditional E-glass	Advantex® glass
50 years time under sustained stress (creep)	44%	46%
Salt water	69%	92%
Tap water	39%	83%
Deionized water	38%	87%
Cement extract (pH 12.6)	34%	54%
1N Hydrochloric acid	2%	28%

Table 3 – Partial retention factors at 50 years
(expressed as % of ultimate tensile strength)

The effective stress limit for a GFRP rod after 50 years under sustained stress in a certain environment will be obtained by multiplying the initial material strength, 1100 MPa, by the creep-rupture/time effect and by the environment effect. As an example, the 50-year stress limit for an isopolyester GFRP rod reinforced with traditional E-glass in cement extract environment will be: 1100 MPa x 0.44 x 0.34 = 1100 MPa x 0.15 = 165 MPa.
The same value for Advantex® glass will be: 1100 MPa x 0.46 x 0.54 = 1100 MPa x 0.25 = 275 MPa.

To put the results in another perspective, Table 4 is provided to show the influence of glass type on the lifetime of the rods in the various environments for a specific stress.

Environment at 23°C	@ % ultimate stress	Lifetime with Traditional E-glass	Lifetime with Advantex® glass
Air	46 %	20 yrs ≈ Equiv't	50 yrs
Salt water	42%	3 months	50 yrs
Tap water	38%	13 days	50 yrs
Deionized water	40%	(5 days) insufficient data	50 yrs
Cement extract (pH 12.6)	25%	11 months	50 yrs
1N Hydrochloric acid	13%	4 days	50 yrs

Table 4 – Influence of glass type over the lifetime under sustained stress at 23°C

Conclusions

The stress-rupture testing, as outlined in this paper, appears to offer a reasonable means of providing data that can be used to predict the long-term performance of composite materials when exposed to the combined effects of stress and corrosion by an environment.

A significant technical contribution offered in this paper is the discovery that Advantex® glass, an E-CR glass, provides significantly improved performance in environments other than acids. Advantex® glass fiber reinforcements offer significantly improved long-term behavior and higher stress limits whenever the composite material is submitted to the combined effects of stress and environmental corrosion in an array of environments.

In an air environment under constant stress (creep-rupture), the maximum stress limits for GFRP isophtalic polyester composite rods are approximately 45% of their ultimate initial tensile strength, whether using a boron-free Advantex® glass or a traditional E-glass.

Various long-term performance retention factors have been determined for both types of E-glass, which allows assessment of the specific effect of each environment on the composites reinforced with these glasses. Among the considered environments, the least aggressive is saltwater, followed by tap water and deionized water, cement extract (pH 12.6), and 1Normal acids.

With pultruded rods made with Advantex® glass reinforcements, the differences in partial retention factors for the three water environments studied, there appears to be little difference and little effect with an average factor of 0.87. For GFRP materials reinforced with traditional E-glass, there is a difference in water effects and they appear to be significant with retention factors of 0.69 for saltwater and 0.39 for tap water and deionized water.

For cement extract, the partial retention factors are 0.54 for Advantex® glass and 0.34 for traditional E-glass. In practice, this means that the maximum stress limits for a 50-year lifetime of GFRP isophtalic polyester composite reinforcing bars used in concrete are approximately 25% of the ultimate tensile strength when using Advantex® glass and 15% when using traditional E-glass as reinforcements.

Whatever the type of reinforcement used, the long-term stress-rupture data provides a more comprehensive and quantifiable understanding of the performance of GFRP composite materials in specific environments. Such data provides a valuable tool for assisting in the design of GFRP composites within certain environments or applications for a specific lifetime.
The results indicate that Advantex® glass-fiber reinforcements offer superior long-term performance and will allow cost savings in existing GFRP applications where corrosion and aging occur and broaden future market applications.

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APPENDIX 1 - Glass Fibers Specifications in Standards

ASTM D 578-00 and DIN 1259/Part 1(2001) describe 2 types of E-glass with some details about their compositions.
In particular, ASTM D578-00 lists the two possible chemical compositions (with ranges) for E-glass.
Amongst the differences between these compositions, the main one is that, in the first composition, applying to glass fiber yarn for printed circuit boards, the boron content may be from 5 to 10%, whilst in the second composition, applying to glass fiber products for general applications, the boron content may be from 0 to 10%, and the silicon oxide content may be somewhat higher, up to 62%.
In addition, a boron-free modified E-glass composition for improved resistance to corrosion by most acids is called E-CR glass.

Note: With its boron-free composition, Advantex® glass falls in the 2nd type of E-glass ("for general applications") and is an original E-CR glass.

ISO 2078-1993 only lists the various types of glasses with their generic letter. Next to E-glass, C-glass, S-glass, etc, E-CR glass is reported "for use in acid environments". This standard is currently under revision and is likely to develop performance-oriented specifications.

Pipes and Tanks standards
Most standards about GFRP materials (e.g. ASTM, ISO, CEN, …) do specify the use of an E-type of glass including either alumino-boro-silicate or alumino-calco-silicate (= boron-free E-glass).

Some standards do precisely mention E-CR glass, e.g. DIN 16 868-Part 1 (1994) - "Glass fiber reinforced unsaturated polyester (UP-GF) pipe – Filament-wound filled pipes" - states in section 4.2 (Laminate structure): "The resin-rich inner layer (s1) shall be 0.2 to 0.4 mm thick and bonded either to a type C glass or a type E-CR glass substrate or a synthetic mat …", and it further states: "When using type E-CR glass, the inner layer (s1) may be dispensed with."

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Appendix 2 - Acid Corrosion resistance of virgin glass fibers

To assess the acid durability of a glass or its resistance to acid corrosion, a relatively simple method, though not standardized yet, is the weight loss test.

The test method consists of measuring the weight loss of virgin or de-sized glass strands after a certain period of immersion in a chemical solution. To accelerate the etching process, the tests are performed at elevated temperature or in a boiling environment. In order to compare results from different product types, the initial weight of de-sized glass must be calculated as a function of fiber diameter to make sure that identical areas of fiber surface be exposed to constant volumes of etching solution.

This procedure allows obtaining a good comparison of the corrosion resistance of Advantex® versus E-glasses in given environments. It provides a quick and meaningful indication for comparing the effects of chemicals on glass and potentially the performance of a GFRP structure. Since this kind of test is performed on glass fibers only, it does not allow prediction of any laminate properties or future performance. It is also an extremely severe test, only intended for relative comparison of the reinforcements' behavior. This comparative performance is expected to be reflected in laminate performance when fibers become exposed to the chemical environment after matrix cracking.

The following results show the weight losses of de-sized glass fibers of the same fiber diameters after 24 hours and 168 hours (7 days) of immersion in 10% H_2SO_4 and in 10% HCl at 96°C. (Figures A2-1and A2-2)

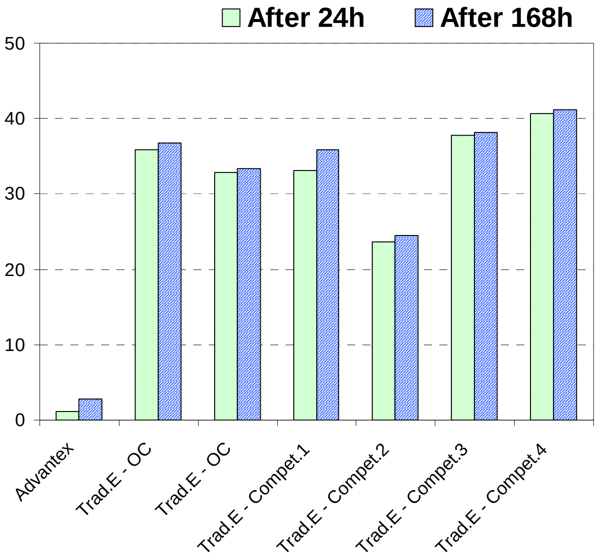


Figure A2-1 - Glass weight losses in 10% H_2SO_4

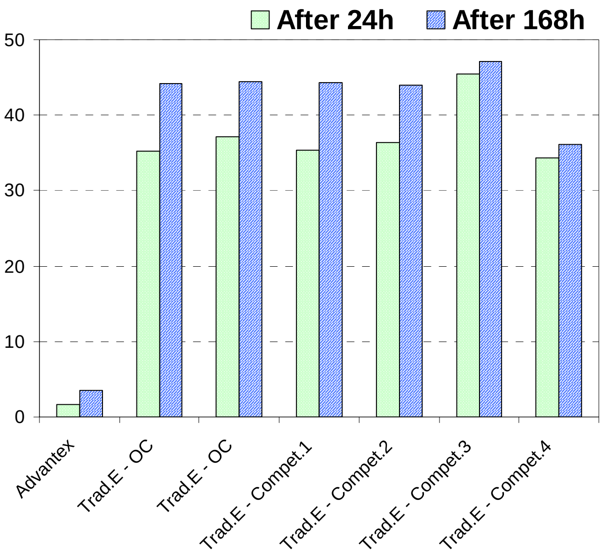
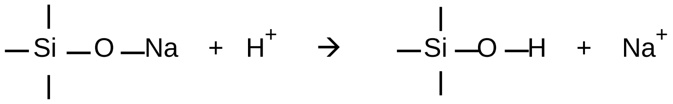


Figure A2-2 - Glass weight losses in 10% HCL

In these graphs, Advantex® glass is compared to various traditional E-glasses: two from Owens Corning (different furnaces), and four from other glass fiber suppliers. Whilst most of the weight losses of traditional E-glass already exceed 30% after 24 hrs and are in the 35 - 45% range after 168 hrs, the weight losses of Advantex® glass fibers in the same conditions are limited to 1.5 to 4%. These data are typically in the same magnitude as the former ECRGlas® for which many more weight loss data had been recorded.

The cause and phenomenon of traditional E-glass acid leaching has been described earlier.
In short, it is related to the presence of Boron in the glass composition, which makes it less resistant to ionic exchange occurring essentially at the glass fiber surface, according to the following schematic formula:



$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\mathrm{Na} + \mathrm{H}^+ \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\mathrm{H} + \mathrm{Na}^+$$

Analysis of the etching solution by inductively coupled plasma emission spectrometry indicated that the depleted ions from the E-glass fibers, after almost 3 months of aging time, were mainly Sodium, Calcium, Aluminum and Boron.

This process gradually produces a depleted surface layer with its remaining silica skeleton around an inner, undepleted fiber core. The depleted fiber surface tends to produce a slight shrinkage that ultimately leads to the occurrence of a helical crack. Helical cracking has been previously reported (Metcalfe, et. al., 1971; Aveston and Sillwood, 1982; and Bledzki, et. al., 1985) on traditional E-glass fibers subjected to acid corrosion but has not been seen with boron-free E-CR glass.

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APPENDIX 3 - Physical and mechanical properties of E-type glass

Property	Units	Test Method	Advantex® glass	Tradition. E-glass
Physical				
Density	g/cc	ASTM D1505	2.62	2.52 – 2.62
Softening Point	°C	ASTM C338	916	830 – 860
Annealing Point	°C	Parallel plate viscometer	736	640 - 675
Refractive Index	-	Oil immersion	1.560 – 1.562	1.547 – 1.562
Linear Thermal Expansion	10^{-6}/°C	ASTM D696	6	5.4
Electrical				
Dielectric Strength	kV/cm	ASTM D149	100 – 106	100 – 111
Dielectric Constant @ 100kHz – 23°C	-	ASTM D150	7.2	6.9 – 7.1
Dielectric Constant @ 100kHz – 250°C	-	ASTM D150	7.5	7.1 – 7.6
Dissipation Factor @ 100kHz – 23°C	-	ASTM D150	0.0010	0.0005 – 0.0020
Dissipation Factor @ 100kHz – 250°C	-	ASTM D150	0.0012	0.0010 – 0.011
Volume Resistivity @ 500V-DC – 23°C	ohm.cm	ASTM D257	10^{29}	10^{23} – 10^{30}
Volume Resistivity @ 500V-DC – 500°C	ohm.cm	ASTM D257	10^{11}	10^{9} – 10^{12}
Mechanical (pristine monofilaments)				
Tensile strength/single filament @ 23°C	MPa	ASTM D2101	3100 – 3800	3100 – 3800
Elongation at break / single filament	%	ASTM D2101	4.6	4.5 – 4.9
Elastic modulus	GPa	Sonic Method	80 – 81	76 – 78

Table A3 – Physical, Electrical, and Mechanical Properties of E-type glasses

The physical properties were generally measured on bulk glass.
In practice most of the properties of Advantex® glass are equivalent to those of standard E-glass, the main noteworthy exception being the softening point of Advantex® glass which is about 70°C above that of traditional E-glass. Boron is a melting and fiberizing aid in the traditional E-glass fabrication process. Its absence in the Advantex® glass formulation increases the viscosity and fiberizing temperature, but also gives this glass a higher temperature resistance.

The refractive index of the glass is an important property for the glass appearance in a laminate, particularly if it must be translucent (e.g. panel application).

The electrical properties are practically equivalent for most applications. Though yarns used for printed circuit board applications are made from the traditional E-glass, Advantex® glass is currently used as a reinforcement in numerous pultruded parts where particularly good electrical properties are required (ladder rails, electrical tool handles, high-voltage insulators, electrical appliance equipments,)

The mechanical properties were measured under laboratory conditions on pristine glass single filaments and are therefore not obtained in field processing conditions. The modulus of elasticity was determined by a special sonic method at a high frequency and this leads to modulus values that are some 7 - 8% higher than the effective tensile modulus values one could measure in practice.

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