

Influence of Glass Fibre Sizing and Storage Conditions on Composite Properties

Luc Peters

Abstract This paper describes a major component of glass fibre reinforcements, the sizing, and its impact on mechanical properties of epoxy or polyester laminates. First the basics of the glass fibre manufacturing process and the types of silanes used for direct rovings are briefly described. The important feature of these coatings is that they can be affected by storage conditions. The study focuses on the effect of roving storage time, temperature and humidity as well as packaging type on the fibre/matrix interphase and on the inter-fibre properties of the composites. The conclusions show that not all fibre sizings offer the same storage stability and that warehousing and packaging details can have a significant impact on the final composite performance.

Keywords Glass fibre • Sizing • Storage • Ageing • Moisture

1 Introduction

3B is part of the Braj Binani Group which is a conglomerate with diversified interests in cement, zinc and glass fibre. 3B is a major actor in composite reinforcement solutions, with a special focus on thermoplastics, wind energy and performance composites [1]. The company has a long heritage of 45 years of expertise and produces more than 160,000 tonnes of glass fibre products per year.

Glass fibre production was developed in the 1930s and has been extensively documented in various textbooks and websites [e.g. 2–4]. The basic process involves melting silica sand, limestone, kaolin clay and other minerals to liquid form at temperatures above 1500 °C, then extruding through bushings to make

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Fig. 1 Glass fiberizing and coating with sizing



fibres, Fig. 1. The most common fibre is E-glass, which is aluminoborosilicate glass with less than 1% by weight of alkali oxides. 3B produces two unique high performance and eco-responsible glass technologies: Advantex® glass, a corrosion resistant grade (E-CR) [5], and HiPer-tex™, a fibre with improved mechanical properties [6].

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Figure 2 shows a schematic diagram of the process.

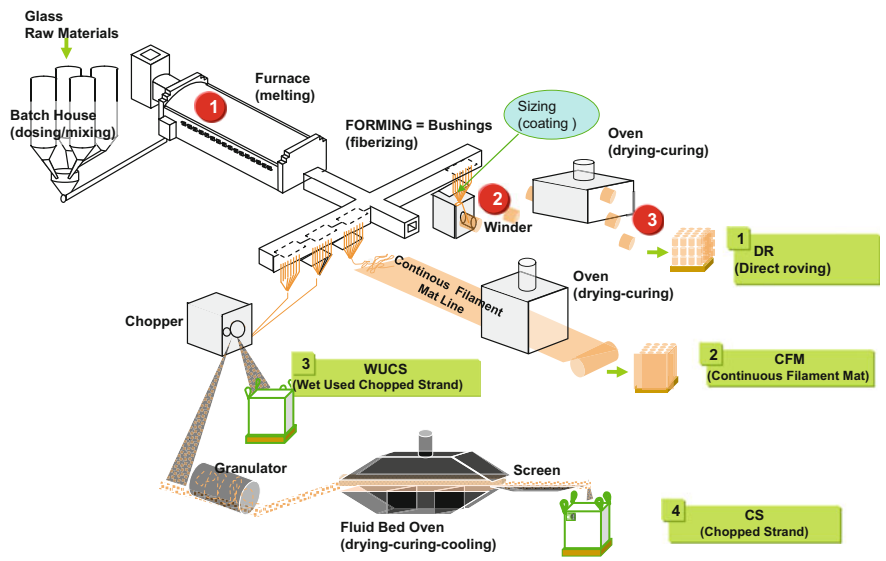


Fig. 2 Schematic figure showing glass fibre production

2 Sizing Composition

Size is a coating applied as a water-based formulation, it contains

- Coupling agent(s): Provides adhesion between glass surface and the resin (usually silanes),
- Film Former(s): Provides protection and strand integrity to the roving as well as compatibility with the resin (epoxy, polyester, vinylester, etc.),
- Lubricant(s): Provides lubrication and protects the filaments during processing,
- Other Additives: antistatic, emulsifier, anti-foaming, bactericide, etc.

Sizing is applied to the fibres as they are drawn down from the hot bushings, as a water-based emulsion with 2–10% of solid. Final solid content on the dry fibre can range from 0.3 to 1.5% depending on final product application and sizing type. Table 1 shows a typical formulation.

Table 1 Typical glass fibre sizing composition

Component	% of sizing
Silane(s)	5–15%
Film former	50–70%
Lubricant	10–30%
Additives	0–5%

The application of this sizing to the fibres is an incredibly complex operation, as Thomason has pointed out [7]. The fibre bundle is pulled at velocities up to 60 m/s, so sizing pick-up occurs in less than 0.5 ms. The sizing must then fully impregnate the bundle before it reaches the first winding sheave, i.e. in less than 0.2 s.

After coating, the fibres are wound onto bobbins, then dried and cured in an oven.

Optimising the sizing is a balancing act between cost, processing and performance.

3 How Sizing Works

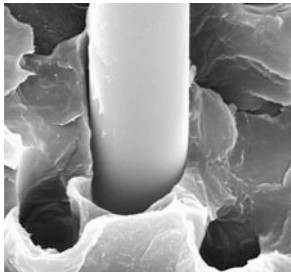
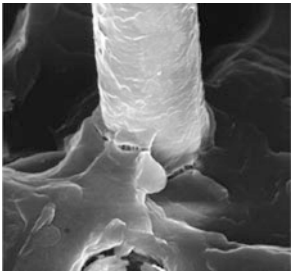
The role of the glass sizing is to ensure good transfer of load applied on the composite from the polymer matrix to the glass. Glass fibre (GF) sizing is specific to the polymer matrix and the final application. Table 2 shows the difference a good sizing can make to an injection molded short fibre reinforced polyamide 66 specimen.

The most common sizing strategy is to use condensation of silanes onto the glass surface as shown in Fig. 3.

Different types of silane are used for different thermosetting matrix resins, such as γ -aminopropyltriethoxysilane for epoxies and γ -methacryloxypropyltrimethoxysilane for unsaturated polyester and vinylesters. The reactive groups from the silane (shown in green on the figures in the electronic version) will react with the resin or hardener reactive groups.

These are shown below, Fig. 4.

Table 2 Example of two glass fibre reinforced PA66 composites with different sizings

Injection molded PA66-50%wt GF (Chopped strands reinforcement)	Poor coating	Good coating
Tensile strength (MPa)	50	180
Notched Impact strength (kJ/m ²)	<5	18
Interface quality		

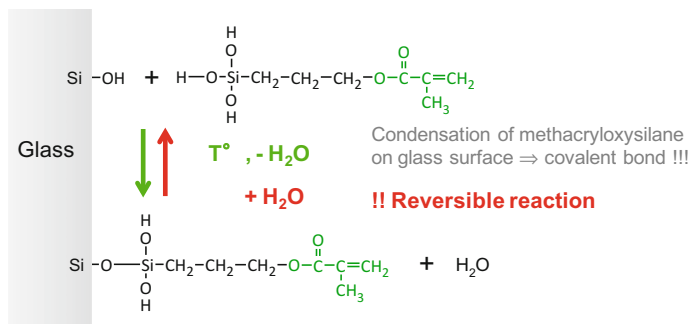
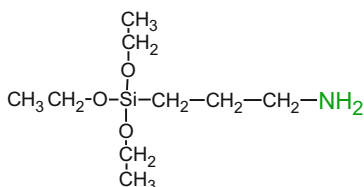
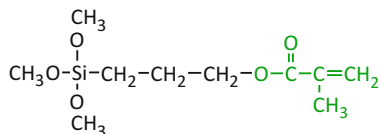


Fig. 3 Application of silane to glass surface

γ -aminopropyltriethoxysilane $\rightarrow$ Application = Epoxy resin



γ -methacryloxypropyltrimethoxysilane $\rightarrow$ Application = Vinyl Ester and Unsaturated polyester



γ -glycidoxypropyltrimethoxysilane $\rightarrow$ Application = Epoxy resin

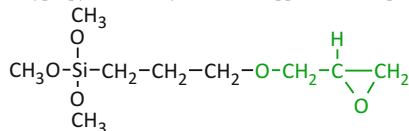
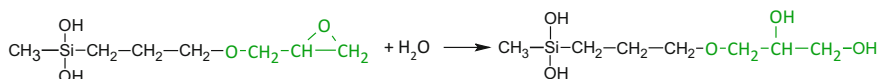


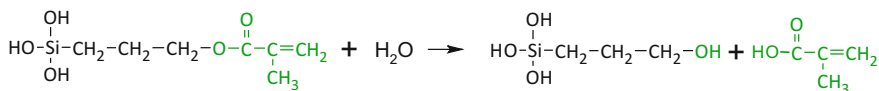
Fig. 4 Typical coupling agents for thermoset matrix composites

4 Long Term Stability of Sizing on Glass Fibres

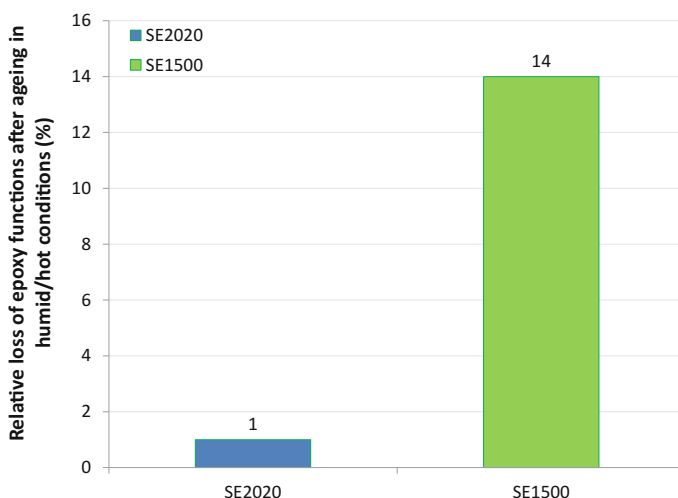
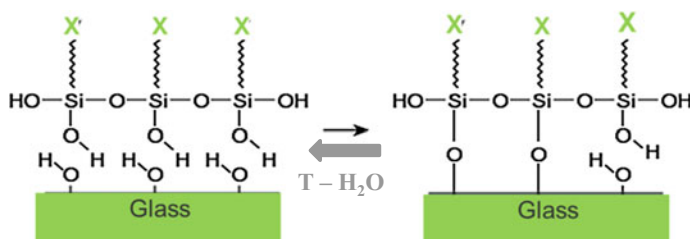
Continuous fibres used for the reinforcement of thermoset resins show usually a decrease of adhesion properties with storage conditions and time (Figs. 5 and 6). This results in an important deterioration of transverse tensile strength and inter-laminar shear strength as highlighted later in this article (Figs. 7 and 8).



(a) Hydrolysis of Epoxysilane when exposed to moisture and heat



(b) Hydrolysis of Methacryloxysilane when exposed to moisture and heat

Fig. 5 Examples of sizing reactivity reduction due to hydrolysis of sizing ingredients when exposed to moisture and heat**Fig. 6** Relative loss of epoxy functions (peak ref. = 912 cm^{-1}) after ageing of sizing films in humid and hot conditions ($30\text{ }^{\circ}\text{C}$ — $80\%\text{RH}$) during 12 weeks**Fig. 7** Hydrolysis mechanism of Si—O—Si bonds at glass—sizing interface when exposed to moisture and heat

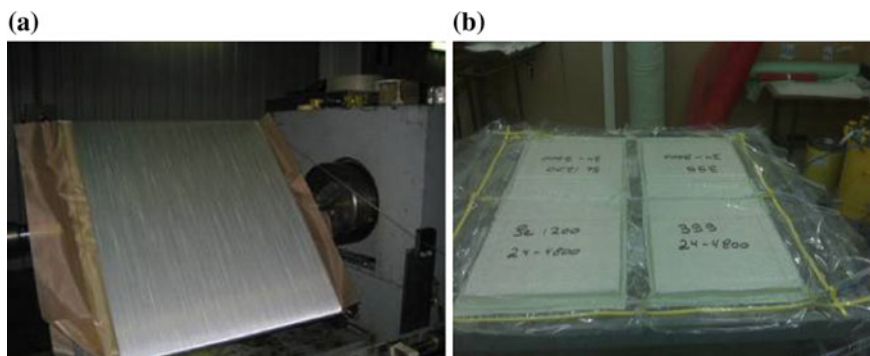


Fig. 8 Sample preparation. **a** reinforcement winding, **b** Infusion (4 products/infusion in most cases)

This decrease of adhesion properties is clear evidence that sizing chemistry on the glass is affected by the storage conditions. There are several mechanisms that could explain this drop of properties

(A) Hydrolysis of chemical functions when exposed to moisture and heat

(A.1) Sizing-matrix interface: reduction of sizing reactivity with the matrix.

The role of the sizing is to chemically bond the glass surface with the polymer matrix. This implies that some sizing ingredients will react with the resin during the processing of the composite. Nevertheless, the majority of the chemical functions used for that purpose are sensitive to moisture and heat. Those so-called hydrolysis reactions will result in a reduction of the sizing reactivity with the polymer matrix and consequently in a decrease of fibre-matrix adhesion. The chemicals functions that are the most impacted are the epoxy functions (epoxy silane and bisphenol-A epoxy resin usually used as film former) and the methacryloxy function (methacryloxysilane). The reaction schemes of epoxy and methacryloxysilane hydrolysis are presented in Fig. 5. Similar mechanism to epoxysilane takes place in the case of bisphenol-A epoxy resin.

The hydrolysis of the epoxy functions has been demonstrated by FTIR at the level of 3B-Fibreglass laboratory on different sizing films stored at 30 °C and 80% RH during 12 weeks. Figure 6 presents the relative loss of epoxy functions for films of SE2020 and SE1500 stored at 30 °C—80%RH compared to reference films stored at 24 °C—47%RH.

Based on those results, it is clear that the sensitivity to moisture and heat depends on the sizing composition. Indeed, the recently developed SE2020 sizing is clearly less affected by the epoxy hydrolysis reactions than an old generation sizing like SE1500.

(A.2) Glass-matrix interface: hydrolysis of Si–O–Si bonds

As presented in Fig. 3, the functionalized silanes react with the silanol bonds present at the surface of the glass. Unfortunately, this condensation reaction is reversible and the formed Si–O–Si bonds could be hydrolyzed when the fibres are exposed to moisture and heat. This results in a weakness at the level of the glass-sizing interface and consequently in a decrease of adhesion properties at the level of the composite. Figure 7 illustrates again the reaction scheme of reversible equilibrium hydrolysis-condensation of Si–O–Si bonds.

(B) Glass-matrix interphase: reduction of sizing solubility when exposed to heat in dry environment

Glass fibre sizings for thermoset applications usually contain a high concentration of epoxy functions. When exposed to heat in dry conditions, those epoxy functions could react with other sizing ingredients bearing, e.g. hydroxyl, amino or carboxylic acid functions. Those post-reactions will generate high molecular species that will reduce the sizing solubility with the liquid resin during composite manufacturing. This phenomenon can cause impregnation issues and defects that will negatively impact the mechanical properties.

In the case of sizing formulations containing methacryloxysilane or more generally unsaturations, heat will accelerate the oxidation of the double bonds and the creation of radicals. The presence of radicals could lead to cross-linking reactions that will again reduce sizing solubility.

On top of that, the two mechanisms described here before will have as consequence a reduction of the reactive species concentration on the fibres.

There is little published information on the long-term stability of glass fibre sizings in the scientific literature. While the importance of the interphase region between fibre and matrix is generally accepted the complexity of the chemistry in that zone has limited the number of studies. Ishida and Koenig [8] published some early results showing loss of silane coating after an 80 °C water treatment.

Plueddemann [9] discussed some of the factors that affect water resistance of coupling agents, and Ishida provided a review of the subject in 1984 [10].

Wang et al. [11] used mass spectroscopy to study the interphase in E-glass surfaces coated with silanes and exposed to different hot wet conditions. They revealed the presence of layers of different hydrolytic stability. In a second paper [12] using X-ray photon spectroscopy, they showed evidence of aluminium ion migration from the fibre surface into the silane layers, and these layers remained after hot water extraction.

Salmon and colleagues at ENSAM, Paris [13, 14] described a series of tests on two common coupling agents for amine-cured epoxy/glass fibre composites: APS (γ -aminopropyltriethoxysilane) with amine groups and GPS (glycidylpropylsilane), in which the coupling function is an epoxide group (glycidyl). These were taken as model compounds for part of the interphase and subjected to wet ageing under various conditions at temperatures from 0 to 100 °C. They clearly showed that the organosilane layer cannot act as a protective barrier to water ingress.

Given the lack of available results, and also the specific nature of the conditions to which glass fibre reinforcements can be subjected before and after manufacturing, 3B launched a detailed study to quantify how the stability of composites is affected by the storage and packaging conditions of the sized glass reinforcements.

5 Materials and Methods

Fibre reinforcements

The composites tested were based on the following fibre products:

Pallets of fibres from the 3B Birkeland plant (rovings have different production dates):

Reference sizing (SE1500) 17–2400, production date: 4/3/2013.

New sizing (SE2020) 17–2400, production date: 11/4/2012.

New Multi-Compatible sizing (W3030) 17–2400, production date: 5/9/2013.

Note: 2020 sizing is epoxy specific, and 3030 sizing is multi-resin compatible (UP, VE, EP).

“SE” indicates that the sizing is applied on Advantex glass, “W” means it is applied on HiPer-tex glass.

Ageing conditions

Trip to/from Dubai for SE1500 and SE2020 from August to December.

1 week at $-18\text{ }^{\circ}\text{C}$ (to check Epoxy crystallisation).

2.5 months in oven at $50\text{ }^{\circ}\text{C}$ in Laboratory (RH = 2–3%).

2.5 months oven $50\text{ }^{\circ}\text{C}$ + 2.5 months at $30\text{ }^{\circ}\text{C}/80\%\text{RH}$ (21.5 g $\text{H}_2\text{O}/\text{kg}$ air).

2.5 months oven $50\text{ }^{\circ}\text{C}$ + 2.5 months at $30\text{ }^{\circ}\text{C}/80\%\text{RH}$ in two sealed PE bags.

Composite panel manufacture

After ageing, composite panels were manufactured from each batch of fibres for testing.

Glass fibres were aligned by dry winding of flat panels, Fig. 8a:

Four layers of 845 g/m^2 UD rovings for a reinforcement weight of 3380 g/m^2

Laminates of 2 mm thickness were produced by infusion with Hexion RIMR 135/137 epoxy resin at $35\text{ }^{\circ}\text{C}$ under full vacuum, Fig. 8b, with a 4 h post-cure at $90\text{ }^{\circ}\text{C}$.

Glass contents were determined to be in the weight range of 72–75.5% in all cases.

The test methods used to evaluate the effect of sized fibre ageing on composite performance were

Tensile testing at $90\text{ }^{\circ}\text{C}$ to the fibre direction, and

Short beam shear test according to ISO 14130.

These tests are known to be very sensitive to the fibre/matrix interface integrity.

6 Test Results

The environmental conditions during the return trip to Dubai were measured using a data logger, which indicated a temperature range from 8 to 42 °C and humidity from 40 to 80%.

Figure 9 shows the transverse tensile test results for all UD samples. This plot provides a very large amount of information. It is clear that some panels have very low transverse tensile strengths, <10 MPa, this was due to transverse cracks already visible in the panels after manufacture. The improved sizing (2020 and 3030) show good strength retention even after 2 years, while the SE1500 properties (diamond symbols) tend to drop under all ageing conditions.

Figure 10 shows the interlaminar shear strength results. The ordinate scale is reduced, and even in the worst case an ILSS value above 40 MPa is obtained, but the overall trends correspond very closely to those seen in transverse tension, with significant ageing effects for the SE1500 reference sizing. It is also of interest to examine how such changes in interface performance might affect fatigue performance, as this is critical for the wind turbine industry. Figure 11 shows an example of test results. The green curve is an actual curve for a UD fabric with W2020 roving which was used for the certification of wind turbine blades. The red curve is an estimation of the possible drop in the case of sizing degradation; such drops have been seen with old sizings, such as SE1500 [15].

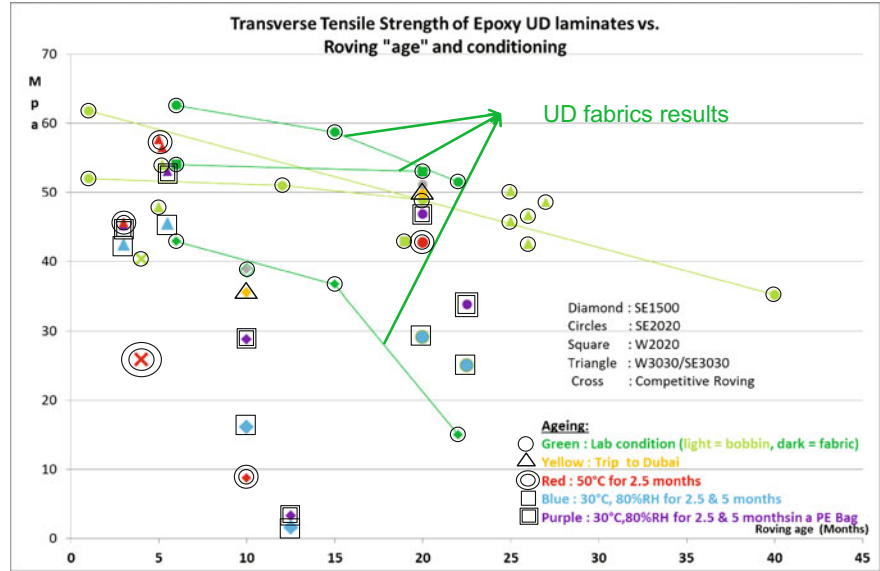


Fig. 9 Transverse tensile test results (Colours shown in electronic version)

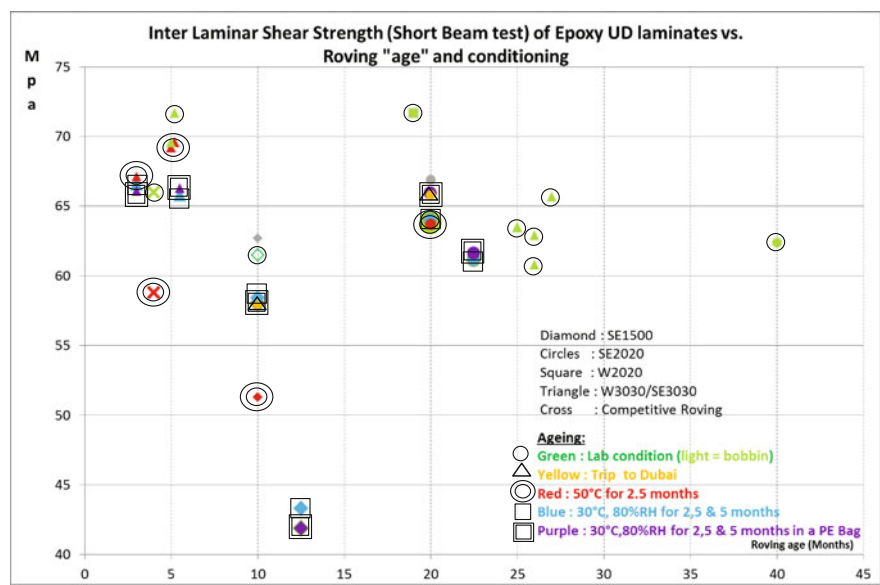


Fig. 10 Interlaminar shear strengths (Colours shown in electronic version)

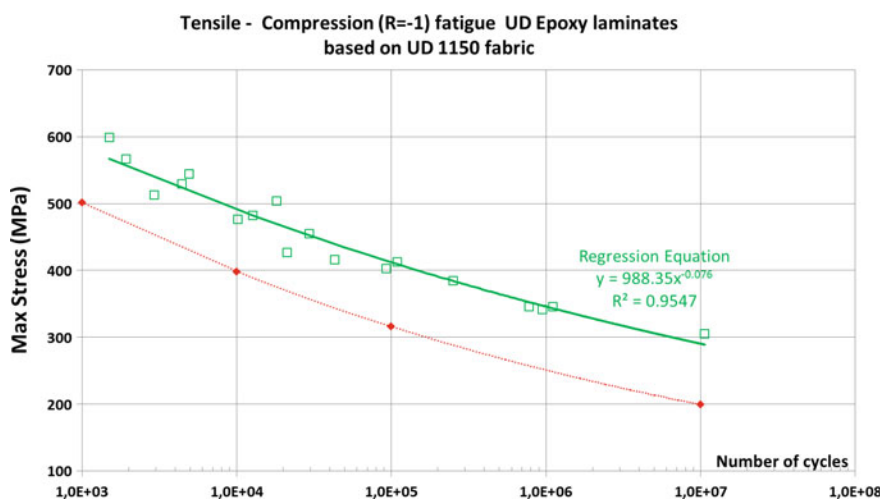


Fig. 11 Fatigue test results. New sizing test data (green squares) and degraded old sizing estimation (red diamonds)

7 Conclusions

This paper describes results from a study of the stability of sizings on glass fibres prior to manufacturing, and the consequences for composite interfacial properties.

As noted in service, some old reference sizings were confirmed to be very sensitive to storage conditions (especially temperature) and demonstrated significant reduction of interfacial properties over time.

The newly developed sizings demonstrate much reduced degradation over time in both rovings and fabric forms of Advantex and HiPer-tex glass fibres. These are much less sensitive to temperature, and provide significantly higher initial interfacial strength.

After 2 years of storage under normal Western European storage conditions, these new sizings still demonstrate excellent interfacial properties.

Degradation in hot and humid environments still occurs, most likely at the interface with the glass surface (hydrolysis of silane) but also at the level of the silane and film formers reactive groups. Tight packaging can help but water will still diffuse through eventually. Storage under controlled moisture levels can also help (i.e. <25 g H₂O/kg or 35 °C/70%RH).

Newly developed sizings ensure better laminate property consistency and should be preferred for critical structural applications.

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