

# Investigation of Strength Recovery of Recycled Heat Treated Glass Fibres through Chemical Treatments

E. Sáez-Rodríguez\*, L. Yang, J. L. Thomason.

Department of Mechanical and Aerospace Engineering, University of Strathclyde, 75 Montrose street, Glasgow, G1 1XJ United Kingdom.

\*Corresponding author (eduardo.saez-rodriguez@strath.ac.uk)

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## 1 Abstract

The strength loss of thermally treated glass fibre (GF) at elevated temperature is well reported in literature. This phenomenon even occurs at short period of time such as 25 minutes. In the recycling technologies for composites, GFs are usually recovered by degradation of polymeric matrix with thermal and/or chemical treatments. Therefore thermal effect on the strength of GF is a significant factor when restricting the possibilities of recycling this material for a second life.

This study reports on the strength of thermally treated commercial GF after acid treatment and silanization of the fibre surface to achieve a proper combination of treatments which may provide us with the ability to recover the mechanical properties of the heat treated GFs. It is thought that silane coupling agents can directly increase and recover the strength of GFs. Two factors associated with this recovery are the possibility of the sizing repairing the damage on the surface of the heat treated GFs and the reduction of the fibre-fibre friction in the bundle through lubricating effect.

GF samples were heat treated at 450<sup>0</sup>C for 25 minutes and coated with silanes, applying different combinations of hydrochloric acid (HCl) and the two silanes used in this study,  $\gamma$ -Aminopropyltrimethoxy Silane (APS) and  $\gamma$ -Methacryloxypropyltrimethoxy Silane (MPS); these fibres were characterized by single fibre testing for strength. The results obtained demonstrated that the fibre strength improves slightly after combination of HCl and MPS treatment, and has a negative effect when the combination of HCl and APS was used. The surface

deposition of silane on the surface of the fibre is also discussed using a Scanning Electron Microscope (SEM).

## 2 Introduction

During recent years there has been an increase in global concern about reducing the 'carbon footprint' of the world to protect the environment.

The disposal of end-of-life composites in an environmentally friendly manner is one of the most important challenges faced by the industry. It is projected that the total global production of composite materials will significantly exceed 10 million tons by 2015, which will occupy a volume of over 5 million cubic meters. Glass fibre reinforced composites (GRP) account for approximately 90% of all the fibre reinforced composites currently produced.

Furthermore, many GRP market sectors such as wind turbine applications have growth rates well into double figures with a predicted 6 million tons of GRP wind turbine blades to be produced globally over the coming decade. Currently most of this material is destined for landfill at the end of its 10-25 year application lifetime.

A number of processes are available for recycling composites. Of these possible routes, thermal recycling is probably the most advanced technologically. However, nearly all options deliver recycled materials which suffer from a lack of cost competitiveness with pristine first-pass materials. A key factor in this equation is that there is a huge drop in the performance of recycled GFs (80-90%) in

comparison to its original state. Consequently, recycled GFs have a very poor performance to cost ratio, and in most cases are considered unsuitable for reprocessing and reuse as a valuable reinforcement of composites. For these reasons, landfill is currently the most common way of composite disposal. However, expanding the use of the landfill option is increasingly being perceived as environmentally and economically unacceptable.

In this study, thermal treated GFs [1], were investigated to recover their mechanical properties and to compare to pristine GFs. The goal of this project is to benchmark the effect and performance of silane coupling agents on the critical performance strength of recycling GFs from GRP. This paper is presenting the follow-on work for two previous research projects [2][3] studying the strength loss due to the thermal treatment combined with the interactions of silanes with the surface of GFs. Two of the main results of these studies showed that coating the fibres with silanes increased the strength of the bare GFs[2] and loss of tensile strength up to 60% at 450<sup>o</sup>C [3].

In this project heat treated GFs were coated with APS and MPS, using HCl to pre-treat them in some cases. The influence of these treatments on the fibre strength will be discussed.

## 2.1 Literature Review

### 2.1.1 Effect of Temperature in Glass Fibre

It is well known that the exposure of GFs to elevated temperatures affects mechanical properties, and results in strength loss[3].

In the case of GFs where the fibre-forming process imposes severe quenching on the glass, any explanation of measured physical and mechanical properties has to be based on the thermal history of the volume and surface glass in the fibre. It is supposed that a distinct surface layer forms when the fibre is fabricated, because the temperature of its surface is lower and its viscosity higher than its interior. The temperature gradient near the surface of the inner of the fibre is the greatest. The viscosity gradient of the surface layer is still greater because of the exponential dependence of the viscosity of the glass on temperature. As a result, the maximum stresses during the drawing of GFs are concentrated

in the thin surface layer with a viscosity exceeding substantially the viscosity of the interior of the inner of the fibre.

The quenching imposed by the fibre-forming process results in a form of glass which is so far from equilibrium at room temperature that most physical properties are affected. This does not mean that the glass is unstable at room temperature; the opposite of this in fact is shown when we measure properties they are well established. Experimental evidence shows that the thermal compaction is both time and temperature sensitive; thermal compaction increases with both time and temperature until the normal softening temperature of the glass is reached [4][5].

Regarding the fibre surface layer, it has to be considered that due to the high temperature, a slow flaw growth is produced, with it consequently decreasing the fibre strength due to the higher flaw severity and higher probability to break under loads applied to the fibre [6]. Exposure to high temperature can cause an increase of these defects.

### 2.1.2 Silane Coupling Agents

The general formula for a silane coupling agent typically shows the two classes of functionality due to its two moieties. R is a nonhydrolyzable organic moiety that can be either an alkyl, aromatic, organofunctional, or a combination of any of these groups. These groups provide the organic compatibility which allows the silane to form interpenetrating polymer networks, or in the case of reactive organofunctional silanes, to co-react with the coating polymer. The X represents alkoxy moieties, most typically methoxy or ethoxy, which react with the various forms of hydroxyl groups and liberate methanol or ethanol. These groups can provide the linkage with inorganic substrates (in this case GF surface), pigment, or filler to improve coating integrity and adhesion[7][8].

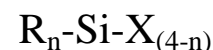


Fig.1. General Formula for a silane coupling agent [8].

Reaction of these silanes to an inorganic substrate involves the four steps shown in Figure 2.

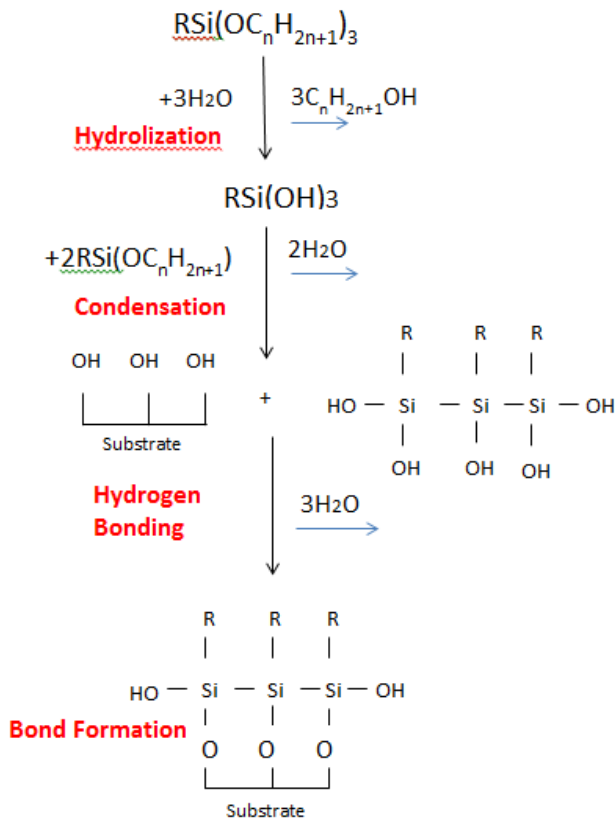


Fig.2. Reaction process of alkoxy silane [7].

Once the hydrolysis stage has occurred we assume the above four stages happen simultaneously. At the interface, normally there is one bond from each silicon of the organosilane to the substrate surface; the other two remaining silanol groups are usually present either condensed or free form.

The “Chemical Bonding Theory” states that coupling agents contain functional groups that can react with silanol groups on glass. This attachment to the glass can be made by covalent bonds. Apart from these bonds, coupling agents contain at least one different functional group which can react with the laminating resin during cure. This is the reason why the coupling agents act as a bridge to bond the glass to the resin with a chain of primary bonds.

### 3 Experimental

#### 3.1 Materials

The GFs used in this study were APS sized GFs provided by Owens Corning. The GFs are boron-

free E-glass under the trade of Advantex® with nominal fibre diameter as 17 µm.

The chemicals used in this project were HCl 37% [9] and two silanes, whose designations and structures are shown below:

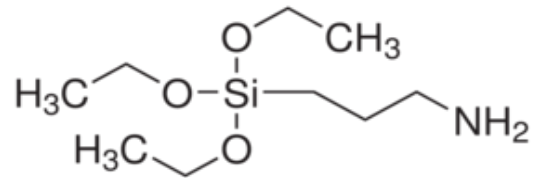


Fig.3.  $\gamma$ -Aminopropyltriethoxysilane (APS).

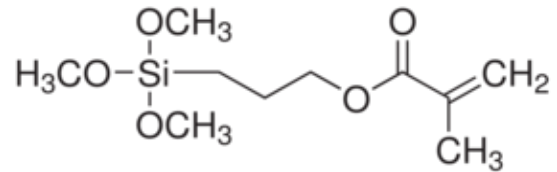


Fig.4.  $\gamma$ -Methacryloxypropyltrimethoxysilane (MPS).

#### 3.2 Thermal Treatment

A specially designed steel rig using a nut, bolt and washer to prevent fibre breakage, was used to heat treat the bundles. Care was taken to ensure that no damage was suffered by the bundle, damage due to tensile stresses and contact between them which may cause friction and consequently damage. Once the furnace had been preheated to 450<sup>0</sup>C for 1 hour, the rig was inserted into the furnace for 25 minutes. Thereupon it was removed from the furnace leaving it cooling under room temperature for at least 30 minutes. These thermally conditioned fibres were then treated with HCl and silanes.



Fig.5. 2 Bundles Steel Rig. A) GF Bundle. B) Nut, bolt and washer.

All the treatments done in this work are summarised below:

1. Heat Treated GF at 450°C (HT).
2. HT followed by HCl 10% v/v for 1 hour.
3. HT followed by APS 1% v/v for 15 minutes.
4. HT followed by MPS 1% v/v for 15 minutes.
5. HT followed by HCl 10% v/v for 1 hour followed by APS 1% v/v for 15 minutes.
6. HT followed by HCl 10% v/v for 1 hour followed by MPS 1% v/v for 15 minutes.
7. Original APS sized GFs.

### 3.3 Acid Treatment (HCl 10% v/v)

The procedure followed for the HCl 10% v/v treatment was the same for every combination in which HCl was used. First of all, a 10% v/v solution has to be made. Using deionized water, the HCl 37% was diluted. Once the concentration of the HCl is 10% v/v, the heat treated GFs bundles have to be immersed in it, leaving them for 1 hour at room temperature[10]. Thereupon the GFs bundles were rinsed in deionized water for at least 1 minute. If this is the only treatment applied to the GFs bundles, a drying process follows, which consists of placing the bundles in an oven at 110<sup>0</sup>C for 15 minutes. The oven should previously be preheated for 15 minutes; the steel rig is used for this process. The HCl treatment was applied to achieve an increase in hydroxyl groups (OH) concentration on the GFs surface as J. Baselga et.al. probed to try to increase the probabilities of reaction between the silanes and the GFs. On the other hand, for similitude with

Hydrofluoric acid (HF) treatment, is expecting to see a slightly etching effect[11].

### 3.4 Silane Treatments (APS and MPS)

The hydrolyzing of silane was done by preparing a 1% v/v of each silane in deionized water. The pH of the deionized water was its natural which is about 8, measuring it with a pH meter which was calibrated using pH 4, 7 and 10 buffer solutions. Once the solution was made, each solution was left for 24 hours hydrolyzing.

With the solution ready to be applied GF samples were completely immersed in the silane for 15 minutes at room temperature. Based on the paper by Yue and Quek[12] determined that the immersion time is not a critical factor in the relationship with the silane deposition on the dried GF surface. The samples were then removed from the solutions and dried following the same process described above.

Regarding the process described above, it is important to leave the silane treated bundles over night before preparing the tensile samples to be sure that the bundle is perfectly dried and any remaining reactions have occurred.

It was observed during this process that the GF bundle treated with APS and with MPS showed a different rigidity, being more rigid the one coated with APS than the one with MPS. Also there were differences in the silane deposition depending on the combination followed, that will be shown later using SEM pictures.

### 3.5 Single Fibre Tensile Testing

Once the GFs samples had been treated, they were prepared in templates for a gauge length of 20mm like the one shown in Figure 6, leaving the glue drying overnight; when the glue is dry the diameter of every sample was measured using an optical microscope. Thereupon 60 samples per treatment were tested following the ASTM standard D3822-07 using the Instron Tensile Testing 3342 at room temperature.

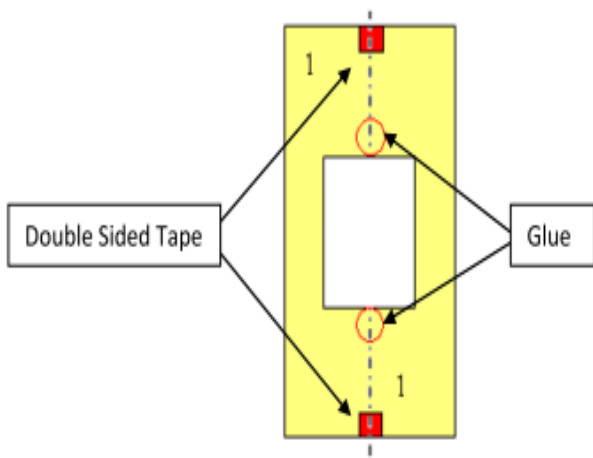


Fig.6. Single Fibre Test Template.

A 10N load cell was used for these tests and a ramp rate of 0.3 mm/min was applied, resulting in a 1.5% strain/min for the gauge length of 20 mm.

### 3.6 Scanning Electron Microscope (SEM)

The Scanning Electron Microscope used was a HITACHI SU-6600, a high resolution analytical variable pressure, field emission scanning electron microscope. The samples were coated in gold using an Edwards S150 sputter coater, to obtain a clearer picture of the fibre surface.

The SEM was used to carry out examination of the GFs surfaces, before and after chemical and silane treatments and combinations of both that were applied, paying special attention to surfaces of the ones treated with silanes.

### 4 Results

The experimental stress strain curves were linear, unsurprisingly in brittle materials. The results of the average fibre strength (error bars show 95% confidence limits) are shown in Figure 7, showing them in increasing order.

Table 1 Treatments Applied.

Treatment	1	2	3	4	5	6	7
HCl 10%	-	1 h	1h	-	-	1h	-
APS1%	-	-	15 min	15 min	-	-	-
MPS 1%	-	-	-	-	15 min	15 min	-

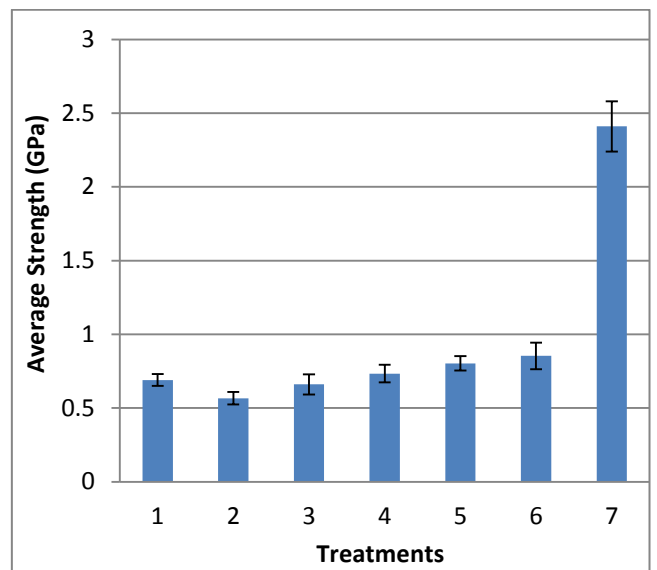


Fig.7. Average Fibre Strength (GPa).

Table 2 Average Diameters.

Treatment	1	2	3	4	5	6	7
Average Diameter (um)	16.9	16.6	16.9	16.8	16.5	16.6	16.9

The results obtained show that the HCl treatment has not got any direct benefit in fibre strength; in fact the fibres suffer a slight decrease in fibre strength after treatment in HCl. On the other hand the results show that the effect of any silanization applied increases the fibre strength. Combination number 6 is the best

one (HCl 10% v/v for 1 hour followed by MPS 1% v/v for 15 minutes).

No etching effect was seen comparing the average diameters of the different treatments (Table 2).

**5 Discussion**

Using the Weibull plots the different results achieved are further compared. Basically all the different treatments applied for the GFs show a very good agreement with a linear fit or unimodal as established by the  $R^2$  curve fit value, which leads us to think that the fibre failure is caused by one type of flaw population. Probably this unimodal distribution can be attributed to a remaining residue of the

coating of the original Owens Corning APS sized E-GFs, which hasn't been completely removed from the surface by the different treatments, heat and chemical treatments applied, still healing the surface flaws [13].

In Figure 8 we can see the differences between the heat treated GFs and the ones with the HCl treatment alone. The ones with only the heat treatment can be seen that are slightly better than the ones with the HCl treatment. The Weibull modulus for the heat treated GFs is a bit bigger than the other, which means that the distribution of the flaws is less evenly [14][15].

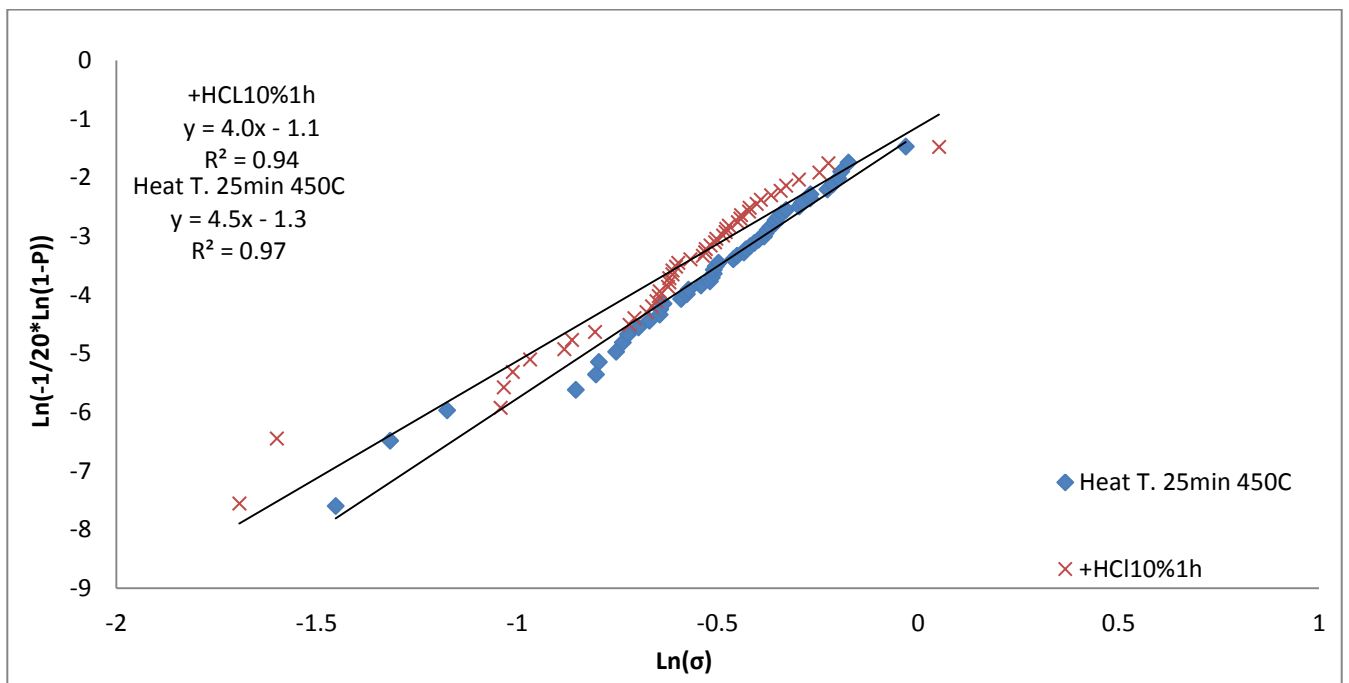


Fig.8. Weibull distribution. Heat Treated fibres (baseline) and HCl Treated fibres.

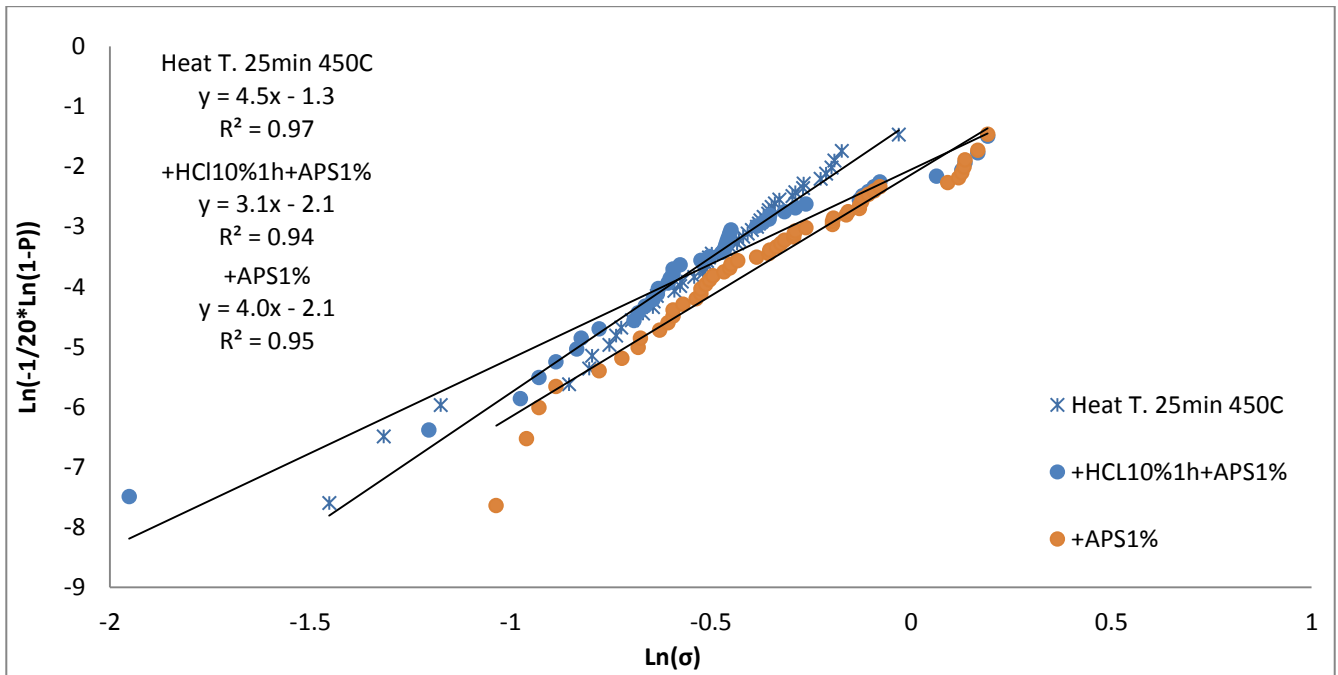


Fig.9. Weibull distribution. Heat treated, APS treated with and without chemical treatment.

For the different two treatments using APS silane, we can see that the difference between both is small (Figure 7). The combination of the chemical treatment with HCl and APS can be confirmed that is not satisfactory. The strength increase is almost negligible. Regarding to the Weibull distribution (Figure 9), both Weibull modulus are lower than the one for only heat treated GFs, which confirm us that the flaw distribution is more irregular and therefore the silane doesn't heal the flaws.

Using MPS two treatments have been applied as well. The average strength for the combination of HCl and MPS gave a higher average strength than the one for MPS. If we focus on the Weibull distribution shown on Figure 10, this average strength could be misleading. We can see two clear different parts for the values obtained. For lower strengths the values for MPS treatment are higher than the ones for HCl combined with MPS, but when the strength increases the opposite occurs, we

start to have higher values for the combination of HCl and MPS. If we analyse the Weibull modulus, it tells us that the flaw distribution is more regular for the MPS treatment than the combination, but the  $R^2$  curve fit value is not bad enough to make us think it has to be bimodal.

In Figure 11 the comparison of the APS 1% and MPS 1% treatments are shown. The strength developed for the MPS treatment is higher than the one with the APS treatment (Figure 7). From the Weibull plot in Figure 17 we can see that at lower strengths, the values for MPS are higher than the ones for APS, but when the strength begins to increase both values become to be similar. Feih et. al.[15] identified a threshold above it the silane doesn't affect the strength of the fibre. Comparing the Weibull modulus we can say that the flaw distribution for MPS GFs is more uniformly distributed, being the MPS Weibull modulus substantially higher than the APS one.

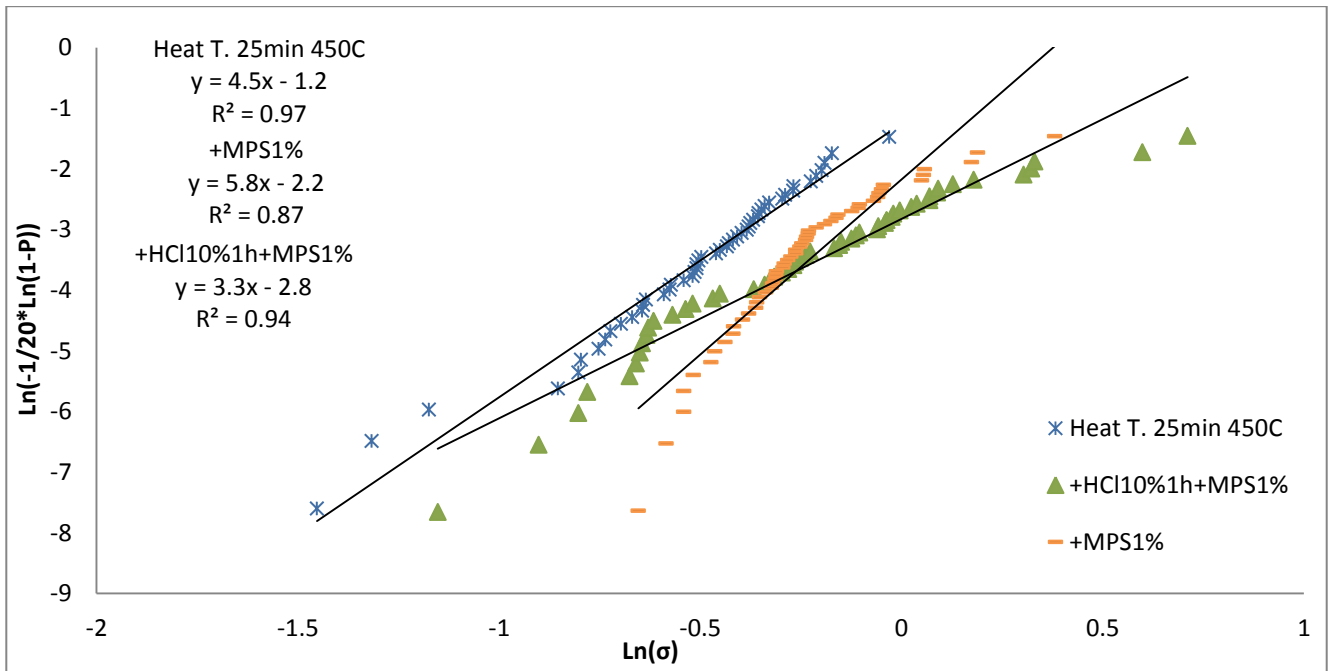


Fig.10. Weibull distribution. Heat treated, MPS treated with and without HCl treatment.

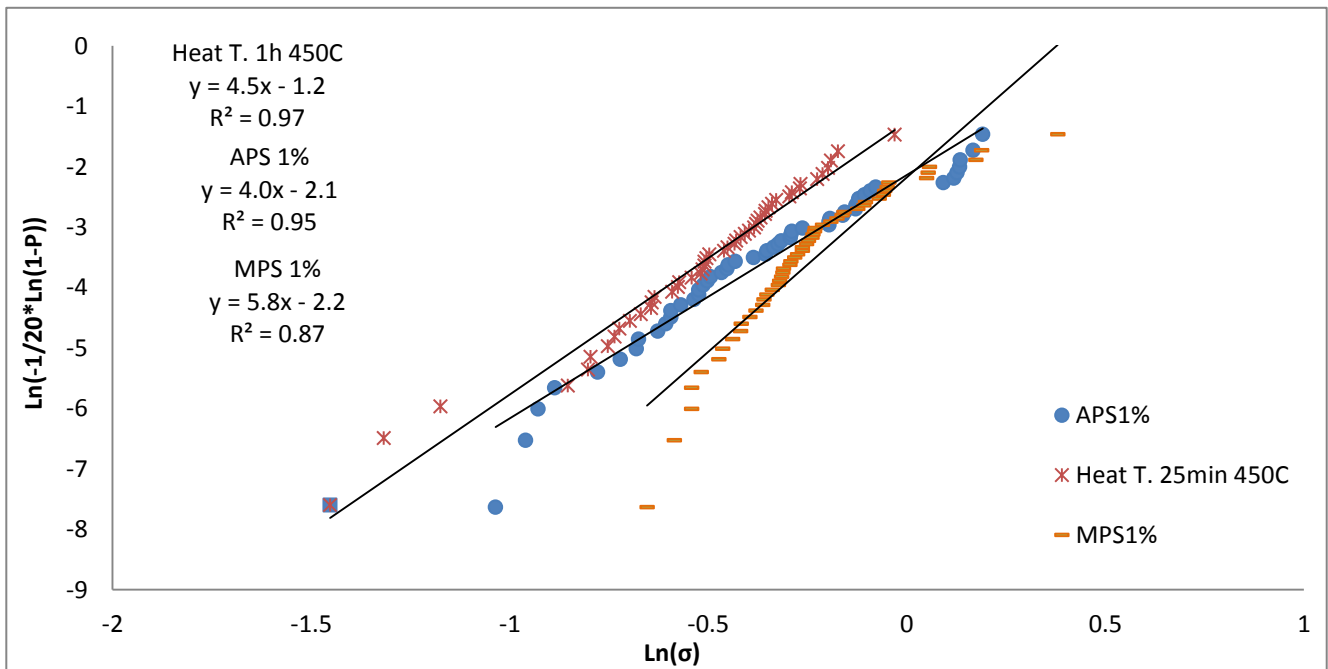


Fig.11. Weibull distribution. Heat treated, APS treated and MPS treated.

The last Weibull plot (Figure 12), compares the HCl treatment and the combination treatments with APS and MPS. As previously explained and shown in other plots, it is clear that the combination of HCl

with MPS is significantly better than the APS one and of course the HCl treatment.

Both combinations have basically the same Weibull modulus, which means that the flaw distribution can



be assume is practically the same. Focus on the data points; the values for the combination with MPS are always higher than the ones for the APS

combination. It tells us that MPS combination has a better effect when healing the flaws.

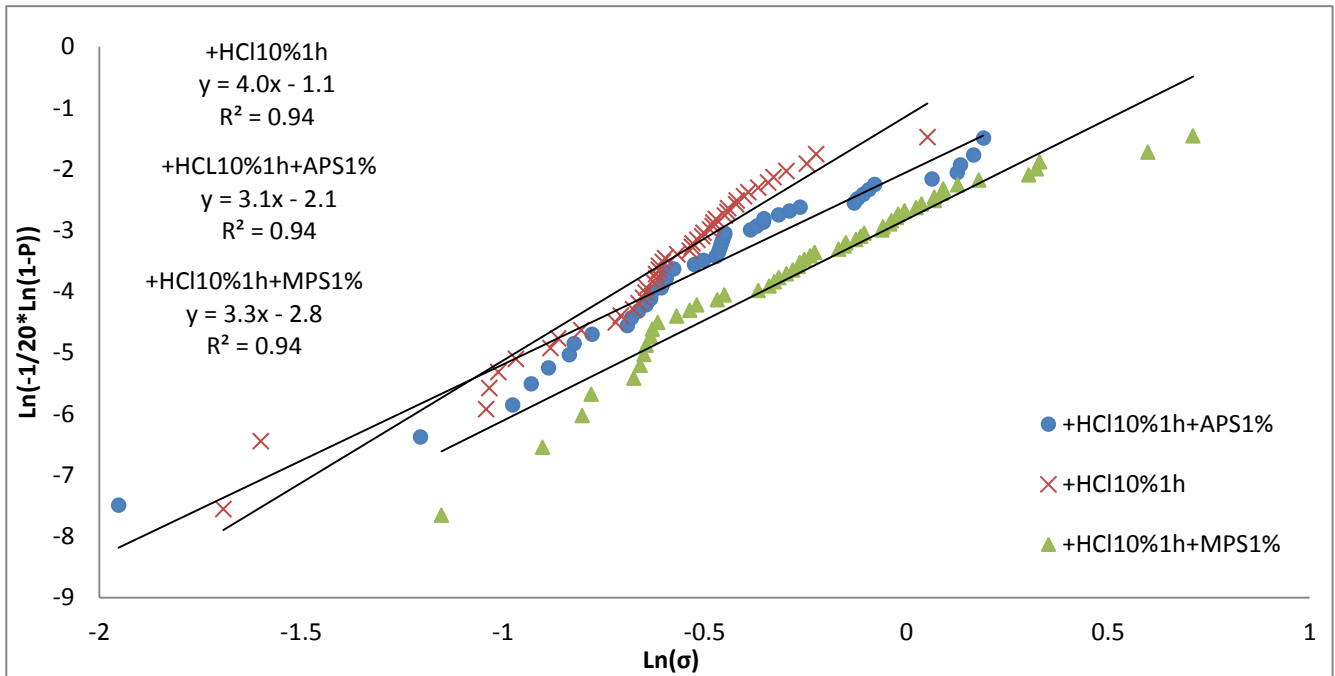


Fig.12. Weibull distribution. HCl treatment and combination with APS and MPS.

Once the Weibull distribution of different treatments has been explained, some typical SEM pictures of the different treated GFs are going to be analyzed.

In Figures 13 and 14 we can see the typical appearance of heat treated GF. In Figure 14 a bump is shown, probably due to the heat treatment or the effect of the electrons through the remaining coated.

The SEM picture of the heat treated fibre with the chemical treatment of 1 hour immersed in HCl 10%, is basically the same (Figure 15).

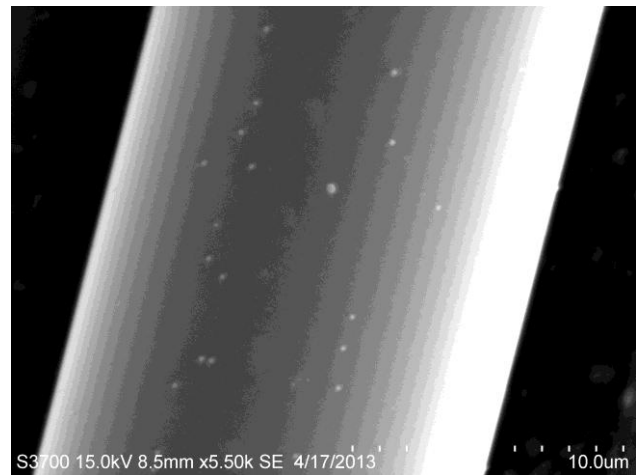


Fig.13. SEM Picture. Heat Treated Fibre at 450<sup>0</sup>C for 25 minutes.

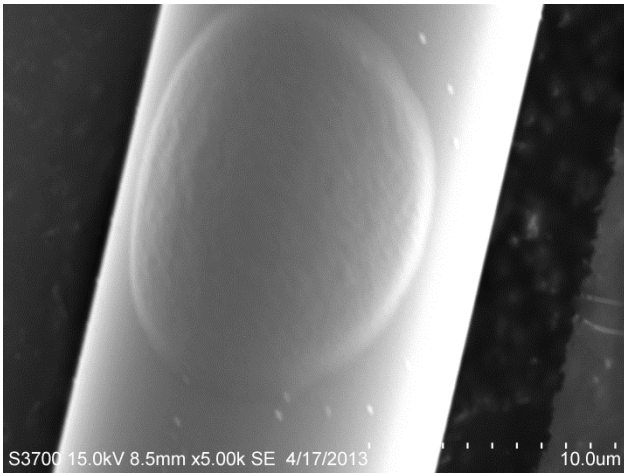


Fig.14. SEM Picture. Heat Treated Fibre at 450<sup>0</sup>C for 25 minutes with a bump.



Fig.15. SEM Picture. Heat and HCl Treated Fibre.

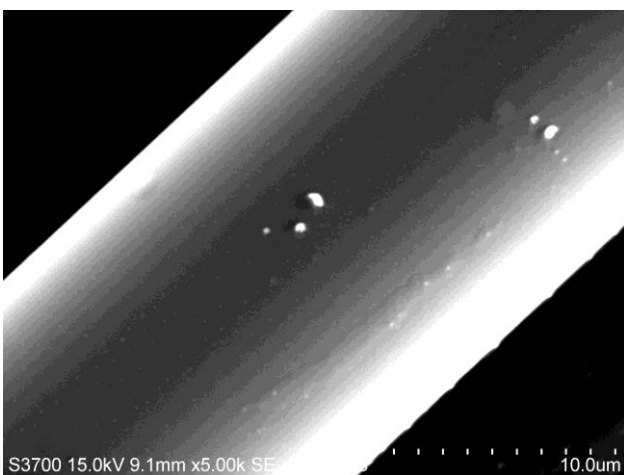


Fig.16. SEM Picture. Heat and MPS Treated Fibre.

Comparing the APS and MPS treatments on heat treated GFs, silane deposition can be seen easily. The difference is that the deposition of the MPS apparently is more homogeneous in comparison with the deposition of APS (Figures 16 and 17).

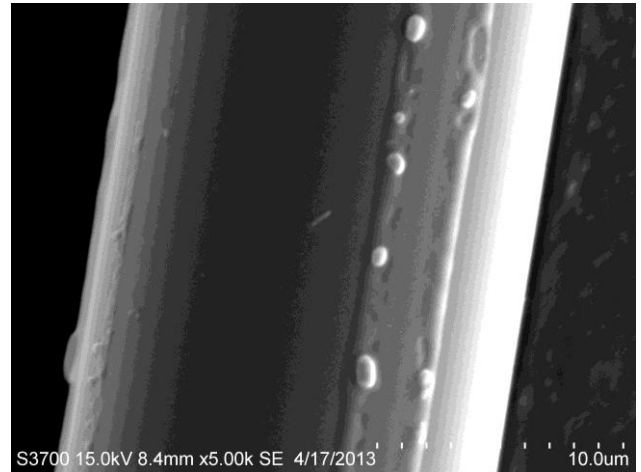


Fig.17. SEM Picture. Heat and APS Treated Fibre.

For combinations of HCl and the silanes, Figures 18 and 19 showed that the amount of MPS on treated fibre surface appears to be higher than that with APS. Comparing Figure 18 and 19 with Figure 16 and 17, HCl treatment prior to silanisation seems to increase MPS deposition on heat-treated GFs and appears to have an opposite effect on APS deposition. On the other hand, the combination of HCl and MPS treatment seems to leave a less homogenous surface coverage. This may explain the relatively low Weibull modulus compared to the one with only MPS treatment in Figure 10.

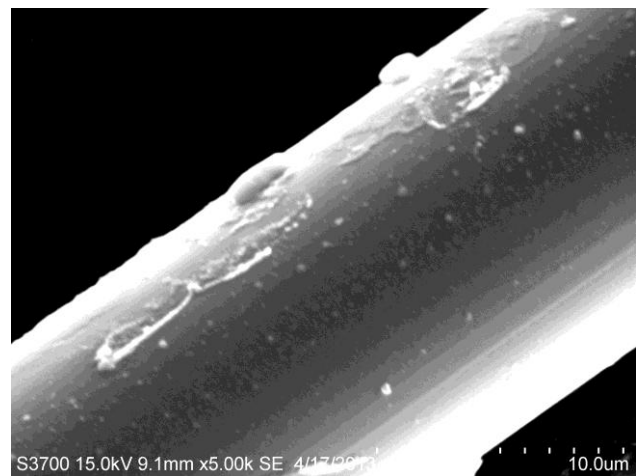


Fig.18. SEM Picture. Heat, HCl and MPS Treated Fibre.

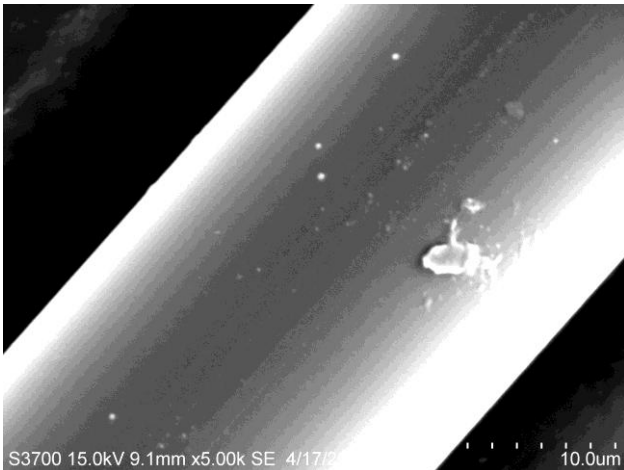


Fig.19. SEM Picture. Heat, HCl and APS Treated Fibre.

## 6 Conclusions

This paper presents our initial attempt at regenerating the strength thermally conditioned GFs. The results showed that using a simple silane treatment cannot recover the strength of conditioned GF.

Based on the work by J. Baselga et.al. which showed the increase of the hydroxyl group (OH) in the GF surface after being immersed for a period of time in HCl, effect of APS on strength recovery cannot be confirm and for MPS the results are slightly better. On the other hand we can confirm that the HCl has not got any etch effect as HF does, without any attack or reduction in the diameter of the GFs.

Results showed that the commonly used silane APS, does not work well with and without HCl treatment, probably due to a bad reactivity performance with the heat treated GF surface.

Regarding the MPS, it has more options of research. A higher average strength was for the combination of HCl and MPS, and the higher distribution shown in the Weibull plot in comparison with the MPS treatment make suggest that it has a good potential to be studied more in-depth. Once better combination is found, the strength could be substantially increased to the higher values of the Weibull plot, making the Weibull values higher what would be translate in an evenly distribution, a higher strength recover.

## 7 Acknowledgements

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