REGENERATION OF THERMALLY RECYCLED GLASS FIBRE FOR COST-EFFECTIVE COMPOSITE RECYCLING: INCREASING THE STRENGHT OF THERMALLY CONDITIONED GLASS FIBRES USING COST EFFECTIVE ReCoVeR TREATMENTS

E. Sáez-Rodríguez[a*], L. Yang[a], J. Thomason[a].

1Department of Mechanical and Aerospace Engineering, University of Strathclyde, 75 Montrose Street, Glasgow, G1 1XJ, United Kingdom
**eduardo.saez-rodriguez@strath.ac.uk*

Keywords: Glass Fibre, Recycling, Strength, Regeneration.

Abstract
The paper reports an extensive study on the regenerating performance of thermally treated glass fibres using two different treatments routes. The effectiveness of these two different treatments was investigated on strength recovery of glass fibres thermally treated with the conditions imitating composite recycling technology. The regenerated strength levels of these ReCoVeRed fibres must also be further protected and maintained by the use of standard fibre sizing technology similar to standard glass fibre products. Consequently, the effect on fibre strength of the combination of our ReCoVeR treatments. Significant increase of fibre strength was obtained through the ReCoVeR and coatings treatments, achieving up to 200% increase in fibre strength in comparison with the glass fibre thermally treated.

1. Introduction

The processing and reuse of end-of-life composite products in an environmentally friendly manner is one of the most important challenges facing the industry and community. The development of an economically viable process for regenerating the properties of thermally recycled glass fibres (GFs) would have major technological, societal, economic, environmental impacts. The ultimate goal of this project is to enable cost-effective regeneration of the mechanical properties of GFs which have been produced from thermal recycling of end-of-life glass reinforced structural composites from automotive and wind energy applications. The global annual production of glass reinforced composite materials is rapidly approaching 10 million tons, of which approximately 60% is thermoset based. A breakthrough in the regeneration of recycled glass fibre performance has the potential to totally transform the economics of recycling such glass fibre reinforced plastics composites (GRP) which would otherwise most likely be disposed of to landfill. This will enable such recycled fibres to compete with, and replace, pristine materials in many large volume composite applications. The reuse of these materials could result in a huge reduction in the environmental impact of the glass-fibre composites supply industry.

Nowadays, 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][2], were investigated to recover their mechanical properties and to compare to pristine GFs. The goal of this project is to benchmark the huge drop in the performance of heat treated GFs and the performance of ReCoVeR treatments on the critical performance strength of recycling GFs from GRP. This paper is presenting the follow-on work for previous research project [3][4] studying the strength loss due to the thermal treatment combined with the interactions of ReCoVeR treatments on GFs. Results of these studies showed the ReCoVeR treatments applied increased the strength of the heat treated GFs and loss of tensile strength up to 200% at 450^0C.

2. Literature Review

2.1. 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 [2].

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 [5][6].

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[7]. Exposure to high temperature can cause an increase of these defects.

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. HCl 37% [8] and Methacryloxypropyltrimethoxy Silane (MPS), whose structure is shown below, were used as well:

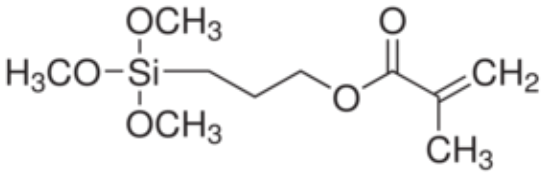

Figure 1 γ-Methacryloxypropyltrimethoxysilane (MPS).

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 (Figure 2). 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.

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

Once the furnace had been preheated at the required temperature (from 350^0C up to 500^0C every 25^0C) 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.

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[9]. 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 110^0C 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[10].

3.4. Silane Treatment (MPS)

The hydrolyzing of MPS was done by preparing a 1% v/v of MPS 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, it 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[11] 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 solution 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.

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 3, leaving the glue drying overnight.

Once the glue is dry the diameter of every sample was measured using an optical microscope. Thereupon 30 samples per treatment were tested following the ASTM standard D3822-07 using the Instron Tensile Testing 3342 at room temperature.

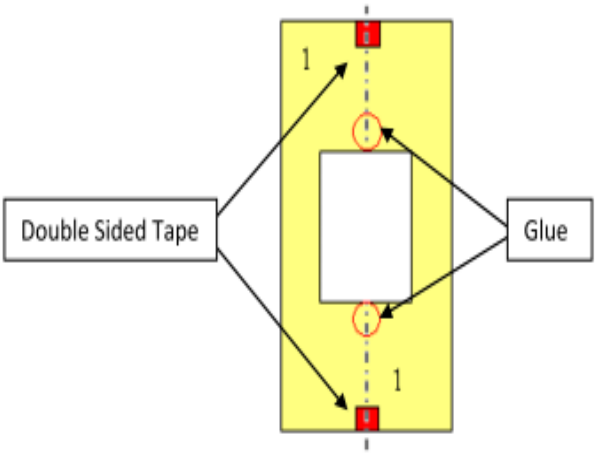

Figure 3 Single Fibre Test Template.

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.

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 below.

4.1. Thermal Degradation of Fibre Strength

Figure 4 shows the average fibre strength values for heat treated GFs at different temperatures from 350^{0}C up to 500^{0}C in intervals of 25^{0}C of temperature increase.

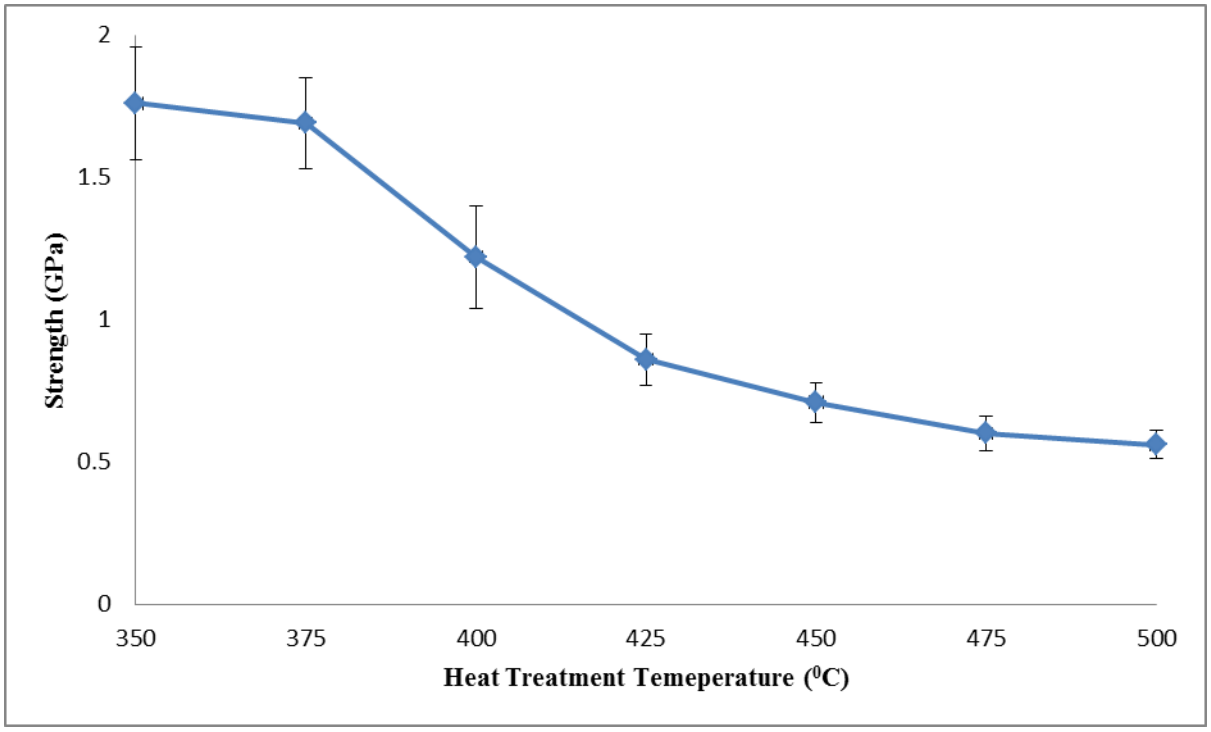

Figure 4 Heat Treated GF Strength.

The results obtained show that there is huge drop in GF strength between 375^{0}C and 450^{0}C reducing its GF strength from 1.7GPa to 0.7GPa. After this temperature the GF strength decreases from 0.7GPa to 0.56GPa between 450^{0}C and 500^{0}C.

4.2. Strength ReCoVeR

Results obtained for heat treated GFs at 450^{0}C are shown in Figure 5, where the best results obtained in previous work [3] and the ones obtained using the ReCoVeR treatments are shown together in increasing order. The treatments shown in Figure 5 are the ones below:

1. Original APS Sized GFs
2. Heat Treated at 450^{0}C for 25min (HT)
3. HT followed by MPS 1% v/v for 15 minutes
4. HT followed by HCl 10% v/v for 1 hour followed by MPS 1% v/v for 15 minutes
5. HT followed by ReCoVeR 1
6. HT followed by ReCoVeR 2
7. HT followed by ReCoVeR 3

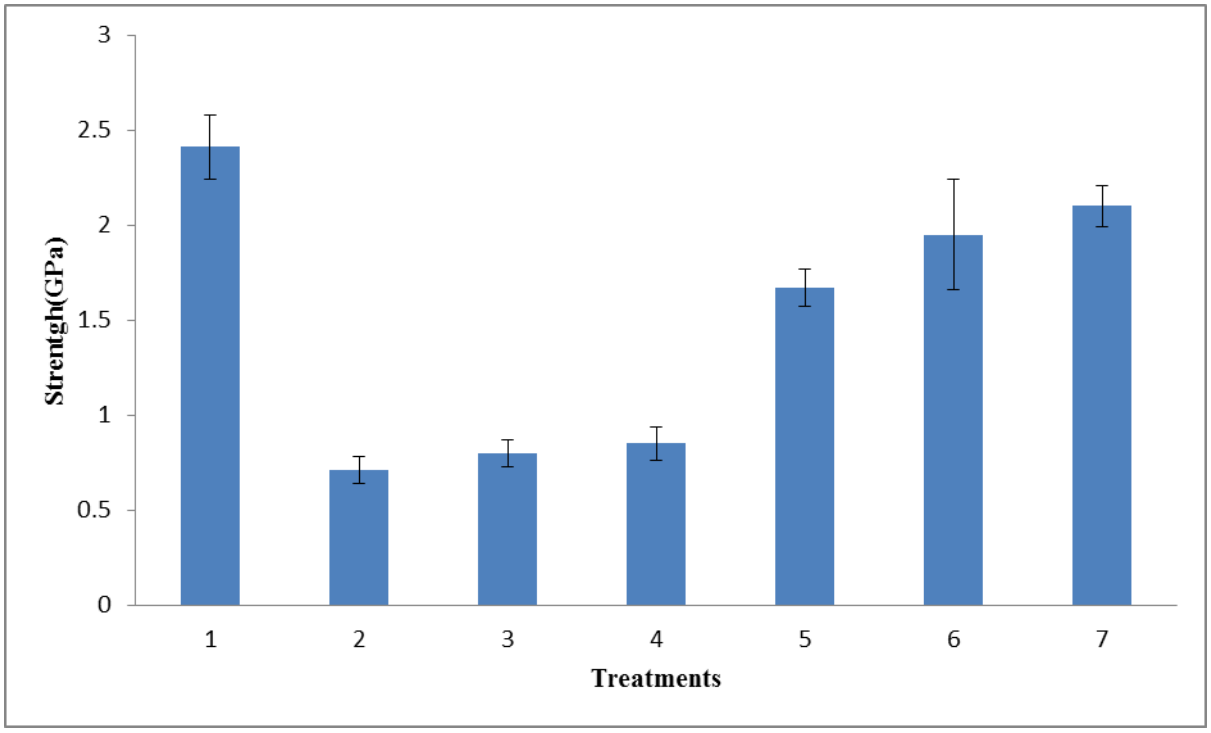

Figure 5 Average Fibre Strength.

The results show that any ReCoVeR treatment applied substantially increases fibre strength, especially in compare with the other treatments, being ReCoVeR 3 the best one.

5. Conclusions

This paper presents the characterization of the huge drop in GF strength due to the thermal treatment. The heat treatment temperature of 375^0C could be considered the critical temperature after which the GF strength starts to decrease faster related to the temperature increase until 450^0C is reached. It seems to be that for temperatures above 450^0C until 500^0C GFs strength decreases but in a less sharply way.

Really promising progress at regenerating the strength of thermally conditioned GFs are shown as well. The results show that using the ReCoVeR treatments the strength of conditioned GFs can be recover. Based on the work done before that did not show any substantial increase in GF strength using simple silanes and the combination of them with Hydrochloric Acid (HCl), ReCoVeR treatments seem to have a remarkable positive effect in GF strength, reaching values up to 200% increase of the conditioned GFs.

This strength recover may give the opportunity to produce composites materials using these ReCoVeR GFs with similar properties than the ones using pristine GF.

6. Ackwonledge

This research work has been financially supported by the EPSRC as part of the Regenerated Composite Value Reinforcement (ReCoVeR).

The Authors would like to acknowledge Dr Chih-Chuan Kao, Simson McCreath and Advanced Materials Research Laboratory (AMRL) for support and guidance throughout the execution of this work and all the members of the Advanced Composites Group for their support and help.

References

[1] S. Feih, E. Boiocchi, G. Mathys, Z. Mathys, A.G. Gibson and A.P, Mouritz. Mechanical Properties of thermally-treated and recycled glass fibres. *Composites: Part B*,42(3): 350-358, 2011.

[2] P. Jenkins, J. Thomason and R. Meier. Separation of mechanical and thermal degradation of thermally conditioned sized glass fibre. *15th European Conference on Composite Materials*, 2012.

[3] E.Saez-Rodriguez, L. Yang and J. Thomason. Investigation of strength recovery of recycled heat treated glass fibres through chemical treatments. *19th International Conference on Composite Materials*. 2013.

[4] S.P. Reilly and J. Thomason. Effects of silane coating on the properties of glass fibre and glass fibre reinforced epoxyresin. *14th European Conference on Composite Materials* 2010.

[5] G.M. Bartenev. Constitution and strength of glass fibres. *International Journal in Fracture Mechanics*, 5(3): 179-186, 1969.

[6] W.H. Otto. Compaction effects in glass fibers. T*he American Ceramic Society*. 44(2): 68-72, 1958.

[7] P.K. Gupta. Strength of glass fibers. M. Elices and J. Llorca, *Fibre Fracture*,129-151, Elsevier Science, 2002.

[8] N.N. Greenwood and A.Earnshaw. *Chemistry of the elements.* Elsevier Science, 1997.

[9] J. Baselga, A.J. Aznar and J. Gonzalez. Microestructural and wettability study of surface pretreated glass fibres. *Journal of Materials Processing Technology*. 92-93: 129-134, 1999.

[10] G.A.C.M. Spiernings. Review: Wet chemical etching of silicate glasses in hydrofluoric acid based solutions. *Material Science*. 28: 6261-6273, 1993.

[11] M.Y. Quek and C.Y. Yue. The interfacial properties of fibrous composites. *Material Science*. 29: 2487-2490, 1994.