Regeneration Of Thermally Recycled Glass Fibre For Cost-Effective Composite Recycling: Increasing the strength of thermally conditioned glass fibres by HF treatment

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Abstract
In this paper the results of an extensive study will be presented of regenerating performance of thermally conditioned glass fibre using hydrofluoric acid (HF). The effectiveness of HF was investigated on strength recovery of glass fibres thermally conditioned in a typical temperature range for glass fibre recycling. The chemical treatment was also applied to glass fibres directly recycled from epoxy composites using a fluidised bed technique. The effect of treatment time on fibre strength was studied. A significant increase of fibre strength was obtained through the HF treatment and apparent reduction of fibre diameter suggested that strengthening mechanism was associated with HF etching. SEM/EDX was used to examine the surface alteration caused by the HF treatment.

Keywords: Glass Fibre, Strength Regeneration, Composites Recycling

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 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 glass fibres 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 GRP composites 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.

Although thermoplastic based composites are, in principle, intrinsically recyclable, the greatest challenge is with the larger fraction of thermoset based GRP composites. The infusible and insoluble high-density networks in molecular structure make thermosetting polymers ideal candidates for composites with more demanding performance required in areas

such as aerospace and wind energy. The same reason for their merits, however, has also been causing difficulties in recycling thermosetting composites. The 3D networking structure does not result in the same reprocessability as offered by thermoplastic polymers. Consequently, various techniques have been developed to recycle thermosetting polymers and these techniques have been seen to serve as the foundation of the recent development of thermosetting composites recycling. A number of processes are available for recycling such composites [Pickering]. Of these possible routes, thermal recycling is probably the most technologically advanced and has been piloted in the UK and Denmark. However, nearly all options deliver recycled fibres (which make up approximately 60% by weight of the composites) that suffer from a lack of cost competitiveness with pristine first-pass materials. A key factor in this equation is the huge drop in the performance of recycled glass fibre (80-90%) in comparison to its original state. Consequently, recycled fibres 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. A breakthrough in this field could enable such recycled glass fibres (RGF) to compete with pristine materials in many large volume composite applications. The development of an economically viable process for regenerating the properties of thermally recycled glass fibres would have major technological, societal, economical, environmental impacts.

In this paper we report the recent development in this critical area with particular focus on strength regeneration for thermally treated and recycled glass fibres. The aim of this study is to prove the concept for building a potential close-loop recycling for glass fibre thermosetting composites.

2. Experimental

2.1. Materials

Boron-free E-glass fibres supplied by Owens Corning Vetrotex were investigated in this work. All fibre rovings were produced on the same pilot scale bushing and were received as 20 kg continuous single end square edge packages. The rovings had a nominal tex of 1200 and a single fibre diameter of 17.4 ± 1.3 μm [1]. The molten fibres had all been hyperquenched by water spray before they were coated with a normal rotating cylinder sizing applicator containing a 1% γ-aminopropylsilane (APS) hydrolysed solution in distilled water. All fibre packages were subsequently dried at 105°C for 24 hours.

2.2. Thermal treatment

The fibres were used as received from the manufacturer. Heat conditioning was carried out in a Carbolite LHT6 high temperature oven at temperatures 450°C. The glass fibre strands were suspended on a specially constructed jig preventing any contact with, and therefore damage to, the fibres. 300 mm lengths of silane sized and water sized fibre strand with no visible damage were removed from the inside of the roving packages. These samples were selected such that the fibre length at the outside edges of the package, with the highest probability of transport and handling damage, were not included in the gauge length. Care was also taken that the sample strands were not touched by anything in the gauge length to prevent additional damage. Heat treatment of both fibre types was conducted simultaneously to obtain samples with identical thermal conditioning history. The oven temperature was allowed to stabilise for 2 hours prior to inserting the samples. After placing the samples in the oven 10 minutes was allowed for the oven

to return to the set temperature and then a further 15 minutes was then allowed for the heat treatment. During the heat treatments no load was applied to the fibre bundles to avoid creep effects.

2.3. Chemical treatment

The heat-treated fibres were then soaked in 1-10% HF solution, which had been aged for 40 minutes. The fibres were chemically treated in the solution for various periods of time from 0.5 minutes to 2.5 minutes. After HF etching, the fibres were immediately rinsed for numerous times with deionized water followed by a drying process in an oven at temperature of 110°C for 15 minutes.

2.4. Scanning electron microscopy

Numerous high resolution images of the surfaces of glass fibres were captured using a Hitachi SU6600 Field Emission SEM (FE-SEM). Images were taken at an accelerating voltage of 15 kV and extraction voltage 1.8 kV. Both as received and fibres conditioned by the single fibre thermal conditioning method were imaged. In all cases the samples were gold coated prior to making observations.

2.5. Single fibre tensile testing

Single fibre tensile properties were determined following ASTM C1557-03. The card mounted single fibres were gripped in an Instron 3342 universal testing machine equipped with a 10 N load cell. After the specimen had been mounted in the test machine, a section of the tab was carefully cut away, leaving the specimen free to be loaded during the test. Sample gauge length was 20 mm for both fibre types and approximately 40 fibres were tested at each condition. The tensile testing strain rate used was 1.5%/min and all the tests were carried out at room temperature and 50% relative humidity. Only the tests where the sample broke along the gauge length at a distance greater than 3 mm from the clamps were used for further data processing.

3. Results and discussion

It was clear from our observation that the effect of HF solution on glass fibre strength and diameter of treated fibre is dependent on both concentration of the solution and treatment duration. The species of HF solution are extremely reactive to oxides in the glass fibre. The treatment with 10 wt% HF solution for 5 minutes proved to be too concentrated to produce fibres without too much removal of the material. Consequently, the solution was reduced down to 1 wt% and 4 wt%. It should be noted that the chemical reaction is also affected by the amount of glass fibres in the given HF solutions. Therefore, the volume of the solution for the same amount of glass fibres measured by the estimated total surface area was controlled throughout the study. Figure 1 shows the results for tensile strength of glass fibres treated by HF solutions for different length of time.

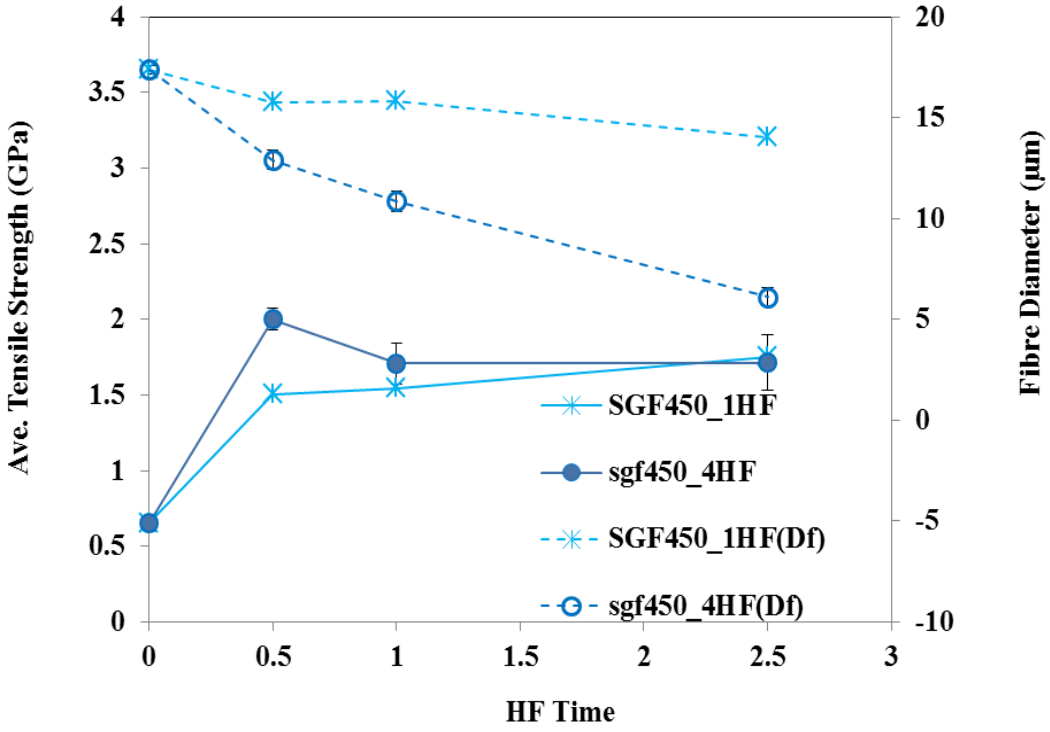

Figure 1. tensile strength of glass fibre treated with HF solutions

The results in Figure 1 show that the HF aqueous solution can significantly increase the strength of heat-treated glass fibres. Almost quadruple increase of the fibre strength was achieved after very short period of 4 wt% HF treatment to glass fibre heat-treated at 450°C. Strength of 2 GPa is just slightly below the commercially APS sized fibres as received. The effectiveness of HF solution on strength regeneration of heat-treated glass fibre is actually well known in the literature [2] and the results from Figure 1 confirm previous observations obtained by other authors. However, the results in Figure 1 reveal more details in this area. It is evident from Figure 1 that the positive effect of HF solutions on fibre strength is a function of both treatment duration and solution concentration. Low concentration would require more time to increase the strength of heat-treated glass fibre to the same level that would be achieved in less time by high concentration. However, such concentration dependence becomes insignificant after 2.5 minutes with the strength in HF-treated glass fibre tends to reach the same level. The strengthening mechanism of HF solution for glass fibre is well known as chemical etching process, in which HF molecules, HF_2^-, and H^+ in HF aqueous solution are generally considered as the reactive species to glass and can lead to dissolution reaction [3]. Figure 1 does seem to show that the strength increase is accompanied by HF etching process, which is characterised by a significant reduction in fibre diameter. However, as the strength gradually levels off, such correlation disappears. This is more clearly shown in Figure 2.

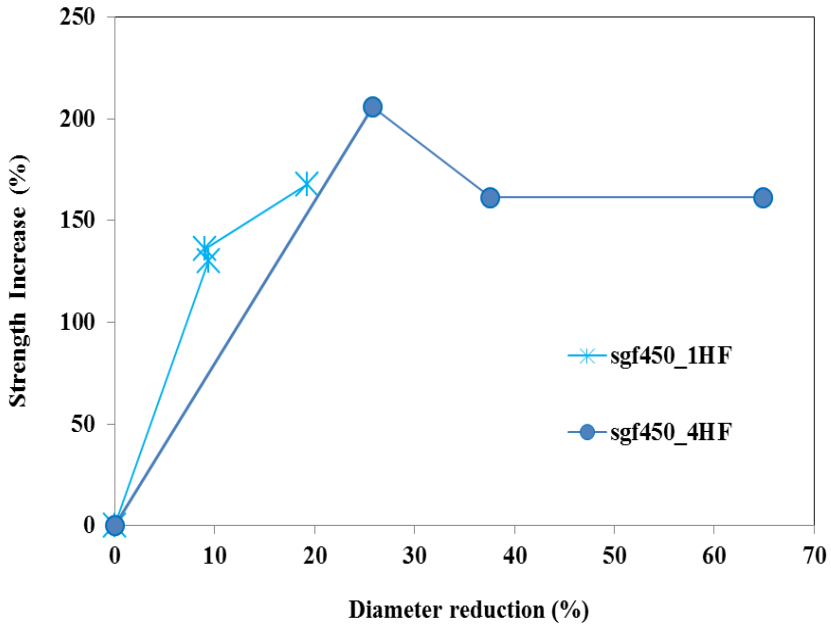

Figure 2. Strength increase as a function of diameter reduction in heat-treated glass fibre

In fact, the results from 4% HF treatment show that the highest strength is not found in the glass fibre with the largest reduction in fibre diameter. On the other hand, the results based on lower concentration in Figure 2 indicate a tendency for further strength increase with diameter reduction. These results imply that there may be an optimised diameter reduction for strength regeneration in heat-treated glass fibre by using HF etching process. It is also reasonable to expect that such optimal point is likely to be influenced by heat-treatment temperatures. It is quite clear that more work is required to further investigate the effect of HF etching and maximise strength increase. Nevertheless, the important message from these results is that the significant strength decrease in glass fibre after heating should mainly be attributed to the damaged surface layer and by removing such layer can tremendously boost mechanical performance of thermally conditioned glass fibres.

These results above strongly indicate that the limiting factors for low strength in heat-treated glass fibres are related to the glass surface layer. However, the increased strength is approaching to the level somewhat below the strength of original sized fibres after a removal of 4-5 μm thickness of the fibre. Theoretically, the depth of surface flaws on heat-treated fibres is expected to be less than 1 μm [4]. The etching process, even in a short period of time, may expose a flaw-free surface, which normally gives rise to the strength above 3 GPa. Such strength level has not been achieved by the treatment carried out so far. This may be due to the following possibilities: 1) although HF is capable of dissolve the network in the glass fibres, it may also leave the treated fibres with a characteristic surface, which might determine a corresponding level of the strength; 2) Assuming a flaw-free surface is obtained after the HF etching, due to lacking of any protection, surface flaws may then be introduced during the subsequent mechanical handling for the measurement. 3) Apart from dissolution of the glass, the species in HF solution may have ability to penetrate into the bulk structure and cause disruption to the internal network and longer term of treatment may lead to a more significant portion of more damaged internal network, giving a less increased strength. The fact that larger reduction in fibre thickness did not bring about any further increase of the strength suggest that the surface damage of HF-treated fibres is independent of the immediately exposed surface at least after 30 seconds of 4% HF treatment.

Figure 3 presents typical fibre surface after the treatment with 4% HF solution. It can be seen that the surface after 30 seconds treatment appear relatively clean and smooth compared to that after 2.5 minutes. The SEM-EDX showed (not shown here) that the particles left behind on the glass surface rich in fluorine and are likely to be reaction products during chemical treatment.

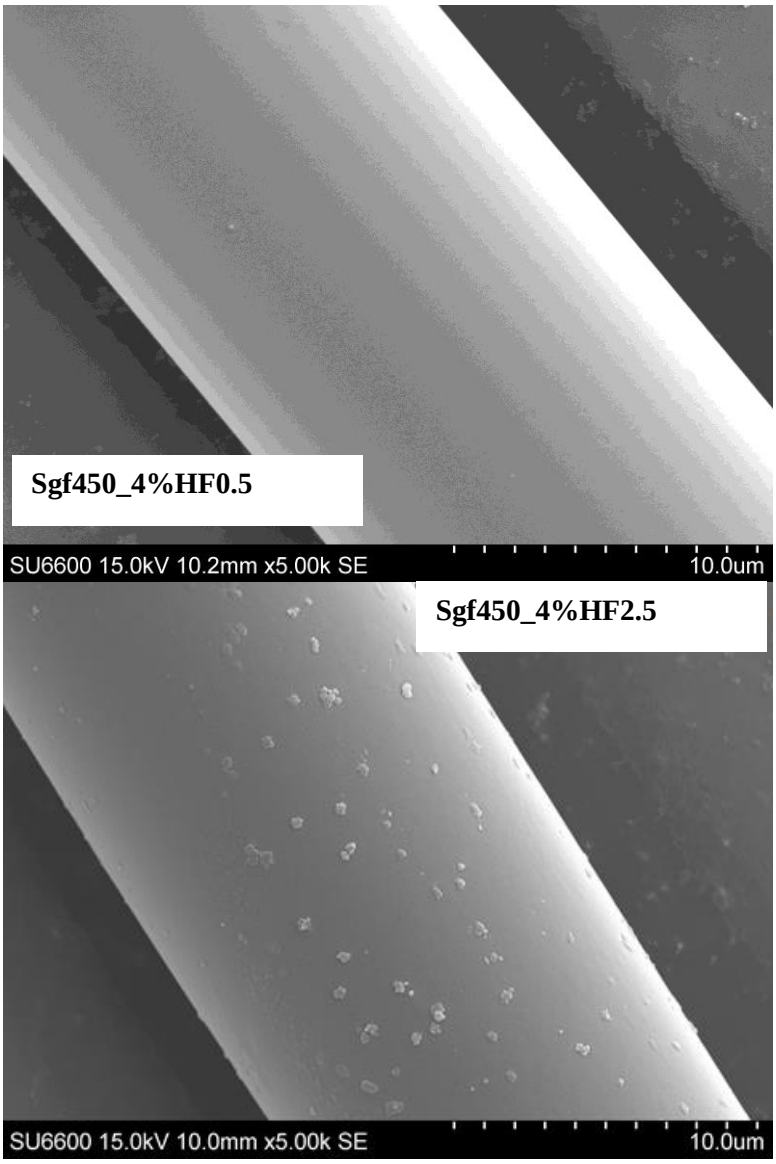

Figure 3. SEM photos of glass fibre treated by 4 wt% HF solution

Figure 4 shows the results for fibre strength of glass fibres recycled from epoxy composites using the fludised bed developed in the University of Nottingham [5]. The fibres were recycled at 500°C and followed 1wt% HF treatment. It is very interesting to see that HF etching process gives rise to almost the same amount of strength increase as that with controlled fibres as shown in Figure 1. It suggests that the thermal degradation of epoxy matrix does not seem to cause additional complication to strength regeneration with HF etching technique. More importantly, it proves that the performance of damaged glass fibre recycled from thermosetting composites using a proper thermal recycling technique can still be potentially regenerated if the severely damaged surface lay can be removed by HF etching or any other possible methods.

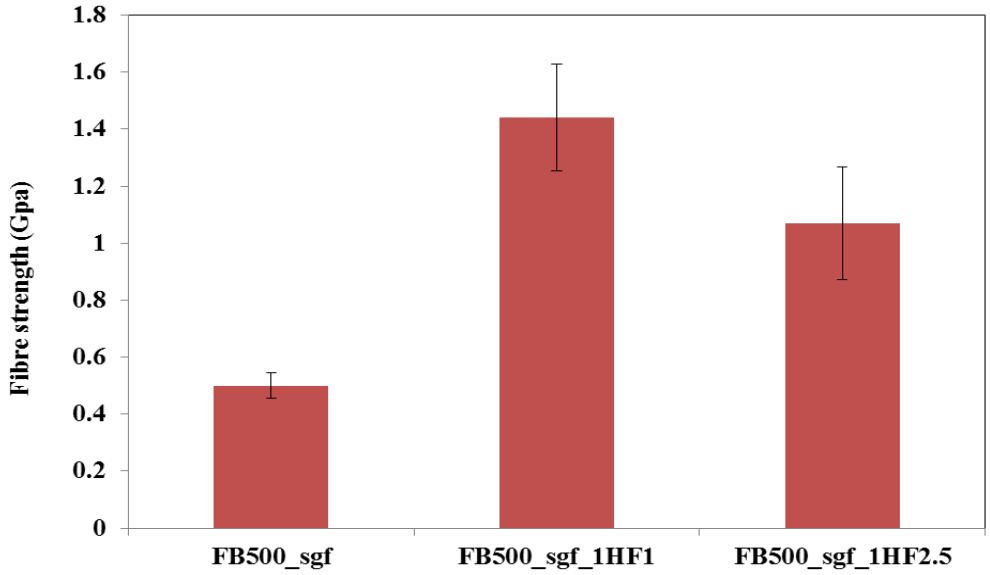

Figure 4. Tensile strength of fludised bed-recycled glass fibre after 1wt% HF treatment

4. Conclusions

HF aqueous solutions with different concentrations was used to regenerate the strength of glass fibres subjected to either thermally conditioning in the lab or recycling process in a fludised bed. The results showed that the HF etching process is able to tremendously increase the strength of damaged fibres by removing the surface lay. Such process was found to be influenced by both solution concentrations and treatment duration. The correlation between change in fibre diameter and strength disappears when the strength gradually reaches a plateau. There might exist an optimised treatment point before that level for HF treatment at relatively high concentration. The results in this work strongly indicate that the performance of damaged glass fibre recycled from thermosetting composites using a thermal recycling technique can still be potentially regenerated if the severely damaged surface lay can be removed by HF etching or any other possible methods.

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