A COST-EFFECTIVE CHEMICAL APPROACH TO RETAINING AND REGENERATING THE STRENGTH OF THERMALLY RECYCLED GLASS FIBRE

S. Bashir[1], L. Yang[2], R. Anderson, N. B. Basri, E. Sáez-Rodríguez, J. J. Liggat[3], and J. Thomason

[1]Department of Mechanical and Aerospace Engineering, University of Strathclyde, 75 Montrose Street, Glasgow, G1 1XJ, United Kingdom
Email: sairah.bashir@strath.ac.uk
Web Page: http://www.strath.ac.uk/compositematerials/staff/sairahbashir/

[2]Department of Mechanical and Aerospace Engineering, University of Strathclyde, 75 Montrose Street, Glasgow, G1 1XJ, United Kingdom
Email: l.yang@strath.ac.uk
Web Page: http://www.strath.ac.uk/compositematerials/staff/liuyang/

[3]Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL, United Kingdom
Email: j.j.liggat@strath.ac.uk
Web Page: http://www.strath.ac.uk/staff/liggatjohndr/

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Abstract

The purpose of this research study was to investigate the efficacy of alkaline treatments on restoring mechanical strength of thermally damaged glass fibres for potential reuse as reinforcement material. Here, E-glass fibres were heat treated in a furnace at 450 °C for 25 minutes in order to simulate the harsh thermal conditions required for the recycling of glass fibre thermosetting composites. Following heat conditioning, fibres were treated with three different alkaline solutions: sodium hydroxide (NaOH), potassium hydroxide (KOH) and lithium hydroxide (LiOH). Results showed little effect of LiOH solution, however both NaOH and KOH were proved to be successful in regenerating strength of fibres heat treated at 450 °C. It is believed these alkaline treatments might improve fibre strength by etching away surface defects. Factors such as concentration of alkali and treatment time were investigated in order to find optimum conditions for strength regeneration.

1. Introduction

Thermal treatment is a common approach to recycling of glass fibre reinforced thermosetting polymers (GRP) waste. By subjecting the material to elevated temperatures, degradation of the polymeric matrix is achieved with subsequent extraction of fibres. However the harsh conditions employed in this recycling procedure normally results in a severe loss in glass fibre strength limiting its current reusability in high performance applications [1, 2].

Increasingly restrictive legislation has been put in place in countries such as Germany regarding the disposal of fibre reinforced composite waste. Hence great demand exists for the development of a cost-effective treatment to restore mechanical strength in glass fibres following the severe thermal conditions in which they are recycled. An economical and effective chemical approach to regenerate strength in thermally degraded glass fibres means that closed-loop recycling of GRP waste can be achieved. This will have a positive environmental impact, as a reduced volume of end-of-life composite material will be destined for landfill. Recently, Yang et al. discovered that the strength of glass fibres heat conditioned at 450-600 °C almost tripled after a few minutes of immersion in dilute HF solution [3]. As HF is a highly toxic compound, its use for regenerating strength of thermally weakened glass fibres might be challenging on an industrial scale. Nevertheless, HF is proven to be an effective chemical etchant, and is able to strengthen glass by removing surface flaws [4].

In the present work, fibre bundles were heat treated at 450 °C before being immersed in relatively safer, alkaline solutions. The dissolution of glass in alkali is well documented in literature [5-7], however the use of these corrosive substances for strengthening glass fibre via etching of surface flaws is a novel concept. We have recently discovered that sodium hydroxide (NaOH), prepared at high temperatures and at caustic concentrations, can significantly improve the strength of glass fibre thermally damaged at 450 °C [8]. To further our understanding of glass etching by alkaline treatment, hydroxides based on other alkali metals were surveyed (LiOH and KOH). Alkaline solutions were prepared at concentrations between 1.5 M and 5 M, and heated in sealed containers before treating the thermally conditioned fibre bundles. Alkali concentration and immersion time were the two parameters investigated. Fibre diameters were measured to find any signs of etching, and single fibre tensile test data was collected to determine if the treatment was effective.

2. Experimental

2.1. Materials

Boron-free E-glass fibres were used in this study, and were supplied by Owens Corning Vetrotex. Fibres were coated with aminopropyltriethoxysilane (APS) coupling agent and had a nominal diameter of 17 μm. The chemicals used in this project were: NaOH pellets, LiOH powder, KOH flakes (all at 90% or above purity), and hydrochloric acid (HCl, 37%). NaOH and HCl were purchased from VWR, and KOH and LiOH supplied by Sigma Aldrich.

2.2. Thermal Treatment

A specially designed rig was used to heat the fibre bundles. Once the furnace was preheated to 450 °C, the rig was inserted for 25 minutes. Following this thermal conditioning, the rig was extracted from the furnace and left to cool at room temperature for around half an hour. The fibre bundles were then removed from the rig, and treated in various alkaline solutions.

2.3. Alkaline treatment

NaOH, LiOH and KOH solutions were prepared in 500 ml volumetric flasks. The solid was weighed into the flask according to the desired molarity (1.5 M, 3 M and 5 M) and then made up to the mark with deionised water. The solution was then poured into a polypropylene (PP) container, sealed, and heated to 95 °C for 2 hours in an oven. The heat treated fibre bundle was then immersed for 10 minutes, before being rinsed for 1 minute in 37 % HCl and then another minute in deionised water. Following this rinsing step, the fibres were left to dry in the oven at 110 °C for 15 minutes.

2.4. Single Fibre Tensile Testing

Glass filaments were carefully separated from the bundle and mounted on tensile test card using superglue. At least 25 samples were prepared at each treatment condition. Fibre diameters were measured using an optical microscope before testing for tensile strength using a Testometric tensile testing machine. The load cell was 5 N with a strain rate of 1.5 %/min applied to the samples. All fibres were tested at 20 mm gauge length at ambient environment.

2.5. Scanning Electron Microscopy (SEM)

A HITACHI SU-6600 field emission scanning electron microscope (FE-SEM) was used for aesthetic analysis of fibres following chemical treatment. Samples were coated in gold in order to acquire a clearer image of the fibre surface.

3. Results and Discussion

3.1. Single fibre tensile test data

At a thermal conditioning temperature of 450 °C, both the KOH and NaOH treatments had a positive impact on fibre strength, as shown in Figure 1 (error bars in all cases display 95 % confidence limits):

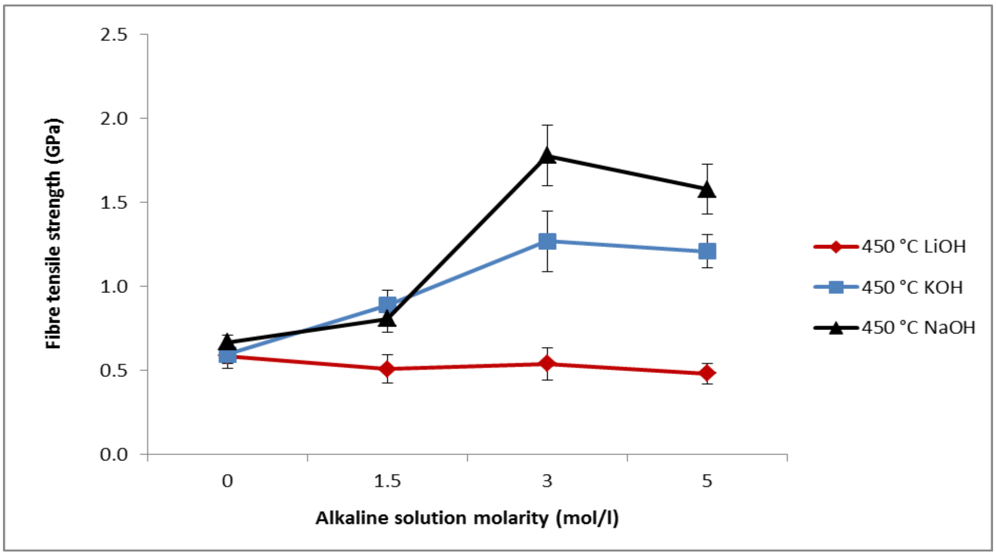

Figure 1. Average strength of fibres thermally conditioned at 450 °C and treated in various concentrations of alkali

From the results provided it is evident that 450 °C heat conditioned fibres treated in NaOH exhibit a significant increase in tensile strength, in particular at 3 M (0.67 GPa to 1.78 GPa). Similarly, treatment in 3 M and 5 M KOH increases strength to 1.27 GPa and 1.21 GPa respectively. However, no improvement in tensile strength of LiOH treated fibres was observed. The better strength recovery of fibres treated in NaOH as opposed to the other alkalis could be attributable to its higher reactivity with glass, leading to a more effective removal of surface defects on the fibre surface.

From previous work conducted by us, 10 minutes was found to be the most ideal treatment time for NaOH solution; accordingly KOH and LiOH treatments were carried out at this condition. Considering the rate of reaction between KOH and glass might differ, the effect of immersion time of this alkali on fibre strength was investigated (Figure 2).

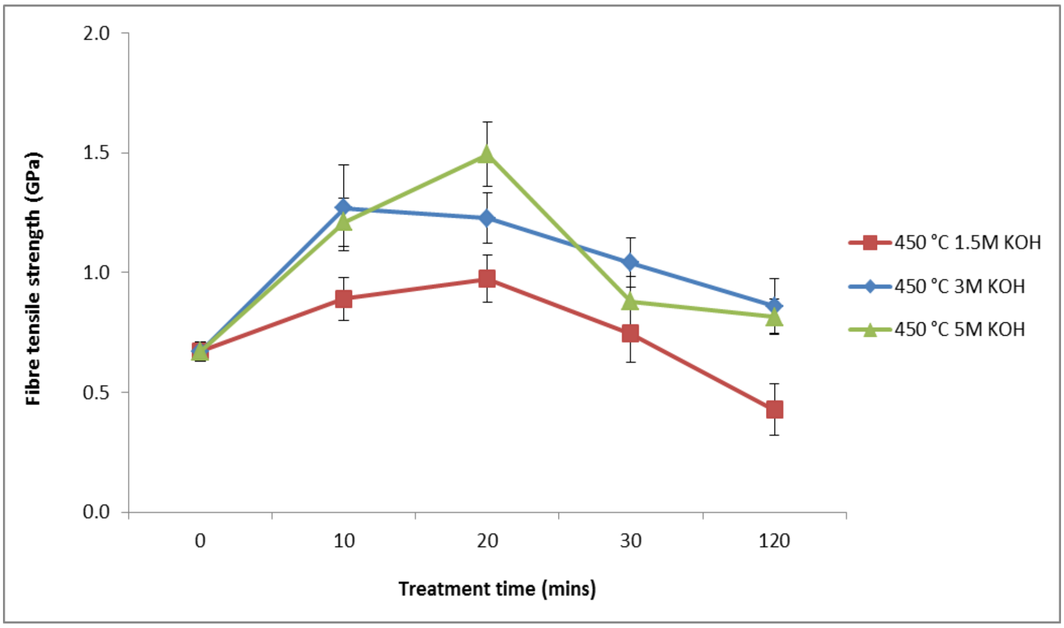

Figure 2. Average strength of fibres thermally conditioned at 450 °C and treated in KOH at different concentrations and times

At 3 M KOH concentration, treatment time at 10 minutes gives the highest strength result. For other molarities used, the tensile strength reaches a peak value at 20 minutes (at 5 M it is 1.49 GPa), before declining at longer application times. At all concentrations, prolonged exposure proves to be detrimental to the fibre. The optimal condition for KOH treatment has been defined; 5 M at an immersion time of 20 minutes. NaOH performs best at an application time of 10 minutes, but at a slightly lower concentration of 3 M.

3.2. Fibre diameter measurement

The diameters of fibres treated in KOH at various concentrations were plotted against immersion time (results shown in Figure 3).

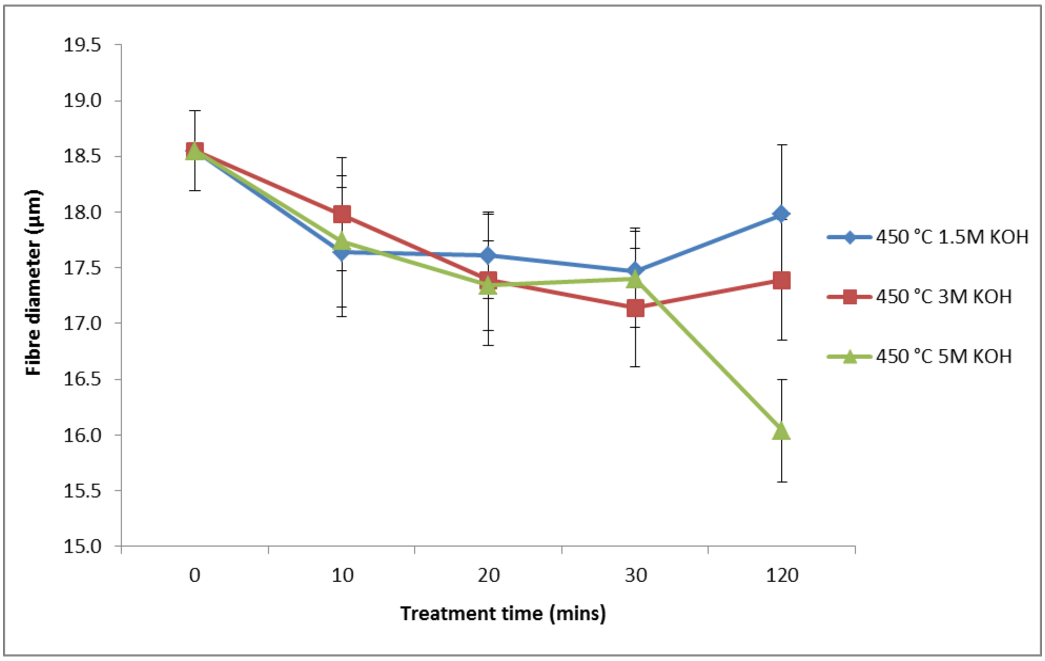

Figure 3. Average diameter of fibres thermally conditioned at 450 °C and treated in KOH at different concentrations and times

An examination of fibre diameter measurements for each permutation suggests there is an overall reduction as alkali concentration or application time increases, however this cannot be confirmed as the majority of the results are within experimental error. For 5 M a considerable decline in fibre diameter at 120 minutes immersion time is observed, but at the other two molarities there is in fact an average increase in diameter of fibre from 30 to 120 minutes. This does not exclude the notion that alkaline solutions etch glass, but rather insinuates that at times erroneous diameter measurements were made due to the presence of residual layers on the fibre surface (as shown by SEM images given in section 3.3). Other possible factors include the natural variation of fibre diameters within a bundle, and the error associated with employing an optical microscope.

3.3. SEM imaging

SEM pictures were acquired for fibres treated in different concentrations of KOH followed by acid-rinse, so as to examine the residual material deposited on the surface. Figure 4 shows the build-up of residue on fibres heat conditioned at 450 °C and treated in increasing concentrations of KOH.

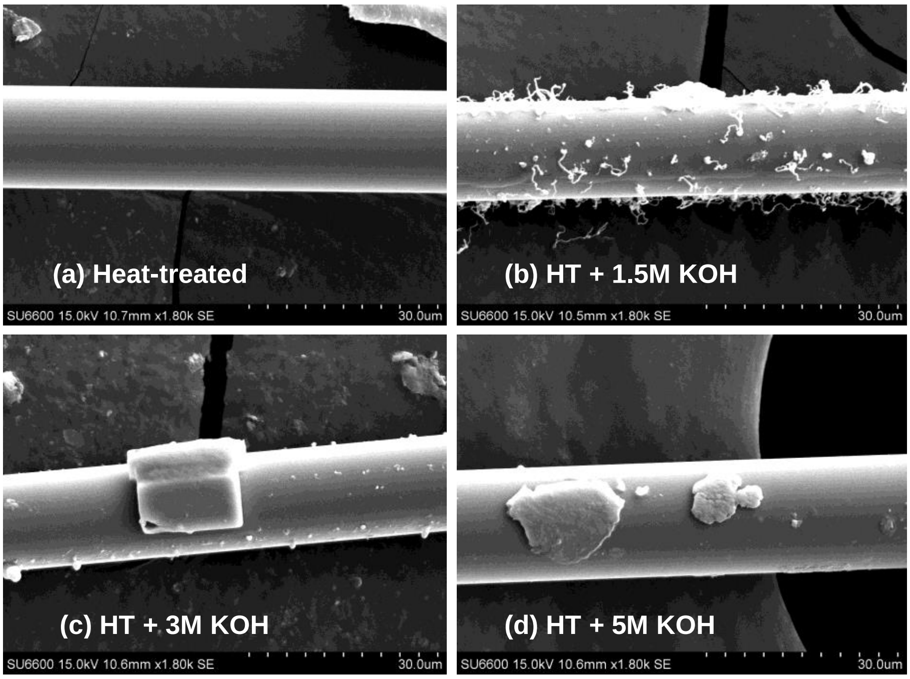

Figure 4. SEM images of fibre after (a) heat-treatment (HT) at 450 °C followed by (b) 1.5 M KOH, (c) 3 M KOH and (d) 5 M KOH treatment for 10 minutes, with acid rinse

A clean surface is shown for fibre heat conditioned only. After treatment for 10 minutes in 1.5 M KOH solution, flakes of residue appear before they coalesce into blocks at 3 M and 5 M. Figure 5 includes SEM images of fibre treated in 1.5 M KOH with increasing immersion time:

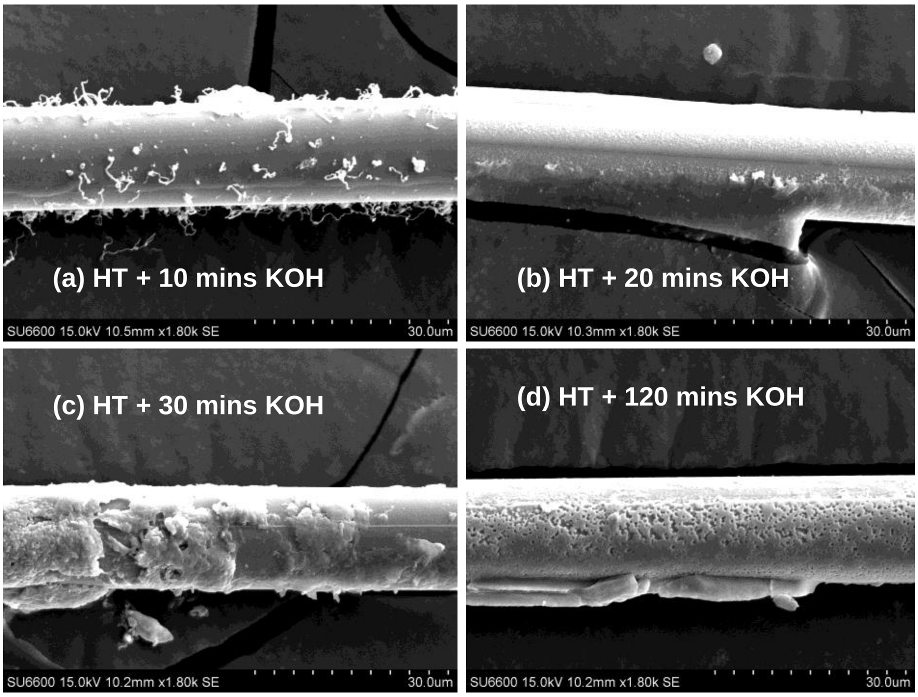

Figure 5. SEM images of HT 450 °C fibre followed by treatment in 1.5 M KOH at (a) 10 minutes, (b) 20 minutes, (c) 30 minutes and (d) 120 minutes, with acid rinse

For short treatments of 10 and 20 minutes spots of residue are visible on the fibre surface, which grow larger with time (30 minutes) and eventually form a coating (120 minutes). It is clear that the acid failed to remove the residual deposit completely and its presence could be obscuring the true diameter of the fibre, potentially leading to anomalous measurements.

4. Conclusions

This paper explores three alkaline treatments applied to thermally weakened glass fibres with the aim of restoring mechanical strength. LiOH solution failed in achieving this, however NaOH and KOH managed to recover a considerable amount of strength in fibres heat treated at 450 °C, at optimum conditions of 3 M at 10 minutes, and 5 M at 20 minutes respectively. A slight reduction in fibre diameter was observed after alkaline treatment, suggesting possible etching of the glass. However, SEM analysis shows the appearance of residue on the fibre surface which is likely to have led to inaccurate measurements of diameter. We have hypothesised that the mechanism of strength regeneration of glass fibre by alkaline solution is similar to that postulated in [3] for HF, where severe surface cracks on the fibre are removed or modified through wet chemical etching.

The main aim of this project was to develop an effective and economical treatment to restore strength in thermally recycled glass fibres for reuse in composite applications. Both KOH and NaOH are strong candidates, though NaOH increases fibre strength to a greater degree, and appears to operate best at lower concentrations and shorter treatment times. NaOH and KOH are relatively safer than HF, and therefore can be employed in an industrial setting. Further investigation of feasibility of alkaline treatments will be conducted to see if closed-loop recycling of GFRC waste can be accomplished. In addition, the reaction between these alkali metal hydroxides and glass will be studied in more detail in order to affirm our notion that the process of strength restoration is as a result of etching of fibre surface flaws.

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