A SIMPLE CHEMICAL APPROACH TO REGENERATING STRENGTH OF THERMALLY DAMAGED GLASS FIBRE FOR REUSE IN COMPOSITES

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Abstract
A key technical barrier to the reuse of thermally recycled glass fibres in composite applications is their low mechanical strength. This research study looks into the effect of alkaline treatments in regenerating the strength of glass fibres which were heated in a furnace to simulate thermal recycling conditions. Up to 100% strength increase of the fibres can be achieved through a simple treatment in alkaline solution. It was found that the nature of alkali, concentration, and treatment duration had a significant effect on the extent of strength recovery of the fibres. These treatments could potentially be implemented to thermally recycled glass fibres on an industrial scale, to allow their reprocessing into second-life composite materials. As well as optimising the reaction conditions to regenerate fibre strength, an examination of the surface morphology was carried out using various techniques. In addition, the kinetics of dissolution of glass fibres in alkaline solutions was investigated in order to further understand the strength regeneration mechanism.

1. Introduction

Glass fibre is used in over 90% of all fibre-reinforced composites produced worldwide, and there would be a high volume of waste once these materials reach the end of their life cycle [1]. Composites

such as glass fibre reinforced thermosetting polymers (GRP) possess high rigidity and chemical resistance; this is required for optimum performance but unfortunately results in poor recyclability. As a result, these materials very often are deposited in landfill sites when they are no longer fit for use. Stringent legislation in addition to rising costs associated with landfill means this method of disposal of composite waste is becoming more undesirable. Clearly there is a need for an alternative approach to deal with composite waste [2], especially given the accelerating growth in use of GRP materials particularly in the production of wind turbine blades [3].

In order to address the environmental and economic issues associated with the disposal of end-of-life composite materials, various recycling technologies have been developed [4, 5]. One of the common techniques exploited commercially is thermal treatment, where the composite is heated to elevated temperatures to degrade the polymeric matrix and allow the extraction of fibrous reinforcement. Due to the severity of the procedure the glass fibres lose a significant amount of strength and therefore cannot be reused in various composite applications [6-8]. We have found that dilute hydrofluoric acid (HF) solution can regenerate the strength of glass fibres thermally damaged at 450 to 600 °C [9]. It is thought that HF strengthens glass by smoothing out sharp, severe surface flaws [10]. Unfortunately as HF is highly toxic it is problematic to use on an industrial scale to regenerate glass fibre strength, thus a safer chemical treatment needs to be developed.

This paper reports on our recent investigations into the effect of hot sodium hydroxide (NaOH) and potassium hydroxide (KOH) solutions to recover strength of glass fibres that were thermally conditioned in a furnace. The dissolution of glass by alkaline solution is well documented in literature [11-13], however the use of these treatments to improve the strength of thermally degraded glass fibres is a novel concept [14, 15]. In this study, glass fibres were thermally treated in a furnace at 450 °C to mimic recycling conditions. Fibres were then treated in various alkaline solutions to see whether strength regeneration was achieved. The surface of the glass fibres following alkaline treatment was also analysed for any morphological changes. Additionally, the dissolution kinetics of glass fibres in alkaline solutions was investigated to improve our understanding of the strength regeneration process.

2. Experimental

2.1. Materials

Boron-free E-glass fibres supplied by Owens Corning (OC) were used in this study. These fibres had a nominal diameter of 17 μm. During production, the fibres were coated with a 1% volume γ-aminopropyltriethoxysilane (APS) hydrolysed solution in deionised water. One of the experiments described in Section 2.7 involved the use of unsized glass fibres; APS solution was not applied to these fibres and they were water sprayed only. The chemicals used in this project were purchased from Sigma Aldrich and included NaOH pellets, KOH flakes (all at commercial grade), and standard 37% concentrated hydrochloric acid (HCl).

2.2. Thermal treatment

APS-coated fibre bundles were arranged in a steel rig for thermal conditioning in a Carbolite furnace under air. The fibres were treated at 450 °C for 25 min, as these conditions were severe enough to result in the amount of strength loss representative to that of thermally recycled glass fibres. The rig was then extracted from the furnace and left to cool at room temperature, before fibre bundles were removed and treated in alkaline solution.

2.3. Alkaline treatment

NaOH and KOH solutions were prepared at various concentrations (1.5, 3 and 5 M) and heated to 95 °C. Fibre bundles were immersed in the hot solution for various treatment times (2, 5, 10, 20 and 30 minutes). To remove alkaline residue from the treatment, the fibres were then rinsed in 3.7% HCl for 10 minutes followed by 1 minute in deionised water. Following the rinsing procedure, the fibres were dried in an 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. 30 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. The fibre strength was calculated for each treatment condition by averaging from the 30 samples, and the error bars associated with the strength measurements represent 95% confidence limits.

2.5. Scanning electron microscopy (SEM)

A HITACHI SU-6600 field emission scanning electron microscope (FE-SEM) was used for surface morphology analysis of glass fibres following chemical treatment, and to measure fibre diameter (see section 2.7). Samples were coated in gold using an Edwards S150 sputter coater in order to prevent charge build-up since glass fibres are non-conductive. Images were captured at an accelerating voltage of 15 kV and extraction voltage of 1.8 kV.

2.6. Atomic force microscopy (AFM)

A Bruker Innova atomic force microscope was used for analysing the surface morphology of fibres following alkaline treatment. Tapping mode was used with a visible apex Si tip that had a mean resonance frequency of 70 kHz and a low spring constant (2 N/m) ideal for fibrous samples. AFM images were acquired at 128 x 128 pixel resolution and a low scan rate (0.1 Hz). For each treatment condition three individual fibres were selected at random and mounted on a metal plate. Two areas of each fibre were scanned in a 3 x 3 μm region. Height and tapping phase images were flattened to remove curvature by using the 'Flatten' function in NanoScope Analysis at 2nd order, and roughness values were measured and plotted as a function of treatment time.

2.7. Measurement of diameter reduction of glass fibres following alkaline treatment

To understand the kinetics of dissolution of glass fibres in alkaline solutions, fibres were treated in KOH and NaOH solution and their diameter change measured through SEM. Due to the difficulty in handling individual heat-treated (HT) fibres, unsized fibres were used in this experiment, though it was not believed that this had an impact on the results obtained. Each fibre was cut into three portions (1- untreated, 2- treated in 3 M KOH and 3- treated in 3 M NaOH). Portions 2 and 3 were treated in the respective alkaline solution for 1, 2, 3 and 5 hours, rinsed in acid and water, and dried. Five fibres were treated in alkaline solution at each treatment time. Diameters were then measured under the SEM, and by comparing values before and after treatment, the fibre diameter reduction (%) was determined. The error bars used for diameter reduction measurements show the standard deviation.

3. Results and discussion

3.1. Strength regeneration by alkaline treatment

Figure 1 displays the strength of HT glass fibres following treatment in KOH solution at various molarities and times.

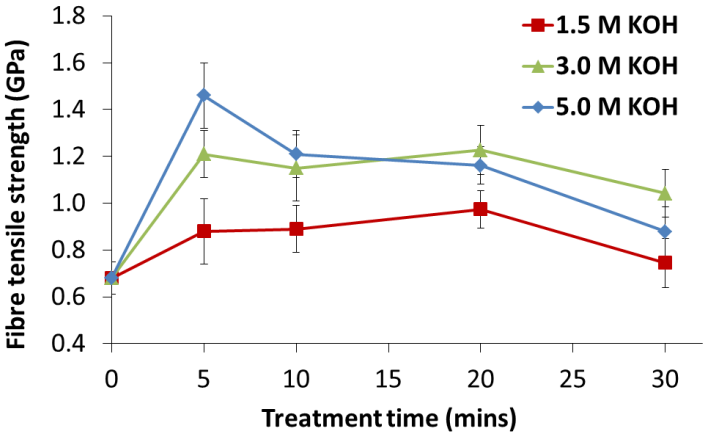

Figure 1. Strength of HT fibres after treatment in KOH solution at different concentrations and times

The strength of the glass fibres is too low for reprocessing after thermal treatment (0.68 GPa). Fortunately, a considerable amount of strength can be recovered through alkaline treatment of the fibres. Figure 1 shows a significant improvement in HT fibre strength after just 5 minutes of treatment in 5 M KOH solution. There appears to be a trend where increasing the molarity leads to an increase in fibre strength at 5 minutes. Beyond this treatment duration, the strength either remains the same for the low molarities (1.5 and 3 M) or decrease at higher molarity (5 M). This decrease in strength could be due to substantial breakdown of the bulk glass network structure [15].

Figure 2 shows the strength of HT fibres following NaOH treatment at different concentrations and times.

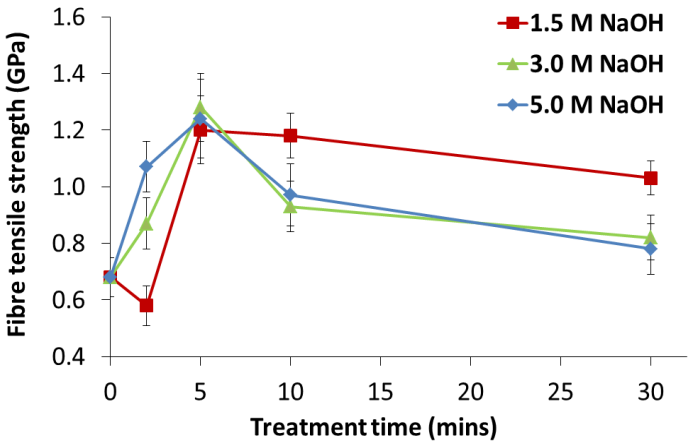

Figure 2. Strength of HT fibres after treatment in NaOH solution at different concentrations and times

There is an increase in fibre strength with molarity at 2 minutes NaOH treatment time. At 5 minutes, the strength recovery is at its optimum for all three NaOH concentrations, being around 1.2 GPa. A similar trend to Figure 1 then follows with the strength eventually declining at longer treatment times for the high NaOH molarities (3 and 5 M) and a very gradual decrease for the lower NaOH concentration of 1.5 M.

3.2. AFM analysis of alkali-treated glass fibres

We have shown that treatment of HT fibres in alkaline solution for a few minutes can result in significant strength recovery. In order to examine the surface morphology of the fibres after alkaline treatment, AFM analysis was carried out. Figure 3 displays representative AFM height images of fibre surfaces before and after treatment in 3 M KOH and NaOH solution for 30 minutes.

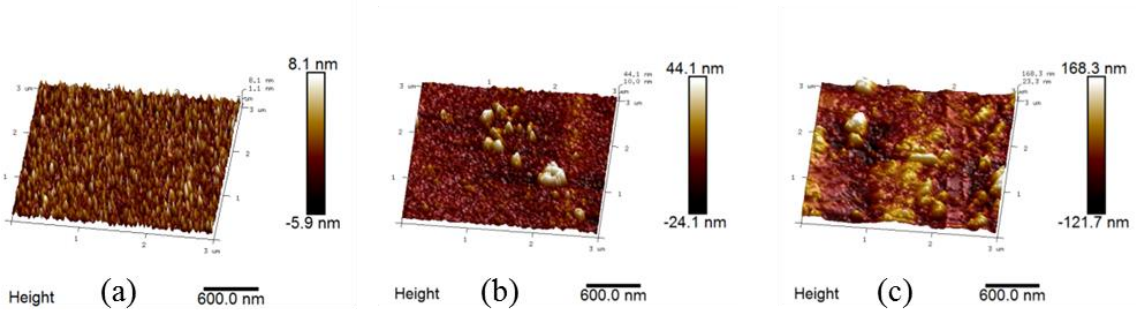

Figure 3. AFM height images of (a) untreated glass fibre, (b) fibre treated in 3 M KOH solution for 30 minutes, and (c) fibre treated in 3 M NaOH solution for 30 minutes

It is clear that untreated fibres possess a fairly smooth surface as indicated by the 3-D height image. After treatment of fibres for 30 min in KOH, we begin to see numerous spots on the height image which are even more prominent for the NaOH-treated fibre. The corresponding phase images (not included here) show some of these elevated regions translate to phase shifts, meaning these areas do not belong to the glass and could have resulted from the interaction of the glass with alkaline solution. There were occasions where these areas did not translate to phase shifts, implying that the topography of the glass itself was being affected by alkaline treatment. Figure 4 shows the root mean square roughness (Rq) values in nm of the fibres after treatment in KOH and NaOH solutions at various treatment durations.

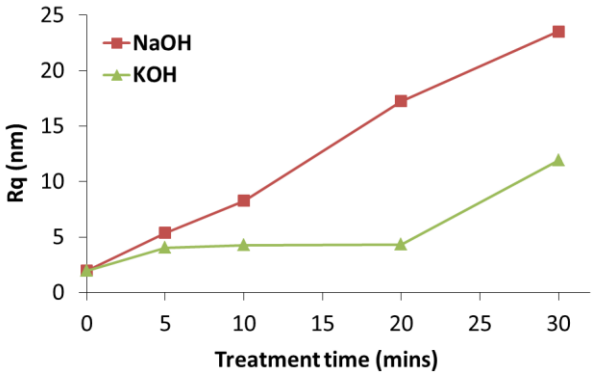

Figure 4. Rq values of fibres before and after treatment in 3 M KOH and NaOH solutions at different times

It is evident that with longer alkaline treatment times there is increased roughness of the fibre due to the presence of residual deposits and topographic changes of the glass itself. The Rq values presented for NaOH-treated fibres are significantly higher than from fibres treated in KOH. This could have been due to the increased amount of residual deposits on the NaOH-treated fibre surface, and also because NaOH might have reacted more readily with the glass fibre. To prove this, a dissolution experiment was conducted with results presented in section 3.3.

3.3. Dissolution kinetics of glass fibre in alkaline solution

It is widely accepted that HF and alkaline solutions can etch glass under particular reaction conditions [9-13]. The etching process involves the breakdown of the silicate network in the glass by the anions of the chemical solution; in alkaline treatments, these would be the hydroxide ions. When glass is in its fibrous form, the corroding effect of HF can be seen through a reduction in fibre diameter [9]. The thought of HF etching resulting in the removal or alteration in surface cracks has been articulated several decades ago with bulk glass [10] and recently Yang et al. adopted this methodology to recover strength of thermally damaged glass fibres [9]. The HF etching of deep, V-shaped surface flaws into smoother, U-shaped structures is reported on bulk glass [10] and it is believed that this is the mechanism by which alkaline solution regenerates the strength of thermally damaged glass fibre. Understanding the strength regeneration process requires the study of the kinetics of reaction between glass fibre and alkaline solution. Figure 5 presents the diameter reduction (%) of E-glass fibres after treatment in 3 M KOH and NaOH solution at 95 °C for various times.

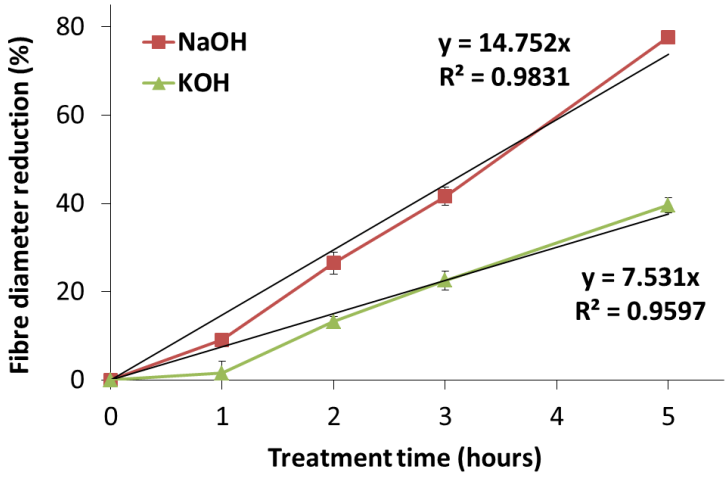

Figure 5. Diameter reduction (%) of fibres after treatment in 3 M KOH and NaOH solutions at different times

For both alkaline treatments the glass fibre diameter reduction proceeds in a linear fashion, with a slight induction period visible at 1 hour. It is apparent that NaOH dissolves glass fibre at almost twice the rate as KOH, proving it is a more corrosive alkaline reagent; in fact we see almost 100% conversion at 5 hours. The greater reactivity of NaOH could explain why it is a more efficient strength regenerator of HT glass fibres. Results in Figure 5 indicate that treatment of individual glass fibres in alkaline solution is an effective way of analysing reaction kinetics [16]. The disparity in behaviour of KOH and NaOH towards glass fibre is further emphasised in Figure 6, which gives representative SEM images of a fibre before and after treatment in 3 M KOH and NaOH solution at 95 °C for 5 hours.

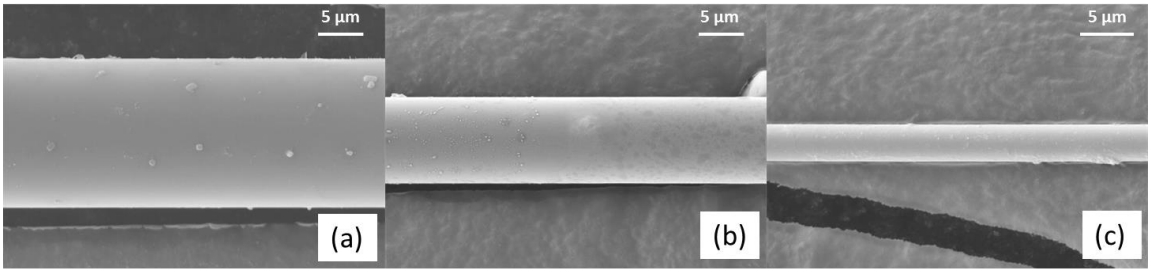

Figure 6. SEM image of (a) untreated fibre (16.5 µm), (b) fibre treated in 3 M KOH solution at 95 °C for 5 hours (9.7 µm), and (c) fibre treated in 3 M NaOH solution at 95 °C for 5 hours (3.5 µm)

The glass fibre, even following an aggressive alkaline treatment, possesses a fairly clean surface; however it is worth bearing in mind that these fibres were individually immersed in alkaline solution, and rinsed. The fact that NaOH reacts more readily with glass fibre than KOH agrees with our AFM results in section 3.2, which show NaOH-treated HT fibres have a rougher surface. NaOH might be more corrosive towards glass due to reaction products being formed more readily and exothermally [13].

4. Conclusions

Thermally damaged glass fibres are generally too low in tensile strength to be reused in composite applications. We have demonstrated that treatments of such fibres in a hot alkaline solution for a few minutes can almost double their strength. A clear trend was observed at short treatment times with both KOH and NaOH treatments where increasing the concentration resulted in greater strength recovery of fibres. NaOH was found to be a more efficient strength regenerator of fibres due to its greater reactivity with glass as indicated by AFM and dissolution kinetics experiments. An excessive treatment of fibres in alkaline solution eventually leads to a decrease in strength, possibly due to significant bulk glass network dissolution.

The results presented in this work clearly indicate that alkaline solutions can significantly regenerate the strength of thermally damaged glass fibres. If these treatments were to be scaled up industrially to treat real thermally recycled glass fibres, a balance needs to be achieved with dissolving just enough alkali into the water to recover fibre strength in a reasonable period of time, whilst not exhausting too many chemicals. With an in-house fluidised bed now fully operational, work is currently underway with recycling fibres out of real composite waste and recovering their strength in a cost-effective and hence industrially-feasible manner.

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