A simple chemical approach to regenerating the strength of thermally damaged glass fibre

S.T. Bashir[a]

L. Yang[a, *]
l.yang@strath.ac.uk

R. Anderson[a]

P.L. Tang[b]

J.J. Liggat[c]

J.L. Thomason[a]

[a]University of Strathclyde, Department of Mechanical and Aerospace Engineering, 75 Montrose Street, Glasgow G1 1XJ, United Kingdom

[b]Agilent Technologies, Mobile Measurement Group, Edinburgh EH12 9DJ, United Kingdom

[c]University of Strathclyde, Department of Pure and Applied Chemistry, 295 Cathedral Street, Glasgow G1 1XL, United Kingdom

*Corresponding author.

Abstract

Process-induced strength loss is a major technical barrier to the effective reuse of thermally recycled glass fibres in composite applications. We have developed a novel approach to effectively restore strength in glass fibres through treatment in alkaline solutions. Glass fibres were treated at elevated temperature and experienced significant strength loss found typically after thermal recycling processes. Different alkaline treatments were then applied to the thermally damaged fibres in an attempt to restore strength which had been lost as a result of the heat conditioning procedure. Results indicated that these treatments were able to generate considerable fibre strength recovery. The degree of strength regeneration was found to be highly dependent on reaction conditions, which were investigated and optimised. The positive effect of these simple chemical treatments demonstrated great potential for facilitating the reuse of thermally recycled glass fibres in composite applications.

Keywords: A. Glass fibres; A. Recycling; B. Strength; E. Surface treatments

1 Introduction

There is growing concern of the negative effect current disposal methods of composite waste are having on the environment. It is estimated that by 2020 the composites market will reach almost £80 billion globally, and as a result, there will be a high volume of waste once these materials reach the end of their life cycle [1]. Glass fibre is currently used as reinforcement in over 90% of all fibre-reinforced composites produced, and production waste represents 5-10% of composites production. The high rigidity and chemical resistance of these composites, particularly glass fibre reinforced thermosetting polymers (GRP), are required for optimum performance but unfortunately result in poor recyclability; when such materials are no longer fit for purpose, they are deposited frequently in landfill sites. The rising costs associated with landfill together with increasingly stringent legislation means this disposal route is becoming ever more undesirable. Consequently, alternative methods for dealing with GRP manufacturing waste are needed [2]. In addition, the accelerating growth in use of GRP materials such as in the production of wind turbine blades [3] means it is imperative that a long-term, cost-effective, recycling solution be developed for end-of-life composites.

In an effort to reduce the environmental damage caused by disposal of end-of-life composite materials, a range of recycling techniques have been investigated, some of which are now exploited on an industrial scale [4,5]. Thermal treatment is one of the most widespread recycling technologies; by subjecting the composite to elevated temperatures, degradation of the polymeric matrix is achieved, facilitating subsequent extraction of any fibrous reinforcement. Due to the harsh conditions employed in this procedure the glass fibres suffer from a severe loss in strength, and therefore cannot be reused in many forms of composite applications [6–9]. These damaged filaments can

however be reused as reinforcements if their strength is restored by means of chemical treatment. Such an example has recently been given in [10] where the strength of glass fibres heat conditioned at 450–600 °C can almost triple after a few minutes of immersion in dilute hydrofluoric acid (HF). HF is proven to be an effective chemical etchant, and is thought to strengthen glass by smoothing out sharp, severe surface flaws [11]. However as HF is highly toxic in nature, its commercial use for regenerating strength of thermally weakened glass fibres is problematic. Consequently there is a need to find less challenging chemical routes to enable a solution to the problem of cost-effective recycling and reuse of the glass fibres in GRP waste.

The present work presents the results of an investigation of the use of hot alkaline solutions in regenerating the strength of thermally degraded E-glass fibres. The dissolution of glass in alkali is well documented in literature [12–14], however the use of these corrosive substances for strengthening thermally damaged glass fibres is a novel concept, given that alkaline treatments are shown to have a detrimental effect on virgin glass fibre strength [15]. It is believed that the reduction in strength of fibres after heat treatment can be attributed to the creation of new flaws on the surface and/or the growth of pre-existing flaws [16,17]. The mechanism by which these flaws develop is not yet fully understood, however it has been postulated that it could involve the interaction of water with the fibre surface during the heat treatment process [16,17]. It can be hypothesised that the reaction of silica (SiO_2) in the glass fibre with hydroxide ions (OH^-) from the alkaline solution [18] leads to the smoothing of the sharp, severe surface flaws, and thus increases the tensile strength of the fibre. The modification of surface flaws has been reported previously on bulk glass with HF as the corrosive medium [11].

We have recently discovered that sodium hydroxide (NaOH), prepared at high temperatures and at concentrations of 1.5 M and above, can significantly improve the strength of thermally damaged glass fibre [19,20]. To further our understanding of the reaction of glass with alkaline solutions, hydroxides based on other alkali metals were surveyed: lithium hydroxide (LiOH) and potassium hydroxide (KOH). It is thought the effect of etching of the glass surface by alkaline treatment is strongly dependent on various reaction conditions including nature of alkaline solution, temperature, molarity and treatment duration. In this research study, we provide initial evidence of glass fibre etching by alkaline solutions, and the resulting deposit formed on the fibre surface was analysed through various techniques. The main aim of this research study is to validate our hypothesis that alkaline treatment can regenerate the strength of thermally degraded glass fibres, offer a potential cost-effective route to GRP recycling, and ultimately reduce the negative environmental impact from landfill disposal. Additional objectives include generating further understanding of the etching mechanism and how differences in chemical properties of alkali metal hydroxides affect their reaction with glass fibre.

2 Experimental

2.1 Materials

Boron-free E-glass fibres supplied by Owens Corning (OC) were used in this study. These OC fibre rovings were manufactured on a pilot scale bushing and received as 20 kg continuous single end square edge packages. Each roving had a nominal tex of 1200 and a nominal fibre diameter of 17 μm. During production, fibres were coated with a 1% volume γ-aminopropyltriethoxysilane (APS) hydrolysed solution in deionised water. The purpose of this APS sizing is to functionalise and protect the fibre surface. One of the experiments described in Section 2.8 involved the use of unsized glass fibres; APS solution was not applied to these fibres and they were water sprayed only. Mechanical properties of these fibres at room temperature are reported elsewhere [21]. The chemicals used in this project were purchased from Sigma Aldrich and included NaOH pellets, LiOH powder, KOH flakes (all at commercial grade), and standard 37% concentrated hydrochloric acid (HCl).

2.2 Thermal treatment

Fibre bundles were arranged in a steel rig for thermal conditioning, which was carried out in air. A Carbolite furnace was used to treat the fibres at 450 °C for 25 min, as these conditions were severe enough to result in the amount of strength loss representative to that of fibres recycled from pyrolysis and thermal oxidative processes. The rig was then extracted from the furnace and left to cool at room temperature, before fibre bundles were removed and treated in various alkaline solutions. Further details of the heat conditioning procedure are given in [6,7].

2.3 Alkaline treatment

NaOH, LiOH and KOH solutions were prepared according to the following molarities: 1.5, 2, 3 and 5 M. Solutions were heated to 95 °C before treating the fibre bundles. The standard treatment duration was 10 min; however this was varied in a subsequent experiment (at 2, 5, 20 and 30 min) to investigate its effect on fibre properties. After fibres were treated in alkaline solution, they were rinsed in 5% HCl solution for 7 min followed by rinsing with deionised water for 1 min. The purpose of this rinsing procedure was to ensure the effective removal of residual deposits which developed on the fibre surface as a result of interaction with alkaline solution [15]. In addition, previous experimentation did not show any significant change in mechanical properties of glass fibres after a short period of acid rinsing alone. Once the fibres were rinsed after alkaline treatment, they were dried out in an oven at 110 °C for 15 min.

2.4 Single fibre tensile testing

Single fibre tensile testing was performed following the standard ASTM C1557-03. After heat and chemical treatment, glass filaments were carefully separated from the bundle and mounted on card tabs with the central window matching the desired gauge length of 20 mm. Fibre diameters were measured using an optical microscope before testing for tensile strength using a Testometric tensile testing machine at ambient environment. The load cell was 5 N with a strain rate of 1.5%/min applied to the samples, and at least 30 samples were tested for each condition; the strength values were then averaged to give the average strength. Error bars associated with the strength measurements represent 95% confidence limits. The tensile test procedure is described in detail elsewhere [21].

2.5 Scanning electron microscopy (SEM)

A HITACHI SU-6600 field emission scanning electron microscope (FE-SEM), equipped with an energy dispersive X-ray spectrometer (EDS), was used for surface morphology and compositional analysis of the fibres following chemical treatment. 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 roughness 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 × 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 × 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 Fourier transform infrared spectroscopy (FT-IR)

Examination of the observable mid-infrared chemical vibrational modes in the alkali treated fibres was achieved by the use of an Agilent Technologies 4100 FT-IR with external reflectance handheld diffuse interface. The diffuse interface with the 4100 FT-IR collected data in a preparation-free manner and force-free manner leaving the sample completely intact. Spectra were acquired of 128 scans at 8 cm^{-1} resolution resulting in a data collection time of 40 s. The bundled glass fibre samples were examined throughout their whole length and then analysed and averaged per treatment. The diffuse interface has about 2 orders greater penetration depth compared to the diamond ATR (Agilent Technologies 4500) and less bias towards the fingerprint region, and is therefore more representative of the sample as well as containing greater data density.

2.8 Mass loss and diameter reduction of fibres after alkaline treatment

To understand the etching effect of hot alkaline solution on glass fibre, two separate experiments were conducted; firstly, three heat conditioned glass fibre bundles were treated in 3 M KOH or NaOH for each treatment duration (1, 2, 3 and 5 h) and thoroughly rinsed in acid and water to remove as much residue as possible. The mass of these bundles was measured before and after alkaline treatment using a microbalance and the loss (%) calculated. The second experiment involved monitoring the same fibre before and after treatment and measuring the diameter change using an SEM. Due to the difficulty in handling individual heat treated 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 h, 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 mass loss and diameter reduction measurements show the standard deviation.

3 Results and discussion

## 3.1 Strength regeneration by alkaline treatment

Fig. 1 shows tensile test results for heat treated (HT) glass fibres treated with KOH, NaOH, and LiOH solution in a wide range of molarities. The average strength of HT fibres is shown to be reduced drastically, from approximately 2.3 GPa (untreated reference value) to as low as 0.68 GPa. Despite the precipitous drop in performance of HT fibres, a significant amount of strength can be restored through a tailored alkaline treatment as shown in Fig. 1. A major increase in HT fibre strength is observed following immersion in 1.5 M NaOH. As the molarity of NaOH increases, the treatment does not significantly improve the strength of fibres. KOH enhances fibre strength at 1.5 M, although to a lesser extent than NaOH at the same molarity. Treatment of fibres in KOH from 2 M onwards results in an increase in fibre strength to values similar to what NaOH can achieve at a lower molarity of 1.5 M. LiOH appears to have little effect on HT fibre properties for the molarity range investigated.
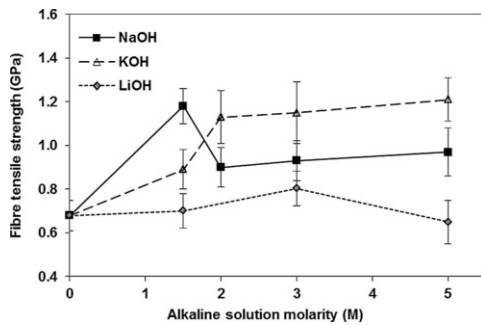
Fig. 1 Average strength of fibres thermally conditioned at 450 °C and treated in various concentrations of alkaline solutions for 10 min.

Studies show NaOH dissolves glass at a faster rate than any other alkali metal hydroxide, with KOH slightly less reactive and LiOH the least [22]. Assuming these alkaline solutions improve fibre strength through an interaction with the damaged glass surface, we would assume NaOH to be the most efficient treatment option overall. This is supported by results in Fig. 1 which indicates NaOH treatment can significantly improve HT fibre strength at a molarity of 1.5 M, whereas for KOH to have a similar effect a more concentrated solution is required. Generally, the chemical strength of basic hydroxides is determined by their dissociation constants (which is their ability to separate into metal cations and hydroxide anions in solution). Li, Na and K belong to the same group in the periodic table (the group 1 alkali metals) and the atomic size of the element increases down a group. Li, being at the top of group 1, has a smaller atomic size and has a stronger affinity for the OH$^-$ in LiOH. As a result, the dissociation of LiOH into Li$^+$ and OH$^-$ ions is poor. It is believed that the OH$^-$ ions are responsible for the modification of the surface of HT glass fibre; consequently the fewer OH$^-$ ions present from LiOH leads to a reduced rate of attack, and therefore a low tensile strength recovery. Conversely, Na and K possess a larger atomic size and are more willing to liberate hydroxide ions. Since K has a greater atomic size than Na, one might assume KOH to be a stronger base. However, studies conducted by numerous authors [12,22,23] show NaOH is the most corrosive alkali towards glass. The reason for this is seldom explained, though it is suggested it could be due to the reaction products from NaOH and glass being formed more readily and more exothermally [22]. Another possible theory is that the smaller Na$^+$ ions have a stronger attraction to OH$^-$ ions in solution, which reduces the likelihood of OH$^-$ ions to interact with neighbouring water molecules and as a result they will travel to the glass surface more easily to react [24]. In a later experiment, glass fibres were treated in NaOH and KOH and their degree of reactivity examined through mass loss and fibre diameter reduction (Section 3.2). For the moment we accept that NaOH and KOH, both being very corrosive alkaline reagents, can restore HT fibre strength through a modification of surface defects. Likewise, poor strength recovery for HT fibres treated in LiOH is attributable to its lower reactivity with glass.

Fig. 2 shows the effect of varying the treatment time of HT 450 °C fibres in KOH with different concentrations. For 1.5–5 M KOH, fibre strength increases significantly as the length of treatment time increases up to 5 min. The rate of strength regeneration is clearly affected by the concentration of the solution with higher molarity giving higher rate of strength increase. Extended treatment with 1.5 and 3 M KOH after 5 min shows little improvement in fibre strength. In fact, prolonged treatment appears to start adversely affecting fibre strength and causes its reduction as indicated by the results after 20 min in Fig. 2. Such behaviour becomes more evident when it comes to 5 M KOH, which shows a sharp increase in fibre strength after a short period of KOH treatment followed by a more significant reverse effect on strength regeneration at an earlier stage compared to 1.5 M and 3 M.
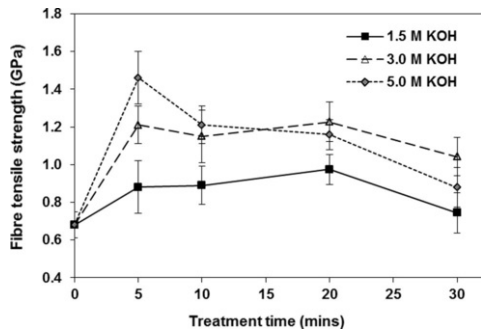
Fig. 2 Average strength of fibres thermally conditioned at 450 °C and treated in KOH at different concentrations and times.

Fig. 3 shows how variations in treatment time affect HT 450 °C fibres treated in NaOH at different concentrations. It presents overall a similar trend to that in Fig. 2 for the influence of treatment concentration and time on the strength of HT glass fibres; considerable strength recovery (100% increase) is observed after the first 5 min followed by no improvement at low concentration or subsequent strength loss at high concentration. In addition, the strength

values presented for all three molarities overlap at 5 min; it was initially thought that these data points intersected because the optimum treatment duration of fibres in NaOH had already passed. At a shorter treatment time of 2 min we clearly see the strength is molarity dependent; it improves as NaOH solution molarity increases. Despite this observation 5 min is yet considered to be overall the optimum treatment duration regardless of NaOH solution concentration, and HT fibre strength begins to decrease from 10 to 30 min. In addition, we found the strength of fibres reduced further after treatment in both NaOH and KOH solution for an extended amount of time (e.g. 120 min whose data was not presented in Figs. 2 and 3 for clarity).
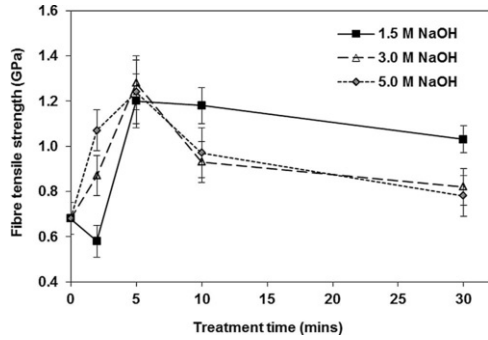
Fig. 3 Average strength of fibres thermally conditioned at 450 °C and treated in NaOH at different concentrations and times.

It is generally agreed that tensile strength of a brittle material such as glass fibre is practically determined by surface flaws of critical size [19]. Therefore, it is reasonable to consider correlating the strength of alkaline treated fibres with flaw geometry through a linear elastic fracture mechanics approach. However, this proves somewhat troublesome since these theoretical defects of submicron scale cannot be readily probed in an experiment. Alternatively, a grossly simplified approach may relate the crack size reduction to glass dissolution caused by the hot alkaline solution. However, we have found there were no optically detectable changes in an average thickness of glass fibres treated by NaOH or KOH at 1.5–5 M within the first 30 min. Despite this difficulty, one can still foresee that this analytical approach will be unlikely fruitful as the fracture mechanics model will predict a monotonic increase in fibre strength due to the crack size reduction. On the contrary, the results in Figs. 1–3 have clearly shown that there exists an optimal condition for the maximum strength regeneration, which tends to appear at an early stage of the treatment with both hot concentrated NaOH and KOH solutions. This should be beneficial from recycling point of view as the strength of thermally damaged glass fibres can be effectively recovered at very little expense of removing surface materials.

## 3.2 Etching effect of alkaline solutions on glass fibre

SiO_2 is the major component in virtually all types of glass fibre, with a small percentage of various metal oxides such as Al_2O_3, CaO and MgO included. For simplicity we refer to silica glass as SiO_2, but in reality SiO_2 exists as a complex network. In addition, Al_2O_3, classed as an intermediate oxide, can function both as a network former or modifier in the glass. CaO and MgO are included in glass as network modifiers only; unlike Al_2O_3 they cannot form part of the network structure with SiO_2. When glass is in contact with hot, concentrated alkaline solution, the hydroxyl ions attack the SiO_2 framework:

$$[-Si-O-Si-] + OH^- \rightarrow [-SiO]^- + [-Si-OH] \qquad \textbf{(1)}$$

E-glass fibre is composed mainly of SiO_2; it is therefore believed the breakdown of the silicate network in Eq. (1) is the key process in the dissolution of E-glass fibre by alkaline solutions. Al_2O_3, which is present in small quantities in E-glass fibre, can react with OH^- from NaOH/KOH solution in a similar fashion to SiO_2. Due to their basic nature, CaO and MgO may not react directly with KOH/NaOH but they are soluble in the alkaline solution, resulting in further disruption of the glass network structure. All the above mentioned processes should occur in theory, though an EDS analysis of the residue (results presented in Section 3.3) can provide further insight into how alkaline solution interacts with E-glass fibre. The reaction of alkaline solution with glass fibre components establishes the theoretical basis for the etching process, and the results displayed henceforth validates the concept of alkaline solutions exhibiting an etching effect on E-glass fibre.

A mass loss study of fibre bundles was performed following treatment in NaOH and KOH at 3 M concentration. Extensive treatment durations were selected in order to observe clearly the etching effect of glass fibres, and it is believed that all the fibres in the bundle were in contact with the solution during the treatment. Fig. 4 gives the mass loss (%) of HT fibre bundles after treatment in alkaline solution for various times (1, 2, 3 and 5 h). The fibre mass loss (%) increases after NaOH and KOH treatment, suggesting both alkaline solutions can dissolve the glass fibres. However, it appears the rate of mass loss of treated glass fibres decreases with treatment time as shown in Fig. 4. The data obtained from both treatments can be fitted by a logarithmic function. The decay of glass conversion rate can be attributed to a combination of precipitation of an incrustation of hydrated silicates and zeolites and local

contamination of alkaline solution during a static treatment [15]. SEM images presented in Figs. 5 and 6 show the gradual build-up of residue on glass fibres after KOH and NaOH treatment respectively. It is also noticed that precipitation of reaction products on glass surface tends to be more severe after NaOH treatment compared to KOH treatment under the same condition. This has a good agreement with the measured glass conversion as indicated by the mass loss in Fig. 4. The results in Figs. 4–6 suggest that NaOH is more corrosive to glass fibre than KOH and this agrees well with the studies of silicate bulk glass in [12,22].
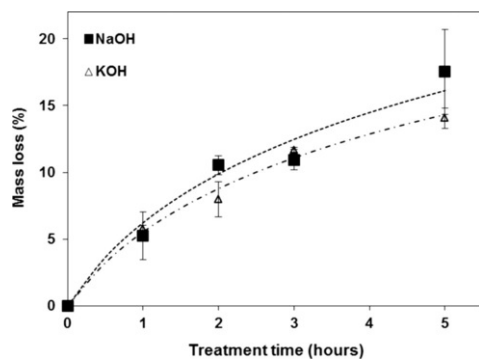
Fig. 4 Mass loss (%) of glass fibre bundle after treatment in 3 M NaOH and KOH at different times.
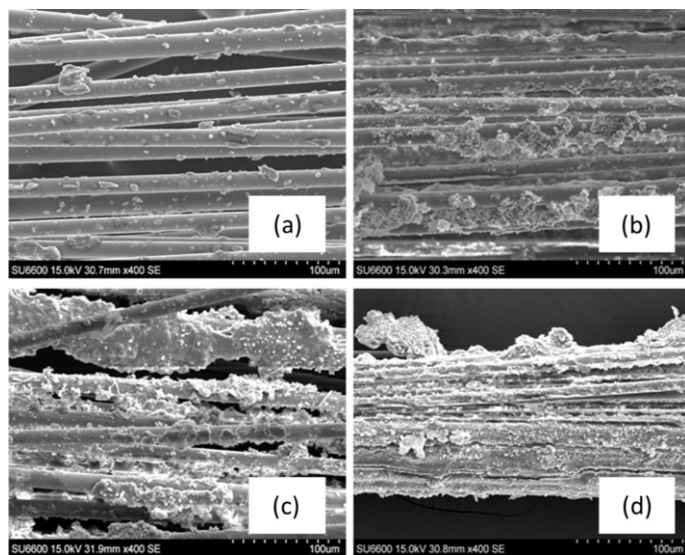

Fig. 5 SEM images of HT 450 °C fibre bundles followed by treatment in 3 M KOH at (a) 0.5 h, (b) 1 h, (c) 2 h and (d) 5 h, without rinsing.
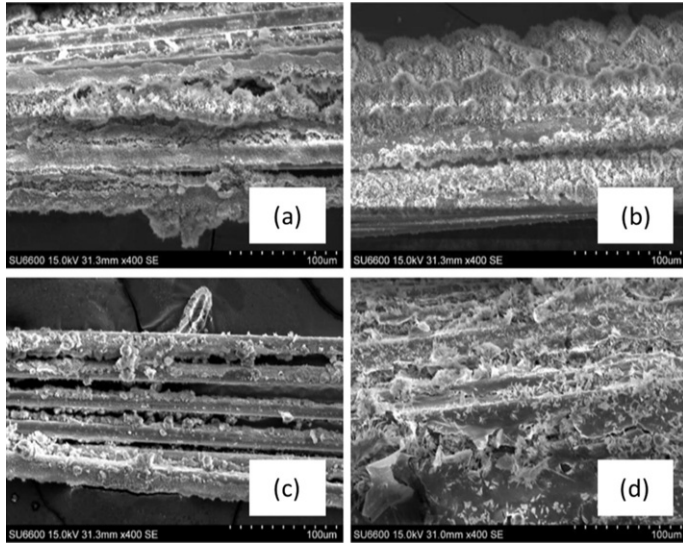
Fig. 6 SEM images of HT 450 °C fibre bundles followed by treatment in 3 M NaOH at (a) 0.5 h, (b) 1 h, (c) 2 h and (d) 5 h, without rinsing.

As mentioned above, the glass dissolution process can be retarded by precipitation of reaction products and local contamination of alkaline solution. Such effect is likely more significant with NaOH than KOH as illustrated in Figs. 5 and 6. Consequently, it obscures fundamental understanding of reactivity of NaOH and KOH with glass fibre. In order to minimise this self-damping factor, individual glass fibres, rather than the fibre strands, were treated with the hot alkaline solutions. Fig. 7 shows the diameter reduction (%) of individual unsized fibres treated in NaOH and KOH solution and corresponding mass loss calculated from the diameter reduction. It can be found that without the damping factor glass dissolution apparently proceeds in a linear fashion and at a higher conversion rate compared to the dissolution behaviour observed in Fig. 4. This behaviour sustains until fibres are almost fully dissolved as in the case of the fibres treated with NaOH. Furthermore, the results in Fig. 7 clearly indicate that the hot concentrated NaOH solution is much more reactive with E-glass fibre than KOH and gives rise to nearly twice as much of glass dissolution as that caused by the KOH solution. The results from Fig. 7 also prove that the method of alkaline treatment to single fibres is a more accurate and effective way of analysing reaction kinetics.
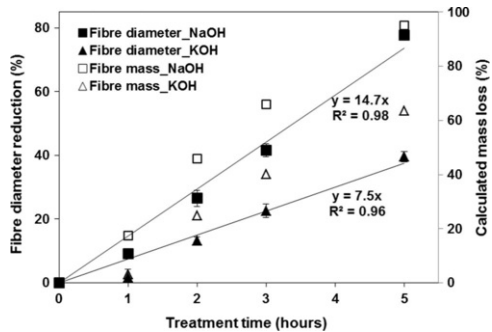
Fig. 7 Fibre diameter reduction (%) and calculated mass loss of single glass fibre after treatment in 3 M NaOH and KOH at different times.

3.3 Elemental analysis of alkaline treated fibres

The products formed between HT E-glass fibre and alkaline solution was examined with the objective of developing a more effective rinsing method in future. Indeed the investigation of the nature of these products and the enhancement of the rinsing procedure to remove these materials will improve the bonding of alkali treated fibres to the polymer matrix in the composite. In this experiment HT fibre bundles were treated in 3 M NaOH/KOH for extended periods of time (0.5, 1, 2 and 5 h) and dried without rinsing. An EDS analysis was conducted of the residue to investigate the composition of different elements. The results are compared to that of fibres HT at 450 °C alone, referred to as untreated. Taking into account the accelerating voltage (15 kV), the EDS penetration depth was around 1 μm. So, it is worth bearing in mind that although the residue was analysed through EDS, there was a possibility of

some fibres underneath to contribute to the elemental composition. Nevertheless, in the following discussion the compositional analysis is denoted as being of the residue only unless otherwise specified.

Table 1 gives the weight (%) of each element of the residue after increasing treatment time of fibres in 3 M KOH (error values represent 95% confidence limits). Overall as treatment time in KOH increases, we find the percentage of Al, Si and Ca becomes less significant. The concentration of O decreases slightly, as is the case for Na and Mg (which are naturally present in trace amounts). Interestingly, the percentage of K increases with time as the concentration of other elements (apart from O) becomes less substantial. This suggests the residue was composed mainly of KOH. In fact, at 2 and 5 h treatment time the amount of KOH in the residue was almost at 100%. One might consider that the increasing concentration of KOH with time was due to the increase in thickness of the KOH residual material layer; in other words, less of the actual fibre contributed to the EDS results and more of the residue was analysed.

Table 1 Weight (%) of each element present in residue on 3 M KOH treated fibres at different times, determined by EDS.

Element	O	Na	Mg	Al	Si	K	Ca
Untreated	52.2 ± 1.4	0.5 ± 0.1	1.6 ± 0.1	5.9 ± 0.3	23.9 ± 2.2	0.1 ± 0.1	15.3 ± 1.5
0.5 h	50.2 ± 4.2	0.6 ± 0.1	1.3 ± 0.1	6.6 ± 1.2	17.5 ± 1.8	12.7 ± 4.5	9.5 ± 1.0
1 h	49.8 ± 2.7	0.1 ± 0.1	0.9 ± 0.3	6.3 ± 2.4	13.2 ± 3.9	21.2 ± 8.1	7.9 ± 2.8
2 h	42.2 ± 4.5	0.1 ± 0.7	0.1 ± 0.1	5.3 ± 2.2	2.2 ± 2.1	48.9 ± 7.2	0.8 ± 0.7
5 h	41.4 ± 4.1	0.4 ± 0.2	0.7 ± 0.5	2.0 ± 1.0	8.3 ± 4.1	40.5 ± 9.8	6.2 ± 2.9

Table 2 gives the composition of different elements in residue on fibres treated in 3 M NaOH at 0.5 to 5 h. Overall, the percentage of Mg and K is negligible, and O decreases rapidly. The concentration of Al, Si and Ca decreases with time, and there is a rapid increase in percentage of Na; already at 0.5 h we see there is nearly 100% NaOH present. This composition remains until 2 h. Unexpectedly, the percentage of Na decreases and Al increases considerably (around 24%) after 5 h NaOH treatment; this suggests there was possibly a mixture of NaOH and Al_2O_3 in the residue, or perhaps they reacted to form a complex sodium aluminate. This is not quite understood, however from SEM imaging in Fig. 6 it is clear that a thick film is covering the fibres at 5 h, which could potentially have contributed to the high percentage of Al.

Table 2 Weight (%) of each element present in residue on 3 M NaOH treated fibres at different times, determined by EDS.

Element	O	Na	Mg	Al	Si	K	Ca
Untreated	52.2 ± 1.4	0.5 ± 0.1	1.6 ± 0.1	5.9 ± 0.3	23.9 ± 2.2	0.1 ± 0.1	15.3 ± 1.5
0.5 h	41.2 ± 3.3	45.5 ± 11.9	–	1.0 ± 0.4	3.9 ± 2.7	–	7.9 ± 7.5
1 h	39.6 ± 1.0	58.1 ± 1.1	–	0.6 ± 0.1	1.2 ± 0.2	0.1 ± 0.1	0.3 ± 0.3
2 h	41.5 ± 1.6	51.3 ± 4.7	0.2 ± 0.2	1.0 ± 0.6	3.7 ± 2.3	0.2 ± 0.2	2.1 ± 1.0
5 h	42.0 ± 2.8	29.3 ± 9.0	–	24.3 ± 8.4	2.1 ± 1.4	–	2.1 ± 1.5

So, KOH treated fibres show a gradual increase in concentration of K as treatment time is extended; however for NaOH treated fibres the percentage of Na increases more abruptly, which is consistent with SEM observations in Fig. 6 of a rapid residue build-up. It is understood that as soon as glass fibre is immersed in alkaline solution, the OH⁻ ions travel to the glass surface and begin to react with the silicate groups. As these ions move toward the fibre surface, so does the counter-ion (Na⁺ or K⁺). Eventually these ions congregate around the glass fibre surface, which explains why, when our fibres were removed from solution and dried without rinsing, there was a substantial amount of residual material that was characterised as being mainly NaOH/KOH from EDS analysis. It is evident in some cases that the EDS registered an overwhelming concentration of KOH and NaOH, which consequently masked the reaction products. The idea of NaOH residue build-up being more severe than KOH is supported by SEM imaging and EDS analysis. This reinforces the observation that NaOH is a more effective E-glass fibre etchant than KOH.

3.4 Surface roughness and phase imaging of alkaline treated fibres

HT glass fibres treated in 3 M NaOH/KOH were analysed with an AFM. We have seen that large amounts of residue on fibres could lead to contamination of the AFM tip and consequently a poor image resolution. From SEM

images it is clear the amount of residue present is significant and would have resulted in difficulty in noticing both the residue phase and the glass phase through phase imaging using an AFM. In tapping mode AFM is able to differentiate between various materials according to their adhesion force and viscoelastic property, and these variances give rise to phase shifts marked by different colours in the phase image. It is worth bearing in mind that if two materials have the same viscoelastic behaviour then there would be no phase difference, and conversely if exactly the same material is present in different forms (such as amorphous and crystalline) these regions would appear as different phases.

In order to prevent debris pick-up by the tip of the AFM probe and allow both the glass and residue phase to be visible, fibres treated in alkaline solution for a short period of time (5–30 min) were rinsed in acid before they were examined using AFM. Fig. 8 shows the height and tapping phase images of untreated glass fibre (not treated with either hot alkaline solution or heat treatment), and after treatment in 3 M KOH at 5, 10, 20 and 30 min. It is clear that untreated fibres possess a fairly smooth surface as indicated by the 3-D height image. The corresponding phase image shows very little change in terms of phase shifts, suggesting the bulk of the sample was composed of the same material; any regions that may have been indicative of a different material being present on the glass surface was likely as a result of contamination. After treatment of fibres for 5 min in KOH, we begin to see numerous spikes in the height image that also appear as phase shifts, indicating they belonged to a different material from the bulk glass; in other words, they are present as a result of interaction between the fibre and the alkaline solution. These residual spots appear to eventually coalesce and become a common feature on the fibre surface up to 30 min. There are occasions where these elevated regions do not translate to phase shifts, implying that the topography of the glass itself was being affected after alkaline treatment.
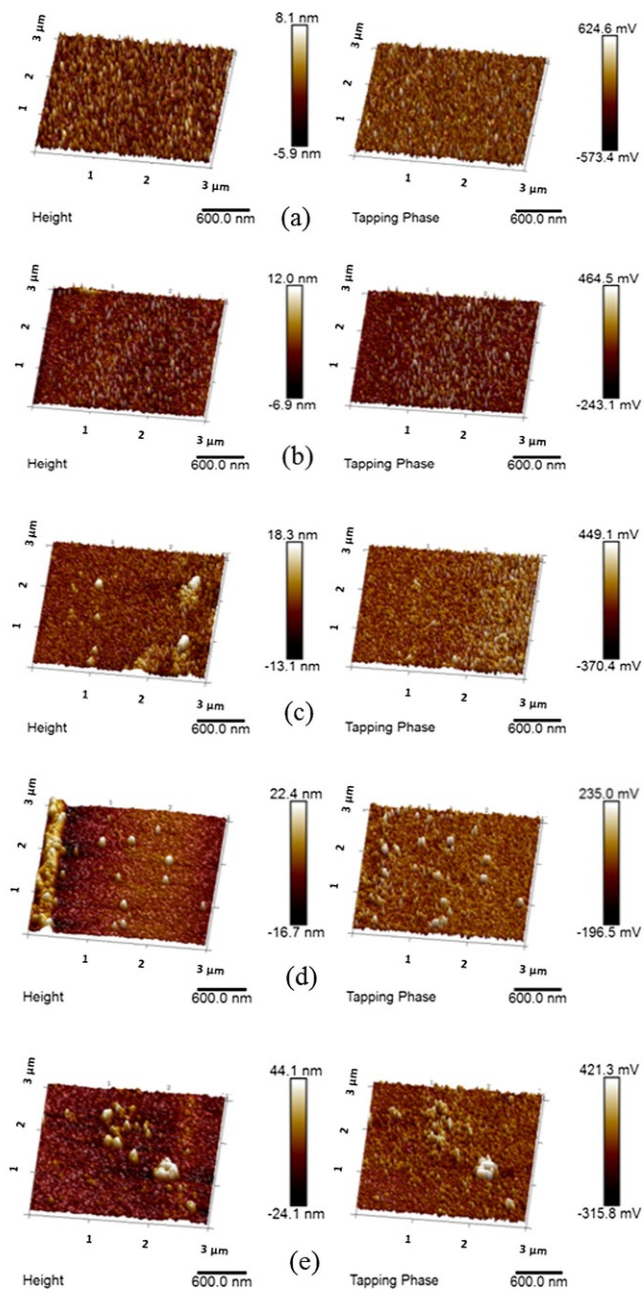
Fig. 8 AFM height and tapping phase images of (a) untreated fibre, and fibre treated in 3 M KOH at (b) 5 min, (c) 10 min, (d) 20 min and (e) 30 min. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 9 shows both the height and phase images of fibres untreated and after 3 M NaOH treatment from 5 to 30 min. There is a substantial amount of these elevated spots already at 5 min, which continues to build up with time. It is interesting to find changes in height do not necessarily emerge as changes in material phase; this could be due to the glass surface itself becoming rough after being etched by NaOH. Nevertheless, phase shifts do appear

commonly, particularly with longer NaOH treatment times. It could be assumed that both the presence of residue and the changes in glass surface topography contributed significantly to the overall roughness of the fibre. Both of these features are very pronounced for NaOH treated surfaces, which further supports that NaOH is a more corrosive alkaline reagent than KOH towards E-glass fibre.
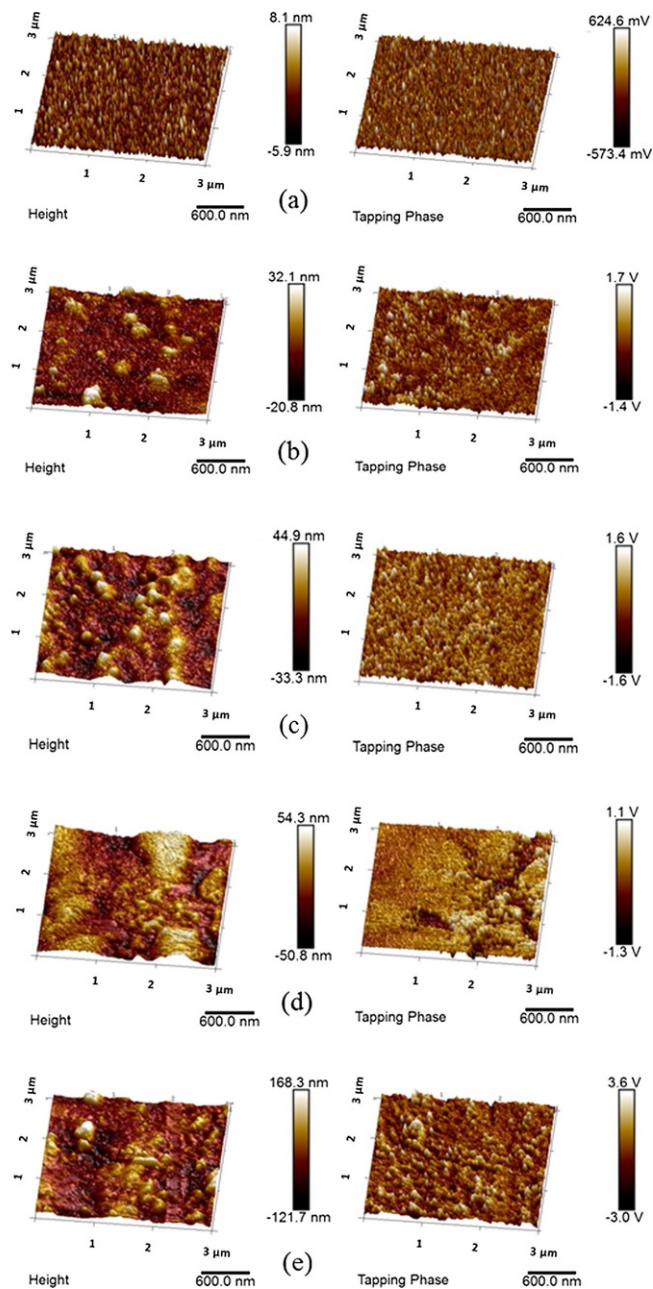
Fig. 9 AFM height and tapping phase images of (a) untreated fibre, and fibre treated in 3 M NaOH at (b) 5 min, (c) 10 min, (d) 20 min and (e) 30 min. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 10 gives the R_q values (root mean square roughness, given in nm) of these fibre samples; it is evident that the increased presence of residual deposits and topographic changes on the fibre surface leads to greater roughness following alkaline treatment. The R_q values presented for NaOH treated fibres are significantly higher than from fibres treated in KOH. This could have been partly due to the increased amount of residual deposits on the fibre surface which appeared for two possible reasons; the acid removed Na-based residual deposits less effectively than K-based deposits, and/or there was a more significant build-up of residue after NaOH treatment which could not have been removed by acid very well compared to residue from KOH treatment. It is also understood from phase imaging that changes in glass surface topography from alkaline treatment contribute to roughness, especially with NaOH. We can therefore conclude that AFM supports our previous results from SEM investigations and etching experiments which show NaOH to be more reactive with E-glass than KOH.
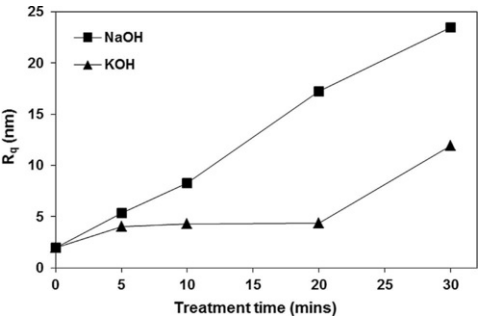

**Fig. 10** Roughness (R_q) values for untreated and alkali treated fibres in 3 M KOH/NaOH at different times.

3.5 FT-IR spectroscopic analysis of alkali treated fibres

At the extreme treatment scenarios both NaOH and KOH show a decline in HT fibre strength with time, which is particularly clear from the 5 M KOH and 5 M NaOH data in Figs. 2 and 3 respectively. In an attempt to relate this strength decrease with bulk structural change of the glass fibres, an FT-IR examination was conducted of the samples with a handheld FT-IR using a diffuse reflectance accessory. An advantage with using such a technique which penetrates hundreds of microns into the sample coupled with a spot size of around 3 mm is that several dozen fibres in the bundle were analysed each time, leading to more consistent and representative FT-IR diffuse reflectance spectra for each treatment condition. An additional benefit of the diffuse reflectance technique employed here is completely non-destructive sample interface interaction coupled with no need for any sample preparation. At this point a possible explanation of the strength decrease of HT fibres after excessive alkaline treatment is as follows: it is believed that similar to HF, NaOH and KOH improved the strength of heat damaged glass fibres by reacting with the surface silicate groups, thereby modifying the damaged surface layer. The reduction of surface flaw severity initially improved the fibre strength, but if conditions were too aggressive or long with respect to time, in other words if the alkali was at a high molarity and/or the fibres were immersed in the alkaline solution for an extended period of time, the restoration of the surface could have extended to the damage of the bulk network structure. KOH, being a milder corrosive agent, could have therefore reduced the severity of bulk attack even at higher molarities and increasing treatment times before it became detrimental to HT fibre properties. NaOH, a more aggressive glass etchant, was optimal at lower molarities and shorter application times; more corrosive alkaline conditions may well have resulted in more extensive glass network damage and also a smaller operational window than KOH. The greater difficulty in handling residue-coated fibres after prolonged alkaline treatment could also have had a negative effect; the acid rinse was designed to remove most of the residual deposits formed on the surface.

Fig. 11 provides a stacked view of the diffuse reflectance spectra of glass fibres as received, after HT, and treatment in 5 M KOH for 5 to 120 min with rinsing. There seems to be no significant bulk structural change in as received fibres after HT. After KOH treatment, the Si-OH vibration band centred around 3400 cm^{-1} [25] (which exists as a result of the reaction of the silicate in the glass fibre with OH$^-$ from the alkaline solution) steadily increases with time; the spectral collection was performed on oven dried samples so it was unlikely that residual water from the treatments led to this band. Also present in the spectra is the reduction of the reststrahlen Si

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Si peak centred around 900-1100 cm^{-1} [25]. What appears as a large peak at 1250 cm^{-1} for each spectrum is in fact a point of inflection as a consequence of the reststrahlen effect [26] where features at lower wavenumbers from this point are all negative primarily due to concomitant changes in refractive index with IR absorbance. The initially small peak related to the Si

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OH deformation vibrational mode becomes more significant at longer treatment times; this vibrational mode is normally only seen in more open silica structures. The stacking of the spectra enables the visualisation and clarification of peak changes in size or shape changes but also compresses the Y-axis hiding another spectral relationship with the degree and severity of treatment. The raw diffuse reflectance mid-infrared spectral data also displays decrease in reflectivity that is directly related to the degree and extent of the KOH treatment.
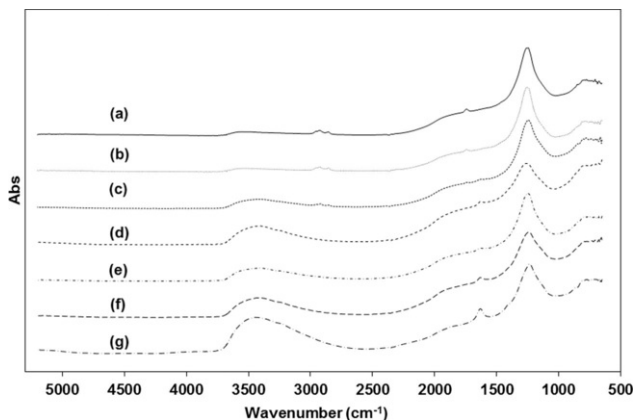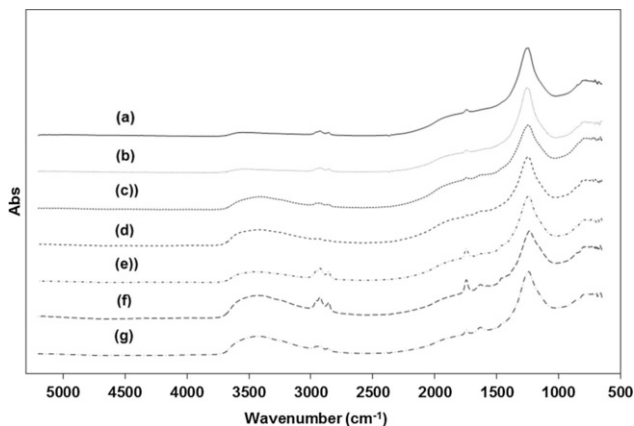
Fig. 11 Stacked view of FT-IR diffuse reflectance spectra of glass fibres (a) as received, (b) after HT, and then treatment in 5 M KOH for (c) 5 min, (d) 10 min, (e) 20 min, (f) 30 min and (g) 120 min, with rinsing.

Fig. 12 shows diffuse reflectance spectra of fibres treated in 5 M NaOH at 5 ~~to~~ 120 min. The key features described in the spectra for KOH treated fibres again appear here, however one of the key differences is in the appearance of the Si-OH vibration band at various treatment conditions. As expected, we do see a gradual increase of this Si-OH band as treatment duration in NaOH lengthens, although the intensity varies with that of KOH treated fibres. For example, after 5 min treatment in NaOH the Si

OH peak is more apparent than in the corresponding spectrum for KOH. On a similar note, the Si-OH signal at 30 min NaOH is more intense than for KOH under the same conditions. The observation of the Si

OH band being very strong after 120 min KOH treatment is unusual; however it is worth considering that traces of residue which remained on alkali treated glass fibres after rinsing could have contributed to this signal.

Fig. 12 Stacked view of FT-IR diffuse reflectance spectra of glass fibres (a) as received, (b) after HT, and then treatment in 5 M NaOH for (c) 5 min, (d) 10 min, (e) 20 min, (f) 30 min and (g) 120 min, with rinsing.

In Fig. 12 there are additional peaks at around 2900 cm^{-1} (which also appear in Fig. 11 for a few spectra) that are variable and are likely to be from residual APS [27,28]. Moreover, there is a peak at around 1750 cm^{-1} which is characteristic of a carbonyl (C

O) functional group that is not present in APS. This peak could be as a result of interaction between APS and alkali to form a halogenated ketone or carboxylic species; Culler et al. [27,28] observed a range of peaks in their FT-IR diffuse reflectance spectra at 1650 to 1300 cm^{-1} corresponding to the bicarbonate salt structure formed between APS and carbon dioxide, and these are absent as is the carbonate absorbance near 2500 cm^{-1}. The carbonyl peaks in our FT-IR spectra appear at a high wavenumber of 1750 cm^{-1} which suggests that carboxylic or halogenated ketone groups were present in the fibre samples.

From the FT-IR diffuse reflectance spectra it can be shown that immersion of HT E-glass fibres in sub-optimal alkaline solution resulted in the breakdown of the silicate network, due to the increase in intensity of the Si-OH

bands and the correlated decrease in Si $\overline{}$

O $\overline{}$

Si peaks. Taking into account the presence of surface flaws in HT fibre, it is believed the alkaline solution initially improved fibre strength by modifying these defects. However, as fibres were treated for a lengthy period, we begin to see clearly from the FT-IR diffuse reflectance spectra that the degradation of the glass network became significant and offers a spectral explanation as to why there was an eventual drop in fibre strength. Furthermore, the rapid increase in intensity of the Si-OH band after NaOH treatment is complementary with previous experimentation indicating it is a more corrosive alkali towards E-glass than KOH. The variety and presence of several FT-IR markers that correlate to the fibre strength offers a possible non-destructive method to pre-validate that the optimal conditions have been applied to the recycled and heat treated glass fibres.

3.6 Fracture surface of alkali treated fibres

Our FT-IR spectra indicate significant bulk glass network damage when glass fibres are treated in alkaline solution for an extended period of time (120 min). To determine whether the origin of failure of these fibres was internal or superficial, the fracture surface was analysed through SEM. HT glass fibres treated in 5 M KOH and NaOH for 120 min were tested for tensile strength, which were measured to be 0.82 and 0.60 GPa respectively. The fracture surfaces of some of these fibres were examined under the SEM after tensile testing, with representative images (both for KOH and NaOH treated fibres) displayed in Fig. 13.
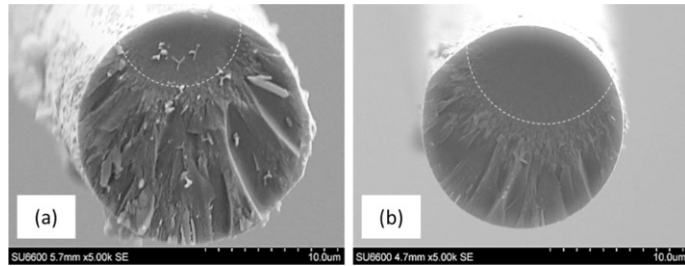
Fig. 13 SEM images of fracture surfaces of fibres HT and treated in (a) 5 M KOH for 120 min and (b) 5 M NaOH for 120 min.

Three distinct regions are generally present in the majority of fibre fracture surfaces- mirror, mist and hackle [8]. The smooth and featureless mirror zone surrounds the original crack that is located at the surface of the fibre. At the edge of the mirror zone there is a pitted surface which is the mist region, and the branches that appear are referred to as hackle. The fact these features are present in both images in Fig. 13 suggests the origin of failure was at the surface, even if the bulk glass network was damaged by the severe alkaline treatment; there was no indication from any of the fibre fracture surfaces that failure initiated internally. It is suggested that although the bulk glass structure was damaged with excessive treatment in both NaOH and KOH as indicated by the FT-IR results, the source of fibre failure was still likely to have been at the surface. Indeed, for there to have been significant internal damage the glass fibre surface would have had to react first with the alkaline solution and consequently remain the weakest region.

The main difference between the fracture surfaces of KOH and NaOH treated fibres is the size of the mirror region, which is inversely related to tensile strength; the larger the mirror zone, the deeper the surface crack, and consequently the lower the strength of the fibre. The measured strength of fibres treated in 5 M NaOH for 120 min was lower than in KOH under the same conditions, and we can clearly see from Fig. 13 that the mirror region is larger for NaOH treated fibre.

4 Conclusions

Glass fibres exhibit up to 70% tensile strength loss after conditioning at a thermal recycling temperature of 450 °C. We have demonstrated that a short treatment of thermally degraded glass filaments in hot NaOH or KOH can almost double their strength, allowing their potential reuse as reinforcement in GRP materials. LiOH, however, was unable to restore strength in heat damaged fibres. KOH, shown to be a milder glass fibre etchant from mass loss and diameter reduction experiments, improved fibre strength at higher molarity and longer treatment times. Conversely NaOH was a highly corrosive alkaline reagent towards glass fibre, and proved to be a much more efficient strength regenerator. For a given etchant, the maximum strength regeneration was affected by molarity and treatment time. Interaction of alkaline solution with the glass surface resulted in the formation of residual deposits, which were more prominent for fibres treated in NaOH than KOH as shown by SEM and AFM investigations. The degradation of the glass network, as indicated by FT-IR spectra, correlated with the decrease in fibre strength when treatment in NaOH and KOH was excessive. On a positive note, the fact that NaOH was highly corrosive meant only low molarity of solution and short treatment time was required to regenerate HT fibre strength; when conditions became severe then we began to see a drop in strength of HT fibres. It is thought the reduction in severity of surface flaws on HT fibre explained why strength initially improved with alkaline treatment. Despite the degradation of the glass fibre network as a

whole after excessive treatment, examination of fibre fracture surfaces indicated that the origin of failure could still have been at the surface.

The results reported in this work have successfully shown that both NaOH and KOH are promising candidates for significantly regenerating the strength of thermally damaged glass fibres. Further investigation of the feasibility of alkaline treatments will be conducted when scaling up the process, in the hope of creating a potential route to GRP recycling. In addition, the kinetics of the reaction between these alkali metal hydroxides and glass fibre will be studied in more detail to help us further understand the etching mechanism.

Acknowledgements

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