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**Jenkins, Peter and Thomason, James and Stafford, Mhari (2016)
Investigation of the effect of hot water and water vapour treatments on
the strength of thermally conditioned E-glass fibres. In: The 17th
European Conference on Composite Materials (ECCM17), 2016-06-26 -
2016-06-30, Internationales Congress Center München. ,**

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INVESTIGATION OF THE EFFECT OF HOT WATER AND WATER VAPOUR TREATMENTS ON THE STRENGTH OF THERMALLY CONDITIONED E-GLASS FIBRES

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Keywords: glass fibre, tensile strength, thermal conditioning, strength recovery

Abstract

The processing and reuse of end-of-life composite products in an environmentally friendly manner is an important challenge facing the industry. The development of an economically viable process for regenerating the properties of thermally recycled glass fibres would have significant technological, economic and environmental impacts.

Thermal recycling processes for composites are relatively technologically advanced; however, they present a substantial challenge when considering their use for recycling of glass fibre reinforced materials. A combination of exposure to elevated temperatures in the region 450 – 600 °C and to mechanical damage has been shown to cause significant strength loss in glass fibres of up to 90 % of their original value. The recovered fibres are thus unsuitable for use as reinforcement in a second generation composite. Methods of strength recovery that may be applied to such recycled fibres are therefore of interest, particularly if these methods are relatively technologically straightforward.

An investigation of possible strength recovery methods using hot water or water vapour was carried out on E-glass fibres. The methods were derived from similar studies on silica in which significant strengthening effects were presented alongside theoretical frameworks to explain the phenomenon [1–3]; a maximum threefold increase in strength following water vapour treatment at 250 °C was demonstrated on silica artificially weakened by abrasion.

1. Introduction

One of the most significant challenges currently facing the composite materials industry is the issue of economically viable and environmentally friendly end-of-life re-processing. The use of composite materials continues to increase, particularly in the automotive, aerospace and wind energy industries; therefore the challenge of dealing with waste is increasing. Glass fibre (GF) constitutes 90 % of the reinforcement fibre used worldwide and global production of the most common type E-glass is of the order of approximately 7 million metric tons annually [4]. A number of methods are available for recycling glass fibre reinforced plastics, of which thermal recycling methods are probably the most technologically advanced [5–7]. These methods also theoretically allow for the recovery of the fibre fraction, which may be considered the most valuable fraction in a composite [7]. Although thermal recycling may allow for the recovery of fibres, their mechanical properties are invariably poor. Most problematic is a significant reduction in tensile strength due to exposure to elevated temperature, with strength decreases of 80 – 90 % commonplace [8–12]. Methods which are capable of regenerating the

strength of GFs weakened due to thermal treatment or recycling are of interest in the context of potentially developing new avenues for the recycling of the composite fibre fraction as a replacement for virgin GF.

Previous work has shown that the strength of surface damaged glass can be increased by exposure to water or water vapour [1,13,14]. It was theorized that the strength increase observed was due to a change in the crack tip geometry. Blunting of the crack tip by a dissolution and re-precipitation [15] or viscous flow mechanism [14] have been proposed. An alternative theory of the formation of surface compressive stress has been proposed in more recent work [3,16]. In the paper presented the results are shown of an investigation into the ability of both liquid water and water vapour at elevated temperature to recover the strength of heat treated E-glass fibres.

2. Experimental

2.1. Materials

Boron-free E-glass (Advantex) fibres supplied by Owens Corning Vetrotex were investigated in this study. 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 g/km and single-fibre diameter of 17 μm . No sizing was applied to the water finished fibres which had only been water sprayed using the normal cooling sprays under the bushing; these samples are referred to as water sized, unsized or bare (since it can be assumed that most water is removed during the subsequent drying step). The sized fibres were coated with a normal rotating cylinder sizing applicator containing a 1 % γ -aminopropyltriethoxysilane (APS) hydrolyzed solution in distilled water. All fibre packages were subsequently dried at 105 °C for 24 hours.

Treatments were applied to single fibre lengths of between 80 – 120 mm mounted on wire frames manufactured from mild steel wire of diameter 1.5 mm. Glassbond Saureisen Electrotemp Cement No. 8 was used to restrain fibres during thermal conditioning and subsequent water/water vapour treatments.

2.2. Thermal conditioning

Fibre thermal conditioning was carried out using a Carbolite CWF 12/13 furnace, at temperatures of between 200 – 600 °C and for durations of either 25 minutes or 1 hour. All thermal conditioning was performed on single fibres: individual fibres were isolated from the roving and attached to wire frames using the cement described in 2.1. Frames were arranged and inserted into a pre-heated furnace for the prescribed time, then removed directly to cool in room temperature air.

2.3 Water and vapour treatments

After applying thermal conditioning as described in 2.2, some samples were then treated by immersing in either liquid water or water vapour at elevated temperature. To treat using water, frames holding single fibres were arranged in a 4 litre polypropylene container. The container was filled carefully, minimizing fibre movement as much as possible, with deionized water until all samples were fully submerged. The container was placed into a pre-heated oven at 90 °C for 4 hours. Following water treatment, samples were carefully removed and dried in an oven at 110 °C for 30 minutes.

Fibres were treated in water vapour using a domestic pressure cooker; this produced a pressure of approximately 82.7 kPa giving a corresponding boiling temperature for water of around 120 °C. Frames with mounted samples were arranged in an aluminium foil tray and rested on aluminium

blocks to keep them above the level of the water. The heating element used to induce boiling was carefully controlled to prevent excessive agitation of the water during boiling from occurring and thus ensuring that only high temperature water vapour contacted the fibre surfaces. The fibres were vapour treated for 4 hours, beginning when the vessel had reached pressure and begun boiling.

2.4 Tensile testing

Tensile testing of single fibres was carried out according to the method described in ASTM C1557-03 [17] using a Testometric M250-2.5CT with a 5 N load cell. A constant strain rate was used in all tests. Further details can be found in the literature [8,18].

2.5 Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDS)

Scanning electron microscopy was utilized to examine the surfaces of fibres following heat and water or vapour treatments. A Hitachi SU6600 Field Emission SEM was used, operating with accelerating and extraction voltages of 15 and 1.8 kV respectively. The instrument was equipped with an Oxford Inca 350 with X-Max 20 mm² detector energy dispersive spectrometer for elemental analysis; the same voltage settings were utilized for EDS as for imaging.

3. Results

3.1 Strength loss of thermally conditioned glass fibre

Results of the effect of thermal conditioning on the retained strength of fibres are shown in Figure 1. Error bars showing the 95 % confidence limits are shown in this and subsequent figures. A significant decrease in retained fibre tensile strength was found; the magnitude of retained fibre strength decreased with increasing thermal conditioning temperature and with increasing conditioning time. The most significant decrease in strength appeared to occur in the temperature range of approximately 450 – 600 °C, when constant thermal conditioning time was used. Similar trends in strength loss were found for both bare and APS sized fibre; this is attributed to the fundamental strength loss which the GFs experience due to thermal effects and a minimization of mechanical sources of damage from using the single fibre thermal conditioning technique [8].

The data points for fibres heat treated at 500 °C for 1 hour have been artificially moved along the x-axis by 10 °C to make the data in this region clearer. It is notable that there is still a significant decrease in strength with time at 500 °C; previous studies have suggested that even a relatively short exposure to this temperature should be sufficient to decrease fibre strength to a minimum value below which it would not decrease with further length of thermal conditioning [11]. Tensile strengths of approximately 0.55 and 0.85 GPa following thermal conditioning for 1 hour at 500 °C were measured for bare and APS sized fibre respectively.

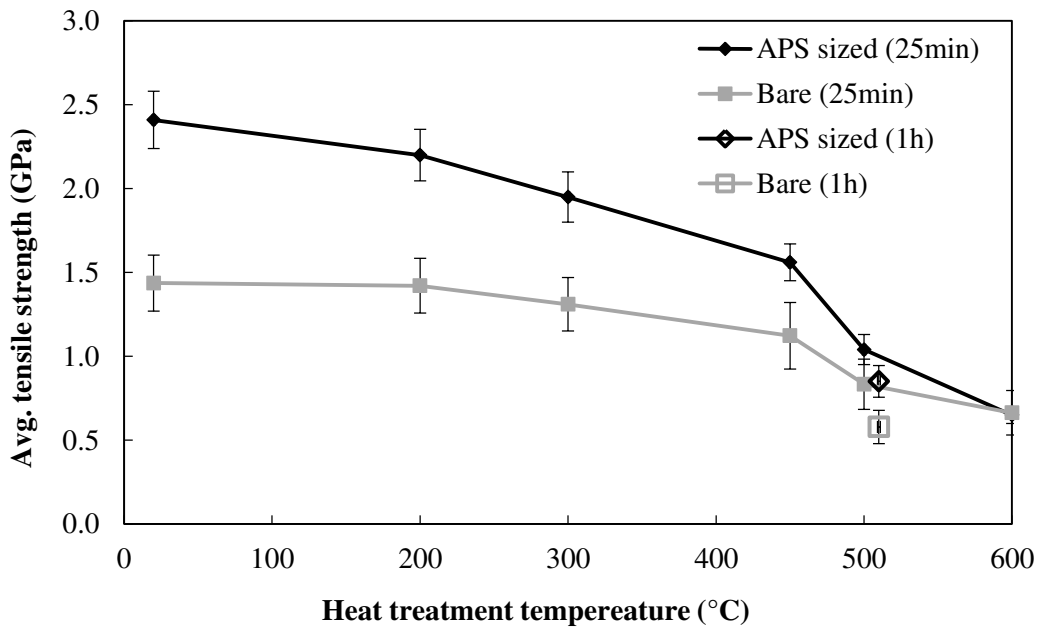


Figure 1: strength loss of bare and APS sized E-glass following thermal conditioning

3.2 Regeneration of fibre strength using water and vapour treatments

The strengths of fibres following treatments using liquid water or water vapour, as described in 2.3, are presented in Figure 2.

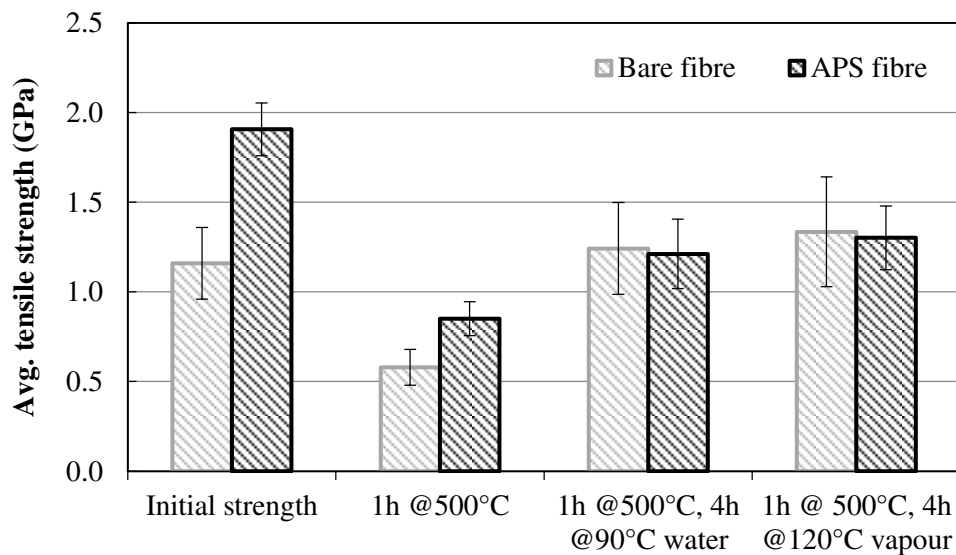


Figure 2: Tensile strength of fibres after various treatments (none, thermal conditioning, thermal conditioning + water treatment, thermal conditioning + vapour treatment)

As discussed in 3.1, thermal conditioning at 500 °C for 1 hour was found to produce a significant decrease in fibre tensile strength of the order of 50 %, or slightly more in the case of APS sized fibre. Fibres thermally conditioned, and therefore subject to this significant strength loss, were subsequently treated using water or water vapour. Both treatments produced a similar increase in the strength of

bare and APS sized fibre, which was significant with respect to the strength of only heat treated fibre. Water treatments and vapour treatments produced a recovery in strength to values of approximately 1.2 GPa and 1.3 GPa respectively, regardless of the fibre used. In the case of APS sized fibre this constituted a strength recovery of up to approximately 50 %, whereas for bare fibre an increase of up to 130 % was achieved.

The surfaces of fibres treated with hot water and water vapour were examined using Scanning Electron Microscopy and some chemical analysis was conducted using Energy Dispersive X-ray Spectroscopy. Images of the surface of fibres after treatment by either hot water or water vapour are shown in Figure 3 (a) and (b) respectively. The particles which appeared as white on the surface fibres such as that shown in Figure 3 (a) were found to have a high weight percentage of zirconium; this originated from the cement used to secure fibres, a portion of which diffused in the water during treatment and appeared to precipitate on fibre surface to some degree. Similar structures were not found on the surface of vapour treated fibres (Figure 3b) but a significant volume of presumably contaminant particles was observed along most of the fibre surface observed using SEM. EDS characterization did not produce conclusive results, but focused spot analyses suggested that larger contaminant particles were generally high in iron and oxygen or zirconium. They may, therefore, be associated with either the cement used or particles of rust from the oxidation of the steel frames which were used to support individual fibres.

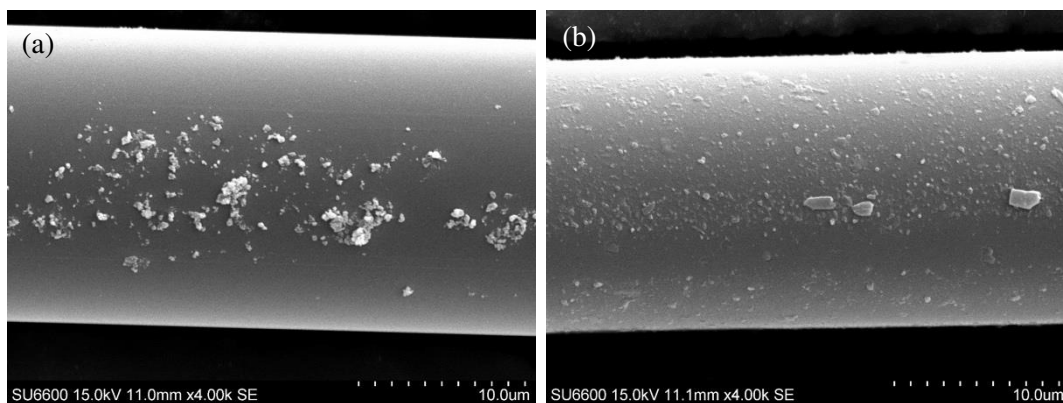


Figure 3: Scanning Electron Microscope image of surface of fibre following (a) water treatment at 90 °C and (b) vapour treatment at 120 °C

4. Discussion

The results presented in Figure 2 show that the hot water and water vapour treatments, applied to glass fibres that had been previously thermally conditioned, were both effective at producing a recovery of fibre strength. The magnitude of strength following treatment was equal whether initially bare or APS sized fibres were used in the investigation. Hot water treated fibres increased in strength to around 1.2 GPa and vapour treated fibres to approximately 1.3 GPa; however, the error bars on these strengths were relatively large and it therefore cannot be claimed that vapour produced a statistically greater strength increase to hot water treatment. It is interesting that the fibre strength after treatment was identical for previously bare or APS sized fibre, given that their relative strengths following thermal conditioning were significantly different – bare fibre having a lower average tensile strength of around 0.55 GPa compared with 0.85 GPa for APS sized.

Significant contamination on the surfaces of both water and vapour treated fibres was observed by SEM. Analysis using EDS suggested that contaminant particles were most often associated with the cement used to affix fibres to their frames for treatment: identification of this was achieved due to the high content of zirconium in the cement, which is not present in E-glass. Tentative evidence of

particles on the surface of vapour treated fibres with high iron and oxygen content was also found; the source of such contamination may be corrosion of the steel frames used to hold fibres during treatments. It is not known whether the presence of surface contamination has an effect fibre strength recovery.

The strength increase phenomenon observed in this work suggests some change in the surface flaws present on the fibres must have occurred. It is known that strength of glass fibres can be increased by etching with a suitable medium such as hydrofluoric acid [19]; however, only deionized water was utilized in this work, therefore an etching phenomenon is most unlikely. As discussed in the introduction, researchers have previously shown it to be possible to increase the strength of abraded silica rods using either hot water or water vapour [1,15]. In addition to the material difference between silica and E-glass, the dimensions of the rods were almost 3 orders of magnitude larger than the glass fibres used in the work presented; the apparent size of flaws causing failure are correspondingly significantly different. The strengths of bare or sized E-glass following thermal conditioning correspond to a critical flaw of the order 300 – 700 nm. Conversely, Li and Tomozawa [1] measured flaws on the fracture surfaces of their glass rods and reported a value of 180 μm . They attributed the strengthening effect to a crack tip blunting mechanism: ingress of water to the crack tip allowed dissolution and re-precipitation of silica, creating an increase in the radius of curvature. It is possible that a similar crack tip blunting mechanism may act on the glass fibres exposed to water and water vapour, despite the significantly smaller apparent flaw dimensions in comparison with silica rods. The atomic radius of a water molecule is of the order of 0.14 nm and water may, therefore, be able to reach the crack tip at which a crack tip blunting mechanism could then occur.

An alternative theory to explain the strengthening effect has been described in the more recent literature [3,16,20,21]. The diffusion of water into silica was studied, when held in humid air or water at elevated temperature. Swelling of the silica with the diffusion of water into its structure was reported and was attributed to the formation of silanol groups, rather than merely due to the presence of water within the structure. This swelling produced a subsequent shielding effect on cracks present in the surface of the glass. Using this mechanism as a basis to explain the strengthening phenomenon of E-glass fibres reported in this work is, however, also potentially problematic. It was reported by Wiederhorn et al. [16] that the strengthening effect in their work was ‘virtually absent’ for cracks of sub-micrometer dimensions: as discussed above, the cracks or flaws in the E-glass fibres investigated are theoretically all less than 1 μm in their critical dimension. On the other hand, the significant material differences between silica and E-glass (both physical and chemical) may mean that this apparent limitation reported by Wiederhorn et al. is not applicable to the case of water and water vapour treated E-glass.

5. Conclusions

It was shown that the strength of single E-glass fibres, previously thermally conditioned at 500 °C for 1 hour, could be recovered by application of a liquid water, or water vapour, treatment at elevated temperature. Water treated fibres were recovered at 90 °C and water vapour treated at approximately 120 °C. The treatments investigated produced an increase in both unsized and APS sized fibres to a similar strength magnitude; the percentage recovery was therefore significantly greater for the originally weaker unsized fibres. Two possible mechanisms, both previously developed based on studies of silica, are reported in the literature; namely, crack tip blunting or crack shielding due to silanol formation from water diffusion. The applicability of either of these mechanisms to the case of E-glass fibres reported here is potentially problematic due to significant differences in scale (crack-tip blunting) and the presence of only sub-micrometer flaws (crack shielding due to diffusion based swelling). Although an explanatory mechanism cannot yet be given, the significant increase in tensile strength obtained is of interest particularly in the context of glass fibre regeneration and recycling from composite materials.

Acknowledgments

The authors gratefully acknowledge the funding through the Engineering and Physical Science Research Council project EP/1038616/1, in addition to Owens Corning for supplying the glass fibre used in this study. Thanks are also given to the University of Strathclyde Advanced Materials Research Laboratory (AMRL) for use of the SEM.

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