

# **Regenerating the strength of thermally recycled glass fibres using hot sodium hydroxide**

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## **Abstract**

Results are presented from the ReCoVeR project on the regeneration of the strength of thermally conditioned glass fibres. Thermal recycling of end-of-life glass fibre reinforced composites or composite manufacturing waste delivers fibres with virtually no residual strength or value. Composites produced from such fibres also have extremely poor mechanical performance. Data is presented showing that a short hot sodium hydroxide solution treatment of such recycled fibres can more than triple their strength and restore their ability to act as an effective reinforcement in second life composite materials. The implications of these results for real materials reuse of recycled glass fibres as replacement for pristine reinforcement fibres are discussed.

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

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## **1. Introduction**

The disposal of composite manufacturing waste and end-of-life composite products in an environmentally friendly manner is one of the most important challenges currently facing the industrial and academic composites community. 2015 global production of fibre reinforced composite materials will significantly exceed 10 million tons [1]. Glass fibre (GF) is the reinforcement of choice in more than 90% of all these composites and more than 5 Mton of reinforcement grade E-glass fibre was produced in 2015 [2]. In fact, some available data indicates that E-glass consumption could already be as high as 7 Mton when yarns are included [3]. The manufacture of this volume of GF results in 0.5-1 million tons of GF manufacturing waste [4] most of which is landfilled. Furthermore, approximately 70% of reinforcement glass fibre is used to manufacture thermoset based composites (GRP) which also produces approximately 15% manufacturing waste [5]. Such GRP materials (both end-of-life and manufacturing waste) are difficult to recycle in an efficient manner and have historically also been disposed of in landfills. Such landfilling is rapidly becoming untenable due to legislative and landfill cost developments. The perspectives on this issue have been recently highlighted due to the accelerating growth in the use of such composite materials in transportation and wind energy sectors [6-9]. A number of processes are available for recycling such composites and thermal recycling is probably the most technologically advanced [6,9]. However, nearly all options deliver thermally recycled glass fibres (TRGF) that suffer from a lack of cost competitiveness with pristine first-pass materials.

A critical technical challenge in the development of GRP recycling technology is the 80-90% drop in the performance (and value) of TRGF in comparison to its original state [9-13]. Processing temperatures in the production of glass fibre are significantly higher than GRP recycling temperatures. Nevertheless, earlier work has indicated that the room

temperature tensile strength of glass fibre can be significantly reduced by annealing at a temperature as low as 150°C [9]. More recent studies have also confirmed that the room temperature glass fibre strength can be drastically reduced by exposure to temperatures in the 300°C-600°C temperature range [11-13] typical of the many different potential GRP recycling processes. Similar behaviour has also been observed in silica and basalt reinforcement fibres [14,15]. Consequently, TRGF have a very poor performance to cost ratio, and in most cases are unsuitable for reprocessing and reuse as a valuable reinforcement for composites. A breakthrough in this field could enable such TRGF to compete with pristine materials in many large volume discontinuous fibre reinforced composite applications. The development of an economically viable process for regenerating the properties of thermally recycled glass fibres would have major technological, societal, economic, environmental impacts. Figure 1 indicates that there is an on-going situation where up to 50% of the global demand for glass fibre reinforcements could potentially be supplied by TRGF from end-of-life and manufacturing waste recycling. The reuse of these materials could result in a huge reduction in the environmental impact of the glass-fibre and composites industry where the replacement of 50% of current glass fibre products by TRGF products would equate to a global reduction in CO<sub>2</sub> production of 2 Mtons/annum from reduced melting energy requirements alone [16]. Furthermore, such a development would also vastly reduce the landfill requirements of the glass fibre and GRP industry. This would clearly be in line with the growing societal and environmental pressure to reduce landfill disposal, increase the reuse of valuable raw materials, and reduce CO<sub>2</sub> release to the atmosphere.

It is generally accepted that the measured strength of glass fibres is dependent on their brittle nature and the state of the fibre surface region. Fundamental research on the thermally induced strength loss of glass fibre indicates that the phenomenon may have a

complex nature but that it appears to be caused mainly by changes on (sizing degradation and surface damage), or just below (“flaw” generation and growth, and dehydroxylation), the fibre surface. Yang et al. [17] recently demonstrated that the reinforcement potential of TRGF could be significantly improved by a post treatment with hydrogen fluoride (HF) to remove this “damaged” surface layer. Nevertheless, given the very aggressive nature of HF and the associated safety issues, it seems unlikely that a cost-effective regeneration process could be based on HF treatment. We have been researching less aggressive chemical routes to achieve similar results. The literature generally refers to the effects of acid or alkali treatments in terms of their deleterious effects on glass fibres [18] and the resultant lowering of composite strength. However, this body of work is almost universally predicated on maintaining the performance of strong fibres. Little if any work has been reported on the use of acid or alkali treatments to change the strength of very weak fibres. However it is well known that under the appropriate conditions a silica network can be attacked, and in some cases dissolved, by the use of sodium hydroxide (NaOH) solutions [19,20].

As part of the EPSRC funded ReCoVeR project we have been focusing on enabling cost-effective recycling of glass fibre thermosetting composites. In particular we wish to show the possibility of regenerating the strength of recycled glass fibres to enable their reuse as a composite reinforcement replacing the use of pristine fibre materials. In this paper we present results showing the ability of hot NaOH and silane treatments to significantly increase the strength of thermally conditioned commercial continuous glass fibres. These chemical treatments are then shown to be equally effective in the strength regeneration of fibres thermally recycled out of model unidirectional continuous fibre reinforced thermoset composites. Finally, results are presented on the influence of fibre thermal conditioning and subsequent fibre strength regeneration through chemical treatments on

the strength performance of laboratory produced discontinuous random in-plane reinforced polypropylene laminates.

## **2. Experimental**

### **2.1 Materials**

Initial screening work on the effect of NaOH treatment on the strength of glass fibre was carried out on boron-free E-glass fibres supplied by Owens Corning (OC). These OC-APS fibre rovings have been previously described in detail [12,13,21]. The rovings had a nominal tex of 1200 g/m and a nominal fibre diameter of 17  $\mu\text{m}$  and had been coated with a 1% volume  $\gamma$ -aminopropyltriethoxysilane (APS) hydrolysed solution in deionized water. A similar glass fibre sample (3B-APS) of 14  $\mu\text{m}$  diameter boron free E-glass coated with a 1% APS solution was supplied by 3B-Fibreglass. A boron containing E-glass roving (TufRov® 4599) supplied by PPG Fiberglass was also used in fibre strength screening work. The 4599 roving is a 17  $\mu\text{m}$  diameter continuous fibre product sized for polypropylene compatibility. To investigate the effect of fibre thermal conditional and subsequent chemical strength regeneration 30% weight discontinuous random in-plane fibre reinforced polypropylene laminates were prepared using a PPG supplied product. PPG 8069 is a chopped glass fibre product designed for easy dispersion in aqueous media for the production of wet-laid non-wovens. These 8069 fibres had a nominal diameter of 10  $\mu\text{m}$  and were received as wet chopped bundles with a nominal fibre length of 9 mm. The homopolymer polypropylene (PP) for the production of composites was purchased in the form of Goonvean DA3/60 chopped PP fibres. The fibres were received chopped with a nominal length of 6 mm and a nominal linear mass of 3.3 dtex.

### **2.2 Glass fibre treatment**

The procedure for thermal conditioning of glass fibres has been previously described in detail [12,13]. To imitate a composite recycling process, glass fibres were thermally conditioned in air. A 'Carbolite CWF 12/13' furnace was preheated to 450 °C, 500 °C, or 600 °C, and the fibres were placed in the preheated furnace for 25 minutes. After thermal conditioning the fibres were allowed to cool down at ambient temperature ( $21 \pm 2$  °C) outside of the furnace. The thermally conditioned fibres were subject to different treatments. The optimisation of the conditions of these chemical treatments has been described elsewhere and is not the subject of this report [22,23]. To regenerate the fibre strength the thermally conditioned fibres were immersed in a 3M sodium hydroxide solution (NaOH) for 10 minutes at 90 °C. These fibres were then drained and rinsed in hydrochloric acid (HCl) to neutralise any remaining NaOH and assist in the removal of any water glass deposits. The SEM micrograph in Figure 2a shows a typical example of these deposits on an NaOH treated heat conditioned fibre. These deposits are commonly observed after concentrated NaOH interacts with E-glass fibre surfaces [24]. Finally the fibres were rinsed three times in demineralised water and dried at 105 °C for approximately 6 hours. A 1 vol% APS solution was used to regenerate the surface functionality of the heat treated and NaOH treated fibres. Deionised water was used to prepare the APS solution. Before the fibre treatment the solution was allowed to hydrolyse for 24 hours at room temperature. The fibres were immersed in the APS solution for 15 minutes. Samples for fibre testing were dried, however samples for Glass Mat Thermoplastic (GMT) production were processed directly into the composites. This was because it was found that the APS treated fibres were more difficult to disperse if they were dried. Figure 2b shows the fibre surface of a heat conditioned fibre after NaOH treatment and silane treatment. This fibre exhibits the virtually featureless surface which is typically observed with new glass fibres and confirms the removal of the deposits seen in Figure 2a which can be very detrimental to the efficacy of the silane treatment [22].

### 2.3 Composite processing

Model composite samples were prepared for thermal recycling of the fibres using an in-house casting method. Lengths of OC-APS glass fibre rovings were aligned unidirectionally in a casting mould. CRYSTIC 701 PAX polyester infusion resin was mixed with 1% by weight methyl ethyl ketone peroxide initiator. The mixture was then degassed in a vacuum chamber for 10 minutes before pouring into the casting mould and cured first at room temperature for 12 hours and then 3 hours at 80°C followed by 3 hours at 120°C. The fibres were then “recycled” from these composites (approximate dimensions 3x6x100 mm) using a Carbolite CWF 12/13 high temperature muffle furnace set at 600°C for 60 minutes in air.

GMT samples were prepared with PPG 8069 chopped fibres, as received, after 500 °C heat treatment (HT), and after HT plus chemical treatment with either NaOH (HT+NaOH) alone or NaOH and subsequent silane coating (HT+NaOH+APS) as described above.

The GMT laminates for composite testing were prepared by wet deposition and compression moulding. A KCL hand sheet former was used to disperse the PP fibres and glass fibres in 20 l of water. All composites were based on 30 wt% glass fibre content. The fibre suspension was agitated using an electrical stirrer at 1200 rpm for 6 minutes and then rapidly strained through the nylon sieve of the sheet former. The mat of glass fibres and PP fibres was then dried for 8 h in an oven at 105 °C until no further weight loss was detected. A Polystat 400S press was used to preconsolidate the mats at a pressure of 6.8 bar and a temperature of 200 °C for 1 minute. The preconsolidated sheets were cut and compression moulded. Four preconsolidated sheets were used to prepare one GMT laminate. The compression moulding was performed at 200 °C. A pressure of 20 bar was applied for 4 minutes. Then the mould was transferred to a second press and the material was quenched

cooled at the same pressure. A water jet cutter was used to cut dog bone shaped tensile test specimens out of the moulded GMT laminates according to ISO 527. A similar procedure was followed to prepare samples of unreinforced PP.

## 2.4 Mechanical testing

The tensile tests of the composites and the unreinforced PP were performed according to the standard ISO 527 using an Instron 5969 universal testing machine equipped with a 50 kN load cell. The crosshead displacement was set to 1 mm/min and the strain was recorded with a video extensometer. The single fibre tensile tests were performed following the standard ASTM C1557-03. The single fibres were mounted on card tabs with a central window of 20 mm (for fibres from continuous rovings) or 5 mm (for samples from the 9 mm chopped fibres). An Instron 3342 universal testing machine equipped with a 10 N load cell was used to perform the tensile tests. The crosshead displacement rate was set to 0.3 mm/min and the tests were performed at room temperature ( $22 \pm 2$  °C). Further details of the method can be found elsewhere [12,13]. For microbond testing of interfacial shear strength, small pieces of preconsolidated PP sheets were molten on a hot plate at 200 °C. Tweezers were used to draw long fibres from the molten polymer. The PP fibres were tied around single glass fibres. The single glass fibres were glued on to washers using two component Araldite epoxy adhesive. The samples were placed in an OV-11 vacuum oven that was purged nitrogen and heated to 220 °C to form microbond droplets. A description of the test procedure can be found elsewhere [25].

## 2.5 Fibre length measurements

The influence of the combined heat and chemical treatment of fibres on the residual fibre length in the GMT composites was investigated using an IDM FASEP fibre length measurement system as previously described [26]. To isolate the glass fibres for length

measurement GMT composite samples were ashed in a Carbolite CWF 12/13 furnace using a 6 hour ashing process with temperatures up to 550 °C. Approximately 25 mg of glass fibres were dispersed into deionised water with glycerine added to improve the dispersion of the fibres. The dispersion was poured into petri dishes and the petri dishes were scanned by a high resolution scanner. The software of the IDM FASEP fibre length measurement system was used to analyse the scanned images and measure the residual length of the glass fibres. Nine such samples were extracted and measured from each ashed composite. Approximately 500-1000 fibres lengths were recorded from each sample and the data averaged to output the number average ( $L_n$ ) and weight average ( $L_w$ ) lengths of the distribution.

### **3. Results and Discussion**

#### **3.1 Single fibre tensile strength of continuous rovings**

The OC-APS fibres were thermally conditioned at three different temperatures and subjected to either hot NaOH alone or hot NaOH followed by application of a simple APS sizing. The obtained results were compared to those obtained by Yang *et al* on the same fibre, thermally conditioned in an identical manner but then treated using HF etching [17]. The results of the investigation of heat conditioning and subsequent chemical treatment on the average single fibre tensile strength are shown in Figure 3. A large drop in average fibre strength (from an untreated reference value of 2.3 GPa) is observed after heat treatment (HT) alone at all three temperatures. It was observed that after thermal conditioning the fibres were extremely brittle and difficult to handle without breakage. Hence thermal recycling not only results in a very large drop in the glass fibre performance but also makes TRGF virtually impossible to process in any standard composite production equipment.

It is also worth noting that, with increasing thermal conditioning temperature, an increasing proportion of the HT fibres failed during selection, mounting and handling. Consequently these average strength values represent a decreasing fraction of the actual fibre strength distribution of these samples. In a review of single fibre testing results in the literature Thomason has previously estimated that minimum fibre strength of approximately 0.3 GPa is required for any individual glass fibre to survive the sample preparation process [27]. Any fibres weaker than this limit which are selected from the population will not survive to contribute to the pool of strength results from any individual fibre population. Consequently the HT only average values in Figure 3 must actually be considered as an upper limit on the actual average strength of these samples which may well be considerably lower due to the absence of the weakest fibre values which cannot be accessed by this test method. It is difficult to put an exact value to the proportion of very weak fibres which are excluded from the average strength measurement due premature breakage as this is highly operator sensitive as well as dependent on the fibre properties. However it was noted that, after fibres had been mounted on the card windows, approximately 30% of the HT samples failed prematurely during the mounting and test. For the “as received fibres” this value was less than 5% and for the chemically treated HT fibre it was approximately 10%. Consequently it was observed by the operators that it was possible to make a prediction on the effectiveness of the chemical treatments on the fibre strength simply from the amount of fibre breakage during the sample preparation and mounting.

The results for the fibre strength recovery achieved with the hot NaOH treatment are impressive, with a strength regeneration after all three conditioning temperatures reaching approximately 1.5 GPa from the initial value of the HT fibre strength of (less than) 0.6 GPa. The addition of a simple APS sizing after the hot NaOH treatment leads to further

significant (at the 95% confidence level) increases in fibre strength regeneration to above 1.5 GPa. We consider this value of 1.5 GPa to be an important target for strength regeneration of recycled fibre in order to compete, on performance, with commercial first-pass glass fibre products. Despite the textbook value for the strength of E-glass being of the order of 3.5 GPa, Thomason and Kalinka have previously shown that the actual average strength of fibres in commercial 4 mm chopped glass products can be as low as 1.8 GPa measured at a gauge length of 0.3 mm and down to 1.5 GPa measured at a 2 mm gauge length [28]. Given the well known inverse dependence of average fibre strength on test gauge length we consider that the average regenerated strength of 1.5 GPa measured at 20 mm gauge length in this work represents a fibre strength distribution that is higher than that obtained in many commercial discontinuous glass fibre products.

The results in Figure 3 appear to indicate a general trend for decreasing strength of the regenerated fibre strength with increasing conditioning temperature. It appears that the higher the conditioning temperature which the glass fibres have experienced then the greater the challenge of regenerating their strength. However, all treatments (even the HF data) show this tendency to some degree. This may be related to the above discussion that the average HT fibre strength values actually represent an upper limit and that the actual value (if it could be measured) is probably much lower and may well decrease with increasing conditioning temperature. Nevertheless, the data reveal that the hot NaOH based treatments deliver significant regeneration of strength in glass fibre thermally conditioned in the 450-600°C range. In particular the treatments can match the best performance of the very aggressive HF etching in terms of strength regeneration. It is most unlikely that the HF route could ever lead to a cost-effective process for regeneration the properties of recycled glass fibre. However, the data from Yang *et al* [17] clearly demonstrated the concept of glass fibre strength regeneration and also went on to

show the effects on composite performance. Certainly their results using HF etching clearly showed that any such treated fibres must also be further protected and maintained by the use of fibre sizing technology similar to standard glass fibre products [4,29]. The results shown in Figure 3 for hot NaOH treatment followed by APS sizing are always slightly higher than NaOH alone. This is likely due to the added protection of the regenerated fibre strength against the handling and sample preparation provided by the sizing.

It can be seen that significant increases of fibre strength were obtained through the hot NaOH regeneration treatments, achieving greater than a tripling of fibre strength in comparison with the thermally treated glass fibre. Furthermore the same treatments have also been applied to glass fibres recovered from model composites using laboratory thermal recycling. Figure 4 compares the average fibre strengths of single fibres which have been heat treated at 600°C and then subjected to the hot NaOH treatment compared with fibres which have been thermally recycled out of unidirectional polyester composites (prepared with the same OC APS fibres) and then also subjected to the same treatments. It is clear that a similar level of strength regeneration is achieved on fibres recycled out of composites compared with heat treated fibres. Consequently, it is apparent that the hot NaOH treatments enable regeneration of fibre strength to a level which makes reusing these fibres as a composite reinforcement a viable option.

A further important point when considering the recycling the glass fibres out of end-of-life GRP composites is that the boron-free type of E-glass fibres examined in the above investigation have only been used in commercial GRP composites since the late 1990's when Advantex® based glass fibre products were introduced by Owens Corning. This means that a large fraction of the E-glass fibres in end-of-life GRP today is still based on

the older boron containing E-glass formulations. Consequently, the efficacy of the ReCoVeR hot NaOH treatment was also checked on boron containing E-glass fibres. Figure 5 shows the average single fibre tensile strength for E-glass fibre obtained from three different manufacturers. The OC and 3B rovings were based on boron-free E-glass (coated with only APS) and the PPG fibres were based on a boron containing E-glass formulation (with a PP compatible sizing which most likely contains APS [4]). It can be seen that heat conditioning at 500°C results in a large drop in the strength of all three fibre samples to approximately 0.6 GPa. Similarly the hot NaOH treatment of these conditioned fibres regenerates their strength in all cases to above 1.5 GPa. This indicates that the presence of boron in the E-glass formulation does not appear to seriously affect the ability of the ReCoVeR hot NaOH treatment to regenerate the strength of thermally recycled glass fibres.

### **3.2 Chopped fibres for GMT**

The influence of the properties of glass fibres after thermal conditioning and chemical regeneration on composite performance was further investigated by the preparation of 30% weight in-plane randomly oriented glass fibre reinforced polypropylene laminates (GMT) prepared as described above by a wet-laid papermaking process and compression moulding. The water-dispersible glass fibre product to make these GMT's was a 9 mm chopped (boron containing) E-glass fibre product from PPG. The 9 mm fibre length was chosen as a compromise between processability (in particular dispersion in the sheet forming process) and the desire to be able to measure the fibre strength at a reasonable gauge length (5 mm) for each step in the processing. Figure 6 shows the average strengths obtained for these fibres following a combination of thermal conditioning (at 500°C) and hot NaOH strength regeneration. The general trends observed in Figure 6 are similar to those seen in Figure 3 with the strength values in Figure 6 shifted somewhat higher. These

higher values are most likely due to the shorter gauge length of 5 mm used for these chopped fibres as it is well known that the measured average strength of glass fibres increases with decreasing gauge length [21,26]. The results in Figure 6 again confirm the effectiveness of the ReCoVeR hot NaOH treatment in regenerating the strength of thermally recycled boron-containing E-glass fibres.

Figure 7 shows the results for the average fibre modulus obtained from single fibre testing for these samples. We have previously reported that thermal conditioning of E-glass fibres appears to increase their modulus [30]. This finding is in line with the fact that, due to the fibre production conditions, the structure of glass fibre is normally in a non-equilibrium state compared to bulk glass. This non-equilibrium condition is characterized by a lower density and modulus [31]. The expected increase in fibre modulus for a thermal treatment at 500°C would be approximately +10% [30]. The average modulus of the three heat treated fibre samples in Figure 7 is always above the “as received” fibres in the range of +4-7%. However, it should be noted that these modulus values are not compliance corrected and that at 5 mm gauge length there is a significant compliance effect in the modulus measurement (approximately -33%) [21]. When the values in Figure 7 are compliance corrected (using an available compliance factor of 0.0346 mm/GPa for the OC-APS fibres) the modulus difference for the range of HT fibres increases to +5-10%. Although not all of these average modulus values are significantly different (at the 95% confidence level) the difference of 10% between the “as received” and the HT fibre is significant.

### **3.3 Microbond analysis of Interface Strength**

We have previously observed that although the regeneration of fibre strength is a necessary condition to generate reinforcement grade TRGF but is not necessarily

sufficient. It is also necessary to regenerate the compatibility of the TRGF with the polymer matrix of the final composite. This is generally accomplished by the application of a chemical coating (or size) to the surface of glass fibres [4,17,29,32]. In particular the application of a silane coupling agent has been shown to be critical to the generation of an adequate stress-transfer capability of the fibre-matrix interface [21,29,32]. Figure 8 shows the results for the interfacial shear strength (IFSS) characterisation of the apparent adhesion of these TRGF fibres to the homopolymer PP used to make the GMT laminates. It can be seen that the “as received” PPG 8069 fibres have an adequate level of IFSS with PP. It should be noted that the coating on these fibres is probably optimised primarily for wet processing and only secondly for adhesion and composite performance.

The datasheet for the PPG 8069 fibres describes the product as having an aqueous silane based sizing optimised for fibre dispersion when producing a wet-laid non-woven. It is further described as compatible with a wide range of binder resin systems and also compatible with gypsum and similar systems. Consequently the IFSS level with PP of 14.7 MPa in Figure 8 can be described as good for a product which is not developed specifically for PP. It can also be observed that the removal of the sizing by the 500°C heat treatment significantly lowers the level of IFSS. The IFSS of 9.2 MPa seen in Figure 8 with the HT fibres is of the same order of magnitude obtained for unsized fibres when the microbond samples are properly prepared under an inert atmosphere to avoid significant PP degradation [25,33]. It can further be observed that the ReCoVeR hot NaOH strength regeneration treatment alone does not regenerate the stress-transfer capability of the GF-PP interface. It is only after the APS coupling is applied to the HT+NaOH treated fibres that we see the IFSS recover. Indeed the average IFSS of the system is regenerated to an average value (16.1 MPa) which is above the “as received” fibres.

### 3.4 Composite performance

Figure 9 presents the results for the tensile strength of the GF-PP GMTs produced using the above range of thermally conditioned and chemically treated fibres. The strength of the GMT containing the “as received” fibres is in good agreement with the range of values reported by Thomason *et al* on GF-PP composites [34] prepared in a similar manner (also with PPG wet chopped fibres). The GMT containing the HT fibres exhibits a large drop in tensile strength presumably due to the much lower strength of the fibres and the interface in this composite. The GMT tensile strength recovers by 44% when the HT fibres are given the hot NaOH treatment. Addition of a silane coupling agent after the NaOH treatment results in a 74% recovery of the GMT tensile strength. It was noted that the average tensile modulus of this range of GMT’s followed similar trends to the tensile strength. However, in the case of the modulus data, the differences were much smaller and in no case significant at the 95% confidence level.

In addition to the fibre strength and IFSS, it is well known that GMT tensile strength is dependent on the fibre content, length, and orientation [34]. Moreover, it is also acknowledged that the level of fibre length degradation during processing, and hence the final average fibre length, in discontinuously reinforced thermoplastic composites is influenced by the strength of the fibres. The fibre orientation of these wet deposited GMTs is assumed to be random in-plane and constant in all cases and the nominal fibre content was fixed at 30% by weight. Figure 10 presents the results for the average fibre lengths in each of the above GMTs. The nominal fibre chop length was 9 mm and the measured average fibre length of the fibres taken from fibre bundles before any composite processing was very close to that nominal value ( $L_n=8.67$  mm,  $L_w = 8.75$  mm). The fibre length samples were obtained by ashing the grip area of a tensile dog-bone sample. Since these samples have dimensions of the same order as the initial fibre length it must be

assumed that a large part of the observed fibre length reduction may be due to the reduction in fibre length produced by cutting the composite sample. Nevertheless, since the samples were all obtained from composite pieces of the same dimension it can be assumed that the relative trends observed in Figure 10 are representative of the relative fibre length differences between the samples. Consequently it can be observed that the average fibre lengths appear to correlate well with the measured average fibre strengths. This is shown directly in Figure 11 by plotting the average length values against the measured average fibre strengths. It can be seen that an excellent direct correlation is obtained in Figure 11. This relationship clearly indicates how the average strength directly influences the probability of fibre breakage, and consequent length reduction, during composite processing.

Thomason *et al* have previously reported that the strength of this type of GF-PP GMT can be well modeled by the Kelly-Tyson theory when measured values of all the required micro-mechanical parameters are available [34]. Although the model was originally developed for aligned discontinuous fibre composites it is often presented with an additional, empirically obtained, orientation factor ( $\eta_o$ ) as shown below

$$\sigma_c = \eta_o \left( \sum_i \left[ \frac{\tau L_i V_i}{D} \right] + \sum_j \left[ \sigma_f V_j \left( 1 - \frac{\sigma_f D}{4\tau L_j} \right) \right] \right) + (1 - V_f) \sigma_m^* \quad (1)$$

where  $\tau$  is the interfacial strength,  $V_{ij}$  the volume fraction of fibres of length  $L_{ij}$ ,  $\sigma_f$  is the fibre strength,  $\sigma_m^*$  is the matrix stress at composite failure. The two summation terms arise from the contributions of fibres of sub-critical and super-critical length where critical fibre length is defined by  $L_c = \sigma_f D / 2\tau$ . Thomason *et al* noted that the orientation parameter should not necessarily have the same value as that used in the modeling of the modulus ( $\eta_o=0.375$  for random in-plane composites) and showed that a fitted value of 0.2 gave an excellent correlation between experimental and modeled strength [34]. Using all of the

measured values presented above and an orientation factor of 0.2 we have followed the same procedure and compared the results for the GMTs in this study with the earlier results of Thomason *et al* [34]. It can be observed that the results presented in Figure 12 show excellent agreement.

### **3.5 Implications for real materials reuse of recycled glass fibres as replacement for pristine reinforcement fibres.**

To the best of our knowledge the results shown here are the first published demonstration of a chemical treatment, other than HF etching, that significantly increases the strength of thermally recycled glass fibres. Moreover, the results on GMT laminates clearly show that this regeneration of glass fibre strength can be translated directly into composite strength. Although full regeneration of the fibre strength has not been achieved in these initial experiments, the results presented here demonstrate that significant (74%) progress has been made in this direction. It is certainly reasonable to suggest that further exploration of such chemical treatments may result in additional fibre and composite strength improvement. Furthermore, optimisation of the sizing for such recycled, regenerated fibres may also be worth exploring given the progress made in fibre and composite performance achieved by the glass fibre manufacturing industry through sizing development. Interestingly, the identification of one chemical route producing such significant fibre strength regeneration poses the question whether other chemical treatments which produce comparable or better effects may exist, and we are actively researching this possibility.

There are currently no known commercially exploited processes in operation for the recovery of TRGF from GRP. There are many non-technical factors which will play a role in the eventual commercial profitability of any GRP recycling process. However, we

believe that maximising the performance regeneration of TRGF will, enable replacement of pristine fibre products from a performance viewpoint, maximise the value of such a recycled fibre product, and increase the economic attraction of composite recycling. The development of a non-HF based glass fibre strength regeneration treatment is an exciting development in the progress towards a cost-effective GRP recycling technology.

#### **4. Conclusions**

Glass fibres lose 80% or more of their strength when exposed to temperatures typically found in GRP thermal recycling processes making them unsuitable for reuse as a composite reinforcement. The results of single fibre tensile testing presented here clearly show that up to 75% of that strength loss can be recovered by a short treatment of the fibres using hot sodium hydroxide solution. This strength recovery can be maintained and improved upon by a further application of a silane sizing. This silane layer also acts to recover the compatibility of the recycled fibre surface with a polymer composite matrix and regenerate a high level of fibre-matrix interfacial stress transfer capability. The regeneration of the recycled glass fibres performance by these simple chemical methods resulted in GF-PP GMT composites which exhibited a 74% strength recovery compared to GMT based on thermally recycled fibres which had received no further treatment. It is proposed that further optimisation of these chemical treatments can lead to further improvements in the fibre performance enabling them to be used to replace pristine first-pass fibre products used in many discontinuous glass-fibre reinforced composite applications.

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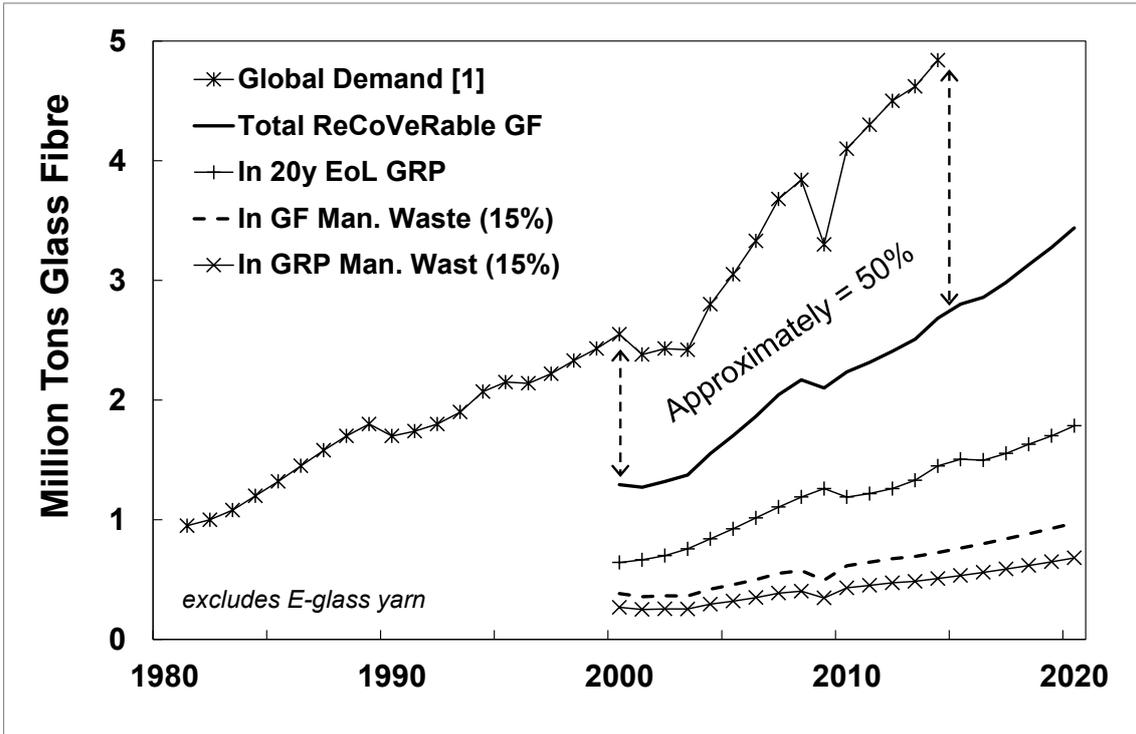


Figure 1 Glass fibre global demand and availability for recycling

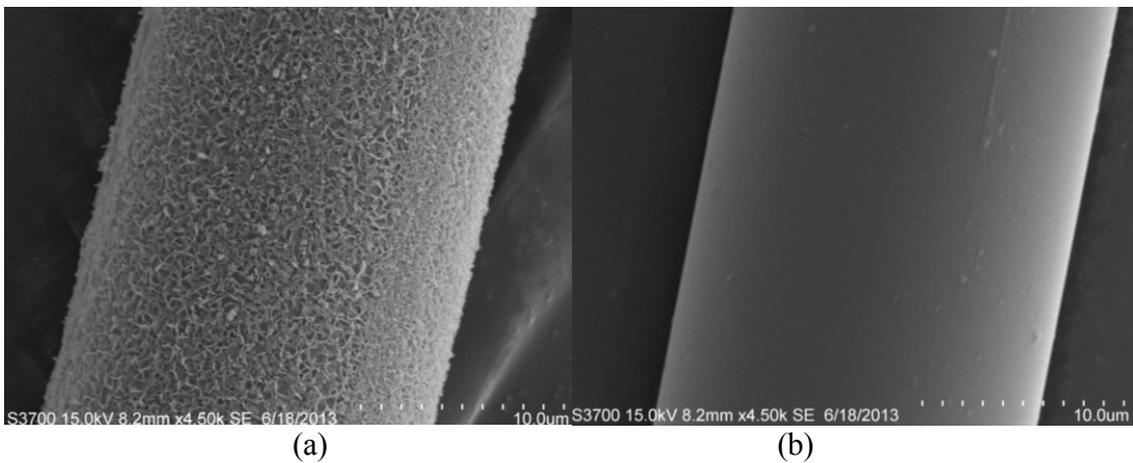


Figure 2 SEM images of heat conditioned fibre after a) NaOH treatment, b) NaOH treatment + HCl rinse + Silane coating.

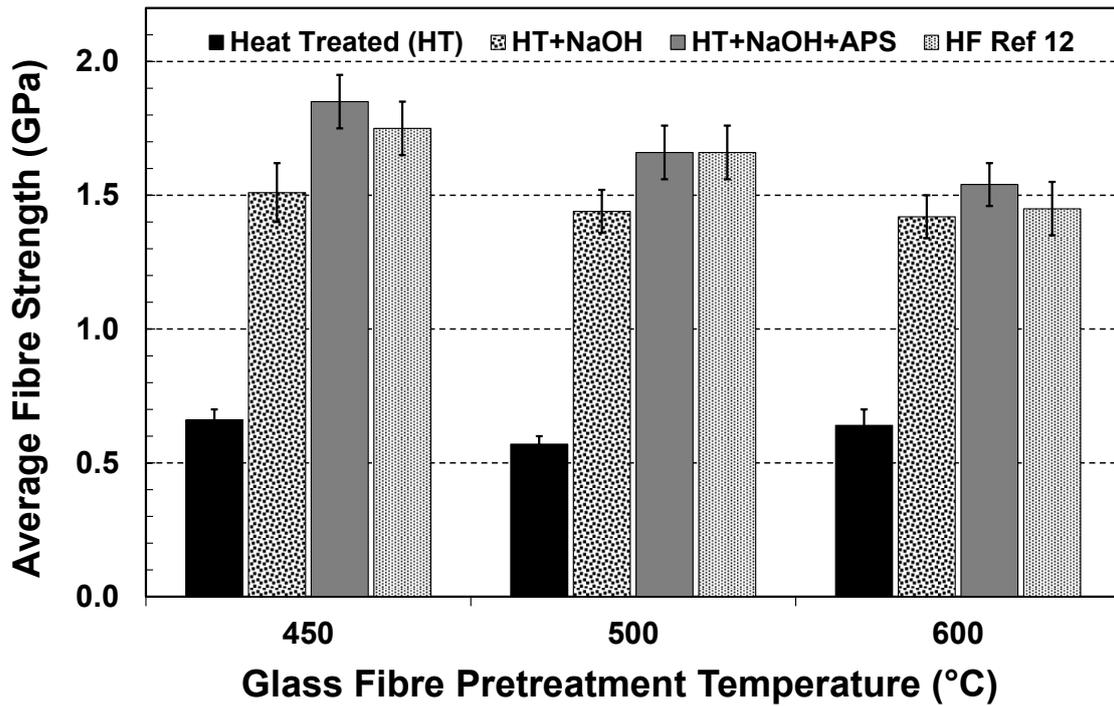


Figure 3 Influence of heat treatment temperature and ReCoVeR chemical treatments on the average glass fibre strength at 20 mm gauge length.

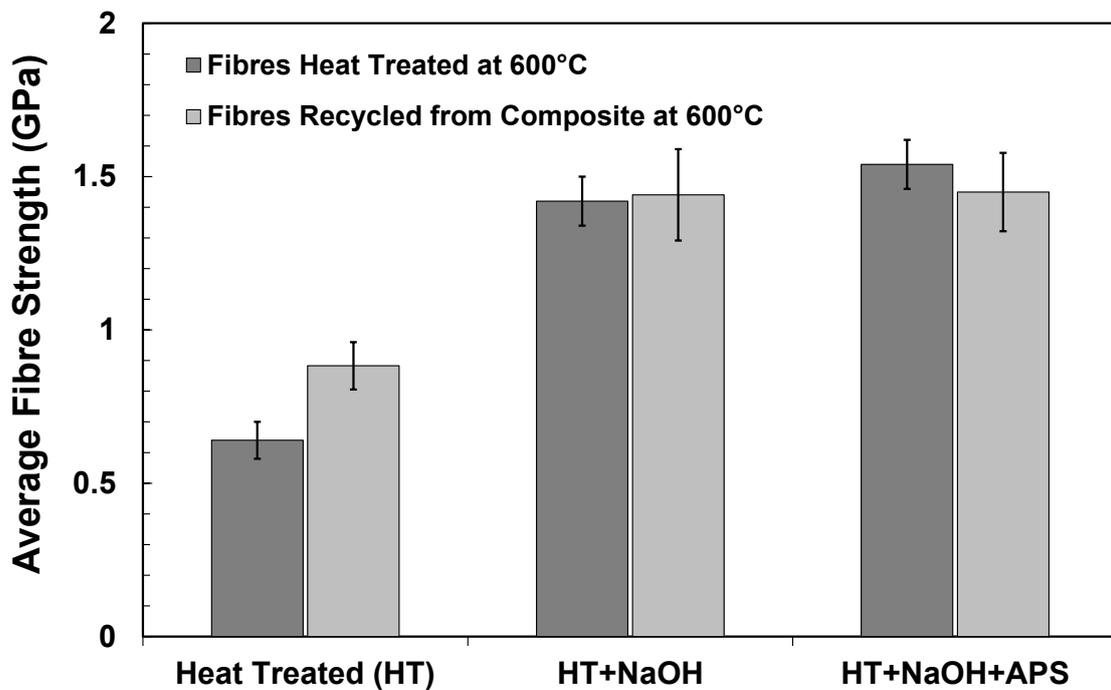


Figure 4 Comparison of ReCoVeR chemical treatments on tensile strength at 20 mm gauge length of heat conditioned fibres *versus* fibres recycled out of composites.

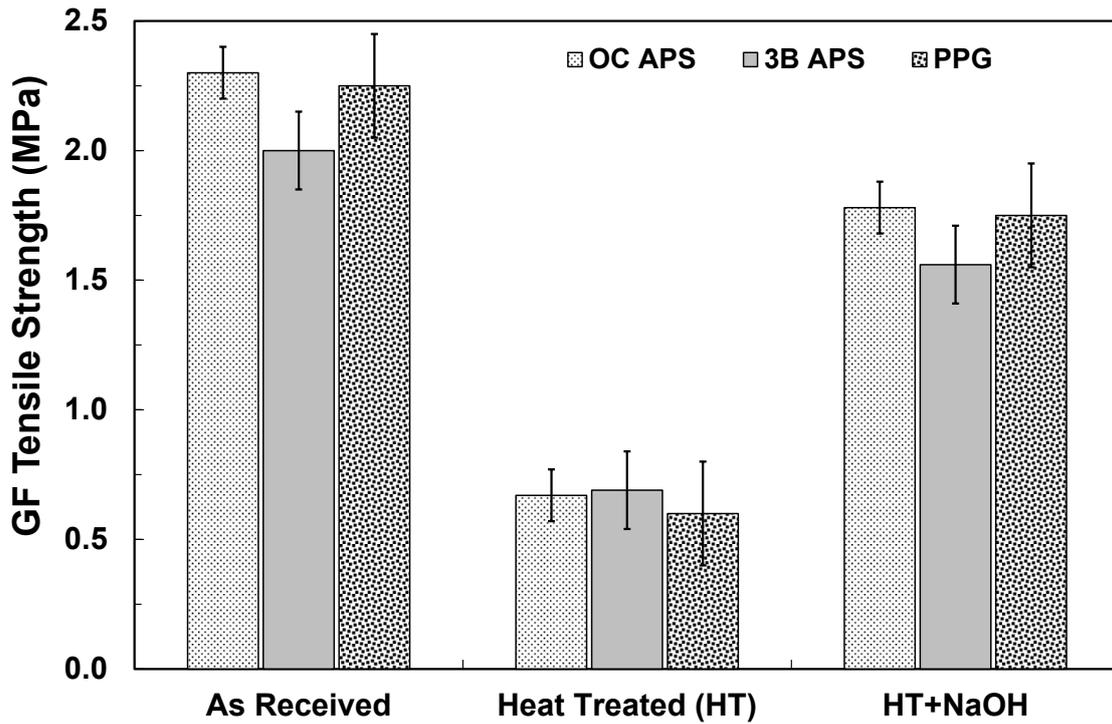


Figure 5 Influence of glass fibre treatments on average single fibre tensile strength at 20 mm gauge length for different E-glass fibres. (HT=25 mins at 500 °C)

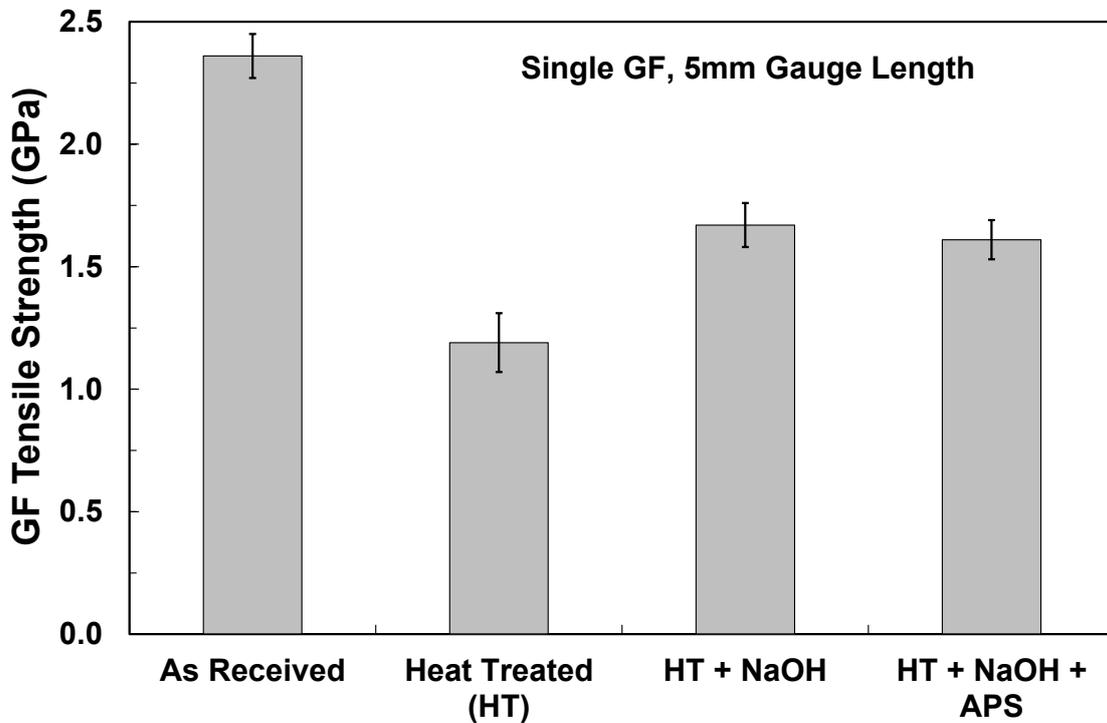


Figure 6 Influence of ReCoVeR treatments on average single fibre tensile strength of PPG chopped E-glass fibres. (HT=25 mins at 500 °C)

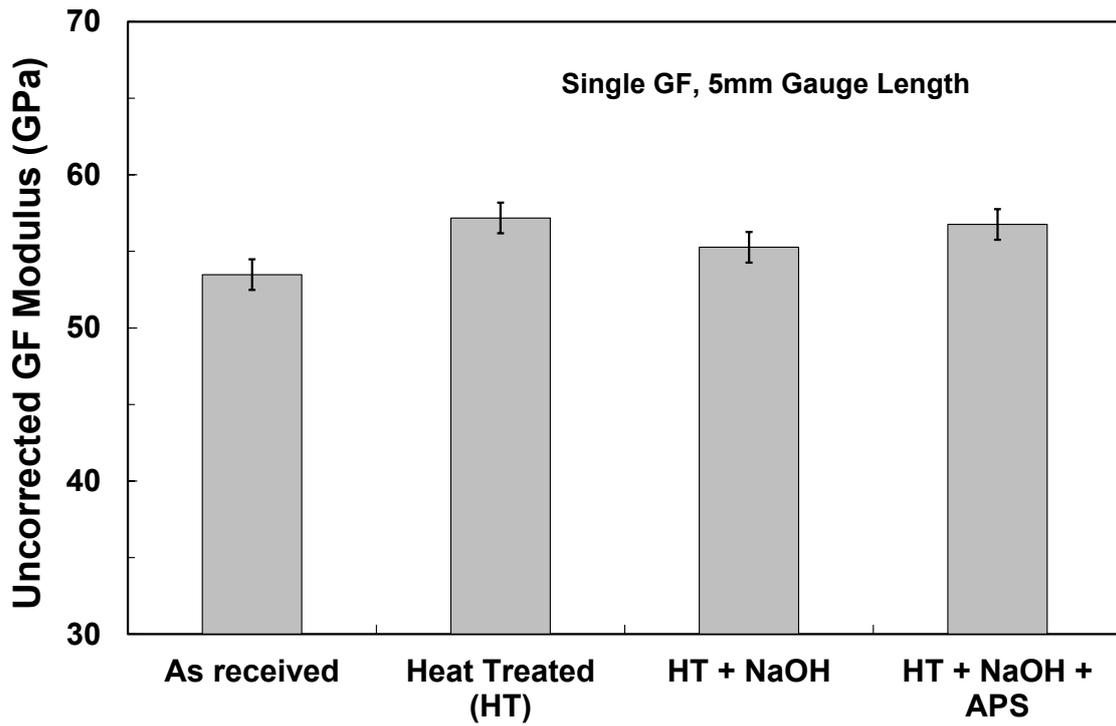


Figure 7 Influence of ReCoVeR fibre treatments on average single fibre tensile modulus.

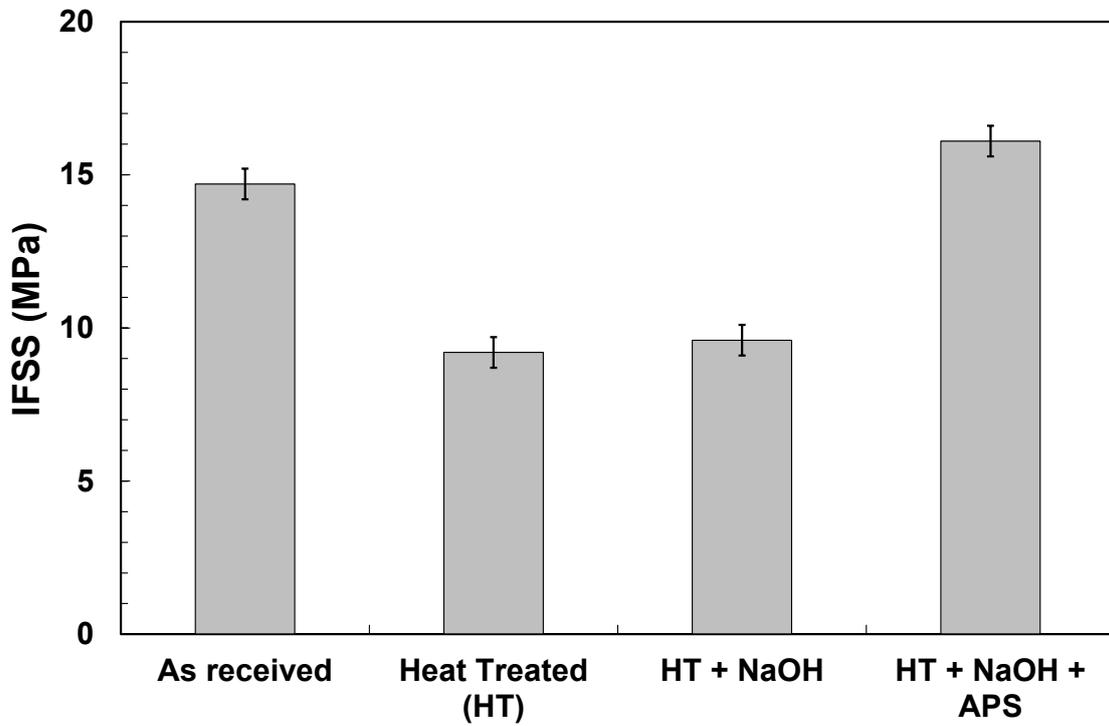


Figure 8 Influence of ReCoVeR fibre treatments on GF-PP interfacial shear strength.

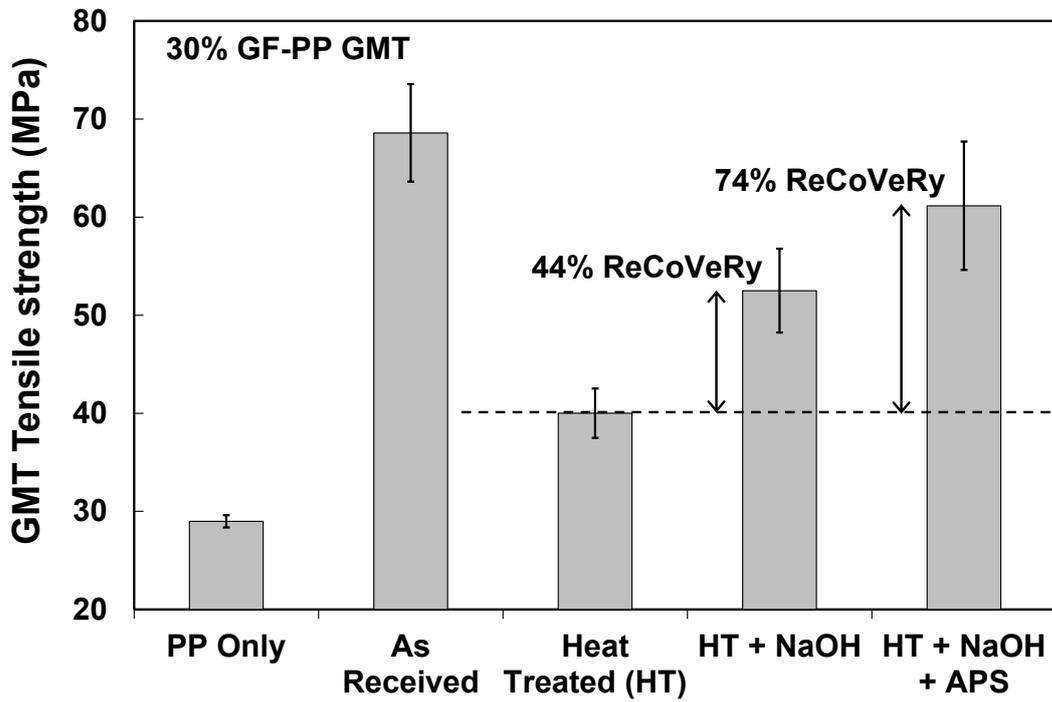


Figure 9 Influence of ReCoVeR fibre treatments on GF-PP GMT tensile strength.

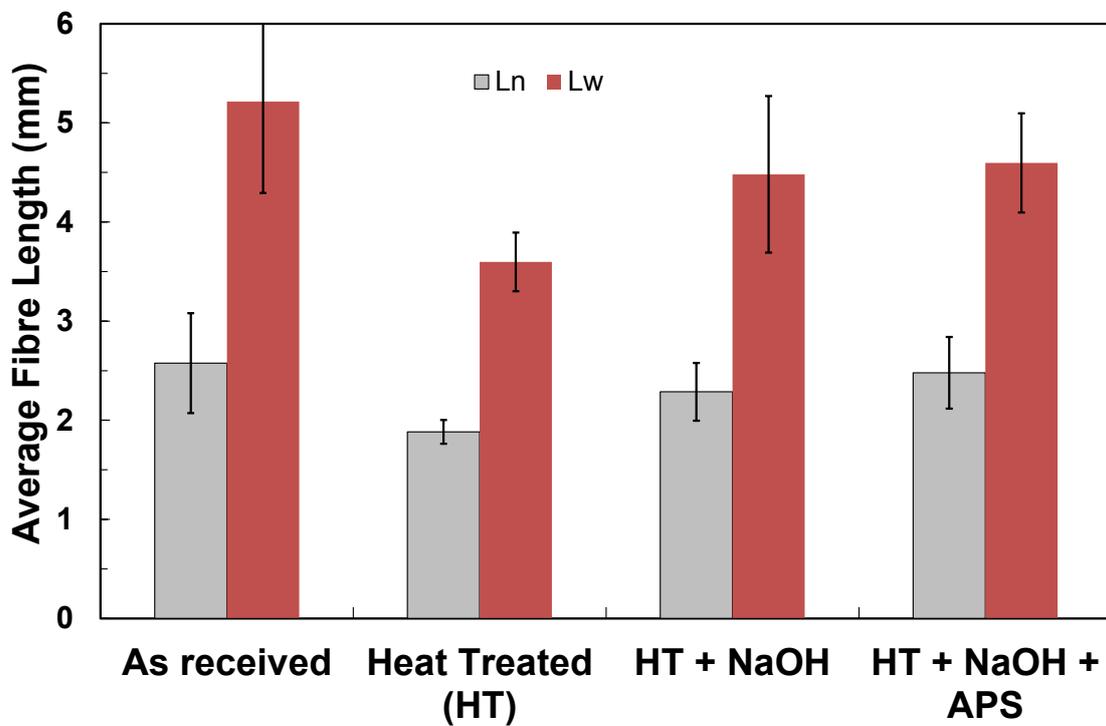


Figure 10 Average fibre lengths in GF-PP GMT laminates

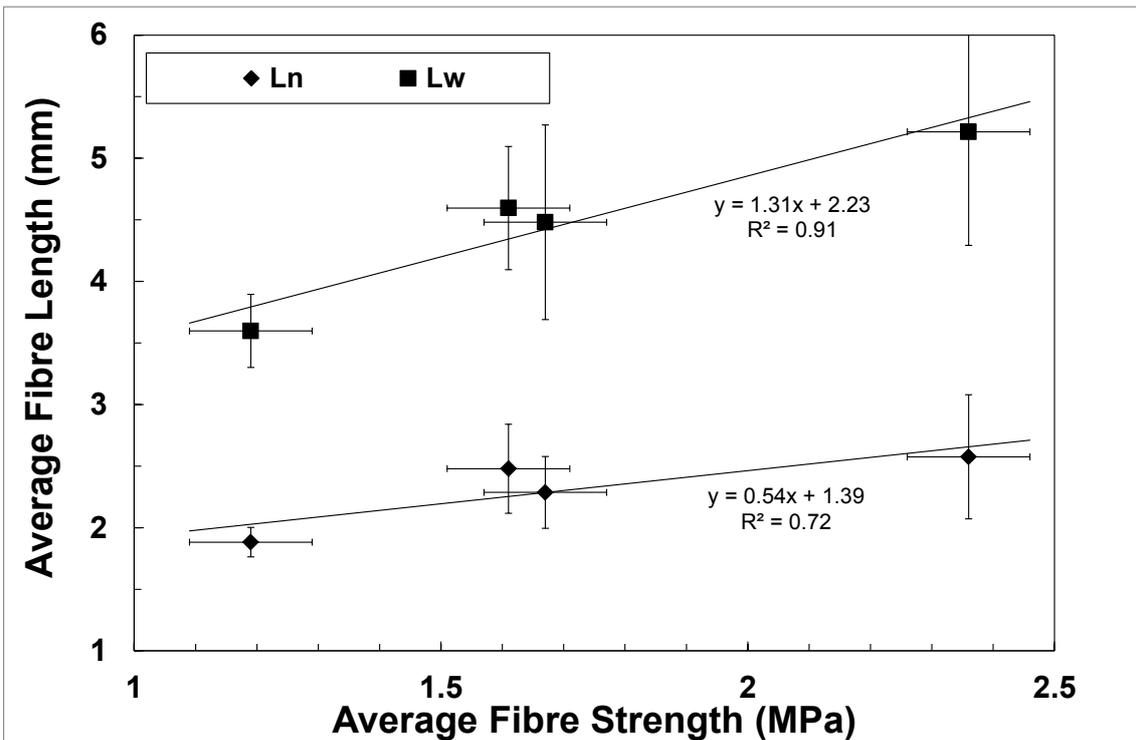


Figure 11 Comparison of average fibre length in GMT to average fibre strength before processing.

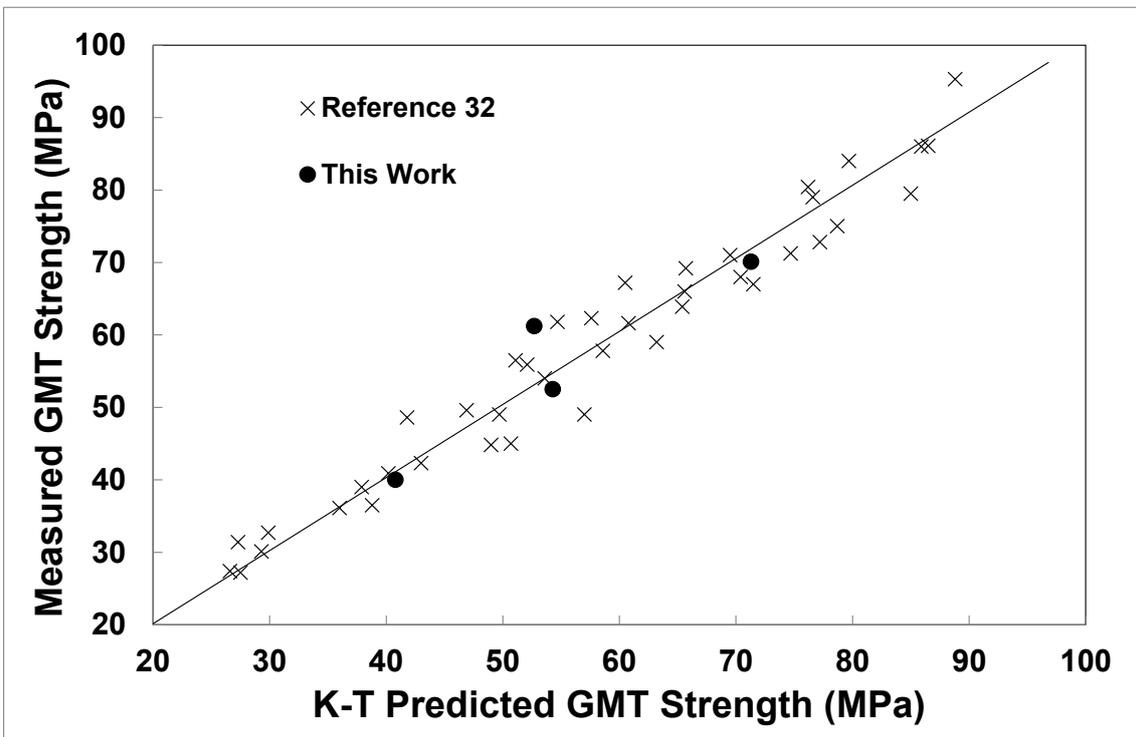


Figure 12 Comparison of measured GMT strength versus Kelly-Tyson model calculated strength.