Composites: Part A 72 (2015) 167–174

Contents lists available at ScienceDirect

Composites: Part A

journal homepage: www.elsevier.com/locate/compositesa

Can thermally degraded glass fibre be regenerated for closed-loop recycling of thermosetting composites?

L. Yang *, E.R. Sáez, U. Nagel, J.L. Thomason

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

ARTICLE INFO

Article history:
Received 9 November 2014
Received in revised form 28 January 2015
Accepted 30 January 2015
Available online 7 February 2015

Keywords:
A. Glass fibres
A. Recycling
B. Mechanical properties
E. Heat treatment

ABSTRACT

Commercially manufactured E-glass fibres were heat-conditioned to mimic the effects of thermal recycling of glass fibre thermosetting composites. Degradation in the strength and surface functionality of heat-treated fibres was identified as a key barrier to reusing the fibres as valuable reinforcement in composite applications. A chemical approach has been developed to address these issues and this included two individual chemical treatments, namely chemical etching and post-silanisation. The effectiveness of the treatments was evaluated for both thermal degraded fibres and corresponding composites. Drastic reduction was observed in the properties of the composites with the heat-conditioned preforms indicating thermally degraded glass fibres have no value for second-life reinforcement without further fibre regeneration. However, significant regeneration to the above properties was successfully obtained through the approach developed in this work and the results strongly demonstrated the feasibility of regeneration of thermally degraded glass fibres for potential closed-loop recycling of thermosetting composites.

1. Introduction

The disposal of 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. It is projected that by 2015 the total global production of composite materials will significantly exceed 10 million tons which, at end-of-life, will occupy a volume of over 5 million cubic meters [1]. Glass fibre reinforced composites account for more than 90% of all the fibre-reinforced composites currently produced. About 60% of this volume employs thermosetting matrix materials producing composites (GRP) that are difficult to recycle in an efficient manner [1]. 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 [2]. For instance, wind turbine applications have growth rates well into double figures with a predicted 6 million tons of GRP wind turbine blades to be produced globally over the coming decade [3]. Currently most of this material is destined for landfill at the end of its 10–25 year application lifetime. However the rapidly increasing cost and reducing availability of landfill, combined with increasing national and international legislation, means that such disposal of end-of-life composites is becoming economically and socially unacceptable. Clearly alternate methods for dealing with end-of-life composites are urgently required.

Although thermoplastic based composites are, in principle, intrinsically recyclable, the greatest challenge is with the larger fraction of thermoset based GRP composites. The infusible and insoluble high-density networks in molecular structure make thermosetting polymers ideal candidates for composites with more demanding performance required in areas such as aerospace and wind energy. The very same reason for their merits, however, has also been causing difficulties in recycling thermosetting composites. The 3D network structure does not result in the same reprocessability offered by thermoplastic polymers. Consequently, various techniques have been developed to recycle thermosetting polymers and these techniques have been seen to serve as the foundation of the recent development of thermosetting composites recycling [4]. A number of processes are available for recycling such composites [5,6]. Of these possible routes, thermal recycling is probably the most technologically advanced and has been piloted in the UK and Denmark. However, nearly all options deliver recycled fibres (which make up approximately 60% by weight of the composites) that suffer from a lack of competitiveness with pristine first-pass materials. A key factor in this equation is the huge drop in the performance of recycled glass fibre in comparison to its original state [5,7]. Consequently, recycled fibres have a very

* Corresponding author. Tel.: +44 1415482324.
E-mail address: l.yang@strath.ac.uk (L. Yang).

http://dx.doi.org/10.1016/j.compositesa.2015.01.030
1359-835X/

poor performance to cost ratio, and in most cases are considered unsuitable for reprocessing and reuse as a valuable reinforcement of composites. A breakthrough in this field could enable such recycled glass fibres to compete with pristine materials in many large volume composite applications. The development of an economically viable process for regenerating the properties of thermally recycled glass fibres would have major technological, societal, economical, environmental impacts. We are currently focusing on enabling cost-effective closed-loop recycling for glass fibre thermosetting composites. The following areas have been identified by us as major technical barriers that have to be overcome in order to achieve this goal. This includes fibre recycling technique, fibre strength regeneration, fibre surface reactivation and fibre reprocessing.

In this paper we report some recent developments in these critical areas with particular focus on strength regeneration and surface reactivation of thermally treated glass fibres. The aim of this study is to verify the concept of regenerating thermally degraded glass fibres for a potential closed-loop recycling of glass fibre thermosetting composites.

2. Experimental

2.1. Materials

Boron-free E-glass fibres supplied by Owens Corning Vetrotex were used for micromechanical tests including single fibre tensile test and microbond test described below. The fibre roving was produced on a pilot scale bushing and was received as 20 kg continuous single end square edge packages. The roving had a nominal tex of 1200 and a single fibre diameter of 17.4 ± 1.3 μm. The molten fibres had all been hyperquenched by water spray before they were coated with a normal rotating cylinder sizing applicator containing a 1% γ-aminopropylsilane (APS) hydrolysed solution in distilled water. The room temperature mechanical properties of these fibres have been reported in somewhere else [8]. 'SABIC® PP 579 S' polypropylene (PP) compounded with 1 wt% maleic anhydride grafted polypropylene (MaPP) was used as the matrix to demonstrate different levels of adhesion with both thermally and chemically conditioned glass fibres. It would be indeed more consistent to use the same matrix for a model composite to investigate the effect of different fibre treatments developed in this work. However, it was thought that using other readily available materials should not jeopardise the main purpose of conveying the concept of closed-loop composites recycling. The composite materials in this study consisted of 'PPG Fibre Glass® Mat 92 chopped strand mat' (CSM) supplied by PPG Industries and IN-2 epoxy infusion resin supplied by Easycomposites. Using virgin CSM gives the advantages of maintaining the original form of the CSM in terms of fibre length, orientation and fibre content after different treatments. This limits the dependence of the composite properties only to the variables related to glass fibres themselves. The chemicals used to treat thermally degraded fibres included ACS reagent 48% hydrofluoric acid (HF) and γ-aminopropyltriethoxysilane supplied by Sigma Aldrich.

2.2. Thermal treatment

Heat conditioning of glass fibres intended for micromechanical testing was carried out in a Carbolite LHT6 furnace in the temperature range 450–600 °C. The chosen temperatures cover a typical range required in thermal recycling techniques such as pyrolysis and fluidised bed. The conditioning procedure within a comprehensive study of thermal effect on fibre strength loss has been detailed in [1]. Heat treatment of CSM was carried out in a furnace at a temperature of 500 °C for 30 min. The preform of total 16 layers of 28 cm × 28 cm CSM was placed in a metal tray, which could be inserted in the furnace as shown in Fig. 1. This facilitated sample handling for the subsequent chemical treatment and vacuum infusion process. The preform was placed in the furnace at room temperature followed by a temperature ramp at 10 °C/min before it reached 500 °C. After the heat treatment, the preform was cooled to room temperature outside the furnace and subject to chemical treatments if required.

2.3. Chemical treatment

It is known that heat-treated glass fibre suffers significant strength loss [1,5,9,10]. In order to regenerate its strength, 1 v% HF aqueous solution was employed to treat degraded fibres. Approximately 100 mg 15 cm long glass fibres were immersed in 300 ml HF solution for up to 2.5 min. The HF-treated fibres had been repeatedly rinsed with deionised water before they were dried in an oven at a temperature 110 °C for 20 min. When such treatment was applied to the heat-treated CSM, the immersion time was extended up to 10 min to compensate for the relatively lower amount of HF solution (3 L) with respect to ~300 g glass fibres. Approximately 2% of fibre diameter was lost after the treatment of the CSM. The drying process was extended up to 24 h to ensure complete drying of the preform and this was confirmed by monitoring the weight change during drying. It has been reported that thermally degraded glass fibre also loses its original surface coating [10] and may even end up with a dehydroxylated surface [11]. In order to reactivate surface functionality after heat and/or HF treatment, the fibres were fully immersed in 1 v% APS solution for 15 min. The APS solution was prepared with deionised water at its natural pH value. The aqueous solution was aged for 24 h before use. The condensation of silane deposition on the glass surface was achieved through the drying process at a temperature of 110 °C for 15 min. In the case of CSM, this stage was extended up to 24 h. When weak heat-treated preforms were handled through the above chemical treatments, extreme care was taken to minimise disruption to the original CSM in terms of fibre length, orientation and fibre content.

Fig. 1. Photo of 16 layers of chopped strand mat heat-conditioned in the furnace. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.4. Composites processing

The control and pre-conditioned preforms were impregnated with epoxy resin through a vacuum infusion process built in-house. The resin was mixed with an amine-based hardener at a weight ratio of 100:30 as suggested by the supplier. The mixture had been then degassed for 10 min before it was used to impregnate the preforms. It took approximately 15–20 min to fully impregnate the preform, which was then left to cure under vacuum at room temperature for 24 h. This was followed by a post-cure at 60 °C for another 24 h. The finished product tended to give a panel with a thickness of 4–5 mm. Samples with the geometries for the corresponding tests were then obtained from the panel by machining.

2.5. Single fibre tensile test

Single fibre tensile properties were determined following ASTM C1557-03. Sample gauge length was 20 mm for all fibre types and at least 30 fibres were tested at each condition. The diameter of individual fibres was measured using Nikon Epiphot inverted optical microscope. The strain rate was 1.5%/min and all the tests were carried out in an Instron 3342 universal testing machine equipped with a 10 N load cell at ambient environment. More details on sample preparation and test procedure can be found in [8].

2.6. Microbond test

In order to assess the effect of fibre treatments on fibre–matrix adhesion, apparent interfacial shear strength (IFSS) was measured by a laboratory-developed microbond test technique. The specific procedures of forming a PP microdroplet on a glass fibre and the development of microbond test for thermoplastic composites have been previously reported in [12,13]. The load–displacement curve from each test was recorded to obtain the maximum force. This was used with the corresponding fibre diameter and embedded length to calculate the apparent IFSS. The tested samples were then examined under the microscope to confirm interfacial debonding. Approximately 30 tests were carried out to obtain the average IFSS for each sample.

2.7. Composites testing

Mechanical characterisation of model composites based on CSM received various conditioning was guided by the relevant standards including ISO 527 for tensile properties, ISO 178 for flexural properties, ISO 179 and ASTM D6110 for unnotched and Type A notched impact properties respectively. Tensile tests were carried out in 50 kN Instron 5969 equipped with a video extensometer with the direction of the loading parallel with the laminate plane. Flexural tests were carried out in the same machine with the direction of the loading perpendicular the laminate plane. Charpy edgewise impact test was conducted using 25 J Tinius Olsen®IT 503 with the direction of the blow parallel with the laminate plane. At least 6 specimens were tested for the tensile and flexural properties and 10–12 specimens were tested to obtain the impact properties. All tests were carried out at ambient environment.

3. Results and discussion

3.1. Strength regeneration

Fig. 2 presents the average tensile strength of HF-treated glass fibres as a function of treatment time and the dashed line indicates the average strength obtained from the original fibre using the same testing scheme. 70–80% of the initial fibre strength was lost depending on the treatment temperature. This result agrees well with the data reported by other researchers [5,10]. It is clear that the HF aqueous solution proves to be very effective in regenerating the strength of glass fibres conditioned at typical temperatures encountered during thermal recycling. The strength of thermally weakened fibres experienced almost two-fold increase after being treated with a low concentration HF solution for a short period of time. This ultimately resulted in nearly tripled strength in HF-treated fibres compared to heat-conditioned fibres at different temperatures as shown in Fig. 2. The report on such large regeneration of glass fibre strength resulting from HF treatment can be dated back to the 1950s in the results of Sakka [14] and thereafter followed by other similar observations [9]. More recently, due to the continuously growing concern on recycling thermosetting composites, the effect of HF treatment on the strength of heat-treated glass fibres was studied again [15]. Despite its confirmed influence on strength recovery, the systematic investigation of HF treatment for thermally degraded glass fibre has not been seen in the literature. The results in Fig. 2 show that the strength of glass fibres heat-treated at different temperatures follows a rather similar trend over the course of the same chemical treatment. The absolute strength increase caused by HF treatment does not appear to be dependent on thermal conditions applied to the fibres. This may imply that the recovered strength shown in Fig. 2 is unlikely to be related to the bulk structural change in heat-conditioned glass. The significant strength increase is probably caused by partial dissolution of glass surface by the HF solution, also known as chemical etching. It has been well known that HF aqueous solution has the ability to dissolve glass and it has been widely used to remove the damaged surface through wet HF-etching and in turn increase glass strength [16].

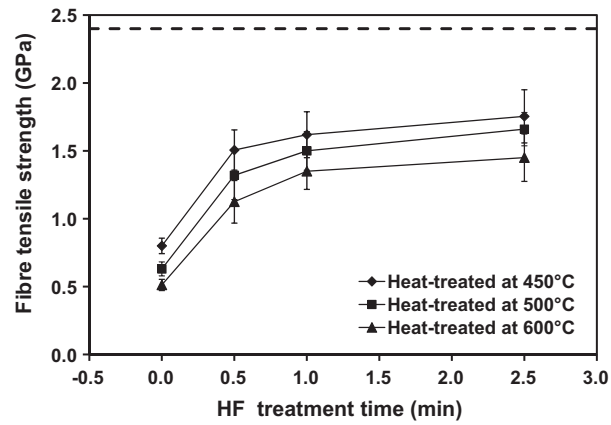

Fig. 2. Tensile strength of heat-treated glass fibres as a function of the treatment time of 1 v% of HF aqueous solution.

One can equally propose the same mechanism in the case of glass fibre, even though the physical properties of surface damage on glass fibre still remain relatively unclear compared to those on massive glass. Fig. 3 presents a plot of relative strength increase as a function of fibre diameter reduction by HF-etching. It can be clearly seen that the fibre strength keeps increasing as the fibre diameter decreases for all three groups of heat-treated glass fibres. The relative diameter decrease caused by HF-etching may be simplistically related to the critical surface crack in a glass fibre by two times of the change in crack length divided by the original fibre diameter. This assumes a homogeneous uniform etching process, which does not account for etching within the defeats. This allows us to calculate fibre strength as a function of fibre diameter reduction with a 2D linear elastic fracture mechanics approach.

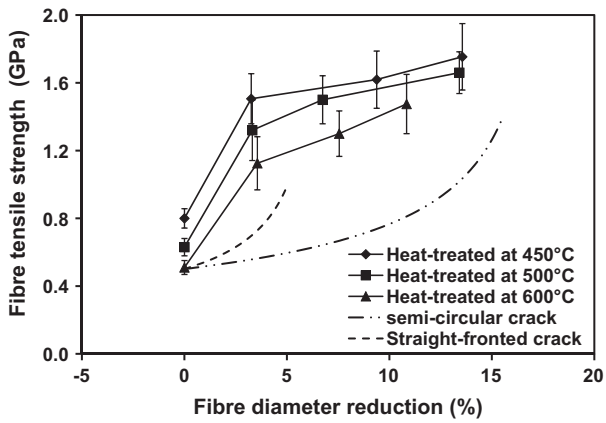

Fig. 3. Tensile strength of heat-treated glass fibres as a function of fibre diameter reduction.

Fig. 3 shows an example for the 600 °C-treated fibres with semi-circular or straight-fronted cracks respectively. The geometry factor accounting for surface cracks in cylindrical bars is calculated with the coefficients established in [17]. It is obvious that correlation between fibre strength and surface etching cannot be described by this simple approach. However, it is interesting to see that the experimental data tend to stay above the predicted values when fibre diameter reduction is relatively low. It implies that HF-treatment does not just simply remove the material from the surface but also significantly change the characteristics of existing cracks on etched surface. It has been reported for bulk silicate glasses that HF-etching can transform a surface with closed microcracks into an open cusp-like glass surface [16]. While these closed cracks, if there are any present, should be much smaller in fine glass fibres, a similar process may take place and would lead to a much higher strength than that based on 2D cracks. Clearly more fundamental work is required to further investigate this discrepancy. Nevertheless, from the viewpoint of closed-loop composites recycling, the recovered fibre strength in Fig. 3 is already sufficient to open up potential opportunities for these regenerated fibres to be used in many composite applications. The results obtained in this work have shown that a large fraction of such strength loss can be effectively recovered by removal of surface layer from the degraded glass fibre.

Another obvious discrepancy between the experimental results and theoretical calculations in Fig. 3 is the rate of change in the fibre strength. It increases as the fibre diameter reduces in the simplified case of 2D cracks. However, the experimental results show the opposite behaviour. Preliminary results of further investigation of more extensive HF etching tend to suggest that the fibre strength should eventually reach a plateau in between 2 and 2.5 GPa. This lies in the same level of tensile strength of original silane-coated fibres used in the present work. However, one may further ask why the maximum strength obtained from glass fibres chemically etched by HF solution has to be found on this level rather than somewhere higher since a flaw-free surface might be expected after substantial amount of materials is removed from the surface. Several possibilities may exist including new surface features created by HF-etching process, irreversible bulk structural relaxation, lack of surface protection after etching, the effect of static fatigue during the test, and the effect of HF-etching on glass bulk structure. These will be discussed in more detail in a separate paper.

3.2. Surface reactivation

In contrast to strength loss, the influence of heat on the surface reactivity of glass fibre in terms of fibre–matrix interface in composites has received much less attention. On the other hand, it has been reported that some commonly used silane/sizing can suffer decomposition at temperatures as low as 250 °C [10,18]. It is almost certain that most silanes employed in the current composites market will not survive the heat required to fully decompose polymer matrices. Consequently, it is quite clear that thermally conditioned/recycled glass fibres require to be re-sized before their potential reuse in polymer composites. Fig. 4 shows the interfacial shear strength (IFSS) in glass fibre-modified polypropylene (GF-mPP) with fibres subject to different treatments. The data for each condition contain 25–30 measurements and the results in Fig. 4 present the average value with 95% confidence limit. It can be seen that the IFSS decreases from 16 MPa in the original system to approximately 8 MPa after the heat-treatment at 500 °C. The decomposition of silane coating is responsible for 50% of IFSS loss. The lower value coincides well with that obtained from unsized GF-unmodified PP [12] suggesting that the surface of heat-treated glass fibre has completely lost its functionality to interacting with MaPP in the matrix. It may be reasonable to expect an even greater reduction in IFSS if a commercial sizing optimised for PP were adopted in the original system instead of a single component of silane. Nevertheless, the decrease of IFSS in Fig. 4 clearly indicates that high temperature conditions not only cause a significant strength loss in glass fibre but also lead to poor fibre–matrix adhesion. These disadvantages can be mainly attributed to thermal degradation of glass fibre sizing.

Fig. 4 also shows that HF-etching does not significantly change IFSS compared to that obtained from heat-treated fibres. On the other hand, the post-silanisation with 1% APS gave rise to nearly 100% recovery from the reduced IFSS. It follows that the re-silanised surface must have restored its functionality through the post-silanisation method developed in the present work. Despite this success, the full recovery in IFSS has led to a very interesting question that is why the post-silanisation is able to fully recover the IFSS loss for heat-treated glass fibres and yet the same method proved to be ineffective in strength regeneration as shown in Fig. 4. We have previously speculated that one of possibilities for the failure of direct silanisation in strength regeneration of the heat-treated glass fibre may lie in the dehydroxylation of glass surface exposed to elevated temperatures [1]. However, the results in Fig. 4 seem to have reduced such possibility to some extent since both silane coupling mechanism and flaw healing theory would require polysiloxane bonds to be formed on glass surface, where adequate silanol groups are necessary for both mechanisms to

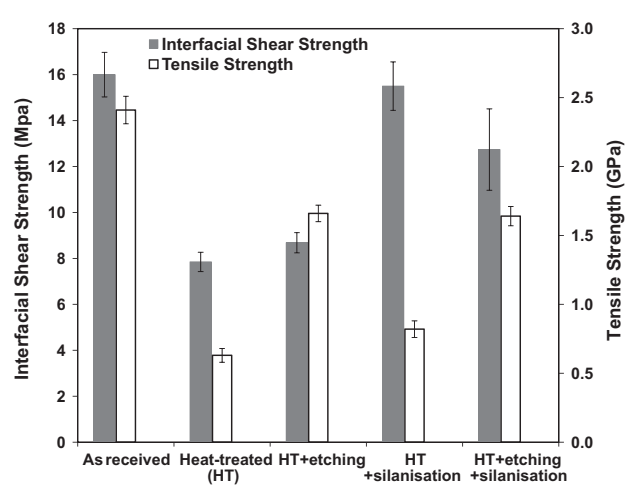

Fig. 4. Interfacial shear strength of GF-mPP and tensile strength of GF after different fibre treatments including heat-treated: 500 °C for 25 min, etching: immersion in 1 v% HF solution for 2.5 min, and silanisation: immersion in 1 v% APS for 15 min.

impose an impact on the corresponding properties. The contradictory effects of post-silanisation on the regeneration of fibre strength and IFSS, together with the results in [1], may raise further doubts on the validity of the flaw healing theory but more importantly indicate that further fundamental work is needed to improve understanding of the role of post-silanisation in the strength of glass fibres.

Furthermore, Fig. 4 also shows that the combination of HF-etching and post-silanisation resulted in less improvement in IFSS than direct silanisation. Since the HF-etching itself showed little effect on the IFSS, the lower increase in IFSS obtained from the combined treatment suggests that HF-etching seems to compromise the effect of post-silanisation on IFSS regeneration. The possibility related to the surface dehydroxylation should probably be ruled out in this case as HF-etching has been shown to leave glass fibres with a hydroxylated surface [19]. The lower increase in IFSS may well be caused by insoluble reaction products left behind on the HF-etched glass fibres as shown in Fig. 5. While an apparently smooth and clean surface can be found on most heat-treated fibres, the HF-etched fibres tend to display residual nanoparticles on the surface as seen in Fig. 5. These substances are most likely to be insoluble inorganic compounds such as CaF_2, MgF_2, or AlF_3 and can be removed by inorganic acid such as hydrochloride. This is partially supported by the quantitative results obtained from the SEM energy dispersive X-ray spectroscopy, which revealed the presence of approximately 7.5 wt% fluorine in the residual particles. This element was not detectable when a bare area of the fibre surface was analysed. The amount and distribution of these insoluble particles is affected by the advances of etching. Fibres that received deep etching can be substantially covered by the residual products, which can mask the fibre surface and impede the etching process. This agrees with the rate of change in diameter reduction as shown in Fig. 6. The decrease of the rate of diameter reduction is indicative of the decreasing etching rate in terms of the mass removed from the glass. It should be noted that the correlation in Fig. 6 should by no means be relatively generalized as it is specific to a set of conditions including the fibre composition, the concentration of HF solution, and the amount of reactants relative to each other. The results from our preliminary study of the last two factors have indicated that for a given amount of glass fibre increasing the amount of etching species either by increasing the concentration or the volume of HF solution can significantly accelerate the etching rate.

3.3. Composite properties

Fig. 7 shows a typical stress–strain curve for CSM-epoxy model composites where the preform received different conditioning. The last data point in each curve was used solely for the purpose of distinguishing the overlapping curves. It can be clearly seen that the stress–strain behaviour varied significantly as the glass fibres in the preform underwent different treatments. In particular, the tensile strength and strain at failure suffered a severe reduction after heat-treated preform had been used. Significant recovery in composite performance was obtained by either fibre regeneration via chemical etching or surface reactivation via post-silanisation. Further increase was obtained by improving both fibre strength and surface functionality. In contrast, there does not seem to be much variation in Young's modulus throughout all the samples.

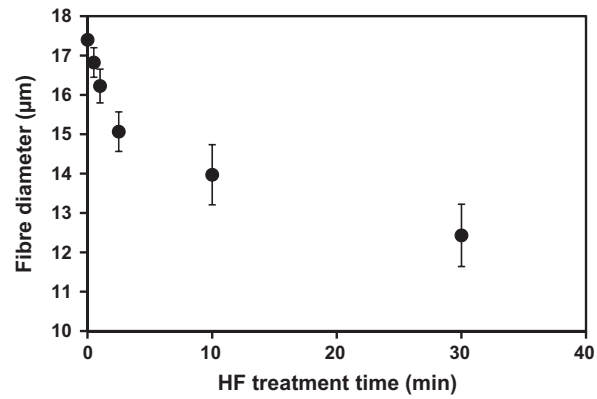

Fig. 6. The fibre diameter as a function of the treatment time of 1 v% HF aqueous solution.

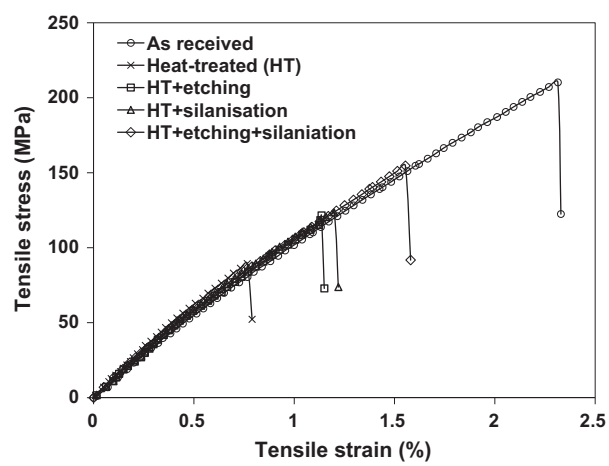

Fig. 7. Typical tensile stress–strain curve obtained from CSM-epoxy composites with glass fibres received different treatments.

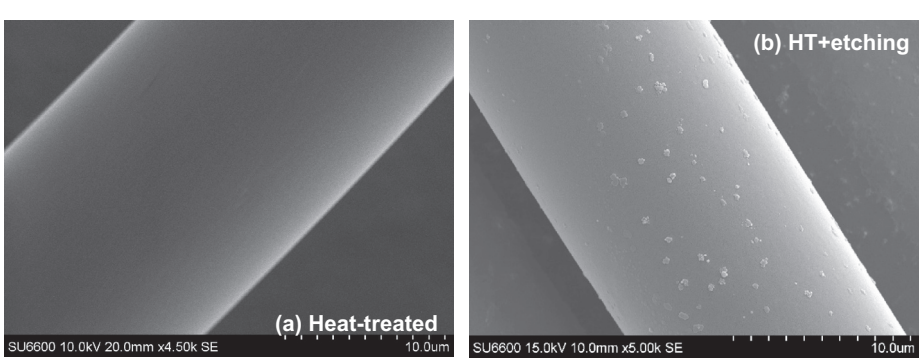

Fig. 5. SEM photo of glass fibres after (a) heat-treatment (HT) at 500 °C and (b) HT followed by 1 v% HF etching for 2.5 min.

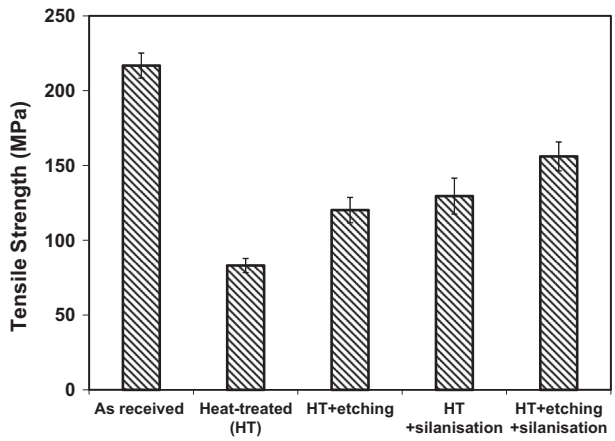

Fig. 8. Tensile strength of CSM-epoxy composites with glass fibres received different treatments.

Fig. 8 and Table 1 summarise average value with 95% confidence limit for tensile properties and the fibre content in each sample. The composites with original CSM gave tensile strength of approximately 220 MPa, over 60% of which was lost after the preform had been heat-conditioned at 500 °C for 30 min. As a result the heat-treated sample ended up with a strength value slightly higher than that of epoxy matrix (65–73 MPa according to the datasheet). Nevertheless, 30–35% of the above strength loss was recovered by increasing the fibre strength or interfacial adhesion alone as shown in Fig. 8. Furthermore, over 50% of the lost strength was regained by combining these two treatments. These results have firmly proved the feasibility of producing discontinuous fibre reinforced composites with a reasonable mechanical performance by reusing glass fibres regenerated through a chemical approach demonstrated in this work. The change in failure strain followed a rather similar trend to the strength as seen in Table 1. The fibre content was influenced by etching itself and manual handling after the original binder was burnt off. However, the variation was controlled within 5% as shown in Table 1 and the Young's modulus appears insensitive to this small change in the fibre content. It is therefore possible to significantly regenerate the composite strength without losing much glass and compromising the stiffness. It should be noted that further strength recovery may be obtained by optimising the combined process of etching and post-silanisation/appropriate sizing. It is rather evident from the above results that the decay in the mechanical performance of the composites with heat-treated glass fibre may be mainly attributed to the loss of fibre strength and surface functionality. Thus, it is necessary to address both issues if thermally-degraded glass fibres are intended for the use as a valuable reinforcement in second-life applications of fibre reinforced composites. Fig. 9 shows a comparison of the fracture surface of a tensile sample with etched or silianised fibres. It clearly reveals a difference in the surface of glass fibres transverse to the loading direction. Fibres without post-silanisation showed clean surface and clear debonding from the matrix whereas those treated with silane couple agent presented considerable amount of residual polymer on the surface which can be interpreted as indicating a very strong adhesion to the matrix. This agrees with the results observed in Fig. 4.

Fig. 10 shows the average value with 95% confidence limit for the flexural strength obtained from the same materials presented in Fig. 8. The general trend is similar to that seen with the composite tensile strength. The flexural strength overall is much higher than the tensile strength at the same condition due to the geometry differences and the fact that in bending tests the surface stress rather than a homogeneous stress is considered. Such an effect could be further enhanced by brittle glass fibres in the polymer matrix due to the different statistical significance involved in the samples for these tests. Another noticeable difference between tensile and bending behaviour lies in the relative strength loss and strength regeneration. 50% decrease of the original flexural strength is found in Fig. 8 and the dual treatments eventually led to 70% recovery compared to 50% realised in the tensile strength in Fig. 7. This might be related to the defects in the specimens such as fibre breakage and voids. These effects would have a more statistically significant impact in tensile test than bending test. Although it was not characterised in this work, these defects are expected to increase during manual handling after the preform is heat-treated. Therefore, flexural strength may to some degree exhibit less loss after heat-treatment and in turn relatively higher percentage of regeneration after chemical treatments. Similar to the Young's modulus obtained from the tensile test, the flexural modulus at different conditions showed insignificant variation and was found to be overall 11% lower than the measured Young's modulus as shown in Table 2. This is not surprising since some of the deflection is related to the shear stress during bending and this effect can be further augmented when the modulus normal to the laminate plane is smaller than that in the plane.

Table 2 summarises the average values with 95% confidence limit for the impact strength obtained from both Type A notched and unnotched CSM-epoxy composites. It is interesting to see that the heat-treatment, which removes original silane coating and reduces fibre strength, is more detrimental to the impact performance compared to the tensile and the flexural properties discussed earlier. Over 80% and 70% decrease in the impact strength was measured for notched and unnotched samples respectively. Although the model composites studied in this work will probably not be loaded along the plane direction in most applications, edgewise impact was still chosen in order to reduce the susceptibility to delamination at the notch tip. Increasing fibre strength alone showed little improvement in the energy absorption in either test as shown in Table 2. This is somewhat expected since the fracture of brittle fibres is not normally considered as a major mechanism contributing to the energy dissipation during a fracture process in composites. The post-silanisation alone led to a small but statistically significant regeneration in the measured impact strength. It is known that very strong fibre–matrix adhesion can also give rise to low fracture toughness as it does not make use of the energy dissipation associated with the fibre pull-out [20]. Extremely low fibre strength could further increase such possibility or at least considerably reduce the critical fibre length of pulled-out fibres. Similar to the other properties discussed previously, the most recovery to the impact performance was

Table 1
Summary of the fibre content and the modulus for CSM-epoxy composites with glass fibres received different treatments.

	Fibre content (wt%)	Tensile failure strain (%)	Young's modulus (GPa)	Flexural modulus (GPa)
As received	64.9 ± 0.4	2.21 ± 0.06	15.1 ± 1.2	13.3 ± 0.9
Heat-treated (HT)	62.7 ± 0.6	0.76 ± 0.04	14.0 ± 0.7	12.9 ± 1.1
HT + etching	60.3 ± 0.5	1.14 ± 0.09	14.6 ± 0.7	13.5 ± 0.7
HT + silanisation	61.8 ± 0.4	1.20 ± 0.09	14.9 ± 1.3	13.2 ± 1.3
HT + etching + silanisation	60.4 ± 0.5	1.46 ± 0.10	15.7 ± 0.6	13.0 ± 0.9

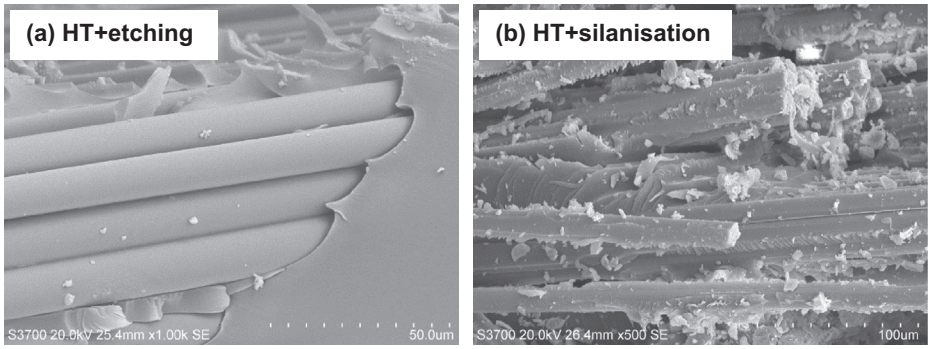

Fig. 9. SEM photo of fractured area obtained from tested samples consisting of the CSM conditioned with (a) heat treatment at 500 °C followed by HF etching and (b) the same heat treatment followed by APS silanisation.

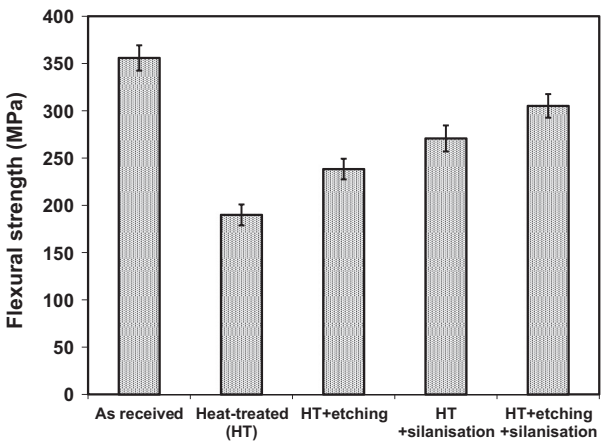

Fig. 10. Flexural strength of CSM-epoxy composites with glass fibres received different treatments.

Table 2
Summary of impact properties for CSM-epoxy composites with glass fibres received different treatments.

	Notched impact strength (kJ/m^2)	Unnotched impact strength (kJ/m^2)
As received	92.6 ± 2.5	150.3 ± 8.8
Heat-treated (HT)	15.3 ± 0.8	38.7 ± 2.3
HT + etching	16.1 ± 0.9	41.9 ± 2.7
HT + silanisation	21.6 ± 1.3	53.8 ± 2.9
HT + etching + silanisation	43.4 ± 1.5	95.2 ± 3.6

achieved through addressing both parameters, namely fibre strength and fibre–matrix interfacial strength. As seen in Table 2, approximately 40% and 50% of lost impact strength was regenerated by the combined treatment. It is reasonable to envisage that further recovery may be obtained through further optimisation of the interfacial strength.

4. Conclusions

The scope of this report is to investigate the feasibility of regenerating thermally degraded glass fibres performance to enable a closed-loop recycling in glass fibre thermosetting composites. Commercially manufactured E-glass fibres were heat-conditioned to mimic the effects of thermal recycling of glass fibre thermosetting composites. The degradation in the strength and surface functionality of heat-treated fibres was clearly identified as a key barrier to reusing the fibres as valuable reinforcement in omposites. 80% of the original tensile strength and 50% of the initial IFSS in GF-mPP were found lost after a heat-treatment at 500 °C. A chemical approach has been developed to address these issues and included two individual chemical treatments, namely chemical etching and post-silanisation. The effectiveness of each treatment was evaluated through direct characterisation of fibre strength and interfacial shear strength. Chemical etching based on 1 v% HF aqueous solution proved to be very effective in regenerating the strength of glass fibres conditioned at a temperature of 450–600 °C and the strength of degraded fibres at each temperature was almost tripled within only 3 min of the treatment. A strong correlation between the fibre strength increase and the fibre diameter decrease was observed and the relationship could not be explained by the removal of surface material alone. Post-silanisation based on 1 v% APS showed nearly full recovery to the measured IFSS, while HF etching demonstrated little effect on the IFSS. The combination of HF-etching and post-silanisation resulted in slightly less improvement in IFSS than direct silanisation.

The same approach was then applied to heat-treated CSM and the effect of different treatments on mechanical properties of CSM-epoxy composites was evaluated through tensile, flexural and impact tests. Over 60% of the original tensile strength (~220 MPa) in the CSM-epoxy composites was lost after the preform had been heat-conditioned at 500 °C for 30 min. 30–35% of this strength loss was recovered by either increasing the fibre strength or interfacial adhesion alone and over 50% of the lost strength was regenerated by combining these two treatments. Similar results were obtained for the flexural properties with 50% decrease of the original strength after the heat-treatment and the dual treatment eventually led to 70% recovery. The measured modulus from tensile and flexural tests showed the maximum 7% variation throughout different conditioning, which had been controlled to minimise any change in fibre content. Impact properties suffered relatively greater loss with degraded glass fibres, which caused 70% and 80% decrease in the notched and unnotched impact strength respectively. Etching itself showed little effect on the regeneration and post-silanisation brought about 10% recovery. However, approximately 40% and 50% of the lost impact strength was successfully regenerated by the combined treatment. The results presented in this work provide strong evidence at the feasibility of achieving closed-loop recycling of glass fibre thermosetting composites through regenerating degraded glass fibres. It has also been clearly demonstrated that degradation in both fibre strength and surface functionality need to be addressed in order to establish a recycling route with added value. The results for the property regeneration are promising and certainly encourage more work to be devoted in this area. The use of HF in an industrial environment can be problematic due to its highly toxic nature. We have recently filed a patent on a technology of glass fibre recovery

without involving any HF or its derivatives. The work on a life cycle analysis for our recycling process and its economical competitiveness is also underway.

Acknowledgement

The authors would like to acknowledge the financial support from EPSRC through the projects EP/I037970/1 and EP/I038616/1 and the assistance of the Advanced Materials Research Laboratory of the University of Strathclyde with the mechanical testing. The authors would also like to thank Owens Corning Vetrotex for providing the glass fibres used in this study.

References

[1] Thomason JL, Yang L, Meier R. The properties of glass fibres after conditioning at composite recycling temperatures. Compos Part A: Appl Sci Manuf 2014;61:201–8.
[2] Job S. Recycling glass fibre reinforced composites – history and progress. Reinf Plast 2013;57(5):19–23.
[3] Albers H, Greiner S, Seifertand H, Kühne U. Recycling of wind turbine rotor blades – fact or fiction? DEWI Mag 2009:32–8.
[4] Pickering SJ. Recycling technologies for thermoset composite materials—current status. Compos Part A: Appl Sci Manuf 2006;37(8):1206–15.
[5] Pickering SJ, Kelly RM, Kennerley JR, Rudd CD, Fenwick NJ. A fluidised-bed process for the recovery of glass fibres from scrap thermoset composites. Compos Sci Technol 2000;60(4):509–23.
[6] Meira Castro AC, Ribeiro MCS, Santos J, Meixedo JP, Silva FJG, Fiúza A, et al. Sustainable waste recycling solution for the glass fibre reinforced polymer composite materials industry. Constr Build Mater 2013;45:87–94.
[7] Thomason J, Yang L, Kao C-C, Jenkins P. Regeneration of the performance of glass fibre recycled from end-of-life composites or glass fibre waste. In: International glass fibre symposium. Aachen; 2012.
[8] Yang L, Thomason JL. Effect of silane coupling agent on mechanical performance of glass fibre. J Mater Sci 2012;48(5):1947–54.
[9] Aslanova MS. The effect of different factors on the mechanical properties of glass fibers. Glass Ceram 1960;17(11):563–9.
[10] Feih S, Boiocchi E, Mathys G, Mathys Z, Gibson AG, Mouritz AP. Mechanical properties of thermally-treated and recycled glass fibres. Compos B Eng 2011;42(3):350–8.
[11] Liu XM, Thomason JL, Jones FR. The concentration of hydroxyl groups on glass surfaces and their effect on the structure of silane. In: Silanes and other coupling agents. Leiden, The Netherlands: Brill Academic Publishers; 2009.
[12] Yang L, Thomason JL. The influence of oxidative-thermal degradation of polypropylene on measured interface strength of glass fibre-polypropylene. In: 14th European conference on composite materials. Budapest, Hungary; 2010.
[13] Yang L, Thomason JL. Development and application of micromechanical techniques for characterising interfacial shear strength in fibre-thermoplastic composites. Polym Testing 2012;31(7):895–903.
[14] Sakka S. Effects of reheating on strength of glass fibers. Bull Inst Chem Res, Kyoto Univ 1957;34(6):316–20.
[15] Pico D, Bartl A. Chemical treatment of glass fibres after composite recycling process. In: Waste site stories. Copenhagen, Denmark: ISWA Annual Congress; 2006.
[16] Spierings GACM. Wet chemical etching of silicate glasses in hydrofluoric acid based solutions. J Mater Sci 1993;28(23):6261–73.
[17] Levan A, Royer J. Part-circular surface cracks in round bars under tension, bending and twisting. Int J Fract 1993;61:71–99.
[18] Rudzinski S, Häussler L, Harnisch C, Mäder E, Heinrich G. Glass fibre reinforced polyamide composites: thermal behaviour of sizings. Compos Part: A Appl Sci Manuf 2011;42(2):157–64.
[19] Knotter DM. Etching mechanism of vitreous silicon dioxide in HF-based solutions. J Am Chem Soc 2000;122(18):4345–51.
[20] Kim J-K, Y-w Mai. High strength, high fracture toughness fibre composites with interface control—a review. Compos Sci Technol 1991;41(4):333–78.