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REGENERATION OF THERMALLY RECYCLED GLASS FIBRE FOR COST-EFFECTIVE COMPOSITE RECYCLING

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ABSTRACT

Global production of composite materials in 2015 will significantly exceed 10 million tons. Glass fibre reinforced composites account for more than 90 % of all the fibre-reinforced composites currently produced. Development of economically viable processes for recycling end-of-life glass fibre composites would have major economic and environmental impacts. This paper introduces and reviews the initial results of the ReCoVeR projects on enabling cost-effective performance regeneration of glass-fibres from thermal recycling of end-of-life automotive and wind energy composites. ReCoVeR technology targets treating glass fibre thermally reclaimed from GRP waste in order to regenerate a performance level which is equivalent to new fibres. Composite materials reinforced with ReCoVeR glass fibres can currently attain over 80 % of the reinforcement performance of composites produced with pristine glass fibres.

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. 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. 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. Two European directives in particular have an enormous influence on the composite industry they are the End-of-Life Vehicles (ELV) and the Waste Electrical and Electronic Equipment. With the main priority aimed at preventing these two forms of waste and to reuse and recycle other forms of waste as to reduce the disposal of waste using the ‘polluter pays’ principle. The ELV directive 2000/53/EC states that by 2015 at least 85 % of end-of-life vehicles should be reused or recovered with a minimum of 80 % being reused or recycled. This is due to increase up to 95 % for reuse and recovery and 85 % for reuse and recycling on vehicles at end of life after 2015. It has been estimated that the number of end-of-life vehicles will reach almost 19 million in Europe by 2015 [1].

Glass-fibre-reinforced composite materials will make up a significant proportion of the residual waste from these vehicles, but these materials tend to be regarded as non-recyclable [1]. Consequently, the ELV Directive has given fresh focus on the need to develop routes to recycle composite waste in an economically and environmentally sustainable manner. 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. Currently most of this material is destined for landfill at the end of its 10-25 year application lifetime; the estimate for Germany alone is approximately 100,000 tons of GRP end-of-life turbine blades to be dealt with in the coming decade [2]. 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.

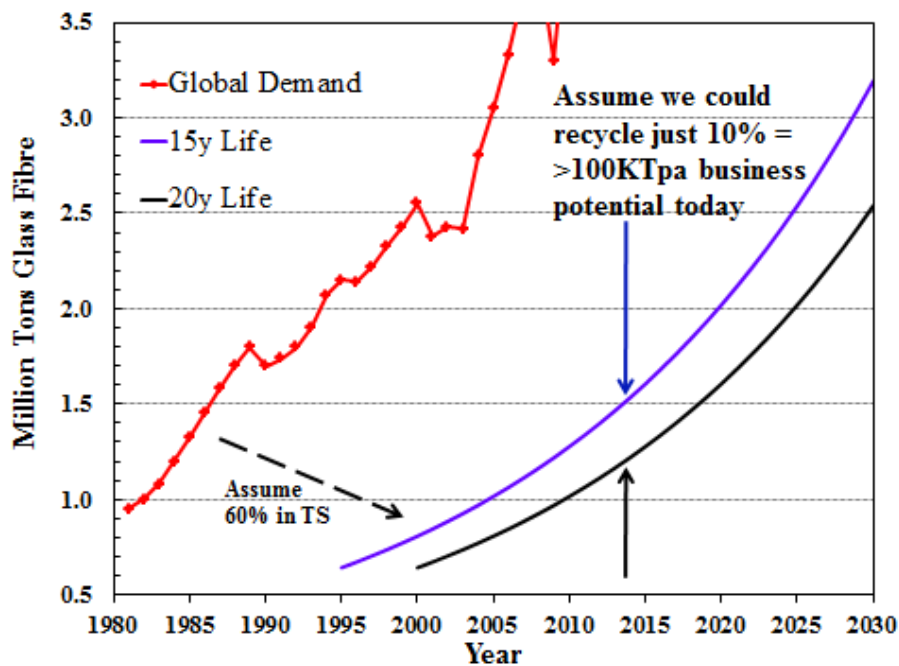


Figure 1. Global glass fibre usage and potential recycled glass fibre availability

Thermoplastic based composites are, in principle, intrinsically recyclable. The greatest challenge is with the larger fraction of thermoset based GRP composites. Figure 1 shows a simple extrapolation over a 15-20 year application lifetime of the global composites industry annual usage of glass fibre [3]. The data in Figure 1 indicate that there must currently be over one million tons per annum of glass fibre in GRP applications reaching end-of-life and this volume is set to double by about 2025. The reclamation and reuse of these glass fibres today could result in a huge reduction in the environmental impact of the glass-fibre and composites industry where the replacement of pristine glass fibre products by RGF products would equate to a global reduction in CO₂ production of more than one million tons per annum from reduced melting energy requirements alone. Furthermore, such a technological development would also reduce the need for an annual landfill disposal of 2 million tons of composite materials. These developments would clearly be in line with the growing societal and environmental pressure to

reduce the use of landfill disposal, increase the reuse of valuable raw materials resources, and reduce the release of CO₂ to the atmosphere.

A number of processes are available for recycling the fibres out of such end-of-life GRP composites. 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 cost competitiveness with pristine first-pass materials. Processing temperatures in the production of glass fibre are significantly higher than GRP recycling temperatures. Nevertheless, early work indicated that the room temperature tensile strength of glass fibre can be significantly reduced by annealing at temperature as low as 150 °C [4]. More recent studies have also confirmed that room temperature glass fibre strength can be reduced by exposure to temperatures in the 300-600 °C temperature range [5-7] which is typical of the many different potential GRP recycling processes. Consequently, recycled glass fibres (RGF) have a very 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 RGF 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, economic and environmental impacts.

We are currently engaged in research projects where the ultimate goal is to enable cost-effective regeneration of the mechanical properties of glass fibres which have been produced from thermal recycling of glass reinforced thermoset composites (such as wind turbine blades). This ReCoVeR team of researchers is currently focused on: (1) generating fundamental understanding of the degradation of glass fibre strength during thermo-mechanical conditioning (300-600 °C), (2) developing cost effective treatments to regenerate the performance of thermo-mechanically treated glass fibres, (3) producing examples of composites using regenerated glass fibres. This paper presents some initial results of these investigations.

2. EXPERIMENTATION

2.1 Single Fibre Testing

Boron-free E-glass (Advantex) fibres supplied by Owens Corning Vetrotex were investigated in this study. The rovings had a nominal tex of 1200 g/km and a single-fibre diameter of 17.4 ± 1.3 μm [8]. 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) hydrolysed solution in distilled water. All fibre packages were subsequently dried at 105 °C for 24 hours.

Thermal conditioning of these fibres was carried out using a CSF1200 Carbolite electric furnace for a period of 25 minutes, after which samples were immediately removed and cooled in room temperature air. Two different procedures, bundle and single fibre, thermal conditioning were used in this work. In the former, lengths of fibre from the roving, as-received, were heat treated and once cooled single fibres were removed and mounted for tensile testing. Alternatively, in the

single fibre thermal conditioning process, single fibres were extracted from a bundle prior to thermal conditioning. These were then attached to wire frames and heat treated in batches of approximately 30 fibres. In both cases great care was taken to avoid any contact between any surface and the fibre lengths to be tensile tested. The single fibres and fibre bundles were supported at their ends and no tensile stress was applied to them during thermal conditioning. The only difference between the two conditioning procedures is the point at which fibres are separated from the bundle.

Single fibre tensile properties were obtained according to the method described in ASTM C1557-03. The details of the procedure utilized are described comprehensively in [9]. All fibres were mounted at a gauge length of 20 mm. After each individual fibre diameter was measured by optical microscopy (to within $\pm 1 \mu\text{m}$) the samples were tested using an Instron 3342 universal testing machine equipped with a 10 N load cell. An extension rate of 0.3 mm/min was used in all cases. The average strength values at each condition are based on between 20 and 80 tensile tests. All tests were carried out at room temperature and approximately 50 % relative humidity.

An APS film was also prepared by oven drying a 1 % hydrolysed solution at 105 °C for 24 hours. Thermogravimetric analysis was carried out on approximately 100 mg of sample using a Netzsch STA 449 F1 Jupiter. Weight loss was measured while heating at 10 °C/min from room temperature to 1000 °C.

2.2 Composite Processing and Testing

Composites were prepared using DS 2200-13P chopped glass fibres provided by 3B Fiberglass company. Where required, heat treatment of the glass fibres was performed in a Carbolite CWF 12/13 furnace. The fibres were placed in an aluminium tray and heat treated for 25 minutes in the furnace at the required temperature. ReCoVeR treatments were also applied to the heat treated glass fibres before further composite processing. A Betol BC25 extruder was used to compound SABIC® PP 579 S polypropylene (PP) pellets with the glass fibres. 1 % Polybond 3200 maleic anhydride-grafted polypropylene by PP weight was added to the composites to improve the adhesion between glass fibres and PP matrix. The extruded material was drawn through a water bath and cut into pellets using a rotary cutter. An Arburg 170-90/200 injection moulding machine was used to produce dog-bone shaped tensile test specimens according to ASTM 638. The processing temperatures were set between 170 °C and 230 °C. All samples were conditioned at room temperature for three weeks before mechanical testing. An Instron 596 testing machine was used to perform the tensile tests. Sample strain was recorded with a video extensometer. A constant head displacement rate of 1 mm/min was used to test the composites. The PP reference sample was tested with a head displacement rate of 1mm/min up to 3 % strain. Then the head displacement rate was increased to 5 mm/min. Unnotched Charpy impact test specimens according to ISO 179-1 were cut from injection moulded tensile bars. A Tinius Olsen Impact 503 impact tester with a 25 J hammer was used to perform the impact tests. Ten individual samples of each system were measured for both tensile and impact testing.

3. RESULTS AND DISCUSSION

3.1 Degradation of glass fibre strength during thermo-mechanical conditioning/recycling

Typical results [7] for the effect of thermal conditioning on the strength of unsized and aminopropylsilane (APS) sized glass fibres are shown in Figure 2. The Figure shows the average single fibre strength of silane sized and water sized fibres after 15 minutes heat treatment. The results indicate that thermal conditioning caused a considerable strength reduction for both silane-sized and water-sized fibre samples, with a loss of over 70 % of the original strength in the case of conditioning at 600 °C. It can be seen that both glass fibre types reduce in strength, with the silane sized glass falling by a greater percentage of its original strength. The water sized fibres exhibit a fairly linear reduction in room temperature strength with increasing conditioning temperature. The strength of silane-sized glass appears relatively stable at low temperatures but exhibits a threshold (at approximately 300 °C) above which a precipitous reduction in fibre strength and strain to failure occurs. These results appear to agree well with results from other investigators [4-7]. Furthermore, Kao et al [9] has extended the study of glass fibre strength loss to the same APS coated glass fibre after they have been processed into and thermally recycled out of polyester composites at 500 °C to 600 °C. An approximate 70 % reduction of strength in recycled fibres was found after recycling composites at these temperatures. Consequently it appears that the average strength of glass fibres is strongly influenced by thermal conditioning at temperatures and times which may commonly be experienced during the thermal processing of end-of-life composite materials in order to obtain recycled fibres [10].

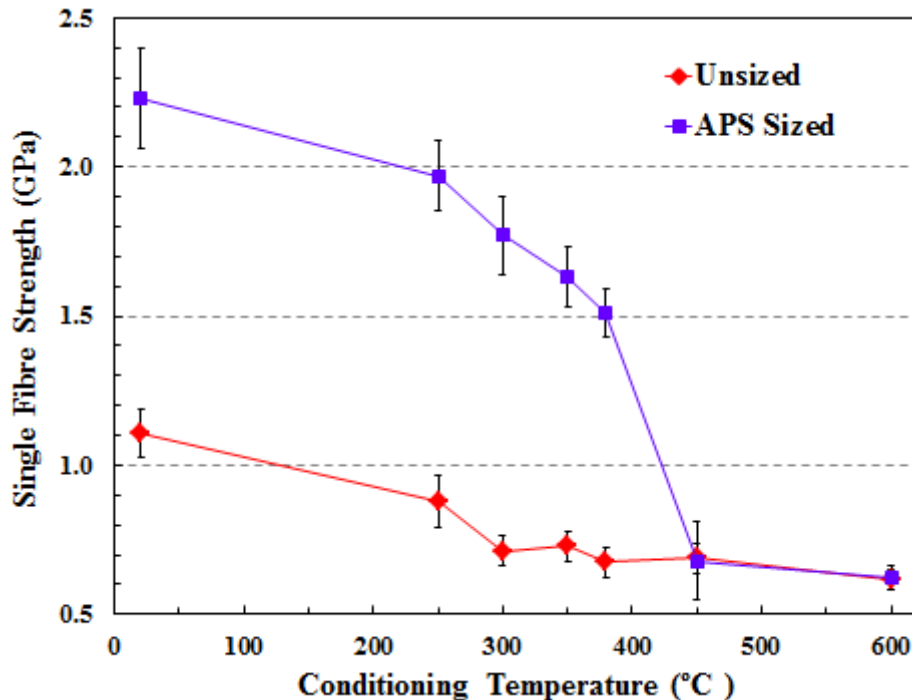


Figure 2. Effect of thermal conditioning on glass fibre strength

The APS sized fibre initially has much higher room temperature strength than bare fibres, which can be attributed to the protection given against fibre surface damage by the silane coating. For

sized fibre, around 20 % of the strength had been lost after a treatment temperature of 300 °C. Strength loss increased greatly above 300 °C and became much less dependent on conditioning temperature beyond 500 °C. The bare fibre, on the other hand, lost over half its original strength by 300 °C and in fact much of this loss was already observed when treating at only 200 °C. At higher temperatures the bare fibre strength decreased further, but to a lesser degree that was just greater than the 95 % confidence limits of the average strength values. Conversely, the strength of the sized fibre decreased most significantly at higher temperatures. Following treatment at 450 °C it retained only one-third its original strength and after 500 °C treatment just one quarter: approximately the same absolute magnitude as measured for the bare fibre.

Since the main difference between these two fibre specimens is the presence of APS coating, it is reasonable to suggest that the degradation of the APS coating may play a role in step decrease in the strength of the APS coated fibres when heated above 300 °C. Figure 3 shows the results of the TGA measurement of weight loss versus temperature of a cast APS film during a dynamic heating experiment. The initial 10% drop in weight up to 200 °C is assigned to further drying of the APS film. The step down in weight at higher temperature is assigned to the degradation and oxidisation of the organic fraction of the APS molecules. This appears to start at temperatures above 300 °C. Due to the dynamic nature of the TGA measurement it can be suggested that the step down in weight loss due to the APS degradation may appear to be shifted to higher temperatures in comparison to the step drop in fibre strength observed in Figure 2.

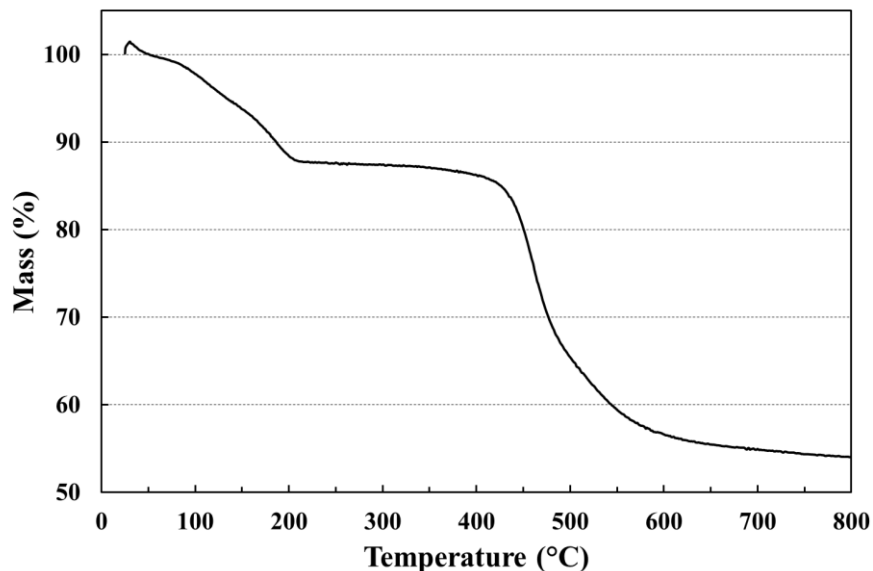


Figure 3. TGA results on polymerized APS film

It is worth remembering that the strength value obtained in a single fibre tensile test is dependent on the full chemical, mechanical and environmental history of the sample. In particular the isolation of single fibres from multifilament sized fibre strands always involves a certain level of unquantified and variable mechanical handling whose negative effects on strength will also vary with the degree and nature of the fibre coating. Consequently it was suspected that part of the fibre strength loss observed at higher temperatures may have been caused by fibre-fibre interaction and damage during extraction of the test fibres from the heat-treated fibre bundle. In

order to test this hypothesis single fibres were first isolated from the glass strands and then heat conditioned [11]. Results for the average single fibre tensile strength of these samples are compared in Figure 4.

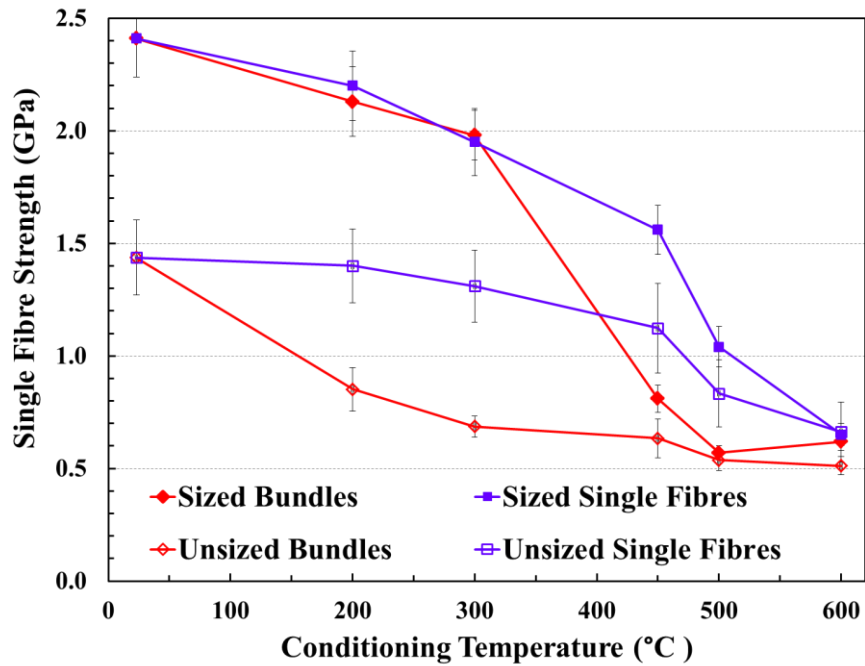


Figure 4. Effect of thermal conditioning as single fibre or in fibre bundle

Average single fibre strength decreased with an increase in thermal conditioning temperature and the data for all samples appears to converge after conditioning above 500 °C. It is noticeable that the strength decay of the bare and the sized fibre after single fibre thermal conditioning shares a similar pattern over the temperature range investigated. This implies that there is a mechanism functioning in both fibre types that is responsible for strength loss. The magnitude of this strength loss may be characterised by the data obtained from individually conditioned bare fibres. Both bare and sized fibre retained a significantly greater strength when thermal conditioning was carried out on single fibres rather than bundles. For bare fibre, this difference is evidenced at temperature as low as 200 °C, whereas for the sized fibres it occurs after heat treating above 300 °C. Interestingly, with single fibre thermal conditioning, both APS coated and bare fibres show evidence of a step down in strength above 450 °C.

Consequently, it seems likely that the thermal degradation of, and loss of protection by, the organic part of the polysiloxane layer on the fibre surface (or a composite polymer matrix), very likely contributes to the loss of average fibre strength through a greatly increased probability of fibre damage due to fibre-fibre interaction. However, since the water sized fibres also exhibit a strength reduction after elevated temperature conditioning it seems probable that there also exists a strength reduction mechanism related to a fundamental change in the glass itself. This conclusion is supported by the results of a deeper investigation of the relationship between the strength of thermally conditioned glass fibres and the degradation of the silane coating [11].

3.2 Effect of fibre strength loss on composite properties

Figure 5 summarises the data on the Tensile Strength and unnotched Charpy Impact performance of the injection moulded, glass reinforced polypropylene composites [12]. These composites were prepared with chopped glass fibres that had been thermally conditioned for 25 minute to mimic composite thermal recycling. It can be seen that the tensile strength of these composites is significantly reduced by the glass fibre thermal conditioning prior to composite manufacture. The glass fibre heat-treatment at 300°C caused a tensile strength reduction of more than 40%. A glass fibre heat treatment at higher temperatures caused a drop of the tensile strength of greater than 50%. However, the tensile strength of unreinforced PP was measured as 35.8 MPa. Consequently the thermal conditioning of the glass fibres has essentially removed 100% of the reinforcement effect of the fibres in terms of increasing tensile strength of the composite in comparison with the tensile strength of the PP polymer alone. Similarly the thermal conditioning of the glass fibres resulted in a loss of more than 50% of the unnotched impact performance of the composite. These results clearly reveal the potential poor reinforcement performance of any glass fibres obtained by thermal recycling of composites. The stiffness of the GF-PP composites was not seriously comprised by the thermal conditioning but the large drop in strength means that there is unlikely to be any significant commercial interest in large-scale application of RGF unless the properties of the RGF can be regenerated in a cost-effective manner.

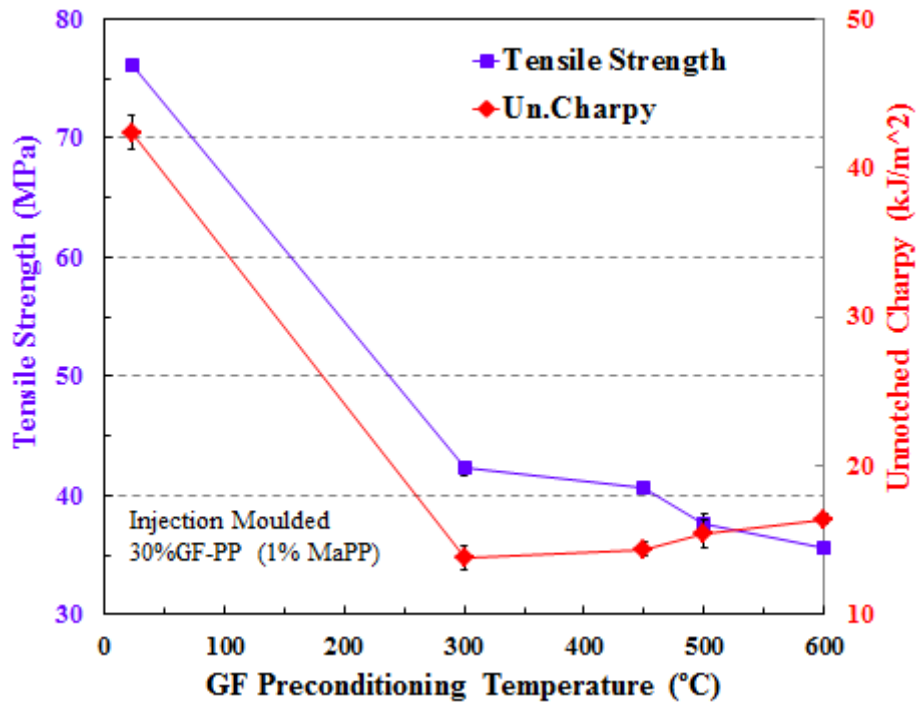


Figure 5. Effect of glass fibre heat treatment on composite performance

3.3 Glass fibre and composite performance ReCoVeRy

Yang et al [13] and Saez et al [14] have reported possible routes to regenerating the reinforcement performance of thermally conditioned glass fibres. Some of the details of the specific routes that have been investigated are subject to confidentiality restrictions due to an on-

going patent application. Yang et al reported on the use of HF etching methods that regenerated single fibre strength of heat-treated glass fibres to above 2 GPa. Saez et al reported that simple silane treatment of heat-conditioned fibres did not significantly regenerate the fibre strength. However, they also reported on other methods (the ReCoVeR treatments) that can regenerate single fibre strength of heat-treated glass fibres to above 2 GPa. The progress made in the different ReCoVeR treatments shows some promise in being able to deliver significant regeneration of strength in glass fibre thermally conditioned in the 450-600°C range. Nagel et al also reported data on the properties of injection moulded glass reinforced polypropylene composites containing ReCoVeR treated thermally condition fibres [12]. Data on the tensile strength of these composites is shown in Figure 6. It can be seen that 71% of the composite strength loss shown in Figure 5 due to thermal preconditioning of the glass fibres at 500°C can be ReCoVeRed by use of the methods discussed by Saez et al [14]. The unnotched impact strength of these composites [12] exhibited an even higher level of ReCoVeRed performance.

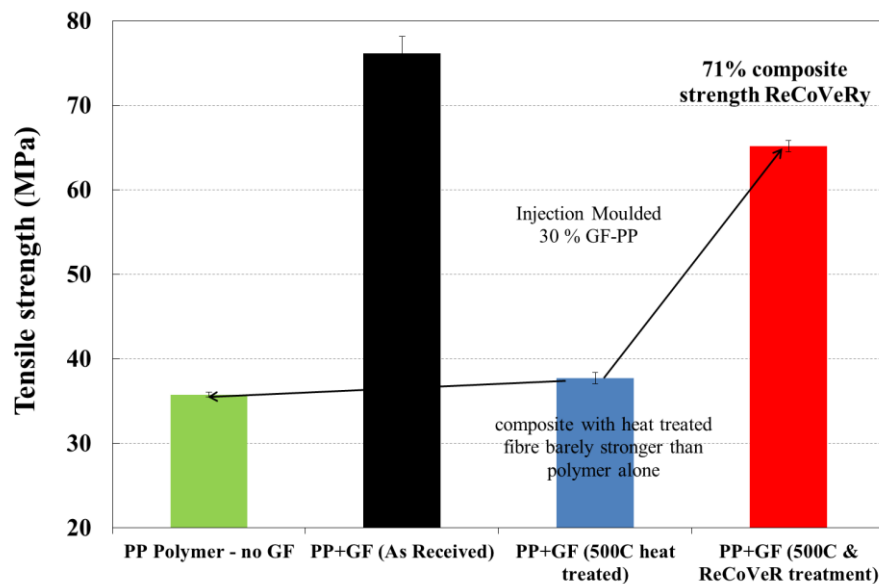


Figure 6. Effect of ReCoVeR glass fibre strength regeneration on composite tensile strength

4. CONCLUSIONS

Development of economically viable processes for recycling end-of-life glass fibre composites will have major societal, economic and environmental impacts. The ReCoVeR team is making significant progress towards the goal of enabling cost-effective performance regeneration of glass-fibres from thermal recycling of end-of-life automotive and wind energy composites. ReCoVeR technology targets treating glass fibre thermally reclaimed from GRP waste in order to regenerate a reinforcement performance level that is equivalent to that of new fibres. Composite materials reinforced with ReCoVeR glass fibres can currently attain over 80% of the reinforcement performance of injection moulded composites produced with pristine glass fibres. Further research of the fundamental underlying technical issues and development of improved ReCoVeR treatments is targeted on raising the reinforcement performance of ReCoVeRed glass fibres to that of pristine fibre products.

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