REGENERATION OF THERMALLY RECYCLED GLASS FIBRE FOR COST-EFFECTIVE COMPOSITE RECYCLING: OVERVIEW OF THE RECOVER PROJECTS

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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 presentation introduces 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 (WEEE). 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.

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. The reclamation and reuse of these glass fibres 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 400,000 Tons/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. Similar behaviour has also been observed in silica and basalt reinforcement fibres [8,9]. Consequently, recycled glass fibres 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 recycled glass fibres (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. The current status of all these aspects of the project will be reviewed during ECCM16 by various members of the ReCoVeR team.

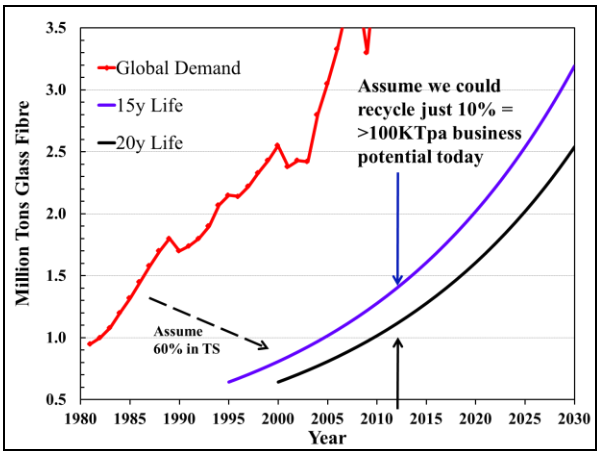

Figure 1: Global glass fibre usage and potential recycled glass fibre availability

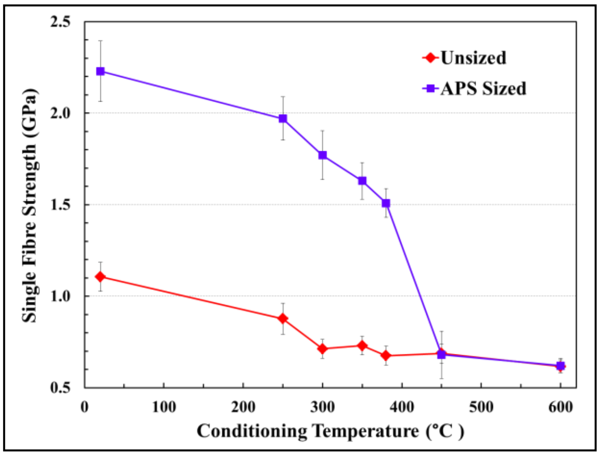

Figure 2: Effect of thermal conditioning on glass fibre strength

2. Review of the ReCoVeR ECCM16 presentations

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

Typical results from the work of Jenkins et al [10] 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 15-25 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 250°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 [11] will extend 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 obtained recycled fibres [12].

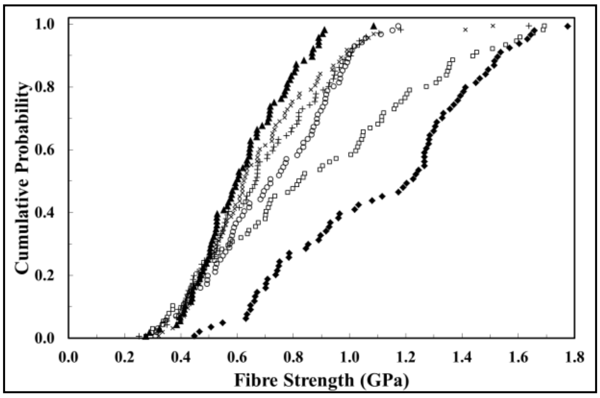

Figure 3: Cumulative failure probability of unsized fibres after thermal conditioning (◆23°C, □ 250°C, ○ 300°C, × 380°C, + 450°C, ▲600°C)

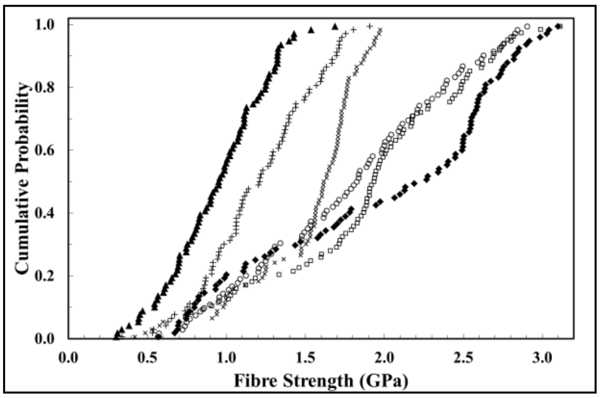

Figure 4: Cumulative failure probability of APS sized fibres after thermal conditioning (◆23°C, □ 250°C, ○ 300°C, × 380°C, + 450°C, ▲600°C)

A more detailed analysis of the single fibre strength data in Figure 2 is given in Figures 3 and 4 which show plots of the cumulative probability of fibre failure (P_F) as a function of fibre strength. It can be observed in Figure 3 that there is considerable separation between the unsized fibres conditioned above 300°C and the as-received fibres. The region between these two groups appears to be spanned by the distribution for the fibres conditioned at 250°C. It can also be observed that all the heat conditioned fibres have a similar low strength distribution for the first 25-30% of the distribution. One possible explanation for these observations is that the low strength region of fibre strength of the heat conditioned fibres is a result of further mechanical damage to the unsized fibres caused by the handling of the fibres in the process of heat conditioning. The strength of any stronger water-sized fibres is then also reduced in greater degree with increasing heat conditioning temperature possibly indicating the presence of some temperature dependent structural change in these fibres [7,10,13].

In the case of the APS sized fibres the data in Figure 4 indicate somewhat different trends in P_F. The as received fibres show a broad strength distribution that appears to be split approximately 50:50 in low and high strength regions. Initially heat conditioning appears to affect the high strength part of this distribution, shifting it to lower values with increasing heat conditioning from 250°C to 380°C. The lowest 30% of these three distributions appear to be unaffected. Heat conditioning at 450°C and above, appears to shift all fibres to lower strengths and removes the appearance of bimodality. Building on the discussion of the water sized fibre results this could be interpreted as indicating that the APS coating protects the fibres from the possibility of mechanical damage during the handling of the fibres in the process of heat conditioning. Consequently there is no reduction in strength of the fibres in the low strength region of the distribution. Nevertheless, heat conditioning will degrade the organic part of the silane coating [7,10,13]. It seems likely that the high strength fraction of the fibres are initially well protected by the silane and so it is the high strength fraction of the distribution that is initially affected by the thermal conditioning at lower (250-380°C) temperatures. At 450°C and above it has been shown that the organic part of the silane is fully degraded resulting in a further reduction in the strength of the high strength fibres [13]. It can also be supposed that the temperature dependent structural effects observed with the water sized fibre data will also increasingly affect the results for the APS sized fibres conditioned at increasingly higher temperatures.

Consequently, it seems likely that the degradation and loss of protection, during thermal conditioning, of the organic part of the polysiloxane layer on the fibre surface, very likely contributes to the loss of average fibre strength in the silane sized fibres. 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 will also be reported by Jenkins et al in ECCM16 [10]. Surface analysis of these heat conditioned, silane-only coated, fibres indicates a full removal of the organic coating. Kao has also investigated the state of the glass fibre surface after recycling out of composites. Figure 5 shows an SEM micrograph indicating the presence of residual contamination after recycling at 500°C. Figure 6 shows a significantly cleaner and smoother fibre surface after an addition cleaning step is introduced.

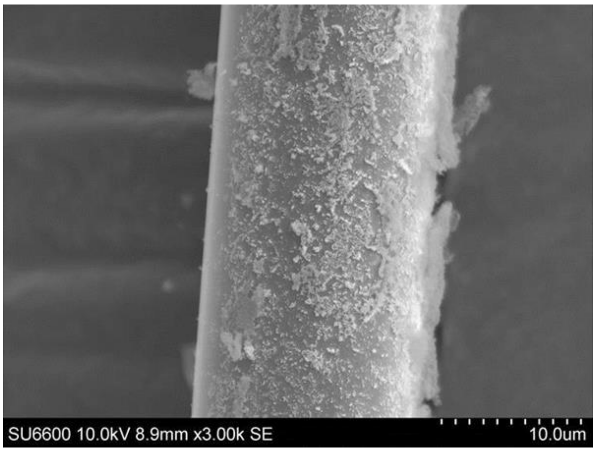

Figure 5: SEM images of APS sized fibres recycled from a polyester composite at 500°C

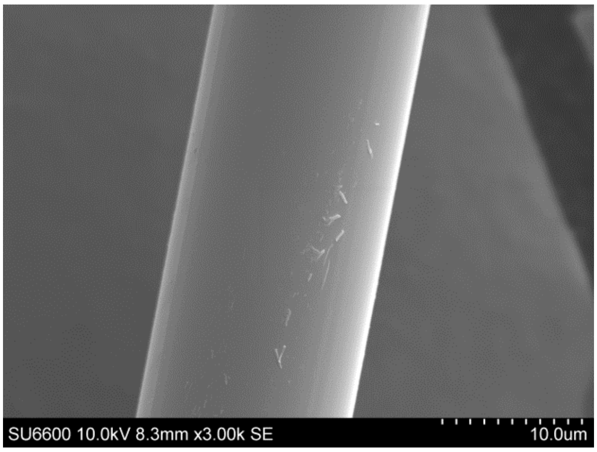

Figure 6: SEM of the same fibres after an additional cleaning step was introduced

2.2 Effect of fibre strength loss on composite properties

In another paper at ECCM16 Nagel et al will report on their work investigating the effect of thermal condition of glass fibres on the performance of extrusion compounded, injection moulded, glass reinforced polypropylene composites [14]. Figure 7 summarises some of the data on the Tensile Strength and unnotched Charpy Impact performance of these composites as a function of the 25 minute heat treatment of chopped glass fibres prior to composite processing. Each data point represents the average of ten individual tests. Figure 5 shows 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.

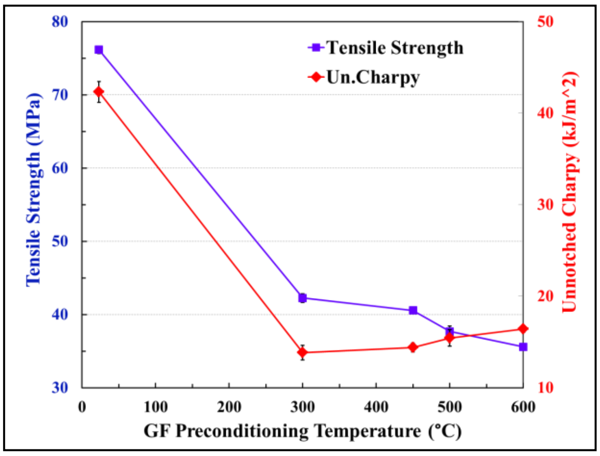

Figure 7: Effect of glass fibre heat treatment on composite performance

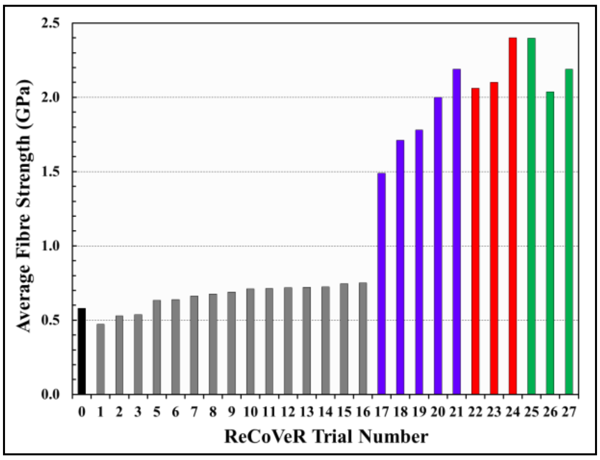

Figure 8: Effect of ReCoVeR treatments on strength of heat treated glass fibres

2.3 Glass fibre and composite performance ReCoVeRy

There are two further papers to be presented at ECCM16 (Yang et al, Saez et al) that will report on work investigating possible routes to regenerating the reinforcement performance of thermally conditioned glass fibres. Some of the details of the specific routes which have been investigated are subject to confidentiality restrictions due to an on-going patent application. Saez et al will report on methods which can regenerate single fibre strength of heat treated glass fibres to above 2 GPa [15]. Yang et al will report on different methods which can also regenerate single fibre strength of heat treated glass fibres to above 2 GPa [16]. The progress made in the different investigated methods which show some promise in being able to deliver significant regeneration of strength in heat-treated glass fibre is indicated in Figure 8. Figure 8 shows a selection of results for the average single fibre strength of APS coated fibres which have been heated treated at 450°C and subsequently subjected to a range of ReCoVeR treatments. Initially the treatments resulted in only small improvements in fibre strength. However, recently a number of routes have been developed which result in significant regeneration of the glass fibre strength. Kao et al [11] will also present data on regeneration of the fibre strength of glass fibre recycled out of glass polyester composites. They have also achieved significant improvements in fibre strength although not, as yet, to the levels achieved with fibres which have only received a thermal conditioning. Nevertheless the paper of Nagel et al [14] will report data on the properties of injection moulded glass reinforced polypropylene composite containing regenerated thermally condition fibres. Data on the tensile strength of these composites is shown in Figure 9. It can be seen that 71% of the composite strength loss shown in Figure 7 due to thermal preconditioning of the glass fibres at 500°C can be ReCoVeRed by use of the methods discussed by Saez et al [16]. Data the unnotched impact strength of these composites indicates an ever higher level of ReCoVeRed performance.

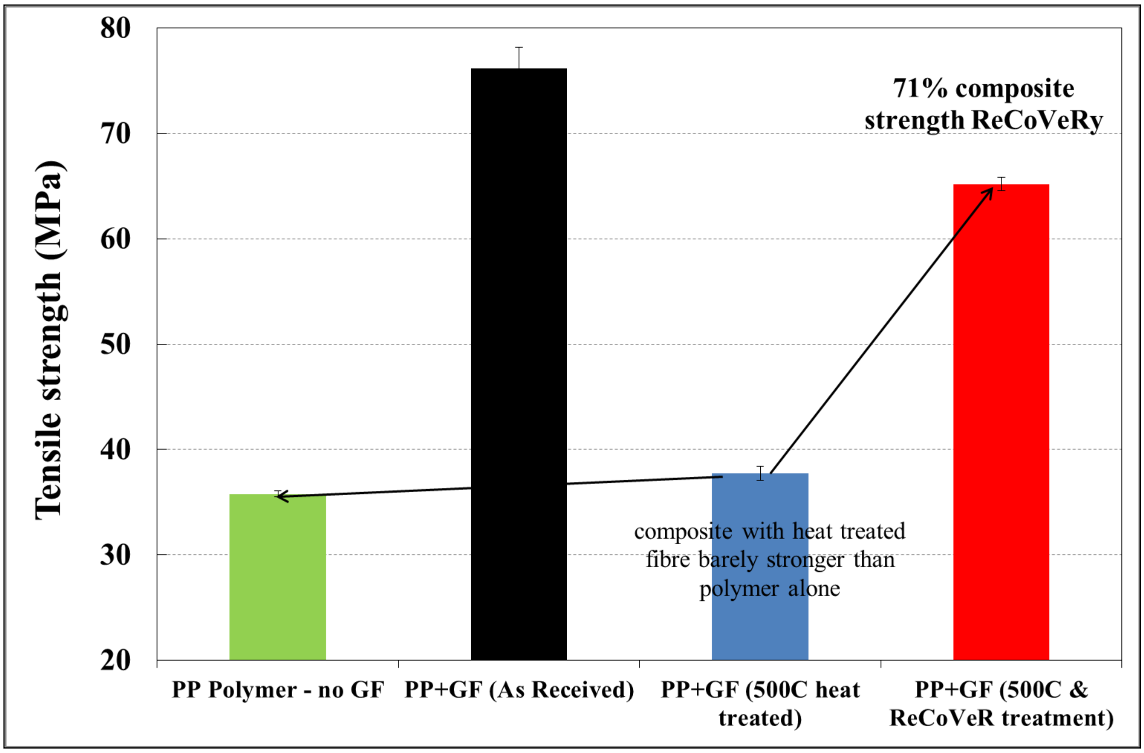

Figure 9: Effect of ReCoVeR glass fibre strength regeneration on composite tensile strength

3. Conclusions

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. Development of economically viable processes for recycling end-of-life glass fibre composites will have major societal, economic and environmental impacts. ReCoVeR technology targets treating glass fibre thermally reclaimed from GRP waste in order to regenerate a reinforcement performance level which 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 underling 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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