MECHANICAL CHARACTERISATION OF GLASS FIBRES RECYCLED FROM THERMOSETTING COMPOSITES USING WATER-BASED SOLVOLYSIS PROCESS

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1 Introduction

This study reports on the recyclability and potential reuse of glass fibres (GF) recovered from thermoset composites using subcritical water as a reaction medium. Unlike thermoplastics, thermoset composites cannot be easily reprocessed or recycled. The complexity of material, the increasing costs of waste disposal and EU legislation puts considerable pressure on thermoset composite users and their supply chains to address this recycling issue.

Recycling of fibre thermoset composites has been an extensive research area over the last decade. It is well established that the measurement of strengths of glass fibres recovered through a fluidised bed process [1-2] at temperatures varying from 450 to 650°C, indicates an approximately 50% decrease in strength due to the effect of high temperature exposure. Similarly, several studies on the effects of heat treatment [3-5] on the glass fibres showed that their strength decreases even after exposure at just 125°C. In addition, glass fibres recovered through a grinding and air separation process [6] follow a similar trend, with a drop in strength of approximately 25-30%.

One of the main advantages of the hydrolysis process is the use of lower temperatures [7-11] to depolymerise the matrix, It has been reported that glass fibres can be recovered using supercritical solvents or water [7-8]. However, the hydrolysis process is a much more complex as it is a combination of both thermal and chemical reactions [11]. Considering that even exposure to 100% humidity for various times has been proved to have an impact on the breaking strength of glass fibres [3], there is no surprise that the thermo-chemical reaction induced in the hydrolysis process can damage the glass fibres recovered.

In this study, we show that using temperatures below the water critical point the recycled fibres can be successfully separated, with approximately 90% removal of the polyester resin. However, there was a significant drop in tensile strength (50-70%) depending on the processing parameters used.

2 Experimental

2.1 Hydrolysis process

Composite samples were prepared by the infusion process using polyester resin and cured at room temperature for 85 minutes. The reinforcement fabric used was E-Glass Advantex®, made of boron-free fibre glass of 17μm diameter, supplied by Owens Corning. The matrix system used in this study was unsaturated polyester resin (Synolite 84880-G) from DSM. The hydrolysis was performed in a 500ml non-stirred stainless steel reactor [11]. The heating was applied through an induction system where the temperature can reach 500°C. The hydrolysis process was carried out at various temperatures and pressures below the critical point of water, as listed in Table 1. The relationship of hydrolysis parameters to recovered fibre mechanical performance was investigated.

It should be noted that the ratio of the water volume to the composite mass was identical throughout the recycling trials. Several washing steps were applied to the samples using distilled water and solvents, such as acetone, for fibre separation after the hydrolysis reaction was completed. The recovered fibres were subsequently dried at ambient temperature before further characterisation of their quality. The percentage eliminated resin ($\%_{ER}$) was determined after washing and drying, using the following equation:

Table 1 Hydrolysis parameters with resulting eliminated resin

Recycling trials	Temperature (°C)	Time (minutes)	Eliminated resin ($\%_{ER}$)
GF-1	350	5	90%
GF-2	350	30	90%
GF-3	300	30	95%

$$\%_{ER} = \frac{(W_R - (W'_F - W_F))}{W_R} \times 100\% \qquad (1)$$

where W_R is the weight of resin before the process. W_F and W'_F are the weights of fibres before and after the process, respectively.

2.2 Scanning electron microscopy (SEM)

Surface characterisation on the recovered fibres was performed using a Hitachi S-3200N scanning electron microscope. Well-isolated single fibres were separately attached onto a carbon tape. A 4nm gold coating was given to each sample before SEM examination to avoid charging from electron beam. The x2000 magnification images of the fibres were recorded.

2.3 Micro-tensile testing

The mechanical testing of the recovered fibres followed ASTM D3379 - "Standard test method for tensile strength and Young's modulus for high-modulus single-filament materials".
Each sample was prepared by centring a single fibre in a window card containing a hole of 10mm gauge length in the middle. The ends of the fibre were glued using an epoxy resin, as in the schematic diagram (Fig. 1). The edges of the window card were burned away once the sample was successfully mounted on the tensile rig.
A tensile testing rig (200N micro-tensile stage manufactured by Deben Ltd.) was used to measure the mechanical properties of the fibres. The rig was positioned under an optical microscope stage to visualise the fibre during set up and testing. The alignment of the fibre was adjusted to the axis of the applied force before the tensile test. The tensile results were obtained with a 20N load cell and linear variable displacement transducer both connected to a computer. The tensile stress was applied at a speed rate of 0.2mm.min^{-1} until the fibre failed. 20 samples were tested for each hydrolysis trial and the mean values are presented here.

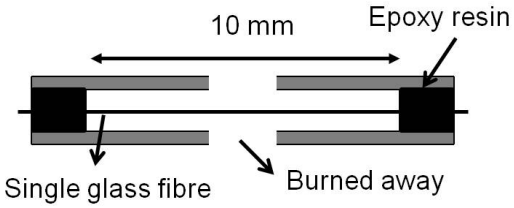
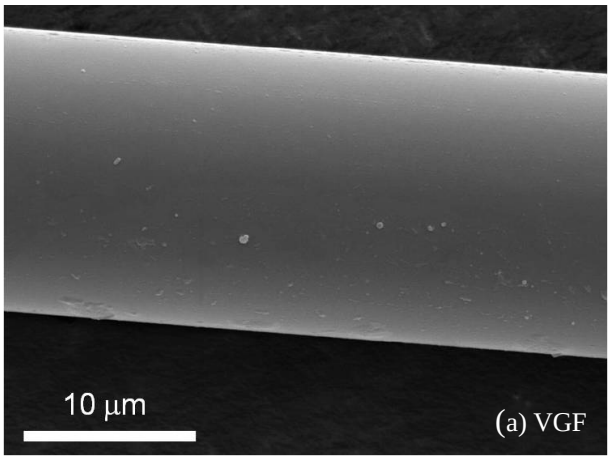


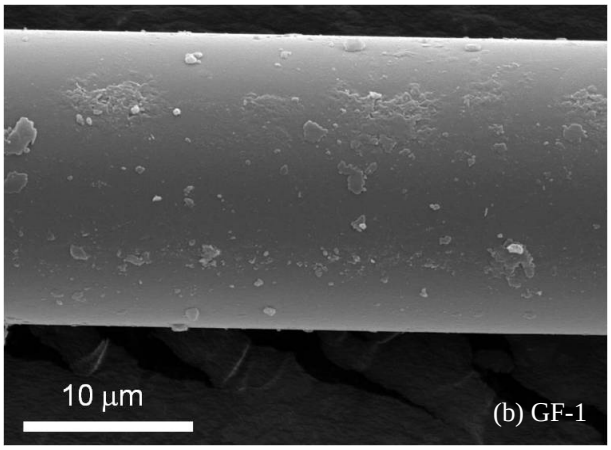
Fig. 1. Schematic diagram of tensile testing sample

3 Results and discussions

3.1 Surface characterisation of the fibres

SEM images of fibre surfaces after the hydrolysis process are shown in Fig. 2. Changes in temperature and time seem to have a significant effect on the cleanliness of the fibres. Lower temperature and longer time produce most clean fibres, an observation confirmed by the percentage of eliminated resin (Table 1). The yield of the eliminated resin and the resulting clean fibre surfaces were comparable with similar research studies on the hydrolysis recycling process using supercritical water [7]. It is interesting to note that under processing conditions (350°C; 30 minutes), the glass fibre surface (GF-2) retains a significant amount of degraded resin residues. This is perhaps surprising as higher temperatures and longer times might be envisaged to produce cleaner fibres. although with poorer mechanically properties. However, it may be that the fibres are actually clean and the rough surfaces observed on GF-2 samples are, in fact, due to corrosion. This is currently under investigation.





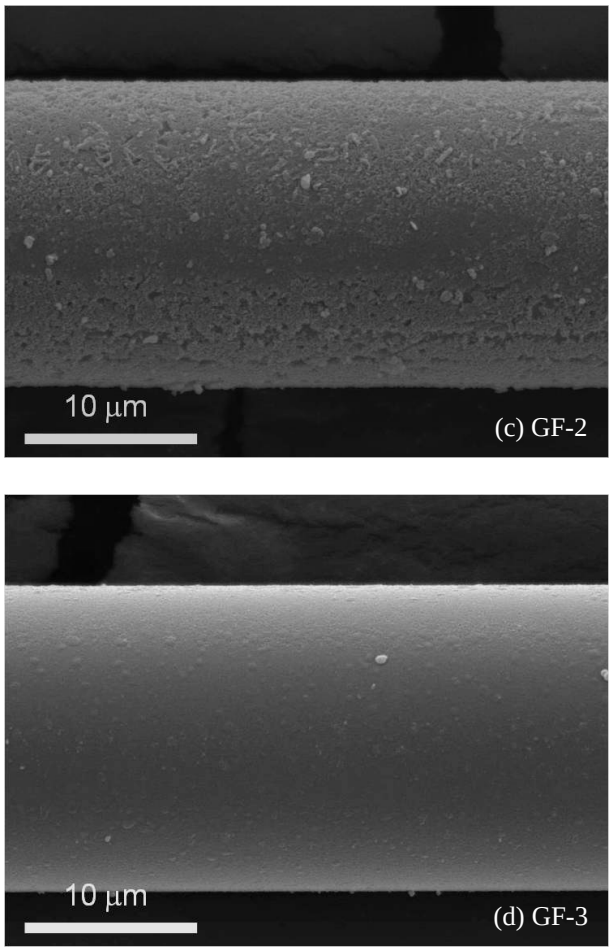


Fig. 2. SEM images of a single fibres including: (a) virgin glass fibre (VGF); (b) GF-1; (c) GF-2; and (d) GF-3

3.2 Mechanical properties of the fibres

The Young's moduli, tensile strength and failure strain of the virgin and recovered fibres are listed in Table 2 and shown in Fig. 3. In comparison with virgin fibres, the recovered fibres have similar Young's moduli while the tensile strength and failure strain recorded a significant drop, up to 70% in both cases.

Table 2 Mechanical properties of the virgin and recovered glass fibres

Recycling trials	Young's modulus (GPa)	Tensile strength (GPa)	Failure strain (%)
VGF	76.1±4.5	2.14±0.51	2.87±0.67
GF-1	73.2±3.9	0.75±0.20	1.02±0.20
GF-2	74.4±5.6	0.68±0.10	0.91±0.12
GF-3	74.4±9.6	1.04±0.31	1.41±0.39

3.3.1 Temperature effect

Table 3 shows the mechanical properties of the recovered fibres using different reaction temperatures. An increase of 50°C in temperature leads to a decrease of approximately 15-20% in fibre strength.

Previous studies on various heat treatments of glass fibres [3-5] revealed similar trends – higher temperatures and times lead to greater damage of the fibre. However, in most cases the drop was not as drastic as in the case of hydrolysis. For example, Thomas [3] has shown that fibres exposed at 350°C for 4 hours had an approximately 45% strength reduction. Furthermore, if fibres are heated at 550°C, the strength drops to 50% compared to the original fibres [4]. Thermal recycling of glass fibre composites using fluidised bed techniques [1-2] has been shown to lead to a drop in strength of 50% when the process is performed at 450°C. Reductions of 80% and 90% are obtained at 550 and 650°C, respectively.

Although the temperatures and times employed in the present hydrolysis process are significantly lower than the previous heat treatments discussed above, the drop in mechanical performance was significant. This is attributed to chemical effects induced during the hydrolysis process. The water ions will chemically attack not only the matrix but

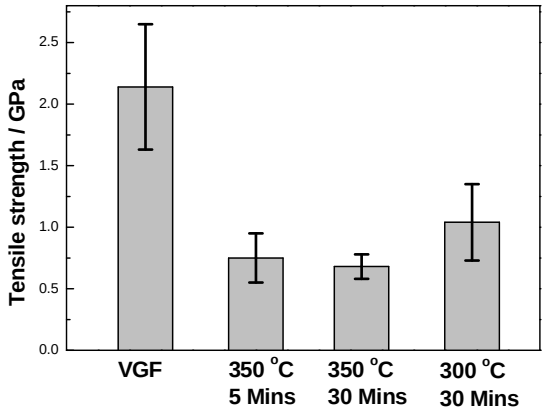


Fig. 3. Tensile strength of recovered fibres.

Table 3 Comparison of temperature effect on strength of the recovered fibre

Recycling trials	Temp. (°C)	Tensile strength (GPa)	Failure strain (%)
GF-2	350	0.68±0.10	0.91±0.12
GF-3	300	1.04±0.31	1.41±0.39

also the glass fibres. In the severe case of complete loss of sizing due to the hydrolysis process, the fibres are exposed even more to chemical and thermal damage.
Independent of the aqueous environment used for studying the degradation of glass (acidic, basic or neutral) [12-13], all investigations seem to agree that in the first instance the surface of glass dissolves in water, leading to leaching of ions and changes of the glass surface to different structures.

3.3.2 Reaction time effect
The relationship between fibre strength and reaction time was shown in Table 4. It was found that longer hydrolysis times (between 5 and 30 minutes) lead to approximately 10% drop in fibre strength. Between the two parameters studied, temperature and time, the processing temperature seems to be the dominant factor affecting the fibre strength (Fig. 3.). There is a fine balance to be achieved between these parameters as for lower temperatures and shorter times the separation of the fibres from the matrix may not be efficient, large bundles of fibres remaining clumped together within the matrix.
Previous investigations on purely the effect of the time of heating on the strength of glass fibres for various temperatures (150-600°C) showed that there is an initial rapid drop in strength in the first hour followed by a small decrease over the following three hours [3]. It could be that an increase in time in our case would not lead to any further variation than the one noticed currently up to 30 minutes of time.

Table 4 Comparison of reaction time effect on strength of the recovered fibre

Recycling trials	Time (Minutes)	Tensile strength (GPa)	Failure strain (%)
GF-1	5	0.75±0.20	1.02±0.20
GF-2	30	0.68±0.10	0.91±0.12

4 Conclusions

The glass fibre/polyester composites were recycled through a hydrolysis process using sub-critical water. The preservation of the fibre mechanical properties is greater when the hydrolysis reaction takes place at lower temperatures and for shorter times. The temperature was identified as the dominant factor weakening the fibre strength. The hydrolysis process is believed to be a much more complex process (thermo-chemical) than thermal or mechanical recycling processes, which subsequently leads to advanced fibre degradation.

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