ANALYSIS OF INTERFACIAL PROPERTIES OF SILANE RECOATED GLASS FIBRES RECOVERED FROM HYDROLYSIS PROCESSES

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Keywords: Recycling, Glass Fibres, Recoating, Hydrolysis

Abstract
This study investigates the effect of recycled glass fibre recoating, on the matrix-fibre interfacial properties. The studied fibres were recovered from glass fibre/polyester composites using a water based solvolysis process known also as hydrolysis. The silane coating distribution on the fibres was identified using Rhodamine B dye test. The interfacial properties were analysed by pull-out test. These results showed that the recoated recycled glass fibres have no significant improvement in interfacial bonding with polyester resin compared to simple recycled glass fibres.

1 Introduction
Previous works on recycling of thermoset composites for recovery and reuse of glass fibres have shown that recycled fibres exhibit much lower tensile and interfacial strengths than the virgin materials [1, 2]. Recycling processes via mechanical granulation, hydrolysis or fluidised bed methods demonstrated that glass fibres are affected by the mechanical manipulation, the use of high temperatures, of solvents and even just water [3]. Due to low fibre strength, the resulting composites produced with only recycled fibres are significantly inferior to those produced with virgin fibres. Up to date, the reuse of recycled glass fibres has therefore been limited to either replacing small amounts of virgin fibres [4] or incorporation as filler in composites [5].
When incorporating the recovered glass fibres into various matrices, enhancement of the bonding between the fibre and matrix is crucial and recoating of the recovered fibres should be explored. Under specific loads, the stress transfers across fibres through the fibre/matrix interface, therefore the mechanical properties of the ultimate composites depend on the morphology and structure of the interface bonding. Although it has been suggested by several studies that recycled glass fibres should be recoated to improve their performance, the effect of fibre recoating processes has not been fully explored and understood in detail. Depending on the recycling process employed, it has been shown that the surface of the recovered glass fibres can be smooth, clean and free of any silane coating, or it can be unevenly covered by resin [6] Previous studies [6] assumed that the resin left on the surface of the recovered glass fibres can act as a protective and chemically suitable coating, although uneven distribution of the resin coating on the fibres might not have the same effect as a smooth silane coating. In addition, any sizing acts also as a protective layer during handling and retains the fibre

strength [7]. A study by Zinck et al, [8] considered that the coupling agent and sizing treatments can recover surface defects, by diminishing separation as well as severity. This effect was associated to the creation of polysiloxane network on the glass surface which allows flaws healing. This is an important aspect when dealing with reclaimed glass fibres which have been found to have reduced mechanical properties [1, 2].
The present investigation used solvolysis process to recover glass fibres from thermoset composites. 98% of resin has been eliminated through the hot-pressured water reactor process. The recovered glass fibres were recoated using a silane agent and their interfacial properties to a fresh polyester resin were investigated.

2. Materials and Testing

2.1 Materials
The recovered glass fibres were taken from a tri-layer composite sheet, which consisted of 30.73% resin by weight. The resin used was Synolite 8488-G-2 developed by DSM©. The reinforcement was a multi-axial E-glass fabric (+45°/90/-45/0°) supplied by AHLSTROM. The composite curing was carried out at room temperature for approximately 92 minutes without any further post-curing.

2.2 Hydrolysis process
40×40mm composite samples were cut for hydrolysis process. The reaction was performed in a non-stirred lab-scale stainless steel hydrolysis reactor (500ml volume) by Institut Catholique d'Arts et Métiers (ICAM) [9]. The heating was carried out by an induction system and the cooling was implemented using compressed air circulation. The hydrolysis was carried out at a temperature of 300°C for 30 min using a ratio mass of 0.05 composite to volume of distilled water (g/ml).

2.3 Resizing Process
The recovered glass fibres were coated with a silane agent and are referred to in the text as recoated glass fibres. The silane coating agent used in this study was Silquest* A-174NT Silane supplied by ACC Silicones Ltd, a methacryloxy functional trimethoxy-silane typically used for SMC and DMC glass fibres and polyester applications. The silane required activation via an acidic reaction. Distilled water at pH 3.4 was mixed with the A-174 Silane (20% by weight) and the solution was left for 2.5 hours to hydrolyse. A bundle of recycled fibres were added to the solution (approximately 0.5g) for 20 minutes. Subsequently, the fibres were washed with 10ml of ethanol and dried at room temperature for at least 24 hours.

2.4 Silane coating identification
In order to check the presence of silane coating on the recovered glass fibres, 0.1g rhodamine B was added to 100ml ethanol and used as a drop test solution on the bundle of the coated fibres. The presence of red spots on the surface of the coated fibres after immediately washing the fibres with hot water, indicates that vinylsilane or methacrylsilane is present and therefore a successful coating [10]. The recoated glass fibres were dried for 24h prior to any further testing.

2.5 Scanning Electron Microscopy (SEM)
Surface characterisation of the virgin, recyclate and recoated glass fibres was performed using a Hitachi S-3200N scanning electron microscope. Single fibres were coated with 4nm gold coating to avoid charging from the electron beam.

2.6 Pull-out Test

The fibre pull-out tests were prepared using a specially designed rig as shown in Figure 1 (a). The rig allowed preparation of 20 single fibres. Each glass fibre was held in place by a needle. The needle was placed over the silicone mold, which was filled with a polyester resin. The samples were cured and prepared for testing by attaching each resin block and fibre to a card support with superglue on either side of the resin block and epoxy fixing the fibre to the card, shown in Figure 1 (b). The freestanding length used was 2mm to enhance pull-out effect and avoid fibre breaking.

The specimen was then inserted into customised jaws on a 200N Deben micro-tensile stage equipped with a 20N load cell. Once the pull-out samples were successfully mounted in the instrument and the fibre was adjusted to align with the force axis, the sides of the window card were burnt away leaving the fibre suspended between the jaws. The crosshead speed for testing was set to 0.2 mm/min

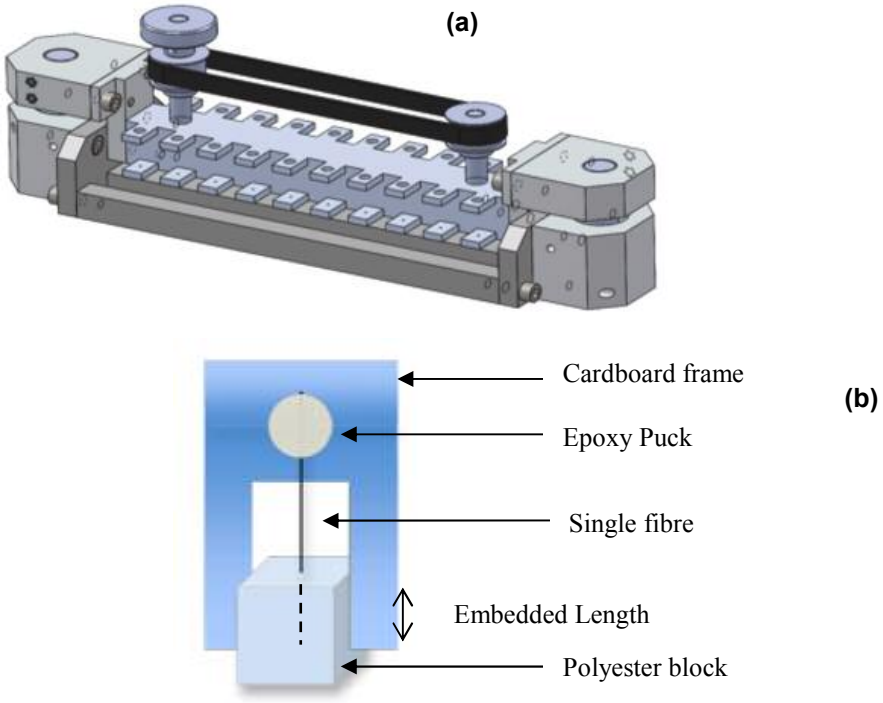


Figure 1. (a) Schematic diagram of the pull out set up- multiple sample preparation; **(b)** single fibre pull out set up

3 Results and Discussion

3.1 Silane detection

Figure 2 presents optical images of a bundle of recycled glass fibres before (a) and after application of Rhodamine dye (b, c). The presence of the strong red colour on the glass fibres after silane coating, application of Rhodamine solution in Figure 2(b) and hot water washing in **Figure 2(c)** indicates a successful recoating process.

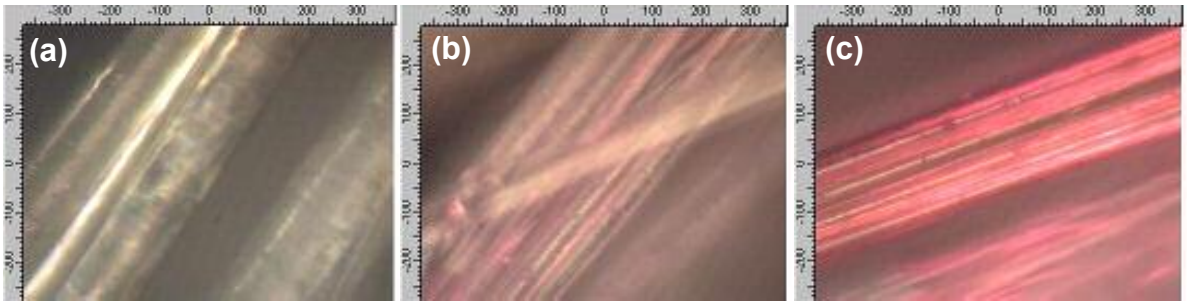


Figure 2. Silane coating identification (a) Silane coated (no Rhodamine solution applied) (b) silane coated (Rhodamine applied) (c) Silane coating (hot water washed)

3.2 Scanning Electron Microscopy results

Figure 3 shows the SEM images of (a) virgin; (b) recycled and (c) recoated recycled glass fibres. The recycled fibres show presence of significant resin residue along the length of the fibre, although it is not as smooth and evenly distributed as the virgin fibres. The recoated recycled glass fibres seem to give an improved coating, with no sign of patchy resin rich regions, the silane solutions coating well the entire glass fibre surface.

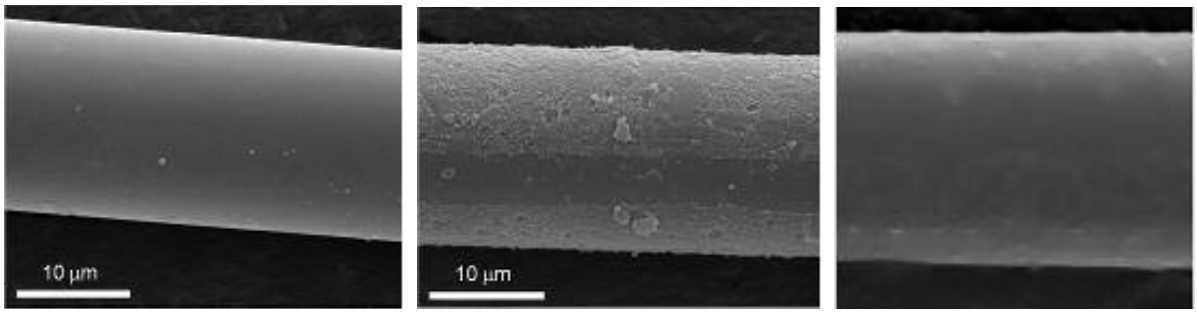
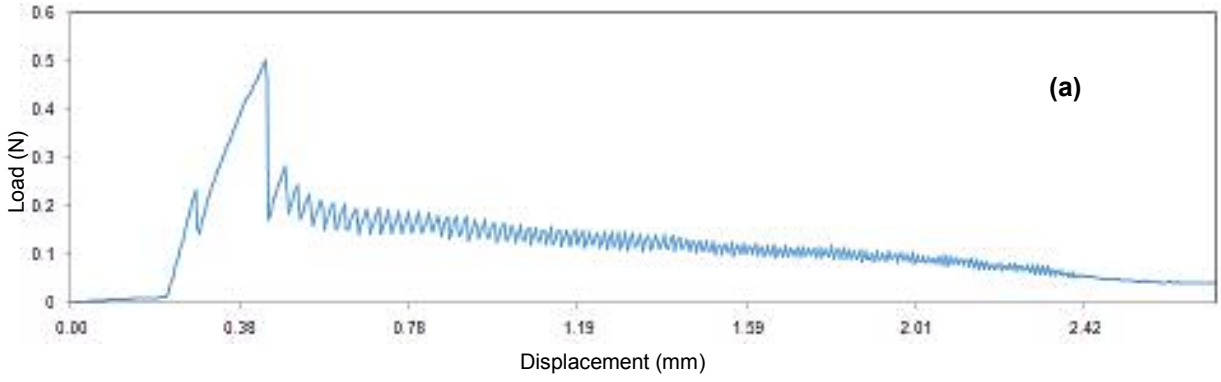


Figure 3. SEM images of (a) virgin, (b) recycled, (c) recoated recycled glass fibres

3.3 Pull-out testing

Figure 4 presents typical load-displacement pull-out curves of virgin and recovered glass fibres. Virgin and recycled fibres pull-out tests were characterized mostly by the type II and III failure modes. These failure modes are common to systems with a weaker fibre-matrix interface and longer embedded fibre length. Type II has a stable debonding process along with frictional resistance, followed by the decrease in load as the fibre is progressively extracted out of the matrix. Type III has been also noticed and it is characterised by a "stick-slip" effect after the initial debonding process, until maximum load is achieved followed by a drop in load with possible frictional resistance.



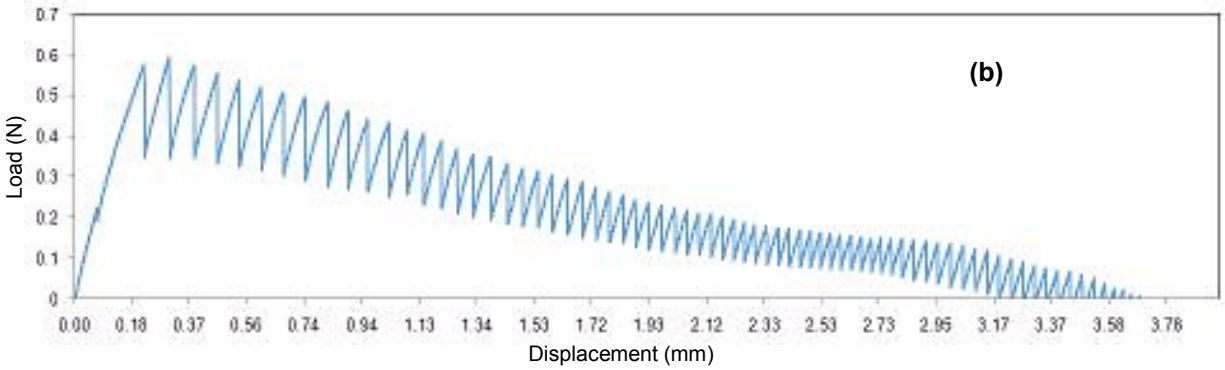


Figure 4. Load –displacement pull-out tests of (a) virgin and (b) recovered glass fibres

Figure 5 and **Figure 6** present the results of successful pull-out and failed pull-out (broken fibres) tests, respectively. The recycled fibres presented a low number of successful pull-out tests, most fibres braking during the pull-out test (see **Figure 5**). In the case of the recoated glass fibres, it was not possible to collect any pull out data. Similar to the recycled fibres, the recoated fibres had a tendency to break prior to any successful pull-out.

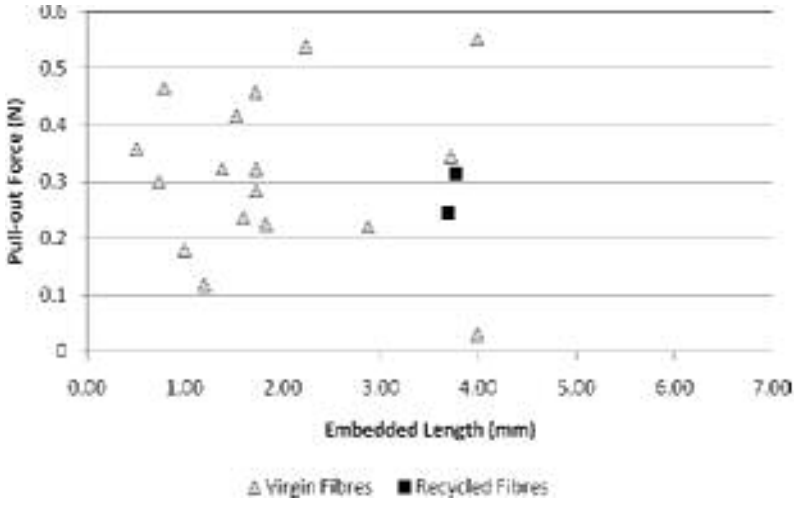


Figure 5. Successful pull-out tests

Although more tests are required to better highlight the trends, it can also be noticed in **Figure 5** that virgin fibres show an increase in the de-bond force with an increase in the embedded length as expected in conventional pull-out, whereas the de-bond force for the recycled fibres remains within a lower load range (0.2-03N). This was previously noticed by James et al, [2], where the de-bonding force of the mechanically recycled fibres was approximately half of the virgin ones.

The lack of successful recoated fibre pull-outs and the low number of successful recycled fibre pull-outs suggests in the first instance a good interfacial bonding between the recycled or recoated fibres and the polyester matrix. However, the analysis of the unsuccessful pull-out samples (broken fibres) in **Figure 6**, lead to the conclusion that the recoated glass fibres are still extremely fragile and break before any attempt of pull-out. The virgin fibres are predominantly stronger but seem to have a weaker fibre-matrix bonding that the recyclate and recoated glass fibres.

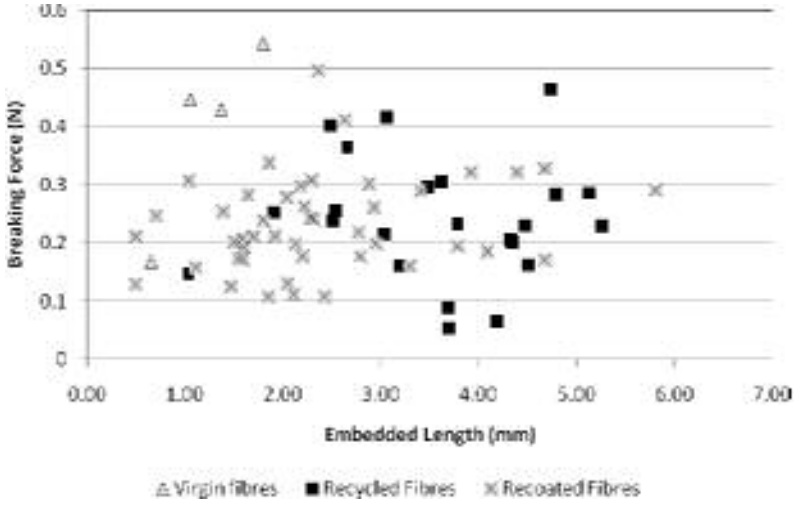


Figure 6. Broken fibres during pull-out testing

Results in **Figure 6** show a slightly higher breaking force for the recoated glass fibres. It is possible that the additional recoating process improved the fibre-matrix bonding and slightly improved the strength of the recoated glass fibres but not sufficiently. The reduction in fibre strength which subsequently leads to fibre failure remains the prominent effect in the case of the recycled and recoated glass fibres.
Considering that in all cases the tensile strength of the recycled or recoated glass fibre has been found lower than the virgin fibres, it is extremely difficult to draw clear conclusions on the effect the remaining resin or silane agent might have on recovered glass fibres and whether these coatings can "reactivate" the fibre surface for enhanced interfacial bonding.

4 Conclusions

The pull-out results presented in this study show that the recoated glass fibres obtained through a hydrolysis recycling process are not significantly improved in interfacial strength in comparison with simple recovered glass fibres and their reuse in composite is unlikely to lead to higher mechanical performance. Although the recoated glass fibres seems to break at slightly higher force, considered a sign of possible fibre strength improvement, their properties are still significantly inferior to the virgin fibres. Unless the strength of the reclaimed fibres can be maintained throughout the recycling process to values comparable with virgin glass fibres, resizing of recovered fibres does not bring significant benefits for their reuse.

Acknowledgements

The study is part of European project: EURECOMP - Recycling Thermoset Composites for Surface Sustainable Transport (SST). The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 218609 (EURECOMP).

References

[1] Pickering S.J., Recycling technologies for thermoset composite materials – current status. *Journal of Composites Part A.* 37, 8. p.1206-1215 (2006)
[2] Palmer J., O.R. Ghita, L. Savage, K.E. Evans, Recyclate fibres –matrix interface analysis for reuse in sheet moulding compounds (SMC) – *ECCM13 Proceedings*, Stockholm, (2008)

[3] Brown E.N., Davis A.K., Jonnalagadda K.D., Sottos N.R., Effect of surface treatment on the hydrolytic stability of E-glass fiber bundle tensile strength, *Composites Science and Technology* 65, 129–136 (2005)
[4] J. Palmer, O.R. Ghita, L. Savage, K.E. Evans, Successful closed-loop recycling of thermoset composites. *Composites Part A: Applied science and manufacturing*, 40, 4. p.490-498, (2009)
[5] Petterson J., Nilsson P., "Recycling of SMC and BMC in Standard Process Equipment", *Journal of thermoplastics Composite Materials*, 7: p.56-63 (1994)
[6] C.C. Kao, O.R. Ghita, K.R. Hallam, Mechanical studies of single glass fibres recycled from hydrolysis process using sub-critical water, *Journal of Composites Part A*. 43, 3. p.398-406 (2012)
[7] Reilly S.P., Thomason J.L, Effects of silane coating on the properties of glass fibre and glass fibre reinforced epoxy resin, *ECCM14 Proceedings,* Budapest, 2010
[8] P. Zinck, E. Maeder, J.F. Gerard, Role of Silane coupling agent and polymeric film former for tailoring glass fibre sizings from tensile strength measurements, *Journal of Mechanical Science*, 36, 21. p. 5245-5252 (2001)
[9] G. Oliveux, E. Le Gal La Salle, J.L. Bailleu, Recycling by solvolysis thermosetting composite materials of sustainable surface transport, *AIP Conf Proc*, 1315, p. 209 (2011)
[10] www.momentive.com – "Detection of Silane Coupling Agents on Treated Fillers and Fibres".