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Published in:

Proceedings of the 20th International Conference on Composite Materials

Publication date:

2015

Document Version

Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):

Beauson, J., Fraisse, A., Toncelli, C., Bech, J. I., & Brøndsted, P. (2015). Thermoset composite recycling: Properties of recovered glass fiber. In *Proceedings of the 20th International Conference on Composite Materials ICCM20 Secretariat*.

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THERMOSET COMPOSITE RECYCLING: PROPERTIES OF RECOVERED GLASS FIBER

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Keywords: Recycling, Thermoset composite, Glass fibers properties

ABSTRACT

Recycling of glass fiber thermoset polymer composite is a challenging topic and a process able to recover the glass fibers original properties in a limited cost is still under investigation. This paper focuses on the recycling technique separating the glass fiber from the matrix material. Four different recycling processes, mechanical, burn off, pyrolysis and glycolysis are selected and compared based on the properties of the glass fiber recovered. The intention is to use the same characterization methodology.

1 INTRODUCTION

The recycling of wind turbines has become a concern over the past decades, with the growth of the wind energy sector [1], [2]. While most of the component made of steel, aluminum and other metallic materials are considered as recyclable, the composite materials found in the WT blades have no established recycling route [3]. In this context, the national consortium GenVind (2012-2016) aims to identify end of life solutions for WT blade and other reinforced polymer composite material. The project includes a large number of industrial partners, such as wind turbine and blade manufacturers, specialists in cutting and recycling, and other potential reuser [4]. The project also includes 3 universities and 2 GTS institutions.

The composites found in wind turbine blades are generally made of thermoset matrix, epoxy, polyester or vinyl ester, reinforced with E-glass fibers. Part of the blade, the shells and the shear webs, see Fig. 1, consists of sandwich laminates. These are built as uniaxial or multi-axial glass fiber laminates with balsa wood or polyvinyl chloride (PVC) foam as core material. The load carrying beam, the trailing edge and the leading edge are made of unidirectional (UD) glass fiber laminates. Surfaces are protected using gel coats, polyurethanes. Thermoplastic foils or special paints are used on leading edges [5].

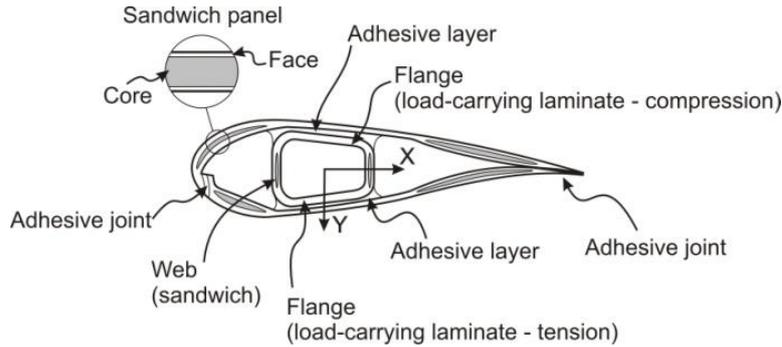


Figure 1. Cross section of a blade [6]

The possible end of life scenarios existing for these composite materials can be compared on the amount of re-processing needed. Solutions involving few or no re-processing of the WT blade have limited field of application. In this case, the WT blade can be refurbished and its service life extended. The WT blades can also, with few modifications, be used as urban installations, see the pictures in Fig. 2.



Figure 2. Urban installations in the Netherlands by Superuse Studios [7]

Solutions involving heavier re-processing of the WT blade are more costly, but also expand the number of possible applications for the recovered material. Separating the glass fiber from the matrix and reusing the glass fiber, is one of these solutions, which open to many reuse possibilities. Extracting glass fiber from thermoset polymer composite has been studied for many years and techniques using mechanical processes, thermal and/or chemical treatment have been developed [8]–[15]. However, the recovered glass fibers were, in all cases, found to have a lower tensile strength than their pristine counterparts. The loss in tensile strength is reported to vary from 17% to 93% [16]. The smallest loss is recorded for the glass fiber recovered with mechanical process.

Nevertheless, single fiber testing of recovered glass fiber can be quite challenging. These results have been collected from studies using different testing methodologies. The various amount of handling needed in these procedures and the different ways of performing the test can/will influence the results.

As a part of the GenVind project, this paper focuses on the processes enabling the separation of the fibers from the matrix. Glass fibers will be extracted from thermoset polymer composite using different techniques. The objective is to compare these recycling techniques by characterizing the recovered glass fiber properties with the same methodology.

2 EXPERIMENTAL PROCEDURE

The four recovery processes used in this study are burn off, pyrolysis, shredding and glycolysis. The latter one, which cannot be used with all thermoset polymers, is included here for comparison as it uses significantly lower temperature than the two other thermal processes.

2.1 Material and specimen preparation

The material for the burn off, the pyrolysis and the shredding is a glass fiber thermoset composites cut out from the load carrying beam of a LM25,8 wind turbine blade. This composite is made of E-glass fibers and a polyester matrix. The fiber volume fraction is around 70 wt%. For the burn off and the pyrolysis experiments, specimens of 100mm long and 15mm wide are cut out through the whole thickness of the composite laminate. For the shredding, a Bolen Super Tomahawk shredder is used with the settings: “Main Frame Screen” and 20 mm hole. A reference E-glass fibers like the ones used in wind turbine blade manufacturing is also selected to compare the results and will be named “Reference E-glass” in the results.

The composite material for the glycolysis experiment is made of a polyurethane matrix reinforced with E-glass fibers. The fiber volume fraction is around 70 wt%. The glass fibers contained in this composite are also tested as new and will be named “Reference Glycolysis”.

2.2 Heat treatment and glycolysis

The burn-off experiments are performed at 350 °C, 400 °C and 450 °C in a furnace with air environment. For these experiments, the furnace is first heated to the needed temperature. Then the specimen placed in a clean and annealed crucible is introduced in the furnace. After the wanted period of time, the crucible is taken out and placed in a desiccator for cooling down. The duration of the heat treatment for each temperature is presented in Table 1.

The pyrolysis experiment is conducted at 450 °C in a furnace with a controlled nitrogen environment. In this case the furnace is first heated up to 450 °C, the crucible with the composite is placed in the furnace and the furnace volume is flushed with nitrogen for 1 min with a flow of 500L/hour. Thereafter the flow is reduced to 100L/hour for the remaining period of time.

Temperature	Air Environment	Nitrogen Environment
450 °C	2 hours	2 hours
400 °C	2 hours	-
350 °C	5 hours	-

Table 1: Overview of the heat treatment

The glycolysis is conducted using a diethylene glycol heated up to 180°C. The composite is left in the solution for 2 hours. Then, it is cooled down to 130°C and Epilox is added to deactivate the isocyanate. Fibers are cleaned with isopropanol.

2.3 Microscopy

A bundle of glass fiber is prepared for scanning electron microscopy. The bundle is stuck on a carbon taped and carbon coated using a BALTEC SCD 005 sputter coater. The observations are performed using a table top microscope Hitachi TM1000.

2.4 Single fiber testing

The tensile test is performed using a single fiber testing machine from Textechno, the Favimat combined with the airobot2. First, the GF linear density is measured using a vibroscopic test. The GF is excited using acoustic wave to a resonance oscillation under the given gauge length L and a known tension F [17]. The method follows the standard ISO 19732. The equation used to derive the linear

density is:

$$f = \frac{1}{2L} \cdot \sqrt{\frac{F}{T}} \cdot \left(1 + \frac{r^2 \cdot E}{[L \cdot F]} \right) \quad (1)$$

, where f is the resonance frequency of the fiber, L the gauge length, T the linear density of the fiber, r the radius of the fiber, E the E modulus of the fiber and F the pre-tensioning force applied on the fiber. If the gauge length is long enough and the pre-tensioning force high enough, then the term dependent on the E-modulus and the radius of the fiber can be neglected.

When the linear density is known then the cross section of the fibers is deducted using the equivalence:

$$A = \frac{T}{\rho} \quad (2)$$

In the end, the tensile test is performed and the E-modulus is calculated using the cross section of the fiber.

At least 30 glass fibers are tested with a gauge length of 50 mm for the fibers recovered using burn off, pyrolysis and glycolysis as well as for the pristine glass fiber. For the mechanically recovered fibers, at least 30 glass fibers are tested with a gauge length of 20 mm. The test speed for all tests is 1mm/min.

3 RESULTS

3.1 Recovery processes

The fibers recovered using the burn off procedure, are shown in Fig. 3. The combustion of the composite specimen is not complete for the treatment temperature 400°C and 350°C and the remaining glass fibers are black, see Fig. 3 b) and c). The composite burnt at 450°C and the composite undergoing the pyrolysis, left white fibers as shown in Fig. 3 a).



Figure 3: a) 2 hours at 450°C, b) 2 hours at 400°C, c) 5 hours at 350°C

The fibers recovered using shredding, are shown in Fig. 4 a). The shredded composite is a mixture of long blocks of fibers, very short fibers and agglomerated short fibers forming clusters. Unfortunately, it was not possible to separate long glass fibers from the blocks of fibers. Only very short fibers of around 10-15mm could be separated and these cannot be tested properly using the testing technique presented in the precedent part.

The fibers recovered using glycolysis, are shown in Fig. 4 c). The fibers are white, but not shiny like the one of the burn off.



Figure 4: a) Shredded composite, b) Fiber blocks from shredded composite, c) Glass fibers recovered with glycolysis

3.2 Microscopy

The glass fiber recovered using burn off at 450 °C, pyrolysis and glycolysis were found to be clean and their surface aspect was observed to be similar. The images presented in Fig. 5 are the one taken from the glass fiber recovered using burn off at 450 °C. The images also indicate the brittleness of these fibers.

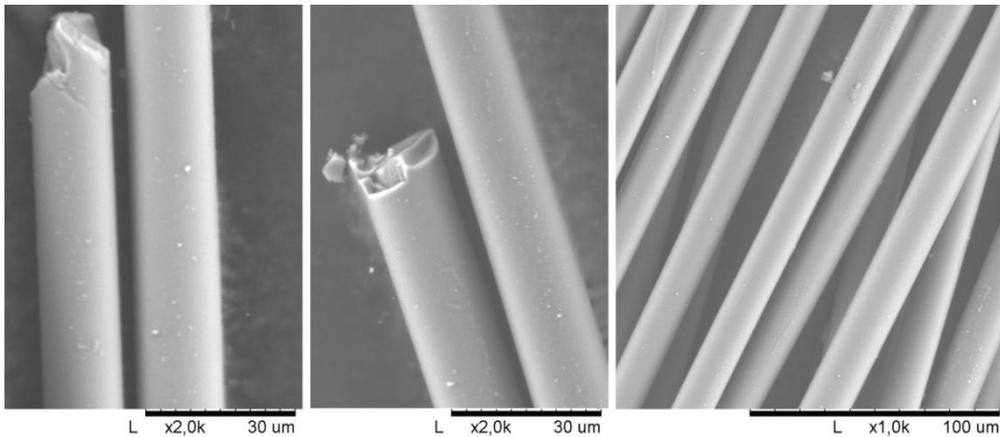


Figure 5: Scanning electron microscopy images of recovered glass fibers using burn off 450°C

Due to the incomplete combustion of the matrix material, the glass fibers recovered using burn off at 350 °C and 400 °C were found to be greyish. The fibers shown in Fig. 6 are the ones recovered using burn off at 350 °C. The microscopy images show some loose matrix material fragments. It seems that some of these fragments are still bonded to the surface of the fibers.

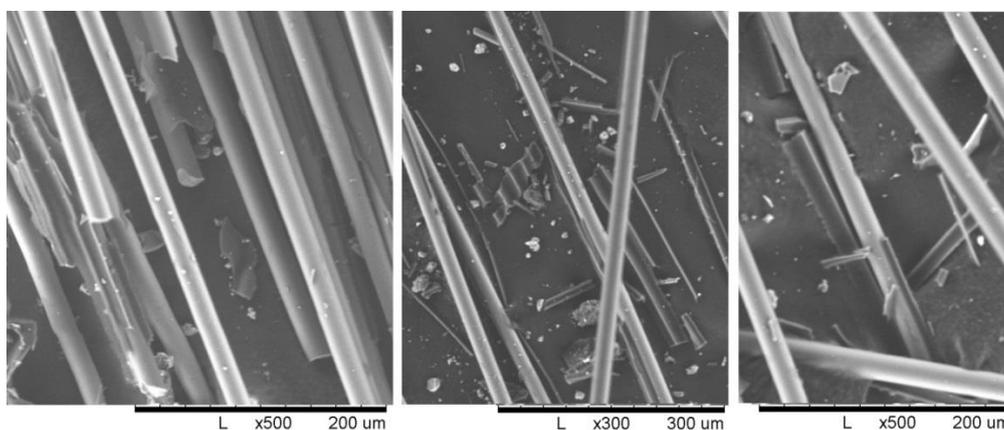


Figure 6: Scanning electron microscopy images of recovered glass fibers using burn off 350°C

The mechanically recovered glass fibers are shown in Fig. 7. Loose matrix material fragments and bonded to the fiber surface can be seen as well as stitching filament.

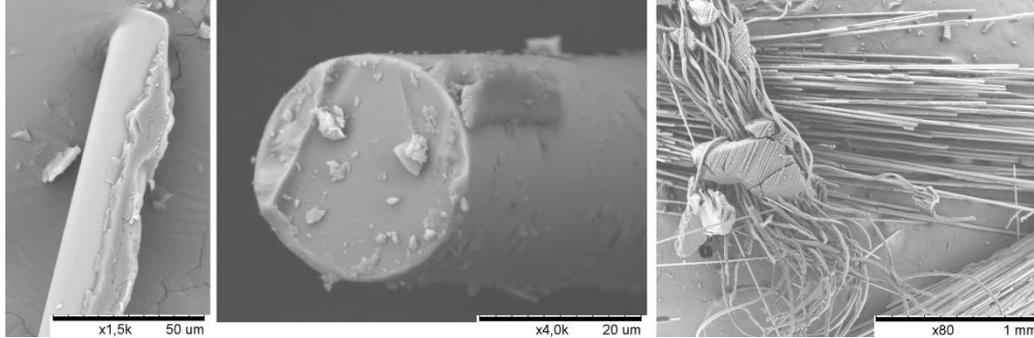


Figure 7: Scanning electron microscopy images of recovered glass fibers using shredding

3.3 Single fiber testing

The results for the single fiber testing are summarized in Table 2 and presented in Fig. 8. The results indicate that the recovery processes used in this study strongly impact the average glass fiber tensile strength, while the fiber modulus remains unaffected or increased.

The average tensile strength of the recovered glass fibers, shown in Fig. 8 a), are reduced by 40 % at least compared to their pristine counterpart. The impact of heat treatment on the average glass fiber tensile strength has been in deep studied and explained elsewhere [18], [19]. The reasons for the loss of strength are believed to be a combination of the removal of the protective silane layer from the fiber surface and some fundamental changes in the glass itself [20]. Studies also reported that the strength of silane sized glass fiber is relatively stable for temperature below 250°C.

The average tensile strength of the fibers recovered using glycolysis shows a 47% decrease compared to their pristine counterpart. The temperature used in this process is lower than 250°C and significantly lower than the ones used for the burn off and the pyrolysis experiments. Therefore, one could expect a higher tensile strength.

Regarding the modulus, it has been reported that the increase in the E-glass fiber modulus is related to a change in the density of the glass due to densification [20]. This is not observed for the recovered fibers using glycolysis.

Type of fiber	Treatment Characteristics	Gauge Length (mm)	Diameter (μm)	Tensile Strength (GPa)	E-Modulus (GPa)
Mechanical	-	20	-	-	-
Reference E-glass	None	50	17,05 ± 2,44	2,07 ± 0,44	76,71 ± 0,78
Burn off	350 °C – 5 hours	50	16,31 ± 1,23	1,28 ± 0,23	78,14 ± 0,81
	400 °C – 2 hours		18,21 ± 1,36	0,86 ± 0,32	78,98 ± 0,76
	450 °C – 2 hours		16,99 ± 1,51	0,99 ± 0,30	80,21 ± 0,38
Pyrolysis	450 °C – 2 hours	50	18,27 ± 1,73	1,02 ± 0,23	79,39 ± 0,53
Reference Glycolysis	None	50	23,02 ± 2,28	1,85 ± 0,43	76,60 ± 0,85

Glycolysis	180 °C – 2 hours	50	21,34 ± 1,56	0,99 ± 0,34	76,59 ± 0,61
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Table 2: Average tensile strength and modulus of the recovered and pristine glass fibers

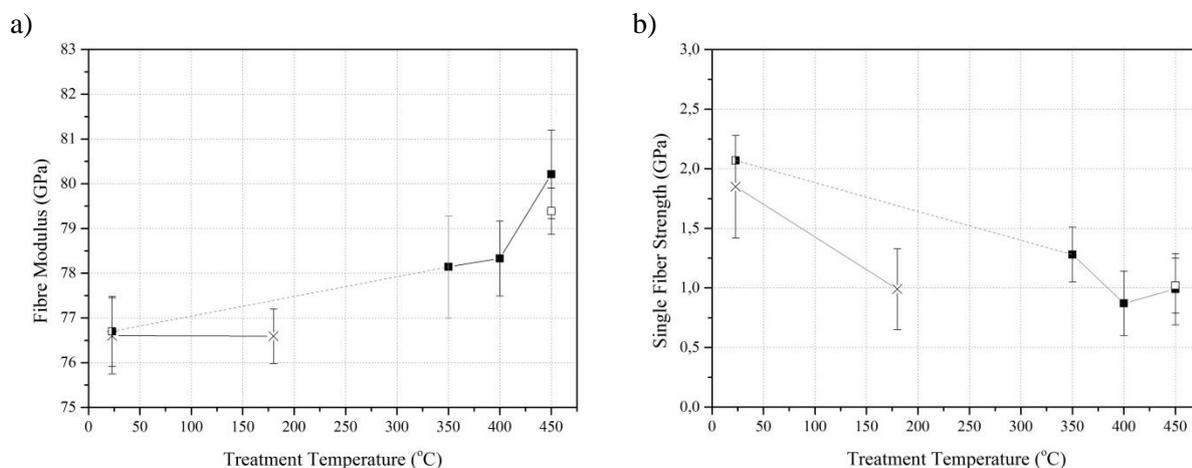


Figure 8: a) Average fiber strength of recovered and pristine glass fibers, b) Average fiber modulus of recovered and pristine glass fibers (■ Burn off, □ Pyrolysis, × Reference Glycolysis and Glycolysis, ■ Reference E-glass)

4 DISCUSSION

The glass fibers recovered in this study were all tested using the same methodology.

Pristine E-glass fibers are not expensive. Therefore, to become an interesting value/product, the recovered glass fibers should at least maintain their original properties. The tensile strength of the recovered glass fiber is strongly influenced by the temperature of the recycling process. The results indicate, in accordance with the rest of the literature, that the lower the temperature of the recycling process, the higher the strength of the recovered glass fibers. Nevertheless, the presence of a solvent such as the one used in the glycolysis seems to be an aggravating factor.

A low temperature process, beneficial for the strength of the fibers, can be challenging. Indeed, for the burn off and the pyrolysis, the combustion is incomplete for temperatures below 400 °C and the fibers were found not to be clean. This can be an issue, if the fibers are to be reused in new polymer composite for example. The clean fibers obtained in this study had low strength.

Regarding the temperature and the duration of the treatment, the most efficient process is the glycolysis with the lowest temperature and the shortest time. The burn off at 350 °C needed more time than the two other burns off experiments and the combustion of the matrix material would still not be complete.

5 CONCLUSION

None of the recycling process investigated in this study led to recovered glass fibers having satisfying properties. Either the cleanliness or the strength of the fibers had to be compromise. As a part of the GenVind project, another recycling process using supercritical fluids is also under investigation. The aim is to optimize a process in order to get clean and strong fibers. The cost is also a concern and the aim is to lower the temperature and limit the duration of the process as much as possible. The fibers using supercritical will then be characterized using the same methodology as presented in this study. If these fibers are interesting, then the next step will be to manufacture a polymer composite plate.

ACKNOWLEDGEMENTS

GenVind consortium has been supported by The Danish Council for Technology and Innovation under the Ministry of Science, Innovation and Higher Education.

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