SOLVOLYSIS OF THE END-OF-LIFE COMPOSITE WASTES FOR GLASS AND CARBON FIBERS RECOVERY

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Keywords: Solvolysis, Composite waste, Recycling, Glass fibers, Carbon fibers, Resins

ABSTRACT

Efficient recovery of carbon and glass fibers from large-size composite materials used in wind energy construction, end-of-life aircraft structures, etc. is a current technological problem. In order to identify the possibility of recovering these fibers, preliminary laboratory tests of batch low-pressure solvolysis process were carried out. The technical possibilities of controlling the solvolysis effectiveness and its time-course were verified by NMR analysis of the process solution. The structure of glass fibers and carbon fibers (SEM) recovered after batch solvolysis and their elemental chemical composition (EDS) were identified. Based on the results of preliminary research, basic recommendations regarding the technological concept of the process of fiber recovery from large-size composite materials are given.

1 INTRODUCTION

According to the European Union (EU) Waste Framework Directive hierarchy, the disposal of waste without recovery of any form of its energetic or material potential should be avoided. Nowadays, one of the biggest challenges of the waste management sector is the incoming supply of large composite wastes (LCWs) from end-of-life wind turbines, decommissioned aircraft, and storage tanks – all similar in structure. The recycling of the LCWs should be aimed to recover and reverse as much of the materials and substances back to the cyclic use, to not deepen the already environmentally intense cost of its manufacturing. Among the recycling methods for the LCWs, the most popular are mechanical and thermochemical (pyrolysis) processing, with numerous highlights on the importance of the development of chemical recycling methods [1-7]. The authors of this article are of the opinion that depending on the type of waste (LCWs), economic, technological and environmental conditions, many recycling technologies should be considered each time, both material and chemical, as well as thermal ones. One of the conversion methods that ensures the recovery of composite fibers is chemical recycling, represented by e.g. the solvolysis process. The paper presents some results of experimental investigation on the correlation between LCW composite structure and its solvolysis processing. Two representative samples of composite wastes *i.e.*, carbon fiber (CF), and glass fiber (GF) reinforced composites were considered. The solvolysis process was tested as the potentially advantageous, effective recycling method to recover the continuous fibers from the polymer resins matrix.

The biggest technical problem of wind energy sector is economic utilization or recycling of post-exploitation composite elements of large wind turbines. The reason is the common use of composite structural materials based on glass and/or carbon fiber in the main structural elements of wind turbines. These specific, modern materials are not easy to recycle due to the strong bond between fiber and resin fractions, thus the difficulty of separating them – especially fiber fraction – for reuse in

production. Over the years, many different technical designs of wind turbines, of various construction details, size and, the most important, made of various combinations of composite fractions were manufactured. The main division into composites based on resins and the type of fibers (carbon / glass ones) does not allow for the optimization of chemical recycling processes. Each specific composition, premix prepared by each manufacturer is its trade know-how. Each dedicated composition may differ in the type and amount of admixtures and modifiers, as well as functional additives of different properties. Moreover, it is characterized by a different course and sequence of cross-linking processes, additionally with subsequent impact of climate factors. Seasonally changing conditions of use and specific resistance to climatic conditions (chemical and physical resistance) significantly affect the degree of wear or material corrosion. Already at the design stage of the composite structure, the environment of future operation should be taken into account. The properties of elements working in coastal zones (chemical resistance to salinity) are different than in deserts (physical resistance, e.g. to intense solar UV radiation). In addition, the change in the material properties used for the production of turbine composite element also depends on changes resulting from the development of engineering knowledge applied in manufacturing techniques. Important may be also the place of production of turbines, manufacturer and the time of their production. An example may be the changes resulting from the EU Directive limiting the use of halogen flame retardants, which is why over time manufacturers have been looking for some effective alternatives and substitute materials. Therefore, the change in the regulations on the use of halogen-free flame retardants affects the chemical composition of the composite material and its structure. This directly affects the dissolution, pulping, digestion and accompanying chemical decomposition processes, as well as the chemical composition of the products of the chemical recycling alternatives. The problems of post-exploitation development of dismantled large in size wind turbine elements (windmill wings) will raise more and more emotions in the nearest years.

According to the literature [1-8] , it can be assumed that there is about 10 tons of waste per 1 MW of installed capacity in wind farms. It is estimated, that composite materials represent over 90% of this mass – of which the vast majority (95 – 98%) are composite materials based on glass fiber.

The basic technical and technological problems to a current and possibly urgent solution is the identification of optimal technological routes for optimizing the recovery of substrates and fibers based on the economic viability of recycling to find a stable market for glass fibers and other, possibly valuable conversion products. One aspect that hinders this process of recovering fibers from composites is the sheer cost of virgin glass fiber – it is cheap. It makes it simply not profitable for end users to buy recycled fiber, which they perceive as inferior and with unstable parameters. Today there is no available fully commercial technology for the method of recovering glass fiber from wind turbines that would recover fiber cheaper than new. Due to the size of the turbines in the material recycling process, so far we have integrated elements of mechanical recycling (cutting and shredding) and chemical dissolving and/or pulping (digestion). Due to the mechanical properties of glass, the glass fiber itself does not tolerate the mechanical/material recycling process and during such processes it loses a significant part of its strength properties, usually due to damage to its structure.

The authors concluded that the reduction of potential mechanical processes will allow for a statistical increase in the average strength of the recovered fibers.

In the presented study, the authors attempted to recover the fiber from the composite using a dedicated chemical bath process – solvolysis – so as not to cause loss of the original structural and mechanical properties of the fibers. This approach was dictated by the problem of a widespread decrease in the strength properties of recycled fibers, noticed in the literature.

2 MATERIALS AND METHODS

2.1 Materials

In order to systematize the results of the solvolysis process for composite samples similar to those from which wind turbine elements based on resin(s) and glass / carbon fibers are made, it was decided to conduct experiments on two types of representative test samples. The materials for the study were two samples of GF and CF composites provided by B&T Composites (Florina, Greece), presented in

Figure 1. An example of the primary structure of the composite containing glass fibers (GF) is shown in Figs. 2a-b, whereas the structure of the composite containing carbon fibers (CF) is shown in Figs. 3a-b (SEM images). The sample images are derived from scanning electron microscope (Silesian University of Technology, Gliwice, Poland). Glass fibers consist of multi-directional strands embedded in a polymer matrix. The diameter of a single glass fiber was found to be about 20 μm. A similar morphology was identified for carbon fibers, also arranged in multi-directional strands, consisting of carbon fiber bundles and embedded in a polymer matrix. The diameter of the fiber bundles is about 8 μm. The composite samples were directed "as are" to the solvolysis process without any pretreatment or size reduction.

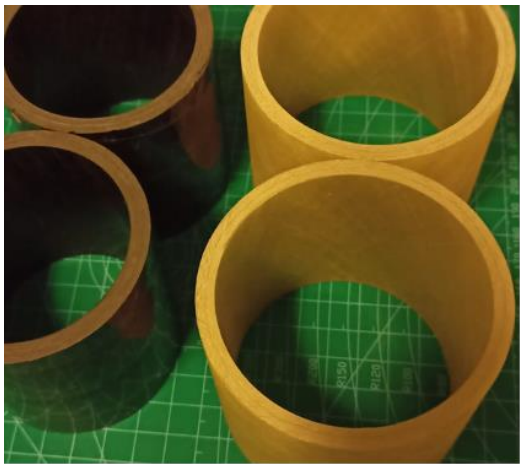

Figure 1: CF (left) and GF (right) composite samples used in this study.

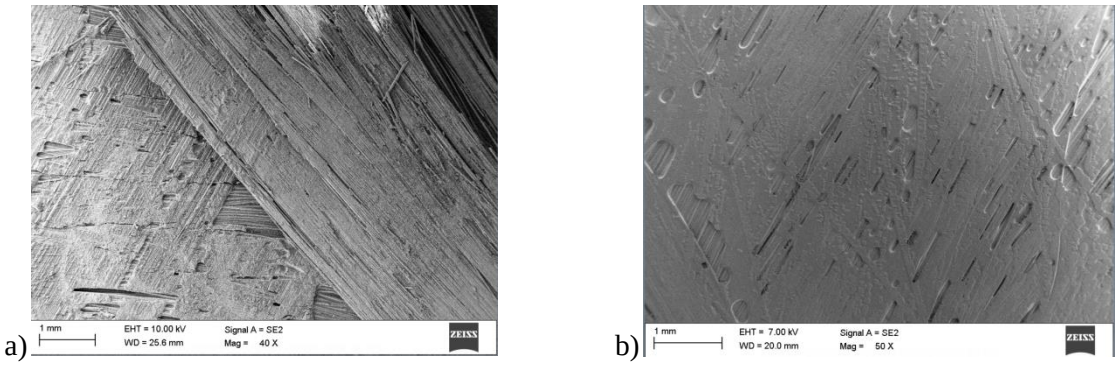

Figure 2: Examples of the primary structure of a composite containing glass fibers, GF (SEM).

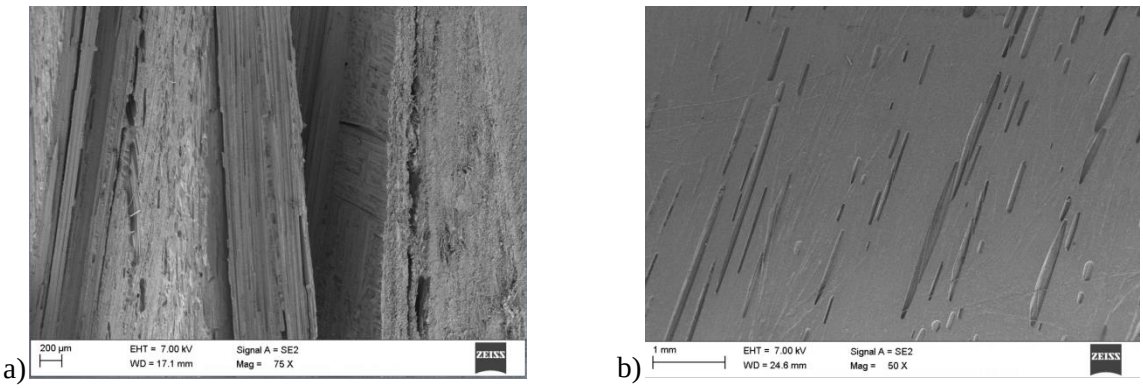

Figure 3: Examples of the primary structure of a composite containing carbon fibers, CF (SEM).

2.2 Research methodology

Structure/morphology studies were carried out using a high-resolution scanning electron microscope Zeiss Supra 35, with an accelerating voltage of 5–15 kV and magnifications in the range of 40 – 35000×. SE and In-Lens detectors were used to study the surface morphology of the composite samples. Analysis of chemical composition in micro-areas was done using the EDX UltraDry diffuse X-ray energy detector by Thermo Scientific™ driven with Pathfinder software. The sample surfaces before the SEM tests were sputtered with conductive material – AuPd alloy. The BAL-TEC SCD 050 sputtering machine was used for this purpose.

2.2.1 Composite samples behavior during the solvolysis process

The low-scale chemical solvolysis was carried out in a laboratory-size batch reactor of 1 dm^3 working volume. The process temperature was maintained at 190 °C by a dedicated heating spiral providing the pressure-less conditions, with the addition of the 0.0125 mol of triazabicyclodecene (TBD) catalyst in the ethylene glycol/NMP (*N*-methyl-2-pyrrolidone) solution. The total batch solvolysis process time for the test was 6 hours. During the process, no problems were detected, and process time was only limited by the diffusion resistance of the catalyst-solvent mixture through the structure of the material. Determination of the rate constant of the process will be the subject of future study.

2.2.2 Fibers characterization

Scanning electron microscope observations on the samples taken during the batch solvolysis process show that the process ran successively. The basic mechanism enabling gradual and deeper penetration of a chemically active solution in this case is surface degradation. In general, a similar course – thus mechanism – was observed for both samples representing glass fibers (GF)/resins (Figure 4) and carbon fibers (CF)/resins (Figure 5).

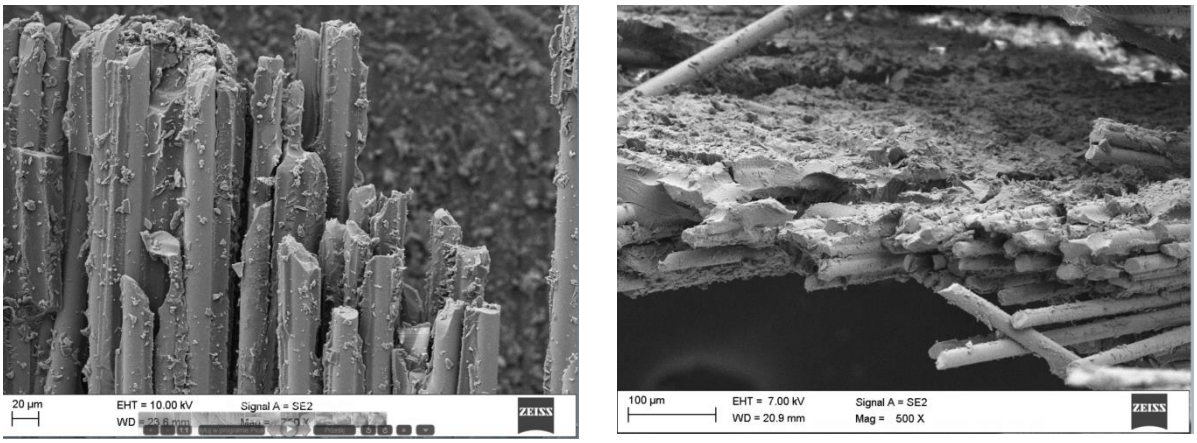

Figure 4: Glass fibers (GF) / resins samples taken for structure analysis during the batch solvolysis process (SEM images).

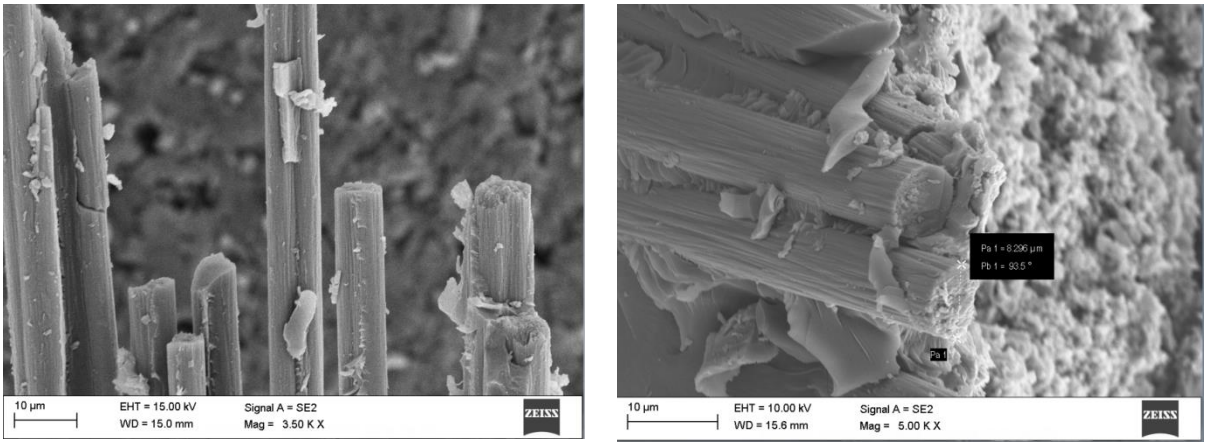

Figure 5: Carbon fibers (CF) / resins taken for structure analysis during the batch solvolysis process (SEM images).

After the solvolysis process, and the separation of the GF and CF fibers, the recycled solids were evaluated with scanning electron microscope (SEM) images using a Zeiss Supra 35 microscope equipped with an EDM detector. Representative SEM images for the batches of fibers were selected after an initial, preliminary selection using a different optical analysis technique - with Zeiss SteREO Discovery optical microscope. The chemical purity of the fibers was determined using Fourier transform infrared (FTIR) spectrometer Nicolet 6700/8700 (ThermoFisher Scientific, USA).

2.2.3 NMR characterization of solutions in solvolysis process

^{1}H-NMR spectra of solvolysis solutions were recorded on an Agilent 400-MR NMR Spectrometer (Agilent Technologies, Inc.) at the operating frequency of 400 MHz using TMS as the resonance shift standard. The samples for analysis were prepared by taking 100 µl of solutions and mixing them with 600 µl of deuterated solvent ($CDCl_3$). By comparing the spectrum of the blank sample (before solvolysis) with the spectra of samples taken during the process, the course of solvolysis can be monitored [9]. An exemplary comparison of this type is shown in Figure 6. The complex study of the solvolysis kinetics using NMR analysis is in progress.

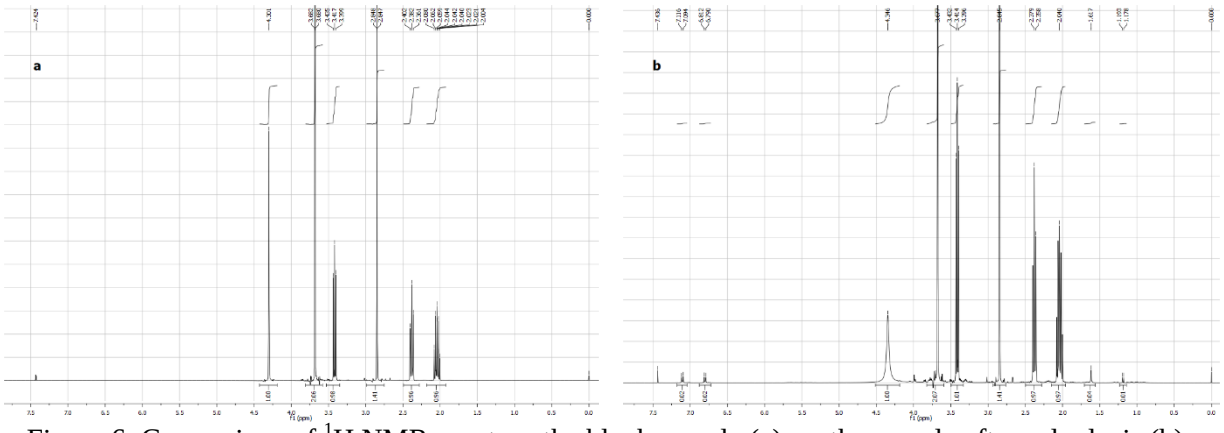

Figure 6: Comparison of ^{1}H NMR spectra - the blank sample (a) vs. the sample after solvolysis (b).

3 RESULTS

3.1 Solvolysis experiments results

After 6 hours of solvolysis processing, the epoxy resin in the polymer matrixes were completely degraded and dissolved. Released GF and CF were separated from the liquid, and dried. The liquid product after the process was stored for future analyses aiming to examine its detailed chemical

composition.

3.2 Testing of recycled GFs and CFs

Figure 7 presents recovered, separated, and dried GF and CF type fibers from the solvolysis process of the representative composite samples. The average length of the obtained fibers was 50 – 60 mm, with the longest fibers obtained from the GF composite solvolysis, reaching 600 – 650 mm size.

Figure 7: CF (left) and GF (right) type fibers retrieved from composite waste samples.

Structural test results demonstrated clearly, that glass fibers (GFs) consist of multi-directional strands embedded in a polymer matrix. The diameter of a single glass fiber was found to be about 20 μm. A similar morphology was identified for carbon fibers (CFs), also arranged in similar multidirectional strands, consisting of bundles of carbon fibers and embedded in a polymer matrix. The diameter of the fiber bundles is about 8 μm in average. The analysis of the chemical composition of both the fibers and the matrix was carried out using an EDS detector – X-ray diffusion energy. In the case of the surface of glass fibers, the presence of elements typical for this type of materials was found: C, Si, O, Ca, Al, Na (Figure 8). In the case of the polymer matrix itself, the presence of mainly carbon and oxygen was found. In the case of carbon fiber tests, the presence of carbon was confirmed, while the polymer matrix consists of carbon and oxygen. In the EDX spectra, the occurrence of characteristic Au and Pd peaks from the deposited conductive coating (SEM technique demand) can be also seen (Figure 9).

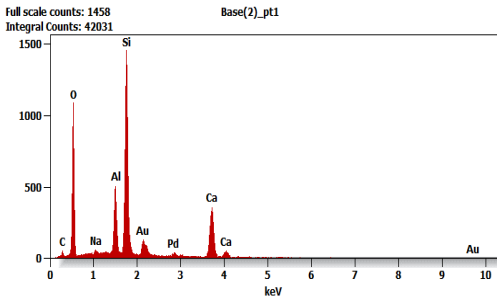

Figure 8: Glass fibers (GFs) composites – EDS chemical composition test results

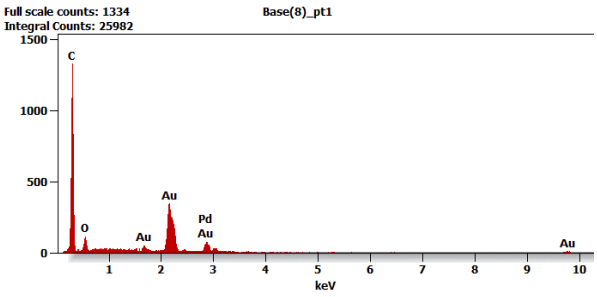

Figure 9: Carbon fibers (CFs) composites – EDS chemical composition test results

Figs. 10 and 11 present the SEM images of the obtained individual CF and GF type fibers, respectively. The overall quality of the fibers is very good, only minor inclusions of unknown substances of different origin can be observed on the GF surface.

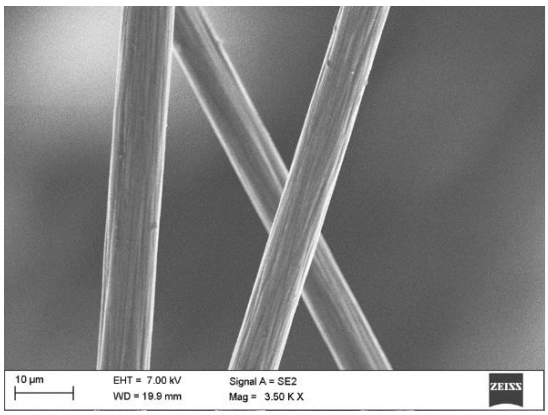

Figure 10: SEM images of the single CF type fiber retrieved from the low-scale chemical solvolysis process (190°C, ambient pressure, after 6 hours).

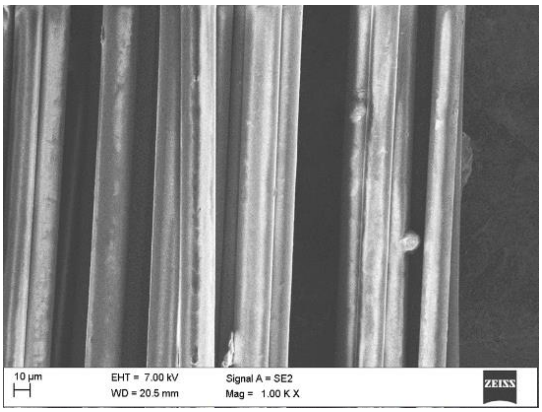

Figure 11: SEM images of the single GF type fiber retrieved from the low-scale chemical solvolysis process (190°C, ambient pressure, after 6 hours).

4 CONCLUSIONS

Analyzes of the GF and CF type samples after batch solvolysis process show that the recovered fibers are heterogeneous in terms of length. The fibers are often tangled and interconnected.

Taking into account the obtained results, attention should be paid primarily to the identified technological difficulties related to the recovery of perfectly clean carbon fibers or glass fibers, without any trace of the residue of the binding resin present in the physicochemically decomposed composite material.

Reliable tests must be carried out to identify whether the fibers, treated only to an acceptable level with resin residues, can be suitable enough for specific applications - without the need for potentially time-consuming and energy-intensive multi-stage cleaning processes.

This way, the integrated economic and technological factors will make it possible to reduce the costs of recycling processes, and thus a more favorable position on the market of post-recycling materials for recycled glass fibers or carbon fibers will be provided.

Before the cutting and pulping process, it is impossible to predict the length of the fibers introduced into the resin. During the experimental tests fibers of various lengths were identified. Mainly, the size

of the composite elements introduced into the reactor should be taken into account – this directly determines the length of the recovered fibers.

ACKNOWLEDGEMENTS

This study has received funding from the European Union's Horizon Europe research and innovation program under grant agreement No 101058089.

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