Investigating Electrochemical Treatment Of Carbon Fiber Composites As A Possible Recycling Technique

S. Soulis, D. Semitekolos, C. Charitidis

Research Unit of Advanced, Composite, Nano-Materials and Nanotechnology (R-Nano Lab), Material Science and Engineering Department, School of Chemical Engineering, National Technical University of Athens, GR-15780 Zographou, Greece.

INTRODUCTION

- The continuous expansion in the use of carbon fiber reinforced composites (CFRPs) with ever increasing applications covering a multitude of sectors (such as aviation, sports or wind power production) has led to a rapid increase in CFRPs consumption, reaching the level of around 150,000 tons per year[1].
- This however, increase is about to create a problem with the end-of-life for these materials.
- Up to now, the volume of CFRP waste was not large enough to be of concern and landfilling or incineration were the most prominent solutions for their disposal[2].
- There is a strong motivation to efficiently recycle CFPRs for a number of reasons, no less due to economic grounds. Indeed, CFs are very stable and (as such) less prone to environmental degradation, and CFRPs end of life depends mainly on the failure of the matrix (attributable to decomposition of the polymer resin).
- Thus, CFs retain their properties almost intact even after the operational lifetime of the CFRPs, and there is a clear incentive to achieve as intact a recovery of the CFs as possible (taking also into consideration their high cost)[2-4].
- This highlights the necessity of finding a proper recycling procedure for CFRPs.
- The problem of CFRPs recycling has been already recognized and there are several methodologies proposed that can be separated into three main categories: (1) mechanical recycling, (2) thermal recycling and (3) chemical recycling[3]. However, the majority of the proposed chemical / mechanical methods demand their feedstock to be in the form of small size particulates (e.g. granules or pellets).
- Thus, the resulting CF product is chopped, low value CFs (e.g. in the form of felt). Additionally, thermal recycling might cause considerable high temperature degradation of the CFs [2].
- Thus, there is a clear motivation in developing alternative (and more efficient) CFRPs recycling methodologies.

The aim of this work is to investigate the possibility of using electrochemical treatment as a method that could be efficient for recycling CFRPs. The idea is to use the high conductivity of CFs and cause partial (or total) decomposition of the interphase and the matrix through electrochemical or chemical degradation of the matrix. Different conditions will be investigated and their result on the decomposition of the CFRPs will be studies via MicroCT analysis.

EXPERIMENTAL

- The CF composite used in this work contained 60% w/w of CF reinforcement; it consisted of epoxy resin matrix and reinforcement with 8 layers of CF plain weave cloth (nominal weight 415 g*m^{-2}, type C415, FIBREMAX, UK, woven using PYROFIL TR50S 12 K carbon fibers, Grafil, UK). It was manufactured with typical vacuum-assisted resin transfer molding (VA-RTM); the manufacturing procedure consisted of the following steps:
  (a) Coating the mold with high-temperature release wax to enable simple demolding.
  (b) Stacking eight layers of dry, unmodified fabric in the mold (without resin).
  (c) Positioning the peel ply to enable the successful peeling of all layers positioned above the CF fabrics.
  (d) Inserting the infusion mesh, that will help the resin circulate more easily throughout the infusion.
  (e) Vacuum-sealing the container to seal out air and stop mold growth.
  (f) Perforating the vacuum bag on two opposite sides. In the first one, a connection was made between the resin catch pot and the vacuum pump. This allowed for the removal of all the air that had been stowed away among the fabric's layers, even though the trap's main purpose was to shield the vacuum pump from the resin that was released during the infusion process. The second one has a beaker with resin attached to it.
  (g) After all the required connections had been secured, pumping the air out of the mold. A manometer mounted on top of the resin catch pot measured the vacuum consistency.
  (h) Once the required vacuum was established, the clamp at the resin beaker was removed, allowing the pump to guide the resin into the mold and through all of the layers of textiles until it was eventually observed to exit the trap.
  (i) The clamps were secured, and the mold was moved into the oven to cure for 4 hours at 80 °C.
  (j) After that, the mold was allowed to cool at ambient temperature so that the composite panels could be taken out and placed in the furnace for a further 4 hours at 120 °C to complete the post-curing process.
- The electrochemical treatment of the CF composite was performed using a POS88 potentiostat. A three- electrode setup was used, with the CF composite as the working electrode, a Pt-plated Pt wire as the counter electrode and an Ag/AgCl electrode as the reference. After each testing, the CF composite sample was thoroughly washed with distilled water and acetone.
- Micro computed tomography (m-CT) can provide a multitude of quantitatively characteristics and images of the internal structure of materials. The internal structure was observed by a compact desk-top 3D X-ray scan system SkyScan 1272 micro-CT (Bruker). The system consists of a microfocus sealed X-ray source which operates at 20-100kV and 10W (<5 μm spot size @ 4W), an X-ray detector with a maximum resolution of 11Mp (4032x2688 pixels) and a 14bit cooled CCD fibre optically coupled to scintillator. Table 1 summarizes the scanning conditions of all CFRPs samples.

Table 1. Scanning conditions of CFRPs.

Voltage	40 kV
Current	166 μA
Filter	Al 0.25mm
Pixel Resolution	1344 x 896
Pixel Size	9 μm

The sample was placed centered and aligned with the rotation axis on top of the holder. The holder was subsequently mounted on a rotational stand in the scanner chamber. A rotation step of 0.3° with 180° tomographic rotation was selected to obtain the 2D x-ray images. 2D images of crosssectional slices were reconstructed via N Recon Reconstruction software (Bruker). The composite materials studied in this article consist of epoxy resin and CF, two components that are largely carbon-based and have a similar attenuation coefficient. As a consequence, to be able to distinguish those two phases, the voltage range was set in a relative low value.

RESULTS AND DISCUSSION

- It is generally believed that epoxy resins are less stable in basic conditions and, for the first testing an aqueous 0.5 M NaOH solution was used. Figure 1 shows the repeated cyclic voltammograms (CV) of the CF composite sample in this electrolyte. Initially, 10 CV scannings were performed in the region: [+3.0 V -> -3.0 V] (with scanning rate 200 mV/s), which showed a gradual increase of the active current (i.e. the area enclosed by the curve of the CV). This is an indication of an increase of either the surface area of the CFs, or of their electrochemical activity or both. However, upon optical inspection, there was no indication of matrix disintegration in the CF composite, neither in the surface nor internally. Further treatment was followed, this tme for another 50 CV scannings in the even wider region of potentials (between [+4.0 V -> -4.0 V], again with scanning rate 200 mV/s). During this test even higher active current was measured, which also increased by the number of the treatment cycle, but the optical investigation did not find any sign of degradation in the CF composite.

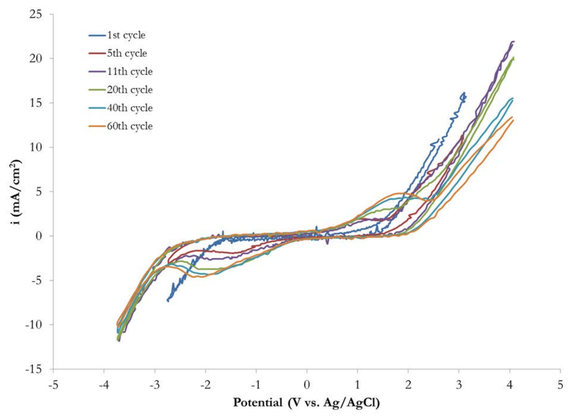

Figure 1. Cyclic voltammograms (CVs) during the treatment of CF composite sample with repetitive scannings in aqueous 0.5 M NaOH solution (scanning rate 200 mV/s).

- The CVs of the treatment indicate that there is an increase of the electrochemical activity; it is possible that this increase could indicate an increase of the CF active surface via the formation of small cracks (invisible to the naked eye) in the bulk of the composite. In order to verify the effect of the treatment on the sample, m-CT analysis on the sample was performed; Figures 2a and 2b show that the CF composite sample remained intact after the treatment with the NaOH solution.

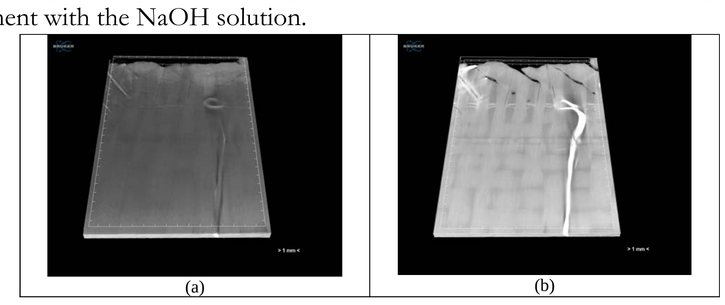

Figure 2. m-CT analysis of the CF composite sample after the electrochemical treatment with aqueous 0.5 M NaOH solution (a) external surface of the composite, (b) internal surface.

- Further treatment was followed using a basic electrolyte at higher concentration, but this time in a solution of an organic solvent. The basic premise was that the organic solvent could have possible added benefits, such as more easily dissolving the products of the matrix decomposition or even chemically attacking the matrix itself. Thus, a 1.0 M NaOH solution in ethanol was used. However, cyclic voltammetry showed very little current passing from electrochemical cell; furthermore, the solution did not show any colour change during the immersion of the sample (even after 1h). This indicates that this solution was not suitable for causing electrochemical (and /or chemical) decomposition of the CF composite (i.e. it could not attack the matrix material). However, it is possible that ethanol is not a proper solvent for electrochemical treatment, thus further investigation (with more polar organic solvents) is necessary.
- The next electrochemical test for CF composite decomposition was performed using concentrated acid solution; the rationale was that electrochemical treatment of CF fibers in acidic solutions with CV could lead to surfacial oxidation and subsequent partial reduction5,6; this change of the CF surface might lead to fiber ablation form the matrix. Up to 100 repetitive potential scannings were performed in the region: [+3.0 V -> -3.0 V] (with scanning rate 100 mV/s). Figure 3 shows the cyclic voltammograms (CV) of the CF composite sample in this electrolyte. The increase in the active current is clear and more prominent compared to the aqueous 0.5 M NaOH solution; thus, it is evident that the electrochemical activity of the CF composite sample increases during the treatment. Moreover, during the CVs the colour of the electrolyte solution progressively darkens, starting form pale yellow and reaching to dark brown. After the CF composite sample was removed from the solution, it was found that the matrix had almost completely disappeared and that the CF cloth layers appeared intact; the m-CT measurements (Figures 4a and 4b) confirmed the optical observation, with the epoxy resin removed from the outer surface and the bulk of the sample. This is a clear proof that electrochemical treatment can be an efficient method for recycling CFRPs.

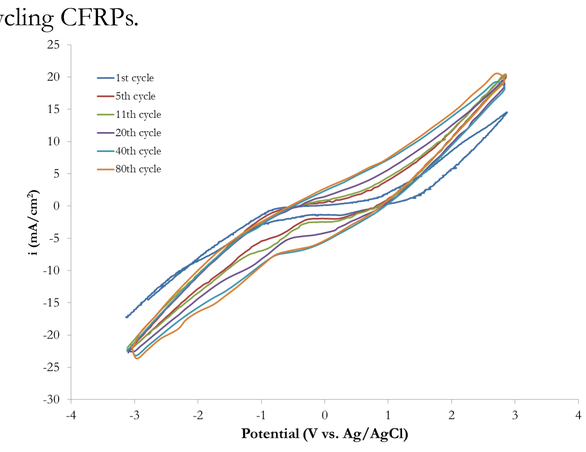

Figure 3. Cyclic voltammograms (CVs) during the treatment of CF composite sample with repetitive scannings in concentrated H2SO4 (96%, scanning rate 100 mV/s).

- It is remarkable in Figure 3 that the CVs indicate the decomposition of the matrix was probably completed before the end of the scannings (probably around the 40th scan); further investigation in necessary to establish the optimum electrochemical treatment conditions for recycling CFRPs.

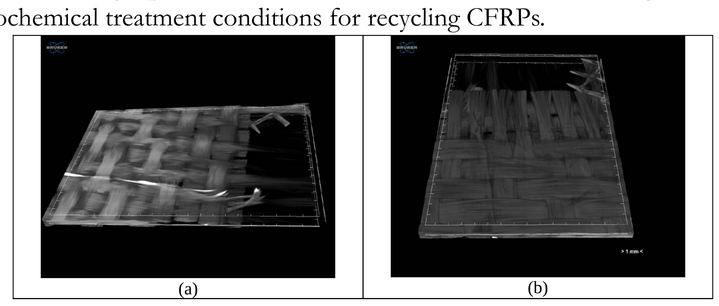

Figure 4. m-CT analysis of the CF composite sample after the electrochemical treatment with concentrated H2SO4 (96%) (a) external surface of the composite, (b) internal surface.

CONCLUSIONS

- *The possibility of electrochemical treatment as a novel method for efficient, cost-effective CFRP recycling was investigated.*
- *The preliminary results show that treatment with repetitive potential scannings (i.e. cyclic voltammetry, CV) in concentrated acid can be an efficient methodology to completely and quantitatively separate the CF reinforcement from the matrix.*
- *Further investigation in necessary to establish the effect of the treatment on the CFs as well as to find the optimum treatment conditions.*

References
(1).Sidorina AI, Gunyaeva AG. Market for Carbon Fibres and Composites Based on them. A review. Fibre Chemistry. 2017;48(4):306-310. (2). Borjan D, Knez Z, Knez M. Recycling of Carbon Fiber-Reinforced Composites-Difficulties and Future Perspectives. Materials (Basel). 2021;14(15):13. (3).Colombo B, Gaiardelli P, Dotti S, Caretto F. Recycling technologies for fibre-reinforced plastic composite materials: A bibliometric analysis using a systematic approach. Journal of Composite Materials. 2022;56(19):3063-3080. (4).Julian I, García-Jiménez A, Aguado A, et al. Advances in the circularity of end-of-life fibre-reinforced polymers by microwave intensification. Chemical Engineering and Processing - Process Intensification. 2022;178:109015. (5).Soulis S, Triantou D, Simitzis J. Electrochemical grafting of 4-phenoxybenzoic acid units onto oxidized carbon fibers as a first step for high temperature composites. Journal of Applied Polymer Science. 2013;130(3):1466-1478. (6).Georgiou P, Simitzis J. Correlation of the Electrochemical Parameters of Carbon Fibre Treatment in Sulphuric Acid by Cyclic Voltammetry with the Created Functional Groups and Their Formation Mechanism. Electrocatalysis. 2022;13(6):838-852.