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Short Communication

Recyclable twin matrix composites

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ABSTRACT

Twin matrix composites (TMC) are novel composite architectures where reinforcing composite elements are embedded in a secondary resin to address various mechanical functions suited for diverse engineering applications such as morphing wings. Here, for the first time, a recyclable twin matrix composite using micropultruded rods as reinforcements will be manufactured. Within the scope of the work, the design of the TMC mould which allows 0°/90°/0° reinforced layup will be discussed and created through additive manufacturing. Recycling and remanufacturing TMC will be conducted up to 4 times, and surface characteristics of the rods will be examined to monitor the effect of recycling. Interlaminar shear strength of TMC made from fresh and recycled rods will be investigated comparatively.

1. Introduction

Fibre reinforced polymer composites (FRPC) shape modern aviation, energy and transport industry by offering lightweight advanced materials [1]. While the fibre selection is continuous glass or carbon fibres for structural parts, polymer matrix can be made of thermoset or thermoplastics [2,3]. Thermosetting resins are based on reactive monomers which react to forge crosslinked network, and can be comprised of epoxy resins, vinyl esters and cyanate esters [4]. Epoxy resins dominate the industry, as well as in the aerospace field, which is fabricated via mixing multifunctional epoxy monomer with hardener [5,6]. Chemical structure, viscosity, cure kinetics are some of critical factors influencing workability and cure conditions of epoxy systems. Despite well-established manufacturing procedures and certified performances, thermosetting composites face significant end-of-life challenges as recyclability is not offered in crosslinked thermoset units [7,8]. Recyclable epoxy resins are widely studied in chemistry literature by employing on-demand degradable chemical bonds [9–11], however their industrial viability and scalability are far from meeting the demands of composite industry. Wu and colleagues elucidated the use of Cleavamine, a hardener with ketal bonds, to generate recyclable glass fibre reinforced composites under mild conditions [12]. Recently, Recyclamine® hardeners stand out as industrially available recyclable amine hardeners with acetal backbone [13,14]. After thermoset formation by reaction of amine hydrogens, acetal groups within hardener can be degraded in mild acidic conditions affording fibre-matrix separation [15]. However, when filaments in UD or fabric reinforcement are recovered, disorganization of the reinforcement is recorded after recycling [16] which prevents reuse of reinforcers in high-performance applications. Next to that the recovered reinforcement needs to be handled with much care as damage to the filaments is prone to happen.

Twin matrix composites (TMC) are formed by utilization of two matrix systems with individual resin properties [17]. TMC possess an additional functionality thanks to the secondary resin compared to single matrix systems [18] and are promising candidates for demanding functional engineering structures such as morphing wings [19]. The added functionality that all previous studies on TMCs have focused on is to obtain higher ultimate tensile strains in the transverse direction. This goal was achieved by incorporating a rubber-based secondary resin yielding an ultimate transverse tensile strain of 3.0 %, which is remarkably higher than that of single matrix variants (0.3 %). While the resultant TMC has shown to have a higher ultimate transverse tensile strain, it has lower stress based strength and modulus properties both in the longitudinal and transverse direction in comparison to the single matrix variant. This is due to the lower total fiber volume of the corresponding TMC (51 %) which is lower than the single matrix variant (67 %). Despite such studies, investigation on recycling and end-of-life options remain unclear.

In this study, the first attempt on brick and mortar inspired recyclable twin matrix composites will be taken. Starting with a digitally manufactured mould design which enables 0°/90°/0° layup of reinforcement rods with a homogenous thickness and distribution, recycling

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Table 1
Properties of epoxy based carbon fibre reinforced polymer (CFRP) micro-pultruded rods used in this study (provided by supplier).

Property	Value	Unit
Fibre volume	63	%
Tensile strength	2500	MPa
Tensile modulus	140	GPa
Compression strength	1600	MPa
Ultimate tensile elongation	2	%
Glass Transition Temperature	120	°C

step and composite formation from recycled rods will be performed up to 4 times. Corresponding surface properties and interlaminar shear strength of TMCs will be analysed to reveal the effect of recycling on reinforcing pultruded rods.

2. Experimental details

2.1. Materials

The main components that the Twin Matrix Composites are made from are:

- **Pultruded Rods**: These rods were obtained from Van Dijk Pultrusion Products (DPP), in the format of a 500 m roll. According to the manufacturer, the width and thickness of the used composite rods are 3.60 and 0.60 mm respectively. The matrix within this pultrusion is a bisphenol A based epoxy resin and the fibre filaments are T700. Properties of pultruded rods are summarised in Table 1.
- **Secondary Matrix**: The secondary matrix is composed from the mixture of a bio-based epoxy resin and an amine based hardener known as Recyclamine by R*Concept, and the commercial name of this resin system is Polar Bear. According to the manufacturer, the resin-hardener mixing ratio must be 100:46 (per weight) and curing occurs at 85 °C for 15 min. Once mixed, the pot life of this resin system is 25 min and its viscosity is 700–1000 mPa*s.
- **Recycling Step**: The acid used to degrade the secondary matrix is a glacial acetic acid, obtained from Fluka. Note that the acetic acid solution has been diluted with water to a 50 % concentration. Recycling the secondary matrix takes place at 90 °C for 2.5 h by placing TMC in a large beaker containing acid solution. After recycling, pultruded rods are collected, washed with distilled water thoroughly and dried. Recycled rods are subsequently employed for twin matrix formation.
- **3D Printing filament for mould design**: The 3D printed mould is made from a filament commercially known as Clear V4. The manufacturer of the filament and printing set up is FormLabs.

Characterisation: Scanning electron microscopy (SEM) was performed on JSM-7500F. Water Contact Angle (WCA) measurements were conducted using KSV Cam 200 and measurements have been done according to ASTM D7334 - 08 standard. Four measurements on two spots of rod surfaces were conducted and the average value was taken. Interlaminar shear strength (ILSS) was calculated using Zwick Roell with TestExpert II software in a three point bending setup with a 1 fps camera to record the fracture initiation and growth in the samples. These tests have been done according to ASTM D2344 – 00 (assuming 0° rods take bending stress and normal strain is linear through thickness, while shear stress is parabolically distributed through the thickness). This test has a load cell of 10 kN and operates at a speed of 1 mm/min. According to this standard, the width of the sample must be twice its thickness and its length must be six times the thickness.

3. Results and discussion

In TMC design, mould plays a pivotal role to attain defect-free composite samples with a good surface finish and uniform layer distances. The desired lay-up order of the TMC is 0°/90°/0° in this study. First attempt to design a mould that can host pultruded rods in desired layup formation led to enormous defects and non-homogenous thickness as seen in TMC cross section image (Figs. S1–2). To prevent such issues, walls are added to the mould (Fig. S3), however resin rich top/bottom layers are obtained (Fig. S4) which is a defect in this regard. Fig. S5 depicts an intended TMC layup with corresponding layer thicknesses, hence an elaborated mould using steps and walls are designed (Figs. S6–7) however TMC showed tilted rods with thick resin top layer (Fig. S8). Finally, the mould designed for this study is a flat plate with walls at each side as shown in Fig. 1a. Next to each edge wall, there are several thinner walls (0.2 mm thick) with the purpose to separate the composite rods. In addition to these thin walls, the mould is equipped with steps where the ends of the composite rods will be placed. This way, the vertical differences between each rod as well as with the upper and lower surface of TMC will be controlled. A Teflon plate is prepared as cover during curing.

To manufacture the TMC samples, one must first cut the pultruded rods in the lengths such that the ends of the rods can be placed on the mould steps. Once the rods are cut into the desired lengths, they must be cleansed with acetone and the 3D printed mould should be treated with a releasing agent (3 layers of Marbocote). The resin and hardener are mixed according to the supplier ratio, the components are placed in a speed mixer for mixing and degassing (≈1000 rpm at ≈40 mbar for 10 min). Note that since the pot life of this matrix system is rather short, it must be used immediately after degassing. For the brick-mortar TMC architecture, the secondary matrix is applied to the bottom of the mould first. Then the first layer of rods (0° rods) is placed followed by the addition of the secondary matrix until the rods are fully immersed. The

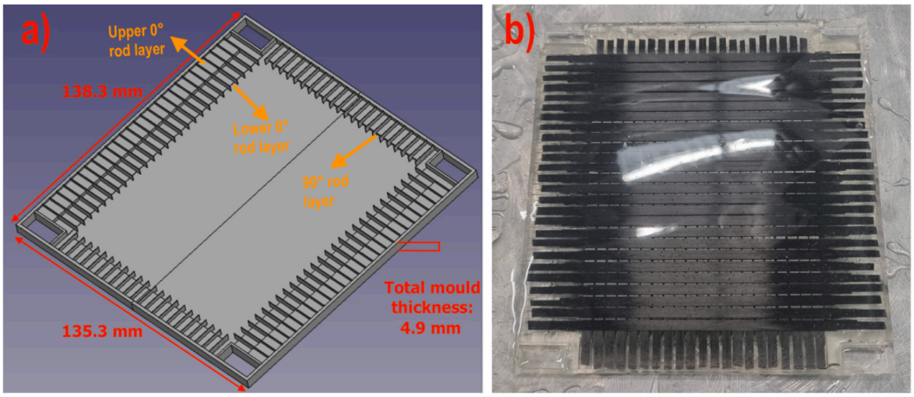

Fig. 1. a) Computer assisted drawing of mould designed for TMC study, b) digital image of TMC prepared using the mould.

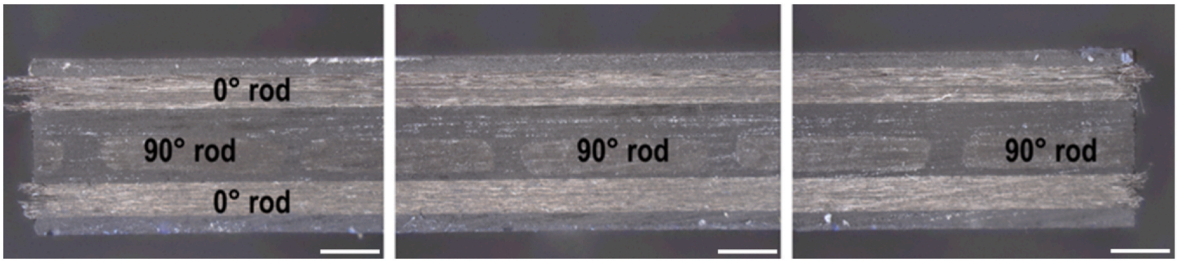

Fig. 2. Optical microscopy images of 3 individual TMC (scale bar corresponds to 1000 μm).

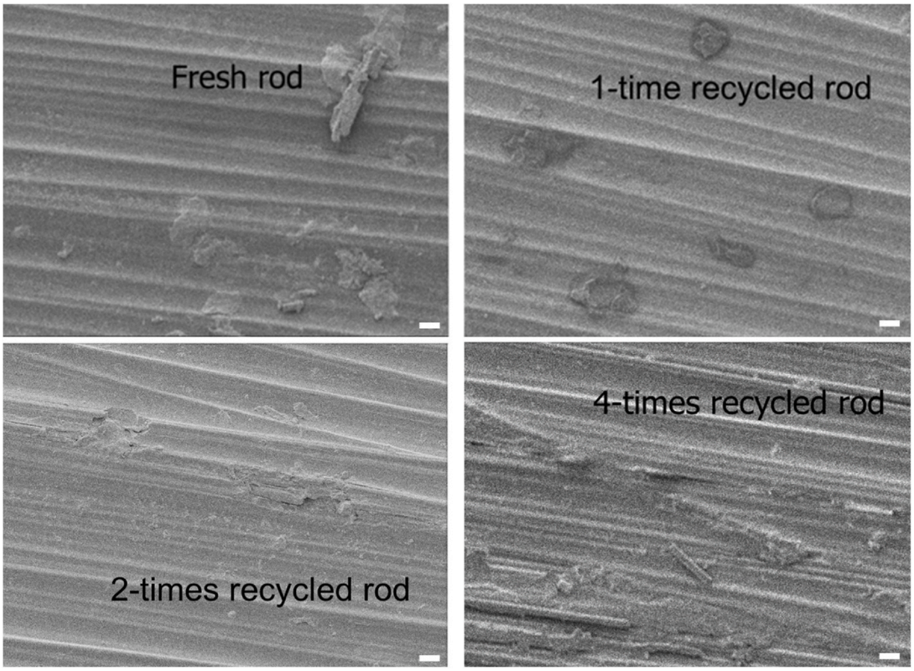

Fig. 3. SEM images of fresh, 1-time recycled, 2-times recycled and 4-times recycled micropultruded CFRP rods (scale bars correspond to 10 μm).

second layer of rods (90° rods) are placed and the secondary matrix is applied again. At the last stage 0° rods are placed and the secondary resin is added until the mould is filled. The top of the mould is covered by a Teflon plate and left for 20 h at room temperature followed by post-cure at 85 °C for 15 min. The final TMC is shown in Fig. 1b. Investigation of the structural homogeneity was conducted via optical microscopy to ensure that the samples meet the standards of mechanical tests by possessing the same thickness between layers of rods. The results of the three individual samples are presented in Fig. 2, which underlines the homogenous TMC formation via the manufacturing approach as presented here.

The recycling process in acetic acid (Fig. S9) will degrade the secondary matrix, however its influence on pultruded rods is unknown. In order to investigate this, the effect of recycling steps on surface properties of pultruded rods are examined via SEM. In Fig. 3, SEM results indicate that there is a small change showing as small dents, fibre distortion and pullout on the surface. These are expected to have a negligible effect on the mechanical properties. No deep cracks or any other defects that would affect rod's performance have been spotted, which underlines that the stiffening elements in TMC can be reused for structural applications. It is important to mention that recycling process is highly contact-dependent process, therefore TMC should be fully in contact with recycling solution. When physical contact and diffusion is not satisfied, resin will remain on rods preventing complete separation (Fig. S10).

Surface wetting properties of rods were analysed using water contact

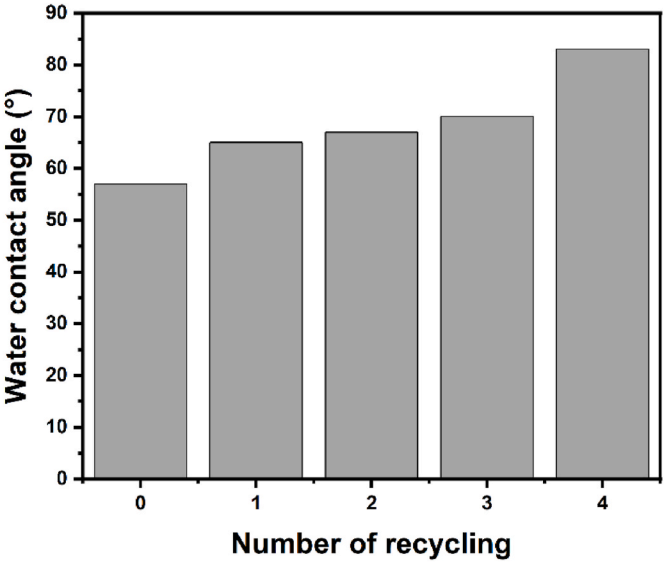

Fig. 4. Water angle measurement results for rods based on the number of recycling.

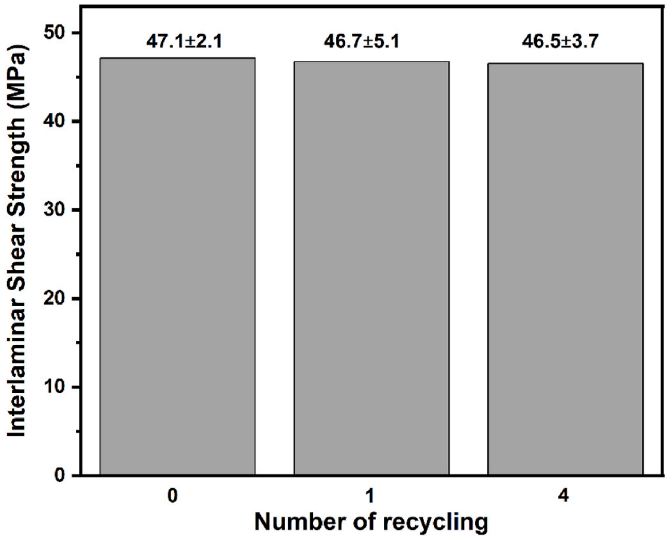

Fig. 5. Average ILSS values of TMC samples employing fresh (0) and recycled (1-time and 4-times) rods.

angle (WCA) measurements. Initial WCA of as-purchased rods is 57°, which increases by recycling treatment. Most pronounced change is observed after 4th time recycling where WCA reaches 83° (Fig. 4), which hints towards changes in surface properties (fibre pullout, roughness etc.). Minor surface defects after 4th recycling observed in SEM align with such a change in WCA results.

Mechanical properties of TMC were examined through ILSS tests. Fibre volume content of tested TMC specimens is 33 % on average. Therefore once the ILSS values of each TMC sample are collected, they must be associated with rod volume in order to have a fair comparison between these data. In this ILSS analysis, we examined TMC with fresh rods and recycled rods (once and four times recycled) to observe the effect of chemical recycling on mechanical properties of TMC. It is important to mention that such analysis is highly sensitive to defects and voids occur during manufacturing process, hence all specimens are investigated optically prior to analysis to ensure sample quality and homogeneity (as presented in Fig. 2). Multiple tests were conducted for each group and results are summarised in Fig. 5. Exemplary raw data obtained on force-displacement ILSS graphs are given in Figs. S11–12.

As can be seen in Fig. 5, TMCs stiffened with fresh rods have ILSS of 47.1 MPa, whereas TMCs stiffened with one-time-recycled rods have ILSS of 46.7 MPa and TMCs stiffened with four-times-recycled rods have an ILSS of 46.5 MPa. Additionally, no notable changes (less than 0.1 %) were seen in two and three times recycled samples, hence data is excluded in graph. This result clearly indicates that recycling the secondary matrix in acid does not degrade the properties of stiffening rods as structural elements. Hence, up to 4 times (experimental limit in this study), TMC with native properties can be engineered using pultruded rods obtained from the recycling process.

Crack growth during test was captured via high speed camera. Fig. 6 highlights the TMC failure during three point bending test. Crack starts from 0° rod/secondary resin interface proceeding through 90° rod and continues towards 0° rod/secondary resin interface. Such crack growth mechanism has been observed in all tested samples and took place within a second upon failure.

Comparing this work to reports in literature, few differences based on manufacturing and properties can be seen. Work of Vasil'ev [17] and Callens [18] focused on using filament winding for TMC, where the first aimed pressure vessel and second one a thin-walled ring. Such approach enables precise manufacturing with high fibre volume contents (40–50 %) tailored for specific mechanical load directions. Schmitz reported using unidirectional composite bundles in elastomer network for curvature morphing skin to generate control over buckling [20]. Recently, Azarov expressed the use of 3D printing to form TMC, where dry fibre bundle is fed into system for thermoset coating followed by curing and co-extrusion with thermoplastic matrix [21]. Our work employs micropultruded composite rods as stiffening elements embedded in recyclable resin. TMC manufacturing in our case is limited by 3D printed mould and low fibre volume content (35 %), yet cheap moulds can be easily accessible. Additionally, interfacial and thickness control over TMC can be achieved, and performing ILSS on so-formed TMCs is a benchmark study in this work.

4. Summary

Twin Matrix Composite (TMC) presents an innovative engineering design that leverages the distinct properties of two individual resin systems. In this study, we utilized micropultruded epoxy-based CFRP composite rods as structural stiffening elements and a recyclable secondary resin to produce novel recyclable TMC using a custom-made precision mould. The surface properties of the rods were assessed through electron microscopy after four recycling cycles in acidic conditions, revealing negligible changes. A significant increase in water

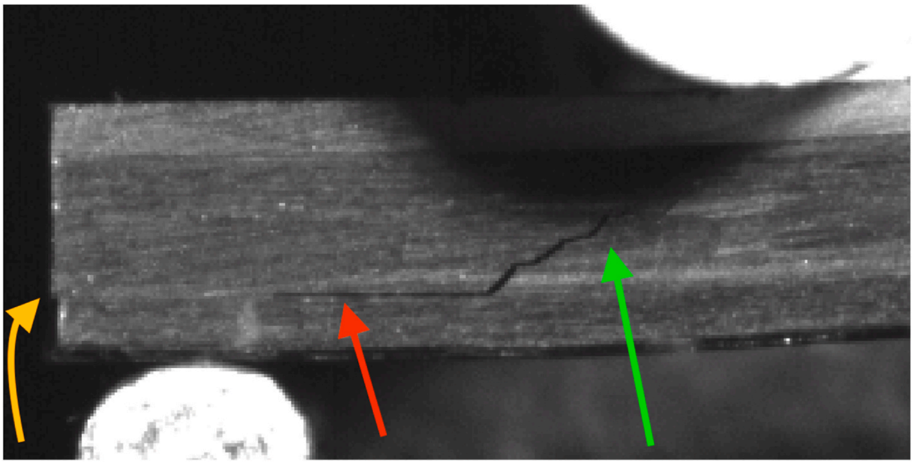

Fig. 6. The captured image of fracture initiation and growth in a TMC made from one-time recycled rods. The red arrow points to an interlaminar fracture which is at the interface between the bottom-most 0° rod layer and the secondary later. The green arrow points to a crack that has gone through a 90° rod. The orange arrow points to the sliding of the bottom-most 0° rod layer with respect to the rest of TMC sample. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

contact angle was observed only after the fourth recycling step, likely due to minor surface dents and fiber pullouts. Importantly, no fiber bundles were detected in the acidic solution, indicating the chemical stability of the Bisphenol-based epoxy resin used in the pultruded rods.

Interlaminar shear strength values for TMC made with fresh and recycled rods (with a 33 % fiber volume fraction) remained consistent around 47 MPa, with less than a 2 % change when four-times recycled rods were utilized. While recyclable resin technologies have been previously studied for fabric-based reinforced systems, their application in TMC is being reported here for the first time.

From a broader perspective, considering that structural composites typically have a lifespan of approximately 20 years, the use of micropultruded rods as reinforcers could extend the applicability of composite materials in the industry to at least 80 years. This represents a significant advancement in the longevity of carbon fiber reinforced thermosetting systems. We believe this research will open new avenues for advanced TMC designs, particularly for demanding applications such as morphing wings.

CRediT authorship contribution statement

Amirsadra Moghaddam: Writing – original draft, Visualization, Validation, Methodology, Formal analysis, Data curation. **Baris Kumru:** Writing – original draft, Supervision, Resources, Investigation, Conceptualization. **Otto K. Bergsma:** Writing – original draft, Supervision, Resources, Conceptualization.

Declaration of competing interest

The authors declare that they have no competing financial interests.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.coco.2024.102010.

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