RESEARCH ARTICLE

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Design and Fabrication of a Customized and Fully-Recyclable Carbon Fibers/Epoxy Composites Prostheses via a Functional Additive Manufacturing Approach

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This study presents an innovative approach based on the combination of two different techniques for fiber-reinforced epoxy composites manufacturing, i.e., additive manufacturing (AM) and hand lay-up-assisted vacuum bagging. It represents a proof of concepts for the manufacturing of a customized and lightweight lower-limb prostheses having built-in functional elements, such as sensors. In particular, a soluble tool for fabricating a complex-shaped carbon reinforced epoxy composite is produced by AM. The 3D printed model is properly designed to integrate a functional element, in a customized way, within the composite structure itself. Moreover, a fully-recyclable epoxy resin system is used as matrix for the fabricated composite part to recover the expensive functional part and carbon fibers as soon as the prostheses has reached the end of its life (EoL). The prostheses recycle is carried out through a chemical recycling process that relies on the presence of acid-cleavable groups within the epoxy-cured network that allows for the cleavage of the crosslink under certain conditions. A similar approach is proposed in the state of art, but by using the traditional autoclave prepreg process and without considering the handling of the part at its EoL.

1. Introduction

Recently, additive manufacturing (AM) has been used to fabricate custom orthoses and prostheses (OP) devices for patients having disabilities. Generally, the most traditional fabrication processes to produce OP relies on manual plaster-molding techniques, but these are time-consuming and requires high delivery times.[1] However, there is an ever-increasing demand for OP devices necessary and helpful for elderly people and patients who have experienced car accidents. So, AM acts for a good alternative, since it represents direct production method for manufacturing customized products, without requiring any specific tool. Furthermore, AM allows for achieving a high level of geometric freedom without involving extra costs, so allowing industries to deliver low production volume of customized components with beneficial costs for end users.[2] Obtaining a quite good level of customization is a benefit of paramount importance, since a study of long-prosthesis use of patients with lower-limb amputation have reported that a worthy level of fitness for OP elements is the most crucial feature for their satisfaction as end-users.[3] In detail, custom prosthetic components must have precise mechanical properties, i.e., stiffness and strength, at low weight to minimize the patient's muscular effort during locomotion as much as possible. So, the crucial features of lightweight condition for lower-limb prosthetics should be satisfied.[1] Even though polymeric components produced through AM could fulfill the latter condition, they are lack in durability and strength. Conversely, fiber-reinforced polymers (FRP) represent a perfect option, since they are high-performance materials with excellent durability, stiffness, and strength-to-weight ratios.[4] For this reason, it is wide spreading a design approach relying on the harness synergies between AM and FRP. Recently, several applications as lay-up tooling exploiting the synergy between fused deposition modeling (FDM) and FRP have been reported, since this AM process allows for not high manufacturing costs and lead times reduction, but still holding quality and repeatability features.[5–7] Moreover, the use of AM can be exploited for producing removable (such as soluble) tool, which is a perfect solution to fabricate hollow composite parts,[8,9] even having embed device within the composite structures itself.[10] Regarding lower-limb prosthesis, the use of sensing systems for interfacial residual limb-prosthesis' socket measurements is commonly used, since this kind of monitoring strategies, for example, for distribution of pressure and shear stresses measuring, permits to improve the quality of life and the comfort for patients,[11] by reducing the pain.

An approach for the design and manufacturing lower limb-prosthesis combining the presented features was already

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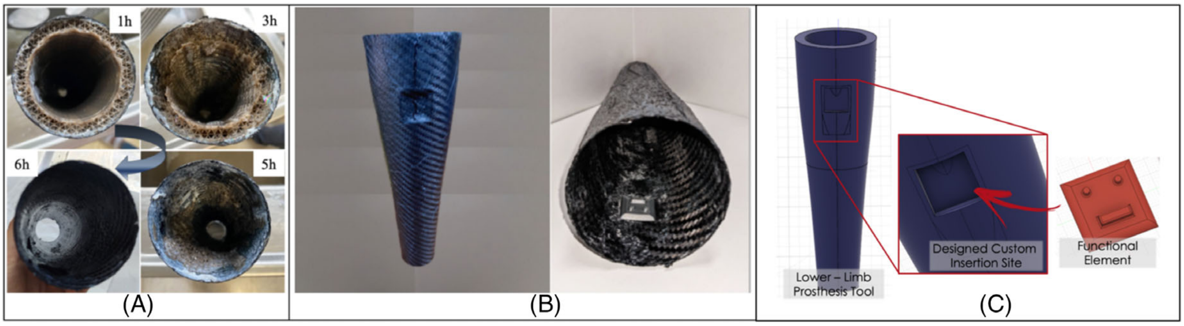

Figure 1. A) Gradual dissolution of the 3D printed mandrel throughout the time. B) Manufactured CRFPs lower-limb prosthesis integrating the functional element within the shell. C) Conceptual sketch for the prostheses design concept.

proposed.[12] It regards an approach combining AM, carbon fiber reinforced polymers (CFRP) and autoclave prepreg process to fabricate complex-shaped hybrid structures with customization capabilities. But, on one hand autoclave involves high quality, since the process can be strongly controlled, while on the other hand this manufacturing process requires very expensive materials, tooling, operational costs, and equipment. These high costs represent an issue for all those patients who cannot afford expensive OP devices. Another concern relative to prepreg use regards its end-of-life (EoL) handling, since being not recyclable, FRP prostheses represent disposal negatively affecting the environment. Next, when carbon fibers (CFs) are used as reinforcement, their non-recyclability involves a significant economic loss, since they are very expensive. Even the non-recovery of the embed functional elements, such as sensors, represent a meaningful economic loss. To overcome these issues, starting from the already proposed approach,[12] a novel manufacturing method combining CFRP produced through hand lay-up-assisted vacuum bagging technique and AM is proposed in this experimental study. To the best of our knowledge, in the state-of-the-art none manufacturing route exploiting this novel fabrication technique to realize custom cost-effective fully-recyclable prostheses with embed functional elements has been previously proposed.

2. Results and Discussion

2.1. Design and Manufacturing of the Lower-Limb Prostheses

The lower-limb prosthesis was designed by using *Autodesk Fusion 360* (Autodesk Inc., San Rafael, CA, USA). Next, the STL file was exported and the 3D printing process was modeled by using the proprietary software *Insight* (Stratasys, Los Angeles, CA, USA). The designed tool was 3D printed on a Fortus 400mc (Stratasys, Los Angeles, CA, USA) with a soluble material the support filament SR-100, which is resistant at high temperature (150 °C). The designed CAD model was 3D printed with a raster angle of 0°/90°, a layer height of 254 µm, and the permeability triangle as infill type (best infill option to promoting the dissolution). Once the tool was ready, it was coated with a release agent and the hand lay-up process was accomplished by stacking four different plies of dry TWILL carbon fibers (CFs) fabric having an areal density of 310 g (Carbon Compositi Srl, Basiliano, Italy). As epoxy resin formulation it was used a mix of bio-based Polar Bear resin (part A) with a fully-recyclable ammine Recyclamine R*101 (part B) with a mixing ratio by weight of 100:22. The resin was uniformly spread, using the hand lay-up method, on each CFs ply. The ratio between epoxy resin and CFs reinforcement was of 50:50 by weight. Next, the prosthesis was closed within the vacuum bag and put under vacuum conditions for 24 h to achieve a complete infusion of the resin into the layers. A post-curing step at 100 °C for 3 h was performed as well. As soon as the curing process was completed, the CFRPs prosthesis was pulled out from the vacuum bag and it still contained the inner composite tool (mandrel) having a thickness of 10 mm. Its dissolution process was carried out in an aqueous basic solution at 80 °C into an ultrasonic bath (75% of power) and required 6 h to be fully accomplished. The gradual dissolution for the mandrel is represented in **Figure 1**A. While, the final CRFPs prosthesis integrating the functional element is shown in Figure 1B. The selected manufacturing approach allowed, during the design phase, to choose in a detailed way the positioning of the functional element, which was firmly connected to the shell during the curing process. At this step a custom insertion site for the functional element was predisposed. The conceptual sketch for the developed design concept is shown in Figure 1C. In the end, both upper and lower load introduction elements (LIE), as attachment points to the socket and knee, might be produced by suing a cost-effective AM approach[13] and added once the CFRPs shell is ready by exploiting properly film adhesive.

To check if the dissolution process affected the *mechanical properties* of the CFRPs material, a flexural test (*ASTM 7264 standard*) of the laminated samples, having size of $(77 \times 13 \times 2)\ \text{mm}^3$, was carried out before and after the dissolution process. Five samples of each type were characterized. The mechanical tests were run using an Instron 5985 universal testing machine (Instron, Milan, Italy) equipped with a load cell of 10 kN, in strain control mode, at 1.0 mm min^{-1} speed, and with a span length of 64 mm. The obtained results are shown in **Figure 2**.

The flexural strength and modulus of the laminated samples slightly decrease after the dissolution process, of about 6% (456.16 ± 5.68 MPa vs 431.31 ± 9.56 MPa) and 4% (28.87 ± 0.45 GPa vs 27.71 ± 0.65 GPa), respectively. Conversely, the deformation at break for the laminated sample after the dissolution process marginally increased of about 3% (1.84 ± 0.05% vs 1.91 ± 0.04%). Nevertheless, the obtained results from a paired *t*-test proved that the difference between the mean values determined for the flexural strength, flexural modulus, and deformation at break for the two considered samples (E_CFs_I and E_CFs_II) is not statistically significant (*p*-value > 0.05). Thus, proving that

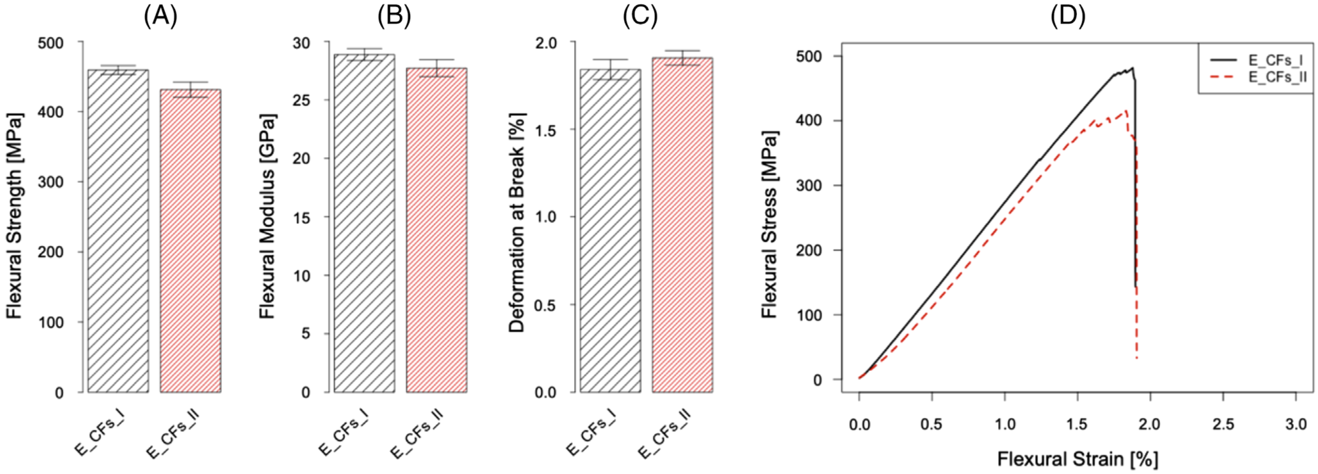

Figure 2. Bar plots obtained for the A) flexural strength, B) flexural modulus, and C) deformation at break (%); D) average flexural stress versus flexural strain (%) curves obtained for the laminated samples before (E_CFs_I) and after (E_CFs_II) the dissolution process.

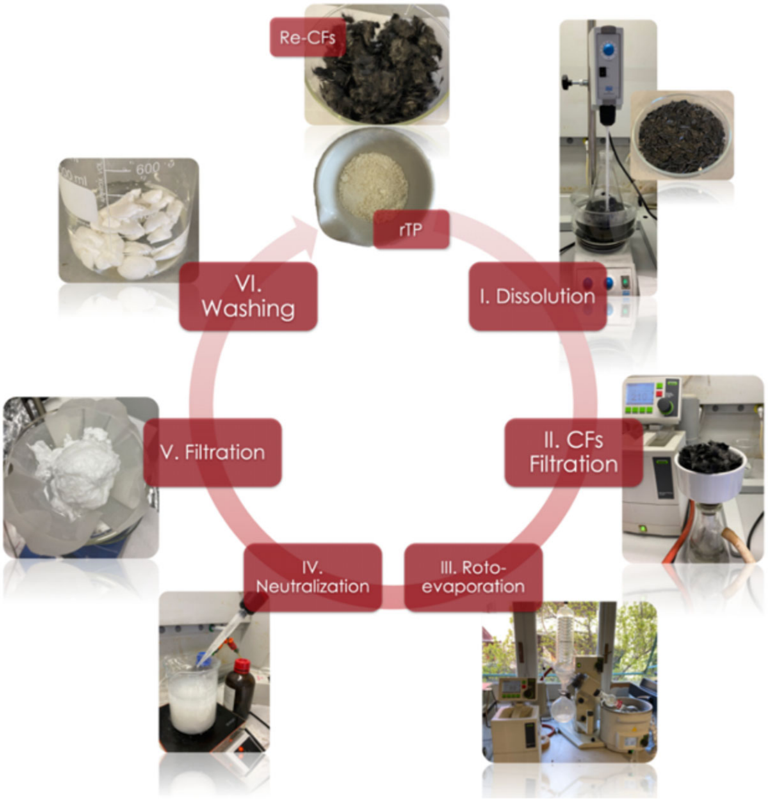

Figure 3. Chemical recycling process for CFs/epoxy composite scheme.

the sodium hydroxide solution used for the mandrel dissolution did not negatively affect in a significant manner the prostheses shell's epoxy matrix.

2.2. Prostheses End-of-Life Handling

A chemical recycling process, already proposed by the author,[14,15] of the composite material was exploited as EoL handling strategy. So, 20 g of carbon fiber/epoxy composite broken in chunks was dissolved in 500 mL of a 75 vol% of acetic acid at 80 °C for 1 h. Once the epoxy matrix was dissolved, the CFs were recovered through a filtration process and dried. The 95% of CFs were recovered as short fibers, and can be further used as fillers for the most disparate polymers matrices. Next, the acid solution containing the dissolved epoxy matrix was roto-evaporated at 60 °C and at a pressure of 60 mbar until a concentrated solution with a volume of 100 mL was obtained. Next, the solution was neutralized by using an ammonium hydroxide solution (50 vol% of distilled water and 50 vol% of ammonium hydroxide solution 28–30% NH_3 basis) and a whitish compound started to precipitate, which is a recycled thermoplastic (rTP). In the end, it was washed with deionized water, dried in oven at 50 °C for 48 h under vacuum conditions and pulverized. The key factor for the recyclability of the epoxy CFRP relies on the use of a fully-recyclable ammine having in its structure cleavable ketal groups that permits the selectively cleavage of the cross-linked network under mild acidic conditions. The recycling process is schematized in **Figure 3**. The recycling process yield was equal to 99%.

3. Conclusions

A hybrid manufacturing approach was proposed to manufacture a fully-recyclable lightweight lower-limb prostheses with an embedded functional element. The used recycling strategy resulted effective as CFRPs disposal route, since rTP and short CFs were recovered with a high process yields. Moreover, the mechanical behavior (flexural test) of the manufactured composite shell was slightly affected by the dissolution process, which involved the treatment of the composite material in a basic environment together with mild high temperature, but not in a statistically significantly way. Future studies must be run to evaluate possible significant changes in terms of thermomechanical properties (i.e., glass transition temperature, T_g) and surface finishing.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

additive manufacturing, carbon fibers, composites, fully-recyclable epoxy resins, recycling

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[1] R. K. Chen, Y. Jin, J. Wensman, A. Shih, *Addit. Manuf.* **2016**, *12*, 77.
[2] A. S. Salles, D. E. Gyi, *Int. J. Comput. Integr. Manuf.* **2013**, *26*, 386.
[3] R. Gailey, K. Allen, J. Castles, J. Kucharik, M. Roeder, *J. Rehabil. Res. Dev.* **2008**, *45*, 15.
[4] I. S. Abbood, S. A. Odaa, K. F. Hasan, M. A. Jasim, *Mater Today Proc.* **2021**, *43*, 1003.
[5] L. J. Love, V. Kunc, O. Rios, C. E. Duty, A. M. Elliot, B. K. Post, R. J. Smith, C. A. Blue, *J. Mater. Res.* **2014**, *29*, 1893.
[6] H. Li, G. Taylor, V. Bheemreddy, O. Iyibilgin, M. Leu, K. Chandrashekhara, *Addit. Manuf.* **2015**, *7*, 64.
[7] G. Cicala, C. Tosto, G. Recca, A. Patti, *Macromol. Symp.* **2021**, *395*, 2000256.
[8] Z. Xiao, L. T. Harper, A. R. Kennedy, N. A. Warrior, *Compos. Struct.* **2017**, *182*, 380.
[9] C. Tosto, A. Latteri, E. Pergolizzi, D. Giordano, G. Abramo, R. Catenaro, N. Pignotti, G. Cicala, *Macromol. Symp.* **2020**, *389*, 1900069.
[10] M. Roy, T. J. Dickens, *Addit. Manuf.* **2017**, *15*, 78.
[11] L. Paternò, L. V. Dhokia, V. A. Menciassi, J. Bilzon, E. Seminati, *Biomed. Eng. Online* **2020**, *19*, 71.
[12] D. A. Türk, H. Einarsson, C. Lecomte, M. Meboldt, *Prod. Eng.* **2018**, *12*, 203.
[13] C. Tosto, J. Tirillò, F. Sarasini, C. Sergi, G. Cicala, *Polymers* **2022**, *14*, 3264.
[14] F. Ferrari, C. E. Corcione, R. Striani, L. Saitta, G. Cicala, A. Greco, *Polymers* **2021**, *13*, 2768.
[15] L. Saitta, V. Prasad, C. Tosto, N. Murphy, A. Ivankivic, G. Cicala, *Polym. Compos.* **2022**, 1.