Supplementary Materials for

3D Printing of Continuous Fiber Composites Using Two-stage UV Curable Resin

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S1. The mechanism of the two-stage UV-curing

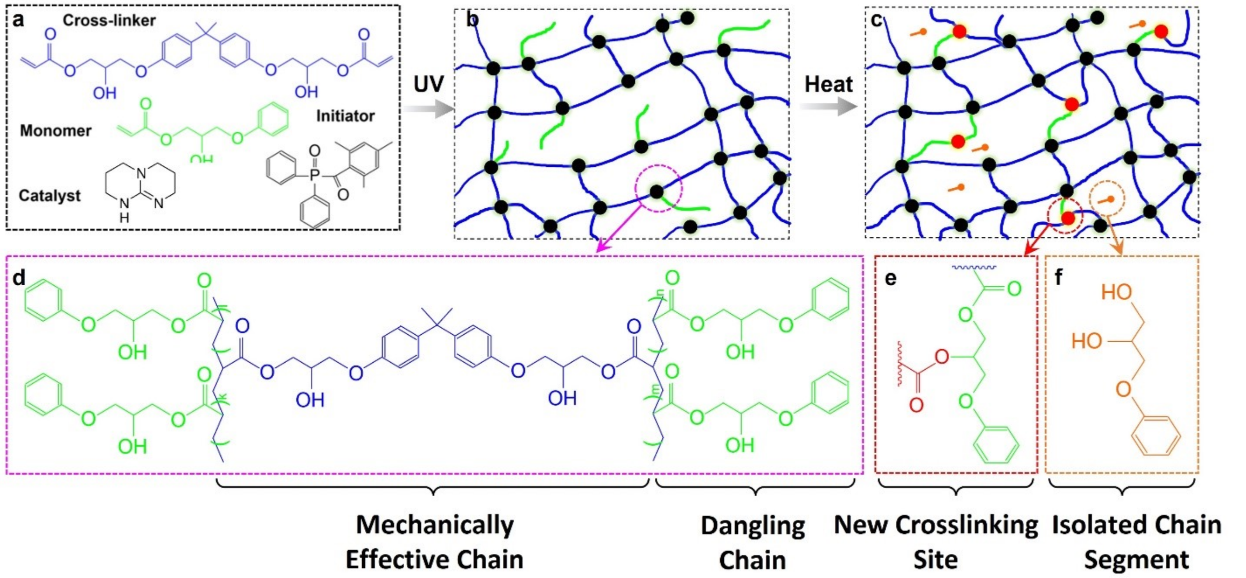

Figure S1. (a) Chemical structures of monomer, cross-linker, photo initiator, and catalyst in the precursor resin. (b) UV curing at Stage 1 forms the network containing mechanically effective polymer chains and dangling chains. (c) During the Stage 2 thermal treatment, dangling chains react with the polymer network through BERs, and increase the density of mechanically effective polymer chains. Isolated chain segments are generated within the network. (d) Chemical structure of the network before thermal treatments. (e) Chemical structure of the newly added crosslinking site after thermal treatment. (f) Chemical structure of the isolated chain segment.

S2. DIW 3D printing setup

The schematic view of the DIW 3D printer for CFRPs is shown in **Figure S2a**. The cross-sectional view of the printhead is shown in **Figure S2b**, which consists of a syringe barrel, a feeding tube, a printing nozzle, and UV light sources with a wavelength of 405nm. The two-stage UV-curable resin is stored in the syringe as printable ink. An aluminum tube with a diameter of

2.7 mm is concentrically attached to the syringe to guide the feeding of continuous fiber. The fiber interacts with the ink at the end of the feeding tube. A straight dispensing needle is attached to the syringe and used as printing nozzles. For this study, a dry 1K carbon fiber tow (CST-The Composites Store, Inc., Tehachapi, CA) without surface treatment was used for the composite printing. To prevent resin curing around the needle tip and nozzle clogging issues, a rubber cap (~2 mm diameter) was installed at the tip of the needle to block the UV light during the movement of the printhead. After the first stage of photopolymerization, the printed composite samples are transferred to the oven at different temperatures for post-curing (**Figure S2c**). This post-curing process facilitates BERs, leading to increased crosslinking density and strengthening of the polymer matrix. Simultaneously, the BERs around the filament interfaces enhance their interfacial strength. **Figure S2d** shows the printed composite lamina sample after the two-stage polymerization scheme.

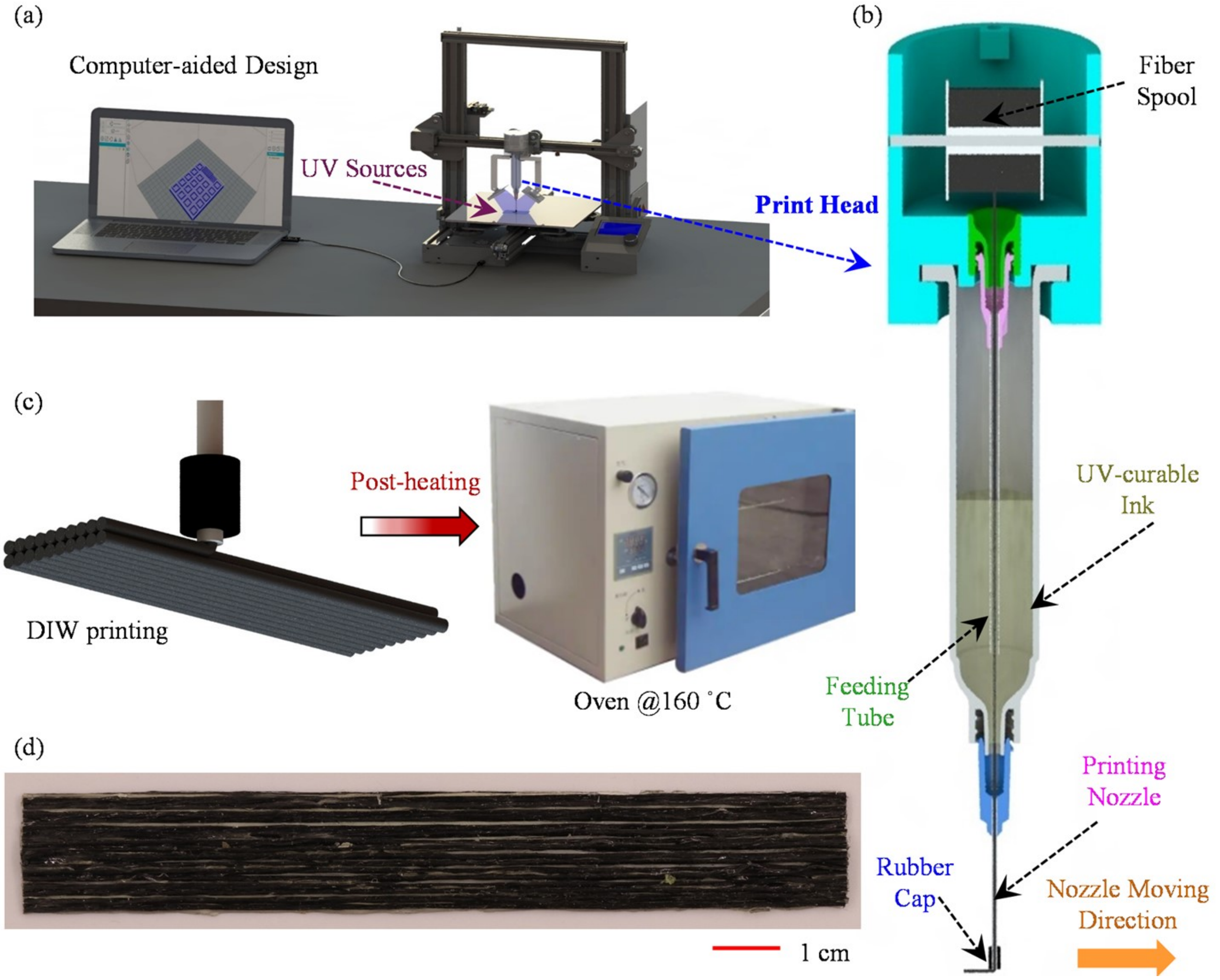

Figure S2. (a) Schematic view of the DIW printer for CFRPs. (b) The cross-sectional view of the DIW printer head. (c) After the printing, the CFRPs are subject to post-heating for the second-stage polymerization. (d) Demonstration of a printed composite lamina.

S3. Fiber volume fraction measurements

Comment [YK]: In Response to Reviewer 1, Comment 2

The fiber volume fractions in the printed composite samples were determined by measuring the volumes of both the fiber and the resin within the printed filaments. Specifically, according to the supplier, the density of the purchased carbon fiber is ρ_f =1.75 g/cm^3. Using Archimedes' principle, we measured the density of the matrix polymer, which was found to be ρ_m =1.24 g/cm^3.

After printing a composite filament, we recorded its length and weight. Subsequently, we measured the weight of a dry carbon fiber with the same length (m_f). The weight of the matrix polymer contained within the printed filament (m_m) was determined by subtracting the weight of the fiber from the total weight of the filament. The volume of the carbon fiber within the filament was calculated as $\varphi_f = m_f / \rho_f$, while the volume of the matrix polymer was determined as $\varphi_m = m_m/\rho_m$. The final volume fraction of fiber content in the printed composite filament is:

$$V_f = \frac{\varphi_f}{\varphi_f + \varphi_r}$$

S4. Experimental characterizations of 1k carbon fiber and 3D printed composites

The carbon fiber bundles for the composites 3D printing were used in their original, untreated state. The modulus of these bundles was determined through uniaxial tension tests conducted at room temperature. To ensure a secure setup, a specimen holder, as depicted in **Figure S3a**, was fabricated to firmly clamp the fiber bundle within the MTS tester. This tensile experiment was carried out twice to ensure the reliability of the data. The stress-strain curves of the carbon fiber are presented in the figure. It is observed that the initial stages of the stress-strain curves from the two experiments are close to each other, indicating good repeatability of the measurement. It was determined from the initial slope of the stress-strain curves that the Young's modulus of the carbon fiber is approximately 174 GPa.

To assess the modulus of an individual composite filament, the filament was initially 3D printed using DIW and subsequently subjected to a post-heating process. To securely grip the filaments in the tensile tester machine, a shouldered specimen fixture was designed as illustrated in **Figure S3b**.

Mechanical performance of the printed composite lamina was characterized. **Figure S3c** showcases the composite lamina with varying fiber contents. The samples look similar due to the presence of black carbon fiber. Corresponding shouldered specimen fixtures were designed to accommodate these lamina samples, as shown in the figure. Additionally, **Figure S3d** displays the composite lamina samples intended for the characterization of the transverse modulus.

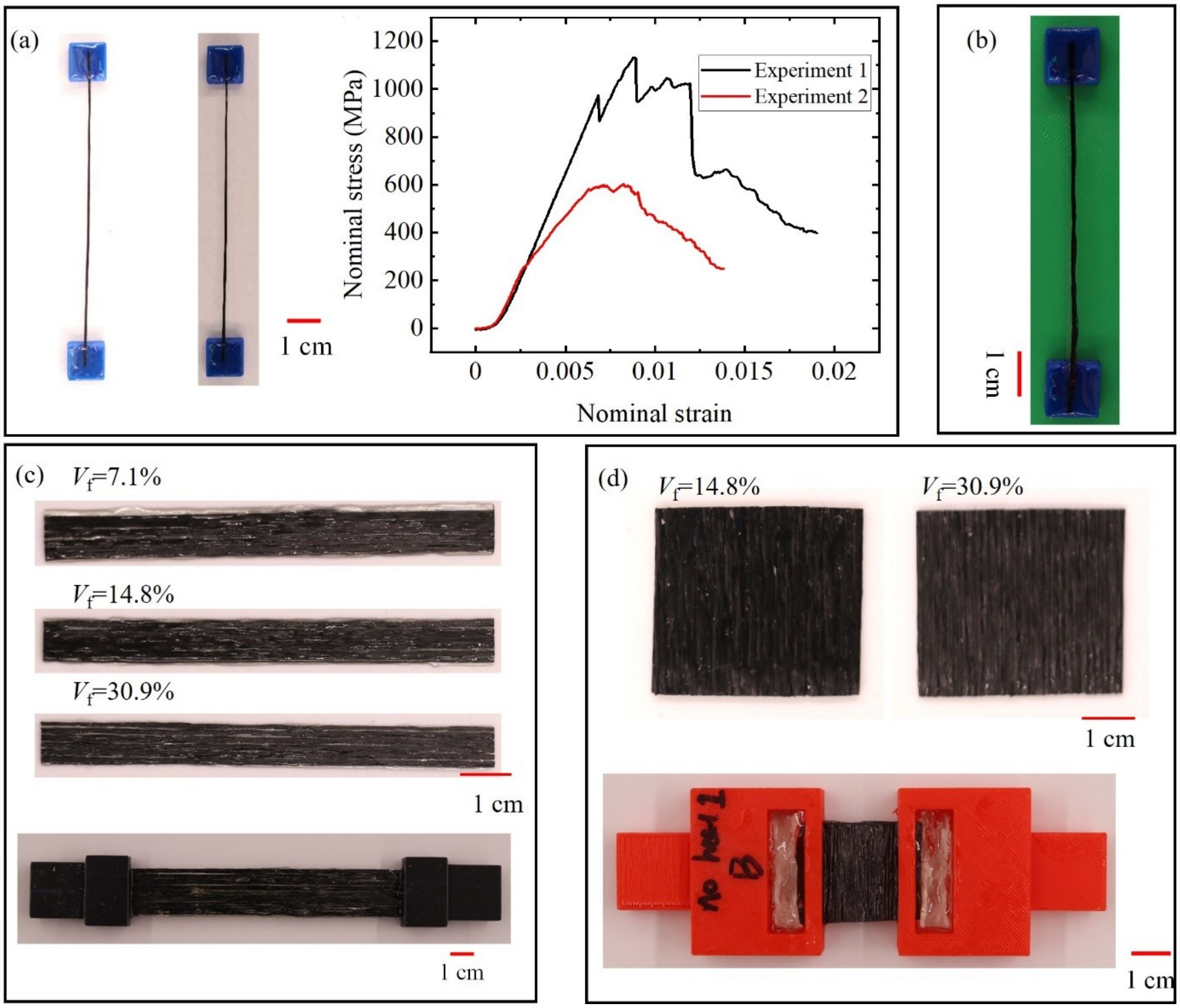

Figure S3. (a) Fiber specimens fabricated for the tensile testing and the stress-strain curve of the 1k carbon fiber bundle. (b) A 3D printed composite filament intended for tensile testing. (c) 3D printed composite lamina for tensile testing along the longitudinal direction. (d) 3D printed lamina samples for tensile testing along the transverse direction.

S5. Schematic view of the network depolymerization

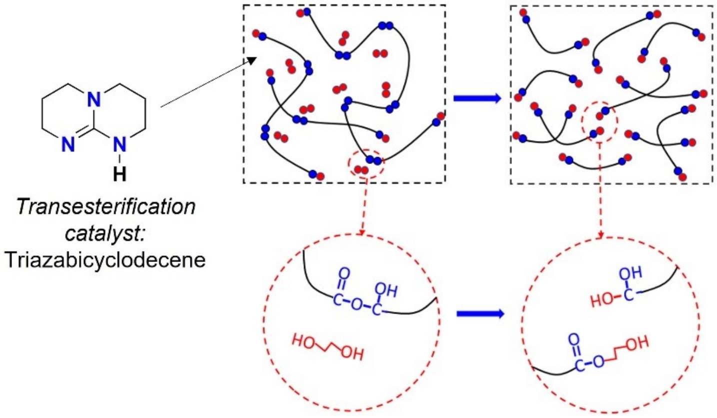

Figure S4. Schematic view showing the mechanism of network depolymerization. The alcohol solvent molecules break the polymer chains from the position of esters via transesterification reactions.

S6. Microscope images of reclaimed fibers after depolymerizing the composite matrix

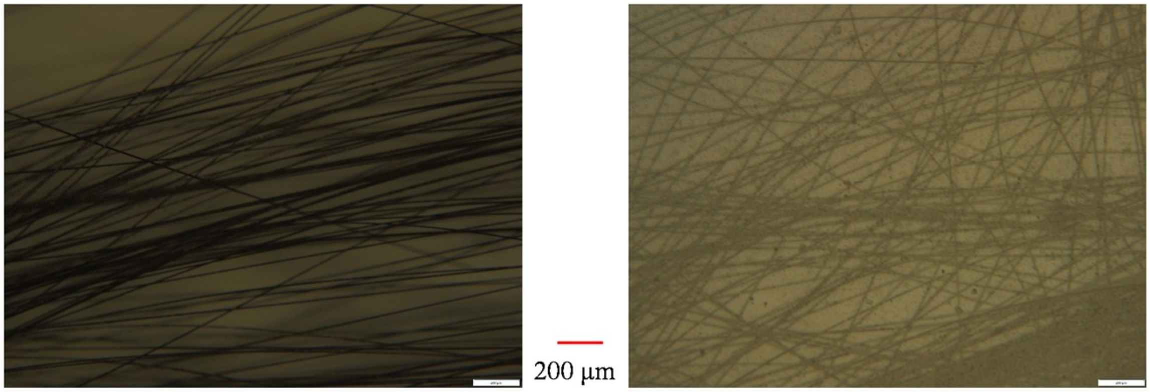

Figure S5. Microscope images of the recycled carbon fibers. Note: The two microscopic images depict the same recycled fiber bundle, captured at different locations, and presented with varying contrasts to emphasize microscale details.

S7. DIW printing with acrylate/epoxy two-stage resin and polyester continuous fiber

The polyester fiber thread was purchased from Coats & Clark Inc. (Charlotte, NC, USA). The acrylate/epoxy two-stage resin was prepared following the previous work by Kuang et al. [1], which consists of 20wt% acrylate resin and 80wt% epoxy resin. The acrylate resin includes 1,6-hexanediol diacrylate and acrylate-epoxy monomer glycidyl methacrylate in a 3:1 mole ratio, while the epoxy resin consists of 4,4-diaminodiphenylmethane and epoxy monomer 4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate with a mole ratio of 1.8:1. The chemical structures of these monomers are depicted in **Figure S6a**. After the initial UV polymerization, the samples were subject to post-heating to trigger the second-stage reaction between amine and epoxy groups. The newly formed interpenetrating network is highlighted in **Figure S6a** in green color.

Figure S6b compares the glass transition behaviors of the cured resin before and after the second-stage thermal polymerization. It is observed that after heating at 100°C for 60 mins, the glass transition temperature is increased from 64°C to 137°C. **Figure S6c** shows the uniaxial stress-strain relationships. The corresponding elastic modulus (within the 5% strain) and sample ultimate strength are summarized in **Figure S6d** After the second-stage polymerization at 100°C, the modulus increases from ~595 MPa to ~4.0 GPa, and the strength increases from 4 MPa to 99 MPa.

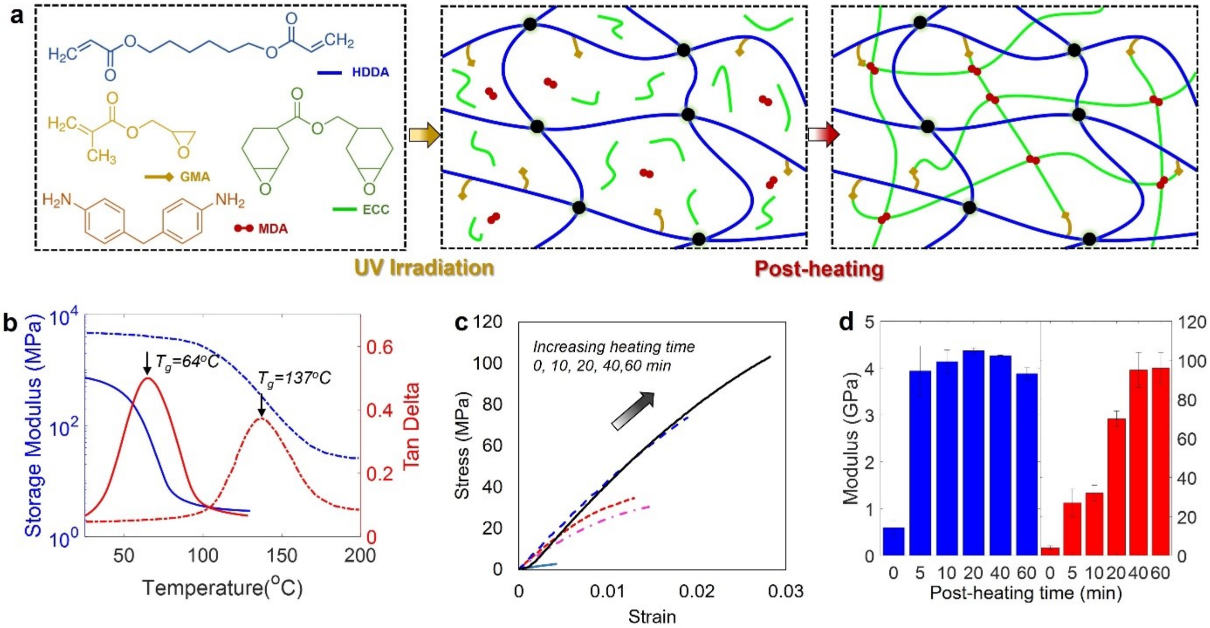

Figure S6. **(a)** Monomers used to prepare the acrylate/epoxy-based two-stage UV-curable resin. The figure also presents the network structure evolution during the curing. The newly formed interpenetrating network is highlighted in green color. **(b)** Storage modulus and tan δ of the cured resin before and after post-curing. **(c)** Room-temperature stress-strain relationship and **(d)** Summary of the elastic modulus and mechanical strength of the resin before and after post-curing at 100°C.

Utilizing the DIW method, we printed two sets of composite samples using the acrylate/epoxy two-stage resin. Both samples were single-layer lamina, embedded with 14.8% continuous carbon fiber and polyester fiber, respectively. The appearances of these printed lamina samples are shown in **Figure S7a** and **Figure S7b**.

After printing, the lamina samples were placed between two molds and subjected to heating at 160oC. A moderate force was applied to maintain their geometry. After one hour, both sets of samples were found to permanently fix the new configuration, indicating excellent reshapability. It's worth noting that the mechanism behind this reshaping differs from what is demonstrated in the manuscript. During the second-stage thermal treatment, an interpenetrating network formed between the epoxy and acrylate species, which contributed to fixing the new configuration of the composite lamina. In contrast, in the manuscript, the reshapability of printed composites is attributed to the stress relaxation of the matrix materials induced by BER.

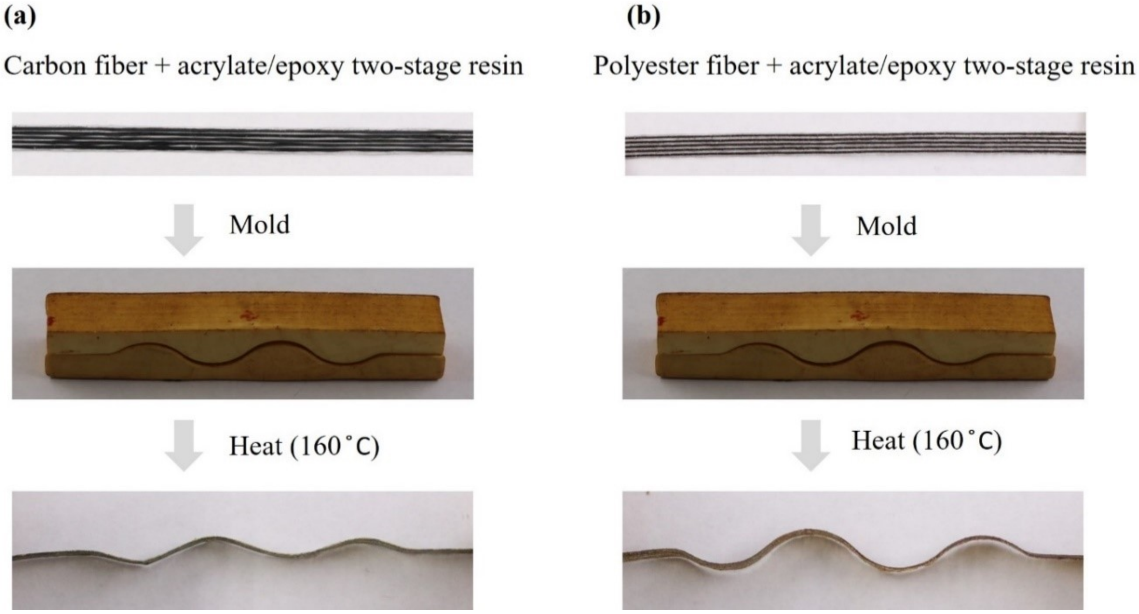

Figure S7. Demonstration of reshaping lamina structure using acrylate/epoxy two-stage resin. (a) Carbon fiber with acrylate/epoxy two-stage resin. (b) polyester fiber with acrylate/epoxy two-stage resin.

Because the cured acrylate/epoxy two-stage network contains ester bonds in the chain backbone, it can be entirely depolymerized by immersing it in a 160°C ethylene glycol solvent mixed with the triazabicyclodecene catalyst to facilitate dynamic transesterification reactions. As shown in **Figure S8**, after immersing the printed composite sample in the 160°C ethylene glycol solvent for approximately one hour, the matrix was completely depolymerized, allowing for the recovery of the embedded carbon fiber. Upon close examination under a microscope, it was evident that the fiber bundle had minimal residual polymer adhering to it.

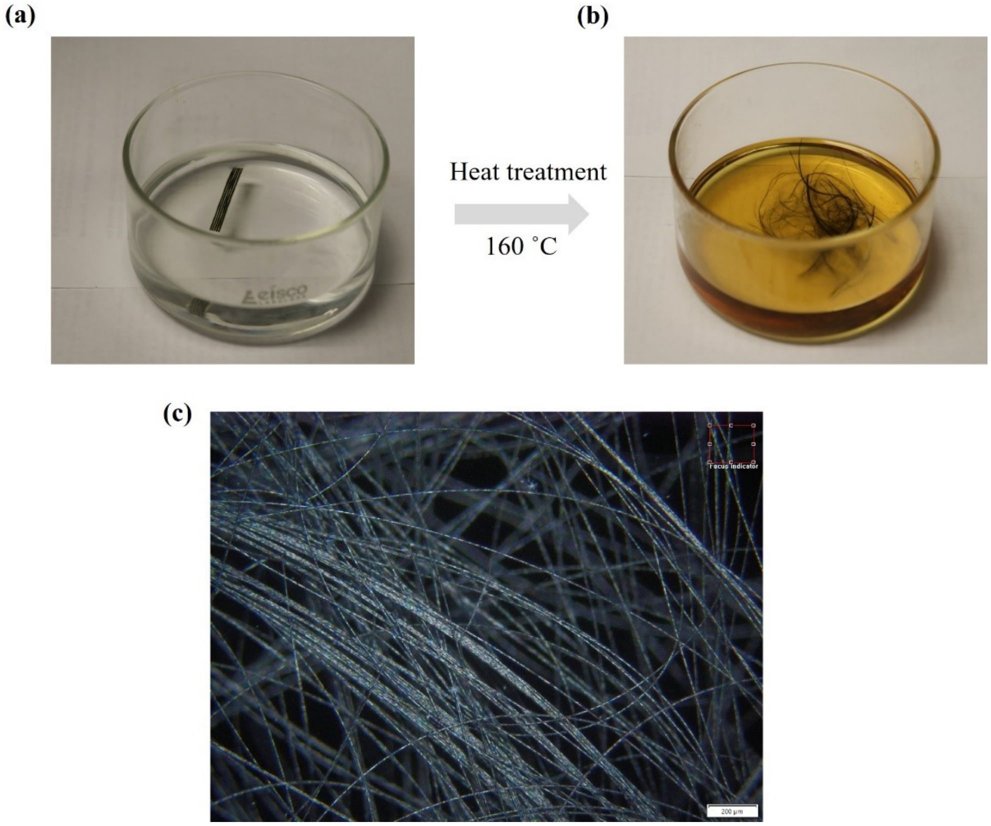

Figure S8. Demonstration of recycling carbon fiber using the acrylate/epoxy two-stage resin. (a) Printed lamina placed into the glassware with EG solvent. (b) Depolymerization of lamina after thermal treatment at 160 ˚C for an hour. (c) Microscope images of the recycled carbon fibers.

References

[1] X. Kuang, Z. Zhao, K.J. Chen, D.N. Fang, G.Z. Kang, H.J. Qi, High-Speed 3D Printing of High-Performance Thermosetting Polymers via Two-Stage Curing, Macromol Rapid Comm 39(7) (2018).