Supplementary information for:

Additive Manufactured Carbon Nanotube/Epoxy Nanocomposites for Heavy-Duty Applications

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S1. Experimental section

Material and preparation of the powder ink

40 g solid bisphenol-A epoxy resin (GT7071, Huntsman, Germany), 1.6 g micronized dicyandiamide latent hardener (Dyhard 100S, Alzchem, Germany), 0.8 g 3,3’-(4-methyl-1,3-phenylene) bis (1,1-dimethylurea) latent accelerator (Dyhard UR500S, Alzchem, Germany) and 1 g multi-walled CNTs (Arkema, Lacq, France) were blended in a blender (Brabender Plastograph Mixer 30/50E, Engelmann & Buckham Limited, UK) equipped with counter-rotating roller blades. The mixture was blended at 62°C for 15 min at a head rotating speed of 53 rpm. After solidification, the mixture was ground into a fine powder (70-500 µm) using a grinder Karcher UM 620 (Austria).

3D Printing of CNT/epoxy parts

The solid resin powder was fed into a syringe; a needle with an inner diameter ($D_i$) of 1.6 mm and an outer diameter ($D_o$) of 1.9 mm was attached to the syringe. The syringe was fitted into a 3D printing platform (Printrbot Simple Bro base model, USA). The layer height ($h$) was set to 0.8 mm; the printing speed ($S$) was 4 mm/s; the dispensing rate ($\alpha$, mm$^3$/s) was calculated using the printing software Cura (version 15.04.2) as follows:

\[ \alpha = S \times h \times D_o \times 105\% \]
The constant 105% was used to allow for overflow of ink to guarantee good adhesion and overlap between walls and infilling lines of the objectives. All printed objects consisted of one layer of outer wall and 100% infilling with a pattern as shown in Figure S1. The objects were printed at 77°C. After the printing, the self-standing, solid yet uncured resin objects were completely covered in wet clay (Fimo air-drying clay, Austria). The objects were placed in oven to cure at 50°C for 24 h, 60°C for 24 h, 70°C for 24 h. The objects were post cured at 120°C and 150°C for 1 h, respectively. Subsequently the cured objects were cleaned with water to remove the clay.

Figure S1. Patterns of a layer of printing epoxy parts contain one outer wall and 45° infilling. Note that the lines show the route of the nozzle during printing, however, the width of the lines does not represent the actual infilling. The actual infilling was always 100%. The parts were printed layer by layer using alternatively pattern 1 and 2. Each layer had a thickness of 0.8 mm.

To print using the single screw extruder printer, the screw was inserted in the barrel, which was inserted in a heating jacket. The screw was connected to the motor of the 3D printer. A hopper was installed on top of the barrel and a needle with an inner diameter of 1 mm attached to the barrel. The solid resin powder was fed into the hopper. The temperature was set to 80°C. The layer height was set to 0.6 mm; the printing speed was 2 mm/s. The printer specimens followed a standard EN ISO 527-2 (1996) 1BA with a thickness of 3 mm (e.g. 5 layer). The printed specimens contained a layer of outer wall to eliminate surface roughness. The raster angles of the infilling were set to 0°, 45° and 90°. The printed specimens were cured following an identical protocol as aforementioned.
Figure S2. Printing dogbone-shaped specimens with 0°, 45° and 90° raster angles. The specimens were all printed flat, resulting in a printing direction perpendicular to tensile direction.

Justification of curing procedure

The as-printed CNT/epoxy parts were self-standing at room temperature. However, once placing the parts in to the oven at 50°C, they began to soften and collapse within 20 min (Figure S2) due to the decreasing viscosity at this temperature. To support the parts at elevated temperatures the parts were covered with a wet clay. The as-purchased wet clay with a water content of 24% was further diluted to a water content of approximately 60 wt% prior to covering the parts. The water in the wet clay did not affect (swell or dissolve) the as-printed parts, as the powder ink is very hydrophobic due to the high loading of the epoxy resin (GT7071), which is only soluble in organic solvents (Datasheet from Huntsman). When dried, the clay formed a stiff shell (the shell may crack because of some shrinkage) to cover but not crush the as-printed parts. To initiate curing the printed parts were heated first to 50°C to soften the resin. Following the onset of curing, the glass transition temperature of the epoxy resin does increase gradually and thus, we increased the curing temperature to 60°C for 1 d and subsequently to 70°C for 1 d. These temperatures were chosen as they allow adequate curing of the clay-wrapped-parts without any deformation. After curing and post-curing the clay was removed by washing and brushing in hot water. However, some clay adhered to the cured parts due to the softening of the resin during curing, allowing the clay to embed in the surface of the resin.
Figure S3. Deformation of as-printed but not clay-covered CNT/epoxy parts (1.5 cm × 1.5 cm × 1.5 cm, 3.1 g) during curing at 50°C. The height of the part was plotted as function of time.

Characterisation

The complex viscosity of the epoxy formulations (mixture of epoxy, hardener, accelerator and CNTs) was measured using TA Rheometer HR-2 (TA Instrument, Germany) equipped with parallel plate geometry with a diameter of 25 mm and measuring gap of 0.3 mm. The formulations were measured by oscillation between the two plates at strain of 1% and a frequency of 2 Hz at 77°C for 20 min.

The bulk density of the objects was determined using a He displacement pycnometer (Accupyc 1340 II, Micrometritics Instrument Corporation, Austria). Fracture pieces of about 0.4 g were measured. The skeletal density of 0.4 g objects was determined using the same equipment, however in this case the samples were ground.

Compression tests were performed following the standard ASTM D1622 using a universal mechanical test machine (Instron 5969, Instron, Germany) equipped with a 50kN load cell. The printed objects with dimensions of 15mm × 15mm × 15mm were polished to obtain a flat surface

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to contact the compression plates. The specimens were compressed either in parallel (XY direction) or perpendicular (Z direction) to the printing direction at a speed of 1.5 mm/min. Flexural tests were carried out on the same test frame but equipped with a 1 kN load cell. Printed objects with a dimension of 80 mm × 10 mm × 3.8 mm were tested following the standard BS EN ISO 178-2010. The span/thickness ratio was 16:1. The test speed was 2 mm/min.

Tensile tests were performed using the same equipment following the standard EN ISO 527. The distance between two clamps was 58 mm. The test speed was 1 mm / min and the actual strain was determined using a video-extensiometer. The stress-strain curves of the specimens were plotted. The Young’s moduli were calculated in the initial linear region of the curves; the ultimate strengths and strains were obtained from the curves at the breaking points. The 0.2% offset yield was determined from the point of 0.2% plastic strain.

The fracture surfaces of flexural specimens were investigated using scanning electron microscopy (SEM, JCM-6000, JEOL, Germany). Prior to SEM, the fracture surfaces were gold-coated. The SEM was operated in secondary beam mode using an acceleration voltage of 15 kV.

The degree of cure of the epoxy resin was confirmed by DSC (Discovery DSC, TA Instrument, Germany). About 10 mg samples were heated / cooled / heated / cooled between 40 °C and 200 °C at a rate of 10°C / min. The glass transition temperatures of the samples were determined using dynamic thermal mechanical analysis (DMTA, Discovery RSA-G2, TA Instrument, Germany). Samples with a thickness of 3.8 mm and a width of 10 mm were tested using 3-point bending with a span length of 25 mm. Samples were tested at a frequency of 1 Hz from 50°C to 160°C at a heating rate of 4°C/min.

S2. Thermal properties of CNT/epoxy composite
Figure S4. Heat flow curve (a) of the printed epoxy parts show no significant exotherm in the first heating curve, indicating a full reaction of the epoxy with the hardener. The glass transition measured from the heat flow curve was 116°C. Storage modulus and tan δ (b) of printed epoxy parts were obtained by DMTA of 10 mm × 3.8 mm × 40 mm (span length). Glass transition temperature is read as the peak of the Tan δ curve, which was 118°C.
### Table S1

| Materials          | Processing                  | Mechanical tests | Mechanical properties                  | Anisotropy                                      | ref    |
|--------------------|-----------------------------|------------------|----------------------------------------|------------------------------------------------|--------|
| CNT/epoxy          | FDM + curing                | Compression      | Modulus: 1.3 GPa                      | No anisotropic                                   |        |
|                    |                             | Flexural         | Strength: 80 MPa                       |                                                |        |
|                    |                             | Tensile          | Modulus: 2 GPa                        |                                                |        |
|                    |                             |                  | Strength: 58 MPa                       |                                                |        |
|                    |                             |                  | Modulus: 1.8-2 GPa                     |                                                |        |
|                    |                             |                  | Strength: 52-58 MPa                    |                                                |        |
| Clay/epoxy         | FDM + curing                | Flexural         | Modulus: 3-4 GPa                       | Anisotropic stiffness from anisotropic fillers  | 1      |
|                    |                             |                  | Strength: 80-150 MPa                   |                                                |        |
| Short CF/epoxy      | Direct writing + curing     | Flexural         | Modulus: 3-10 GPa                      | Anisotropic stiffness                            | 2      |
|                    |                             |                  | Strength: 120-160 MPa                  |                                                |        |
|                    |                             | Tensile          | Modulus: 4-9 GPa                       |                                                |        |
|                    |                             |                  | Strength: 70-140 MPa                   |                                                |        |
| Epoxy              | Dual curing                 | Demo             | 1.2 g epoxy sample can hold 3200 g weight |                                                | 3      |
| Graphene/epoxy      | FDM + curing                | Flexural         | Modulus: 5 GPa                         |                                                | 4      |
|                    |                             |                  | Strength: 80 MPa                       |                                                |        |
| Porous epoxy       | FDM + curing + salt leaching| Tensile          | Strength: 0.6 MPa                      |                                                | 5      |
| Short CF/epoxy      | Direct writing + curing     | Tensile          | Modulus: 2-5.5 GPa                     |                                                | 6      |
|                    |                             | Compression      | Strength: 100-180 MPa                  |                                                |        |
| Whisker/epoxy       | FDM + curing                | Wearing          | Wearing rate: 3-6×10⁻⁶ mm³/Nm          | Anisotropic wearing from anisotropic fillers    | 7      |
| Continuous CF/epoxy | FDM + curing in vacuuming   | Flexural         | Modulus: 60-70 GPa                     |                                                | 8      |
|                    |                             |                  | Strength: 600-950 MPa                  |                                                |        |
| Continuous CF/epoxy | FDM + curing                | Flexural         | Modulus: 30-43 GPa                     |                                                | 9      |
|                    |                             | Demo UAV frame   | Strength: 300-500 MPa                  | Can hold 32 kg weight                            |        |

### S4. Chemical resistance of 3D printed CNT/epoxy composites.

Acetone and isopropanol were purchased from Donau Chemie (Austria), dimethylformamide (DMF), tetrahydrofuran (THF), toluene, benzene and dimethyl sulfoxide (DMSO) from Sigma-Aldrich, 37% HCl from VWR and diesel from a local petrol station. 3D printed CNT/epoxy
composite pieces with a dimension of about 6 mm × 5 mm × 3 mm were immersed in these solvents. The dimension changes of the pieces were recorded. Disintegration was defined as the time when a part of the piece fell off which changed the inherent dimension of the piece.

**Figure S5.** CNT/epoxy composites kept in acetone, isopropynol, DMF, THF, DMSO, toluene, benzene, diesel and 37% aq. HCl (from left to right) for 10 days. The composites disintegrated in DMF, THF and DMSO. The composites swelled slowly in acetone by 30 vol%. However, the composites were stable in the other solvents.

S5. ESI video 1 shows a printed CNT/epoxy composite chain ring was connected with carabiner rings; one author, QJ, dangled himself onto the ring connected onto a construction frame.

S6. ESI video 2 shows the application of 3D printed CNT/epoxy composite spanner at elevated temperature and in acetone.

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