

Electronic Supplementary Information

Carbon nanotube-Vitrimer composite for facile and efficient photo-welding of epoxy

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1. Sample preparation

Dispersion of CNTs

MWNTs were obtained from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences (CVD, purity 95+ %, diameter <8 nm, as-produced length 10-30 μm) with no functionalization. Ultrasonic Processor (*Ningbo Scientz Biotechnology Co. LTD, SCIENTZ-IIID, 950 W*) with titanium micro-tip was used for sonication. The following sonication parameter settings were kept the same throughout all experiments: pulse with 1 s on and 1 s off, probe temperature held at 23 $^{\circ}\text{C}$ and vibration amplitude at 25 %. PIM₁ was synthesized according to *Nat. Commun.* **2013**, *4*, 1918. 4.9 mg CNT and 4.9 mg PIM₁ were suspended in 4 mL Chloroform and sonicated for 1 hr of actual pulsing time. The resulting solution was used immediately for the synthesis of CNT-Vitrimer.

Synthesis of CNT-Vitrimer

As a typical example, stoichiometric amount of diglycidyl ether of bisphenol A (0.340 g, 1 mmol, DGEBA, Sigma-aldrich, DER 332) and adipic acid (0.146 g, 1 mmol) (TCI >99.0 %) were mixed with 4 mL CNT dispersion obtained from the above procedure. The mixture was heated to 100 $^{\circ}\text{C}$ till the chloroform was totally evaporated. Then, triazobicyclodecene (Sigma-aldrich 98 %) (5 mol% to the COOH) groups was introduced and stirred manually till homogeneous. The mixture was cooled to room temperature and sandwiched between two glass slides. The glass slides were covered by PTFE tape before use. The two glass slides with the reaction mixture in the middle were clamped together and left at 180 $^{\circ}\text{C}$ for at least 4 h. For all the samples prepared, the CNT loading was kept at 1 wt%. Fourier transform infrared spectroscopy (FTIR) (*Perkin Elmer spectrum 100*) showed that the epoxy peak totally disappeared. To verify whether the sample was fully cured into a covalently cross-linked network, swelling experiment was carried out in 1, 2, 4-trichlorobenzene. The sample was first immersed in the solvent at 100 $^{\circ}\text{C}$ for 1 h, then the temperature was increased by a 20 $^{\circ}\text{C}$ interval. At each temperature, the sample was immersed for 1 h.

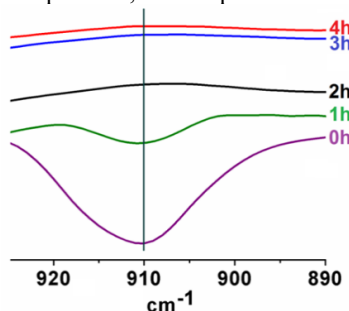


Figure S1. The epoxy signal during the reaction monitored by FTIR.

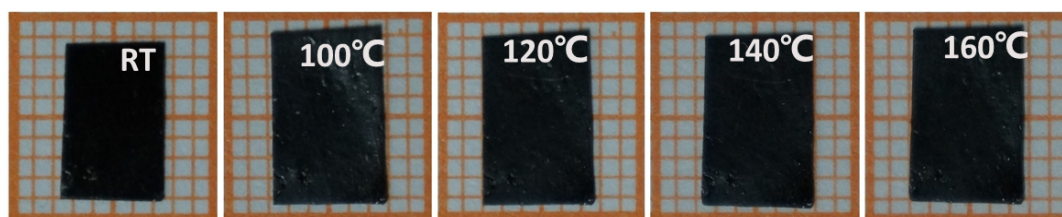


Figure S2. Swelling of CNT-Vitrimer in trichlorobenzene.

2. Thermal properties of CNT-Vitrimer

Differential scanning calorimetry (DSC) was performed using *TA instruments Q2000* operated at a scanning rate of 10 °C /min.

The tensile storage modulus and $\tan \delta$ trace of CNT-Vitrimer were measured by dynamic mechanical analysis (DMA) on a *TA-Q800 DMA* apparatus in the film-tension geometry at a rate of 1 °C/min and an oscillation frequency of 1 Hz.

Stress relaxation experiments were performed on a *TA-ARG2* rheometer using a 8 mm parallel-plate geometry. The sample was equilibrated at the aimed temperature (80, 100 and 170 °C) for 10min. Since 1 % deformation was within the linear range according to a previous strain sweep experiment, we applied a constant 1 % strain step as we monitored the stress relaxation over time. To ensure the good contact, a constant normal force of 10 N was applied.

Dilatometry experiment was performed on a *TA-Q800 DMA* apparatus in the tension film geometry under the controlled force mode, with a rectangular tension film dimension of 10.0 mm \times 2.60 mm \times 0.08 mm. The length was measured while the sample was heated from 25 to 250 °C at a rate of 3 °C/min. To avoid buckling, a weak stress of 24 KPa was applied throughout the experiment.

The thermal stability of CNT-Vitrimer was measured with a *TA-Q50 TGA* under air atmosphere and nitrogen atmosphere.

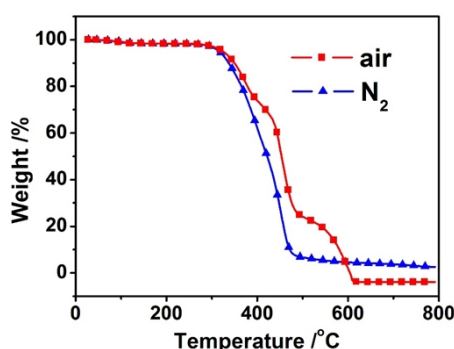


Figure S3. TGA curve of CNT-Vitrimer (heating rate: 20 °C/min).

3. Compress molding of CNT-Vitrimer

Two CNT-Vitrimer films (15.0 mm \times 3.0 mm \times 0.08 mm) were partially overlapped and sandwiched between two glass slides. The glass slides were covered by PTFE tape before use. The glass slides were clamped together by foldable clips and left at 230 °C for 3 min.

4. Light controlled reshaping, welding and healing

All the CNT-Vitrimer samples had a thickness about 80 μ m. Light controlled reshaping, welding and healing were done by IR light (808 nm laser). For the permanent reshaping, welding and healing, the samples were irradiated at an intensity of 3.8 W/cm². To reshape the sample in Figure 3b ii, only the ridge was irradiated (at an intensity of 3.8 W/cm²) for 20 s while the sample was under stress. To get the shape in Figure 3b iii, the left ridge was irradiated at an intensity of 0.38 W/cm² while the right ridge was irradiated for 5 s at an intensity of 3.8 W/cm². Stress-strain and lap shear test were performed using a TA Instruments model Q800 dynamic mechanical analyzer (DMA) in the tensile mode.

For the preliminary welding test, the CNT-Vitrimer samples with diverse CNT concentration (0 wt%, 0.1 wt%, 0.5 wt%, 1 wt% and 3 wt%) were irradiated at an intensity of 3.8 W/cm².

For the investigation on the effect of catalyst, all the CNT-Vitrimer samples (cat.0%, 2%, 5%, 10%) were irradiated at an intensity of 3.8 W/cm² for 1 min while the sample was under stress.

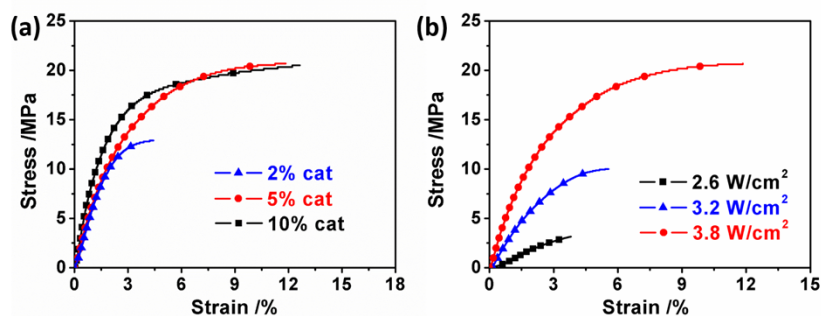


Figure S4. Lap shear test of different welded samples. (a) The effect of different catalyst concentration on photo-welding. (b) The effect of different light intensity on photo-welding.

To make a pocket, a rectangular mask was placed on the top of two overlapped films. When the light was on, only the edges uncovered by the mask were joined together, leaving the shielded zone unaffected. The result pocket was water-proof.

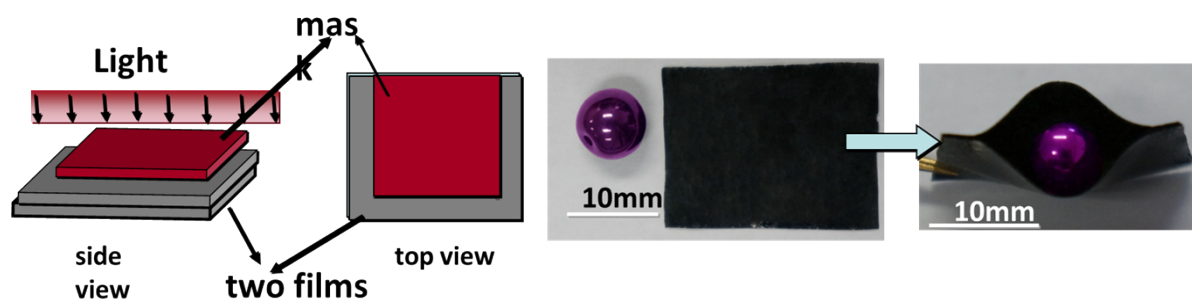


Figure S5. Illustration of welding on the selected area. A purple ball was put in the pocket to show that unexposed parts were not joined together.

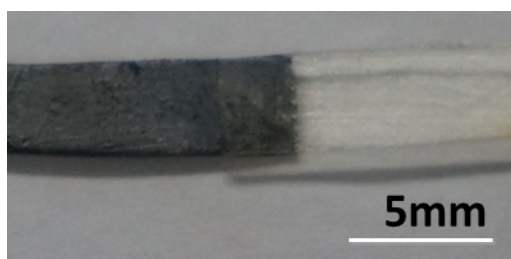


Figure S6. Welding of CNT-Vitrimer (thickness: 0.08mm) with non-CNT Vitrimer (thickness: 0.82 mm).