Supporting Information

Recyclable 3D Printing of Vitrimer Epoxy

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S1. Nanoclay-Vitrimer ink preparation and 3D printing

Table S1 lists the composition of the ink used in this study. Fig. S1 shows the chemical structures of the monomers and the epoxy.

We wrapped two flexible heating elements (with resistance of $16\,\Omega$) around the syringe and the nozzle to increase the temperature and reduce the viscosity of the ink. We applied a 4V current. Fig. S2 shows the IR image of the temperature field around the syringe and the nozzle, showing the temperature of around ~70°C.

Table S1. Printable ink constituents of vitrimer epoxy based thermosets.

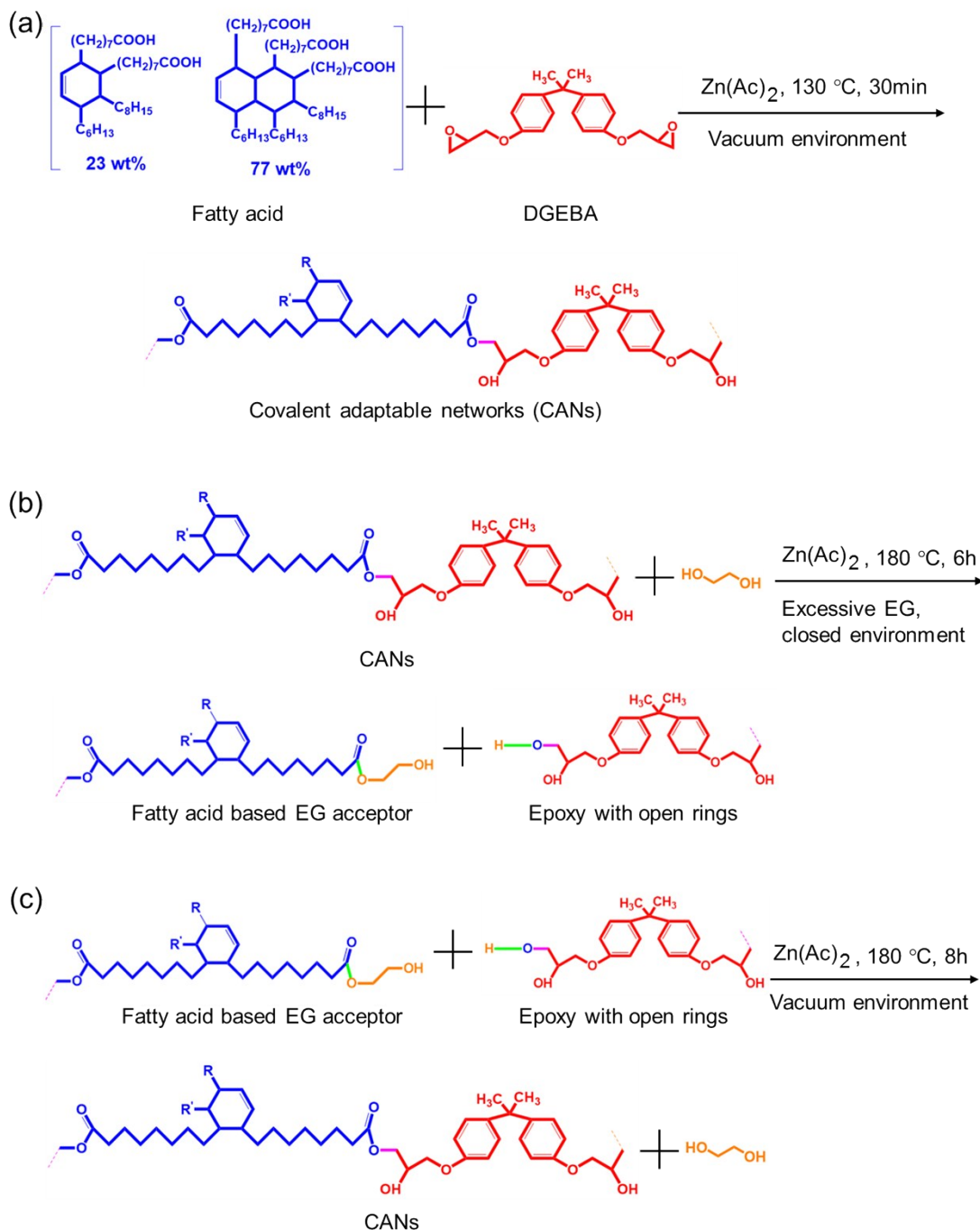| Ink constituent	Printable Vitrimer ink (weight fraction)	Functions
DGEBA	29.50%	The epoxy resin
Fatty acid	50.18%	The crosslinker
Zn(Ac)$_2$	2.24%	The catalyst for BERs
Nanoclay	18.08%	A rheology modifier imparting a strong shear thinning behavior to the ink to form a viscoelastic fluid

Figure S1. Typically chemical reactions during precrosslinking/dissolution/recrosslinking cycles of recyclable 3D printing thermosets. a) For the first printing cycle, the epoxy resin DGEBA is covalently crosslinked to dicarboxylic and tricarboxylic acids. b) At the later cycles, EG molecules participate in the polymer networks at the ester sites to break them. c) Then, the depolymerized chains recrosslink together at the same ester sites and simultaneously regenerate the EG molecules that is evaporated completely with reactions proceeding.
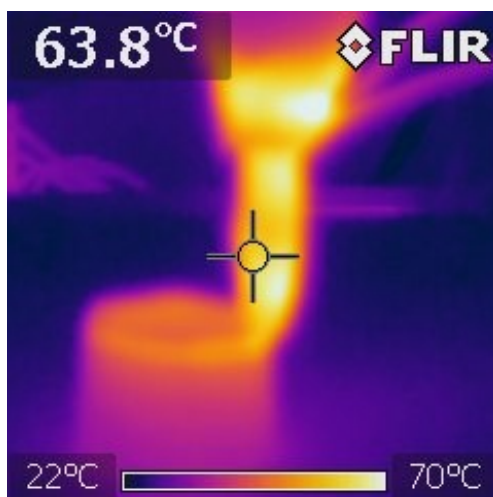
Figure S2. Tested temperature field (around 70°C) of the outer surface of the extrusion nozzle equipped with two heating elements.

S2. Characterization of the EG-assisted bond exchange reactions (BERs) in nanoclay-vitrimers

Fourier transform infrared spectroscopy (FTIR):

To determine the actual composition and the structure of the nanoclay reinforced vitrimers during the dissolution/re-crosslinking cycles, infrared spectroscopy were tracked via FTIR to monitor and characterize the conversion of functional groups (esters and hydroxyl groups) in both epoxy-acid reaction (the 1st cycle) and EG- participated transesterification (the 2nd and following cycles). The FTIR measurements were performed at the room temperature by using Thermo Scientific Nicolet iS50 FT-IR spectrometer fitted with an ATR cell. The spectrum of each sample is the averaged result from 32 scans collected from 550 cm^{-1} to 4000 cm^{-1} at 1 cm^{-1} resolution.

Three samples were prepared for each 3D printing cycle respectively before the FTIR measurements. For the 1st cycle, 1) as-mixed epoxy, 2) pre-crosslinked epoxy that is heated at 130 °C for 30 min under vacuum, 3) fully cured epoxy after printed; for the 2nd and following cycles, 1) fully dissolved epoxy after soaking in EG at 180 °C for ~6h, 2) pre-crosslinked epoxy that is repolymerized at 180 °C for ~8h under vacuum from the vitrimer epoxy dissolution. 3) fully cured epoxy after printed. Tests were carried out for all three samples for each cycle.
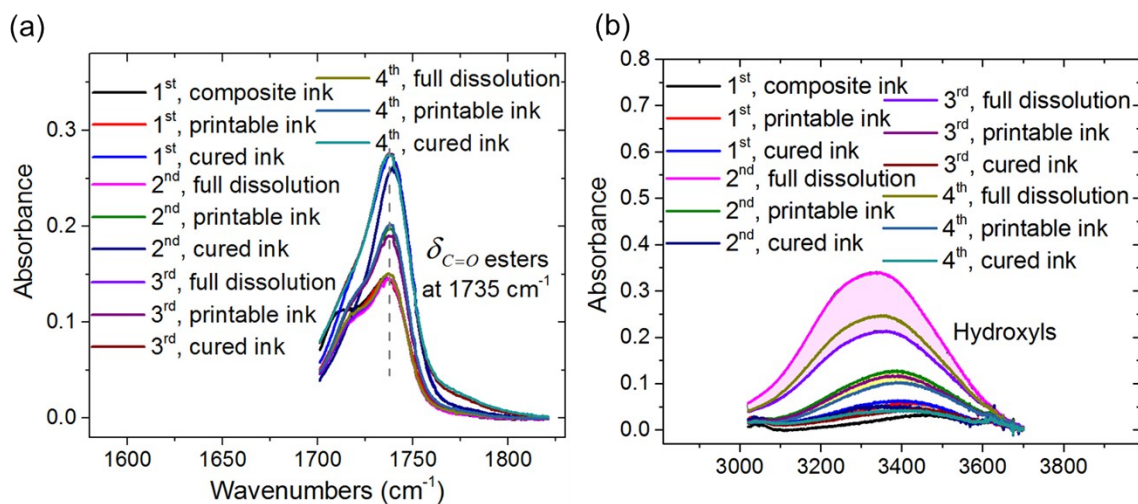
Figure S3. FTIR tracks the functional groups in the polymerization/dissolution/repolymerization process over varied printing cycles. a) Ester (1735-1750 cm-1) signals. b) Hydroxyl (3200-3550 cm-1) signals.

Thermal and mechanical characterization:

To evaluate the mechanical property and recyclability of the 3D printed samples within different printing cycles, the MTS tester (MTS Criterion™ Model 41, MTS Systems Corp., Eden Prairie, MN, USA) was used in tensile mode to test the mechanical behaviors at room temperature. Also, thermomechanical properties of the glass transition and temperature dependent stress relaxation behavior of nanoclay-epoxy within different printing cycles are examined. Here, large pieces of CAN films composed of 3 crosswise printing layers (showing in **Figure S4** a and b) were printed and then cured for both tensile tests and thermomechanical tests, following by trimming them into regular samples with varied dimensions. For tensile tests, trimmed samples with ~20.0mm×4.0mm×1.5mm were used. A small value of loading rate, 0.5mm per min, for all tests was chosen to minimize viscoelastic effects.

The glass transition behaviors of the printed nanoclay-epoxy were tested by dynamic mechanical analysis (DMA). For the first printing cycle, a strip sample with the dimension of ~10.0mm×4.0mm×1.5mm was trimmed and then tested by a DMA tester (Model Q800, TA Instruments, New Castle, DE, USA) on the tensile mode, compared with that of a molded epoxy at the absence of nanoclay with the same size. The strip

sample was first equilibrated at 100 °C for 10 minutes, and then a preload of 0.001N was applied. A peak-to-peak amplitude of 0.1% strain was oscillated at a frequency of 1 Hz during tests. Next, the environment temperature was gradually decreased from 100 °C to -50 °C at a rate of 2 °C/min. And then, the temperature maintained at -50 °C for 10 minutes. After that, it increased to 100 °C at the same rate. This procedure was repeated multiple times, and the data from the last rising step was reported, see **Figure S4** c. For the stress relaxation tests, a polymer sample with the same dimensions mentioned above was first preloaded by 0.001N force to keep it straightness. After reaching the designed testing temperature (120 °C, 140 °C, 160 °C, 180°C and 200 °C separately), it was allowed 20 min to reach thermal equilibrium. The specimen was stretched by 1.5% and then maintained during the tests on the DMA tester. The decrease of stress was recorded, and the stress relaxation modulus was calculated. In total, samples of the first and third printing cycle are tested for the stress relaxation behaviors, separately (**Figure 4**a and b).

According to the simple Arrhenius law, the stress relaxation behavior of the nonoclay-CAN can be captured by using an exponential function [1, 2], namely

$$\frac{\sigma}{\sigma_0} = \exp\left[-\frac{t}{\tau}\right]$$

where $\tau = \frac{1}{k}\exp\left[\frac{E_a}{R(T+273.15)}\right]$ is the relaxation time. σ_0 is the stress before relaxation, k is the kinetic coefficient, R is the gas constant of 8.314 J/(mol K), T is the temperature, and E_a is the activation energy for BERs.
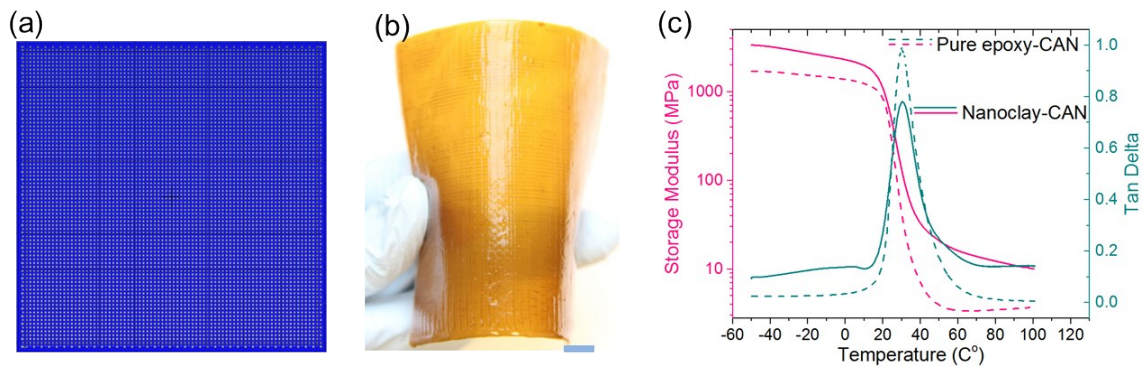

Figure S4. Schematic illustration of the print paths and photo graphs of printedspecimens for room-temperature tensile tests and thermomechanical tests. a) Sliced paths with three

crosswise layers. b) Printed and cured regular samples. c) Storage modulus and tan delta as a function of temperature.

Quantitative calculation of interfacial fracture energy

According to our previous work [1, 2], the interfacial fracture energy G_c can be calculated as

$$G_c = \frac{2\bar{P}(1+e)}{b} - E_0 he^2,$$

where $\bar{P} = \dfrac{\int_{t_1}^{t_2} P(t)dt}{t_2 - t_1}$ is the average peeling force during the steady propagation of the crack (from t_1 to t_2), E_0 is the modulus of the material, h is the thickness, b is the width, and e is the elastic strain under force $\bar{P}$. Since the calculated energy depends on the t-peeling speed, here a very low peeling speed of 0.5mm/min was conducted on the same MTS tester (MTS Criterion™ Model 41, USA) to minimize the viscoelastic effects[1, 2].

Reference

1. Shi, Q., et al., *Solvent Assisted Pressure-Free Surface Welding and Reprocessing of Malleable Epoxy Polymers.* Macromolecules, 2016. **49**(15): p. 5527-5537.
2. Yu, K., et al., *Interfacial welding of dynamic covalent network polymers.* Journal of the Mechanics and Physics of Solids, 2016. **94**: p. 1-17.