

## **SUPPORTING INFORMATION for**

### **Biomass-based Nanocomposites of Polydithioacetals Derived from Vanillin and Cellulose Nanocrystals: Synthesis, Thermomechanical and Reprocessing Properties**

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## 1. Measurements and Techniques

### *Nuclear magnetic resonance (NMR) spectroscopy*

$^1\text{H}$  NMR measurements were performed on a Bruker Advance 500 spectrometer at room temperature. Deuterium chloroform was used as the deuterated solvent.

### *Gel Permeation Chromatography (GPC)*

The gel permeation chromatography (GPC) analyses were performed using a Waters 1515 HPLC system with an RI detector, along with three Waters RH columns (RH1, 3, 4). For elution, a solution of N,N dimethylformamide (DMF) containing 0.01 M lithium bromide (LiBr) was employed at a constant flow rate of  $1.0 \text{ mL} \times \text{min}^{-1}$ . The molar mass values were determined in relation to polystyrene standards.

### *Fourier transform infrared (FTIR) Spectroscopy*

Fourier transform infrared (FTIR) measurements were conducted on a Perkin-Elmer Paragon 100 spectrometer from 4000 to  $400 \text{ cm}^{-1}$ . The films of specimens were obtained by casting the THF solutions of the samples onto KBr windows. The thermosetting blends were compressed into ultrathin transparent films on a hot press at  $130^\circ\text{C}$  with a pressure of 10MPa for 30 min. The as-obtained ultrathin transparent films were directly measured.

### *Thermal gravimetric analysis (TGA)*

Thermogravimetry analysis (TGA) was performed on a Discovery TGA550 instrument in the temperature range of  $50 \sim 800^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$  under an air atmosphere.

### *Differential scanning calorimetry (DSC)*

Thermal analysis was performed on a TA Instruments Q2000 differential scanning calorimeter in a dry nitrogen atmosphere. The instrument was calibrated with a standard indium.

#### *Stress Relaxation Measurements*

Stress relaxation tests were performed with a TA Q800 dynamic mechanical thermal analyzer. The measurements were performed with a constant strain of 5 % at different temperatures.

#### *Tensile Mechanical Tests*

Tensile mechanical tests were performed with a WDW-2 electron universal testing machine (Songdun Instruments Co. Ltd., Shanghai, China). The specimens, with dimensions of  $40 \times 4.5 \times 1 \text{ mm}^3$ , were prepared in accordance with the ASTM D638 standard. The uniaxial stretching experiments were carried out at a loading rate of 100 mm/min at room temperature. For each sample, five parallel specimens were tested, and then the average results were reported.

#### *Rheological Measurements*

The rheological measurements were performed on a DHR-2 stress-controlled rheometer (TA, USA) at 100 °C. The linear viscoelastic (LVE) regime of each circular specimen was determined by applying strain sweeps at a constant frequency of 1Hz.

#### *Transmission Electron Microscopy (TEM)*

Transmission electron microscopy (TEM) was performed on a JEOL JEM-2010 high-resolution transmission electron microscope at an acceleration voltage of 120 kV. The samples were first frozen and ground into powders in liquid nitrogen. The as-obtained powders were then dispersed in ethanol and dropped on the copper grids. After evaporating the solvent, the morphologies of the samples were observed.

## Synthesis of PTDAs

Typically, PDTA-DI (6.012 g), DGEBA (3.528 g) and tetrabutylammonium bromide (TBAB) (0.286 g) were dissolved in 1,4-dioxane (10 mL). The mixture was heated at 120 °C for 10 hours, during which it was gradually gelled. After the solvent was removed under vacuum at 40 °C, the crosslinked network, denoted *c*-PDTA-DI, was obtained. With a similar procedure, the crosslinked networks containing 1,6-hexanedithiol, 1,10-decanedithiol and 2,2'-thiodiethanethiol were synthesized and denoted *c*-PDTA-HE, *c*-PDTA-DE- and *c*-PDTA-TH, respectively.

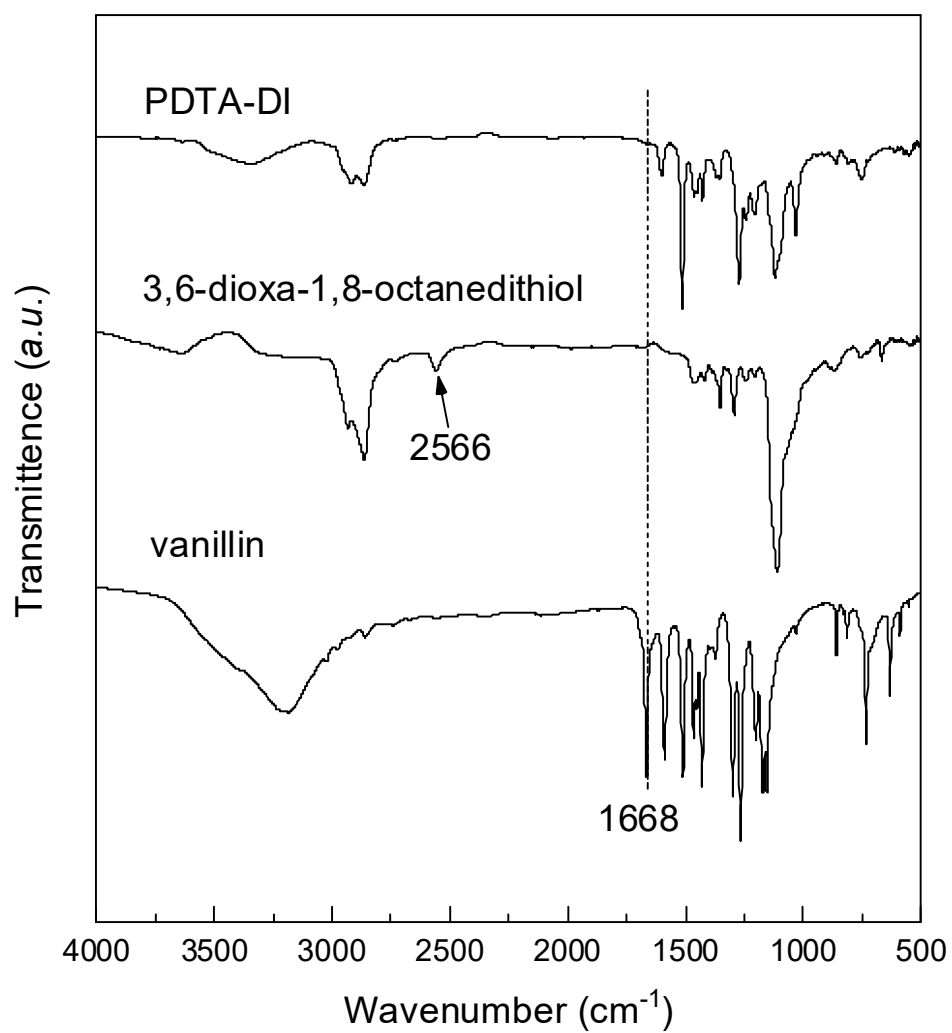


**Figure S1.** FTIR spectra of vanillin, 3,6-dioxa-1,8-octanedithiol and PDTA-DI

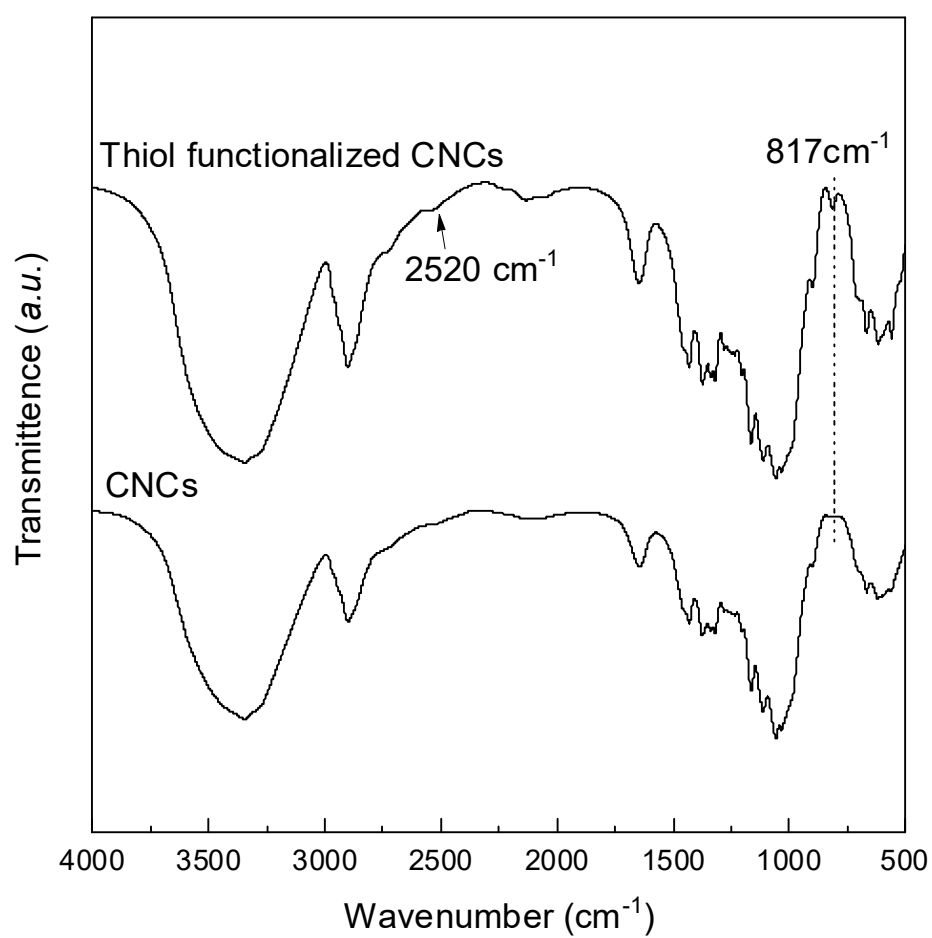


**Figure S2.** FTIR spectra of CNCs and thiol-functionalized CNCs

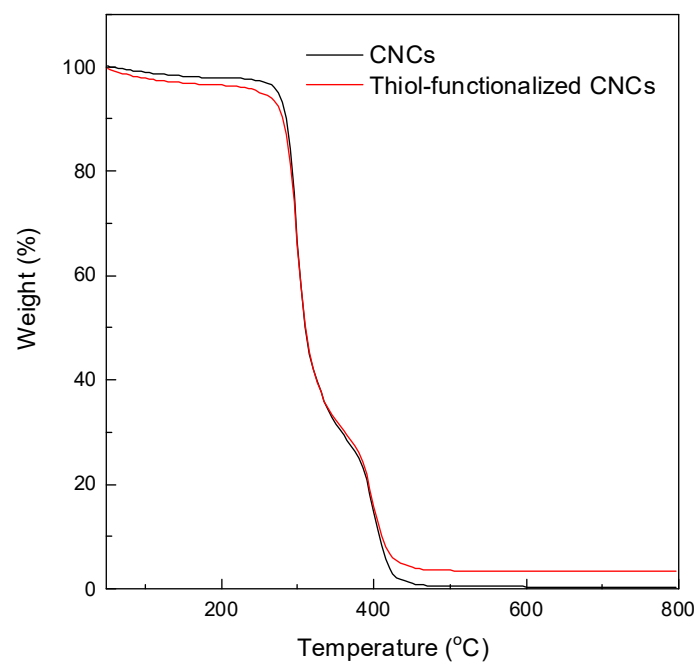


**Figure S3.** TGA curves of CNCs and thiol-functionalized CNCs.

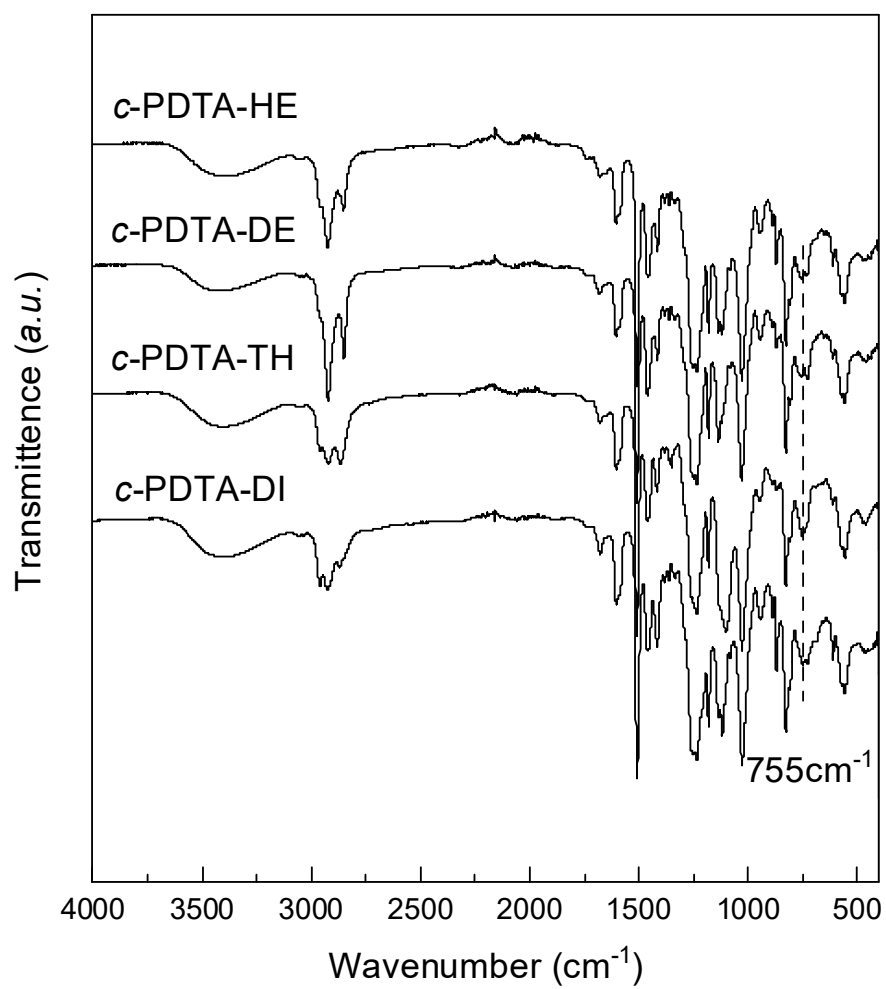


**Figure S4.** FTIR spectra of *c*-PDTA-HE, *c*-PDTA-DE, *c*-PDTA-TH and *c*-PDTA-DI networks.

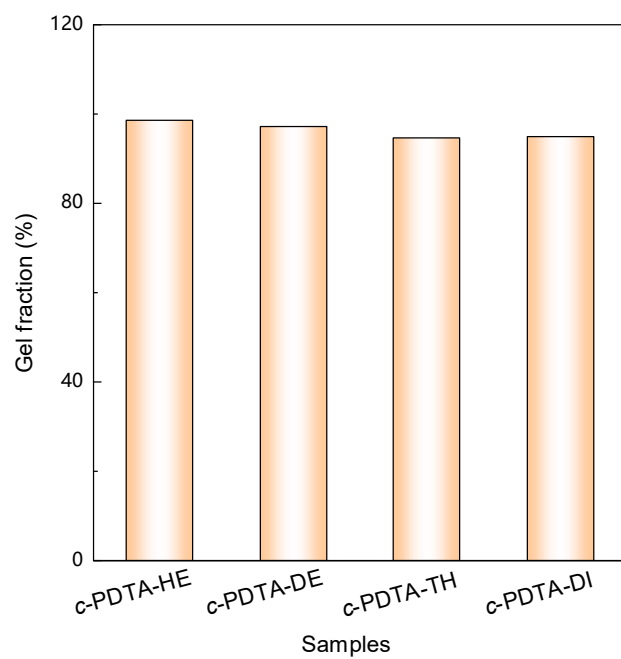


**Figure S5.** Gel fractions of *c*-PDTA-HE, *c*-PDTA-DE, *c*-PDTA-TH and *c*-PDTA-DI in THF at room temperature

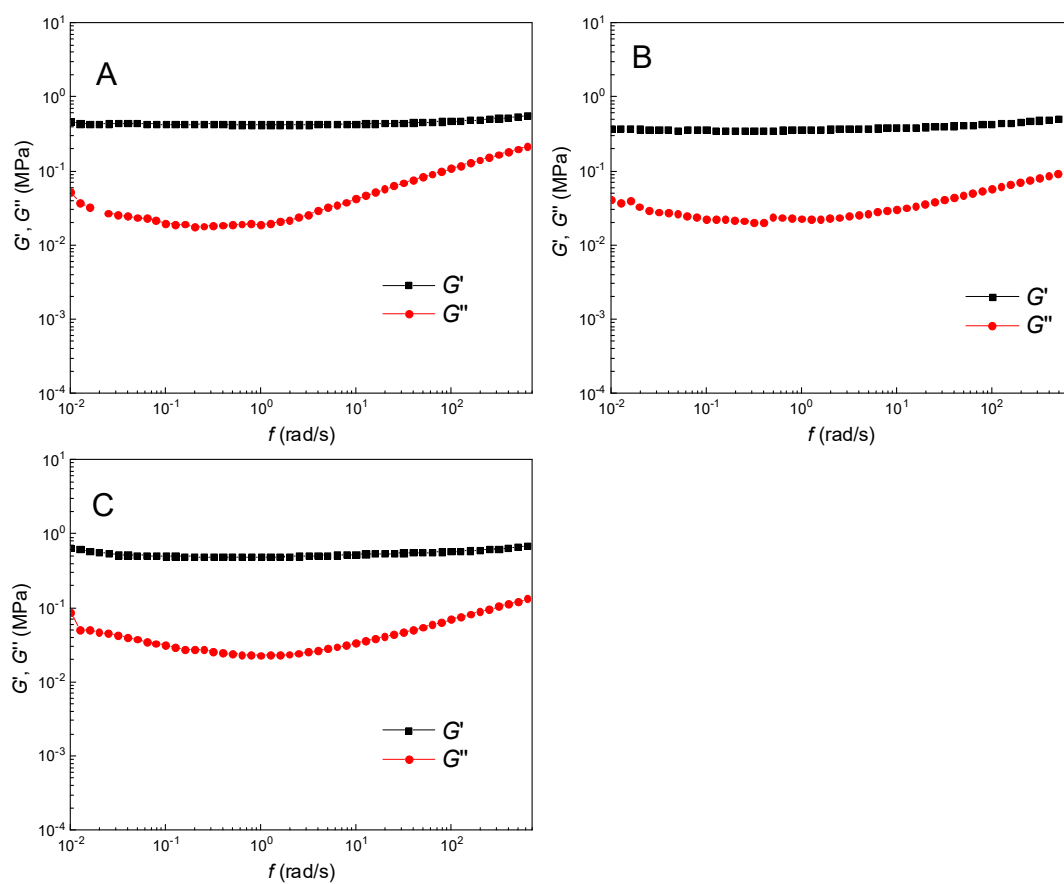


**Figure S6.** Rheological frequency sweeps of (A)  $c$ -PDTA-DI-CNC0, (B)  $c$ -PDTA-DI-CNC5 and (C)  $c$ -PDTA-DI-CNC15

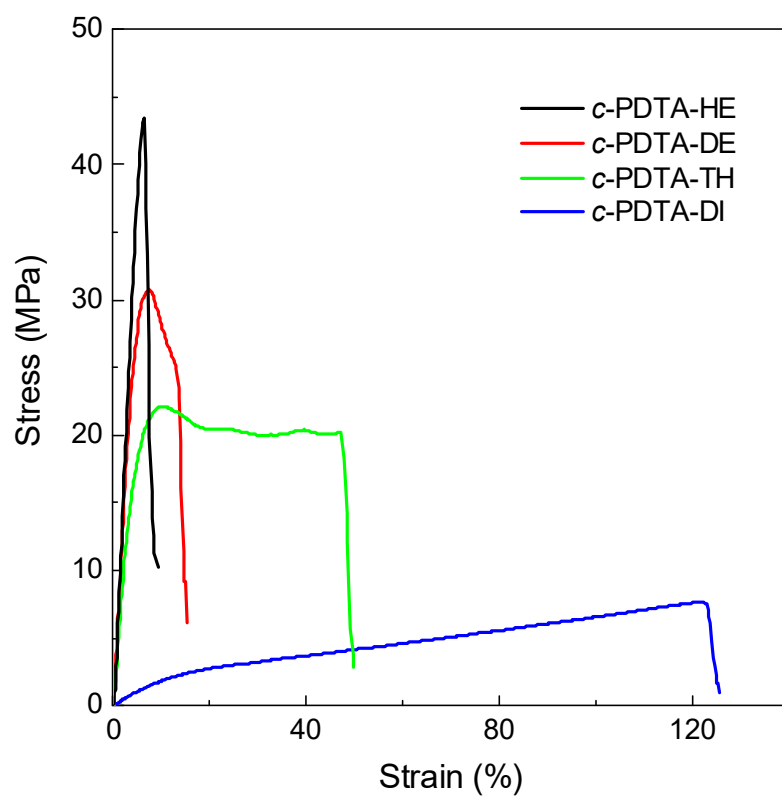


**Figure S7.** Stress–strain curves of *c*-PDPA networks

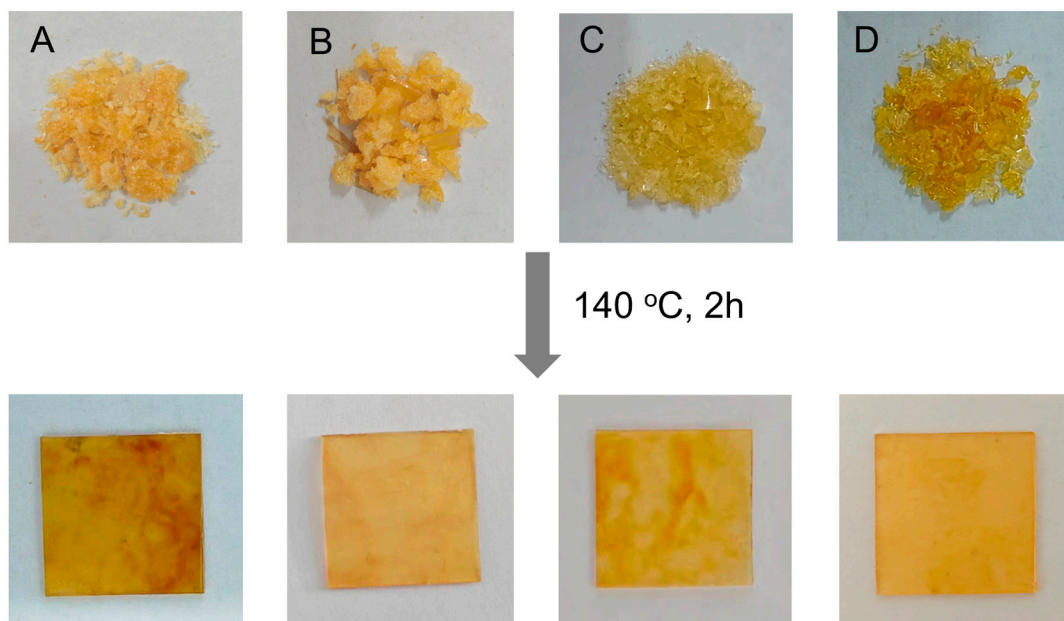


**Figure S8.** Reprocessing photos of (A) *c*-PDTA-HE, (B) *c*-PDTA-DE, (C) *c*-PDTA-TH and (D) *c*-PDTA-DI

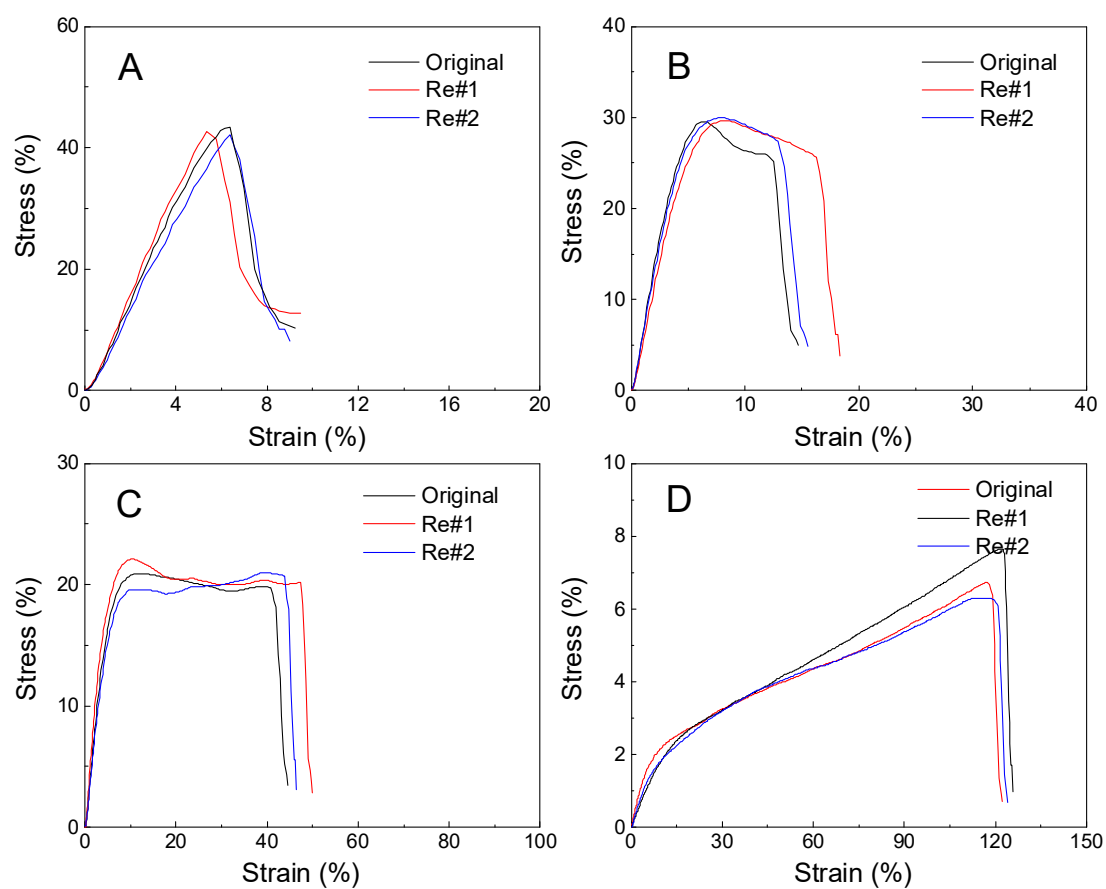


**Figure S9.** Stress–strain curves of the networks before and after reprocessing: (A) *c*-PDTA-HE, (B) *c*-PDTA-DE, (C) *c*-PDTA-TH and (D) *c*-PDTA-DI.