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Electronic Supplementary Information

A Magnetic Solder for Assembling Bulk Covalent Adaptable Network Blocks

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1. Chemicals

Poly(ethylene glycol)diol (PEG) (Mn = 400, TCI), giycerine (GLY) (99.5%, Aladdin), hexamethylene diisocyanate (HDI) (99%, J&K Scientific LTD), 4,4`-methylenebis(phenyl isocyanate) (MDI) (98%, J&K Scientific LTD), N,N,N,N-tetrakis(2-hydroxypropyl)ethylenediamine (HPED) (>98%, damas-beta), dibutyltindilaurate (DBTDL) (95%, damas-beta), Fe_3O_4 nanoparticles (Dalian Meilun Biological Technology Company), tetrahydrofuran (THF, Energy Chemical), ethyl acetate (EA, Shanghai Tian Scientific Company) and dyes. All chemicals were used as received without further purification.

2. Polymer network synthesis

Synthesis of PU CAN solders

PEG (Mn = 400) (0.8 g, 2 mmol), GLY (0.092 g, 1 mmol, tri-functional cross-linker) and stoichiometric amounts of HDI (0.588 g, 3.5 mmol) were mixed in the PTFE centrifuge tube, and then the mixture was put on the vortex for 5 min to make sure the even distribution. Afterwards, different amount of Fe_3O_4 nanoparticles (10 wt%, 20 wt%, 50 wt%) were added to three different mixtures respectively and mixed for 10 min. Last, 1 wt% BDTDL was added into the tube and the mixture was put on the vortex until the polymerization was completed. Finally, the mixture was poured into an aluminum pan and cured at 140°C for 2 h under a pressure of 6 MPa.

Synthesis of bulk PU CAN blocks (PU-1, PU-2, PU-3 and PU-4)

A set of PEG (Mn = 400), GLY (tri-functional cross-linker) with different PEG to GLY ratio and stoichiometric amounts of HDI were mixed in different PTFE centrifuge tubes. Dry THF containing different dyes was added into tubes and they were put on the vortex for 5 min to make sure the even distribution. Afterwards, we added 1 wt% BDTDL into these tubes to mix for 2 min. Finally, the mixtures were poured into molds of different shapes and cured at room temperature for 7 days to make sure that the polymerization is completed and followed by vacuum drying to remove the remaining solvent.

Synthesis of bulk PU CAN blocks (PU-5)

MDI (1.752 g, 7 mmol) was dissolved in ethyl acetate at room temperature. After MDI was totally dissolved, PEG (Mn = 400) (2 g, 5 mmol), HPED (0.292 g, 1 mmol, tetra-functional cross-linker) were added to the solution and well mixed. Finally, the mixture was poured into the mold and cured at 60°C for 2 h followed by a postcure at 120°C for 2 h.

Synthesis of PU CAN foams

PEG (Mn = 400) (0.8 g, 2 mmol) and GLY (0.092 g, 1 mmol, tri-functional cross-linker) and stoichiometric amounts of HDI (0.588 g, 3.5 mmol) were mixed in the PTFE centrifuge tube, and then the mixture was put on the vortex for 5 min to make sure the even distribution. Afterwards, a few drops of dry THF and 1 wt% BDTDL (0.015 g) were added into tube and the tube was put on the vortex for 20 s. Finally, the reaction generated heat to volatilize the solvent to form a foam.

3. Gel content tests

A series of polyurethane samples were soaked in ethyl acetate (40 mL) for three days with the solvent being refreshed daily. Afterwards, the residual polymer samples were dried at 60°C in vacuum oven until the weight reached a constant value. The gel content was calculated as the weight ratio of the polymer after and before the solvent extraction. Each value was the average of three repeated tests.

4. Swelling experiments

The swelling experiments for the welded bulk PU CAN blocks were done in solvent EA at 40°C for 48 h with the top of the bottle sealed to prevent the evaporation of the solvent. The solvent was evaporated very slowly by volatilizing at room temperature for 3 days. Afterwards, the PU bulks were vacuum dried (50°C) for 24 h until the weight reached a constant value.

5. Stress relaxation tests

Stress relaxation results were acquired on a TA Instruments Q800 machine (DMA). After mounting, the samples were brought to the taut length (5%) and allowed to relax at 130°C until full equilibrium were assured.

6. Characterization

The thermal transition temperature of samples with different Fe3O4 nanoparticles contents were measured on a different scanning calorimetry (DSC, TA Q2000) instrument. The first scanning was to eliminate the thermal history of samples, where both the heating and cooling rate were 30°C/min. The second scanning was to measure the thermal transition temperatures, where both the heating and cooling rate were 10°C/min. DSC was used to observe the glass transition temperature (Tg) of different samples. The thermal stability of samples with different Fe3O4 nanoparticles contents were measured on a thermogravimetric analyzer (TGA, TA Q50) under air atmosphere, where the heating rate is 20°C/min. Lap-shear tests were performed using a TA Instruments model Q800 dynamic mechanical analyzer (DMA) in the tensile mode. A series of polyurethane films were measured at room temperature, where the ramp force is 1 N/min. DMA was also used to obtain the stress-strain curves of different samples. The strain was measured while the sample was stretched at a ramp force of 1 N/min to 18 N.

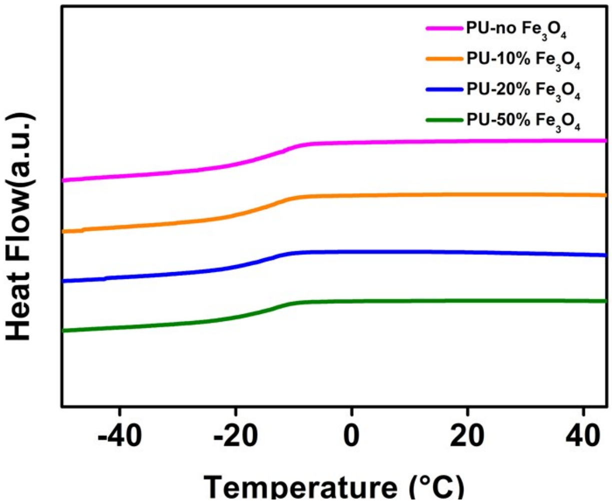

Fig. S1 The thermal transition temperature of samples with different Fe_3O_4 nanoparticles contents were measured on a different scanning calorimetry (DSC, TA Q2000) instrument. Both the heating and cooling rate were 10°C/min to measure the glass transition temperature (T_g) of different samples.

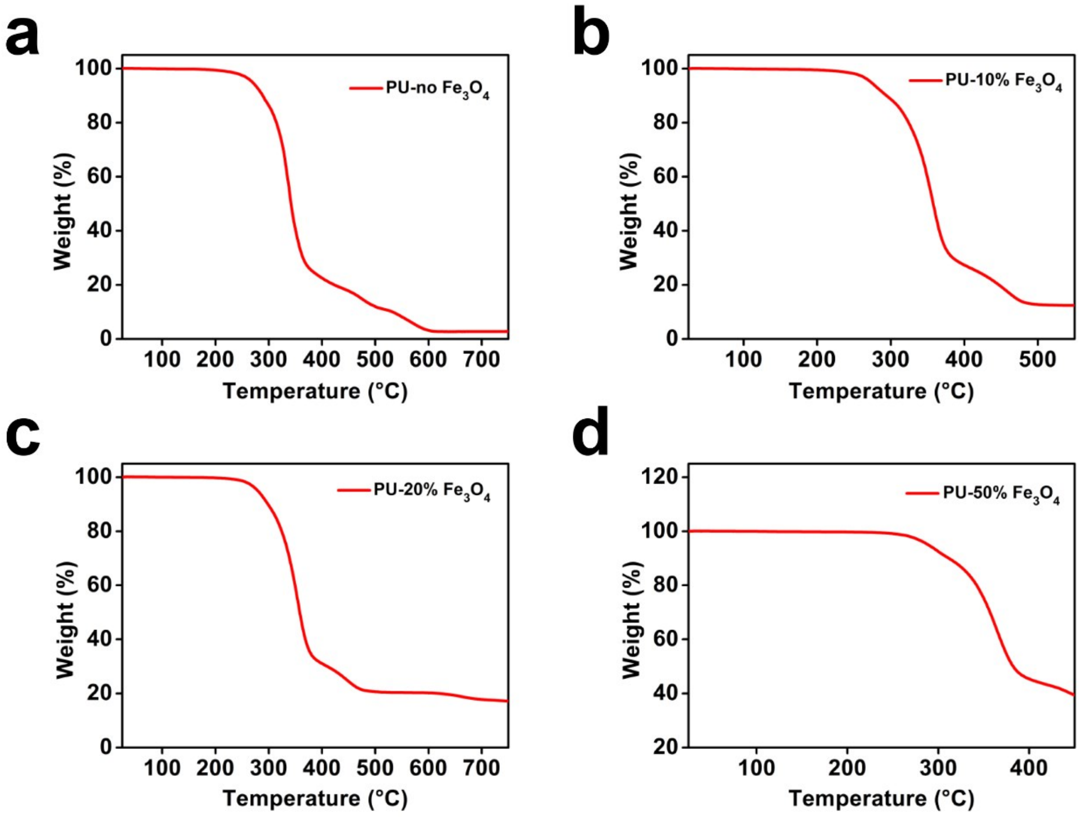

Fig. S2 The thermal stability of samples with different Fe_3O_4 nanoparticles contents were measured on a thermogravimetric analyzer (TGA, TA Q50) under air atmosphere, where the heating rate was 20°C/min. **a** TGA curve of PU-no Fe_3O_4. **b** TGA curve of PU-10% Fe_3O_4. **c** TGA curve of PU-20% Fe_3O_4. **d** TGA curve of PU-50% Fe_3O_4.

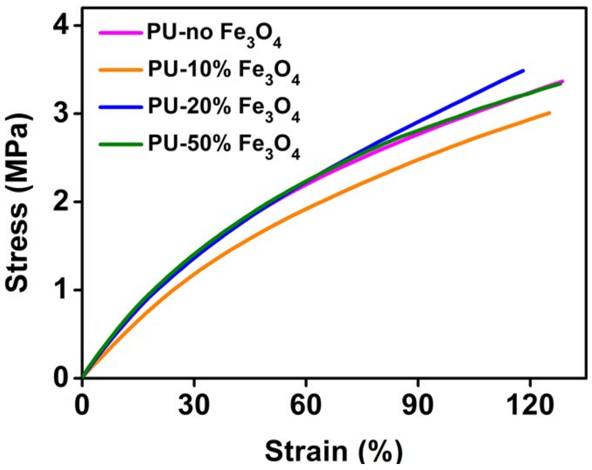

Fig. S3 Stress-strain tests were performed using a TA Instruments model Q800 dynamic mechanical analyzer (DMA) in the tensile mode. A series of polyurethane films were measured at room temperature, where the ramp force was 1 N/min.

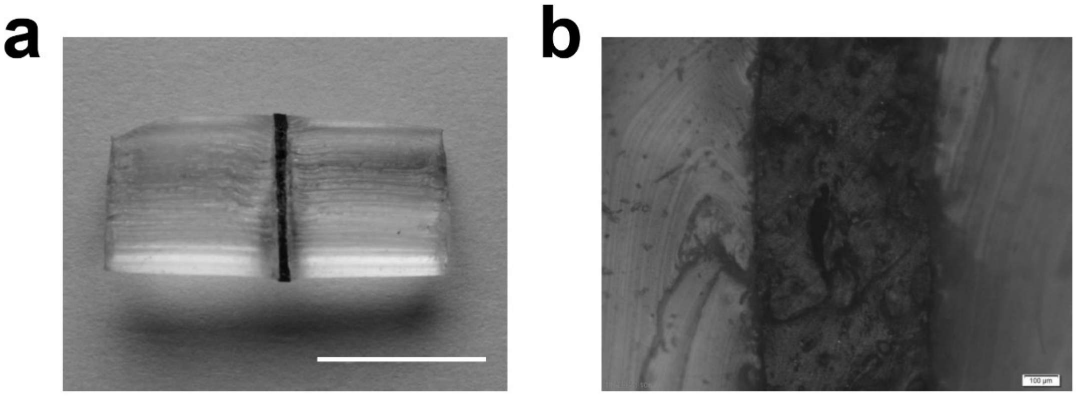

Fig. S4 **a** Longitudinal-section area of the welded bulk. Scale bar: 5 mm. **b** POM image of the longitudinal-section area of the welded bulk.

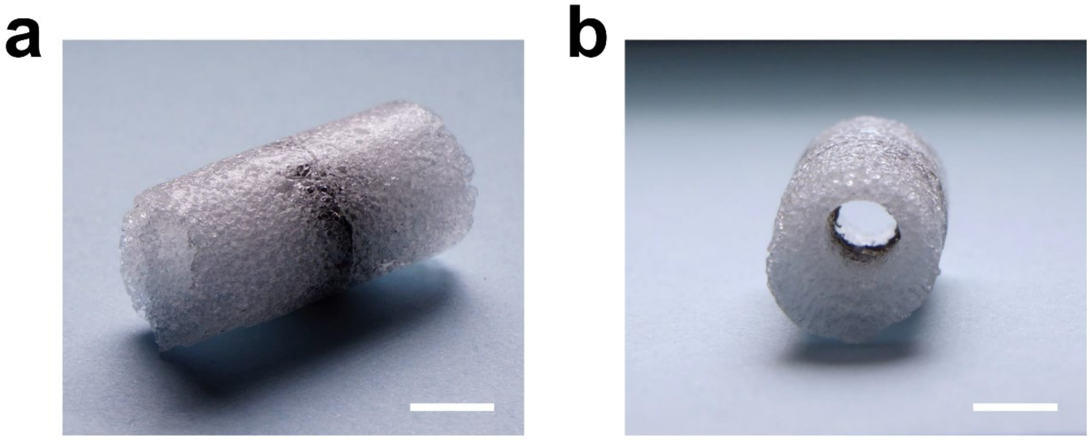

Fig. S5 **a** Side view of the PU foam repaired with the PU solder. **b** Front view of the PU foam repaired with the PU solder. Scale bar: 5 mm.