

## Supplementary Information

### Self-Healing, Malleable and Creep Limiting Materials using both Supramolecular and Reversible Covalent Linkages.

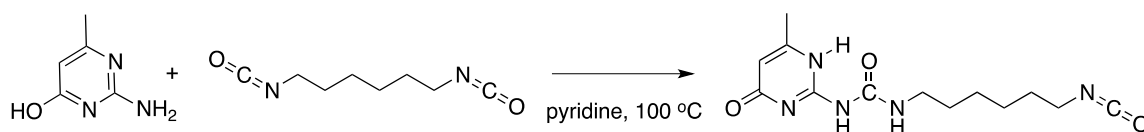
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#### Experimental Section

##### *Materials*

All materials were purchased from commercial suppliers unless otherwise specified. All materials were used as received unless otherwise specified.

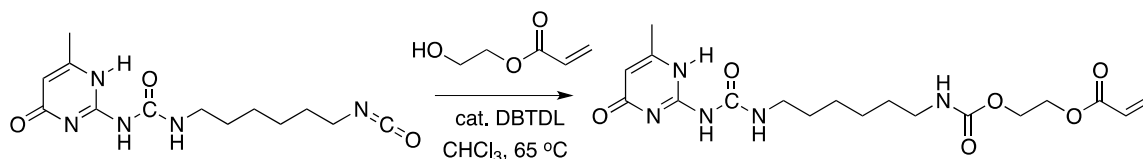
##### *Synthesis of 1-(6-isocyanatohexyl)-3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)urea (UPy-NCO)*



2-amino-4-hydroxy-6-methylpyrimidine (11.19 g, 0.0895 mol) was added to a round bottom flask equipped with a magnetic stirrer bar. To this solid 1,6-hexadiisocyanate (108.5g, 0.646 mol) was added. The reaction mixture was capped with a rubber septum and purged with nitrogen for 10 min. At this point, 8 mL of anhydrous pyridine was added and the reaction mixture was heated at 100 °C for 16 h. To this reaction mixture 30 mL of hexane was added, and the precipitate was washed with diethyl ether. The white solid was dried under reduced pressure to give UPy-NCO (25.48g, 0.0869 mol, 97%

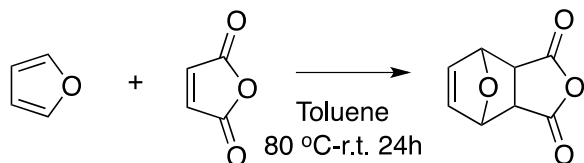
yield). The compound was confirmed by  $^1\text{H}$ -NMR in agreement with the literature.<sup>1</sup>  $^1\text{H}$ -NMR(300 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 13.10 (1H, sing), 11.86 (1H, sing), 10.17 (1H, sing), 5.82 (1H, sing), 3.28 (4H, multi), 2.23 (3H, sing), 1.62 (4H, quin,  $J=6.9$  Hz), 1.41 (4H, multi)

*Synthesis of 2-(((6-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)hexyl)carbamoyl)oxy)ethyl acrylate (UPyA)*



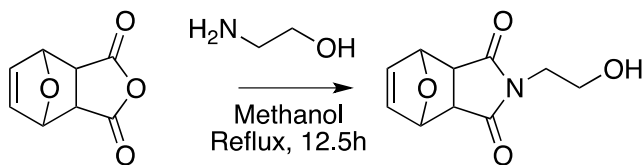
UPy-NCO (6.98g, 0.0238 mol) was added to a round bottom flask. To this solid 105 mL of chloroform, 2-hydroxyethyl acrylate (HEA) (6.9 mL, 6.9 g, 0.059 mol) and 3 drops of dibutyltin dilaurate (DBTDL) were added. The reaction mixture was homogenized and heated at 65 °C for 16 h. After the reaction, the solids were removed by filtration and a large excess of diethyl ether was added to generate a white precipitate. The precipitate was collected by vacuum filtration and washed with diethyl ether, hexane and again by diethyl ether. The solid was dried to give the desired UPyA product (8.71g, 0.0212 mol, 89% yield). The compound was confirmed by  $^1\text{H}$ -NMR in agreement with the literature.<sup>2</sup>  $^1\text{H}$ -NMR(300 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 13.17 (1H, sing), 11.90 (1H, sing), 10.16 (1H, sing), 6.43(1H, doub,  $J=15.9$  Hz), 6.14(1H, multi) 5.85 (2H, multi), 4.97(1H. br), 4.32(4H, multi) 3.25 (2H, quart,  $J=5.8$  Hz), 3.17 (2H, multi), 2.23 (3H, sing), 1.62 (2H, multi), 1.51 (2H, multi), 1.41 (4H, multi).

*Synthesis of 3a,4,7,7a-tetrahydro-4,7-epoxyisobenzofuran-1,3-dione (Furan-protected maleic anhydride (Fp-MAn)).*



Maleic anhydride (MAn, 68.6g, 0.700 mol) was added to a round bottom flask containing a magnetic stirrer bar and dissolved in 350 mL of toluene. The reaction mixture was heated to 80 °C, at which point furan (76.3 mL, 71.4g, 1.05 mol) was added. The reaction mixture was capped with a glass stopper and allowed to cool to room temperature. The reaction proceeded at room temperature for 24 h, yielding a white precipitate. The precipitate was filtered and washed with diethyl ether. The white solid was collected to give Fp-MAn (91.5 g, 0.55 mol, 79% yield). The compound was confirmed by <sup>1</sup>H-NMR in agreement with the literature.<sup>3</sup> <sup>1</sup>H-NMR(300 MHz, CDCl<sub>3</sub>) δ ppm 6.58 (2H, sing), 5.46 (2H, sing), 3.17 (2H, sing).

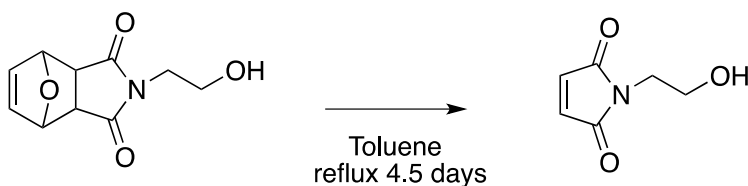
*Synthesis 2-(2-hydroxyethyl)-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindole-1,3(2H)-dione (Furan-protected N-(2-hydroxyethyl) maleimide (Fp-HEMI)).*



Fp-MAn (45.0 g, 0.271 mol) was placed a round bottom flask containing a magnetic stirrer bar and dissolved in 150 mL of anhydrous methanol. The flask was capped with a rubber septum and deoxygenated by bubbling with nitrogen for 10 min, and the placed in an icebath. To this solution, 2-aminoethanol (17 mL, 17.2 g, 0.281 mol) was added via

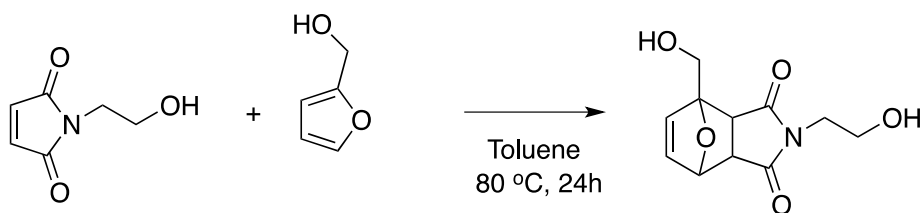
syringe. The reaction mixture was stirred at 0 °C for 30 min, and then refluxed for 14 h. After reacting, the solution was cooled to room temperature, and then cooled to -20 °C. The product Fp-HEMI crystalized out of solution at -20 °C. The solid was collected by filtration and washed with isopropanol and allowed to dry. The solid was collected to give Fp-HEMI (33.3g, 0.160 mol, 59% yield) The compound was confirmed by <sup>1</sup>H-NMR in agreement with the literature.<sup>3</sup> <sup>1</sup>H-NMR(300 MHz, CDCl<sub>3</sub>) δ ppm 6.52 (2H, sing), 5.28 (2H, sing), 3.74 (4H, multi), 2.89 (2H, sing), 2.18 (1H, sing).

*Synthesis of 1-(2-hydroxyethyl)-1H-pyrrole-2,5-dione (N-(2-hydroxyethyl) maleimide (HEMI)).*



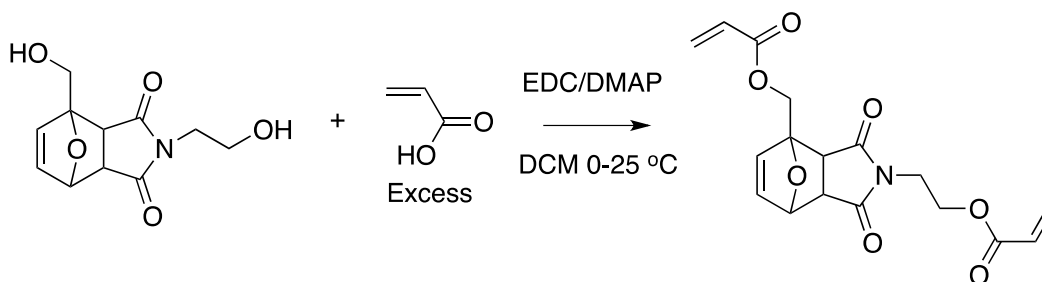
Fp-HEMI (33.3 g, 0.160 mol) was placed a round bottom flask containing a magnetic stirrer bar and dissolved in 320 mL of toluene. The flask was connected to a short condenser and allowed to reflux for 4.5 days. After reacting, the solution was transferred to a clean flask and allowed cooled to room temperature, and then cooled to -20 °C. The product HEMI crystalized out of solution at -20 °C. The solid was collected by filtration allowed to dry. The solid was collected to give HEMI (17.1 g, 0.121 mol, 76% yield) The compound was confirmed by <sup>1</sup>H-NMR in agreement with the literature.<sup>3</sup> <sup>1</sup>H-NMR(300 MHz, CDCl<sub>3</sub>) δ ppm 6.74 (2H, sing), 3.75 (4H, multi), 2.18 (1H, sing).

*Synthesis 2-(2-hydroxyethyl)-4-(hydroxymethyl)-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindole-1,3(2H)-dione (FMI-diol).*



HEMI (9.00g, 0.063 mol) was placed a round bottom flask containing a magnetic stirrer bar and to this solid 135 mL of toluene and fufuryl alcohol (5.4 mL, 6.10g, 0.062 mol) were added. The reaction mixture was heated to 80 °C for 24 h. The product precipitated out of solution as the reaction progressed. The solid was dissolved in a mixture of acetone, DCM and methanol, and precipitated using diethyl ether. The solid was collected by filtration and washed with diethyl ether followed by hexanes and allowed to dry. The solid was collected to give FMI-diol (6.1 g, 0.025 mol, 40% yield) The compound was confirmed by <sup>1</sup>H-NMR in agreement with the literature.<sup>3</sup> <sup>1</sup>H-NMR(300 MHz, d<sub>6</sub>-DMSO) δ ppm. 6.52 (2H, multi), 5.07 (1H, br-sing), 4.92 (1H, trip, J=5.8 Hz), 4.75 (1H, multi), 4.03 (1H, doubdoub, J= 12.8, 6.0 Hz), 3.69 (1H, doubdoub, J= 12.4, 5.6 Hz), 3.40 (4H, multi), 3.04 (1H, doub, J= 6.7 Hz), 2.87 (1H, doub, J= 6.5 Hz),

*Synthesis (2-(2-(acryloyloxy)ethyl)-1,3-dioxo-2,3,3a,4,7,7a-hexahydro-1H-4,7-epoxyisoindol-4-yl)methyl acrylate (FMIDA).*



FMI-diol (4.4 g, 0.018 mol) and DMAP (1.1 g, 0.0090 mol) were placed in a round bottom flask containing a magnetic stirrer bar and to these solids 176 mL of DCM and acrylic acid (10.7 g, 0.149 mol) were added. The reaction mixture was cooled to 0 °C and EDC (20.4 g, 0.131 mol) was added. The solution was allowed to warm to room temperature and stirred for 24 h at room temperature. After the reaction, the DCM phase was washed with 0.2 M HCl (6 x 150 mL), followed by 2 washes with 150 mL of water and 1 wash of brine (150 mL, 1 wt%). The solvent was removed under reduced pressure to give the FMIDA (3.75 g, 0.0108 mol, 60% yield) product as a brown viscous liquid. The compound was confirmed by  $^1\text{H-NMR}$  in agreement with the literature.<sup>4</sup>  $^1\text{H-NMR}$  (300 MHz,  $d_6$ -DMSO)  $\delta$  ppm 6.59 (1H, br-doub,  $J=5.8$  Hz), 6.47 (1H, doub,  $J=5.7$  Hz), 6.42-5.82 (6H, multi), 5.13 (1H, doub,  $J=1.6$  Hz), 4.85 (1H, doub,  $J=12.8$  Hz), 4.40 (1H, doub,  $J=12.8$  Hz), 4.19 (2H, multi), 3.67 (2H, multi), 3.08 (2H, doubdoub,  $J=22.1, 6.5$  Hz).

#### *Preparation of PHEA-FMIDA-UPyA Materials*

To a vial AIBN (40 mg), UPyA (200 mg), FMIDA (82 mg) and HEA (4.00 g) were added. To this mixture dimethylformamide (DMF, 8 mL) was added and the mixture was homogenized by mixing and gentle heating. The solution was transferred to a Teflon

mold and heated for 30 min at 65 °C. The material was removed from the mold and allowed to dry for 2 days at room temperature and pressure followed by 16h in a vacuum oven at 35 °C. The monomer conversion was determined by gravimetry to be greater than 90%.

#### *Cutting and Notching and healing procedures*

Materials were either cut or notched with a razor blade. Cut samples were completely cut through the thickness of the material. Notched samples were notched through 50% of the thickness of the material. In both cases the two sections were placed in contact by gentle pressure for several seconds. Materials that were healed at room temperature were kept on a bench top at 22 °C. Materials that were healed at elevated temperatures were placed in a preheated oven at 90 °C.

#### *Analytical Methods*

All nuclear magnetic resonance (NMR) was performed on a Bruker 300 MHz spectrometer. Infrared (IR) spectroscopy was performed on a Perkin Elmer Spectrum 100 Spectrometer.

#### *Differential Scanning Calorimetry (DSC)*

Differential scanning calorimetry (DSC) was performed on a TA instruments Q20 system. 5.3 mg of PHEA-FMIDA-UPyA material was placed in a DSC pan and sealed. The sample was subjected to the following cycle. Cooled to -44 °C, heated to 150 °C at a rate of 10 °C per min. Cooled to -41 at a rate of 5 °C per min, followed by heating at a rate of 10 °C to 190 °C. Only data from the second heating cycle was used for analysis. The glass transition temperature ( $T_g$ ) was determined from the inflection point determined as

the minimum in the first derivative. The first derivative was smoothed using a 5 point average.

#### *Tensile Tests*

Materials were subjected to tensile testing using an Instron 3344 apparatus equipped with a 100 N load cell. The extension was increased at the rate of 1 mm/s. All samples were measured until the material broke.

#### *Stress-Relaxation Test*

An Instron 3344 apparatus equipped with a 100 N load cell was used to analyze stress relaxation. The extension was increased at the rate of 1 mm/s until 100% strain was achieved. This strain of 100% was maintained while the stress was measured over a 4h period.

#### *Creep Test*

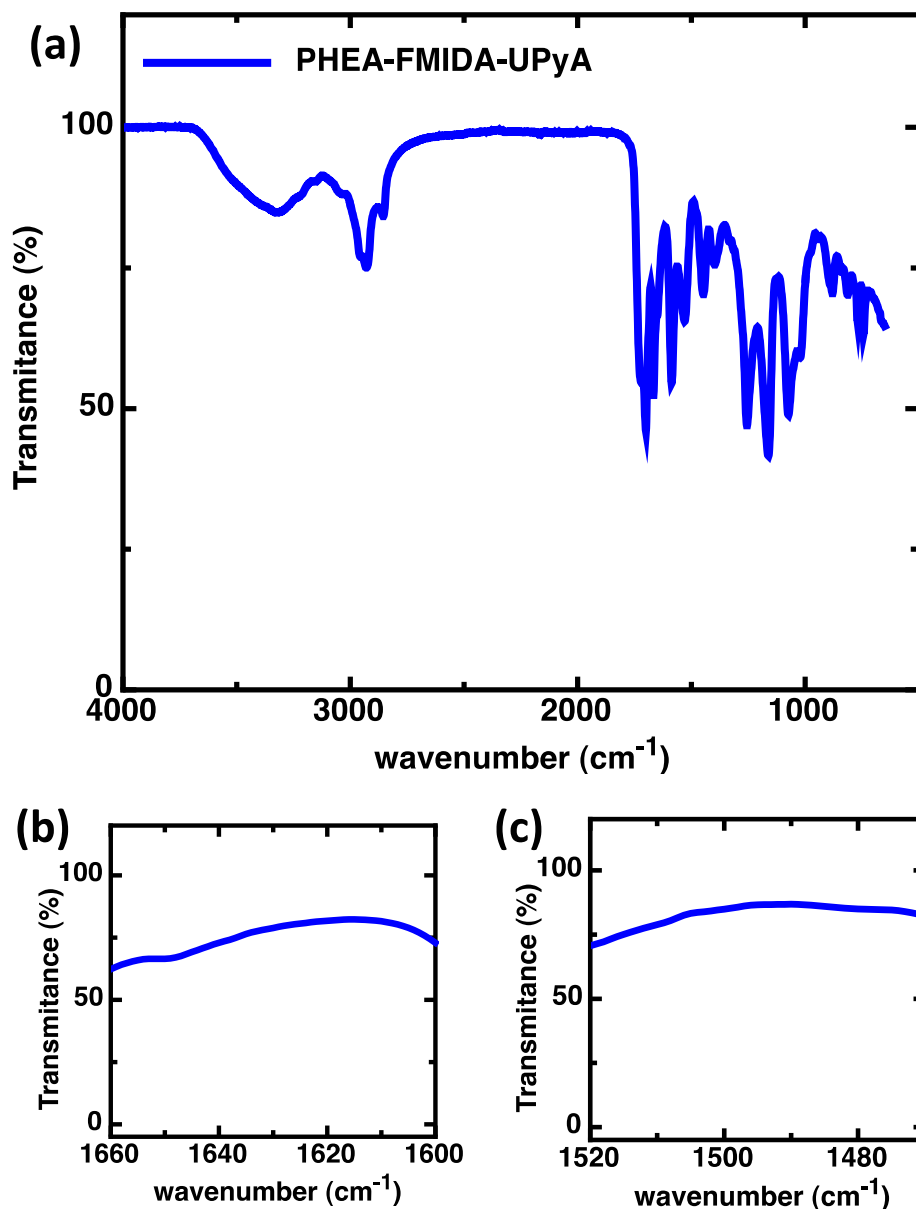
An Instron 3344 apparatus equipped with a 100 N load cell was used to analyze the extent of creep under load. The material was extended at the rate of 0.25 mm/s until a stress of 100 kPa was measured. This stress of 100 kPa was maintained while the strain was measured over a 4h period.

#### *Reshaping materials*

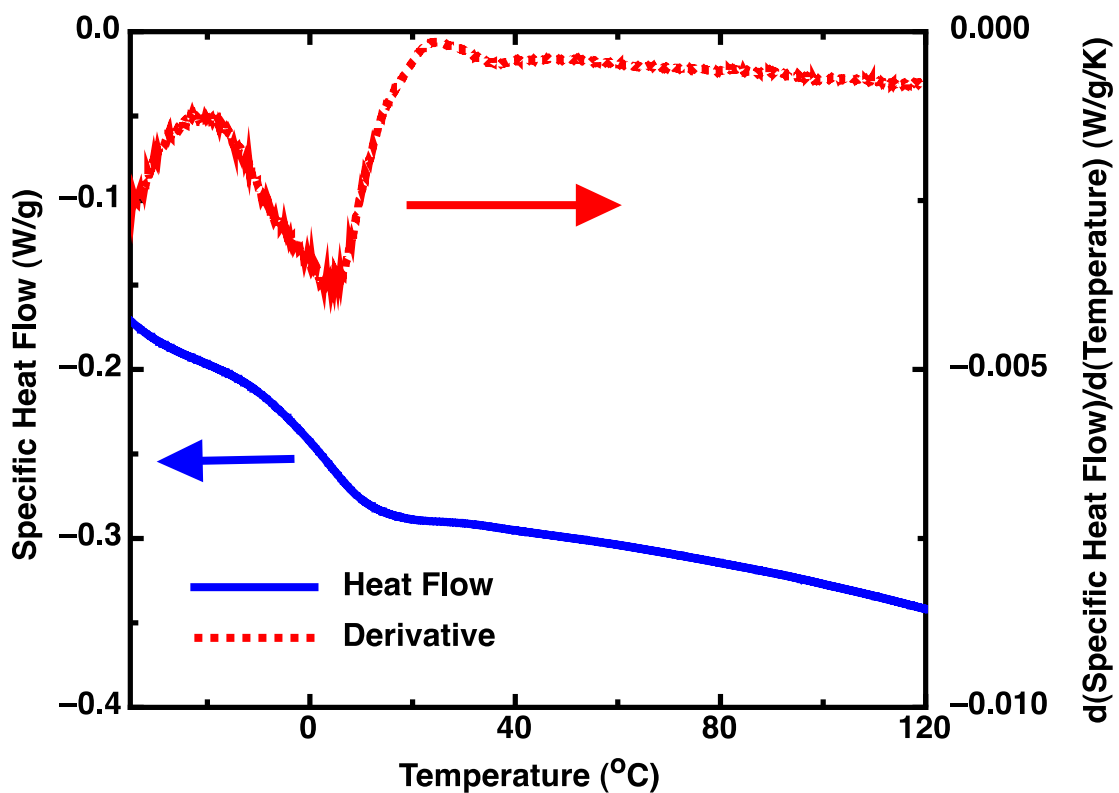
Materials were reshaped by deforming the material to the new configuration, followed by the placement of two paperclips on either side of the material. A 14 g weight was placed on either side of the material and the material was heated in an oven preheated at 90 °C for 7 h.



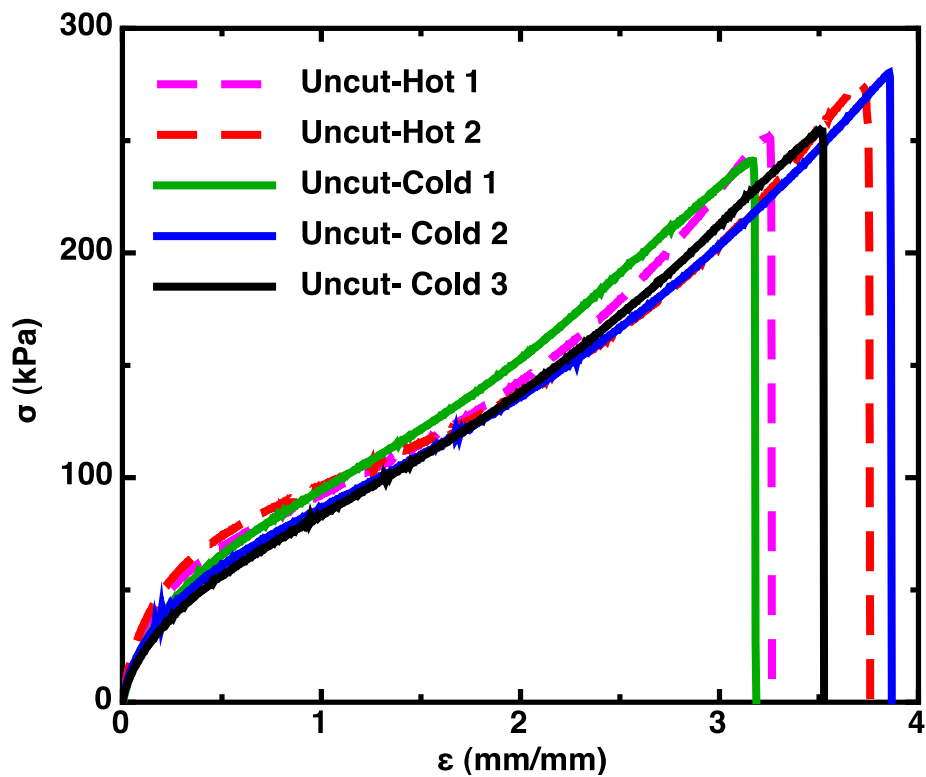
## Supporting Figures



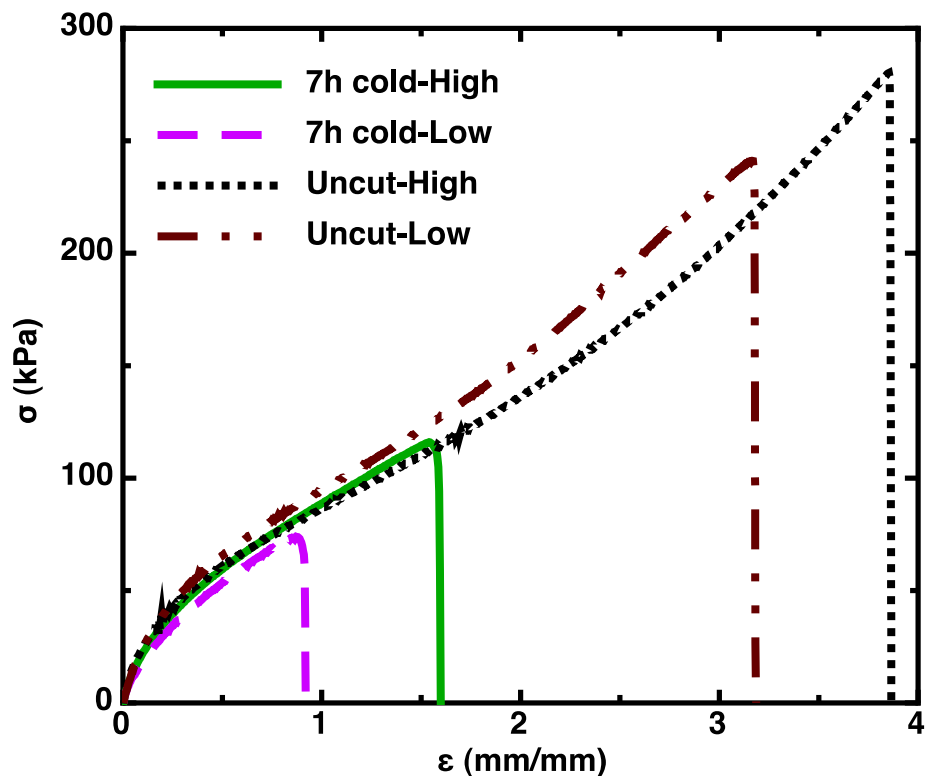
**Figure S1.** Infrared spectrum for PHEA-FMIDA-UPyA material. (a) Shows the complete spectrum. (b) Shows a zoom in around the 1640  $\text{cm}^{-1}$  region characteristic of the C=C stretch in HEA.<sup>5</sup> (c) Shows a zoom in around the 1500  $\text{cm}^{-1}$  N-C stretch in DMF.<sup>6</sup>



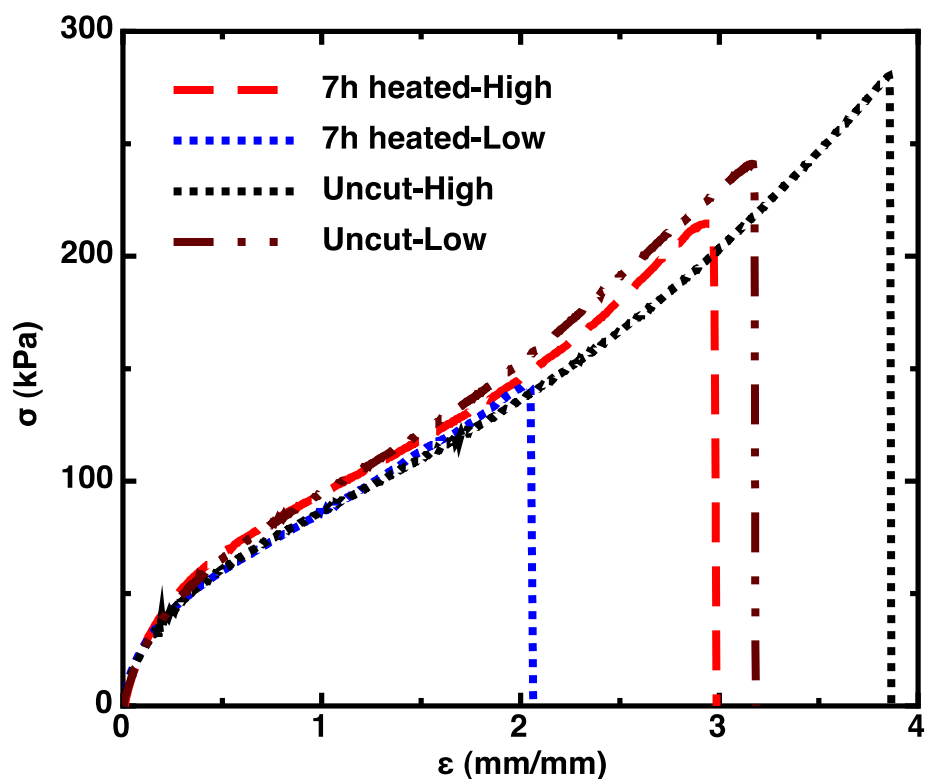
**Figure S2.** Differential scanning calorimetry (DSC) curve and first derivative (heating cycle) for PHEA-FMIDA-UPyA materials in the range -35 to 120 °C. Heating was performed at 10 °C/min. The minimum in the derivative occurs at 4 °C and is taken to be the glass transition temperature ( $T_g$ ).



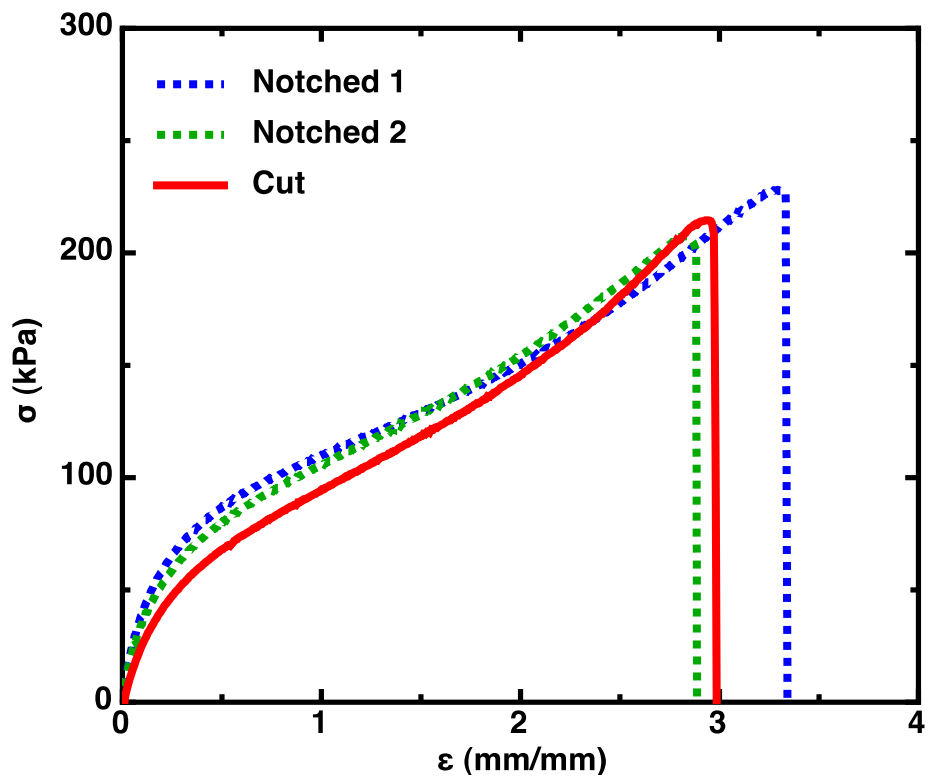
**Figure S3.** Stress-Strain curves for 5 typical uncut PHEA-FMIDA-UPyA materials. The Hot samples were heated for 7h at 90 °C while the uncut ones were kept at room temperature always.



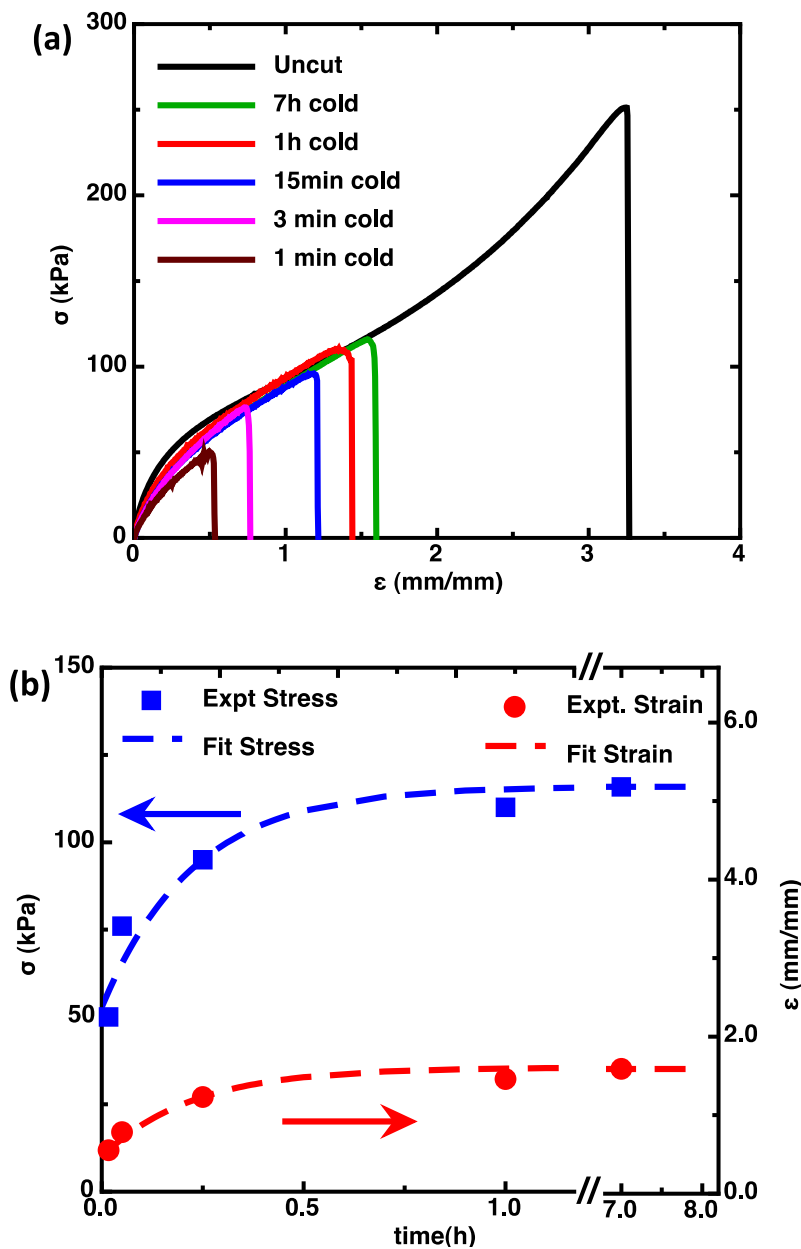
**Figure S4.** Stress-Strain curves for 2 PHEA-FMIDA-UPyA materials cut and healed at room temperature for 7 h. The data show a high recovery and low recovery sample. Also shown are uncut materials with the lowest and the highest strain at break for comparison.



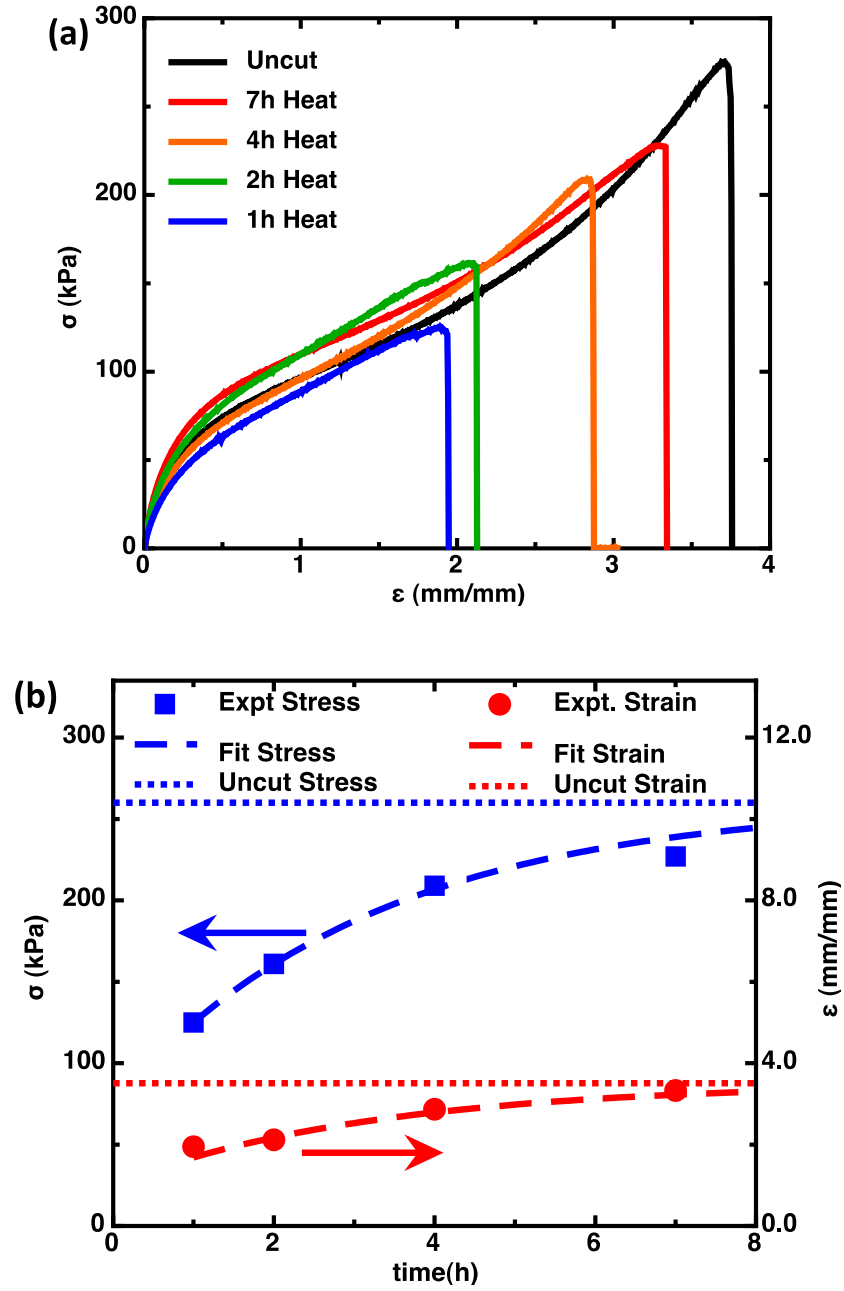
**Figure S5.** Stress-Strain curves for 2 PHEA-FMIDA-UPyA materials cut and healed at 90 °C for 7 h. The data show a high recovery and low recovery sample. Also shown are uncut materials with the lowest and the highest strain at break for comparison.



**Figure S6.** Stress-Strain curves for 3 PHEA-FMIDA-UPyA materials damaged and healed at 90 °C for 7 h. The figure includes 2 notched samples (half of the material thickness cut) and 1 cut sample.



**Figure S7.** a) Stress-Strain curves for PHEA-FMIDA-UPyA materials damaged and healed room temperature for different lengths of time. b) Maximum stress and strain at break fitted to exponential functions  $\sigma_t = \sigma_\infty - b_\sigma \text{Exp}[-t / \tau_0]$  and  $\epsilon_t = \epsilon_\infty - b_\epsilon \text{Exp}[-t / \tau_0]$  with  $\tau_0 = 0.22$  h,  $\sigma_\infty = 116$  kPa,  $b_\sigma = 63$  kPa,  $\epsilon_\infty = 1.58$ , and  $b_\epsilon = 1.16$ .



**Figure S8.** a) Stress-Strain curves for PHEA-FMIDA-UPyA materials damaged and heated 90 °C for different lengths of time. b) Maximum stress and strain at break fitted to exponential functions  $\sigma_t = \sigma_\infty - b_\sigma \text{Exp}[-t / \tau_0]$  and  $\epsilon_t = \epsilon_\infty - b_\epsilon \text{Exp}[-t / \tau_0]$  with  $\tau_0 = 3.2 \text{ h}$ ,  $\sigma_\infty = 260 \text{ kPa}$ ,  $b_\sigma = 184 \text{ kPa}$ ,  $\epsilon_\infty = 3.51$ , and  $b_\epsilon = 2.49$ .



## References

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