

Supporting Information

Simple and versatile approach to self-healing polymers and electrically conductive composites

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Testing conditions

NMR spectroscopy. ^1H NMR spectra of samples were recorded on a 400MHz Bruker Avance II 400 spectrometer at 25 °C using CDCl_3 residual protonated solvent signals as internal standard.

Small Angle X-ray Scattering (SAXS). The synchrotron scattering experiments were operated at beamline BL16B1 at Shanghai Synchrotron Radiation Facility (SSRF). The beam energy and the current were 3.5 GeV and 150 mA, respectively. The wavelength λ_w of the X-ray was 0.124 nm and the magnitude of the scattering vector is defined as: $q = 4\pi\sin\theta / \lambda_w$ where 2θ is the scattering angle. The raw sample to detector distance was about 5100 mm and further refined using a standard chicken tendon collagen sample (<http://www.rz.uni-karlsruhe.de/~cg02/korea.html>). A MarCCD detector was used to record 2D scattering patterns. Typical exposure time was 2 minutes. Due to the limitation of the setup at the beamline, parasitic scattering from the slits could be observed in the SAXS patterns close to the beamstop.

NMR and IR spectra

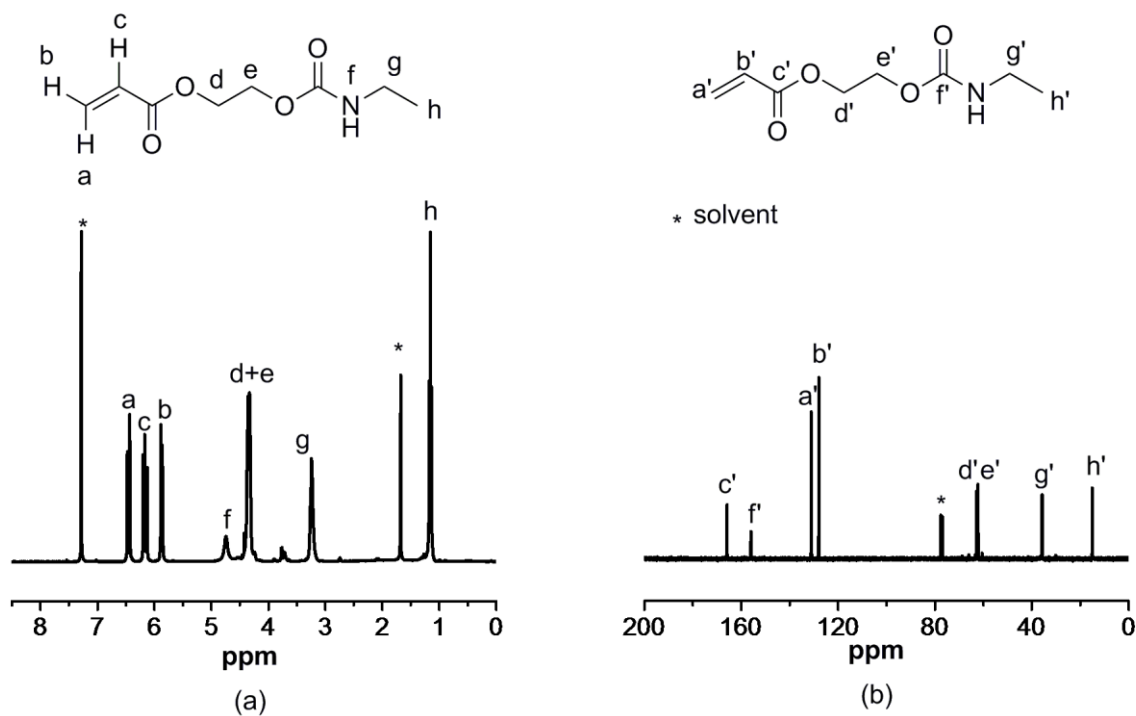


Figure S1. NMR spectra of CMA: (a) ^1H NMR (400 MHz, CDCl_3) and (b) ^{13}C NMR (400 MHz, CDCl_3).

^1H NMR (400 MHz, CDCl_3 , δ): 6.43 (dd, $J_{ac} = 17.32$ Hz, $J_{ab} = 1.51$ Hz, 1 H, H_a), 6.14 (dd, $J_{ca} = 17.32$ Hz, $J_{cb} = 10.43$ Hz, 1 H, H_c), 5.85 (dd, $J_{bc} = 10.43$ Hz, $J_{ba} = 1.51$ Hz, 1 H, H_b), 4.72 (s, 1H, H_f), 4.32 (m, 4 H, H_{e+d}), 3.22 (m, 2 H, H_g), 1.10 (t, 3 H, $J_{gh} = 7.22$ Hz, H_h)

^{13}C NMR (400 MHz, CDCl_3 , δ): 165.6 ($\text{C}_{c'}$), 155.8 ($\text{C}_{f'}$), 130.9 ($\text{C}_{a'}$), 127.7 ($\text{C}_{b'}$), 62.5 ($\text{C}_{d'}$), 62.0 ($\text{C}_{e'}$), 35.5 ($\text{C}_{g'}$), 14.8 ($\text{C}_{h'}$)

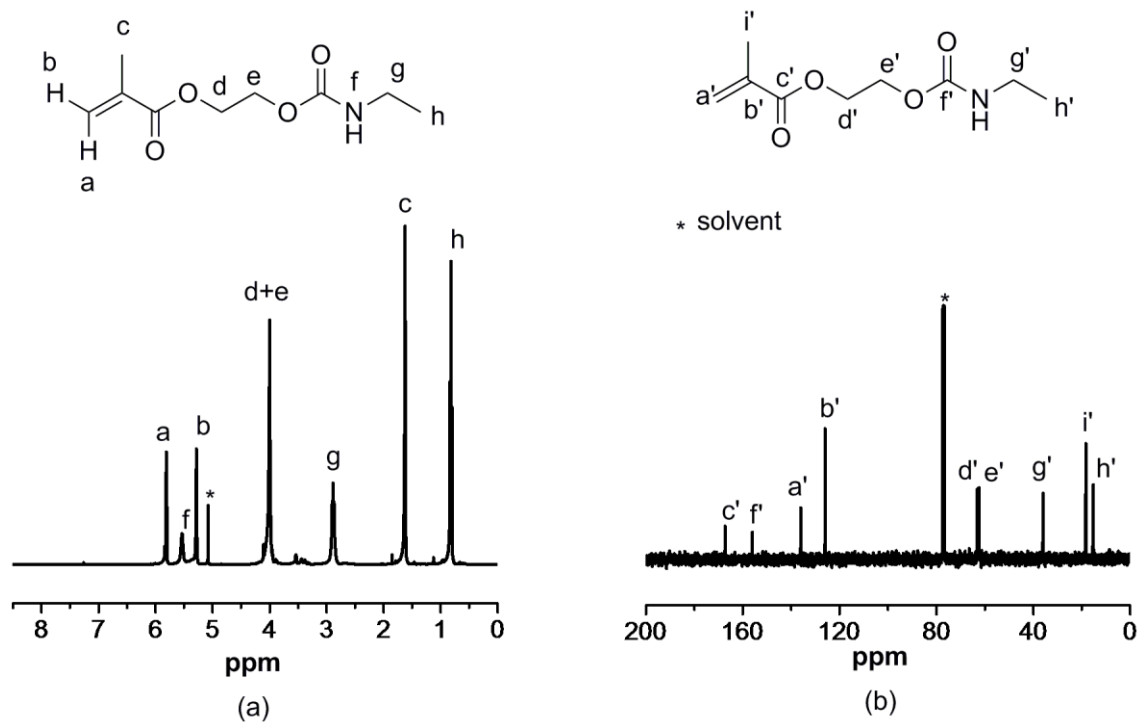


Figure S2. NMR spectra of MCMA: (a) ^1H NMR (400 MHz, CDCl_3) and (b) ^{13}C NMR (400 MHz, CDCl_3).

^1H NMR (400 MHz, CDCl_3 , δ): 5.81 (s, 1 H, H_a), 5.54 (s, 1 H, H_f), 5.08 (s, 1 H, H_b), 4.00 (m, 4 H, H_{d+e}), 2.88 (m, 2 H, H_g), 1.62 (m, 3 H, H_c), 0.82 (t, $J_{gh} = 7.20$ Hz, 3 H, H_h)

^{13}C NMR (400 MHz, CDCl_3 , δ): 166.3 ($\text{C}_{c'}$), 155.6 ($\text{C}_{f'}$), 135.3 ($\text{C}_{a'}$), 125.0 ($\text{C}_{b'}$), 62.4 ($\text{C}_{d'}$), 61.5 ($\text{C}_{e'}$), 35.1 ($\text{C}_{g'}$), 17.4 ($\text{C}_{i'}$), 14.3 ($\text{C}_{h'}$)

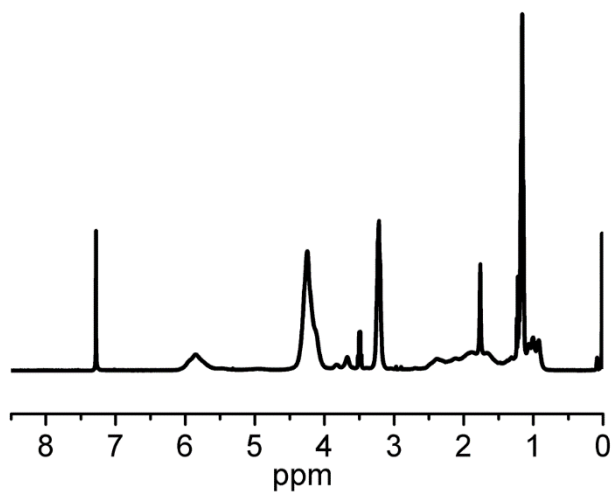


Figure S3. ¹H NMR (400 MHz, CDCl₃) spectrum of **P40/60**.

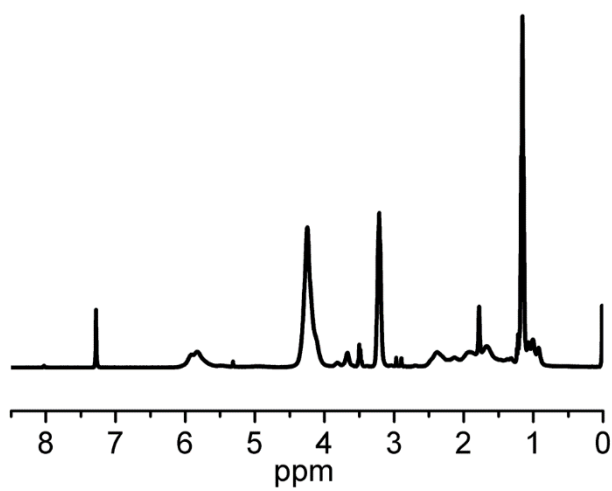


Figure S4. ¹H NMR (400 MHz, CDCl₃) spectrum of **P30/70**.

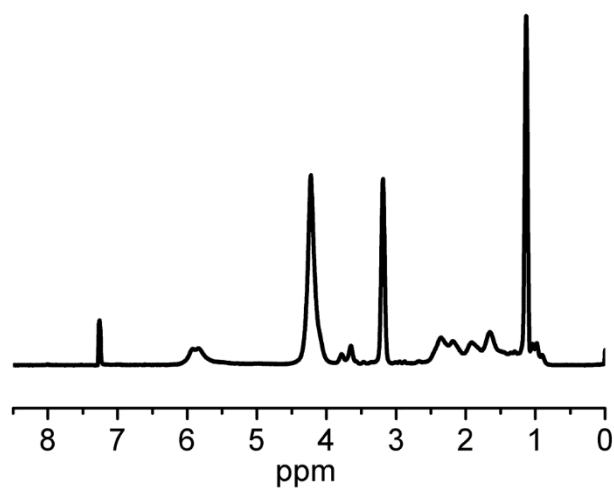


Figure S5. ^1H NMR (400 MHz, CDCl_3) spectrum of **P20/80**.

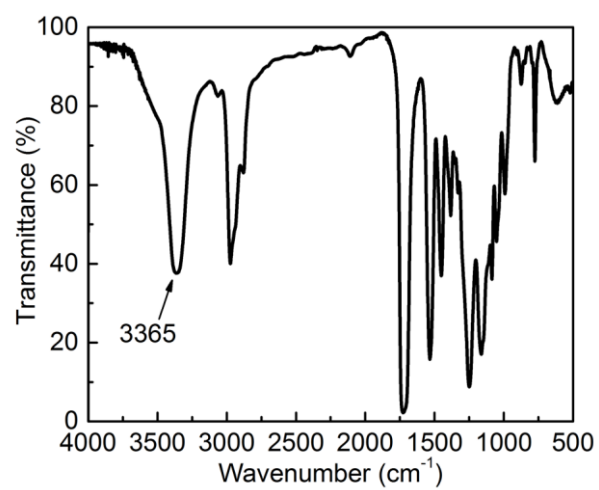


Figure S6. FTIR of **P20/80**.

Mechanical properties

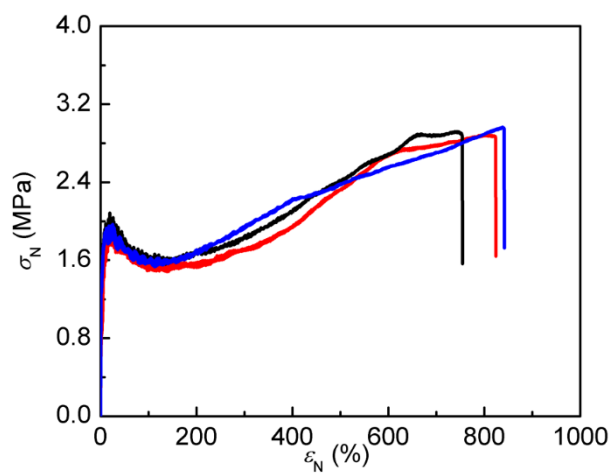


Figure S7. Monotonic stretching of **P20/80** under strain rate of 0.05 s^{-1} from three trials.

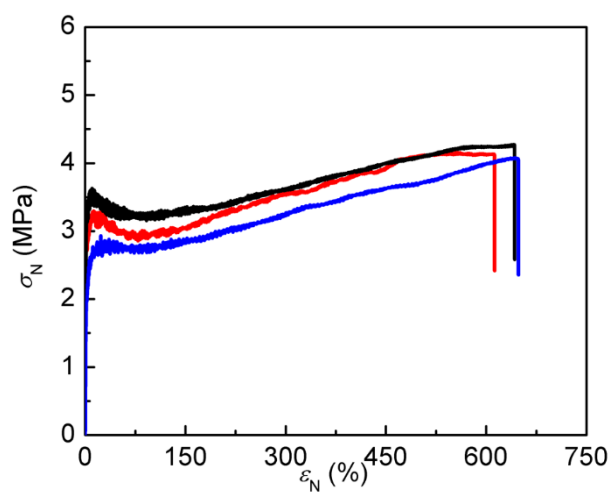


Figure S8. Monotonic stretching of **P20/80-CB5** under strain rate of 0.05 s^{-1} from three trials.

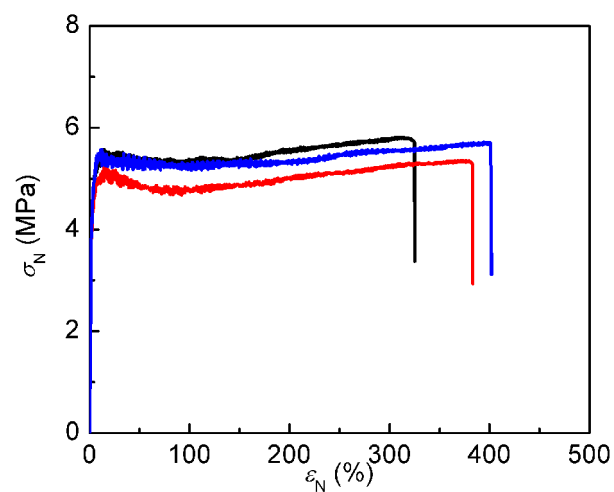


Figure S9. Monotonic stretching of **P20/80-CB10** under strain rate of 0.05 s^{-1} from three trials.

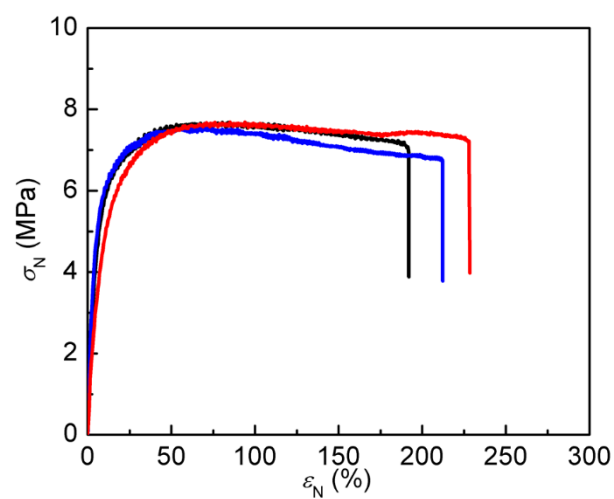


Figure S10. Monotonic stretching of **P20/80-CB20** under strain rate of 0.05 s^{-1} from three trials.

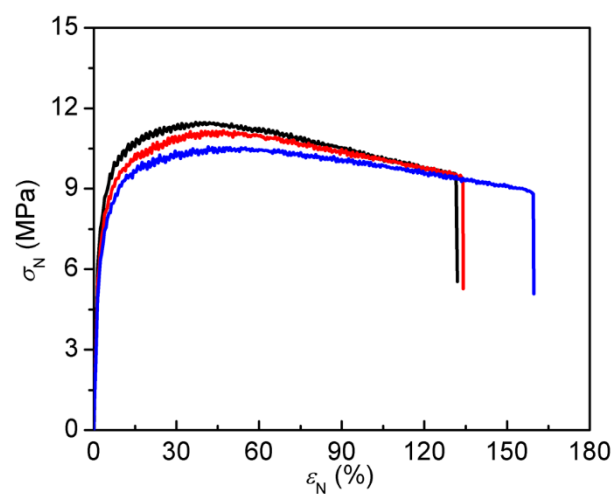


Figure S11. Monotonic stretching of **P20/80-CB25** under strain rate of 0.05 s^{-1} from three trials.

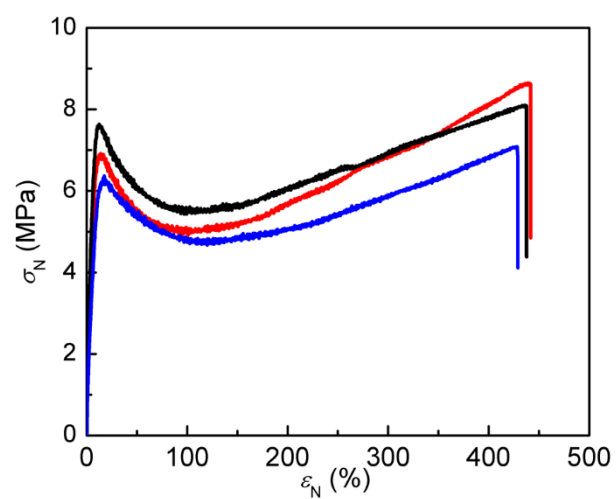


Figure S12. Monotonic stretching of **P30/70** under strain rate of 0.05 s^{-1} from three trials.

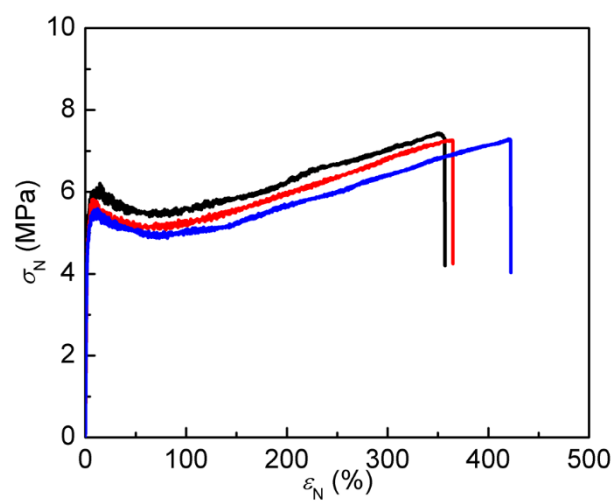


Figure S13. Monotonic stretching of **P30/70-CB5** under strain rate of 0.05 s^{-1} from three trials.

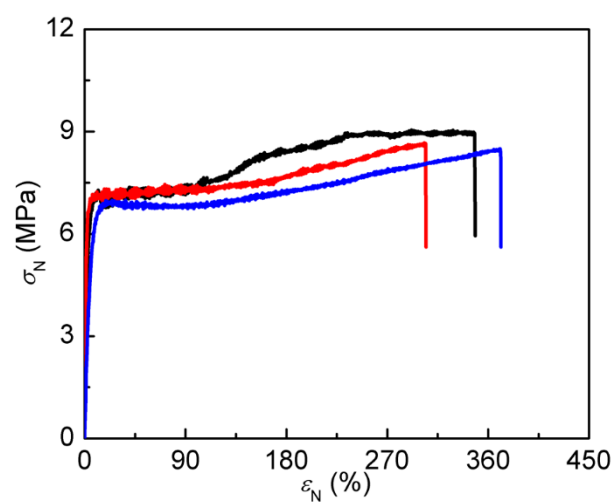


Figure S14. Monotonic stretching of **P30/70-CB10** under strain rate of 0.05 s^{-1} from three trials.

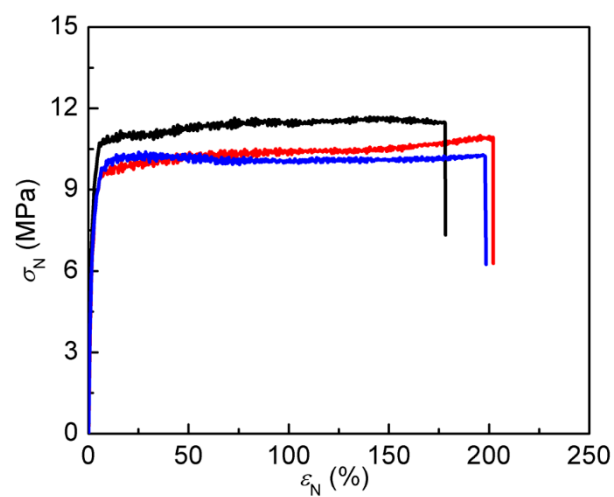


Figure S15. Monotonic stretching of **P30/70-CB20** under strain rate of 0.05 s^{-1} from three trials.

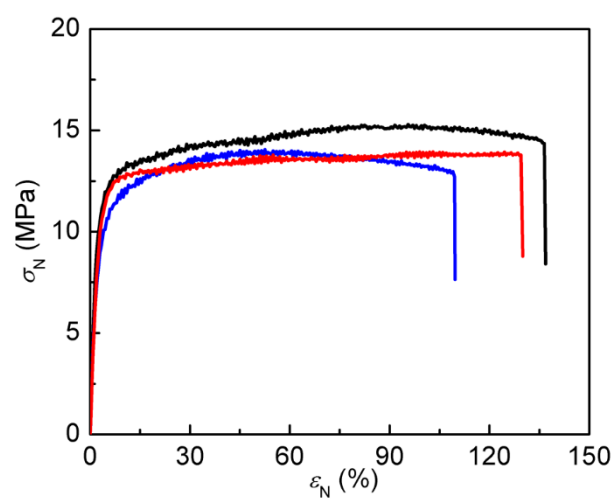


Figure S16. Monotonic stretching of **P30/70-CB25** under strain rate of 0.05 s^{-1} from three trials.

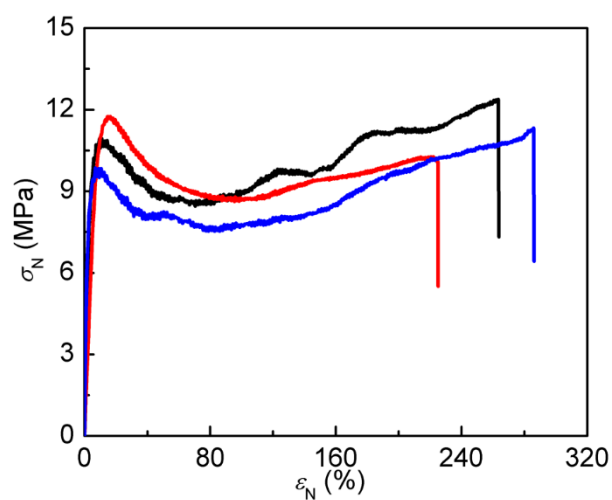


Figure S17. Monotonic stretching of **P40/60** under strain rate of 0.05 s^{-1} from three trials.

Table S1. Young's modulus, yield strength, strain at break, and strength at break for unfilled polymers.

| Sample | Young's modulus(Mpa) | Yield Strength (Mpa) | Strain-at-break (%) | Stength-at-break (Mpa) |
|---------------|----------------------|----------------------|---------------------|------------------------|
| P40/60 | 336.3 ± 22.6 | 10.8 ± 0.9 | 250 ± 30 | 11.3 ± 1.1 |
| P30/70 | 122.5 ± 13.5 | 6.9 ± 0.6 | 435 ± 10 | 7.9 ± 0.8 |
| P20/80 | 33.2 ± 5.4 | 2.0 ± 0.1 | 805 ± 45 | 2.9 ± 0.1 |

**Table S2. Young's modulus, yield strength, strain at break, and strength at break
for filled P20/80.**

| Sample | Young's modulus(Mpa) | Yield Strength (Mpa) | Strain-at-break (%) | Stength-at-break (Mpa) |
|--------------------|-------------------------|-------------------------|------------------------|---------------------------|
| P20/80-CB25 | 330.6 ± 36.8 | 11.1 ± 0.1 | 135 ± 10 | 9.4 ± 0.1 |
| P20/80-CB20 | 185.7 ± 17.1 | 7.7 ± 0.4 | 210 ± 15 | 7.2 ± 0.4 |
| P20/80-CB10 | 117.4 ± 11.2 | 5.1 ± 0.5 | 370 ± 40 | 5.5 ± 0.2 |
| P20/80-CB5 | 93.5 ± 9.3 | 3.2 ± 0.4 | 635 ± 20 | 4.1 ± 0.1 |

**Table S3. Young's modulus, yield strength, strain at break, and strength at break
for filled P30/70.**

| Sample | Young's modulus(Mpa) | Yield Strength (Mpa) | Strain-at-break (%) | Stength-at-break (Mpa) |
|--------------------|-------------------------|-------------------------|------------------------|---------------------------|
| P30/70-CB25 | 457.6 ± 13.9 | 13.1 ± 0.4 | 125 ± 15 | 13.6 ± 0.9 |
| P30/70-CB20 | 353.1 ± 5.4 | 10.4 ± 0.3 | 190 ± 15 | 10.9 ± 0.6 |
| P30/70-CB10 | 218.7 ± 10.8 | 6.9 ± 0.4 | 350 ± 30 | 8.4 ± 0.2 |
| P30/70-CB5 | 209.4 ± 9.3 | 5.8 ± 0.3 | 380 ± 40 | 7.3 ± 0.1 |

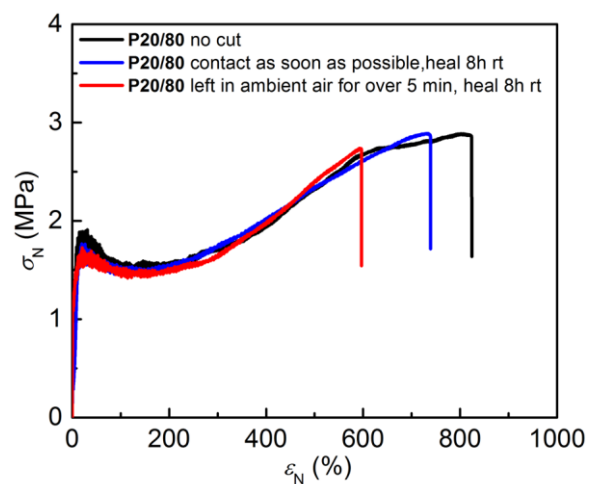


Figure S18. Self-healing of **P20/80** under various conditions indicated in the legend.

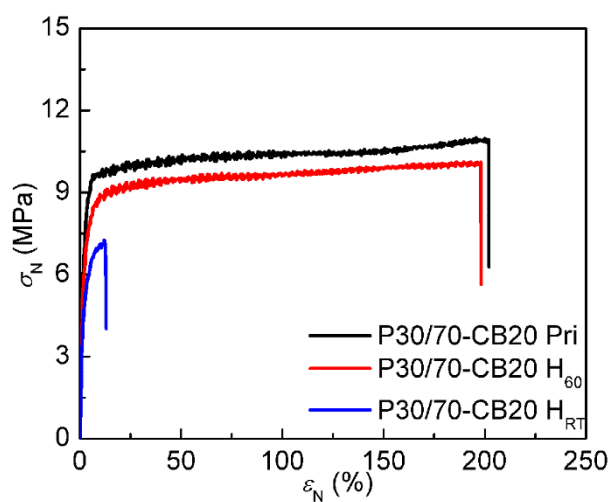


Figure S19. Typical stress-strain curves of **P30/70-CB20**. Pri: pristine sample (black line). H₆₀: healed at elevated temperature (60 °C) for 1 h (red line). H_{RT}: healed at room temperature for 24 h (blue line).

DMA test

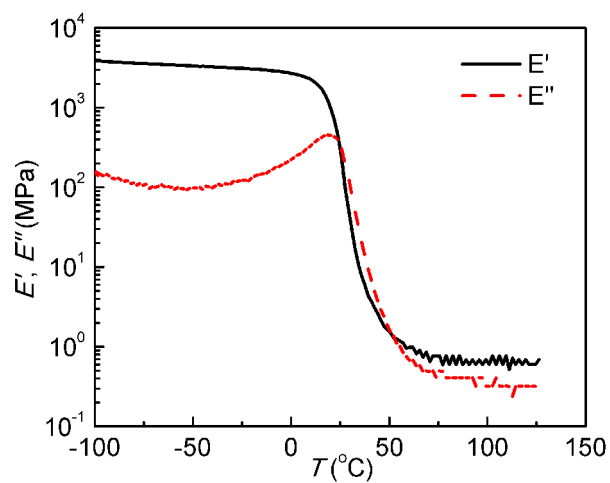


Figure S20. Young's modulus E' and E'' as a function of temperature T for **P20/80**.

Heating rate $5\text{ }^{\circ}\text{C min}^{-1}$. Frequency $f = 1\text{ Hz}$.

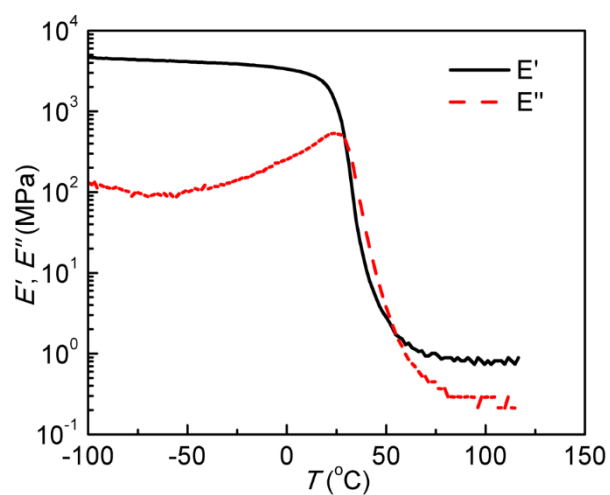


Figure S21. Young's modulus E' and E'' as a function of temperature T for **P30/70**.

Heating rate $5\text{ }^{\circ}\text{C min}^{-1}$. Frequency $f = 1\text{ Hz}$.

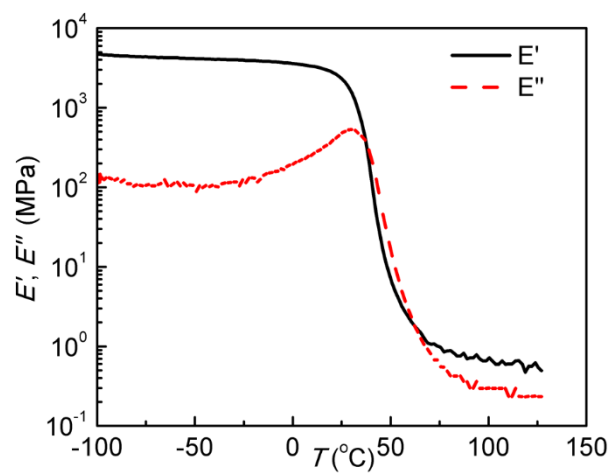


Figure S22. Young's modulus E' and E'' as a function of temperature T for **P40/60**.

Heating rate $5\text{ }^{\circ}\text{C min}^{-1}$. Frequency $f = 1\text{ Hz}$.

Small angle X-ray scattering

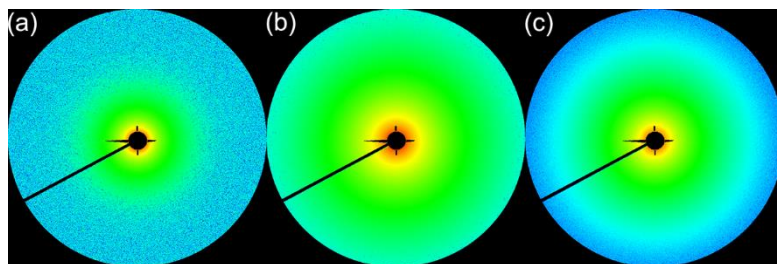


Figure S23. 2D SAXS of (a) **P20/80** (b) **P30/70** (c) **P40/60**. Synchrotron X-ray source.

Electrical properties

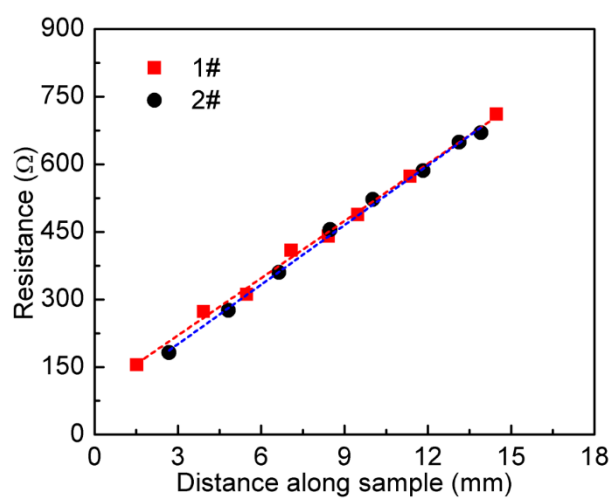


Figure S24 Resistance of **P20/80-CB20** as a function of the distance along the sample.

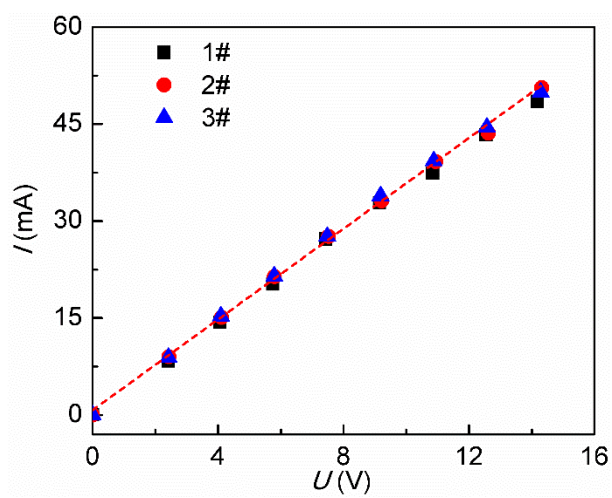


Figure S25. The I - U curve of a **P20/80-CB20** sample.

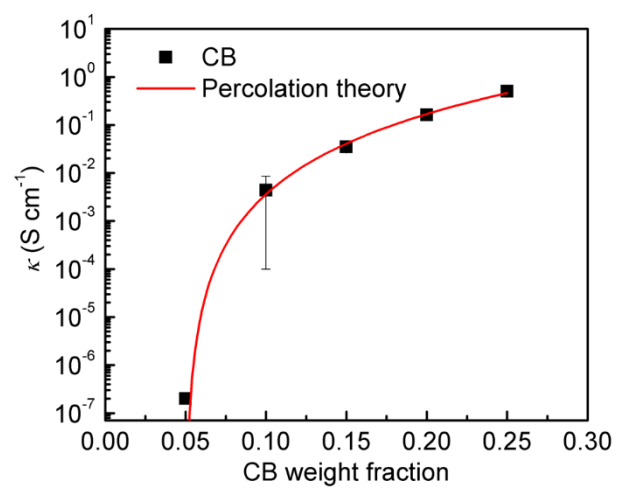
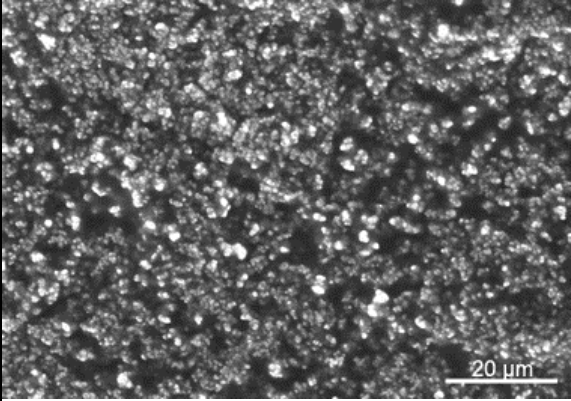
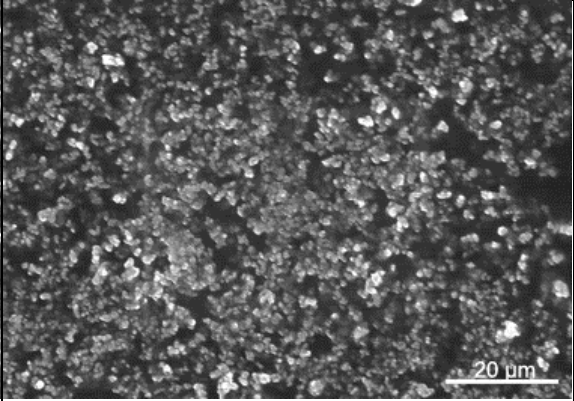
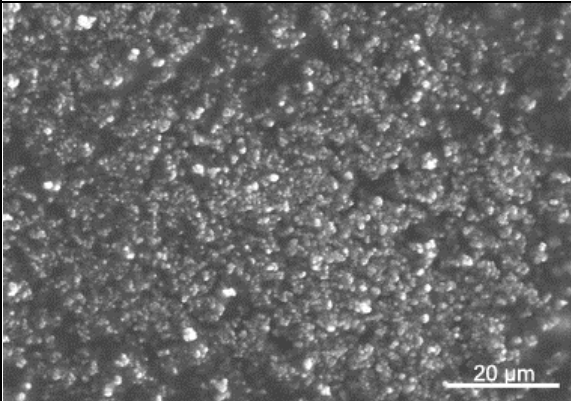
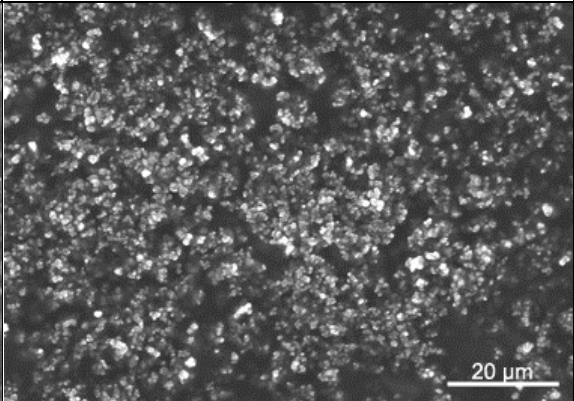
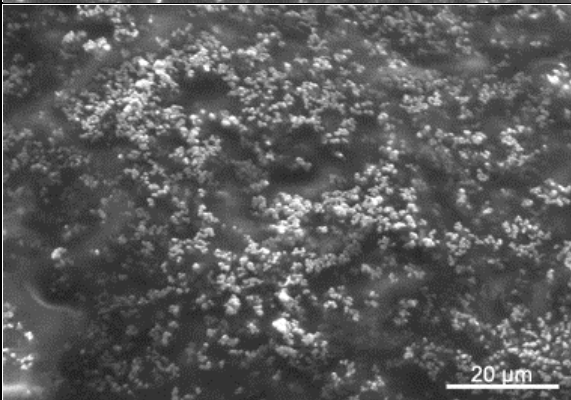
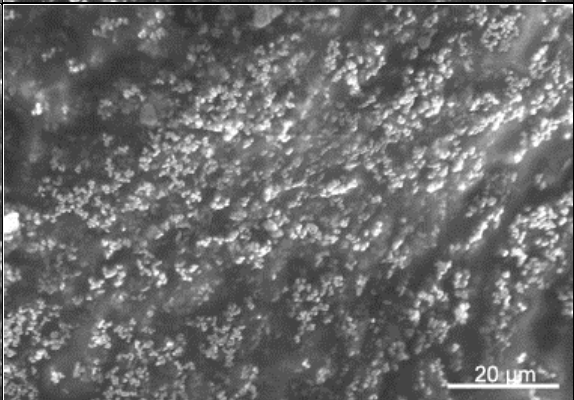
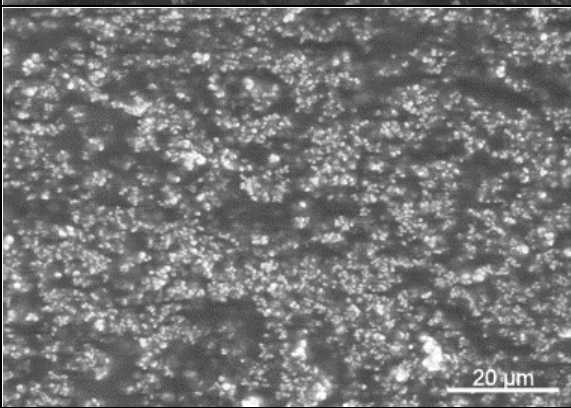
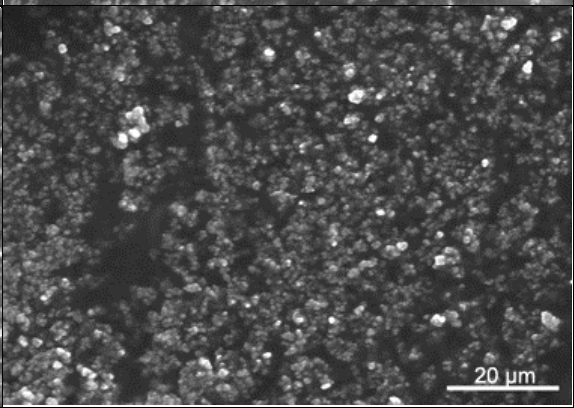


Figure S26. Conductivity as a function of filler weight fraction for **P30/70** materials.

SEM

| <div>Polymer</div> <div>CB %</div> | | (a) P20/80 | (b) P30/70 |
|------------------------------------|--|----------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|
| CB 25 | |  20 μm |  20 μm |
| | |  20 μm |  20 μm |
| | |  20 μm |  20 μm |
| | |  20 μm |  20 μm |

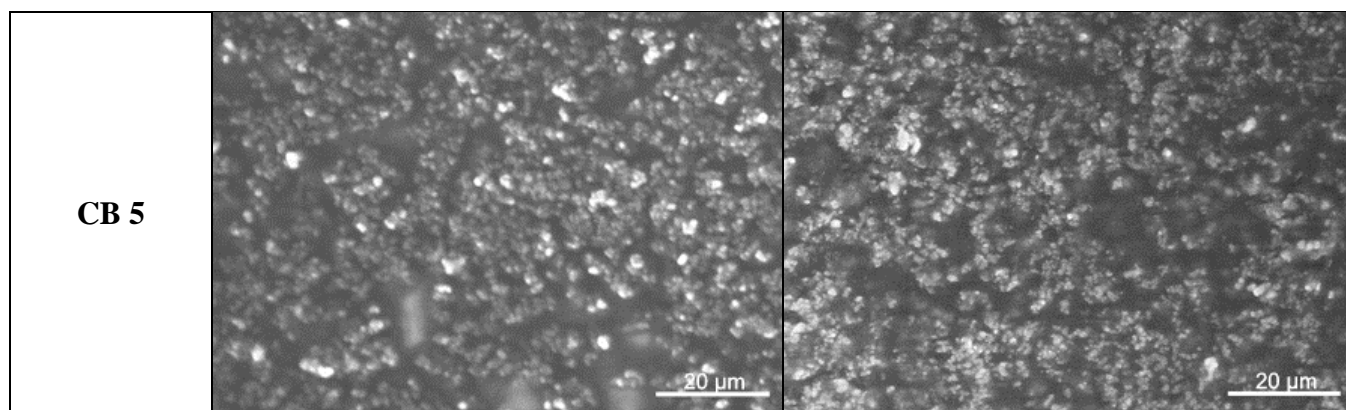


Figure S27 (a): SEM images of the cross-section for **P20/80-CB 25, P20/80-CB 20, P20/80-CB 15, P20/80-CB 10, P20/80-CB 5** samples. (b): SEM images of the cross-section for **P30/70-CB 25, P30/70-CB 20, P30/70-CB 15, P30/70-CB 10, P30/70-CB 5** samples.