Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

1 Materials and methods

1.1 Material and synthesis

Tetrahydrofuran (THF), terephthalaldehyde (TPA), diethyltriamine (DETA), Poly(propylene glycol) bis(2-aminopropyl ether) with average molecular weight of 230 (D-230), tris(2-aminoethyl)amine and 1,6-hexanedianmine (HDA) were purchased form Aladin Industrial Co. (China). Biphenyl A type epoxy resin D.E.R.™ 331™ (epoxy resin) is from the Dow Chemical Company (the USA). All regents used as received.

Synthesis of crosslinking polyimine-epoxy network (C-PIs)

Table S1 Compositions of different C-PIs.

Polymer [a]	TPA (g)	DETA (or HDA) (g)	D-230 (g)	Epoxy (g)	THF (g)
100% C-PI	13.4	10.3	0	18.7	98.9
70% C-PI	13.4	7.21	6.90	13.1	94.8
50% C-PI	13.4	5.15	11.5	9.35	91.9
30% C-PI	13.4	3.09	16.1	5.61	89.1
20% C-PI	13.4	2.06	18.4	3.74	87.7
50% HDA C-PI	13.4	5.81 (HDA)	11.5	9.35	93.5

[a] The percentages stand for the mole ratio of epoxy group and imine group.

Detail Compositions of C-PIs are shown in Table S1. All C-PIs were prepared as follow: THF and TPA were first added into a flask with stirring and a condenser, followed by protection of nitrogen gas. DETA (or HDA) were then inserted into the flask with injectors, and the reaction was kept for 3 h at 60 °C to synthesize linear polyimine (L-PI). Then, D.E.R.™ 331™ was inserted into the reaction, and another 3 h was kept at 60 °C. After cooling, 30 wt% C-PI in THF was obtained as a clear, yellow to red solution.

Reference C-PI used in temperature dependent FT-IR was prepared according to Zhang's work. [1]

1.2 Samples for characterizations and methods

Mechanical properties For mechanical properties estimation, C-PIs solutions were dried in 60 °C vacuum oven with continuously vacuuming for 12 h, and the dried polymers were cured in 80 °C oven for another 12 h. Cured C-PIs were ground to powders or cut into small pellets (if material is too malleable to be ground) for hot press molding, with molding condition of 150 °C, 20 MPa, 10 min. Dumbbell type specimens with significant dimension of 25 mm*4 mm*1 mm were prepared and stored in ambient atmosphere for 48 h to reach humidity equilibrium. The tensile experiments were carried out according to ISO 527-1:2012 on SANS electromechanical universal testing machine CMT4204, with 100 mm/min rate of extension.

Recyclable properties Tested specimens of mechanical properties were cut into pellets in resemble sizes before hot press, and same molding was performed again. Each cycle is called a generation. Three generations were studied in mechanical property change.

Gel content 1.0 g C-PIs of 1st generation as described were put into Soxhlet extractor for 24 h extraction with THF. Gel content is calculated by 100%*m_r/1, m_r is residual mass of the sample.

Water absorption (Equilibrium) Samples in dimension of 12 mm*12 mm*1 mm were cut from dumbbell type specimens of 1st generation as described. The samples were immersed in water at room temperature, and changes in weight were recorded in percentage.

Self-healing behavior Self-healing behavior was observed with Mshot MF10 fluorescence microscope. Films of 500 μm thickness were prepared on cover glasses via solution casting method. Films were cast at room temperature for 12 h, and cured in 80 °C for another 12 h. Scratches with width of 60 um were induced by scalpel under microscopy. And the scratches were observed by fluorescence

microscope after freshly cut and after heating at 30 °C, 60 °C, 90 °C for 1 h, respectively. Mechanical properties of self-healing samples are prepared by solution casting mentioned above. The dimension of specimens and testing method are the same as described in **Mechanical properties**. The specimens were cut apart into two pieces from the middle, and healing process is performed by joining the cracked surface together, undergo 30 °C, 60 °C, 90 °C for 3 h without extra pressure.

Electrochemical analysis Common epoxy resin for comparison consists of 7.48 g D.E.R.™ 331™, 2.30 g D-230 and 22.8 g THF. 30% C-PI which observed to have self-healing ability was directly used in state of 30 wt% solution as described in synthesis of C-PIs. Blends of C-PI and common epoxy resin containing 75%, 50% and 25% amount of C-PI were achieved by simply mixing and stirring them into homogenous state.

75mm*75mm*75 μm wet coating film were prepared on 100 mm*100 mm*1 mm Q235 carbon steel via solution casting method resembled to self-healing behavior. Distinctively, the thickness of dried films was adjusted to 20±1 μm. In scratched samples, the scratches were through to the bottom and the width was 60 μm.

Anti-corrosion feature of C-PIs was analysis by impedance spectroscopy (EIS) and potentiodynamic polarization measurements using a standard three-electrode system which adopts saturated Ag/AgCl electrode, graphite electrode and specimens as reference electrode, counter electrode and working electrode, respectively. The area of working electrode is 0.785 cm^2. After immersion of the films and electrodes in 3.5 wt% NaCl solution for 4 h, EIS and potentiodynamic polarization measurements were carried out with Chenhua(Shanghai) CHI660E electrochemical workstation. EIS was conducted at open circuit potential (OCP) of each samples with an amplitude of 100 mV over a frequency range of 100 kHz to 0.01Hz. And Tafel curve was record by potentiodynamic polarization scanning from -1 V to 0 V, with a scan rate of 1 mV/s.

NMR spectra NMR Spectra were taken on Bruker, AVANCE III HD 400 in deuterated

solvents (DMSO-d_6 and $CDCl_3$).

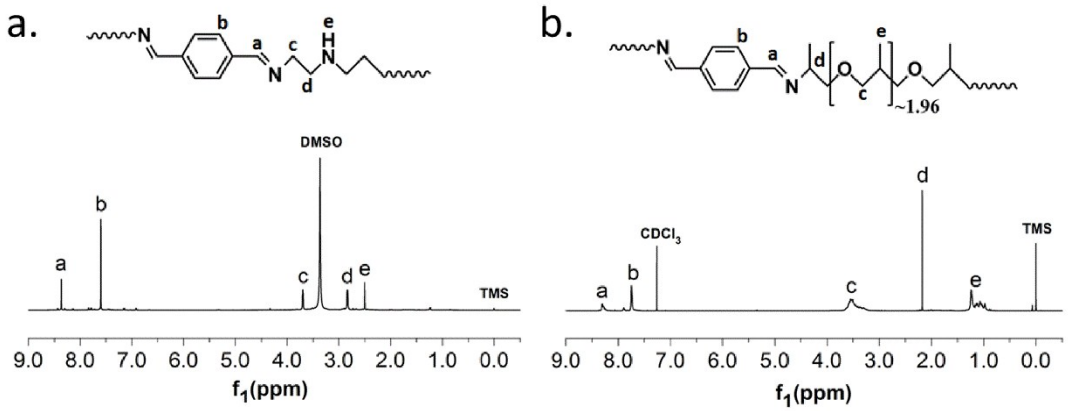
Quantitative FT-IR Quantitative FT-IR was recorded on FT-IR Spectrometer, Bruker, TENSOR 27. Samples before disk press were diluted with KBr into concentration of 5 wt% and ground in agate mortar. 0.3 g diluted samples were used for disk press with applied pressure of 8 MPa.

Temperature dependent FT-IR Temperature dependent FT-IR was recorded on NICOLET 6700 FT-IR with module PIKE TECHNOLOGIES DiffuIR. Samples before hot press were diluted with KBr, and put in diffuse reflectance FT-IR module for measurement.

DSC measurement DSC measurements were carried out on Melttler Toledo DSC 3 with a heating rate of 20 °C/min under nitrogen atmosphere.

NaCl solution immersion quartz columns (circle area with radius of 1.5 cm, height of 10 cm) are anchored to the specimens prepared as described in electrochemical analysis with commercial epoxy resin structural adhesive. 50 ml of NaCl solution were then poured into each column for 7-day immersion of the film.

2 Nuclear magnetic resonance (NMR) spectra



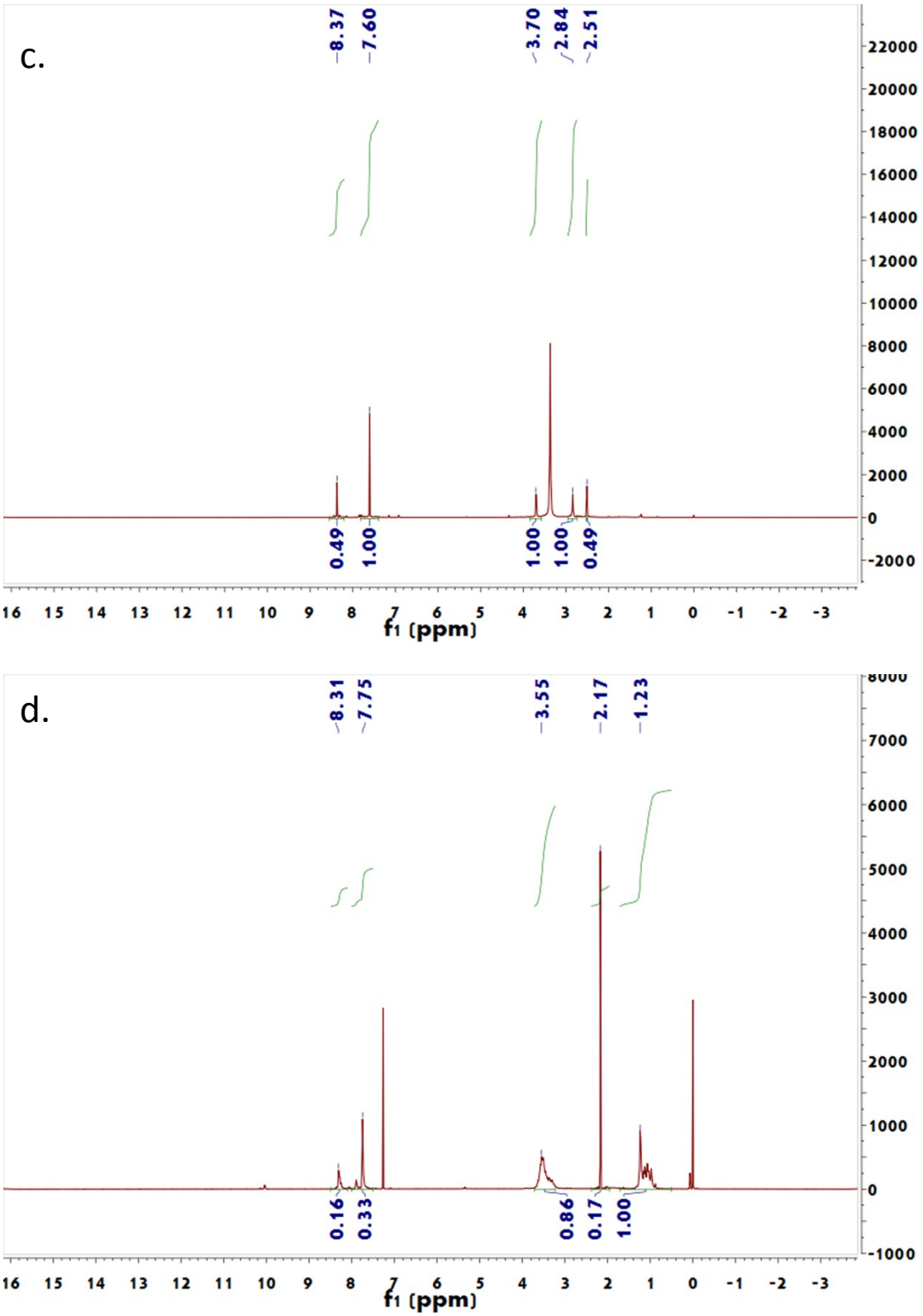


Fig. S1 Conceived structure, chemical shifts and peaks integrals of linear polyimine of TPA-DETA (a, c) and TPA-D-230 (b, d).

3 Quantitative FT-IR spectra of L-PIs and C-PIs

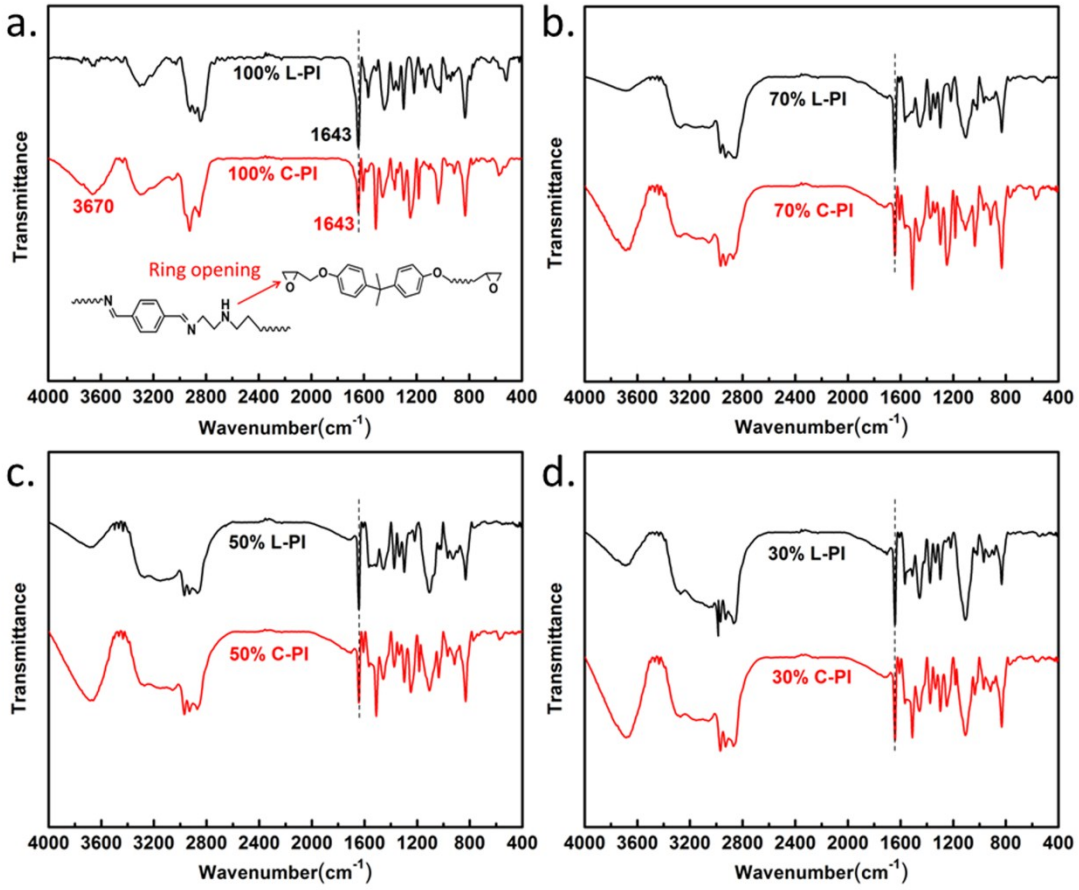


Fig. S2 Quantitative FT-IR spectra of 100% L-PI and C-PI (a), 70% L-PI and C-PI (b), 50% L-PI and C-PI (c) and 30% L-PI and C-PI (d). Scheme of ring opening reaction between epoxy resin and polyimine with secondary amines is shown in (a).

4 Water absorption

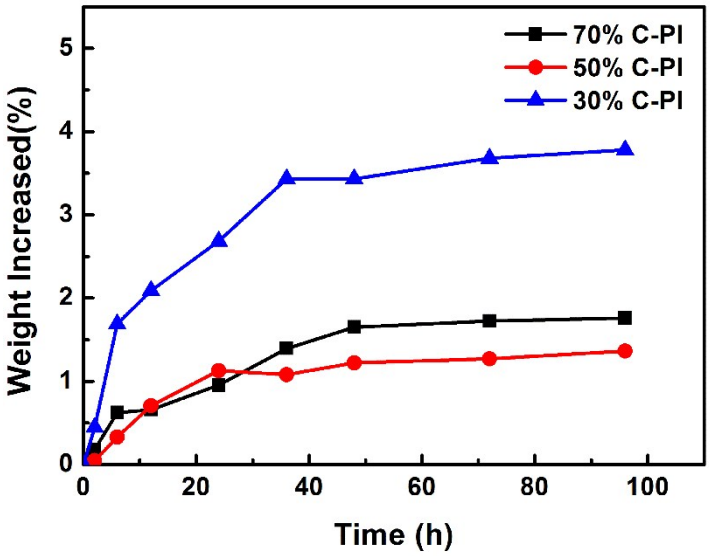


Fig. S3 Water absorption of different C-PIs in 96 h.

5 Differential scanning calorimeter (DSC) analysis

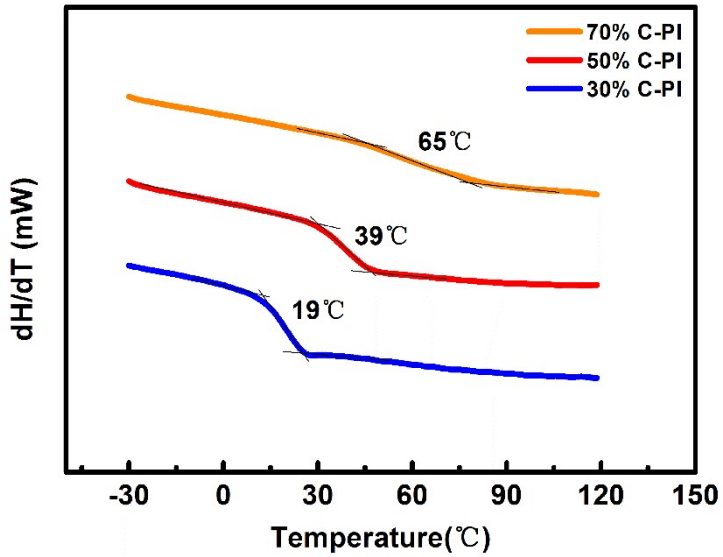


Fig. S4 DSC curves and glass transition of different C-PIs.

6 Pictures of samples

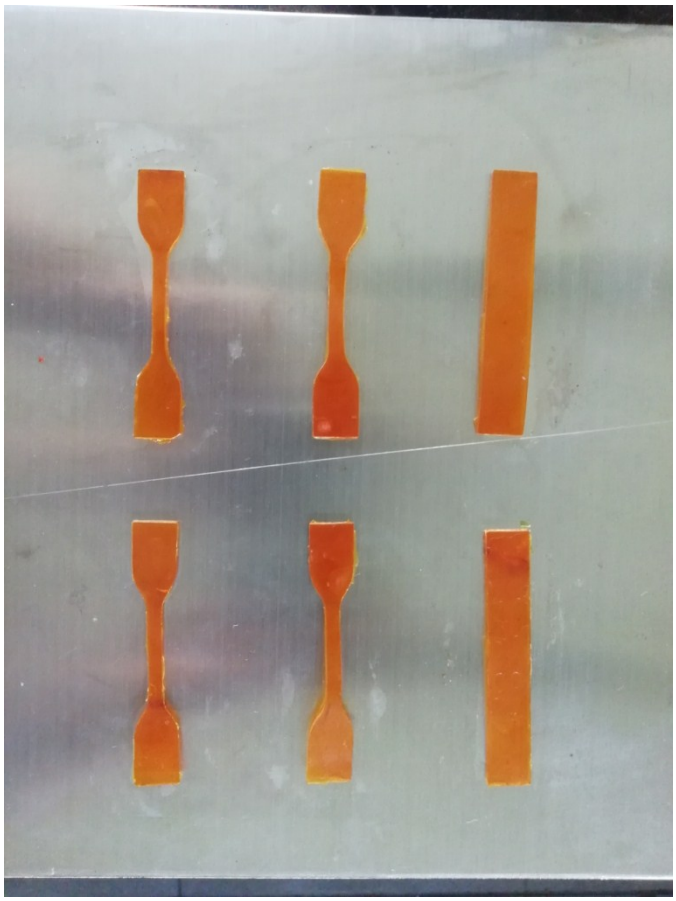


Fig. S5 Mechanical testing specimens prepared by hot pressing.

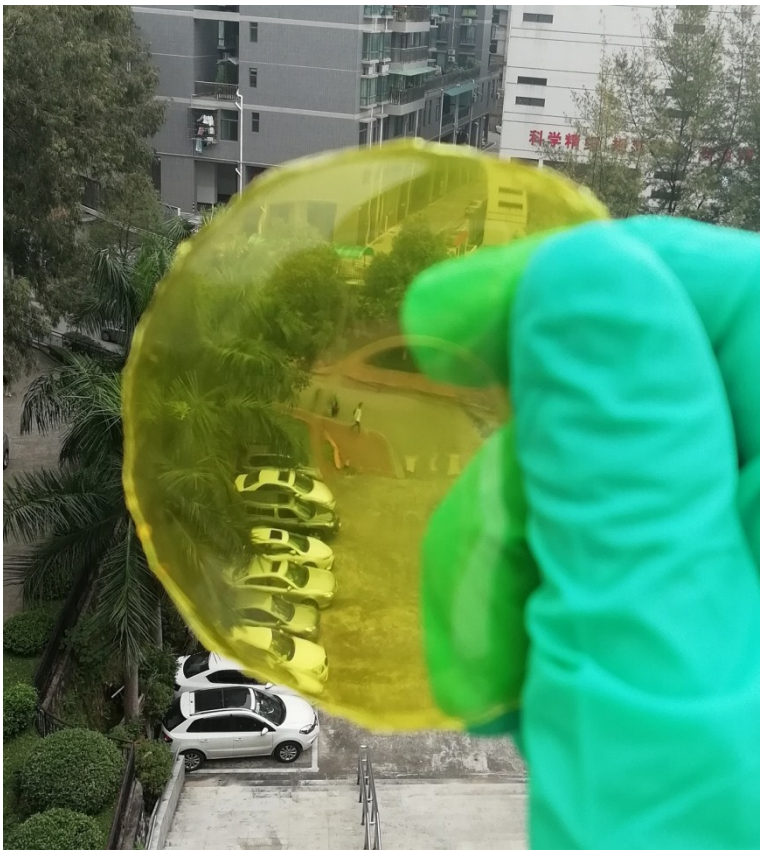


Fig. S6 Transparent film prepared by solution casting

7 Healing Behavior

Table. S3 Percentage change in average strength and elongation of each reprocess generation

Polymer	Strength (%)			Elongation (%)		
	1st gen	2nd gen	3rd gen	1st gen	2nd gen	3rd gen
70% C-PI	100	102.9	100.9*	100	94.9	74.8*
50% C-PI	100	98.2	95.7	100	90.3	97.0
30% C-PI	100	106.5	99.6	100	91.23	68.0

*Drop one unusual data in Fig. 3

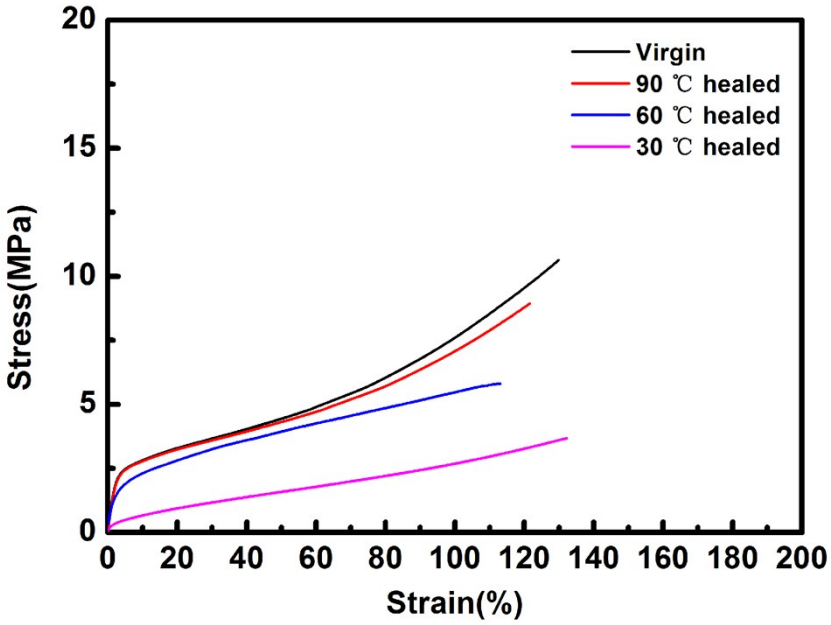


Fig. S7 Stress-strain curves of 30% C-PI healed at different temperature.

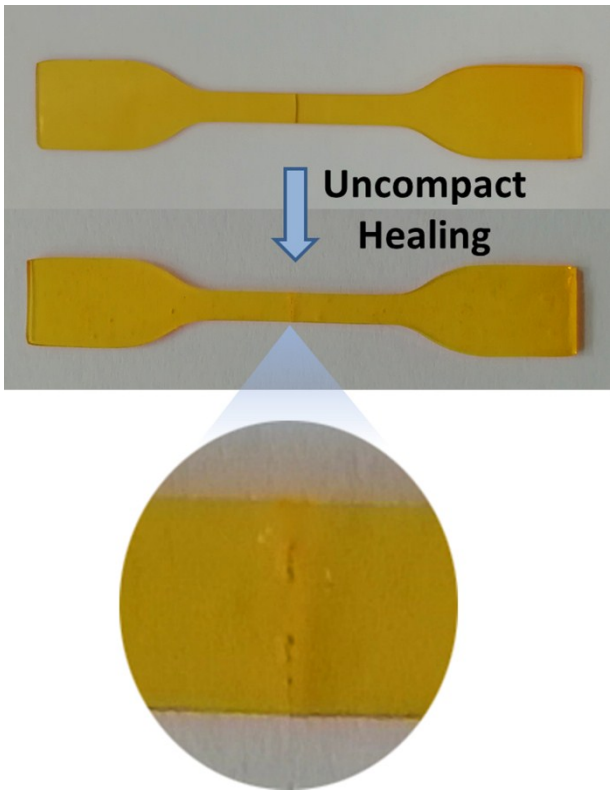
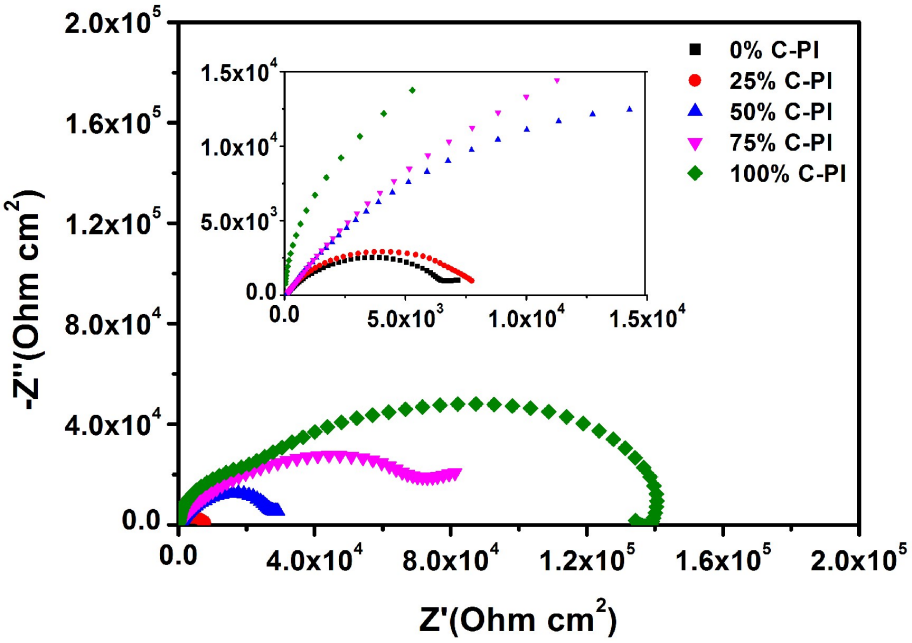


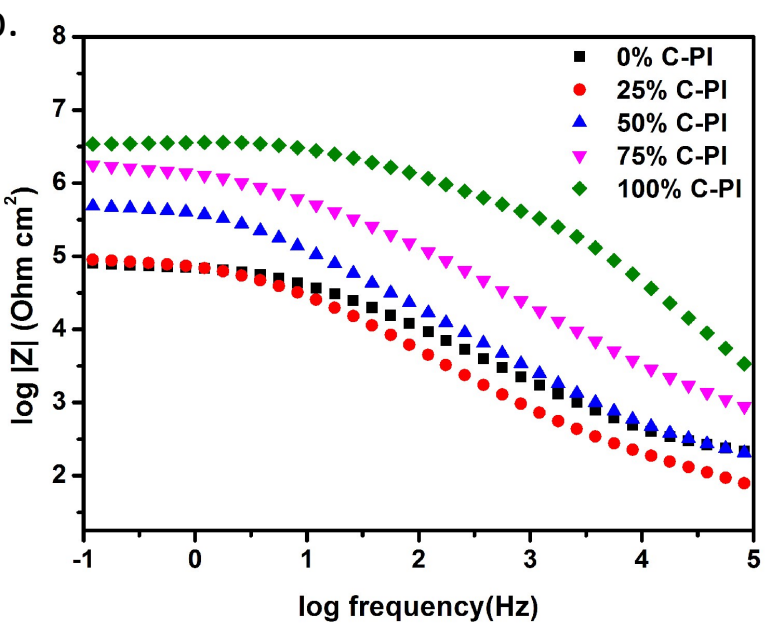
Fig. S8 Uncompact healed sample to show rehealability and defects.

8 Corrosion Inhibiting Feature

a.



b.



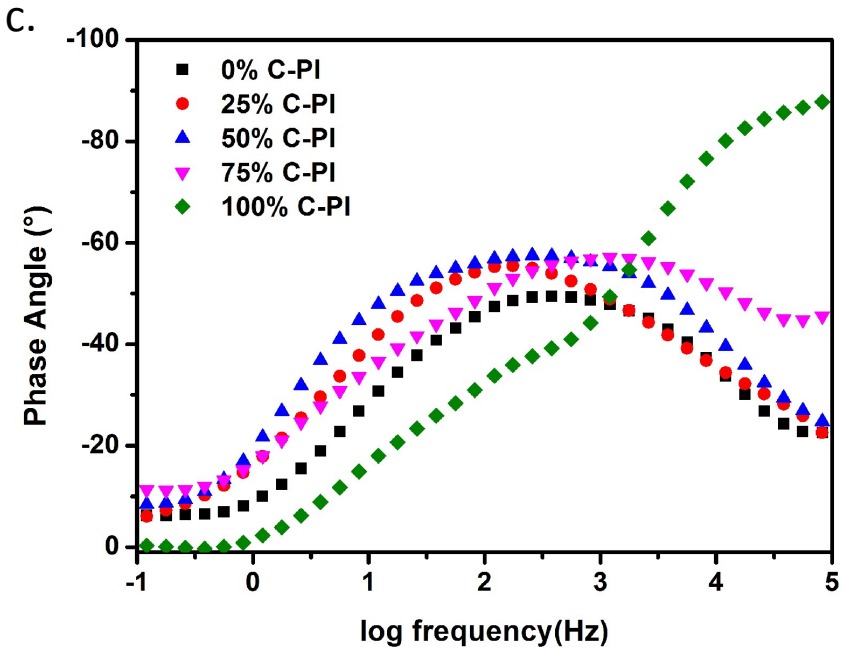


Fig. S9 Electrochemical impedance spectroscopys of blends of common epoxy resin and C-PI. (a) Nyquist plot; (b) Bode modulus; (c) Bode phase angle.

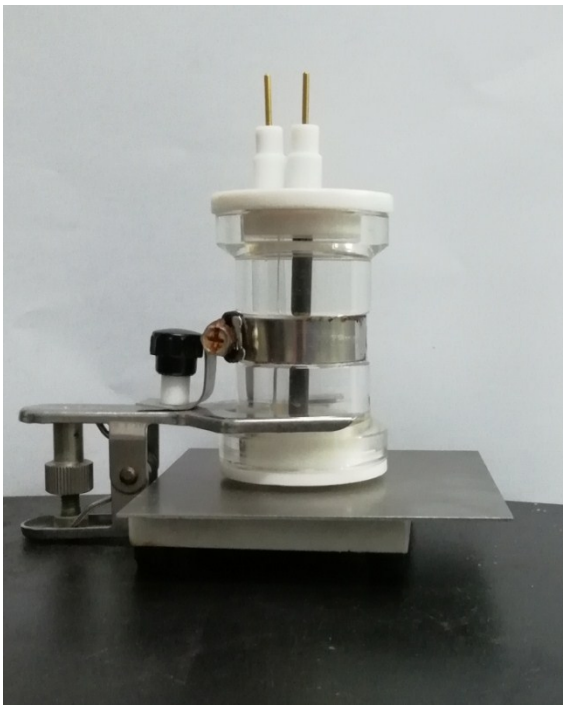


Fig. S10 Electrolytic cell with Ag/AgCl electrode, graphite electrode and specimens.

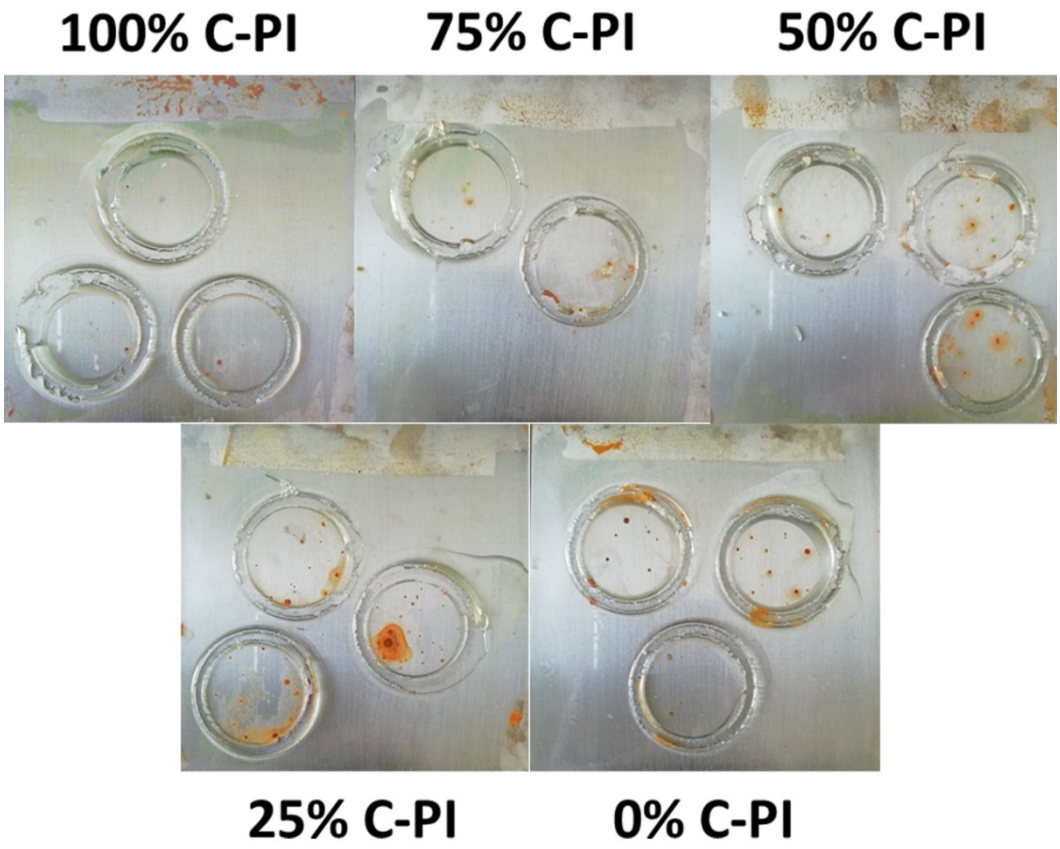


Fig. S11 Specimens immersed in 3.5% NaCl solution for 7 days.

1. P. Taynton, K. Yu, R. K. Shoemaker, Y. Jin, H. J. Qi and W. Zhang, *Advanced Materials*, 2014, **26**, 3938-3942.