Silicone Elastomer with Compromised and Tunable Mechanical Strength and Self-healable Ability Based on Strong and Weak Coordination Bonds

Support Information

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Synthetic route and characterization

Synthesis of 3-aminopropyl-terminated polydimethylvinyl siloxane (APT-PDMVS)

APT-PDMVS was synthesized according to the literature[1] with some modifications by the following procedure. D4 (89 g, 0.300 mol), V4 (12 g,0.034 mol) and benzyltrimethyl ammonium hydroxide (40% in methanol) were added into a three-neck flask with a stir bar and vacuum apparatus. After removal the methanol and water in D4 and V4 at 50 °C for 2 h in vacuum condition, BAPTMDS (4 g) was added to flask and heated to 80 °C and held for 10 h under nitrogen atmosphere, and then system was heated to 160 °C for 1h to destroy the catalyst. Low-molecular-products were eliminated at vacuum at 180°C for 0.5 h. The transparent sticky liquid was collected in glass vessel for characterization. The number of molecular weight of APT-PDMVS is 8.4 x 10^3 g/mol, PDI 1.47 (characterized by GPC). Yield: 70% FTIR (KBr, cm^{-1}): 3056,2963,1598,1408,1260,1096,1026,799. ^{1}H NMR (600 MHz, CDCl$_3$, δ_H, ppm): 0.06–0.09(m,-SiC$\bm{H_3}$) ; 0.53(m, -SiO-C$\bm{H_2}$-CH$_2$-CH$_2$-); 1.18 (br, -CH$_2$N$\bm{H_2}$); 1.46 (m, -CH$_2$-C$\bm{H_2}$-CH$_2$-); 2.67 (t, -CH$_2$-CH$_2$-C$\bm{H_2}$-NH$_2$); 5.80 (m, -C$\bm{H}$=CH$_2$); 5.98 (m, -CH=C$\bm{H_2}$). The molar percentage of vinyl groups is calculated from corresponding integration values (S) in ^{1}H NMR spectrum of APT-PDMVS as follows **(Figure S1a)** and determined as the percentage of the vinyl groups in the sum of methyl groups and vinyl groups. The peak that represented the TMS was overlapped with the methyl groups and can't be separated, but the content was too few to affect the calculating results.

the percentage of the vinyl groups

$$= \frac{S_{vinyl\ groups}}{S_{vinyl\ groups} + S_{methyl\ groups}} = \frac{(S_b + S_c)/3}{(S_b + S_c)/3 + (S_a - (S_b + S_C))/6} * 100\%$$

Synthesis of pyridinedicarboxamide-polydimethylvinyl siloxane (pdca-PDMVS, control-1)

pdca-PDMVS was synthesized according to the literature[2] with some modifications by the following procedure: Et$_3$N (1.1 g) was added to a solution of APT-PDMVS (25 g) in CH$_2$Cl$_2$ (70 mL) at 0 °C under nitrogen atmosphere. After stirring for 1h, a solution

of pyridinedicarboxamide (0.90 g) in CH_2Cl_2 (70 mL) was added in dropwise in 2 hours. The temperature was kept at 0°C during this process. The solution was then allowed to warm to room temperature and stirred for 1 day. After the reaction, the product was poured into 400 mL methane. White precipitate-like viscous solid appeared and the liquid was removed. 100 mL CH_2Cl_2 was added to dissolve the product. The dissolution-precipitation-decantation process was repeated for three times and the final product was subjected to vacuum evaporation at 40 °C to remove the solvent and trace of Et_3N. The molecular weight of pdca-PDMVS is 70×10^3 g/mol, while the PDI is 2.70 (Characterized by GPC). FTIR (KBr, cm^{-1}): 3056, 2963, 1684, 1662, 1537, 1408, 1260, 1096, 1026, 799. ^{1}H-NMR (600 MHz, $CDCl_3$, δ_H, ppm) 0.06–0.09 (m, -SiC**H$_3$**); 0.63 (m, -C**H$_2$**-CH_2-CH_2-NH-); 1.69 (m, -CH_2-C**H$_2$**-CH_2-NH-); 3.49 (m, -CH_2-CH_2-C**H$_2$**-NH-); 5.80(m, -C**H**=CH_2); 5.98(m, -CH=C**H$_2$**); 7.71(br, -CON**H**-); 8.02(t, =C-CH=C**H**-CH=C-N-); 8.36((t, =C-C**H**=CH-C**H**=C-N-). The integration value of peak at 8.02 (peak g) that represents the pyridine group was directly set as 1 hence the relative numbers of link of pdca was 1. Based on this setting the relative numbers of links of -Si$(CH_3)_2$- (x, **Figure 1 a**) and -$SiCH_3(CH=CH_2)$- (**y, Figure 1 a**) were calculated from these formulas as following:

$$x = (S_a - (S_b + S_c))/6$$

$$y = (S_b + S_c)/3$$

And the molar percentage of pdca ligands in pdca-PDMVS chains could be determined as this formula as following:

$$the\ molar\ percentage\ of\ pdca\ ligand = S_g/(x + y + S_g)$$

Synthesis of N-Acetyl-L-cysteine pyridinedicarboxamide-polydimethy siloxane (NAC-pdca-PDMS)

NAC-pdca-PDMS was synthesized by the following procedure[2]. The pdca-PDMVS (10 g, ~9.6% vinyl group), N-Acetyl-L-Cysteine (NAC, 3.21 g), DMPA (0.20 g, as a photo-initiator) and 150 mL THF solution were added into a 250 mL conical flask under nitrogen and stirred for 10 min. The mixture was subjected to UV light for 45 min. In order to remove the excess NAC and DMPA, the resulting mixture was poured into the

mixture solution of deionized water and MeOH (V_{water}/V_{MeOH}=4:1). The precipitate was collected and then re-dissolved in THF and precipitated in the mixture solution. The dissolution/precipitation process was repeated for three times to obtain the NAC grated pdca-PDMS. The latter was dried under vacuum at 50 °C until a constant mass. The number molecular of NAC-pdca-PDMS is 71 x 10^3 g/mol, while the PDI is 3.13 (characterized by GPC) FTIR (KBr, cm^{-1}): 2963, 1731, 1658, 1539, 1408, 1260, 1096, 1026, 799. ^{1}H NMR (600 MHz, CDCl$_3$, δ_H, ppm): 0.06–0.09 (m, -SiC**H$_3$**); 0.98-1.10(m, -SiC**H$_2$**CH$_2$-); 2.0-2.1(m, -COC**H$_3$**);2.55(m,-SiCH$_2$C**H$_2$**S-);2.97(m,-SC**H$_2$**CH-);4.78-4.81(m,-C**H**(COOH)-);0.58-0.61(m,-C**H$_2$**-CH$_2$-CH$_2$-NH-);1.60-1.68(m,-CH$_2$-C**H$_2$**-CH$_2$-NH-);3.75(m,-CH$_2$-CH$_2$-C**H$_2$**-NH-);8.02(t,=C-CH=C**H**-CH=C-N-);8.36((t,=C-C**H**=CH-C**H**=C-N-). The molar percentage of NAC groups on PDMS chains was determined as the previous the molar percentage of vinyl groups (9.6%) subtract the content of residual vinyl groups.

The molar ratio of NAC to pdca ligand was calculated from formula as following*:*

$$the\ molar\ ratio\ of\ NAC\ to\ pdca\ ligand$$
$$=\ the\ molar\ percantage\ of\ NAC\ /_{the}\qquad molar$$
percentage of pdca **Synthesis of N-Acetyl-L-cysteine polydimethy siloxane (NAC-PDMS, control-2)**

The preparation of NAC-PDMS was based on the similar previous work[3]. The same amount of NAC molecules was grafted to the backbone of polymer by thiol-ene click reaction. The process was the same as referred. The number molecular weights of NAC-PDMS was 9.1 x 10^4 g/mol, while the PDI is 2.32 (Characterized by GPC) FTIR and ^{1}H-NMR. FTIR(KBr,cm^{-1}):2963,2909,1731,1660,1540,1410, 1257,1096,1026,799. ^{1}H-NMR (600 MHz CDCl$_3$ δ_H ppm): 0.06–0.09 (m, -SiC**H$_3$**); 1.01-1.06(m,-SiC**H$_2$**CH$_2$-); 2.04-2.15(m,-COC**H$_3$**); 4.78-4.81(m,-C**H**(COOH)-). The molar percentage of NAC groups in NAC-PDMS could be determined as the molar percentage of vinyl groups in PDMVS subtract the molar percentage of residual vinyl groups in NAC-PDMS.
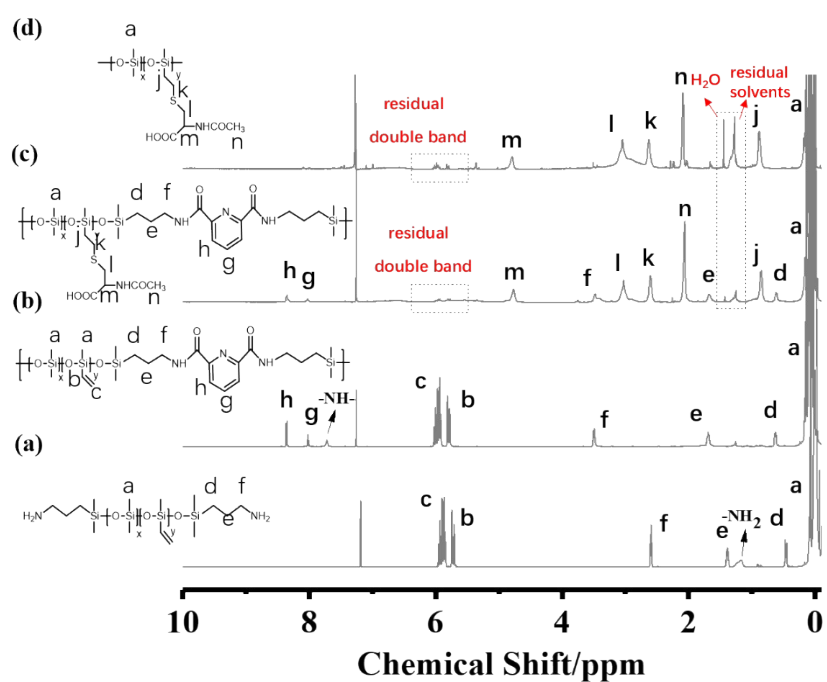
Figure S1 ^{1}H NMR spectra of (a). APT-PDMVS (b). pdca-PDMVS (control-1) (c). NAC-pdca-PDMS and (d). NAC-PDMS (control-2)
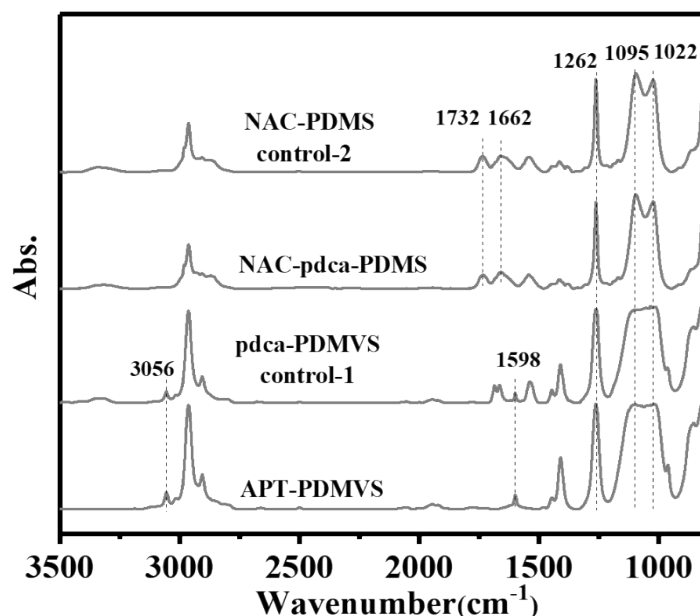
Figure S2 FTIR spectra of APT-PDMVS, pdca-PDMVS (control-1), NAC-pdca-PDMS, NAC-PDMS (control-2)

In addition to ^{1}H NMR spectra, FTIR spectra were also used to characterize the structures of APT-PDMVS, pdca-PDMVS (control-1), NAC-pdca-PDMS and NAC-PDMS (control-2). All of them all contained the characteristic vibration absorptions of Si-C and Si-O bonds. The vibrations absorptions at 1262 cm^{-1} were corresponded to the Si-C bonds, while vibrations absorptions at 1095 cm^{-1} and 1022 cm^{-1} were the Si-O bond.[4] For APT-PDMVS and pdca-PDMVS, the peaks at 1598 cm^{-1} and 3056 cm^{-1} represented the characteristic absorptions of C=C bonds. The introduction of pdca were confirmed by the appearance of new peaks at 1688 cm^{-1} and 1658 cm^{-1}. For NAC-pdca-PDMS and NAC-PDMS, after the thiol-ene reaction, the characteristic absorption peaks at 3056 cm^{-1} and 1598 cm^{-1} that represents the C=C double bonds in polymer backbones nearly disappeared, simultaneously, two sharp new peaks at 1732 cm^{-1} and 1660 cm^{-1} were observed in the curves after the reaction. They represent the stretching vibration of carbonyl groups in –COOH and –COCH$_3$ of NAC groups, respectively. These results demonstrated the double bonds were nearly replaced by the NAC groups.
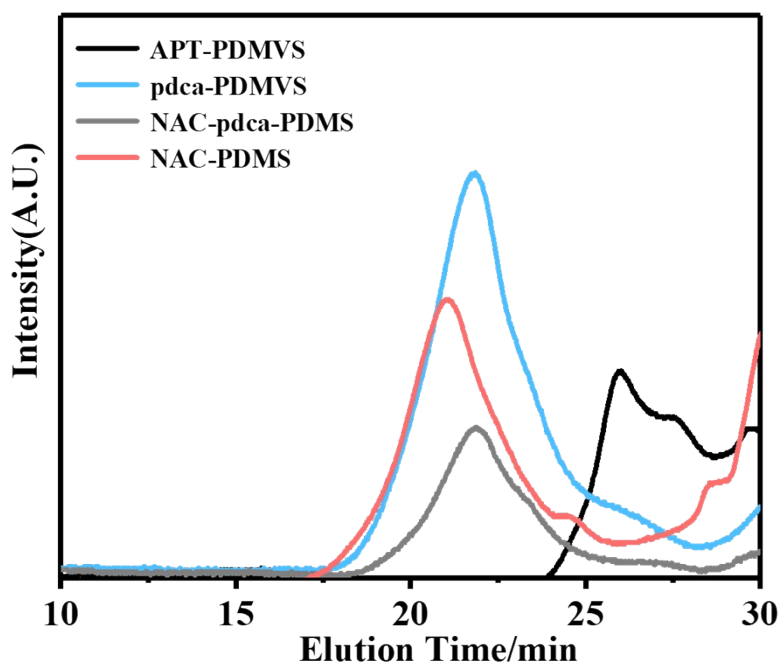
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Figure S3 GPC elution curves of APT-PDMVS, pdca-PDMVS (control-1), NAC-pdca-PDMS, NAC-PDMS (control-2)

Preparation of Fe/NAC-pdca-PDMS x films and reference group

The typical procedure for the preparation of Fe/NAC-pdca-PDMS x polymer films or reference group films (Fe/control-1, and Fe/control-2) was shown as follows in ***Figure S4***: A certain amount of $FeCl_3$ (50 mg/ 1mL) solution (according to molar ratio of metal to ligand, 0.5: 1, 1:1, 1.5:1) in methanol was added to a solution of polymers （10 g） in CH_2Cl_2 (100 mL). The molar amounts of pdca ligand in one gram of polymers (pdca-PDMVS or NAC-pdca-PDMS or NAC-PDMS) were calculated based their corresponding ^{1}H-NMR spectra (***Figure S1 b and S1 c***). The formula was shown as following:

$the\ molar\ amounts\ of\ pdca\ ligand (mol/1g)$

$$= \frac{1}{1*398 + x*74 + y*86}\ for\ pdca\text{-}PDMVS$$

$the\ molar\ amounts\ of\ pdca\ ligand\ (mol/1g)$

$$= \frac{1}{1*398 + x*74 + y*248}\ for\ NAC\text{-}pdca\text{-}PDMS\ or\ NAC\text{-}PDMS$$

In addition to this, these data were also used for calculating the addition of metal-salts in the UV-Vis measurement.

The mixed solution was stirred for 24h at room temperature and concentrated for about 20 mL. The concentrated solution was poured into the PTFE mold and dried at room temperature for 12 h (keeping room relative humidity<50%) followed by dried at 85 °C in the oven to remove the residual solvents. The thickness of films was set in advance. For achieving the required thickness, a PTFE box whose floor side was a 9×9 cm square was prepared by a smooth and flat PTFE membrane considering the weight of samples (10 g, the solute) and the density of silicone rubber (0.98 g/cm^3) as well as the inevitable mass loss in the process of rotary evaporation. The obtained membrane was cut into dumbbell shape by a knife. The final thickness of dumbbell type of samples was measured on a thickness gauge, and the final thickness was determined as 0.85±0.05 mm.

1. Drying for 12h RT

2. 80°C heating
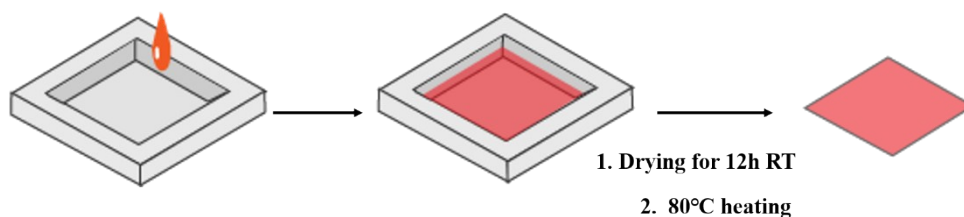
Figure S4 A typical producer of preparation of Fe/NAC-pdca-PDMS x films
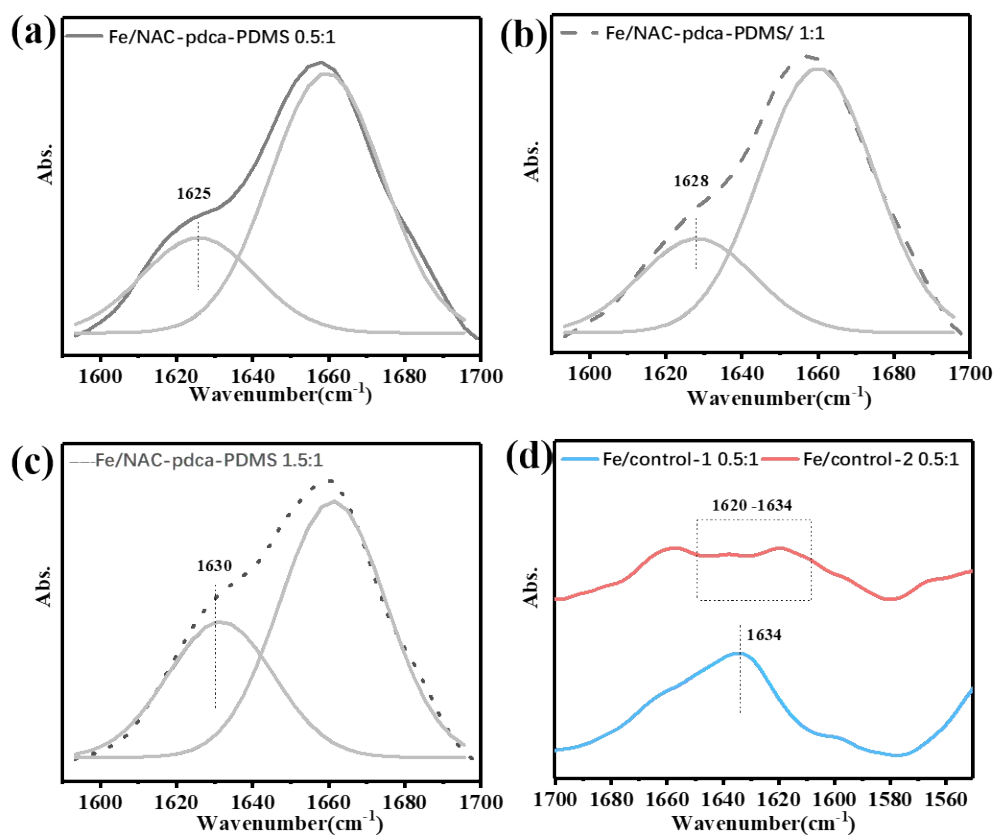
UV-Vis spectra measurements

Figure S5 (a). Curve fitting of wavenumbers region between 1700 cm^{-1}-1600 cm^{-1} of Fe/NAC-pdca-PDMS 0.5:1 (b). 1:1 and (c). 1.5:1 (d). ATR-FTIR spectra of Fe/control-1 0.5:1 and Fe/control-2 0.5:1
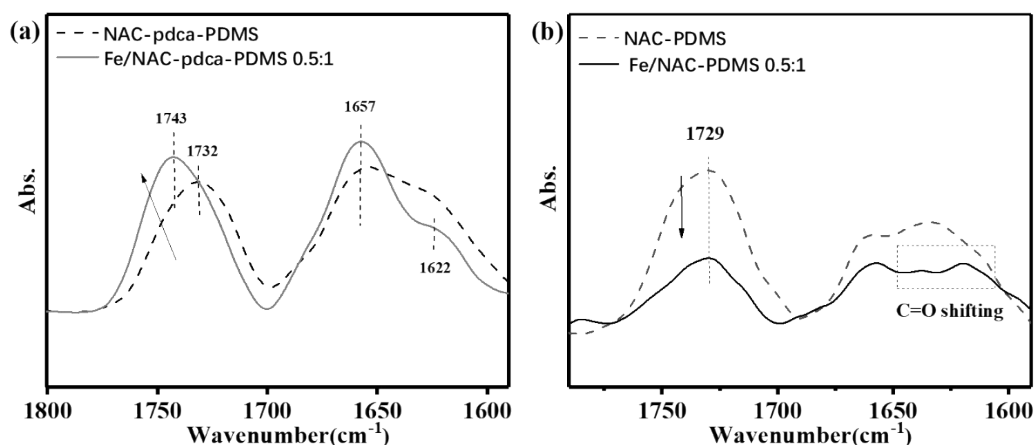
Figure S6 (a). ATR-FTIR spectra of NAC-pdca-PDMS and Fe/NAC-pdca-PDMS 0.5:1 (b) ATR-FTIR spectra of NAC-PDMS and Fe/NAC-PDMS 0.5:1
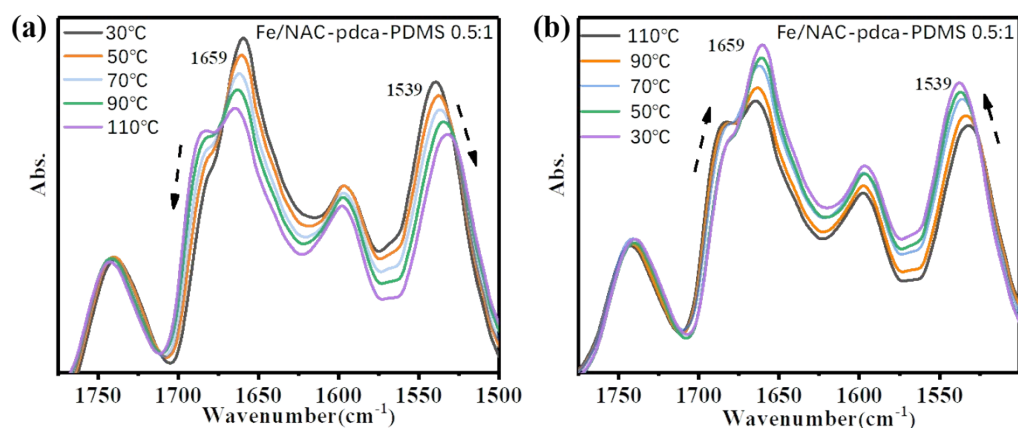

Figure S7 In-situ FTIR spectra of Fe/NAC-pdca-PDMS during (a). heating process (b). cooling process

As shown in ***Figure S7***, in heating process, the characteristic absorption peak of amide I (-CONH, -C=O stretching) exhibited a continuously blue-shift with increasing temperatures and its peak intensity also decreased, and a new peak at higher wavenumber (1686 cm^{-1}) appeared, indicating the formation of non-bonded C=O upon heating. In contrast, when sample was cooled, the intensity of peak that represents the hydrogen-bonded C=O at 1660 cm^{-1}, illustrating the reforming of hydrogen-bonding network. The peak at 1539 cm^{-1} represented the amide II (N-H bend stretching) was shifted to lower wavenumbers (1531 cm^{-1}) when increasing temperatures, and again

shifted to their original wavenumbers when decreasing temperatures. These results further confirmed the dynamic hydrogen bonding between amides in NAC groups.

DFT calculations

For better understanding coordination behavior of ferric ions, the equilibrium of constant of Fe/pdca and Fe/NAC were calculated via DFT calculations, respectively.

The optimized configurations of Fe/pdca and Fe/NAC were firstly calculated. The calculation was performed with DFT method at B3LYP level. LANL2DZ pseudo-potential was used for metal atom and 6-31* basis set for non-metallic atoms. The complexed Fe atom was set as high spin condition(S=5/2) and the PDMS chain were molded as -CH$_3$ group directly. All The two optimized configurations were shown as following:
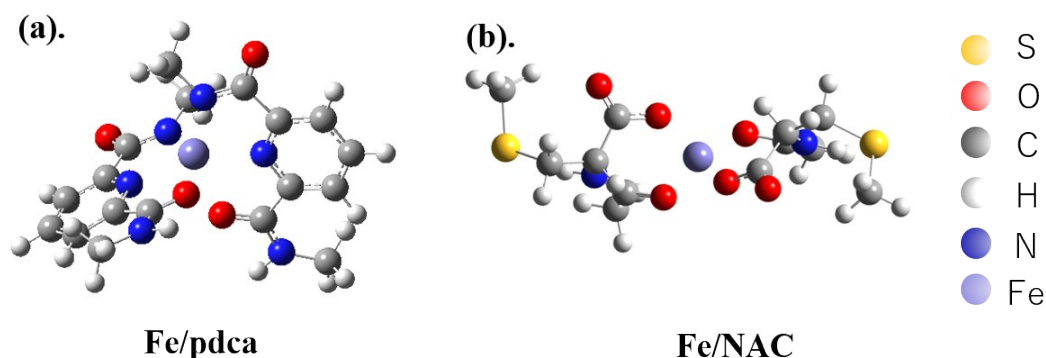
optimized configurations of (a). Fe/pdca and (b). Fe/NAC

After these configurations optimized, the frequency calculation was processed with corresponding metal ions, ligands and complex at the same of level of theory so that the thermodynamics parameter ΔG (including the electronic energy) of two complexes were seized. The equilibrium constants(k) of these two reactions could further calculated according to equation 1:

$$\Delta G = - RT \ln k \qquad\qquad (1)$$

The calculated equilibrium constant k of Fe/pdca and Fe/NAC was 7.64 and 7.11 respectively. This result indicated that these Fe^{3+} ions could nearly simultaneously

coordinate with these ligands. All the calculations were processed on the Gaussian 09 program package[5].

UV-Vis Measurement

The UV-Visible spectra were used to detect the distribution of ferric ions in two ligands (NAC and pdca) in the process of solution blending. A typical procedure was shown in followings and ***Figure S8 a***. According to the ^{1}H NMR proton integration, the molar content of pyridinedicarboxamide (pdca) within 1 g of NAC-pdca--PDMS was about ~0.12 mmol, while the molar fraction of N-Acetyl-L-cysteine (NAC) was around ~1.05 mmol. According to these results, 200 mg of NAC-pdca-PDMS was dissolved in 25 mL mixing solution of 23 mL dichloromethane (DCM) and 2 mL methyl alcohol (MeOH) and stored in a volumetric flask. 50 mg of ferric dichloride (FeCl$_3$) was dissolved in 25 mL methyl alcohol (MeOH). In UV-Vis measurements, the 0.5 mL of NAC-pdca-PDMS solution and determined metal salts solution (determined by molar ratio of metal ion to pdca ligand, 0.5:1,1:1, 1.5:1) was mixed and then another 3.5 mL DCM was added to the mixed solution for the UV-Vis titration. The same process also applied to the reference groups. The UV-Vis spectra of pdca-PDMS (control-1), NAC-pdca-PDMS, NAC-PDMS (control-2) and FeCl$_3$-MeOH in DCM were shown in ***Figure S8 b and Figure S8 c***.
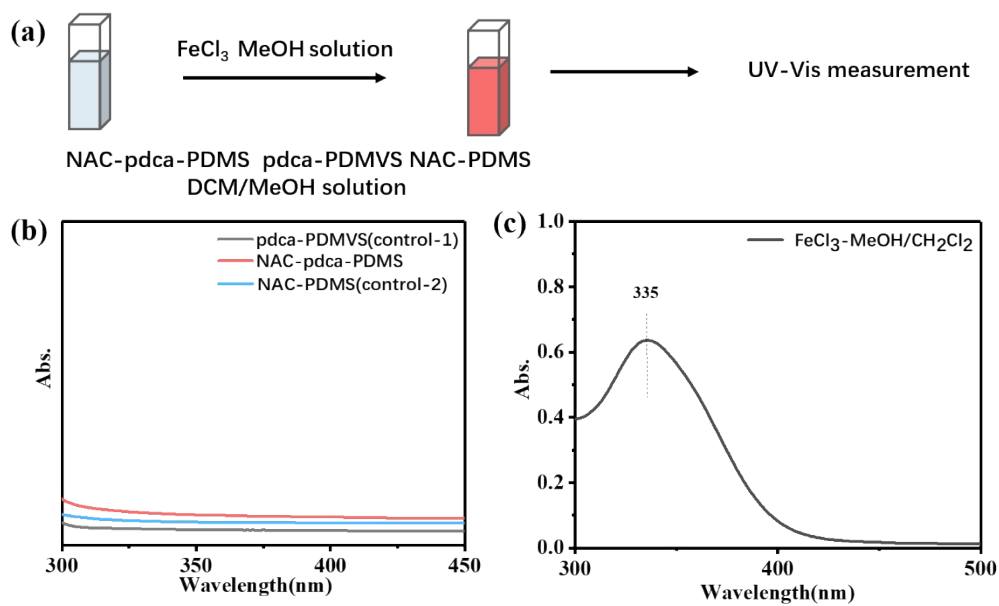
Figure S8 (a). A typical procedure of UV-Vis measurement (b). UV-Vis spectra of pdca-PDMVS (control-1), NAC-pdca-PDMS, NAC-PDMS (control-2) in DCM solution (c). UV-Vis spectra of FeCl₃-MeOH/CH₂Cl₂
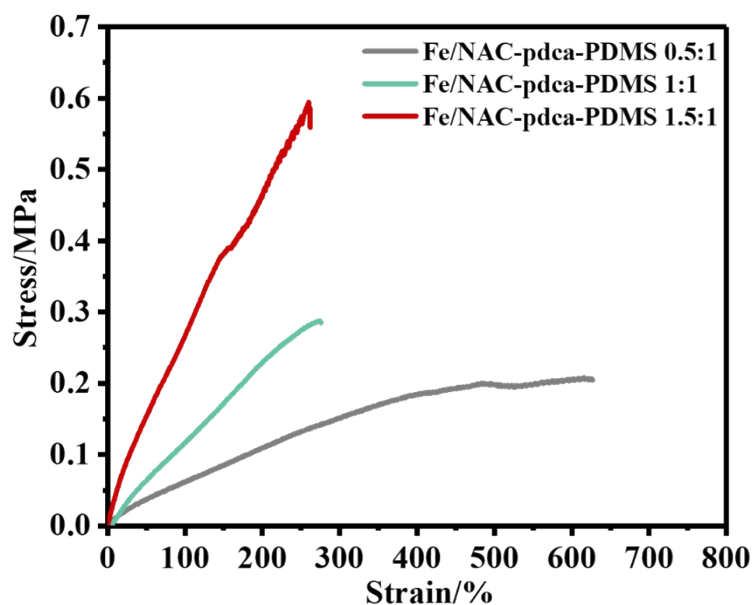
Figure S9 Stress-strain curves of Fe/NAC-pdca-PDMS 0.5:1, Fe/NAC-pdca-PDMS 1:1 and Fe/NAC-pdca-PDMS 1.5:1
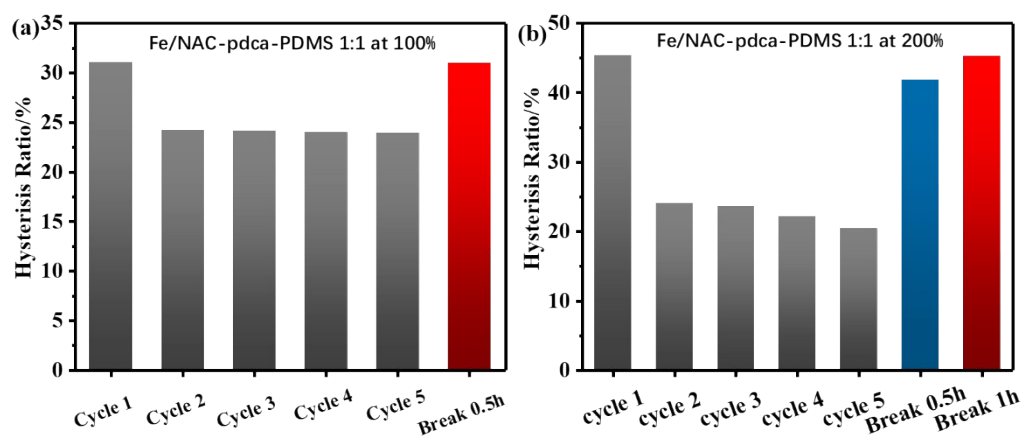

Figure S10 Hysteresis ratio of each cycle in loading and unloading process of Fe/NAC-pdca-PDMS 1:1 at (a). 100% and (b). 200%
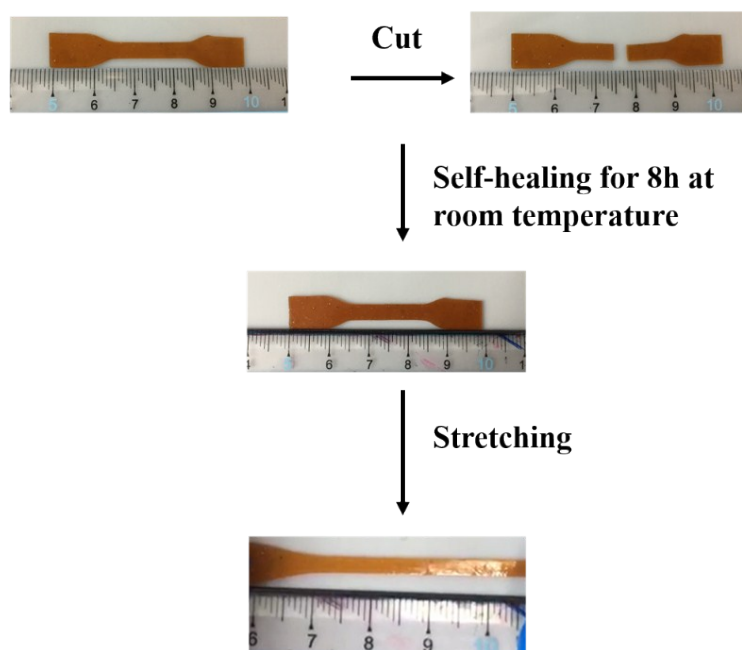
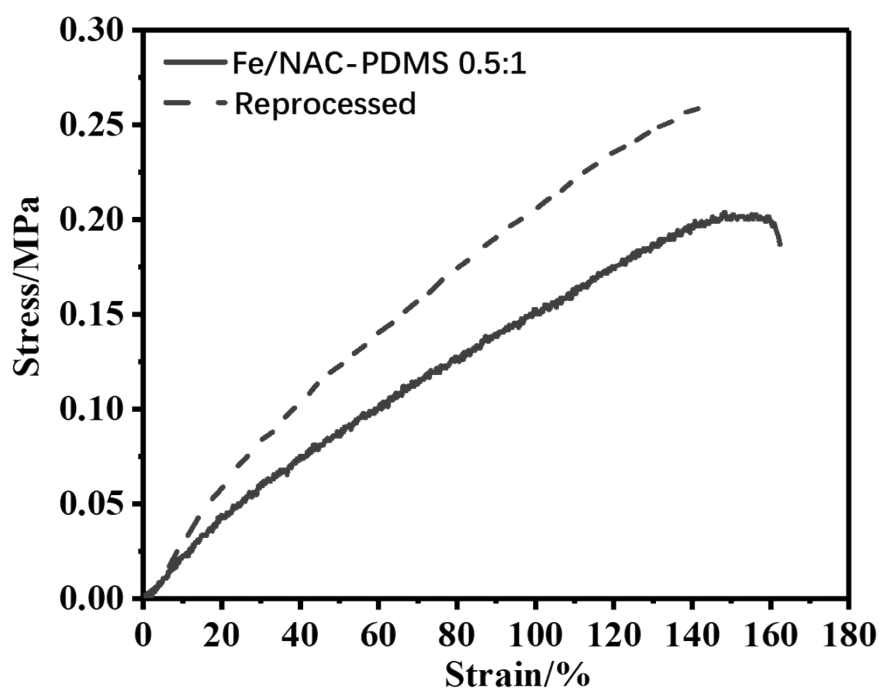**Figure S11 Photographs of self-healing process of Fe/NAC-pdca-PDMS 0.5:1**

Figure S12 Stress-strain curves of Fe/NAC-PDMS 0.5:1 and reprocessed sample
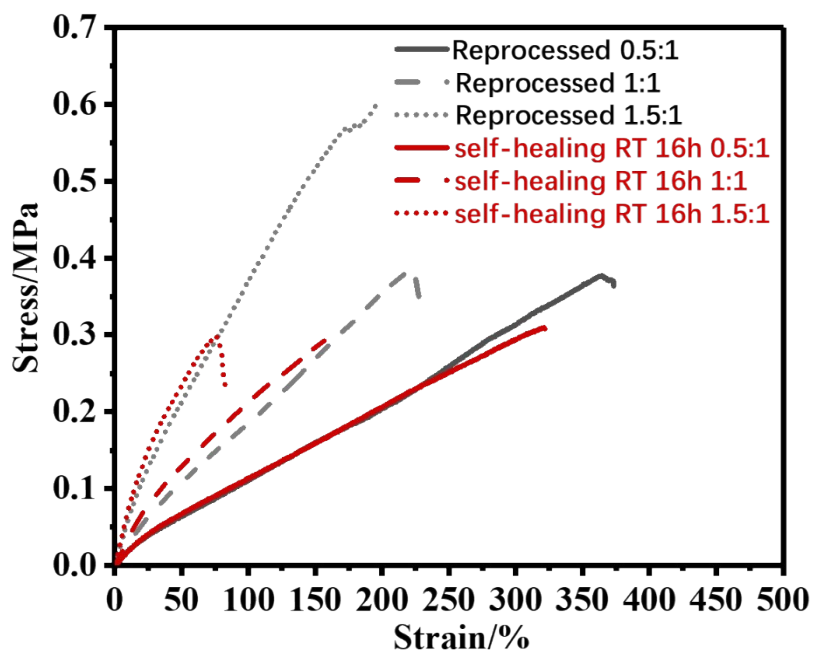
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Figure S13 Stress-strain curves of self-healed reprocessed samples

Table S1 Molecular Structure and Characterization of NAC-pdca-PDMS and reference groups

Sample	pdca[a]	NAC[b]	Mn[c]/ g/mol	PDI[c]
pdca-PDMVS	1.06	0	70000	2.71
NAC-PDMS	/	10.3	71000	3.13
NAC-pdca-PDMS	1.06	9.4	92000	2.32

[a] the molar percentage of pdca [b] the molar percentage of NAC [c] estimated from GPC

Table S2 Comparison of mechanical properties of Fe/NAC-pdca-PDMS films

Sample	Young's modulus/MPa	Maximal Strength/MPa	Breaking Strain/%
Fe/control-1 0.5:1	0.14±0.01	0.08±0.01	547±27
Fe/control-2 0.5:1	0.23±0.01	0.20±0.01	162±13
Fe/NAC-pdca-PDMS 0.5:1	0.11±0.01	0.21±0.01	627±19
Fe/NAC-pdca-PDMS 1:1	0.17±0.01	0.29±0.02	277±18
Fe/NAC-pdca-PDMS 1.5:1	0.40±0.02	0.58±0.02	260±27

and reference group

Table S3 Mechanical properties of Reprocessed Samples

Reprocessed Sample	Young's modulus/MPa	Maximal Strength/MPa	Breaking Strain/%
Fe/control-1 0.5:1	/	/	/
Fe/control-2 0.5:1	0.31±0.01	0.26±0.01	141±11%
Fe/NAC-pdca-PDMS 0.5:1	0.19±0.02	0.36±0.02	369±15%
Fe/NAC-pdca-PDMS 1:1	0.27±0.02	0.38±0.01	224±9%
Fe/NAC-pdca-PDMS 1.5:1	0.61±0.04	0.60±0.03	238±27%

Referrence

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