Supporting Information (SI)

Mechanically and thermo-driven self-healing polyurethane elastomeric composites using inorganic-organic hybrid material as crosslinker

Shiwen Yang[1], Shuang Wang[1], Xiaosheng Du[1], Xu Cheng[1,2], Haibo Wang[1,2], Zongliang Du[1,2*]

[1]College of Biomass Science and Engineering, Sichuan University, Chengdu 610065, PR China. Tel: +86-28-85401296.

[2]The Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Sichuan University, Chengdu 610065, PR China.

[*]Correspondence to: Z. Du (E-mail: dzl407@163.com)

Synthesis of Furan-A

A solution of maleic anhydride (50 g) in 100 ml ethyl acetate was charged into a round bottom flask, furan (46.25 g) was added at a constant speed. The reaction was carried out 24 h at room temperature until the white crystals separating, which was collected via suction filtration and dried in an oven to get a product (Furan-A, yield 87%). Furan-A synthesis confirmed by ^{1}H NMR spectroscopy. ^{1}H HMR (500 MHz, DMSO-d_6) δ: 6.586 (s, 2H, -CHC*H*=C*H*CH-), 5.353 (s, 2H, -C*H*CH=CHC*H*-), 3.317 (s, 2H, O=CC*H*).

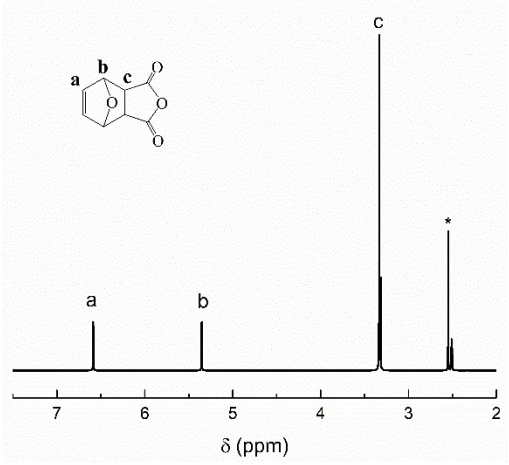

Figure S1 ^{1}H NMR spectrum of Furan-A in DMSO-d_6.

Synthesis of HEPD-A

Furan-A (50 g) and EtOH (80 ml) were mixed into a round bottom flask with a stir bar. MEA in EtOH was added dropwise to the Furan-A solution at a 1.03 molar excess of MEA to Furan-A in an ice bath. Then, heat the resulting mixture to 85 ^{o}C with refluxing for 24 h, until the solution turned dark orange. Upon termination, the solution was cooled overnight and the product was collected by suction filtration. The collected crystals were washed by diethyl ether and dried under vacuum. The colorless product (HEPD-A) was used without further purification (yield 48%). HEPD-A synthesis confirmed by ^{1}H NMR spectroscopy. ^{1}H HMR (500 MHz, DMSO-d_6) δ: 6.550 (s, 2H, -CHC*H*=C*H*CH-), 5.121 (s, 2H, -C*H*CH=CHC*H*-), 4.799 (br, 1H, NCH_2CH_2O*H*), 3.417 (m, 4H, NC*H*$_2C$*H*$_2$OH), 2.926 (s, 2H, O=CC*H*).

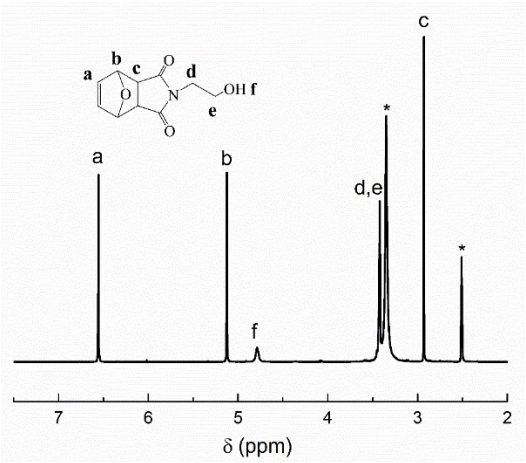

Figure S2 ^{1}H NMR spectrum of HEPD-A in DMSO-d_6.

Synthesis of 1-(2-Hydroxyethyl)-1H-pyrrole-2,5-dione (HEPD)

HEPD-A (5 g) was suspended in toluene (100 ml) in a flame dried 3-neck round bottom flask. The resulting wad refluxed at 115 ^{o}C for 5 h. Put the solution into frozen environment overnight until it cools down to room temperature, then the product (HEMI) was precipitate through suction filtration and washed diethyl ether and dried in an oven(yield 80%). HEMI synthesis confirmed by ^{1}H NMR spectroscopy. ^{1}H HMR (500 MHz, DMSO-d_6) δ: 7.009 (s, 2H, O=CC*H*=C*H*O=O), 4.786 (s, 1H, NCH_2CH_2OH), 3.452 (m, 4H, NCH_2CH_2OH).

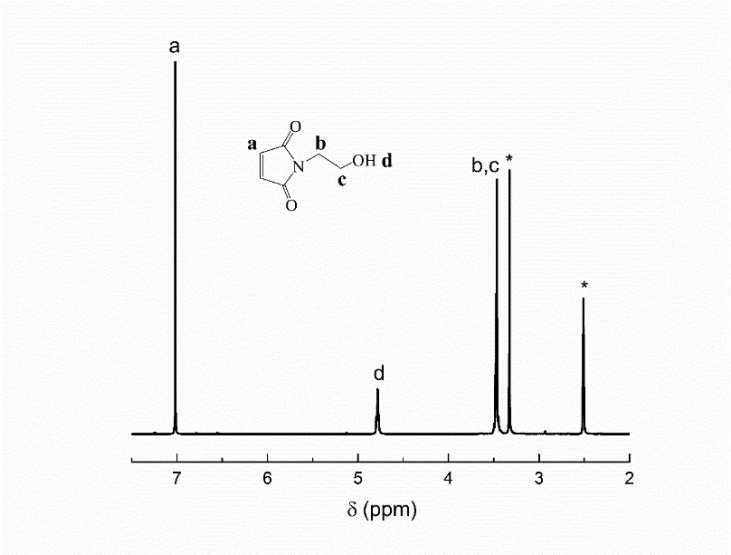

Figure S3 ^{1}H NMR spectrum of HEPD in DMSO-d_6.

The degree of cross-linking of DA-PU-xSiO_2 elastomeric composites calculated by swelling experiment

According to previous studies[1-3], Cross-link density (V_e), defined as moles of effective network chain per cubic centimetre, it could be calculated based on the Flory-Rhener relation:

$$V_e = \frac{-\ln(1-\varphi) + \varphi + \chi\varphi}{V_S \rho_p (\varphi^{1/3} - \varphi/2)}$$

where V_S is the molar volume of solvent (106.8 cm^3/mol for toluene), φ is the volume fraction of polymer in the swollen gel and χ is the polymer-solvent interaction

parameter calculated by the following equation, respectively:

$$\chi = 0.34 + \frac{V_S(\delta_p - \delta_s)^2}{RT}$$

where R is the gas constant [J/(K mol)], T is the temperature (K), δ_p and δ_s is the solubility parameter of polymer and solvent, respectively.

$$\varphi = \frac{m_0/\rho_p}{m_0/\rho_p + m_1/\rho_s}$$

Where m_0 is the initial weight of elastomeric composite (g), m_1 is the weight of the swollen sample (g), ρ_p and ρ_s is the density of the elastomeric composite and solvent, respectively.

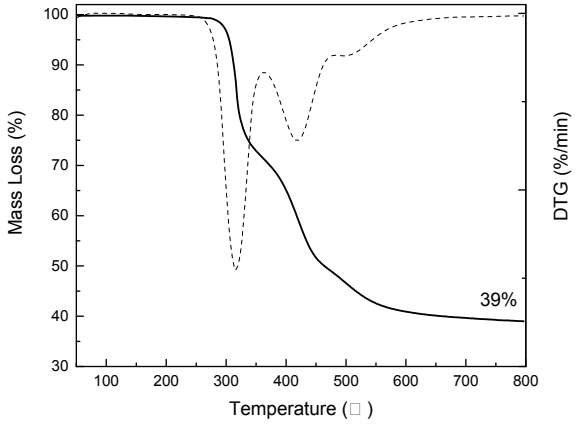

Figure S4 The TGA and DTG curves of furan@SiO_2

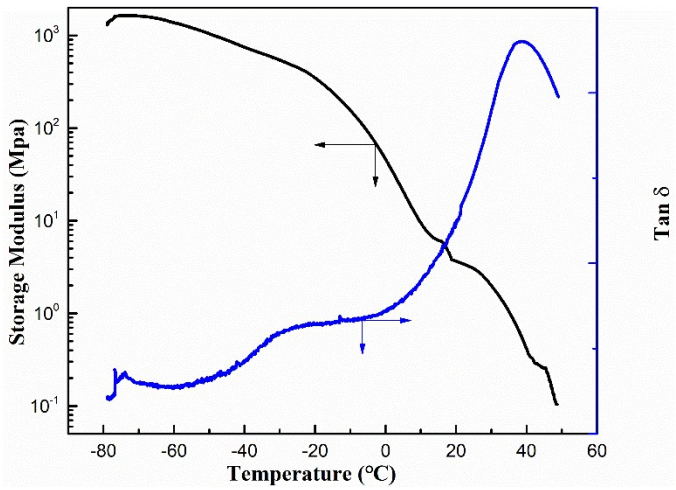

Figure S5 Elastic storage modulus and the glass transition temperature versus temperature of mPU

References:

1. S. R. Jain, V. Sekkar and V. N. Krishnamurthy, *J. Appl. Polym. Sci.*, 2003, **48**, 1515-1523.
2. P. Król and J. Wojturska, *J. Appl. Polym. Sci.*, 2006, **101**, 3511-3519.
3. S. K. Rath, J. Bahadur, H. S. Panda, D. Sen, T. U. Patro, S. P, M. Patri and D. V. Khakhar, *Soft Matter*, 2018, **14**, 3870.