Supporting Information

Mechanically robust and tough waterborne polyurethane films based on diselenide bonds and dual H-bonding interactions with fast visible-light-triggered room-temperature self-healability

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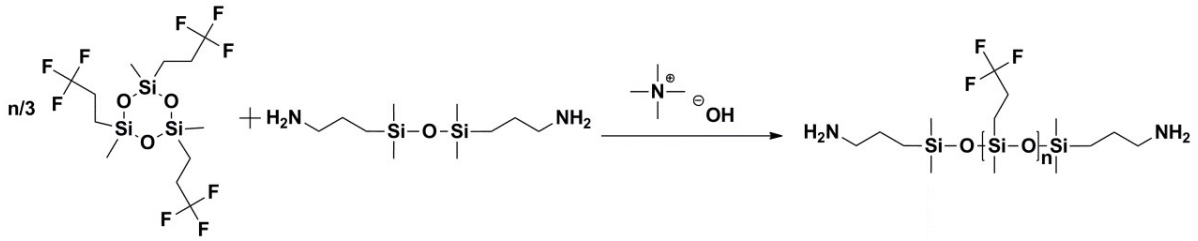
Synthesis of bis(3-aminopropyl)-terminated polytrifluoromethylpropylsiloxane (AMFSi)

AMFSi was synthesized by the anionic ring-opening polymerization of trifluoropropylmethylcyclotrisiloxane (D_3^F) using bis(3-aminopropyl)tetramethylsiloxane as the blocking agent, as shown in Scheme S1. D_3^F (87.65 g，0.187 mol), bis(3-aminopropyl)tetramethylsiloxane (12.43 g，0.050 mol) and TMAH (0.1 g) were charged in a three-neck flask (250 mL), and then the mixture was distilled at 50 °C and a vacuum degree of -0.09 MPa for 1 h. Subsequently, the temperature was kept at 110°C and reacted for 4 h. After that, the temperature was kept at 145℃ and a vacuum degree of -0.09 MPa for 1 h to decompose TMAH. After cooled down to room temperature, a colourless viscous liquid of AMFSi was obtained. ^{1}H-NMR (300 MHZ, $CDCl_3$) δ (ppm): 2.65 ($SiCH_2CH_2C\boldsymbol{H}_2NH_2$), 2.05 ($SiCH_2C\boldsymbol{H}_2CF_3$), 1.42 ($SiCH_2C\boldsymbol{H}_2CH_2NH_2$), 0.75 ($SiC\boldsymbol{H}_2CH_2CF_3$), 0.53 ($SiC\boldsymbol{H}_2CH_2CH_2NH_2$), 0.05～0.16 ($SiC\boldsymbol{H}_3$) (Fig. S1a) [1]. FTIR (KBr, cm^{-1}): 3377.4 (ν[N-H]), 1267.2 (δ[Si-C] of Si-CH_3), 1209.4 (δ[C-F] of -CF_3), 1068.6 and 1026.1 cm^{-1} (ν[Si-O-Si]) (Fig. S1b) [1]. The number-average molecular weight (M_n) was calculated according to the formula as follow:

$$M_n = \frac{I_b}{I_d} \times 2/3 \times M_{D3F} + M_T \quad (1)$$

I_b and I_d represent the integral area of peaks at 0.75 ppm and 0.53 ppm, respectively. M_{D3F} and M_T represent the molar mass of D_3^F and bis(3-aminopropyl)tetramethylsiloxane, respectively. M_n calculated from ^{1}H-NMR is 2 151.5 g/mol, which is close to the theoretical value of M_n (2 000 g/mol).



Scheme S1 Synthesis route of AMFSi.

Characterization and measurements

Nuclear magnetic resonance (NMR) spectroscopy

The ^{1}H-NMR spectra was determined on a JNM-ECA 300 Spectrometer (JEOL, Japan) with $CDCl_3$ as a solvent at 300 MHz.

Fourier transform-infrared spectrometry (FT-IR)

The FT-IR spectra were recorded using an IRAffinity-1 FT-IR spectrometer equipped with an attenuated total reflection (ATR) accessory (Shimadzu, Japan) over a spectral range of 400 to 4000 cm^{-1} at 25°C.

Transmission electron microscopy (TEM)

Morphology of emulsion particles was observed using a H7650 TEM (Hitachi, Japan) with an accelerating voltage of 75 kV and the sample was stained by 0.2 wt % phosphotungstic acid hydrate before observation.

Dynamic Light Scattering (DLS) analyzer

Particle size of the obtained emulsion was determined using a Nano S90 DLS analyzer (Malvern, UK) at 25°C, and the results were the mean value of three measurements.

UV/Vis spectrometer

Transmittance of film samples with a thickness of ～100 μm was determined by a SP-756P UV/Vis spectrometer (Spectrum, China) in the wavelength range of 380 to 780 nm at 25°C.

Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) curves were obtained on a DMA 242C (Netzsch, Germany) in the tensile resonant mode, at a heating rate of 5 K/min from -80 °C to 80 °C, and the loss factor (*tan δ*) was obtained at 1 Hz frequency.

Tensile tests

The stress-strain tests were conducted by a UTM 6203 electronic universal tester (SUNS, China) with a 2 KN load cell at a cross-head speed of 50 mm min^{-1} at room temperature. The tested samples were tailored into an oblong shape with a length of 30 mm, a width of 5 mm and a thickness of ～1.5 mm. Mechanical properties including ultimate tensile stress and elongation at break were obtained and the results were the mean values of five measurements. Toughness, which is defined as the area surrounded by the tensile stress-strain curve, was also calculated by using the software of Origin Pro 9.0 and its value were the mean values of five times.

Optical microscope

In order to investigate the morphology during the healing process, morphology of the crack surfaces were also

observed using a DC6000 optical microscope (Jiangnan, China).

Infrared thermographic camera

In order to investigate the surface temperature during the healing process, the temperature on the surface of healed film sample was detected using an E5 infrared thermographic camera (FLIR, USA).

Water contact angle

Water contact angle was tested on an Attension Theta (Biolin, Sweden) optical contact angle measuring device, and the results were the mean values of three measurements.

Water absorption

Film sample of approximately 1.0 g was immersed in water for 24 h at 25 °C, after the residual water was wiped from the films using filter paper, the weight was measured immediately. Water absorption of the film sample was calculated as follows:

$$Water\ asorption = \frac{m_1 - m_0}{m_0} \times 100\% \tag{2}$$

where m_0 and m_1 represent the mass of film sample before and after the water absorption test.

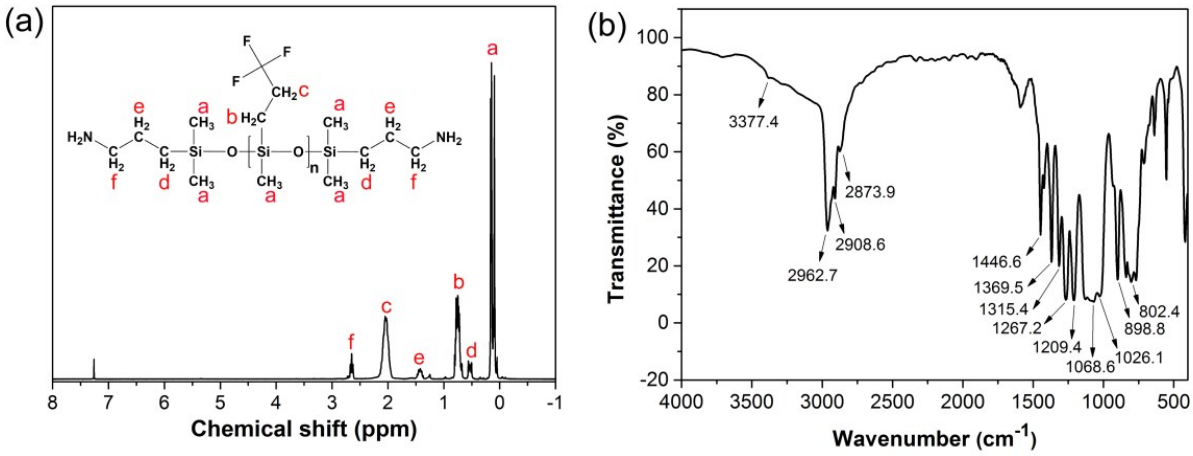


Fig. S1 (a) ^{1}H-NMR spectra and (b) FTIR spectra of AMFSi. ^{1}H-NMR (DSe-WPU-FSi-4, $CDCl_3$): δ (ppm) = 4.04 (-C***H***$_2$- of DMPA), 3.76 (-C***H***$_2$CH$_2$SeSe), 3.40 (-C***H***$_2$CH$_2$CH$_2$C*H*$_2$- of PTMG), 3.11 (-CH$_2$C***H***$_2$SeSe and -C***H***$_2$ of IPDI), 2.89 (-NH-C***H***$_2$- of IPDI), 2.02 (-SiCH$_2$C***H***$_2$CF$_3$), 1.60 (-C***H***$_2$- of IPDI and -CH$_2$C*H*$_2$C***H***$_2$CH$_2$- of PTMG), 1.25 (-C***H***$_2$- of IPDI), 1.05 (-C***H***$_2$ of IPDI), 0.92 (-C(C***H***$_3$)$_2$ of IPDI), 0.88 (-C(C***H***$_3$)$_2$ of IPDI and -C***H***$_3$ of DMPA), 0.54 (-SiC***H***$_2$CH$_2$CF$_3$), and 0.16 (-Si-C***H***$_3$).

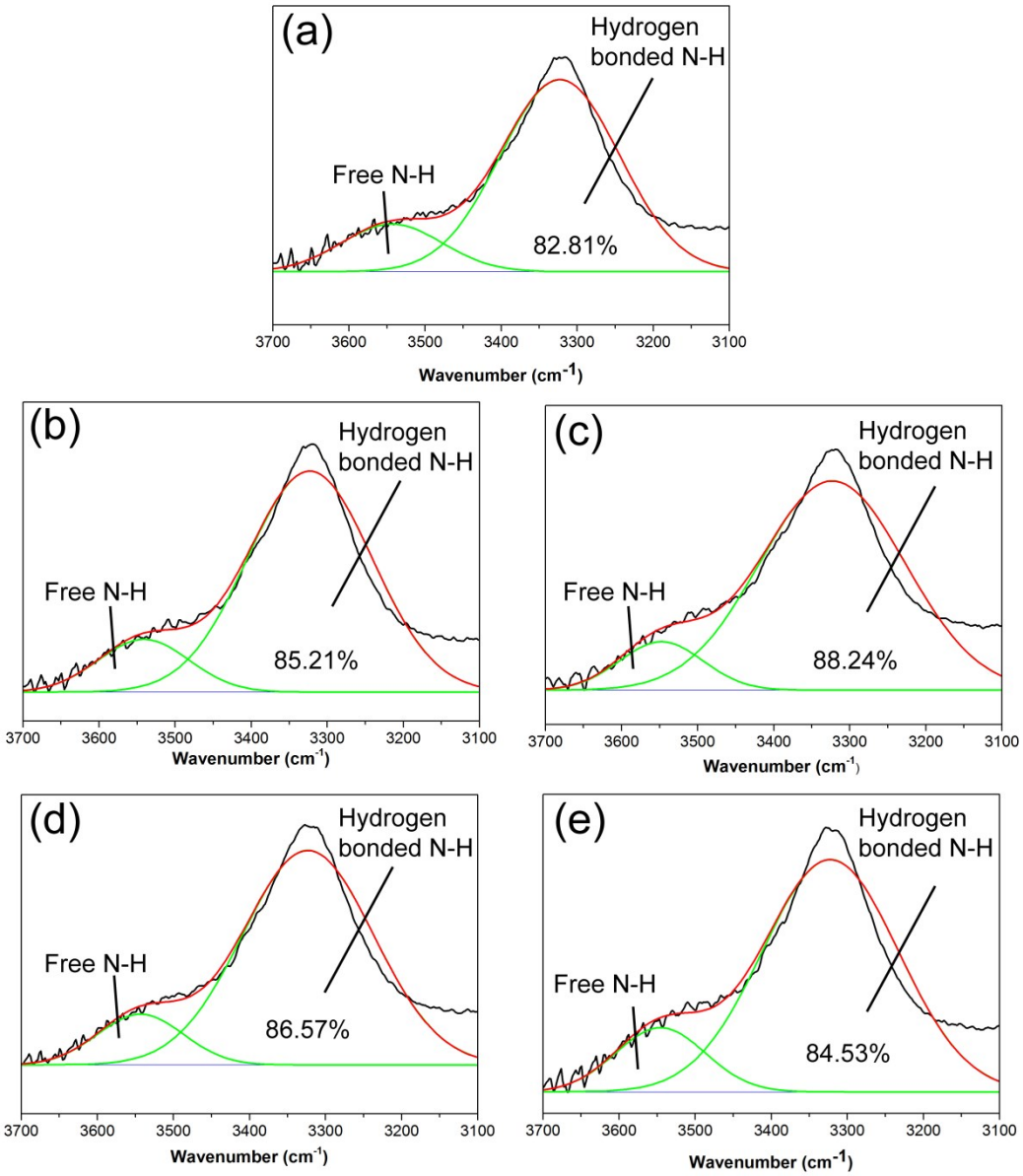
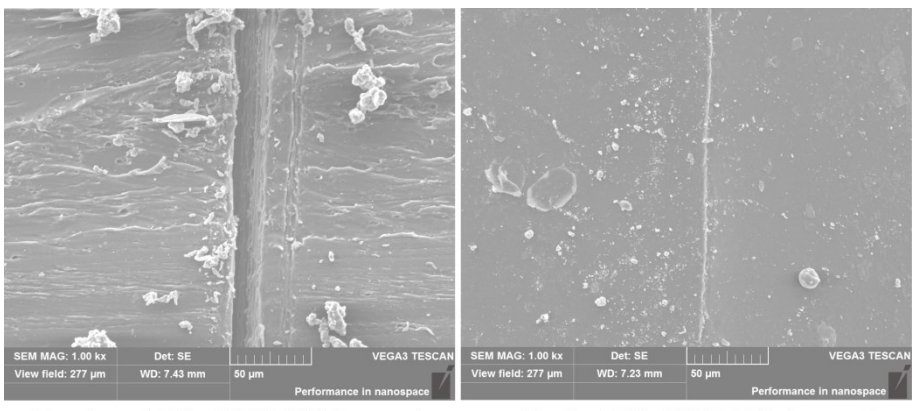


Fig. S2 Deconvolution of amino region for (a) DSe-WPU-FSi-0 film, (b) DSe-WPU-FSi-2 film, (c) DSe-WPU-FSi-4 film, (d) DSe-WPU-FSi-8 film, and (e) DSe-WPU-FSi-16 film by least-square curve-fitting.



Fractured DSe-WPU-FSi-4 sample **Healed DSe-WPU-FSi-4 sample**

Fig. S3 SEM photographs of the cross section of DSe-WPU-FSi-4 sample before and after healed.

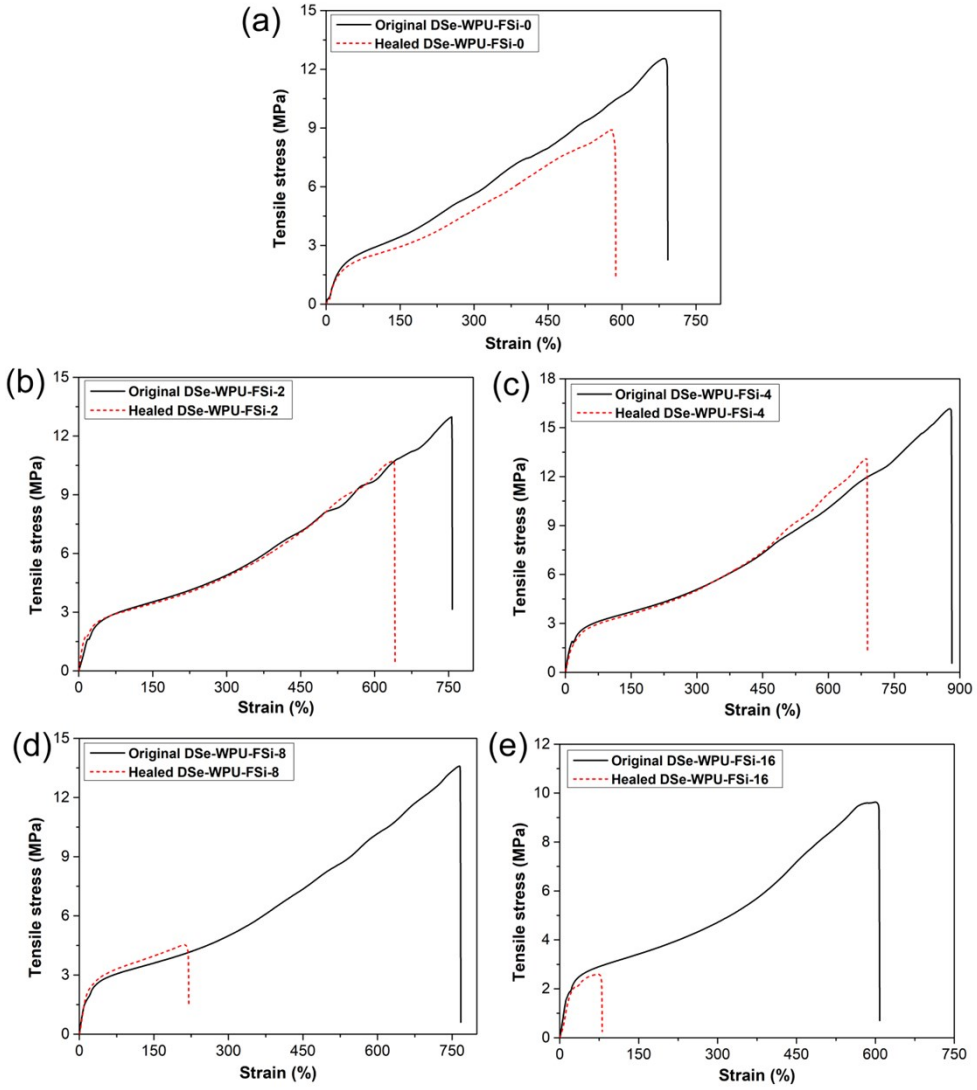


Fig. S4 Stress-train curves of the healed samples of (a) DSe-WPU-FSi-0 film, (b) DSe-WPU-FSi-2 film, (c) DSe-WPU-FSi-4 film, (d) DSe-WPU-FSi-8 film, and (e) DSe-WPU-FSi-16 film.

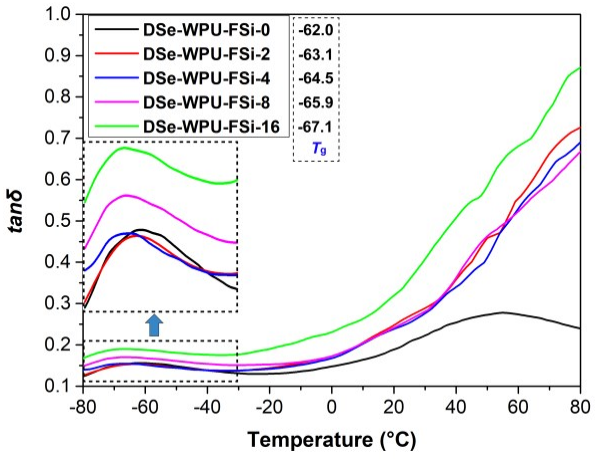


Fig. S5 *tanδ* curves of DSe-WPU-FSi films.

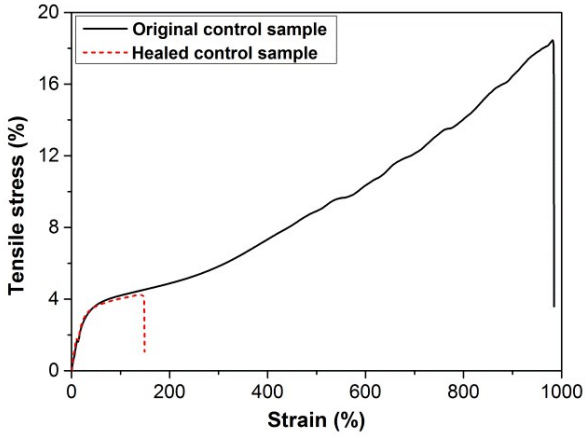


Fig. S6 Stress-train curves of the original and healed control film sample.

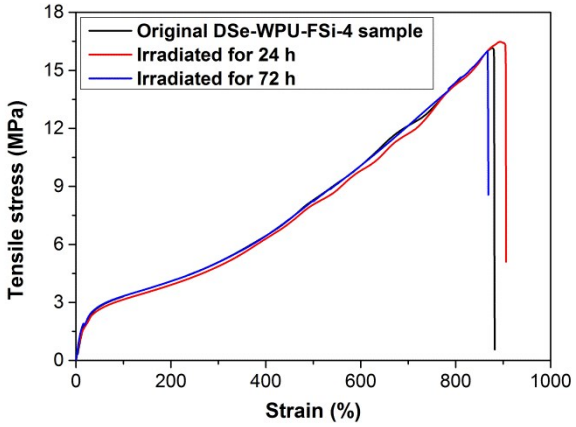


Fig. S7 Typical stress-strain curves of DSe-WPU-FSi-4 specimens irradiated under a table-lamp (intensity = ～10 000 Lux) for different times.

The synthesized DSe-WPU-FSi polymers contain element C, H, N, O, Se, F, and Si in the macromolecule chains. Due to the test principle of EDS involved, element H can't be detected in the test procedure. Therefore, in the calculation of theoretical weight value of element F and Si of DSe-WPU-FSi polymers, H element is excluded. The chemical structure of PTMG, IPDI, DMPA, DiSe-DiOH and AMFSi is $C_{108}H_{218}O_{28}$, $C_{12}H_{18}N_2O_2$, $C_5H_{10}O_4$, $C_4H_{10}Se_2O_2$ and $C_{54.9}H_{106.5}N_2O_{11.2}F_{33.6}Si_{11.2}$, respectively. N_1, N_2, N_3, N_4 and N_5 are the mole number of PTMG, IPDI, DMPA, DiSe-DiOH and AMFSi, and M_C, M_N, M_O, M_{Se}, M_F,and M_{Si} are the molar mass of element C, N, O and Se. A represents the theoretical mass of DSe-WPU-FSi polymers, and $A=N_1(108M_C+28M_O)+N_2(12M_C+2M_N+2M_O)+N_3(5M_C+4M_O)+N_4(4M_C+2M_{Se}+2M_O)+N_5(54.9M_C+2M_N+11.2M_O+33.6M_F+11.2M_{Si})$. TWV_{Si} and TWV_F are the theoretical mass ratio of element Si and Fi, respectively, and calculated using the formula as follow:

$$TWV_{Si}=\frac{11.2N_5M_{Si}}{A}\times 100\% \quad (3)$$

$$TWV_F = \frac{33.6 N_5 M_{Si}}{A} \times 100\% \quad (4)$$

Supporting References

1 T. Su, G. Y. Wang, X. D. Xu and C. P. Hu, *J. Polym. Sci. Polym. Chem.* 2006, **44**, 3365–3373.