Supporting Information

Dual regulation of flexible chain segments and dynamic covalent bonds for self-healable copolyimide

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1. Experimental section

1.1. Materials

4-aminophenyl disulfide (4PDA, >98%), 4,4'-(4,4'-isopropylidenediphenoxy) diphthalic anhydride (BPADA, >98%), 1,2-dichlorobenzene (DCB, >99%) and N, N-dimethylacetamide (DMAc, >99%) were supplied from Aladdin Shanghai company in China. Poly(dimethylsiloxane) etherimide (NH_2-PDMS-NH_2, Mn=1000) was obtained from Macklin

Shanghai company in China. The carbon fiber (CF) was obtained from Shanghai RELIEYSEX company, China.

1.2. Synthesis of Polyamide acid (PAA) solution

SHPI films were produced by using a two-step process. 1,2-dichlorobenzene and DMAc were prepared as co-solvent in a ratio. Dissolving 4PDA (0.093g) and PDMS (0.875g) in the co-solvent in sequence. The flexible dianhydride monomer BPADA (0.651g) was slowly added into the mixture in three stages after complete dissolution. Reacting at room temperature for 24 hours with stirring. Then the polyamide acid (PAA) of PI precursor was prepared.

1.3. Preparation of self-healing polyimide (SHPI) films

The PAA solution was poured into a dry and clean PTFE mold. The mold was placed in a vacuum drying oven for 5 minutes to remove the air bubbles. Puting it in a fume hood for 12 hours to allow the evaporation of the initial solvent and cure. Afterwards, the product was placed into the oven to raise the temperature for thermal imidization (60 ℃ for 12h, 100 ℃ for 2h, 150 ℃ for 2h, 200 ℃ for 2h). The prepared film was named SHPI-3:7. Four types of PI films were prepared by adjusting the ratio of two functional diamine monomers. Table S1 shows the specific monomer content and nomenclature of the four systems.

1.4. Preparation of carbon fiber reinforced composite (CFRC) film

Firstly, two pieces of carbon fiber were cut to the right size in the shape of a PTFE mold. A small amount of the PAA solution was spread flat on the bottom of the mold. One piece of carbon fiber material was then laid flat on the solution. The above steps were repeated to flatten the PAA solution again with the carbon fiber sheet. Finally, the remainder of the PAA solution is poured into the mold to completely cover the carbon fiber material. The mold was placed in a fume hood for 12h for initial processing and then placed in an oven for thermal

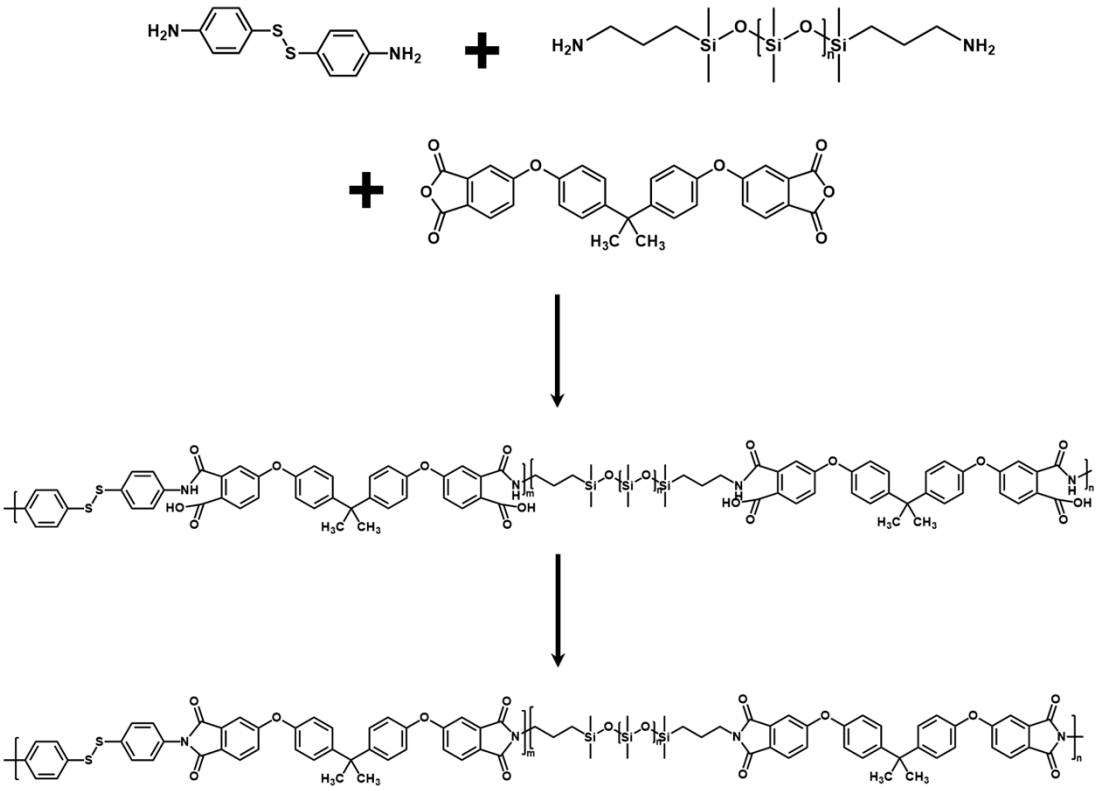
imidization as above. The composite film was hot pressed and compression molded to obtain the final carbon fiber reinforced composite (CFRC) film.

1.5. Characterization

The morphology and structure of SHPI-3:7 film before and after damage were analyzed using field emission scanning electron microscopy (FESEM-SU8010; Hitachi, Japan). At the same time, we observed the morphological structure of CFRCs as well as CF using the same instrument. The SHPI films were analyzed by Fourier transform infrared spectroscopy using an infrared spectrometer (Nicolet-6700; Thermo Scientific, USA). The instrument for characterizing the thermal stability of films is a thermogravimetric analyzer (TGA-55; TA, USA). The tensile properties of SHPI films were tested using MARK-10 from MARK Corporation in the United States. The test speed for tensile testing is 55mm·min^{-1}. X-ray diffraction (XRD) analysis using an X-ray diffractometer (Smartlab SE; Rigaku, Japan) at 2° from 10 ° to 80 ° θ scan at a speed of 5 °/min within the range. The glass transition temperature, storage modulus, and stress relaxation analysis of SHPIs were tested using a dynamic thermomechanical analysis (DMA) instrument (Q800; TA, USA). The breakdown resistance test of SHPI films was carried out using a withstand voltage testing device (RK2674-A; MEIRUIKE, China). The corona test was performed using a needle plate electrode corona resistance testing system (HYJH-4; HUIYUAN, China). Among them, the corona damage parameter of the needle tip electrode was determined to be 4.78 kV/0.179 mA/30 min. The distance between the tip of the needle and the film is determined to be 1 cm. The hot pressing operation of composite film was completed using a hot pressing machine (NLH-600D; LEINUOXINDA, China).

2. Synthesis of self-healing polyimide films

Scheme S1 shows the synthesis of SHPI films, which are prepared using a two-step copolymerisation method. The performance of the films can be precisely controlled by controlling the ratio of two types of diamine monomers. Table S1 shows the specific monomer dosages for the four systems, which SHPI-3:7 film has excellent self-healing performance and recyclability among them.



Scheme S1. Synthetic routes of SHPI films.

Table S1. Raw material ratio of SHPI with four different diamine ratios.

Polyimide	4PDA (g)	PDMS (g)	BPADA (g)
SHPI-3:7	0.0930	0.8750	0.6505
SHPI-4:6	0.1242	0.7500	0.6505
SHPI-5:5	0.1552	0.6250	0.6505
SHPI-7:3	0.2172	0.3750	0.6505

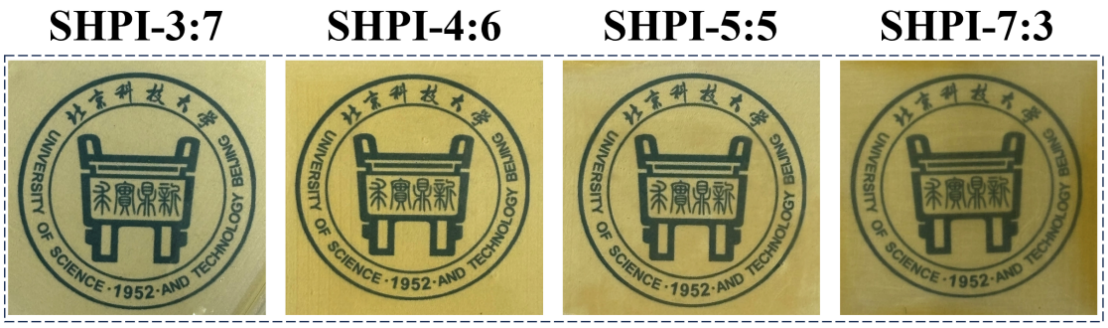


Fig. S1. Digital photographs of SHPI films.

3. XRD analysis of SHPI films

Essentially, XRD analysis is a way of revealing the distance between molecular chains. The Bragg equation ($2dsin\theta = n\cdot\lambda$) can be used to describe the relationship between the diffraction angle and the *d*-spacing, where *d* is the spacing between the molecular chains, λ is the wavelength and *n* is the reflection level (λ = 0.15406nm, *n*=1). The XRD curves and related data of each system are shown below.

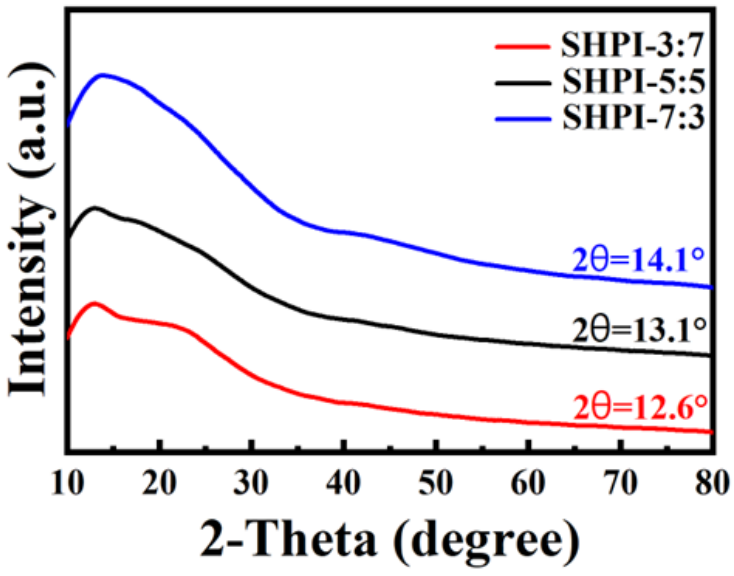


Fig. S2. XRD curve of SHPI films.

Table S2. Relevant data in XRD spectra of SHPI films.

Polyimide	θ (°)	sin (θ)	*d* (nm)
SHPI-3:7	6.33	0.11	0.700
SHPI-5:5	6.55	0.114	0.676
SHPI-7:3	7.05	0.123	0.626

4. Mechanical and thermal properties of SHPI films

Stress relaxation curves of films at three temperatures are obtained by DMA test. Three sets of data corresponding to temperature versus relaxation time are obtained when the film modulus decreased to 1/e of the original modulus corresponding to the relaxation time at the corresponding temperature of the material in the stress relaxation curves. The data was substituted into Arrhenius formula ($\ln k = \ln A - E_a/RT$) and obtained Fig. 3g by linear fitting. According to the equation: activation energy (E_a) = $R \cdot k$. where R is the gas constant with a value of 8.314 J/(mol·K) and k is the slope of the fitted line. The activation energy is obtained as 28.6 kJ/mol.

Polyimide	Elongation at break (%)	Tensile strength (MPa)	Young's Modulus (MPa)	T_g (°C)	$T_{d5\%}$ (°C)	$T_{d10\%}$ (°C)
SHPI-3:7	358.526	22.647	4.525	66	427	443
SHPI-4:6	219.33	23.74	5.098	89	-	-

SHPI-5:5	156.40	27.04	5.618	107.9	-	-
SHPI-7:3	9.579	39.821	158.701	161	-	-

Table S3. Mechanical and thermal properties of SHPI films.

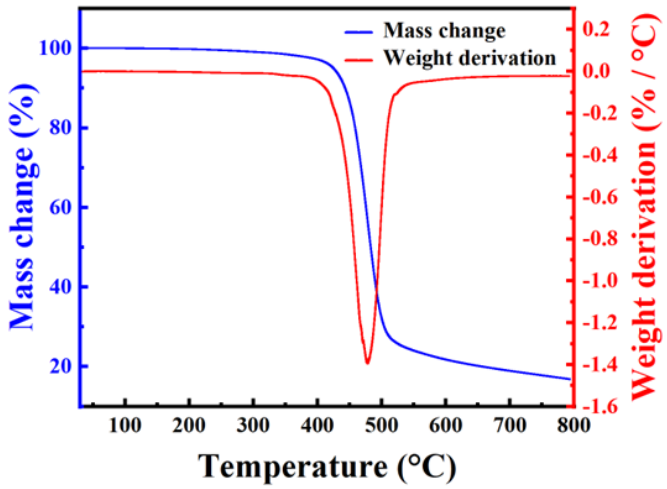


Fig. S3. TGA and DTG curves of SHPI-3:7 film.

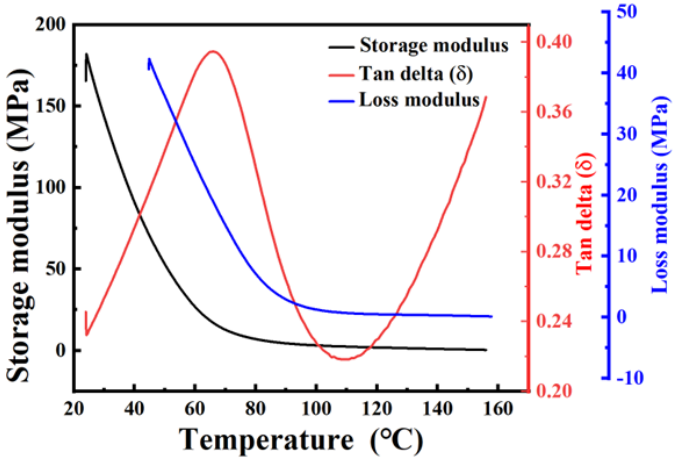


Fig. S4. Storage modulus, loss modulus, and tan δ curves of SHPI-3:7 film.

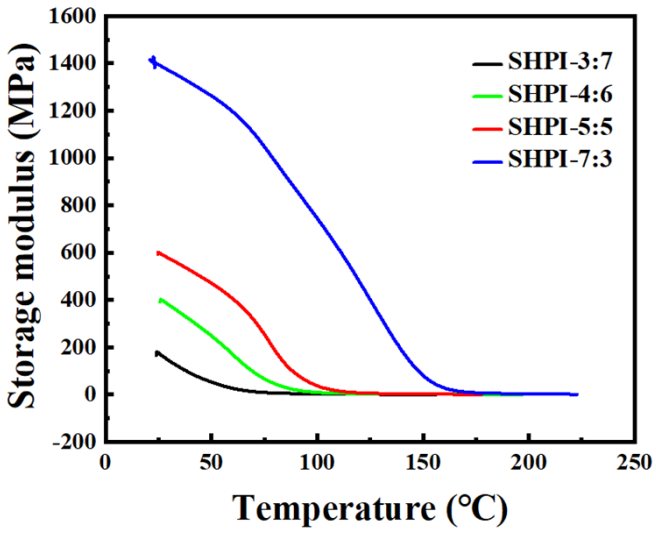


Fig. S5. Storage modulus versus temperature curves of SHPI films.

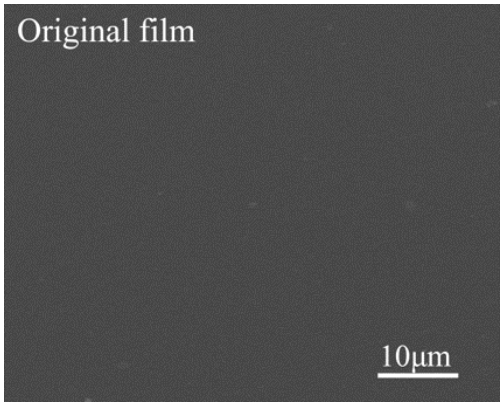


Fig. S6. SEM images of SHPI-3:7 film.

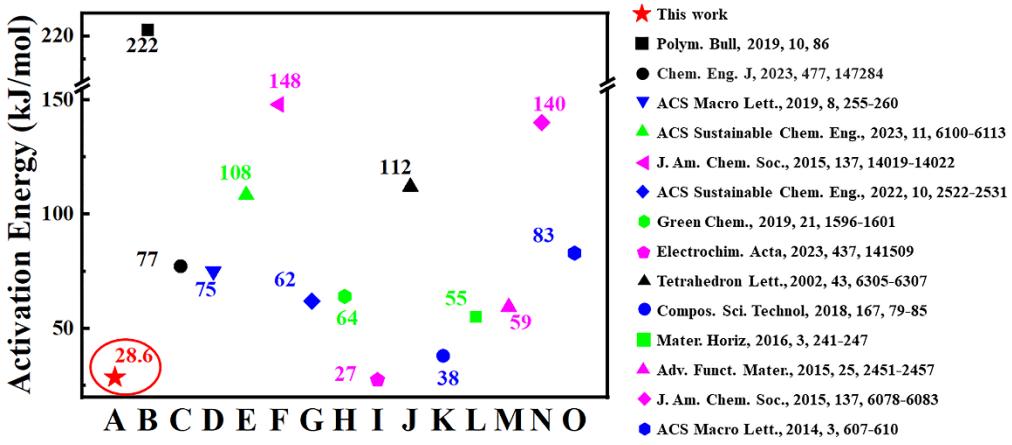


Fig. S7. Comparison of activation energies in the literature.

5. Solubility resistance of SHPI-3:7 film

PIs used in insulation inevitably come into contact with various liquids in the environment. Therefore, solubility is also an important criterion for testing the reliability of PIs. So the SHPI-3:7 is tested by setting up solubility experiments. As shown in Fig. S8, the SHPI-3:7 films are immersed in water, methanol, ethanol, acid and alkali. The films are soaked for more than one week. There is no significant deformation or dissolution of the films in the various liquids. This confirms the excellent solubility resistance of SHPI-3:7 film.

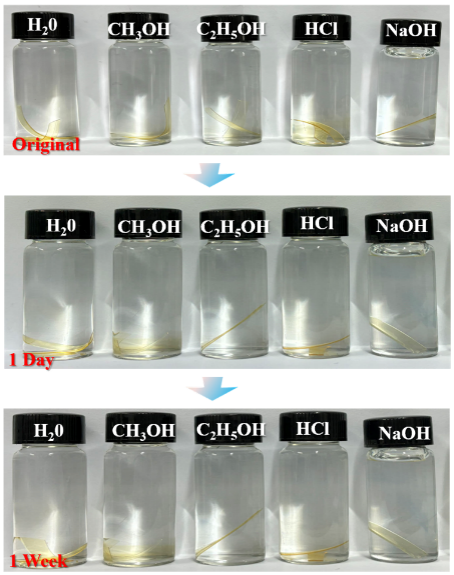


Fig. S8. Digital photographs of resistance tests of SHPI-3:7 film.

6. Shaping capability and recyclability of CFRCs

CFRCs have thermally driven shaping capability due to the excellent shaping ability of the PI matrix. As shown in Fig. S9, these are the “U”, “S”, “T” and “B” patterns obtained by heating the composite film strip to 120 °C. On the other hand, the recovery of CFRC films requires the selection of suitable solvents. The tetrahydrofuran can effectively dissolve the PI matrix, and thus separate CF from the matrix. The recovery process of CFRC films is shown in Fig. S10. The matrix gradually dissolves as the soaking time of CFRCs in tetrahydrofuran

increases. The PI matrix is completely dissolved in the solvent and the CF is completely separated until 5 hours later.

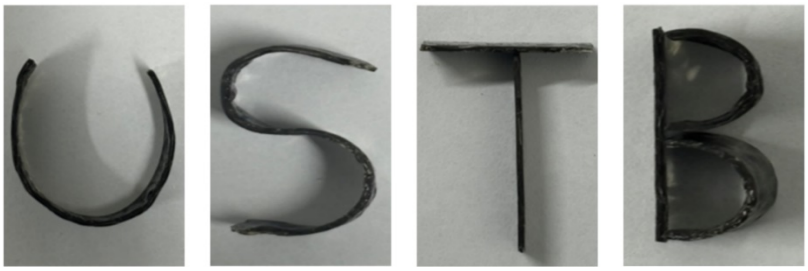


Fig. S9. Digital photographs of shape reprocessing demonstration of CFRCs.

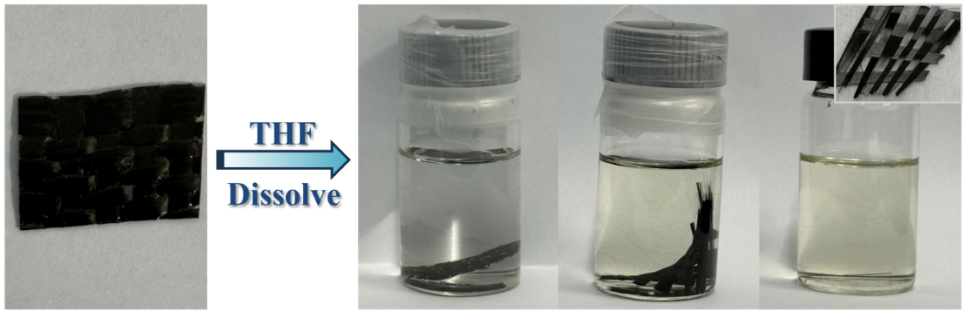


Fig. S10. Digital photographs of degradation process of CFRCs.