

## Supplementary Materials for

# **Reversible Fluorescent Adhesives Based on Covalent Adaptable Networks with Dynamic AIE Crosslink: In-situ Visualization of Adhesion Capability**

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## EXPERIMENTAL SECTION

**Materials:** 4-Aminobenzophenone (98%), zinc powder, titanium tetrachloride ( $\text{TiCl}_4$ ,  $\geq 98\%$ ), potassium carbonate (anhydrous,  $\geq 99\%$ ), sodium acetate (anhydrous,  $\geq 99\%$ ), acetic anhydride (99%), maleic anhydride ( $\geq 99\%$ ), neopentyl glycol diglycidyl ether (NGDE,  $\geq 53\%$ ), furfurylamine (FA,  $\geq 99\%$ ) were purchased from Aldrich and used as received. *N,N*-dimethylformamide (DMF, 99%) was distilled over calcium hydride ( $\text{CaH}_2$ ) before use. Tetrahydrofuran (THF) was refluxed over sodium/benzophenone and distilled under a nitrogen atmosphere just before use. TPE-2MI was synthesized according to our previous report.<sup>42</sup>

**Measurements:** Size exclusion chromatography (SEC) measurements were carried out with the VISCOTEK VE2001 equipped with Styragel HR2 THF and Styragel HR4 THF using THF (1 mL/min) as an eluent. The system was calibrated with linear polystyrene. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker AVANCE III-500 spectrometer and Fourier transform infrared (FT-IR) spectra with a NICOLET iS10 FT-IR instrument. Differential scanning calorimetry (DSC) measurements were performed using a Mettler Toledo DSC1/TC100 system under an inert atmosphere (nitrogen). The lap-shear strength measurements were performed using Instron 5960 dual-column testing systems at room temperature. The crosshead speed was 2 mm  $\text{min}^{-1}$  for all cases. Photoluminescence spectra were recorded on a Thermo Lumina Fluorescence Spectrometer equipped with an external water circulator for the thermostatted cell holder. The light source was a 30 mW He-Ne laser emitting vertically polarized light of 632.8 nm wavelength. To realize the in-situ fluorescence

measurement of the adhesive, the fluorescence spectrum is tested based on the gap between the two steel plates. A self-made mold was used to fix the steel plate on the sample table, in which the mold can ensure that the adhesive in the slit of the steel plate was exposed to the excitation spot. In particular, the position of the steel plate in the mold can be easily adjusted to make sure that the fluorescence intensity of the different positions of adhesives can be monitored (as shown in Figure S8). The result is the average of three tests. In addition, the heated adhesive sample needs to be cooled to room temperature before fluorescence testing, to avoid the influence of high temperature on fluorescence intensity. The density of the adhesive was measured by the Dahometer high-precision solid density tester DH300, which is used to calculate the cross-linking density. The fracture surface morphologies of FEP<sub>1.3</sub>-B<sub>98</sub>T<sub>2</sub> films were observed by scanning electron microscope on SU8010 (SEM, Japan Hitachi) at an acceleration of 2 KV.

**Synthesis of furan-modified epoxy resin FEP:** NGDE and FA were added to a three-necked flask with an epoxide-to-amine ratio of 1.5 : 1. The reaction was carried out under a nitrogen atmosphere at 70 °C for 16 h. The linear polymer FEP was obtained at the end of the reaction as a light yellow colored viscous liquid (Scheme S1). FEP was characterized by <sup>1</sup>H NMR, FT-IR, and SEC (Figure S1-3).

**Substrate cleaning for lap-shear test:** 304 stainless steel with dimensions of 100 mm × 25 mm × 1.6 mm was used as metal substrate and was prepared according to GB/T 7124-2008 standard protocol. The steels were polished with M40 abrasive paper.

**Lap-shear test:** The adhesive property was monitored by the most common lap-shear

test. FEP and MI-containing cross-linkers were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (40 wt% solutions), the resulting solution (60 μL) was then spread on two steel substrates, and most of the solvent (CH<sub>2</sub>Cl<sub>2</sub>) was removed at room temperature. The overlap area was fixed (312.5 mm<sup>2</sup>) for all cases. The substrates were overlapped in a single lap-shear configuration and the overlapped area of the specimen was clamped by a pair of metal clamps. Subsequently, the attached specimens were cured at 80 °C for a specified time. After curing, the samples were allowed to cool down at room temperature, and lap-shear test was performed after 1 hour. The reported values are the average of five measurements with standard error for each study. The lap shear strength was determined using the following equation.

$$\text{Lap shear strength (MPa)} = \text{Load (N)} / \text{Area (mm}^2\text{)} \text{ [Used area=312.5 mm}^2\text{]}.$$

**Rheological test:** Rheological properties were measured with an DHR-1 rheometer (TA Instruments) equipped with either a 25 mm parallel plate fixture. In the study of crosslinked states, adhesive samples are tested in the range of 30-85 °C with a heating rate of 0.2 °C/min. When the sample was heated to 30, 40, 45, 55, 70, and 85 °C, the samples were removed from the rheometer and cooled to room temperature for fluorescence testing. In the test of Figure S11, to exclude the influence of high temperature on the modulus, the samples were removed from the rheometer after being heated to 70, 80, 85, and 90 °C and then cooled to room temperature, for the subsequent rheological tests.

**Equilibrium swelling tests:** FEP and MI-containing cross-linkers were dissolved in a small amount of DCM. After the solvent was evaporated, the adhesive was heated to

80 °C for different times. Equilibrium swelling experiments were conducted by immersing the adhesive in toluene at room temperature for 24 h. After swelling, the solvent was quickly wiped off from the sample surface using filter paper; the samples were immediately weighed and then dried in a vacuum oven at 60 °C to constant weight. The volume fraction of the adhesive in the swollen gel,  $V_r$ , was calculated by the following equation:

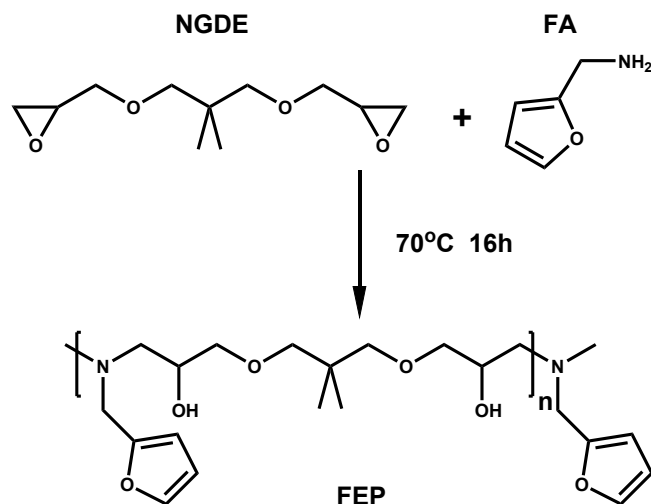
$$V_r = \frac{(m_2 - m_0\varphi)/\rho_a}{(m_2 - m_0\varphi)/\rho_a + (m_1 - m_2)/\rho_s}$$

where  $m_0$  is the sample mass before swelling,  $m_1$  and  $m_2$  are the weights of the swollen and deswollen sample, respectively;  $\varphi$  is the weight fraction of the insoluble components,  $\rho_a$  and  $\rho_s$  are the densities of the rubber and solvent, respectively.

The elastically active network chain density can be calculated by the well-known Flory-Rehner equation:

$$V_e = \frac{\ln(1 - V_r) + V_r + \chi V_r^2}{V_s(V_r^{1/3} - V_r/2)}$$

where  $\chi$  is the Flory-Huggins polymer-solvent interaction parameter, and  $V_s$  is the molar volume of the solvent.

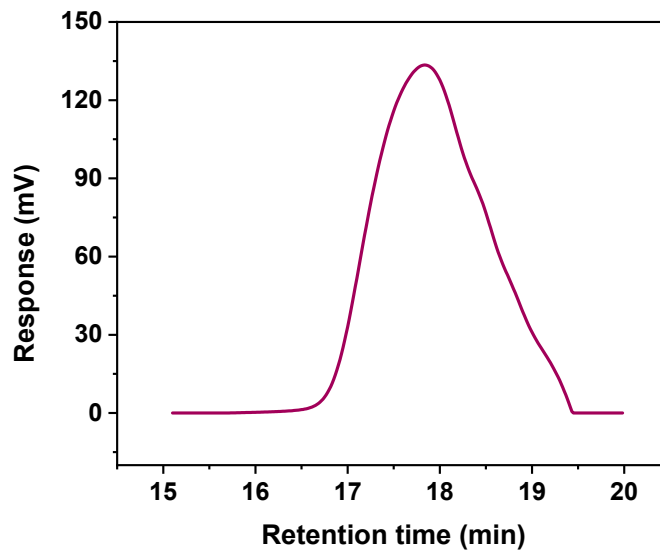


**Scheme S1.** Synthesis of FEP.

**Table S1.** SEC Characterization of FEP.<sup>a</sup>

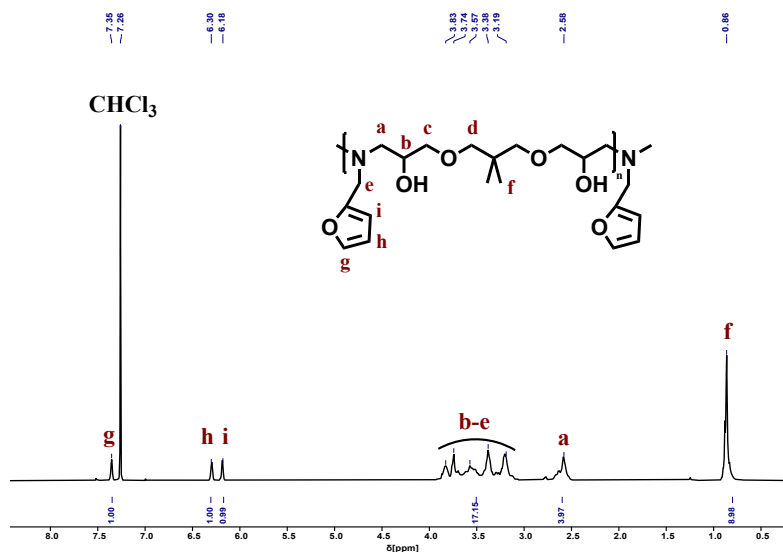
$M_n$	$M_w$	$M_z$	$\mathcal{D}$
774	1193	1687	1.54

<sup>a</sup>  $M_n$ ,  $M_w$ ,  $M_z$ , and PDI were determined by SEC (THF, 25 °C, PS standards).



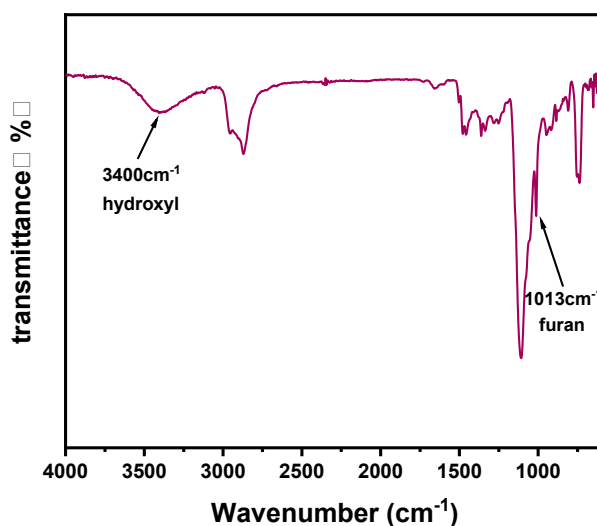
**Figure S1.** SEC trace of FEP.

The SEC data (Figure S1 and Table S1) revealed a monomodal molecular weight distribution with a polydispersity ( $\mathcal{D}$ ) of 1.54.



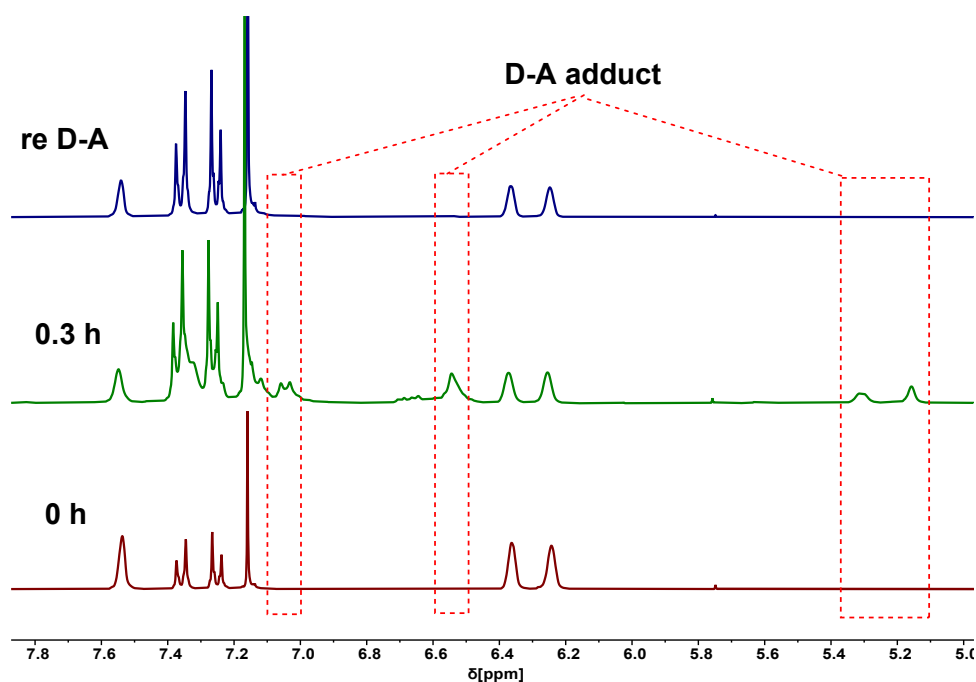
**Figure S2.**  $^1\text{H}$  NMR spectrum of FEP (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )

The chemical structure of FEP was further characterized by  $^1\text{H}$ -NMR (Figure S2). The final composition of the two monomers was calculated using the integration ratio of two peaks "f" and "g" resonating at  $\delta$  0.86 and 7.35 ppm, respectively. An average number of furan groups per polymer chain of 20 ( $n \cong 19$ ) was obtained.



**Figure S3.** FT-IR spectrum of FEP.

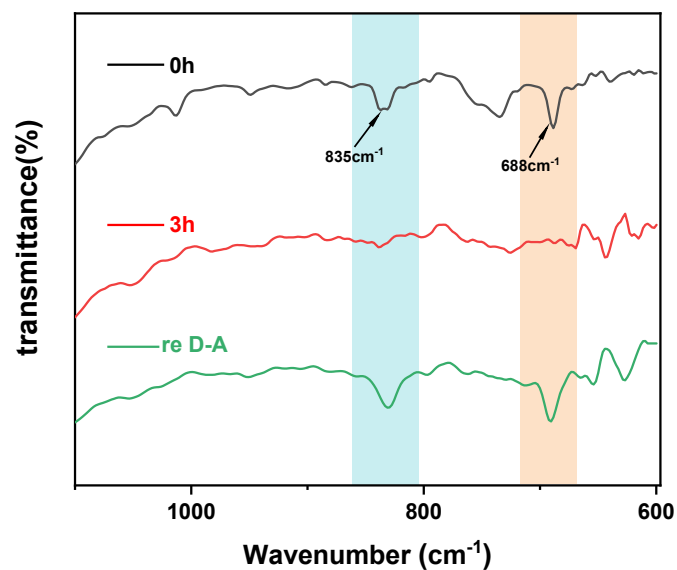
FT-IR spectroscopy also confirmed the chemical structure of the linear epoxy resin. Peaks appeared at 1013 and 3400  $\text{cm}^{-1}$ , indicating the existence of furan and hydroxyl moieties, respectively.



**Figure S4.**  $^1\text{H}$ -NMR spectra of the mixture of FEP and BMI (maleimide/furan ratio,  $n_{\text{mal/fur}} = 1$ ) in  $\text{DMSO-}d_6$  heated at  $80\text{ }^\circ\text{C}$  for 0 h, 0.3 h and at  $130\text{ }^\circ\text{C}$  for 10 min (400 MHz).

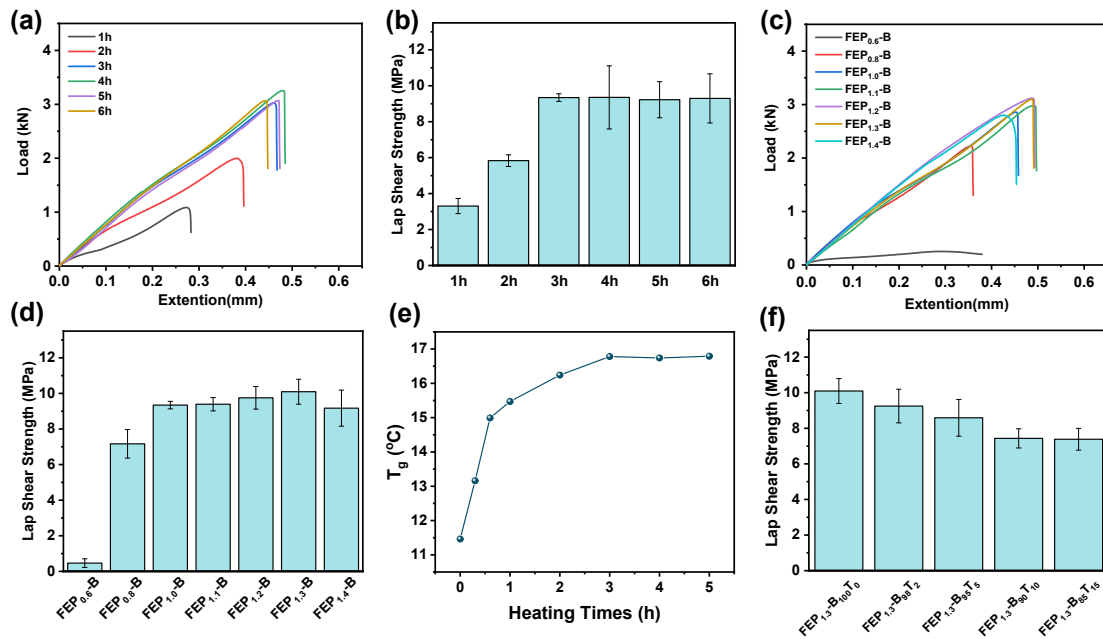
The thermally-induced crosslinking process between FEP and MI-containing cross-linker BMI was then monitored.  $^1\text{H}$  NMR spectroscopy was used to characterize the molecular level of the D-A reaction of furan and MI units. As shown in Figure S4, the mixture of FEP, BMI (maleimide/furan ratio,  $n_{\text{mal/fur}} = 1$ ) in  $\text{DMSO-}d_6$  exhibits peaks at  $\delta$  6.25, 6.37, 7.55 ppm, which belong to the furan and MI groups, respectively. The mixture was then heated at  $80\text{ }^\circ\text{C}$ . After 0.3 h, new signals gradually appeared around  $\delta$  5.16, 5.31, 6.51, 7.03 ppm, belonging to the DA adduct structure. The solution cannot be monitored after 2 h due to its high viscosity. Then, the retro-Diels-Alder (retro-DA) reaction between furan and MI units was also confirmed by  $^1\text{H}$  NMR. The signals of the DA adduct disappeared after the solution was heated at  $130\text{ }^\circ\text{C}$  for 10 min.





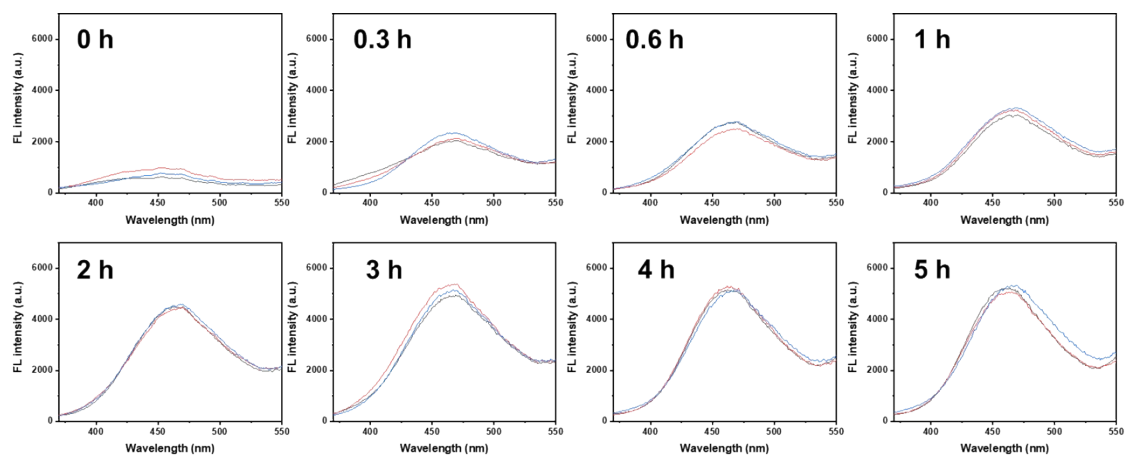
**Figure S5.** FT-IR spectra of the mixture of FEP and BMI ( $n_{\text{mal/fur}} = 1$ ) heated at 80 °C for 0 h, 3 h, and reversal of the mixture after 10 min heating at 130 °C.

Furthermore, in FT-IR measurements (Figure S5), the peak at 835  $\text{cm}^{-1}$  assigned to the C=C bond of MI was observed in the original mixture, and the peak of the C-H bond of MI was also found at 688  $\text{cm}^{-1}$ . However, all these peaks disappeared after 3 h of heating at 80 °C, which strongly supports the DA reaction. Furthermore, the peaks of MI units reappeared in FT-IR spectra when the reacted mixture was further heated at 130 °C for 10 min. The successful cross-linking and de-cross-linking processes have ensured the preparation of the reversible epoxy adhesive.

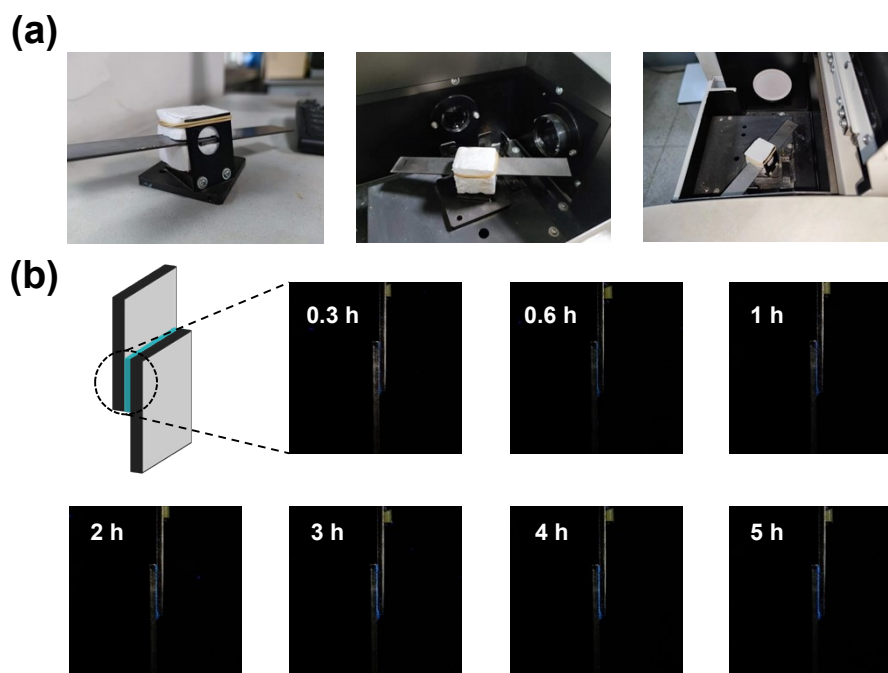


**Figure S6.** (a) Raw profiles (load vs. extension plot) of lap-shear tests, (b) lap-shear tests for FEP<sub>1</sub>-B heated at 80 °C for different times, (c) Raw profiles (load vs. extension plot) of lap-shear tests, and (d) lap-shear tests for FEP<sub>x</sub>-B. (e) Effect of heating time on  $T_g$  of FEP<sub>1.3</sub>-B<sub>98</sub>T<sub>2</sub>. (f) Lap-shear test results of FEP<sub>1.3</sub>-B<sub>m</sub>T<sub>n</sub>.

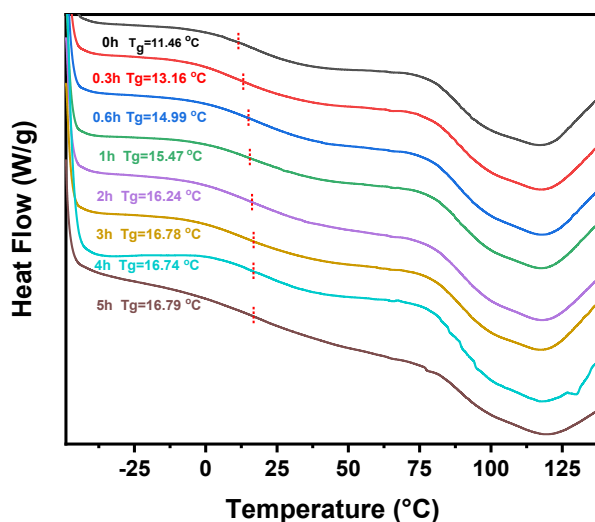
The bonding strength of this reversible epoxy adhesive was then measured by the lap-shear test with stainless steel substrates (Figure S6). First, FEP was mixed with BMI to give the FEP<sub>x</sub>-B adhesives (x denotes the  $n_{\text{mal}/\text{fur}}$  value), and their lap shear strengths were evaluated (Figure S6 a-b). It was found that the lap shear strength of FEP<sub>1</sub>-B gradually increased with the time the substrates were heated at 80 °C, and it reached a plateau of 9.2 MPa at 3 h and did not increase further after that. The  $n_{\text{mal}/\text{fur}}$  was then adjusted to find the best adhesive composition. As shown in Figure S6 c-d, the lap shear strength of FEP<sub>0.6</sub>-B was very low when a low ratio of  $n_{\text{mal}/\text{fur}} = 0.6$  was applied, due to the insufficient cross-linking density. The strength of FEP<sub>x</sub>-B gradually increased with  $n_{\text{mal}/\text{fur}}$ , and the maximum lap shear strength was observed for  $n_{\text{mal}/\text{fur}} = 1.3$ . Thus, the ratio of  $n_{\text{mal}/\text{fur}} = 1.3$  was chosen for further study. Among them, the heating temperature of all samples in Figure S6 is 80 °C, and the  $n_{\text{mal}/\text{fur}}$  of samples in Figure S6 c-d is 0.6, 0.8, 1.0, 1.1, 1.2, 1.3 and 1.4 respectively.



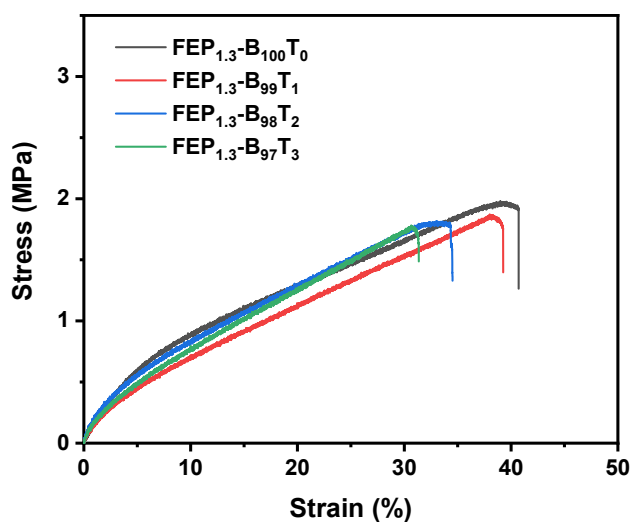
**Figure S7.** Fluorescence spectra of FEP<sub>1,3</sub>-B<sub>98</sub>T<sub>2</sub> heated at different heating times.



**Figure S8.** (a) Test method for FL intensity of adhesives. (b) The photograph of FEP<sub>1,3</sub>-B<sub>98</sub>T<sub>2</sub> heated at different heating times.



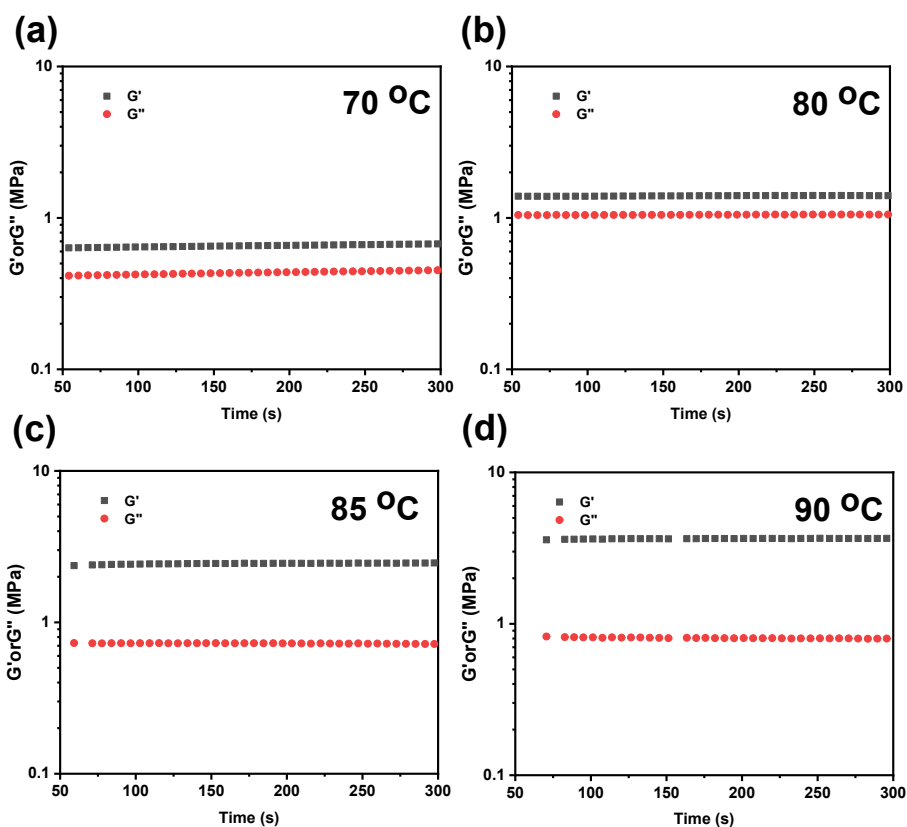
**Figure S9.** DSC thermograms of  $\text{FEP}_{1.3}\text{-B}_{98}\text{T}_2$  heated at different heating times.



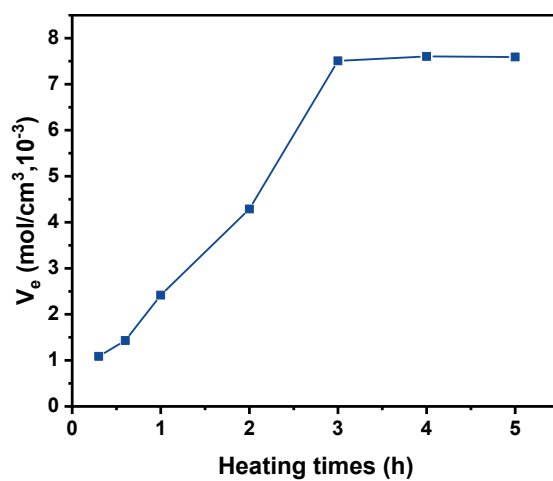
**Figure S10.** The stress-strain curve of  $\text{FEP}_{1.3}\text{-B}_m\text{T}_n$  samples.

**Table S2.** The tensile stress and breaking strain of  $\text{FEP}_{1.3}\text{-B}_m\text{T}_n$  samples.

Samples	$\text{FEP}_{1.3}\text{-B}_{100}\text{T}_0$	$\text{FEP}_{1.3}\text{-B}_{99}\text{T}_1$	$\text{FEP}_{1.3}\text{-B}_{98}\text{T}_2$	$\text{FEP}_{1.3}\text{-B}_{97}\text{T}_3$
Stress (MPa)	$39.90 \pm 1.05$	$36.59 \pm 2.79$	$31.70 \pm 1.89$	$29.84 \pm 1.17$
Strain (%)	$2.21 \pm 0.23$	$1.85 \pm 0.16$	$1.85 \pm 0.04$	$1.72 \pm 0.09$



**Figure S11.** The  $G'$  and  $G''$  of FEP<sub>1.3</sub>-B<sub>98</sub>T<sub>2</sub> after being heated to different temperatures.



**Figure S12.** Variation of cross-link density of FEP<sub>1.3</sub>-B<sub>98</sub>T<sub>2</sub> during the heated process at 80 °C.

**Table S3.** The physical properties of FEP<sub>1.3</sub>-B<sub>98</sub>T<sub>2</sub> heated at 80 °C for different times.

<b>Heating Time (h)</b>	<b>0.3</b>	<b>0.6</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
$V_e$ (mol/cm <sup>3</sup> , 10 <sup>-3</sup> )	1.09	1.43	2.42	4.29	7.51	7.60	7.59
$T_g$ (°C)	13.16	14.99	15.47	16.24	16.78	16.74	16.79
<b>FL Intensity</b> (a.u., 10 <sup>3</sup> )	2.05 ±0.18	2.79 ±0.15	3.39 ±0.15	4.51 ±0.07	5.01 ±0.22	5.17 ±0.07	5.11 ±0.18
<b>Lap Shear Strength</b> (MPa)	2.30 ±0.36	4.06 ±0.48	6.14 ±0.71	9.02 ±0.85	11.10 ±0.10	10.88 ±0.70	11.10 ±0.05

**The derivation of equation (4) and equation (5).**

$$W(V_e) = A_1[1 - e^{-k_1(V_e - d_1)}] \quad (1) \text{ (As shown in Figure 2a)}$$

$$I(V_e) = A_2[1 - e^{-k_2(V_e - d_2)}] \quad (2) \text{ (As shown in Figure 2b)}$$

The relationship between  $W(V_e)$  and  $I(V_e)$  could be derivated from the above two equations, as shown in equation (4):

$$W(V_e) = A_1 - A_1 e^{k_1(d_1 - d_2)} \cdot \left(1 - \frac{I(V_e)}{A_2}\right)^{\frac{k_1}{k_2}} \quad (4)$$

When  $k_1 = k_2$ , equation (4) could be transferred to their linear expression, as shown in equation (5):

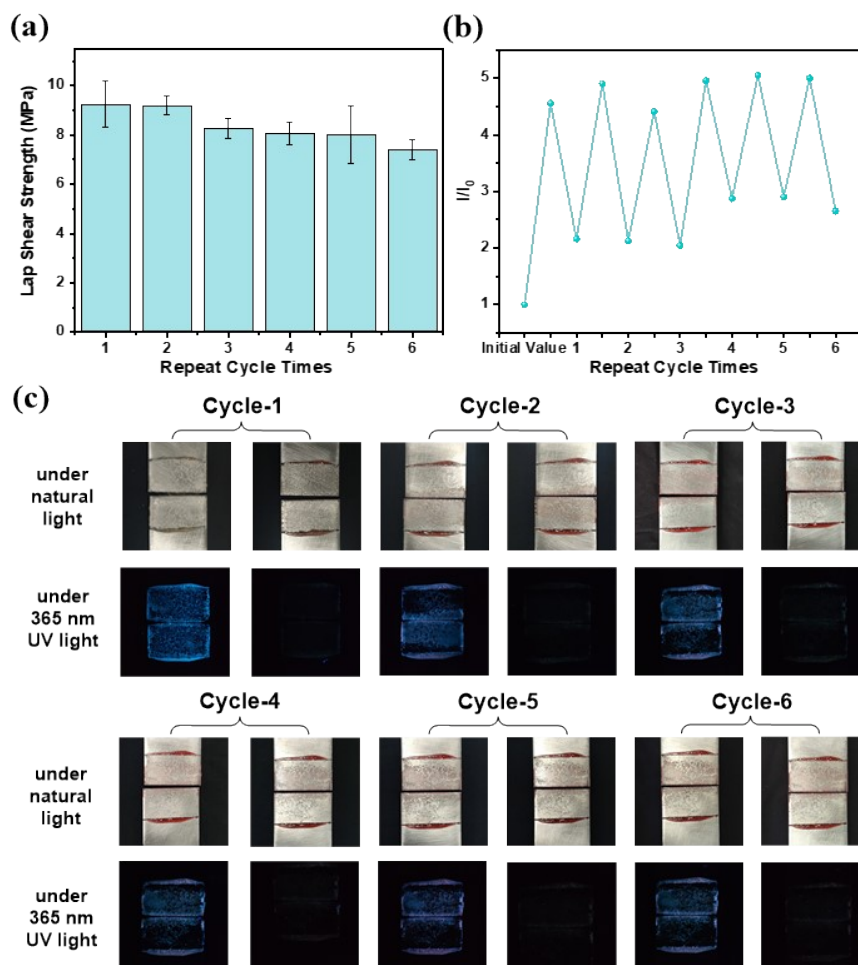
$$W(V_e) = \frac{A_1}{A_2} e^{k_1(d_1 - d_2)} \cdot I(V_e) + A_1 - A_1 e^{k_1(d_1 - d_2)} \quad (5)$$

Bring the fitting parameters in equations (1) and (2), that is:  $A_1 = 6.52$ ,  $k_1 = 0.38$ ,  $d_1 = 0.82$ ,  $A_2 = 4.68$ ,  $d_2 = 0.29$ , the slope and intercept in equation (5) can be calculated:

$$\text{Slope: } \frac{A_1}{A_2} e^{k_1(d_1 - d_2)} = 1.71$$

$$\text{Intercept: } A_1 - A_1 e^{k_1(d_1 - d_2)} = -1.49$$

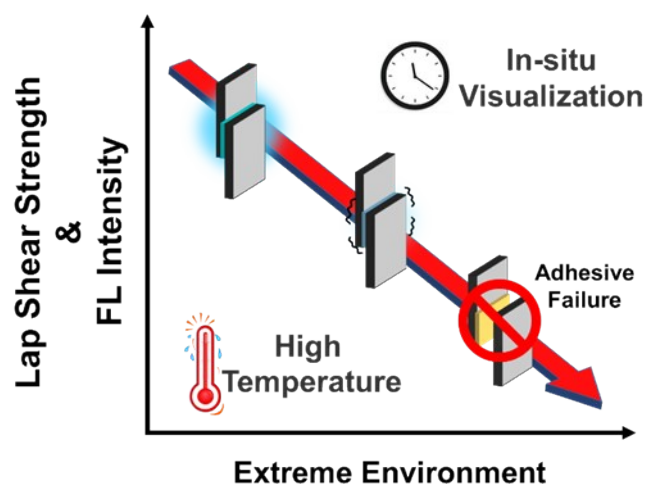
Thus, the calculated slope and intercept in equation (5) were close to the fitting equation (3).



**Figure S13.** (a) Lap shear strength of FEP<sub>1.3</sub>-B<sub>98</sub>T<sub>2</sub> in cyclic test. (b) FL intensity of cross-linking network for several cycles. (c) photos of adhesive fracture surface in lap shear test of reattached specimens. In each cycle, left column: attached specimens after lap shear test; right column: attached specimens after heating at 130 °C for 10 min.

Once the lap shear test was completed, the adhesive was bonded again and fixed with clamps. Subsequently, the sample was heated at 130 °C for 10 min, the retro-DA reaction was dominant and the cross-linking network was de-cross-linked. Then, the sample was heated at 80 °C for 3h to complete the DA reaction again. This process was repeated several times and the reversible DA process was further proved by the SEM results (Fig. S14(e)–(h), ESI†). The lap shear test of the reattached specimens proved the reusability of FEP1.3-B98T2. It is worth noting that the adhesive turns red after heating at 130 °C, which is caused by the high temperature that leads to the oxidation of the epoxy resin.



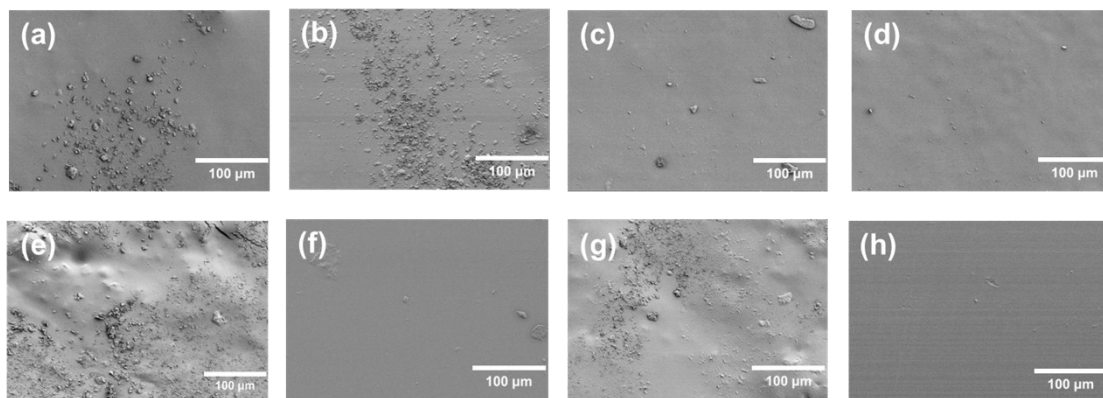


**Scheme S2.** Diagram of the adhesive failure under high temperature.

To explore the failure process of the adhesive at extreme environments (e.g. high temperatures), the cured adhesive samples were heated at 130 °C for 3 min, 4 min, and 5 min, respectively. Then, the samples were cooled to room temperature, and their FL intensity and bonding strength were measured.

**Table S4.**  $W(V_e)$  and  $I(V_e)$  of FEP<sub>1.3</sub>-B<sub>98</sub>T<sub>2</sub> after heating at 130 °C for different times.

Heating Times	3 min	4 min	5 min
$W(V_e)$	$5.22 \pm 0.22$	$2.76 \pm 0.40$	$1.38 \pm 0.12$
$I(V_e)$	$3.82 \pm 0.29$	$2.59 \pm 0.37$	$1.60 \pm 0.30$



**Figure S14.** SEM micrographs of FEP<sub>1.3</sub>-B<sub>98</sub>T<sub>2</sub> films during the curing process with heated at 80 °C for (a) 0.3 h, (b) 0.6 h, (c) 1h and (d) 3h. SEM micrographs of the cured FEP<sub>1.3</sub>-B<sub>98</sub>T<sub>2</sub> films after heating at (e) 120 °C for 10 mins, (f) 80 °C for 3 h, (g) 120 °C for 10 mins, (h) 80 °C for 3 h.

The morphology of FEP<sub>1.3</sub>-B<sub>98</sub>T<sub>2</sub> adhesive during the curing process and the reversible cycles was explored by SEM. As shown in Figure S14a-b, a large number of granular bulges were observed in the initial mixture of FEP, BMI, and TMI, indicating the phase separation structure and un-cross-linked structure. With the extension of heating time, the granular bulges gradually disappeared in 3 h, indicating the occurrence of cross-linking. Figures S14e-h show the morphology of FEP<sub>1.3</sub>-B<sub>98</sub>T<sub>2</sub> during the reversible DA/*retro*-DA cycles. It was observed that the granular bulges appeared once the FEP<sub>1.3</sub>-B<sub>98</sub>T<sub>2</sub> was heated at 120 °C for 10 mins, due to the de-cross-linking process.