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Supporting Information

Self-healing of internal damage in mechanically robust polymers utilizing a reversibly convertible molecular network

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Note S1 The reaction of 3-furoic acid with maleic anhydride is a typical Diels-alder reversible reaction. In order to separate the products easily, it is better to choose the solvent to make the reactants soluble and the products insoluble, so that the products can be precipitated and filtered. Different solvents for the above reaction were studied and finally acetone were chosen as the best solvent for the reaction. In solution, the equilibrium constant of the reversible reaction is shown as follows. In order to improve the yield of the dynamic cross-linker, we need to increase the concentration of reactants. In acetone, the solubility of maleic anhydride is much higher than that of 3-furoic acid. Therefore, excess maleic anhydride helps to increase the concentration of reactants, thereby increasing the yield of the product. The final ratio of maleic anhydride to 3-furoic acid is 2:1, and the yield of the product is about 38%.

$$K_c = \frac{c(3 - furoic\ acid) * c(maleic\ anhydride)}{c(dynamic\ cross - linker)}$$

Note S2 According to the preparation process in Method, DGEBA (average molar mass is 374) and the dynamic crosslinker (molar mass is 210) were mixed in the ratio of 2:1(in mass). Thus, the molar ratio of the above two is about 1.1:1. In theory, each epoxy monomer molecular has four points connected with the dynamic crosslinker, and each dynamic crosslinker molecular has three points connected with the epoxy monomer. Therefore, the epoxy monomer is excessive relative to the crosslinker. The crosslinking points in the self-healing epoxy can be directly calculated through the dynamic crosslinker. Because each dynamic crosslinker molecular have two permanent covalent bonds and one reversible bond, so the ratio of DA bond to covalent bond is 1:2 theoretically. Since the small amount of accelerator (EMI) added during the curing process can also promote the cross-linking of epoxy groups, the actual content of DA bonds may be slightly less than 1/3.

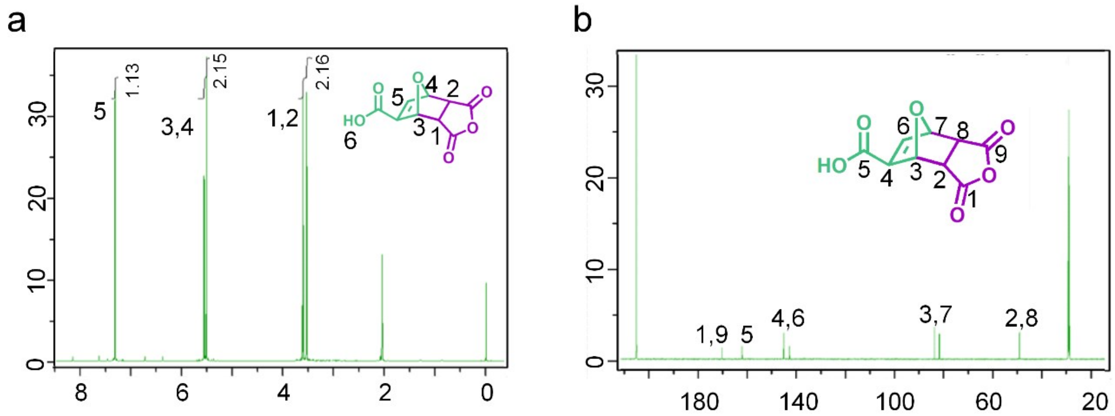

Figure S1. ^{1}H and ^{13}C NMR spectroscopy exhibits results that are consistent with the theoretical product. The ^{1}H spectroscopy (**a**) shows three major peaks at 3.57, 5.58 and 7.35 ppm which respectively represent the hydrogen atoms No.1-5 of the product. The peak of hydrogen atom on the carboxyl (No.6) is not exhibited on the spectrum since it is very active and exchanges with the hydrogen in the solvent. The ^{13}C spectroscopy (**b**) also exhibits results that are consistent with the theoretical product, suggesting the dynamic cross-linker was indeed synthesized and purified well.

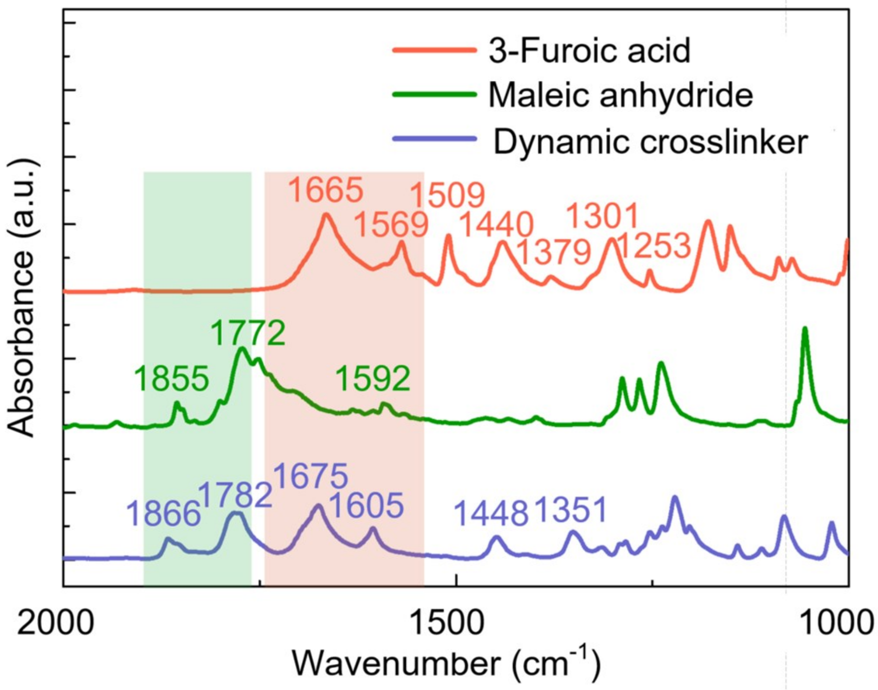

Figure S2. FTIR spectroscopy of the 3-Furoic acid, maleic anhydride and their reaction product, which is called the dynamic cross-linker. As for 3-furoic acid, the conjugated structure of the dienes and carboxyl groups results in its absorption peaks moving towards the lower wavenumber at 1569 cm^{-1}, 1509 cm^{-1}, 1440 cm^{-1}(furan group) and 1665 cm^{-1} (C=O). For maleic anhydride, the carbonyl group of anhydride exhibits absorption at 1855 cm^{-1} and 1772 cm^{-1}. The absorption at 1592 cm^{-1} is attributed to the conjugated double bond. After the Diels-Alder reaction, the diene on 3-furoic acid has reacted with the double bond on maleic anhydride, so the corresponding absorption peak disappears. At the same time, due to the weakening of the conjugation effect, the absorption peaks of the remaining double bonds and carboxyl groups move to 1605 cm^{-1} (C=C) and 1675 cm^{-1} (C=O). The absorption peaks of carbonyl group of anhydride are remained at 1866 cm^{-1} and 1722 cm^{-1}. Above results confirm that the product is indeed synthesized by the Diels-Alder reaction mechanism.

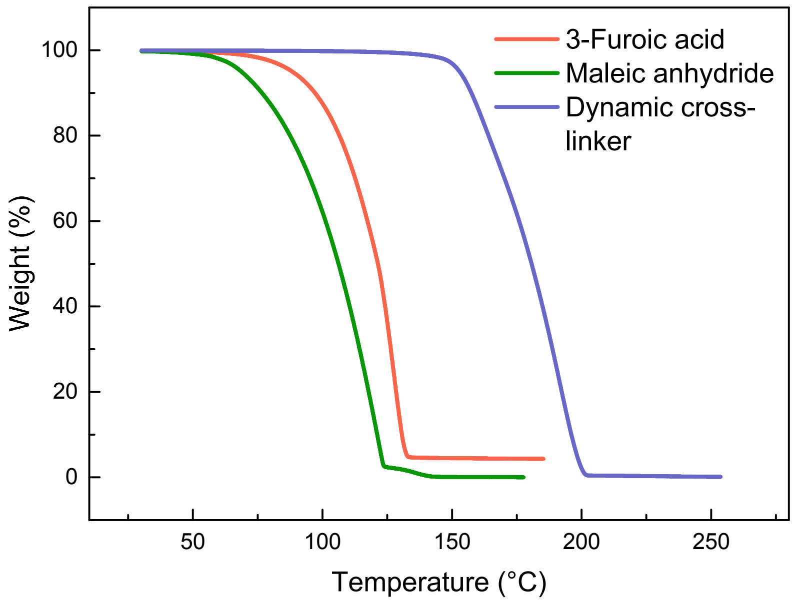

Figure S3 Thermogravimetric analysis curves of the 3-Furoic acid, maleic anhydride and the dynamic cross-linker. The decomposition temperature of the dynamic cross-linker is much higher than that of its two reactants, which proves that the reactants have been successfully synthesized and purified. The high thermal stability ensures that the dynamic cross-linker will not decompose when curing the epoxy monomer.

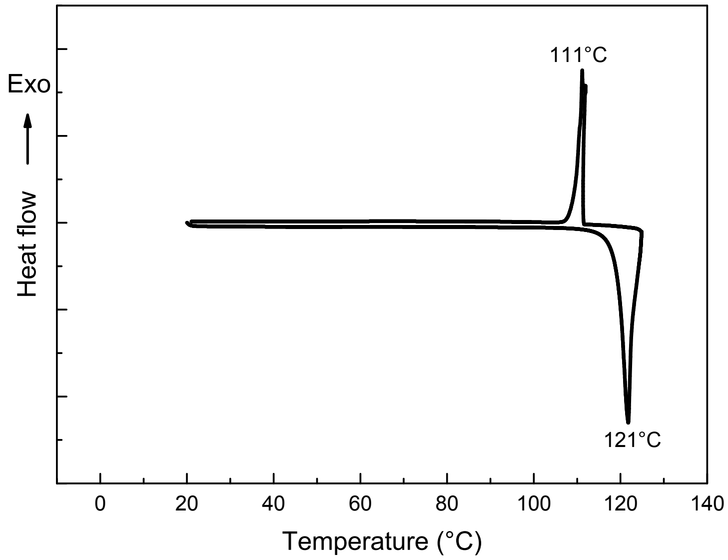

Figure S4 DSC analysis of the 3-furoic acid, which confirms that its melting point and freezing point are respectively at 121 °C and 111 °C. The rate of temperature rising is 10 °C / min

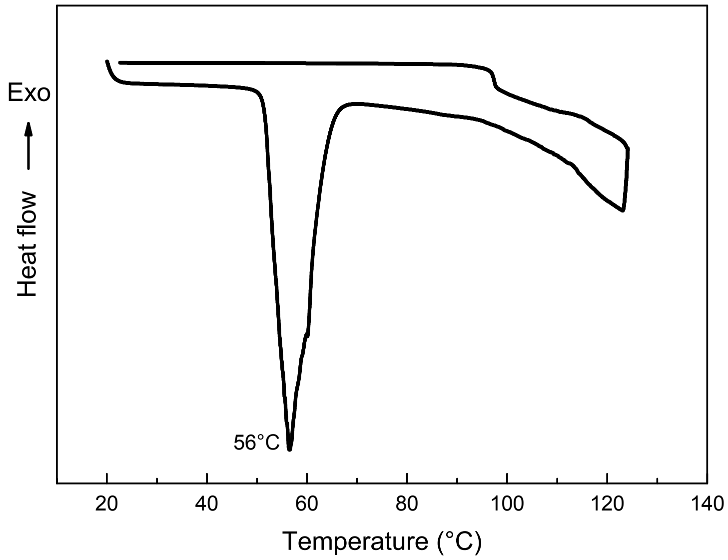

Figure S5 DSC analysis of the maleic anhydride, which confirms that its melting point is at 56 °C The rate of temperature rising is 10 °C / min

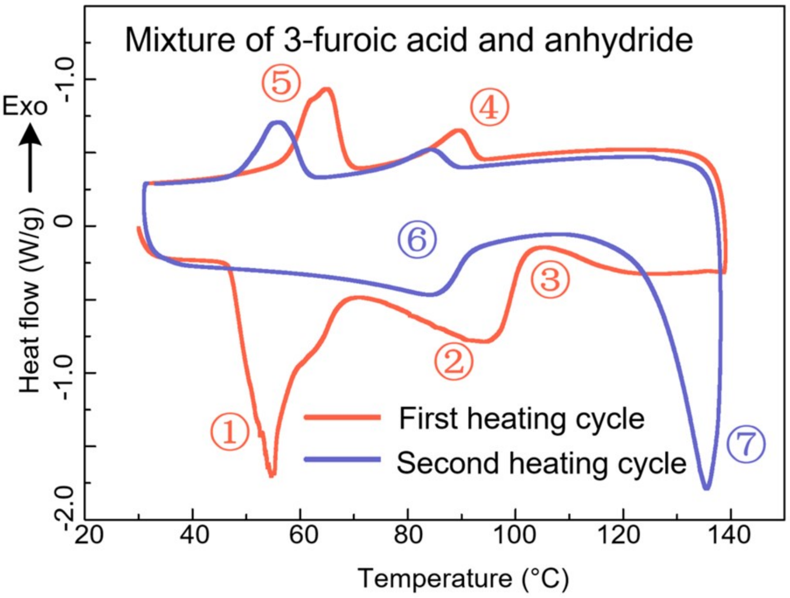

Figure S6 DSC analysis of the mixture of maleic anhydride and 3-furoic acid was implemented to support our explanation of the characteristic peaks in **Figure 1b**. In the first heating cycle, when the temperature increased gradually, maleic anhydride melted first, corresponding to the endothermic peak at ①. After that, 3-furoic acid gradually dissolved in the liquid maleic anhydride ②, and Diels-Alder reaction occurred partially, corresponding to the exothermic peak at ③. When temperature rose to 140 °C, no obvious endothermic peak appeared, indicating that the formation of dynamic cross-linker is very little. During the cooling process, there are two exothermic peaks, one represents the Diels-Alder reaction ④, the other represents the whole solidification process of the mixture ⑤. The melting point of single 3-furoic acid is above 120 °C, and there is no similar peak here, which indicates that 3-furoic acid dissolves in maleic anhydride and forms a single solidification temperature ⑤, which is consistent with the result of the second heating cycle. In the second heating cycle, only a wide endothermic peak appeared at ⑥, confirming that maleic anhydride and 3-furoic acid in the mixture would melt together. Diels-Alder reaction occurred again after the mixture melted ③. Different from the first heating cycle, a intensive endothermic peak appeared above 130 °C, which represented the retro Diels-Alder reaction of the formed dynamic cross-linker. The above results strongly support our analysis of DSC curve in **Figure 1b.**

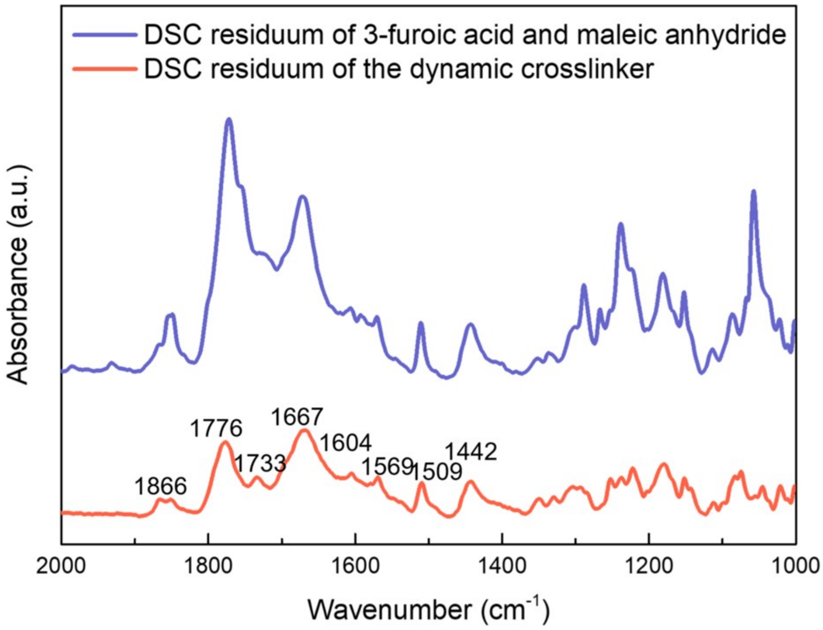

Figure S7 the FTIR spectra of DSC residuum of the mixture of 3-furoic acid and maleic anhydride and residuum of the dynamic cross-linker. Compared with the FTIR spectrum of the dynamic cross-linker in **Fig.S2**, the FTIR spectra of the residuum after DSC test have new peaks representing the maleic anhydride (1733 cm^{-1}) and 3-furoic acid (1569 cm^{-1}, 1509 cm^{-1} and 1442 cm^{-1}), which confirms the decomposition of the dynamic cross-linker and the formation of maleic anhydride and 3-furoic acid after heating.

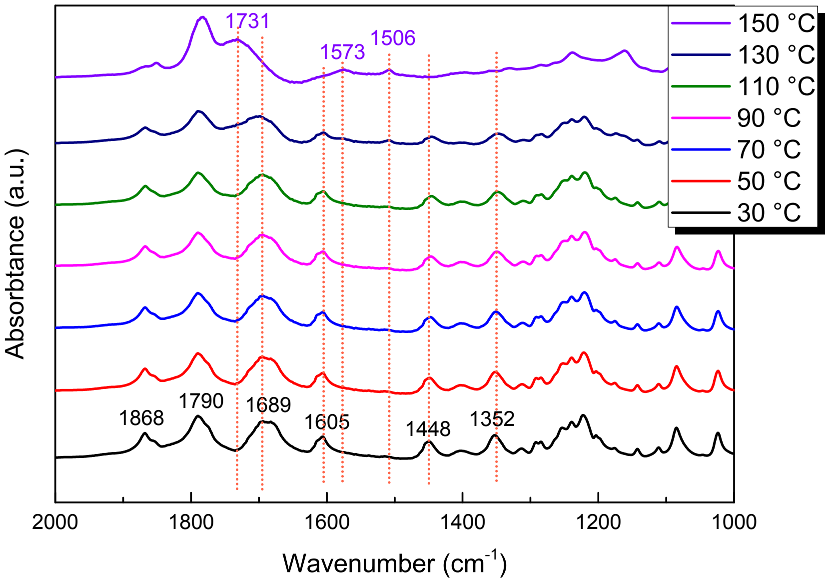

Figure S8 FTIR spectra of the dynamic crosslinker during the heating process. The absorption peaks of 1689 cm^{-1}, 1605 cm^{-1}, 1448 cm^{-1}, 1352 cm^{-1}, which represent the dynamic crosslinker, disappear gradually above 130 °C, while 1573 cm^{-1} and 1506 cm^{-1}, which represent 3-furoic acid, and 1731 cm^{-1}, which represent maleic anhydride, appear gradually, proving that the dynamic crosslinker can be decomposed into maleic anhydride and 3-furoic acid above 130 °C indeed.

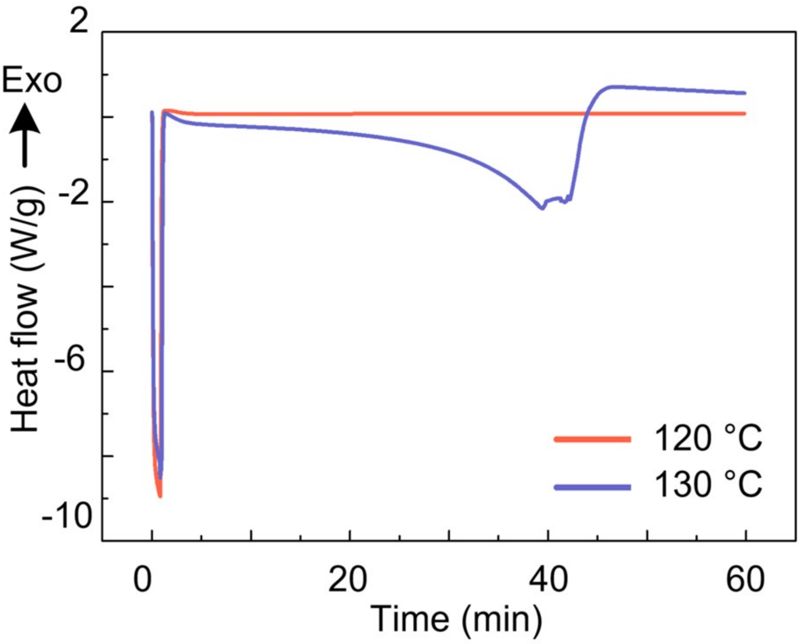

Figure S9 Constant-temperature DSC of the dynamic cross-linker. The dynamic cross-linker does not decompose when kept at 120 ℃ for one hour, while a large amount of heat is generated if the temperature rises to 130 ℃, which means that the dynamic cross-linker has decomposed. Above results indicate that the onset temperature of the retro-Diels-Alder reaction is about 130 °C.

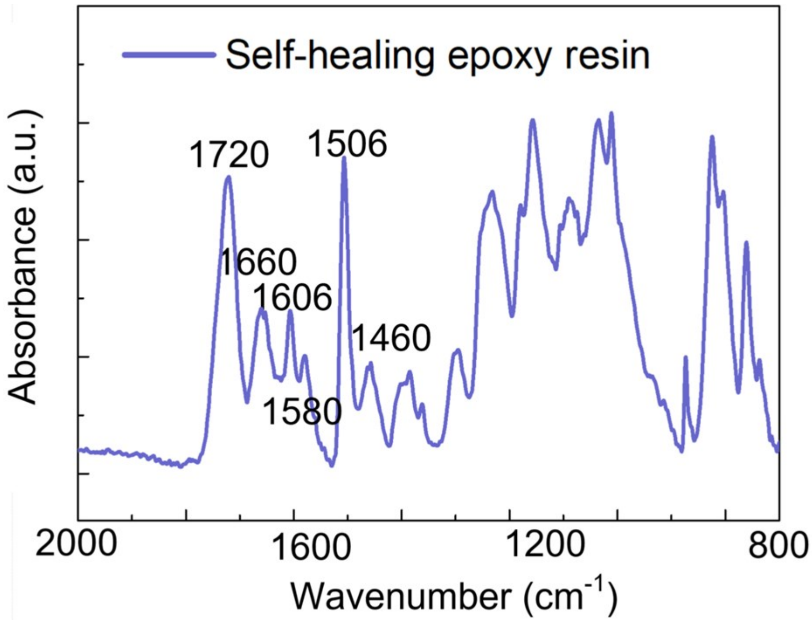

Figure S10 The FTIR spectroscopy of the cured self-healing epoxy resin using the dynamic cross-linker, which confirms the reaction mechanism between the dynamic cross-linker and bisphenol A epoxy monomer. Except the absorption peaks of the benzene ring (1606 cm^{-1}, 1580 cm^{-1}, 1506 cm^{-1} and 1460 cm^{-1}), the cured epoxy resin only exhibits the absorption peak of the double bond at 1655 cm^{-1} and the absorption peak of the ester carbonyl at 1720 cm^{-1}, indicating that the carboxyl and anhydride on the dynamic cross-linker can both react completely with epoxy monomer.

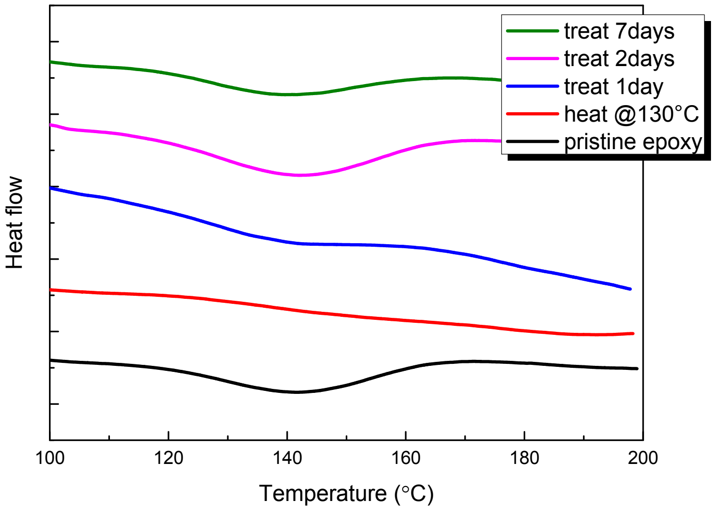

Figure S11 The DSC curves of samples treated for different time at 70 °C. The recovery of endothermic peaks representing the decomposition of reversible bonds during the first heating is used to evaluate the reconstruction of reversible bonds. After 2 days of treatment, the recovery of endothermic peak is the same with that after 7 days of treatment, indicating that 2 days of treatment is enough.

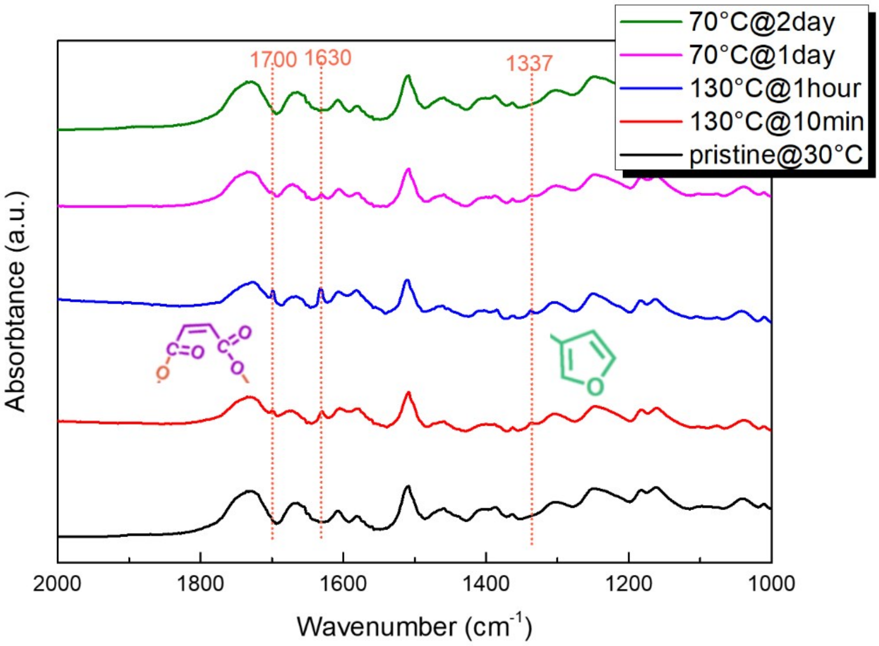

Figure S12 FTIR spectra of the self-healing epoxy resin in the different cross-linked states was studied in a nitrogen atmosphere. The FTIR spectrum of the pristine self-healing epoxy was measured firstly at 30 °C. After that, the temperature was increased to 130 °C and the FTIR spectra were measured again after keeping for 10 minutes and 1 hour, respectively. Finally, the temperature was decreased to 70 °C to recover the fully-crosslinked state and the FTIR spectra were measured again after different treating time. It can be seen that the absorption peaks of the residue of maleic anhydride (1700 cm^{-1} represents the conjugated C=O, 1630 cm^{-1} represents the conjugated C=C) and 3-furoic acid (1337 cm^{-1} represents the furan ring) appeared after the material was treated at 130 °C, indicating that the cross-linked state of the material had changed into the partially cross-linked state. After treating at 70 °C for 2 days, the absorption peak returned to the pristine state, indicating that the material returned to the fully cross-linked state.

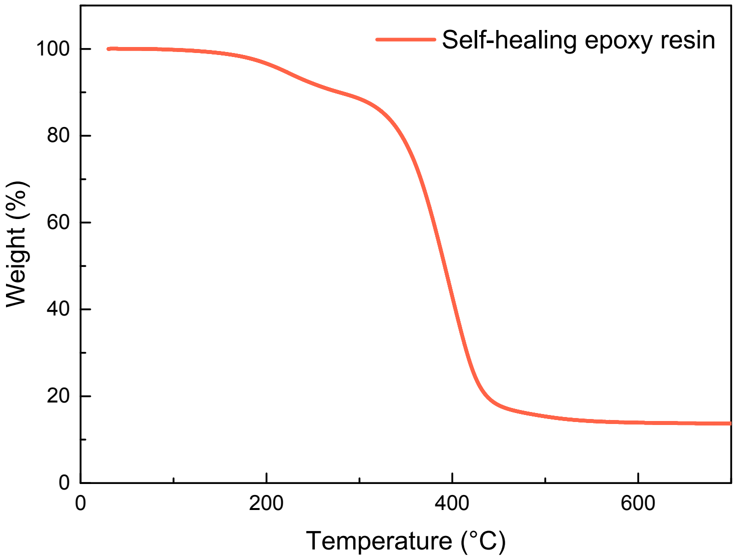

Figure S13 Thermogravimetric analysis curves of self-healing epoxy resin cured by the dynamic cross-linker. The main weight-loss temperature of the self-healing epoxy falls near 400 °C, indicating the epoxy has a good thermal stability. The slight weight loss between 200-300 ℃ is due to the volatilization of residual DMF in the material.

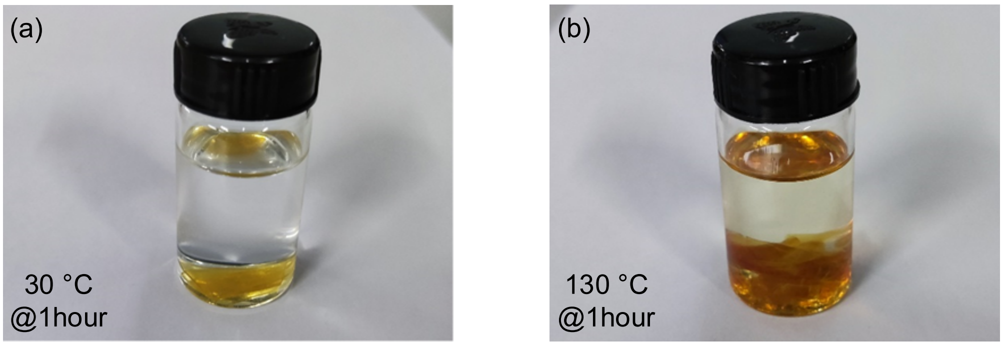

Figure S14 Using DMF as solvent, whether placed at 30°C (a) or at 130°C (b) for 1 hour, the self-healing epoxy did not dissolve. Instead, the volume of the self-healing epoxy expanded significantly after being converted to the partially-crosslinked state, which was due to the breaking of reversible bond inside the material.

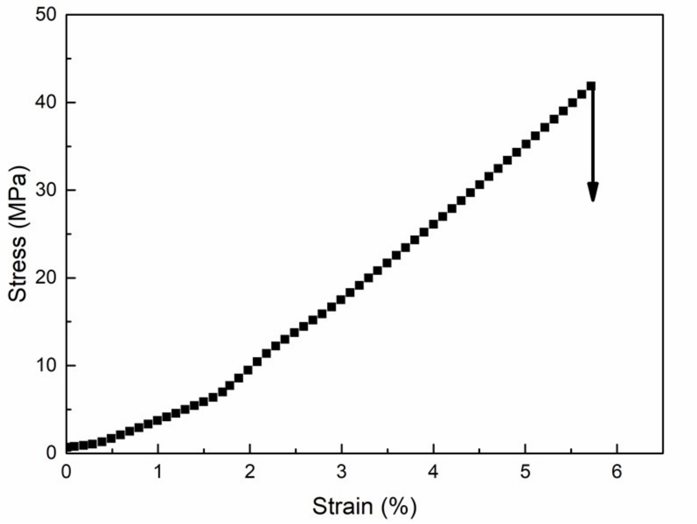

Figure S15 The Stress-Strain curve of the self-healing epoxy.

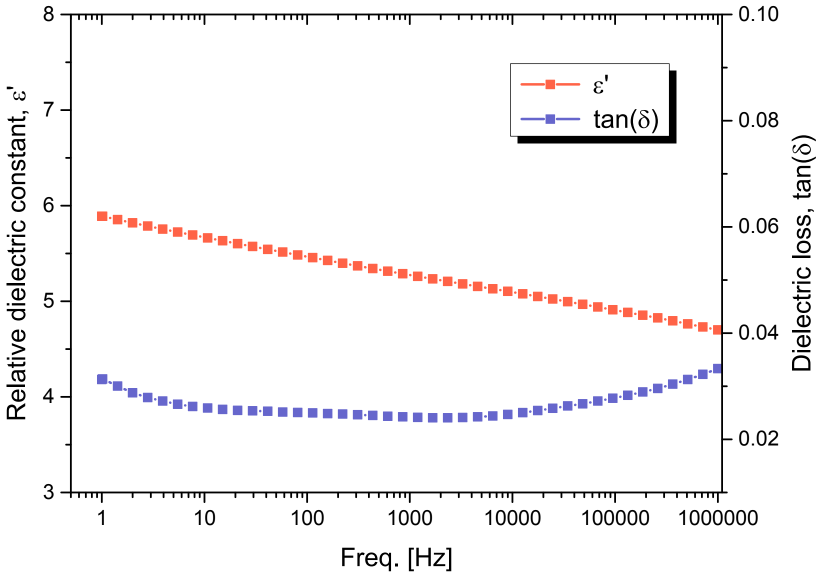

Figure S16 The relative dielectric constant and dielectric loss of the self-healing epoxy resin.

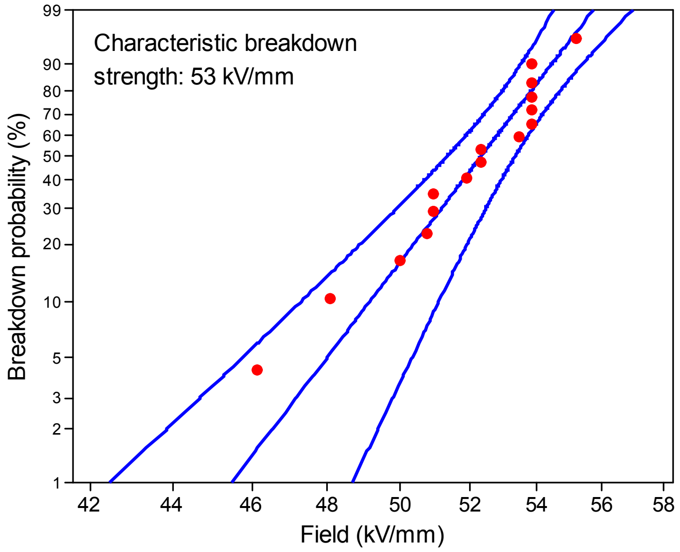

Figure S17 Weibull distribution of AC breakdown strength of the self-healing epoxy resin. The characteristic breakdown strength is about 53 kV/mm.

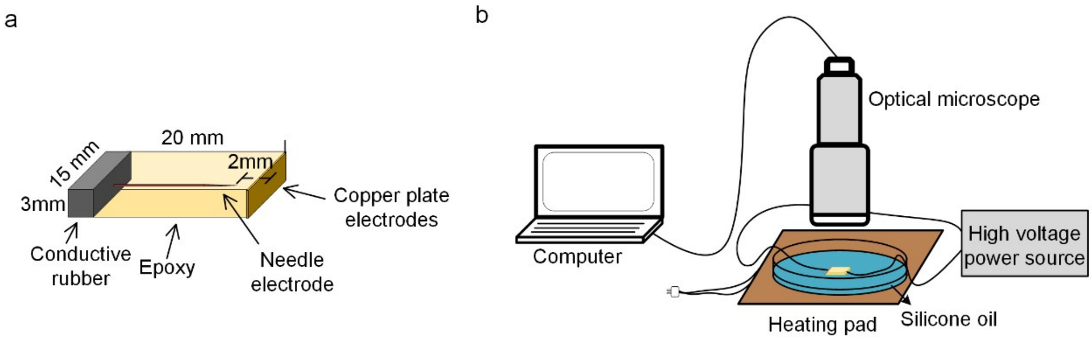

Figure S18 a The structure of self-healing epoxy samples for electrical tree aging experiment. A needle tip is used to simulate the defect in the material. b The electrical tree aging platform with the function of real-time observation of electrical tree aging.

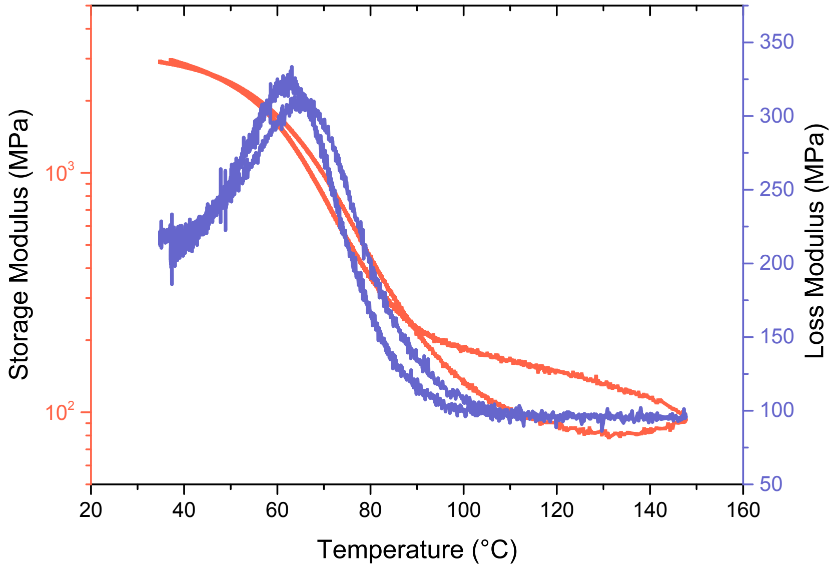

Figure S19 The storage modulus and loss modulus of a normal epoxy resin cured by amine curing agent, of which the cross-linked network is permanent. The glass transition temperature of this normal epoxy resin is about 60 ℃, and the storage modulus is below 100 MPa at 130 °C The temperature rise curve and temperature drop curve coincide basically, indicating that the crosslinking structure of the material has not changed.

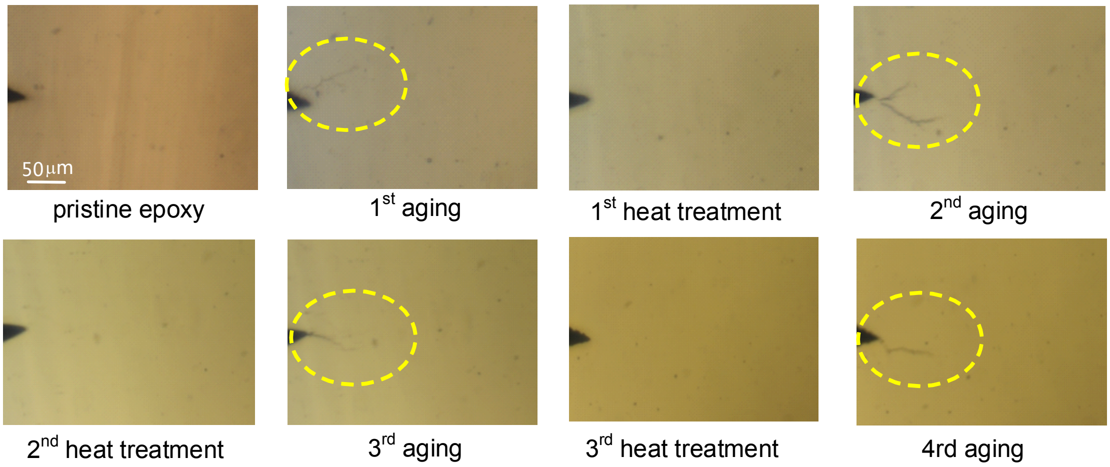

Figure S20 Multiple complete healing of micro electrical tree defects in the three aging-healing cycles.

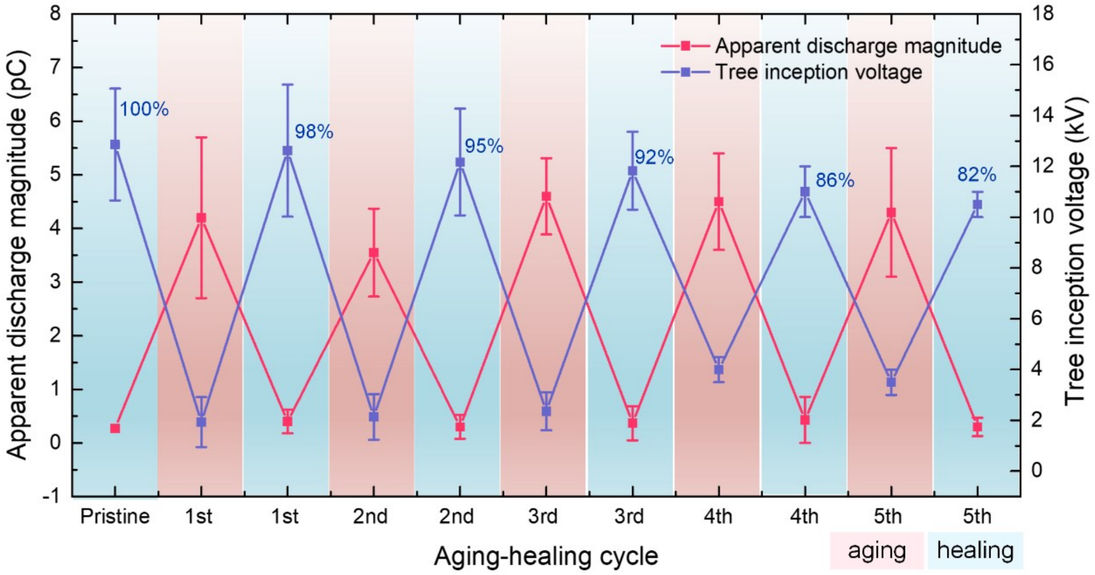

Figure S21 The apparent discharge magnitudes and tree inception voltages of the self-healing samples during five aging-healing cycles. After healing, all the self-healing samples can eliminate the partial discharge in the material and restore the tolerance to electrical stress. After five aging-healing cycles, the tree inception voltages of the samples can still be maintained at 82% of the pristine value. The average values and max-min error bars of the results were obtained from 3-5 samples.

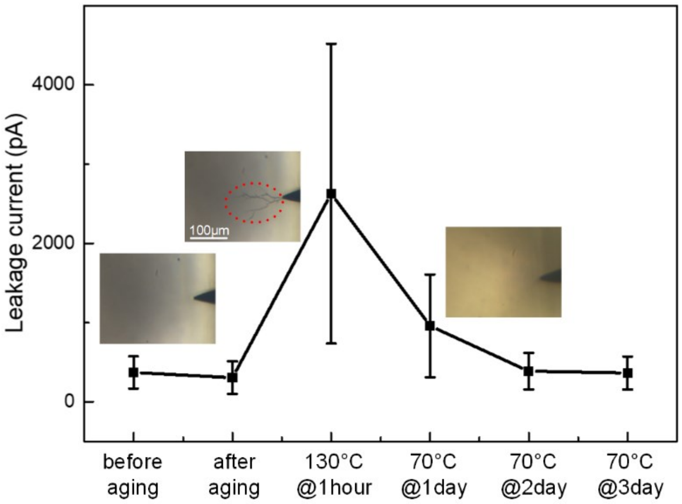

Figure S22 The leakage currents of the self-healing samples before aging, after aging and during different healing stages. After aging, the leakage current has no obvious change compared with that before aging, which confirms that the leakage current (related to resistance) cannot reflect the electrical tree defects inside the material evidently. In addition, when the self-healing epoxy is transformed into the partially-crosslinked state, the leakage currents of the samples increase greatly, and gradually return to the original values in the process of returning to the fully-crosslinked state, which further verifies the interconversion of cross-linked states in the self-healing epoxy resin. The average values and max-min error bars of the results were obtained from 5 samples.