

Supporting Information

Mussel-Inspired High Bio-based Content Thermosetting Polyimide Polymer with Excellent Adhesion, Flame Retardancy, Room-temperature Self-healing and Diverse Recyclability

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1 Experimental

1.1 Materials

Acrylic acid, hydroquinone, diethylene triamine, vanillin, Ferrous sulfate, potassium persulfate, glacial acetic acid, hydrochloric acid, sulfuric acid, orthophosphoric acid, nitric acid and p-toluenesulfonic acid was purchased from Shanghai Macklin Biochemical Co., Ltd., Shanghai, China. Castor oil, N, N-dimethylformamide (DMF), sodium hydroxide, anhydrous magnesium sulfate, sodium chloride, phytic acid were supplied by Sinopharm Chemical Reagent Co. Ltd., China. All the chemicals were reagent grade and were used as received.

1.2 synthesis of ACO

Add 13.95 g (0.015 mol) castor oil, 10.8 g (0.15 mol) acrylic acid, 0.7 wt.% p-toluenesulfonic acid catalyst and 0.3 wt.% hydroquinone polymerization inhibitor into a 40 mL microwave reaction flask with magnets. The microwave reaction temperature was 120 °C, and the reaction was carried out for 20 min. After the completion of the reaction, it was washed with saturated brine until the pH became neutral, the water was removed by anhydrous magnesium sulfate, and suction filtration was performed to obtain a yellow oily liquid ACO.

1.3 synthesis of DAC

Add 11 g (0.01 mol) ACO and 3.1 g (0.03 mol) diethylenetriamine into a 50 ml Erlenmeyer flask with magnets, stirring at 400 rpm, and react at room temperature for 12 hours. After the reaction, it was washed with saturated brine until the pH became neutral. Anhydrous magnesium sulfate was used to remove water, filtered by suction, and rotary steamed to obtain a reddish-brown viscous liquid. The measured ammonia

value was 98 mgKOH/g, which was close to the theoretical value (108.9 mgKOH/g).

1.4 synthesis of DV

Add 15.2 g (0.1 mol) vanillin, 0.76 g (5 mmol) ferrous sulfate, 13.5 g (0.05 mol) potassium persulfate and 400 ml deionized water into a 500 ml Erlenmeyer flask with magnets, stirring at 400 rpm /min, react at 80 °C for 20 min. Suction while it is hot, the filter residue is dissolved with sodium hydroxide solution and then precipitated with dilute hydrochloric acid solution. Filter by suction and wash with hot water 3~5 times. The obtained product is a pale off-white solid powder.

1.5 Preparation of the Schiff Base polymer

DAC-DV is cured according to the formula designed in the **Table 1**, and the name of each sample is marked according to the content of DV for identification. For example, DAC-0.5DV means that the ratio of DAC primary amine group content to DV aldehyde group content in a sample is 1:0.5. The amount of DAC shown in the formula was dissolved in DMF, and then the corresponding mass of DV solid was added, and the mixture was sonicated and stirred for 5 min to obtain a uniform and clear solution with initial crosslinking. The solution was cast in a polytetrafluoroethylene mold, and then heated in a vacuum oven at 80 °C for 24 h to remove the solvent. No bubbles were observed inside the sample, and then a dumbbell-shaped press knife was used to form the corresponding shape and heated at 120 °C 2 h.

2 Characterization and Measurements

2.1 Characterization Methods

We conducted FT-IR spectroscopy experiments on Nicolet iS10 IR spectrometer

(Nicolet Co., USA), with a range of 4000-500 cm^{-1} and a resolution of 4 cm^{-1} . ^1H NMR spectra were obtained using a Bruker ARX 300 NMR spectrometer with CDCl_3 as the solvent and tetramethylsilane as the internal standard. We used the NETZSCH TG 209F1 instrument (Germany Netzsch Instrument Corp.) to conduct thermogravimetric analysis (TGA) research in a nitrogen atmosphere at a heating rate of 5/10/20/40 $^\circ\text{C}\cdot\text{min}^{-1}$ within a temperature range of 35-800 $^\circ\text{C}$. The dynamic mechanical analysis (DMA) was performed on a DMA Q800 instrument (TA Instruments, US) equipped with a gas cooling accessory. The sample size is $60\times 6\times 1\text{ mm}^3$, the oscillation frequency is 1 Hz, and the temperature is increased from 40 $^\circ\text{C}$ to 100 $^\circ\text{C}$ at a rate of 3 $^\circ\text{C}\cdot\text{min}^{-1}$. According to ASTM D2863-97, the limited oxygen index (LOI) is measured on the JF-3 oxygen index meter (Jianning, China), and the sheet size is $130\times 6.5\times 3\text{ mm}^3$. The UL-94 rating is tested according to the UL-94 (ASTM D 63577) standard. The sample size is $130\times 13\times 3.0\text{ mm}^3$. Laser Raman Spectroscopy (LRS) measurements are performed at room temperature using LabRAM HR800, excited by a 325 nm HeNe laser line in a scanning range of 200–4500 cm^{-1} . To avoid heating of the sample, the power is kept below 4 mW. A systematic visual inspection of the surface was subsequently performed to check that no changes had occurred around the focal point. Pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) analysis was carried out with an Agilent PY-3030D/7890B-5977A (Agilent Technologies Co. Ltd, USA). The injector temperature was 250 $^\circ\text{C}$, 5 min at 60 $^\circ\text{C}$, and then the temperature was increased to 270 $^\circ\text{C}$ at a rate of 30 $^\circ\text{C}\cdot\text{min}^{-1}$. The temperature of the GC/MS interface was 270 $^\circ\text{C}$, and the cracker temperature was 800 $^\circ\text{C}$. A field emission scanning electron microscope (FEI-SEM, SU8010) was used to observe the surface of the residual carbon, and the accelerating voltage was 3 kV. The SEM instrument also integrates an energy spectrometer (EDS) trace element analyzer. The UTM6503

universal testing machine of Shenzhen Sansi Zongheng Company was used to carry out the tensile stress-strain experiment, the load was 5KN, the test condition was 25 °C, and the tensile rate was 5 mm·min⁻¹. The sample is cut into a dumbbell shape (50×8.5×4 mm³, the original gauge length is 17 mm), the data of 5 parallel samples are tested, and the median value is taken. Scratch the polymer with a knife and make obvious scratches appear on the surface of the polymer. Use a German Leica DM750M microscope to observe the repair of the scratches on the surface of the sample. Differential Scanning Calorimetry (DSC) was carried out on a DSC8000 (PerkinElmer) at a heating of 10 °C/min from room temperature to 160 °C.

2.2 Lap-shear strength performance test

Lap-shear strength was measured by a universal tensile testing machine with a load of 5 KN. After sanding a 1mm thick stainless-steel plate with 240 grit sandpaper, it was placed in ethanol solution for ultrasonic treatment for 10 min. After drying at room temperature, the surface was wiped with acetone, dried in an oven at 50 °C, and the weight of the iron plate was recorded. The sample film is sandwiched between dry-treated steel plates with an overlapping area of 10×25 mm². The iron sheets are bonded by hot pressing at 80 °C at 0.2 MPa for 1.5 min, and the bonded weight is recorded. The shear strength performance test was carried out at room temperature with a tensile rate of 10 mm·min⁻¹. Replace the steel plate with glass, wood board, epoxy fiberglass board, aluminum alloy and test the lap shear strength according to the above steps.

2.3 Preparation of particle board and its anti-mildew ability test

Dissolve 5 g polymer in 5 g DMF, add 20 ml ethanol and 50 g solid wood particles, stir evenly, heat in a vacuum oven under reduced pressure at 100 °C for 8 h to evaporate

the solvent, and the polymer evenly coat the wood powder particles. Place the sample in a stainless-steel mold, heat-press at 120 °C for 15 min, release the mold after cooling, and saw it into a small square of 5×5 cm² to test the internal shear force. The prepared particleboards were packaged and sterilized by steam at 120°C for 30 min. Under sterile conditions, first place two sterilized glass rods (3 mm in diameter) in parallel on the plate medium that has been covered with *Trichoderma viride* mycelium. The cooled sterilized sample is then placed on top of the glass rod. After inoculation, put it back in the incubator (keep 25-28°C, relative humidity 85%) and cultivate.

2.4 Molecular dynamics simulation

In order to study the adhesion mechanism of the polymer, the interaction between DAC-DV and the steel or glass can be calculated by the following Formula 1 for molecular dynamics simulation¹. The molecular model was constructed using Materials Studio software. Choose DAC-0.7DV as the simulation object, build a molecular chain with DAC: DV as 3:3, and the polymer is composed of 15 chains. In order to analyze the role of imine bonds and benzene rings, replace C=N with C-N and benzene ring with cyclohexane, and construct the same polymer model as above. The stainless-steel plate uses iron element crystals to replace the construction surface, and the glass uses SiO₂ molecules to construct the surface. Construct the lowest energy models of three polymers on two different substrates respectively. The optimized potential of the condensed phase is used in the Atomic Simulation Study (COMPASS II) force field. The COMPASS II force field is usually used to provide atomic interactions. Then, the Ewald method and the atom-based method were used to analyze the Coulomb interaction and Van der Waals (VDW) interaction between the polymer and the substrate. A geometry optimization using smart method with an energy convergence

criterion of $2.0 \times 10^{-5} \text{ kcal} \cdot \text{mol}^{-1}$ and force convergence criteria of $10^{-3} \text{ kcal} \cdot \text{mol}^{-1} \cdot \text{\AA}^{-1}$ was used to get a global minimum energy configuration. To equilibrate the model, a equilibrate process was followed under constant temperature and constant volume (NVT ensemble) at 298 K for 600 ps. During the simulation, Nosé-Hoover thermostat was applied in the temperature control. Then, the cohesive energy density of DAC-DV with different substrates and interaction energy between DAC-DV and different substrates were calculated by the following formula, taking the Fe substrates as an example.

Formula 1: $IAE = E_{\text{Fe-polymer}} - (E_{\text{polymer}} + E_{\text{Fe}})$

IAE: Interaction energy between Fe and polymer, minus means adsorption.

$E_{\text{Fe-polymer}}$: The total potential energy of the polymer on the Fe substrate.

E_{polymer} : The potential energy of the polymer.

E_{Fe} : The potential energy of Fe.

2.5 Calculation of thermal degradation activation energy

The Flynn-Wall-Ozawa method is used to process the TGA curves of different heating rates, and the expression is shown in Formula 2.

Formula 2: $\lg\{\beta\} = \lg\{A \cdot E/R \cdot F(\alpha)\} - 2.315 - 0.4567E/RT^2$

In the above formula, β is the heating rate, A is the pre-factor, which is a parameter related to the rate at which activated molecules are transformed into product molecules, E is the apparent activation energy, R is the universal gas constant, T is the absolute temperature, and α is the decomposition F (α) is the integral formula of the thermal degradation mechanism function f (α). When α is a constant, F (α) is a constant. If $\lg\beta$ is plotted against $1/T$, a straight line is obtained, and the slope is $-0.4567E/R$, and then the E value can be obtained.

2.6 Self-healing test

The self-healing test can be divided into two parts. One is to leave scratches on the surface of the polymer. Use a microscope to observe the healing of different samples at room temperature and the healing of the same sample (DAC-0.7DV) at different temperatures. Record the changes in scratch width, and calculate the repair efficiency (Table S7 and S8). The other is to leave a penetrating wound in the middle of a dumbbell-type DAC-0.7DV sample and place them in an oven at 80 °C. The effect of different repair times on the recovery of mechanical properties was recorded.

2.7 Reprocessing performance

The reprocessing recovery test is carried out in a flat vulcanizer. The sample was broken into powder, placed between two steel plates covered with two Teflon cloth (to prevent the polymer from adhering to the steel plate), and treated at 80 °C and 0.2 MPa pressure for 1.5 min. The recovered film was obtained after cooled to room temperature, and the dumbbell-shaped spline was made to test the mechanical properties. Repeat the test 3 times.

2.8 Solvent recovery

Break 200 mg DAC-0.9DV into powder, place it in a 10 mL vial with 10 ml DMF solution, heat to 80 °C and keep it, observe, and record the powder dissolution. After dissolving, pour the solution into a polytetrafluoroethylene mold and place it in a vacuum oven at 80 °C under reduced pressure for 12 h to remove DMF and re-obtain the polymer film. No bubbles are observed inside the sample, and then use a dumbbell-shaped press knife makes the corresponding shape. Heat at 120 °C for 2 h, and perform

a tensile test after cooling. Repeat the above operation 3 times.

2.9 Monomer recovery

The monomer recovery test was carried out in three steps. The first is to select the best acid type, smash 1200 mg DAC-0.9DV into powder and place them in 6 10 mL vials, and add in 10 ml of 5% hydrochloric acid, sulfuric acid, nitric acid, acetic acid, phosphoric acid, and phytic acid aqueous solution. Compare the degradation ability of polymers in different acids at room temperature (about 20 °C). Then it explores the effect of temperature on degradation. Take 200 mg DAC-0.9DV sample powder, add 10 ml 5% glacial acetic acid aqueous solution and place it at 40 °C. After 80 min, it completely degraded. The solid is recovered by centrifugation. The supernatant is collected and added to sodium hydroxide solution for neutralization, and then washed with saturated brine. The upper organic layer is recovered. Both the recovered solid and organic layers were detected by ¹H NMR. Finally, the recovery efficiency is tested. The monomer recovery experiment was repeated with 3 g sample powder. Since 2 g DAC and 0.73 g DV were obtained, the recoveries were 71% and 90.5%, respectively.

3. Supplementary Figures and Tables

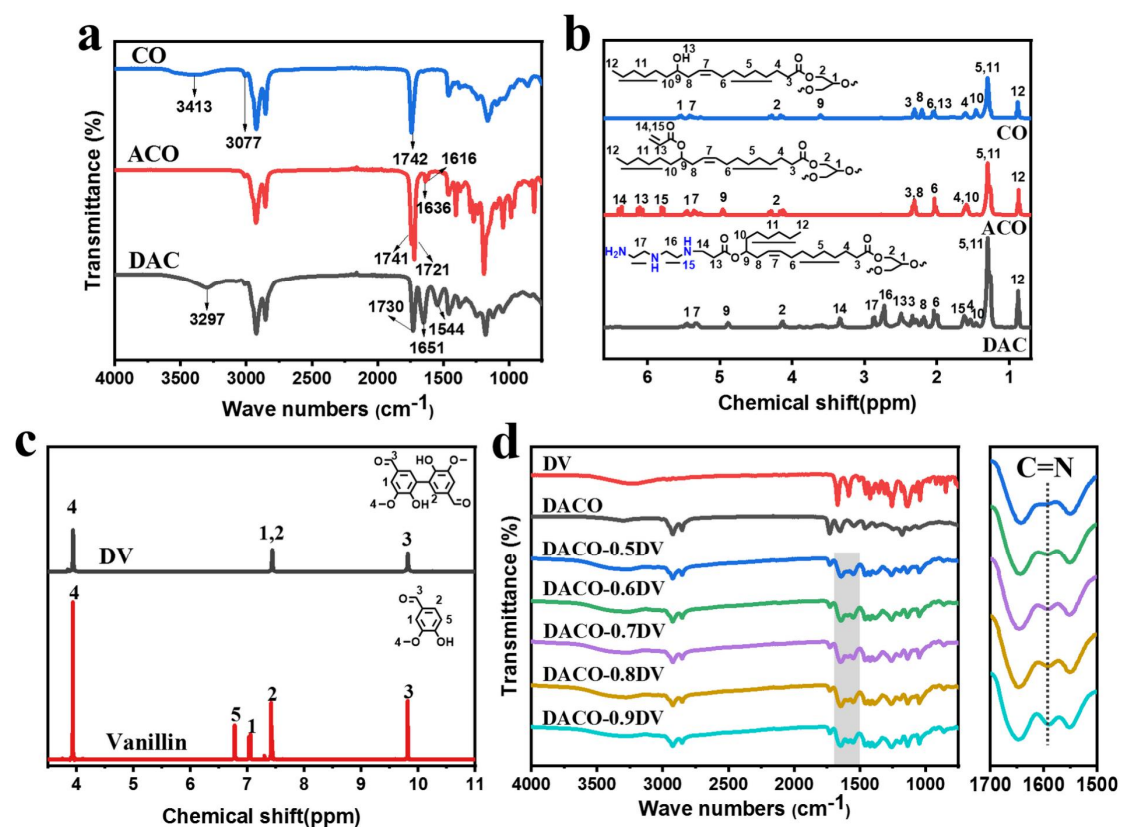


Fig. S1 a) the FTIR spectra of CO, ACO and DAC; b) the ^1H NMR spectra of CO, ACO and DAC; c) the ^1H NMR spectrum of vanillin and DV; d) the FTIR spectra of the polymer and two monomers.

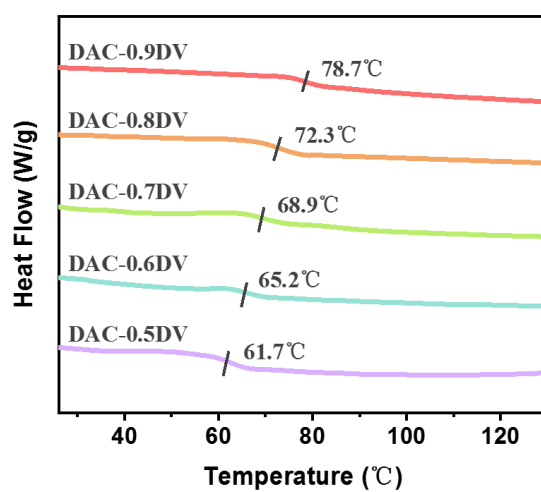


Fig. S2 The DSC curves of the polymer.

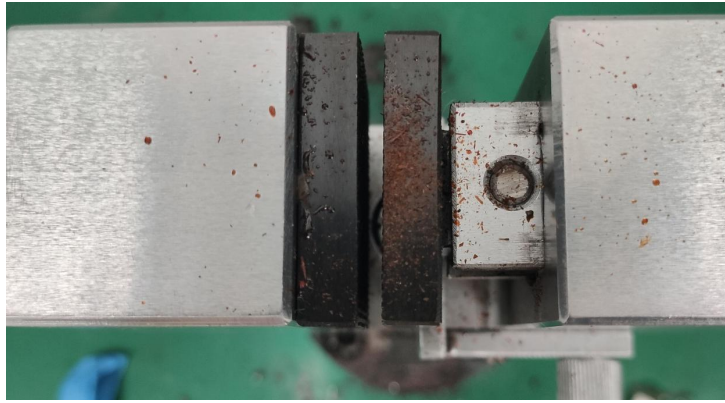


Fig. S3 Picture of the fixture area of the universal testing machine after multiple cyclic lap-shear tests, with obvious accumulation of polymer fragments.

Table. S1 the relationship between the content of adhesive and the lap-shear strength.

	The relationship	R²
DAC-0.5DV	$y = 92.694x + 2.3955$	0.9727
DAC-0.6DV	$y = 96.362x + 3.2324$	0.9716
DAC-0.7DV	$y = 182.62x + 5.958$	0.9938
DAC-0.8DV	$y = 209.63x + 4.0506$	0.9833
DAC-0.9DV	$y = 214.89x + 2.9297$	0.9788

Table. S2 The molecular dynamics simulation of hydrogen bonds in DAC-DV

	Number of H-bonds	Inert H-bonds	Intra H-bonds
DAC-DV	219	36	183
Proportion	-	16.44%	83.56%

Table. S3 The cohesive energy density of DAC-DV with different substrates

	CED ($\text{GJ}\cdot\text{m}^{-3}$) with Fe	CED ($\text{GJ}\cdot\text{m}^{-3}$) with Glass
DAC-DV	2.65	4.83
No C=N	2.26	4.07
No benzene ring	2.3	4.4

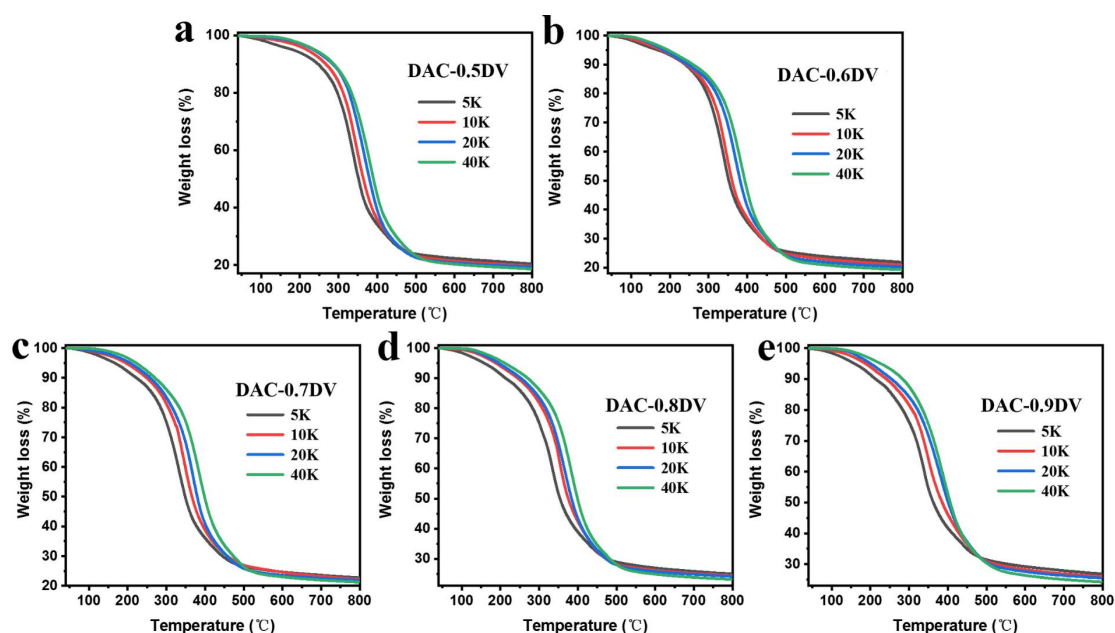


Fig. S4 TGA curves of DAC-DV series polymers at different heating rates.

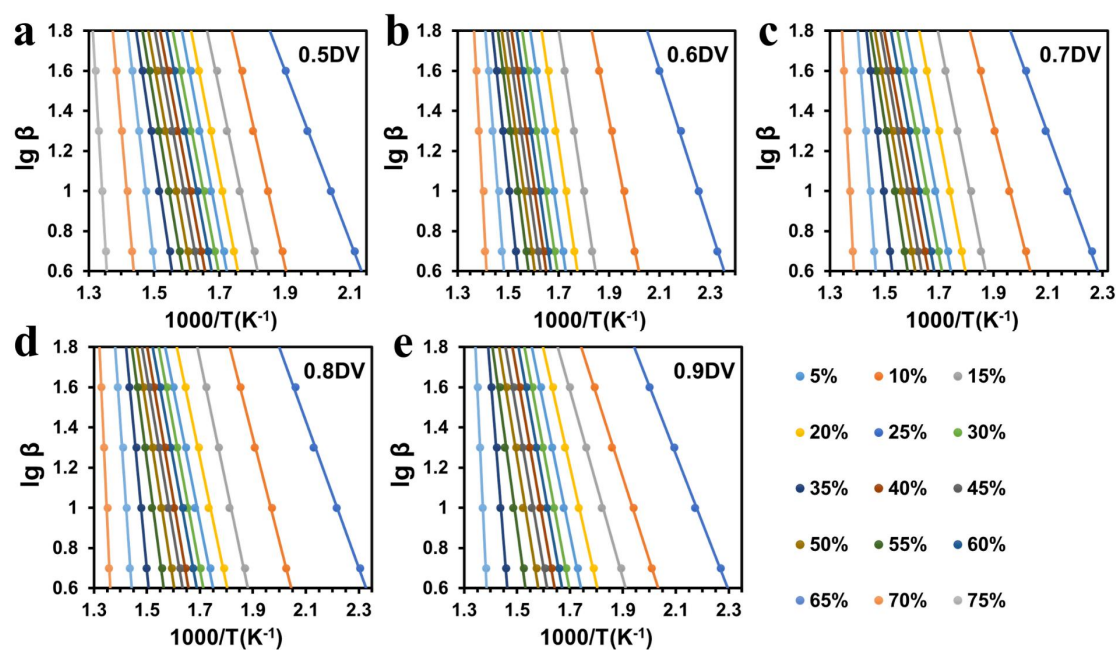


Fig. S5 The relationship between different thermal degradation and temperature of DAC-DV series polymers at different heating rates.

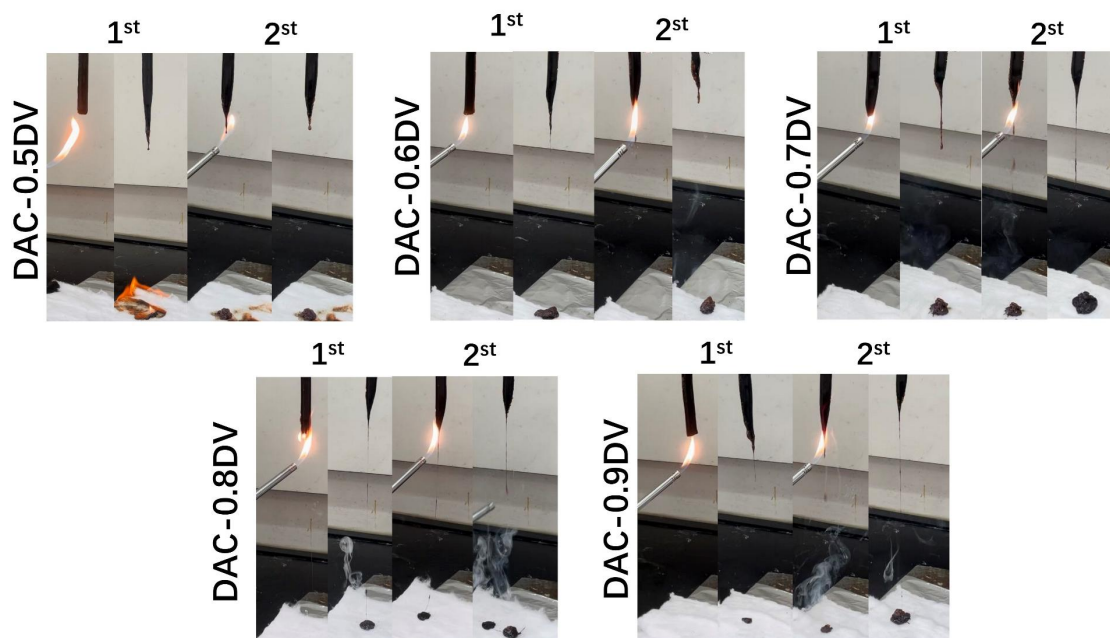


Fig. S6 Photo of UL-94 vertical burn test.

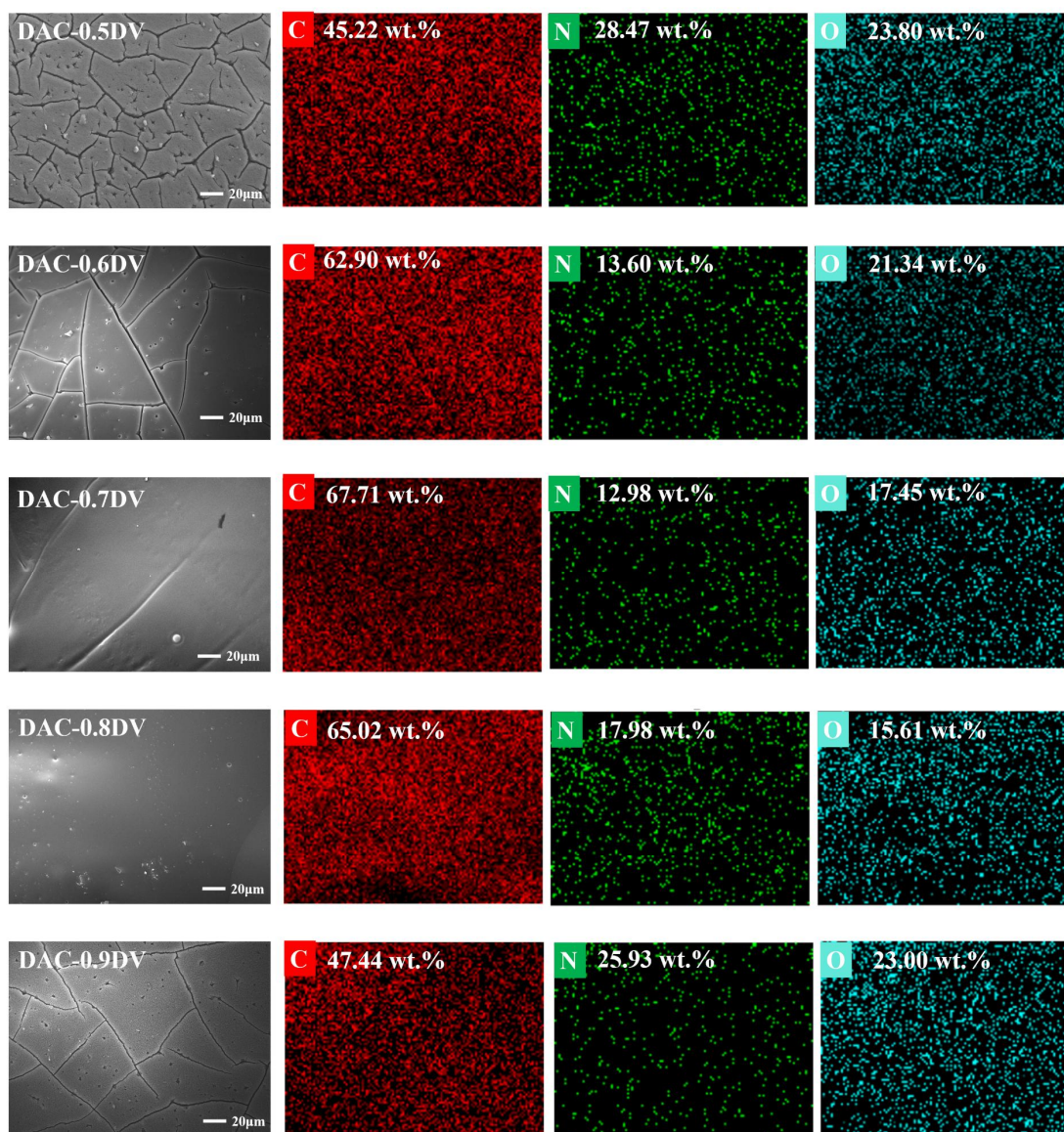


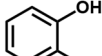
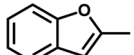
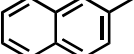
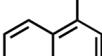

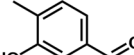

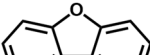
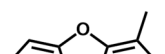
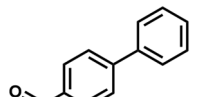
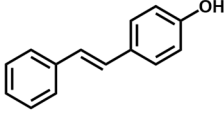
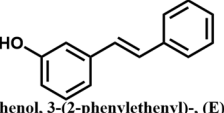
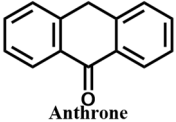
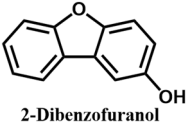
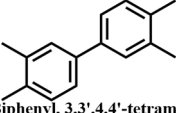
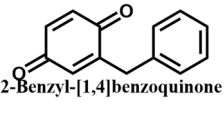
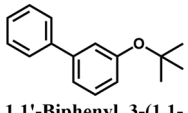
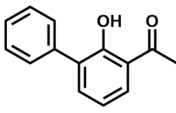
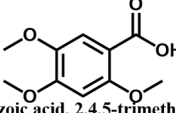
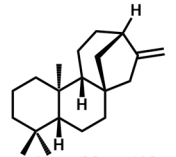
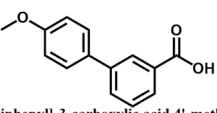


Fig. S7 EDS electron image of carbon residue: a) DAC-0.5DV; b) DAC-0.6DV; c) DAC-0.7DV; d) DAC-0.8DV; e) DAC-0.9DV.

Table S4 The pyrolysis product and mass spectrum information of DV at 800 °C

No.	Retention time (min)	Major mass fragments	Compounds	Number of C atoms
1	1.372	66	 1,3-Cyclopentadiene	5
2	1.82	78	 Benzene	6
3	7.667	108	 Phenol, 2-methyl-	7
4	8.039	132	 Benzofuran, 2-methyl-	9
5	11.256	142	 Naphthalene, 2-methyl-	11
6	11.461	142	 Naphthalene, 1-methyl-	11
7	12.767	152	 Vanillin	8
8	13.824	136	 3-Hydroxy-4-methylbenzaldehyde	8
9	14.001	136	 Benzaldehyde, 4-methoxy-	8
10	14.262	168	 Dibenzofuran	12
11	15.561	182	 Dibenzofuran, 4-methyl-	13
12	15.792	182	 [1,1'-Biphenyl]-4-carboxaldehyde	13

13	16.610	196	 <p>Phenol, 4-(2-phenylethenyl)-, (E)-</p>	14
14	17.005	196	 <p>Phenol, 3-(2-phenylethenyl)-, (E)-</p>	14
15	17.196	194	 <p>Anthrone</p>	14
16	17.458	184	 <p>2-Dibenzofuranol</p>	12
17	17.894	210	 <p>1,1'-Biphenyl, 3,3',4,4'-tetramethyl-</p>	16
18	18.435	198	 <p>2-Benzyl-[1,4]benzoquinone</p>	13
19	19.168	194	 <p>1,1'-Biphenyl, 3-(1,1-dimethylethoxy)-</p>	16
20	19.288	212	 <p>3-aceto-2-hydroxybiphenyl</p>	14
21	19.381	212	 <p>Benzoic acid, 2,4,5-trimethoxy-</p>	10
22	19.561	272	 <p>Kaur-16-ene, (8.beta.,13.beta.)-</p>	16
23	20.069	228	 <p>[1,1'-Biphenyl]-3-carboxylic acid,4'-methoxy-</p>	14

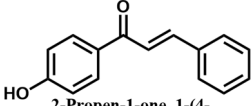
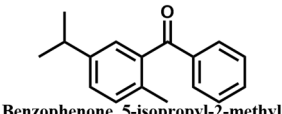


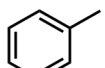
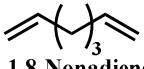
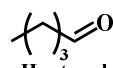
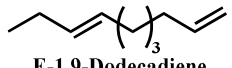
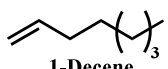
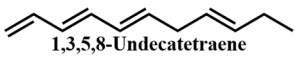
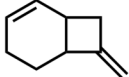

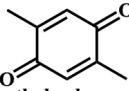
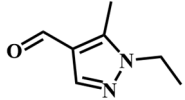
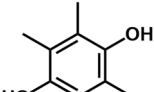
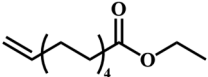
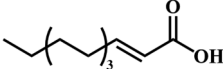
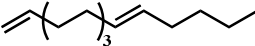
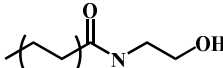
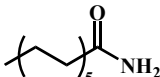
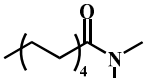
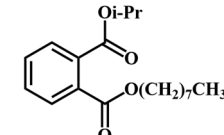
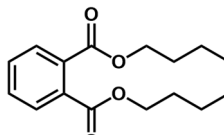
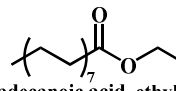
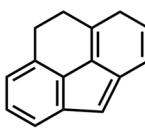
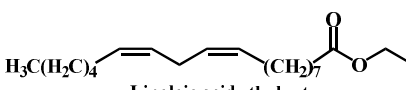
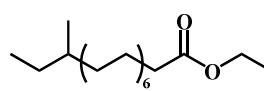
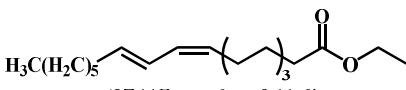
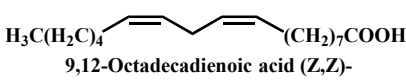
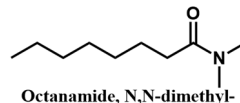
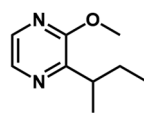
24	20.421	224	 2-Propen-1-one, 1-(4-hydroxyphenyl)-3-phenyl-	15
25	21.158	238	 Benzophenone, 5-isopropyl-2-methyl	17

Table S5 The pyrolysis product and mass spectrum information of DAC at 800 °C

No.	Retention time (min)	Major mass fragments	Compounds	Number of C atoms
1	1.529	66	 1,3-Cyclopentadiene	5
2	1.963	78	 Benzene	6
3	2.761	92	 Toluene	7
4	4.281	124	 1,8-Nonadiene	9
5	4.606	114	 Heptanal	7
6	5.974	166	 E-1,9-Dodecadiene	12
7	6.108	140	 1-Decene	10
8	8.930	148	 1,3,5,8-Undecatetraene	11

9	10.521	120	 7-Methylenebicyclo[4.2.0]oct-2-ene	9
10	12.018	110	 Hydroquinone	6
11	12.288	136	 2,5-Dimethyl-p-benzoquinone	8
12	13.074	138	 Pyrazole-4-carboxaldehyde, 1-ethyl-5-methyl-	7
13	13.333	152	 1,4-Benzenediol, 2,3,5- trimethyl-	9
14	13.67	212	 10-Undecenoic acid, ethyl ester	12
15	13.842	184	 Undecylenic Acid	11
16	14.789	194	 E-1,9-Tetradecadiene	14
17	15.426	187	 N-(2-Hydroxyethyl)octanamide	10
18	15.958	199	 Dodecanamide	12
19	16.853	199	 N,N-Dimethyldecanamide	12

20	18.272	334	 <p>Phthalic acid, isobutyl octyl ester</p>	20
21	19.27	278	 <p>Dibutyl phthalate</p>	16
22	19.495	284	 <p>Hexadecanoic acid, ethyl ester</p>	18
23	20.147	192	 <p>8,9-dihydro-1<i>H</i>-cyclopenta [<i>de</i>]phenanthrene</p>	15
24	20.444	278	$\text{H}_3\text{C}(\text{H}_2\text{C})_7\text{---}\equiv\text{---}(\text{CH}_2)_9\text{CH}_3$ <p>9-Eicosyne</p>	20
25	20.857	238	$\text{H}_3\text{C}(\text{H}_2\text{C})_7\text{---}\equiv\text{---}(\text{CH}_2)_6\text{OH}$ <p>7-Hexadecyn-1-ol</p>	16
26	21.236	308	 <p>Linoleic acid ethyl ester</p>	20
27	21.450	312	 <p>ethyl 15-methylheptadecanoate</p>	20
28	21.626	308	 <p>ethyl (9<i>Z</i>,11<i>E</i>)-octadeca-9,11-dienoate</p>	20
29	21.877	280	 <p>9,12-Octadecadienoic acid (Z,Z)-</p>	18
30	22.123	171	 <p>Octanamide, N,N-dimethyl-</p>	10
31	22.325	166	 <p>Pyrazine, 2-methoxy-3-(1-methylpropyl)-</p>	9

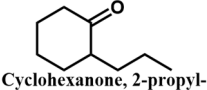
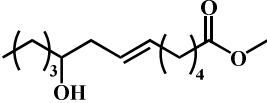
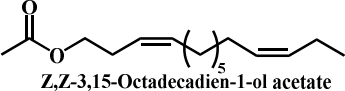
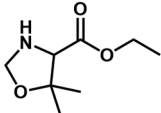
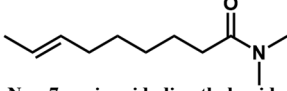
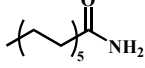
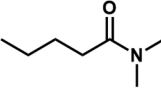
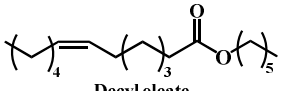
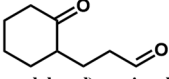

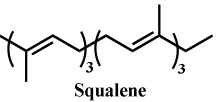



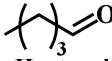
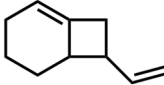
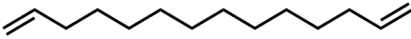
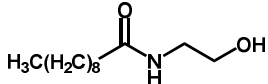
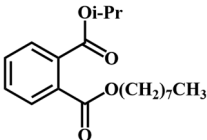
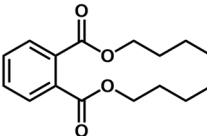
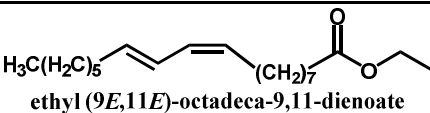
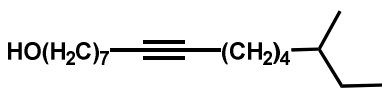
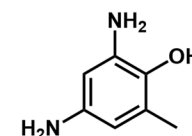
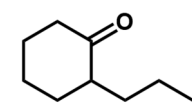
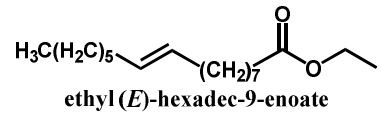
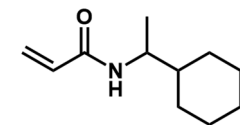
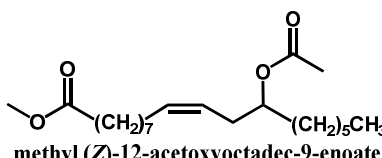
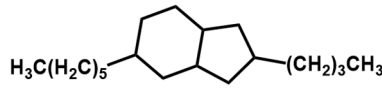
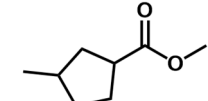
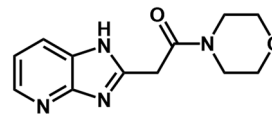
32	22.729	140	 Cyclohexanone, 2-propyl-	9
33	23.025	312	 Methyl 12-hydroxy-9-octadecenoate	19
34	23.403	308	 Z,Z-3,15-Octadecadien-1-ol acetate	20
35	23.538	174	 3,4-Dihydro-5,5-dimethyl-4-ethoxycarbonyloxazole	8
36	23.689	183	 Non-7-enoic acid, dimethylamide	11
37	23.877	227	 Dodecanamide	14
38	24.031	129	 N,N-Dimethylvaleramide	7
39	24.172	422	 Decyl oleate	28
40	24.481	154	 3-(2-Oxocyclohexyl)propionaldehyde	9
41	26.644	282	 Eicosane	20
42	27.042	410	 Squalene	30

Table S6 The pyrolysis product and mass spectrum information of DAC-DV at 800 °C

No.	Retention time (min)	Major mass fragments	Compounds	Number of C atoms
1	1.550	66	 1,3-Cyclopentadiene	5
2	1.980	78	 Benzene	6
3	2.771	92	 Toluene	7
4	4.613	114	 Heptanal	7
5	8.933	134	 2-Methyl-7-endo-vinylbicyclo[4.2.0]oct-1(2)-en	10
6	14.8	194	 1,13-Tetradecadiene	14
7	15.454	215	 $\text{H}_3\text{C}(\text{H}_2\text{C})_8$ N-(2-hydroxyethyl)decanamide	12
8	18.271	334	 Phthalic acid, isobutyl octyl ester	20
9	19.269	278	 Dibutyl phthalate	16
10	20.445	278	$\text{H}_3\text{C}(\text{H}_2\text{C})_7$ 9-Eicosyne	20
11	21.235	280	$\text{H}_3\text{C}(\text{H}_2\text{C})_4$ 9,12-Octadecadienoic acid (Z,Z)-	18

12	21.620	308	 ethyl (9 <i>E</i> ,11 <i>E</i>)-octadeca-9,11-dienoate	20
13	21.873	252	 14-methylhexadec-8-yn-1-ol	17
14	22.321	138	 4,6-Diamino-O-cresol	7
15	22.741	140	 Cyclohexanone, 2-propyl-	9
16	22.982	282	 ethyl (<i>E</i>)-hexadec-9-enoate	18
17	23.111	181	 2-Propenamide, N-(1-cyclohexylethyl)-	11
18	23.628	354	 methyl (<i>Z</i>)-12-acetoxyoctadec-9-enoate	21
19	24.181	264	 2-butyl-5-hexyloctahydro-1 <i>H</i> -indene	19
20	25.288	142	 Cyclopentanecarboxylic acid, 3-methyl-, methyl ester	8
21	29.342	246	 Ethanone, 2-(1 <i>H</i> -imidazo[4,5- <i>b</i>]pyridin-2-yl)-1-(4-morpholyl)-	12

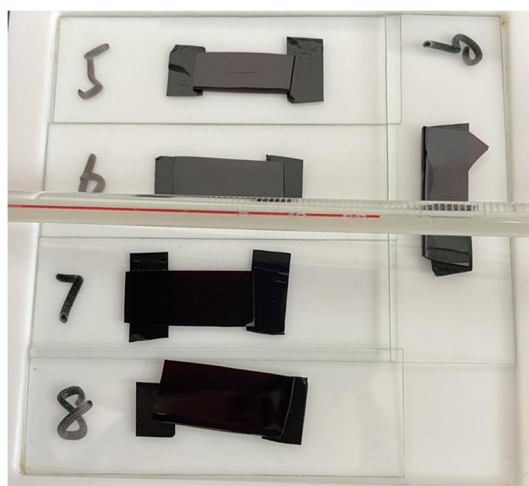


Fig. S8 The photo of the surface scratch self-healing test at room temperature, the temperature is about 23 °C, and clear scratches can be seen on the polymer surface.

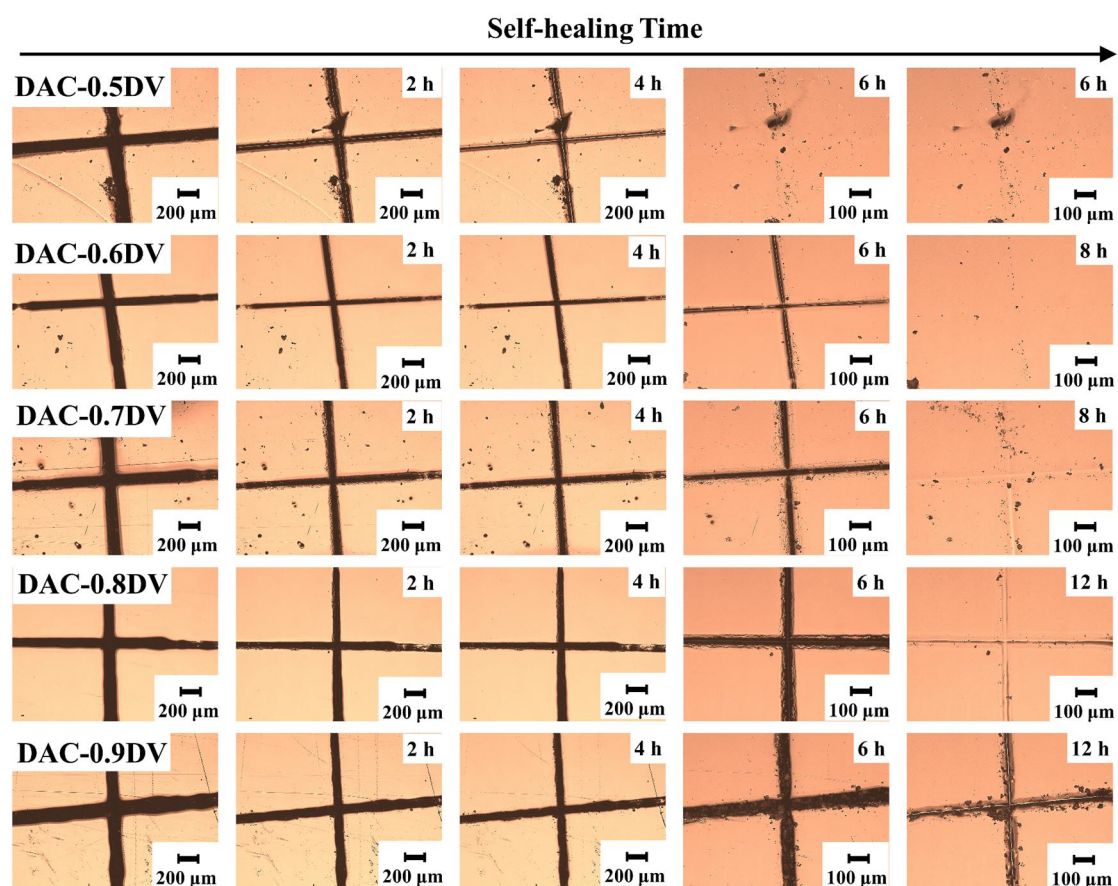


Fig. S9 Photos of the room-temperature surface scratch self-healing test of DAC-DV taken with the microscope.

DAC-0.7DV Self-healing Time

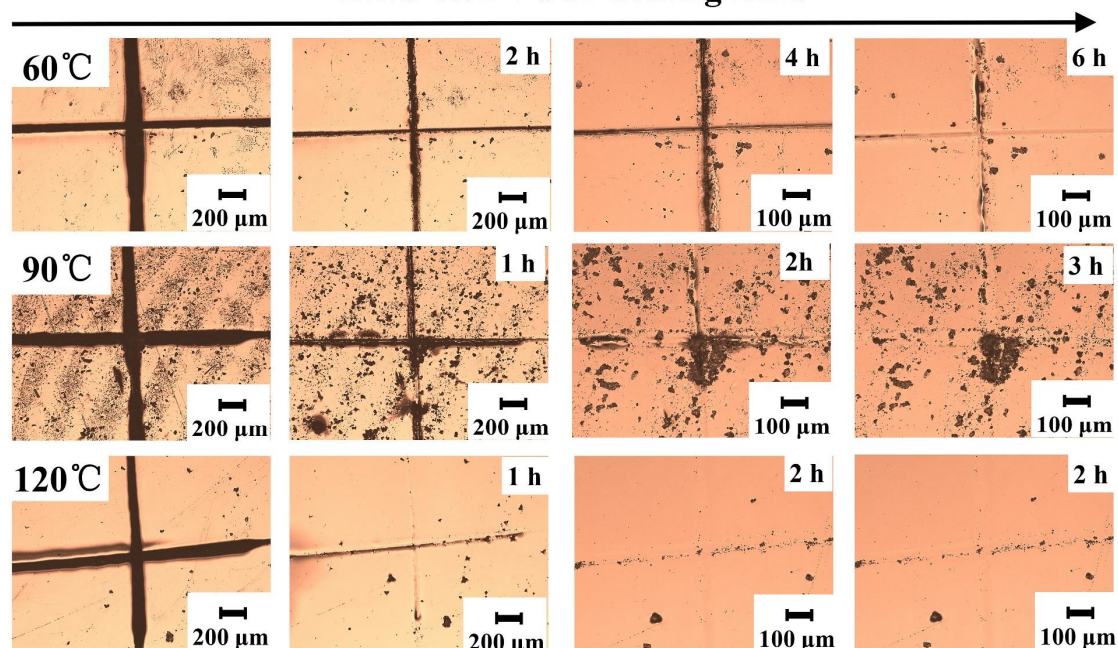


Fig. S10 Photos of the surface scratch self-healing test of DAC-DV at different temperatures taken with the microscope.

Table S7 The detailed data of the room-temperature surface scratches self-healing test of DAC-DV

Time (h)	DAC-0.5DV		DAC-0.6DV		DAC-0.7DV		DAC-0.8DV		DAC-0.9DV	
	Width (μm)	Rate (%)	Width (μm)	Rate (%)	Width (μm)	Rate (%)	Width (μm)	Rate (%)	Width (μm)	Rate (%)
0	176.06	0.00	172.54	0.00	172.54	0.00	169.17	0.00	160.20	0.00
1	145.75	17.22	151.65	12.11	152.67	11.51	153.49	9.27	152.53	4.79
2	101.32	42.45	106.05	38.54	123.68	28.32	127.36	24.72	126.94	20.76
3	71.69	59.28	78.93	54.26	90.03	47.82	106.68	36.94	107.07	33.16
4	49.45	71.91	54.10	68.65	68.26	60.44	90.58	46.45	104.40	34.83
5	25.45	85.54	45.06	73.88	53.96	68.73	76.20	54.95	90.68	43.40
6	0	100	34.59	79.95	45.54	73.61	60.20	64.41	84.80	47.07
7			12.57	92.72	25.13	85.44	51.96	69.29	78.46	51.02
8			1.75	99.00	43.54	74.26	71.03	55.66		
9			35.13	79.24	66.15	58.71				
10			22.49	86.71	59.16	63.07				
11			15.08	91.08	42.16	73.68				
12			7.28	95.69	35.49	77.85				

Table S8 The detailed data of the surface scratch self-healing test of DAC-DV at different temperatures

Time (h)	60 °C		90 °C		120 °C	
	Width (μm)	Rate (%)	Width (μm)	Rate (%)	Width (μm)	Rate (%)
0	210.36	0.00	157.00	0.00	152.52	0.00
1	153.99	26.80	16.92	89.22	12.69	91.68
2	115.82	44.94	7.32	95.34	0	100
3	78.54	62.66				
4	47.27	77.53				
5	30.13	85.68				
6	11.54	94.51				
7	0	100	0	100		

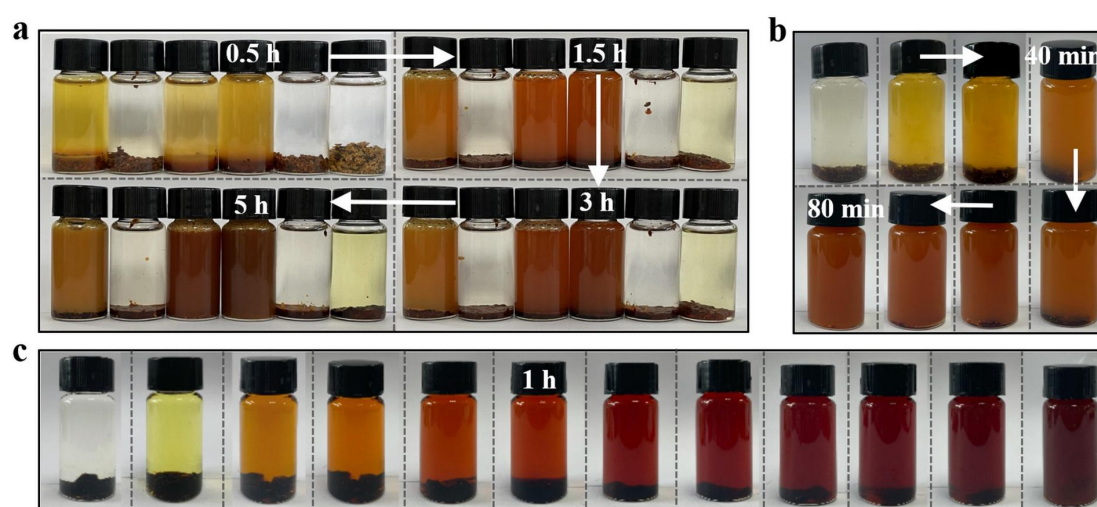


Fig. S11: a) Photos of DAC-0.9DV monomer recovery test using different acids, from left to right are phytic acid, sulfuric acid, phosphoric acid, acetic acid, hydrochloric acid, and nitric acid; b) Photos of monomer recovery test of DAC-0.9DV using acetic acid at 40 °C; c) Photos of solvent recovery test of DAC-0.9DV at 80 °C using DMF.

References

1. J. Zhang, Z. Chen, Y. Zhang, S. Dong, Y. Chen and S. Zhang, *Adv. Mater.*, 2021, **33**, 2100962.
2. M. K. Baloch, M. J. Z. Khurram and G. F. Durrani, *J. Appl. Polym. Sci.*, 2011, **120**, 3511-3518.