Electronic Supplementary Information

1 Materials and methods

1.1 Material and synthesis

Vanillin, epichlorohydrin, benzyltriethylammonium chloride (TEBAC), 1-methoxy-2-propanol (PnM), 5-Amino-1,3,3-trimethylcyclohexanemethylamine (isophoronediamine, IPDA), poly(propylene glycol) bis(2-aminopropyl ether) with average molecular weight of 400 (D-400), ethanol, acetic acid, styrene, ammonium persulfate(APS), and polyvinylpyrrolidone (PVP, K29-K32) were purchased from Aladdin Industrial Co. (China). All regents used as received.

Synthesis of epoxides of vanillin (E-Van)

The synthesis method is simplified from the works by Maxence Fache[1, 2]. Vanillin (60.0 g, 0.394 mol), epichlorohydrin (146.4 g, 1.582 mol) and TEBAC (3.0 g, 0.013mol) were mixed in a 1 L flask with mechanical agitation and a condenser. The mixture was kept at 80 °C for 2 h, and then cooled to room temperature. 100 g NaOH(40 wt%) solution was added dropwise to the mixture in 30 min at room temperature, followed by adding 100 g butyl acetate for dilution, and the reaction was kept at room temperature for another 1 h. After that, the mixture was filtered and the organic phase was precipitated with petroleum ether for more solid product. All solid was collected wash with ethanol for 1 time and pure water for 3 times. 55.3 g light-yellow solid with yield of 67.1% was obtained after drying in vacuum oven.

Synthesis of epoxy-imine network polymers

Table S1 Compositions of the epoxy-imine network polymer series.

Polymer	E-Van (g)	IPDA (g)	D-400 (g)	PnM (g)
0% IPDA	20.8	0	30.0	50.8
25% IPDA	20.8	3.19	22.5	46.49
50% IPDA	20.8	6.39	15.0	42.19
75% IPDA	20.8	9.58	7.5	37.88
100% IPDA	20.8	12.77	0	33.57

Detail Compositions of the epoxy-imine network polymer series are shown in **Table S1**, and the resin content was fixed at 50 wt%. All epoxy-imine polymers were prepared as follow: PnM and E-Van were first added into a flask with a stirrer and a condenser. IPDA and D-400 were then added into the flask, and the reaction was kept for 0.5 h at 60 °C for precuring. After that, the mixture was poured into a PTFE mold, treated in oven at 80 °C for 12 h and then in vacuum oven at 100 °C for 6 h, for drying and further curing. Films of polymers were obtained and then cut into small pieces for molding.

Synthesis of monodispersed polystyrene particles

Styrene (10 g), polyvinylpyrrolidone (0.6 g) and deionized water (75 g) were added into a 250 ml flask with a stirrer and a condenser. The mixture was stirred at room temperature with nitrogen protection for 1h. Then, the temperature is lifted to 76 °C, followed by adding 0.15 g of ammonium persulfate and 5 g of water. The emulsion polymerization was kept at 76 °C for another 8 h. Latex of monodispersed PS particles was obtained after cooling and filtration.

1.2 Characterizations and methods

NMR spectrum NMR Spectra were taken on Bruker, AVANCE III HD 400 in deuterated solvents ($CDCl_3$).

FT-IR spectrums FT-IR was recorded on FT-IR Spectrometer, Bruker, VERTEX 70, with ATR module. Spectrum of E-Van intermediate was collected via transmission method, and all the other spectrum of polymers are collected via ATR method.

DSC measurement DSC measurements were carried out on Melttler Toledo DSC 3 with a heating rate of 20 °C/min under nitrogen atmosphere.

DMA measurement DMA measurements were run on Q800 DMA (TA Instruments, America). The significant dimension of sample is 10 mm*3 mm*1 mm, and the measurement parameters are 4 °C/min, 1 Hz, 5 μm (amplitude).

Stress relaxation The Instruments and samples used are the same to the ones in above DMA measurement, and the initial deformation is 1%.

Tensile properties For tensile properties testing, the pieces of polymers were molded at condition of 150 °C, 20 MPa, 10 min. Dumbbell type specimens with significant dimension of 25 mm*4 mm*1 mm were prepared and stored in ambient atmosphere for 48 h to reach humidity equilibrium. The tensile experiments were carried out according to ISO 527-1:2012 on SANS electromechanical universal testing machine CMT4204, with 50 mm/min rate of extension.

Water absorption Samples in dimension of 8 mm*8 mm*1 mm were cut from dumbbell type specimens of 3rd generation. The samples were immersed in water at room temperature, and changes in weight were recorded in percentage.

TGA measurement TGA was taken on NETZSCH STA 449F3, with a heating rate of 10 °C/min and an air flow of 100 ml/min.

Acid-degradation treatment 1 g of polymers after 3rd reprocessing generation was added into 9 g of 10 wt% acetic acid solution, and the mixture was heated and shaken for 10 to 15 min at 60 °C for degradation. And a series of degradation product aqueous solutions without sedimentation were obtained.

Preparation of composite film with structural color 15 g of degradation product solutions (0% IPDA, 10 wt% resin content) is mixed with 10 g of monodispersed PS emulsion (190nm, 10 wt% resin content). Then the mixture was poured into a PTFE mold, heated in oven at 80 °C for 12 h and in vacuum oven 80 °C for another 12 h. A composite film with structural color was obtained after drying and recuring. FT-IR and tensile experiments are directly run on the film with adequate dimension. Swelling and drying for responsive color change effect were achieved by rinsing with ethanol and drying with an air blower, as shown in the video (**ESI video**).

2 Characterizations for E-Van intermediate

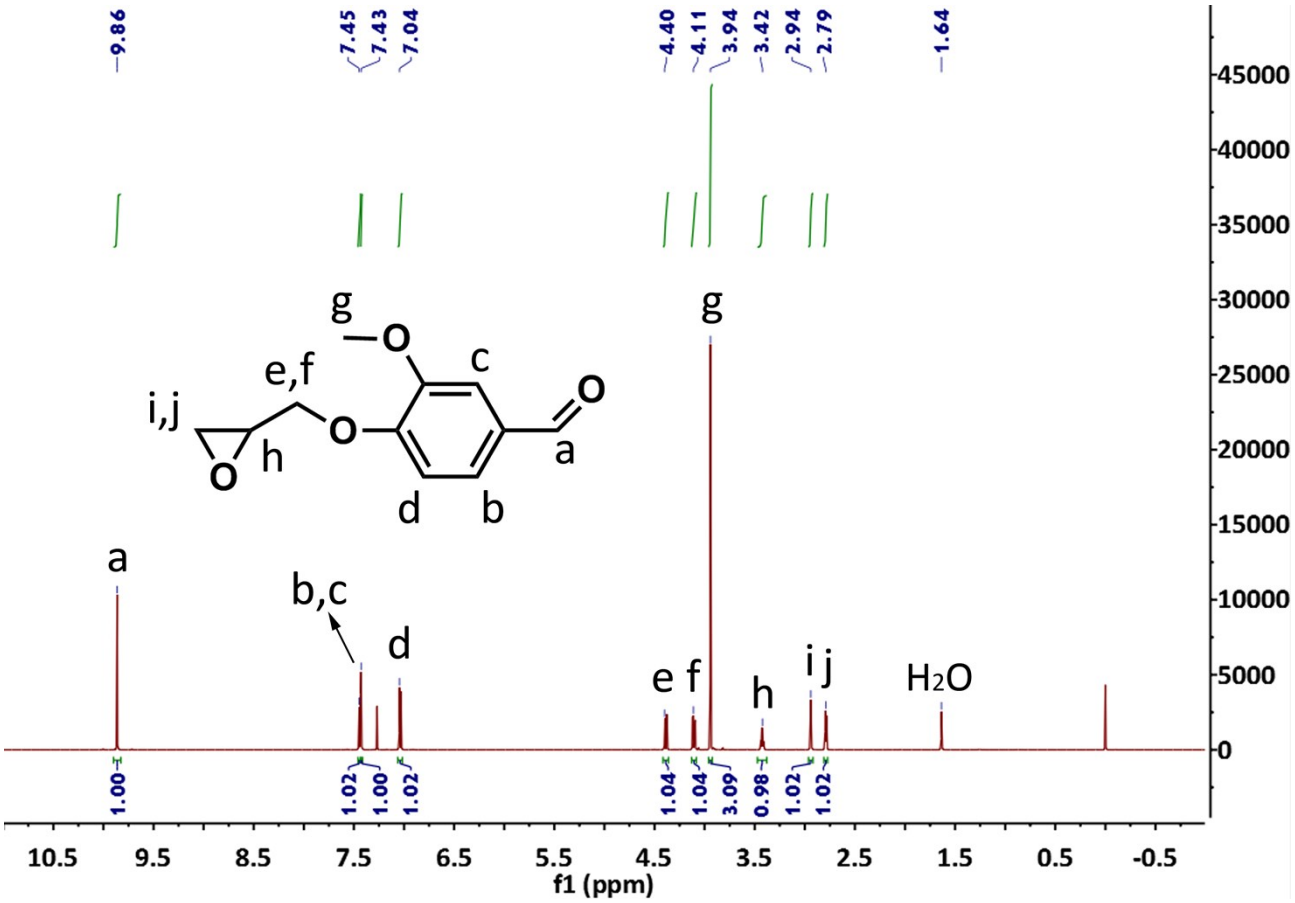

Fig. S1 NMR spectrum of E-Van

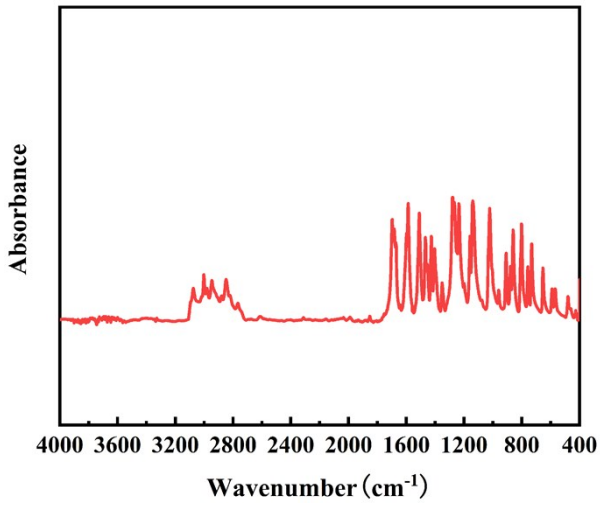

Fig. S2 FT-IR spectrum of E-Van

3 Characterizations for epoxy-imine network polymers

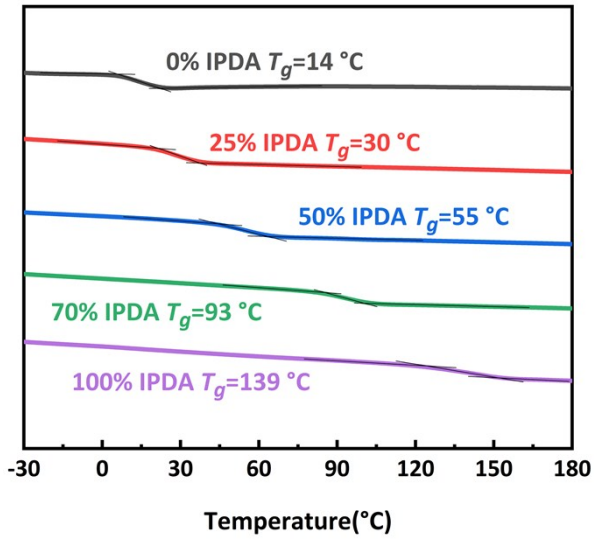

Fig. S3 DSC measurements for the epoxy-imine network polymers

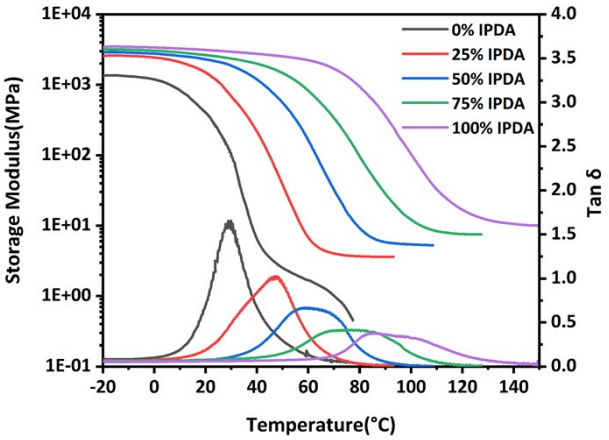

Fig. S4 DMA measurements for the epoxy-imine network polymers.

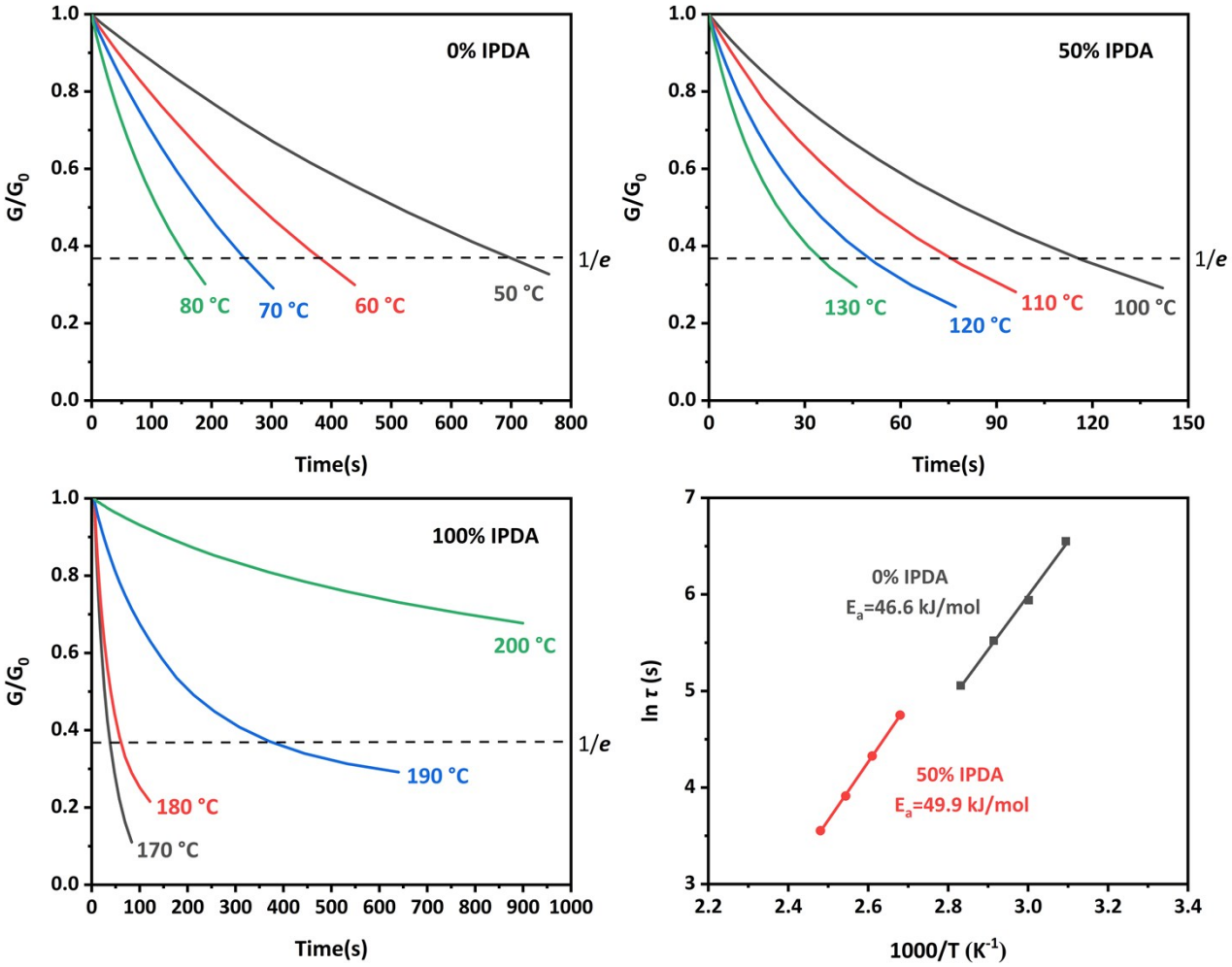

Fig. S5 Stress relaxation curves for 0% IPDA, 50% IPDA and 100% IPDA epoxy-imine network polymer, and calculation of the activation energy.

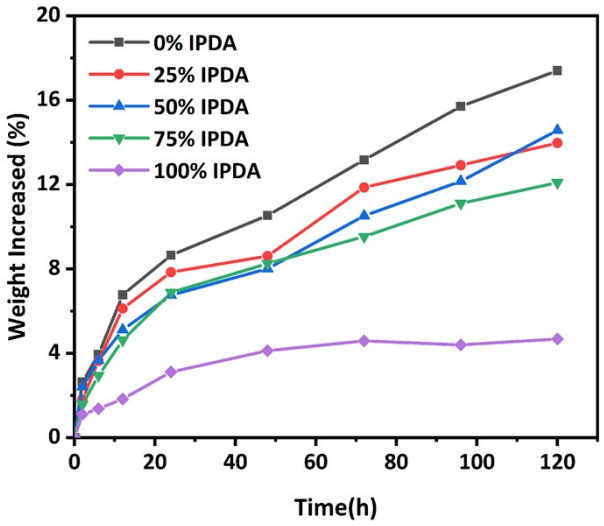

Fig. S6 Water absorption of the epoxy-imine polymers in 120 h.

Table S2 Average strength and elongation of the epoxy-imine polymers after each reprocessing generations.

Polymer	Strength (MPa)			Elongation (%)		
	1st gen	2nd gen	3rd gen	1st gen	2nd gen	3rd gen
0% IPDA	2.2±0.13	2.05±0.10	2.41±0.11	157±17	139±12	166±6
25% IPDA	5.1±0.4	5.4±0.3	5.2±0.4	247.5±9.5	230±10	219±12
50% IPDA	21.1±1.1	22.1±1.0	22.8±1.6	118±2	118±16	101±2
75% IPDA	43.1±3.2	45.9±0.1	45.3±1.2	7.9±0.2	8.2±0.5	9.2±0.4
100% IPDA	63.8±0.1	63.2±0.1	64.0±0.4	10.6±0.3	8.5±0.8	5.3±0.5

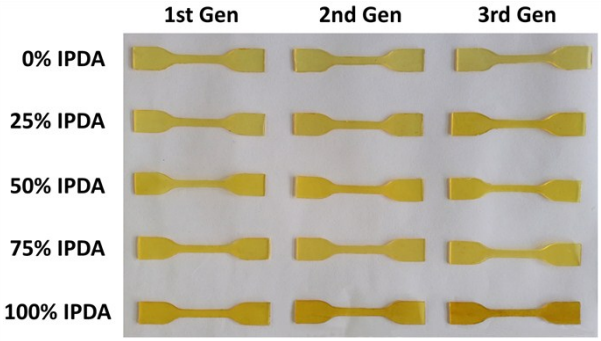

Fig. S7 Specimen of the epoxy-imine polymers after each reprocessing generations.

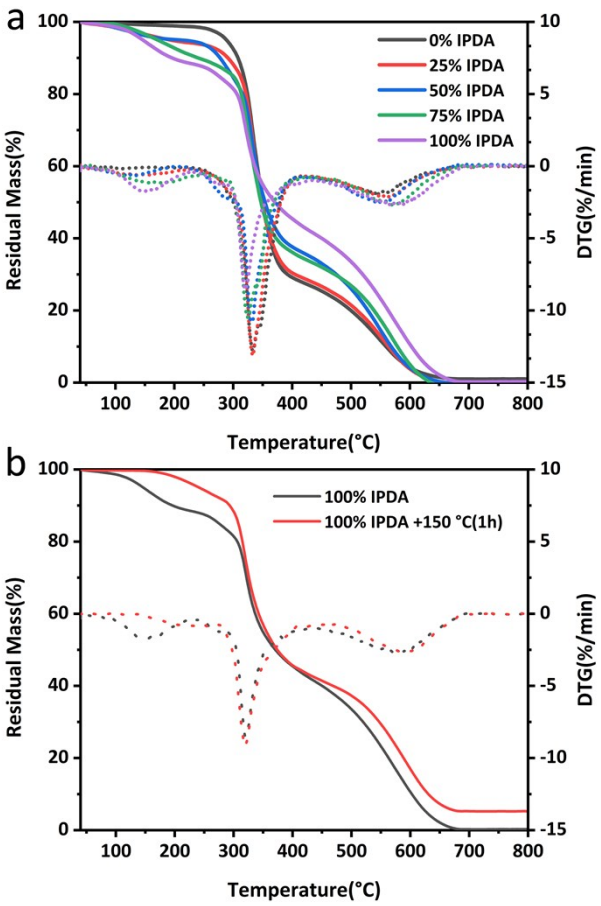

Fig. S8 (a)TGA curves of the epoxy-imine polymers; (b)TGA curves of 100% IPDA cured by method we adopted and 100% IPDA cured for another 1 h at 150 °C.

Fig. S9 Specimens of 100% IPDA prepared by hot pressing.

4 Characterizations for degraded products, monodispersed PS and composite film

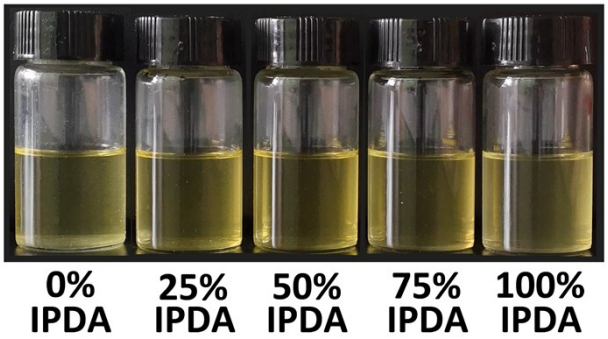

Fig. S10 Acid-degradation product solutions of epoxy-imine polymers with 10 wt% resin content.

Fig. S11 Appearance before and after acid-degradation process of 0% IPDA.

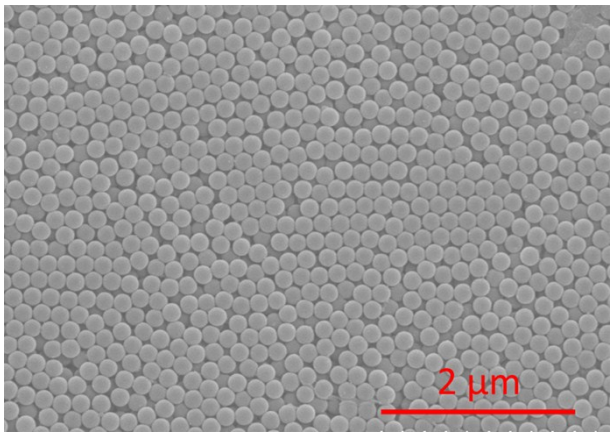

Fig. S12 SEM picture of monodispersed PS prepared.

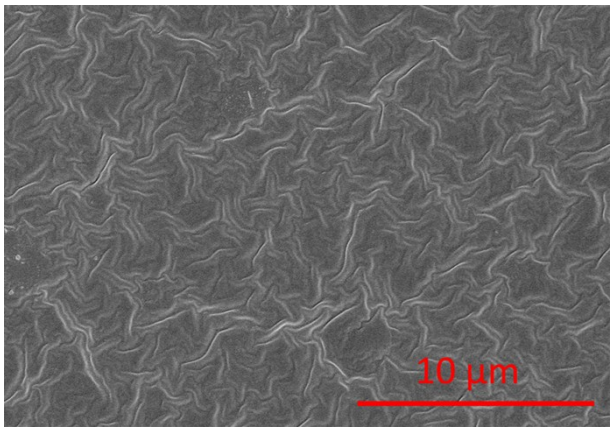

Fig. S13 SEM picture of the surface of the regenerated composite film.

1. M. Fache, R. Auvergne, B. Boutevin and S. Caillol, *European Polymer Journal*, 2015, **67**, 527-538.

2. M. Fache, A. Viola, R. Auvergne, B. Boutevin and S. Caillol, *European Polymer Journal*, 2015, **68**, 526-535.