The preparation of flame-retardant materials with complex shapes based on a dual-modulus network strategy

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Materials

Difunctional acrylate resin and pentafunctional acrylate resin monomers were purchased from Sartomer Guangzhou Chemical Co., Ltd., epoxy resin E51 was purchased from Nantong Xingchen Co., Ltd., tripropylene glycol diacrylate, 2,2-dimethoxy-2-phenylacetophenone, methanol, vinyl phosphate, and 2-ethyl-4-methylimidazole were purchased from Aladdin Industrial (Shanghai, China). All reagents were used directly without purification.

Characterization

Fourier transform infrared (FTIR) spectra were recorded using a Nicolet Magna 760 FTIR spectrometer produced by Nicolet Instrument Co., USA, in absorption mode with a resolution of 4 cm^{-1} and a wavelength range of 400 to 4000 cm^{-1}. 1H and 31P nuclear magnetic resonance (NMR) spectra were recorded using a 400 MHz AVANCE III HD spectrometer from Bruker, Germany, using D_2O as solvent. Non-isothermal DSC curves were recorded using a differential scanning calorimeter from METTLER TOLEDO, China, in a nitrogen atmosphere. Indium and zinc were used for calibration of temperature and enthalpy. The heating rate for DSC non-isothermal tests was 10°C/min. The curing kinetics of the EMI/EP and VPPA-EMI/EP systems were studied from 25–300°C at heating rates of 5°C, 10°C, 15°C, and 20°C per minute. X-ray photoelectron spectroscopy (XPS) analysis was performed on an AXIS ULTRA DLD spectrometer from SHIMADZU, Japan, using a monochromatized Al K-ray source (1486.6 eV photons). Dynamic mechanical analysis (DMA) was performed on a TA Q800 dynamic mechanical analyzer from TA, USA, at a frequency of 1 Hz and a heating rate of 3 °C per minute. The size of the sample for dynamic mechanical analysis was 10 mm × 10 mm × 2 mm. The surface morphology of the carbon residue of the sample was observed at an accelerating voltage of 20 kV using a scanning electron microscope (SEM, JEOL JSM 5900LV, Japan). Thermogravimetric analysis (TGA) was performed using a TG 209 F1 instrument (TG209F1 Instruments, Germany) at a nitrogen or air flow rate of 50 mL min−1. The sample (about 5 mg) was heated from 30 °C to 800 °C at a heating rate of 10 °C min−1. The tensile properties of the intermediate and final products of the acrylate-epoxy resin system were tested using an Instron 5965 universal material testing machine. During the test, pneumatic clamps were used to fix the specimens. The specimen sizes of the intermediate and final products were in accordance with the national standard GB/T 1042.2-2006. Type 5A specimens were selected. The tensile rate of the intermediate product was 5 mm·min-1, and the tensile rate of the final product was 1 mm·min-1. Each group of specimens was tested at least 3 times, and the average value was taken after the test. Limiting oxygen index (LOI) was evaluated by a JF-3 oxygen index meter (Jiangning Analysis Instrument Co.) according to ASTM D2863, with a sample size of 130 × 6.5 × 3 mm^3 . The UL-94 vertical burning rating was measured by a NK8017A apparatus (Nklsky Instrument Co., Ltd.) with a sample size of 130 × 13 × 3 mm^3 according to ASTM D3801. Combustion behaviors were evaluated by a FTT cone calorimeter (Fire Testing Technology) according to ISO 5660. The specimen with the dimensions of 100 × 100 × 3.0 mm^3 was tested under an external flux of 50 kW/m^2 . Thermogravimetric analysis/infrared spectrometry (TG-IR) was obtained from a Q5000IR TG instrument equipped with a Nicolet 6700 infrared spectrometer (Thermo Fisher Scientific) at a programmed heating rate of 10 °C/min from 30 to 800 °C under nitrogen conditions.

Table S1 Composition of single-component epoxy resin

Sample	EMI(g)	VPPA-EMI(g)	EP(g)
EMI-5/EP	5	/	100
VPPA-EMI-6/EP	/	6	100
VPPA-EMI-7/EP	/	7	100
VPPA-EMI-8/EP	/	8	100
VPPA-EMI-9/EP	/	9	100
VPPA-EMI-10/EP	/	10	100

Table S2 Composition of each system of Photo-thermal sequential curing

Sample	Di-functional acrylate resin(g)	Penta-functional acrylate resin(g)	tripropylene glycol diacrylate (g)	Photo-initiator (g)	Epoxy resin (g)	VPPA-EMI (g)	EMI (g)
A2-M8	17.1	1	1.9	0.4	80	/	4.0
A2-E8	17.1	1	1.9	0.4	80	5.6	/
A3-E7	25.7	1.4	2.9	0.6	70	4.9	/
A4-E6	34.2	2	3.8	0.8	60	4.2	/
A5-E5	42.7	3.5	3.8	1.0	50	3.5	/

Note: A2-M8 system is the flame retardant test comparison system

Table S3 Heat Release Value during Curing of VPPA-EMI-x/EP System Liquid Resin.

Sample	Mass (mg)	Total Heat Release (mJ)	Specific Heat Release (J/g)
VPPA-EMI-6/EP	15.20	5482.98	360.72
VPPA-EMI-7/EP	12.30	5222.76	424.61
VPPA-EMI-8/EP	12.00	4877.19	406.43
VPPA-EMI-9/EP	13.50	5288.90	391.77
VPPA-EMI-10/EP	14.20	5618.37	395.66

Table S4 Ti, Tp, and Tf Values during Curing of EMI-5/EP System at Different Heating Rates.

Heating Rate (℃/min)	Ti(℃)	Tp(℃)	Tf(℃)
5	97.95	109.17	113.15
10	110.15	121.32	124.64
15	116.37	127.93	131.98
20	121.60	136.50	139.02
Extrapolate	92.23	101.58	106.46

Table S5 Ti, Tp, and Tf Values during Curing of VPPA-EMI-7/EP System at Different Heating Rates.

Heating Rate (℃/min)	Ti(℃)	Tp(℃)	Tf(℃)
5	131.02	138.10	144.39
10	143.40	151.27	158.72
15	149.02	158.92	166.23
20	152.73	166.12	172.83
Extrapolate	126.34	130.68	137.34

Table S6 Heat Release Value during Subsequent Thermal Curing of Flexible Material after UV Curing.

Sample	Sample Mass (mg)	Epoxy Content in Sample (mg)	Total Heat Release (mJ)	Specific Heat Release (J/g)
A2-E8	12.00	9.60	4164.81	431.32
A3-E7	10.00	7.00	2836.53	405.22
A4-E6	8.50	5.10	2164.14	424.34
A5-E5	11.00	5.50	2310.99	420.18

Table S7 Ti, Tp, and Tf Values of Flexible Material during Curing at Different Heating Rates.

Heating Rate (℃/min)	Ti(℃)	Tp(℃)	Tf(℃)
5	128.62	142.14	172.25
10	141.81	157.84	193.42
15	150.66	168.33	203.04
20	154.93	175.49	218.17

Table S8 The Cone Calorimetry, LOI, and UL-94 data for A2-E8 and A2-M8

Sample	TTI (s)	THR (MJ/m^2)	PHRR (KW/m^2)	TSP (m^2)	TSR (m^2/m^2)	PCO_2PR （g/s）	PCOPR （g/s）	LOI (%)	UL-94
A2-E8	34	97.5	633.2	14.1	1579.3	0.28	0.11	24.8	No-rating
A2-M8	42	112.5	1259.3	14.4	1591.5	0.60	0.15	21.1	No-rating

Table S9 Thermogravimetric Data of A2-M8 and A2-E8 Rigid final Materials in Nitrogen Atmosphere.

Sample	T5wt%(℃)	Tmax(℃)	Char yield at 800℃(%)
A2-M8	346	431	2.39
A2-E8	314	389	18.15

Kissinger equation is shown as Eq. (1).

$$ln\frac{\beta}{T_P^2} = ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_P} \#Eq.(1)$$

Where β (K/min) represents the heating rate, Tp (K) represents the peak exothermic temperature, A represents the pre-exponential factor, and R (8.314 J·mol^{-1}·K^{-1}) represents the ideal gas constant.

Ozawa equation is shown as Eq. (2)

$$E_a = -\frac{R}{1.052} \times \frac{d\, ln\beta}{d\left(\frac{1}{T_P}\right)} \#Eq.(2)$$

Where β (K/min) represents the heating rate, and Tp (K) represents the peak exothermic temperature.

Derivation Equation of Rubber Elasticity Theory is shown as Eq. (3)

$$\nu_e = \frac{E'}{6RT} \#Eq.(3)$$

Where E'(0.1pa) is the storage modulus in the rubbery plateau region above Tg , R is the ideal gas constant, and T is the absolute temperature (K). To reach the rubbery plateau region, T is typically set to Tg+40℃.

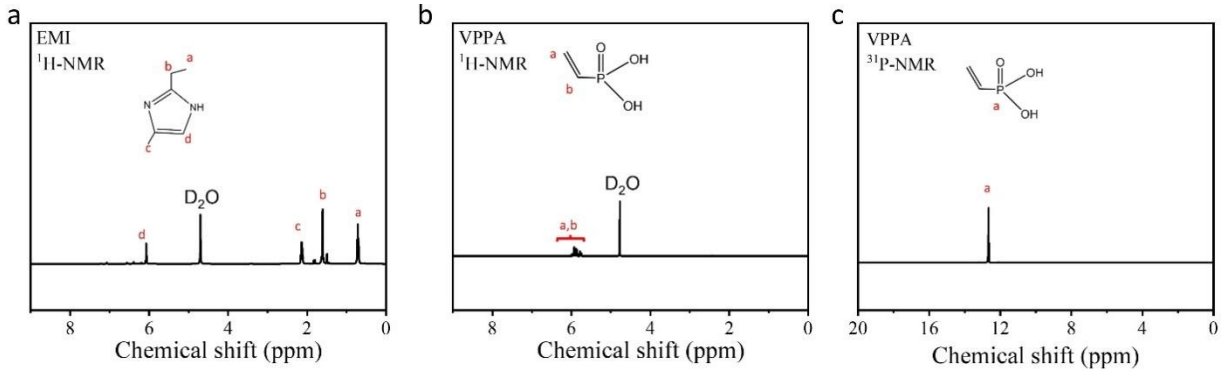

Fig.S1 (a) 1H-NMR of EMI;(b) 1H-NMR of VPPA;(c) 31P-NMR of VPPA

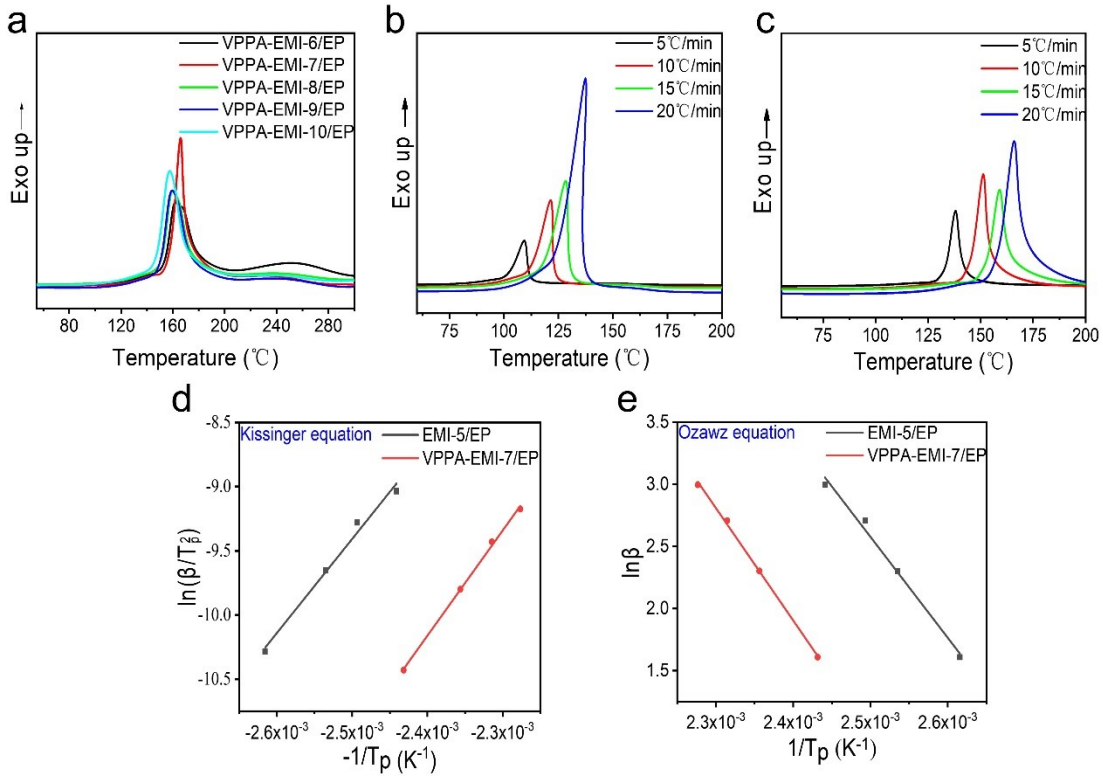

Fig.S2 (a) Non-isothermal DSC test graph of VPPA-EMI-x/EP system, heating rate is 20°C/min.; (b) Non-isothermal DSC test graph of EMI-5/EP system at 5℃/min, 10℃/min, 15℃/min, and 20℃/min; (c) Non-isothermal DSC test graph of VPPA-EMI-7/EP system at 5℃/min, 10℃/min, 15℃/min, and 20℃/min; (d) Fitting line of $ln\frac{\beta}{T_p^2}/-\frac{1}{T_P}$ in Kissinger equation; (g) Fitting line of $ln\beta/\frac{1}{T_P}$ in Ozawa equation

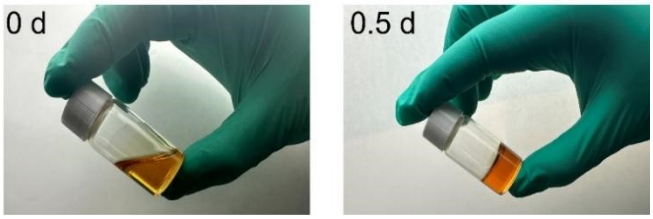

Fig. S3 Flowability of the EMI-5/EP System at Room Temperature.

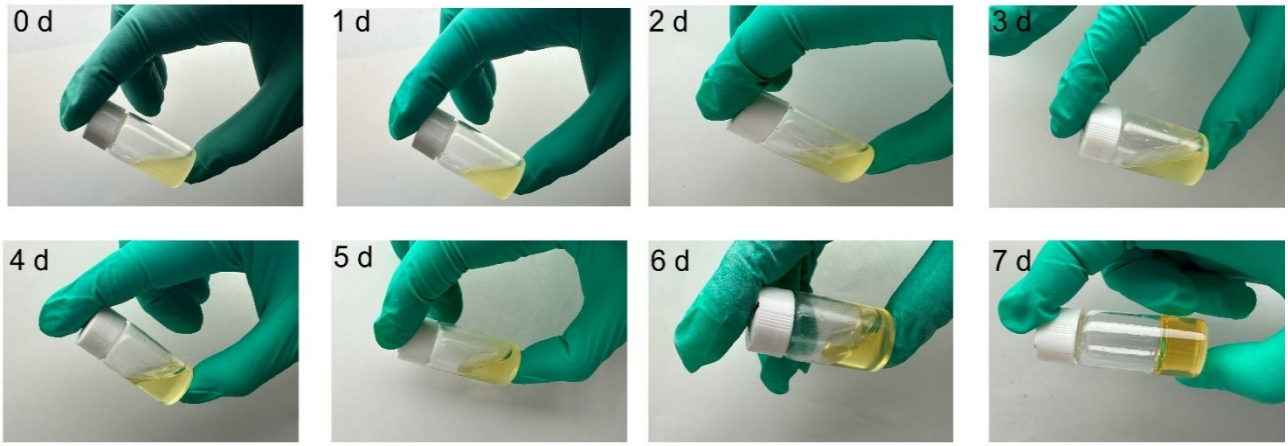

Fig. S4 Flowability of the VPPA-EMI-7/EP System at Room Temperature.

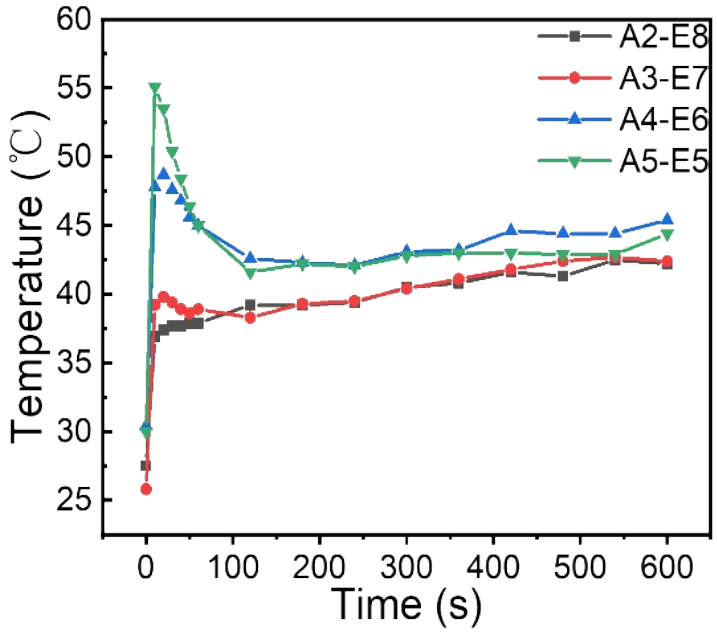

Fig. S5 Temperature vs. Time Curves for Various Systems during UV Curing.

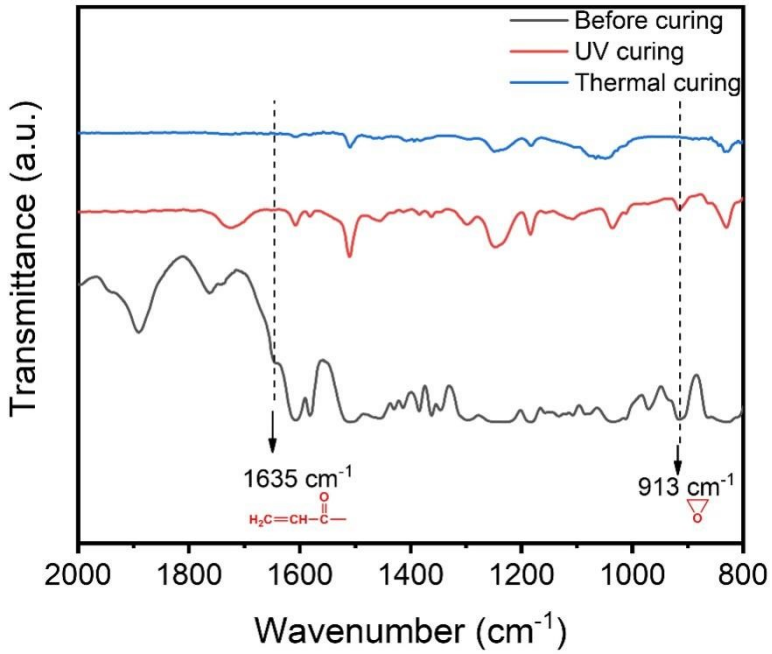

Fig. S6 FTIR spectra of A3-E7 before curing, after UV curing, and after thermal curing.

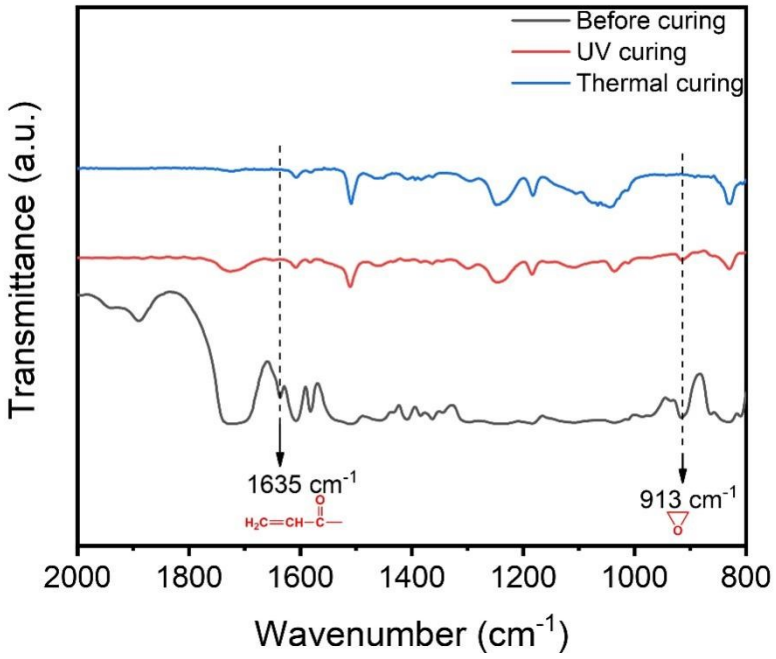

Fig. S7 FTIR spectra of A4-E6 before curing, after UV curing, and after thermal curing.

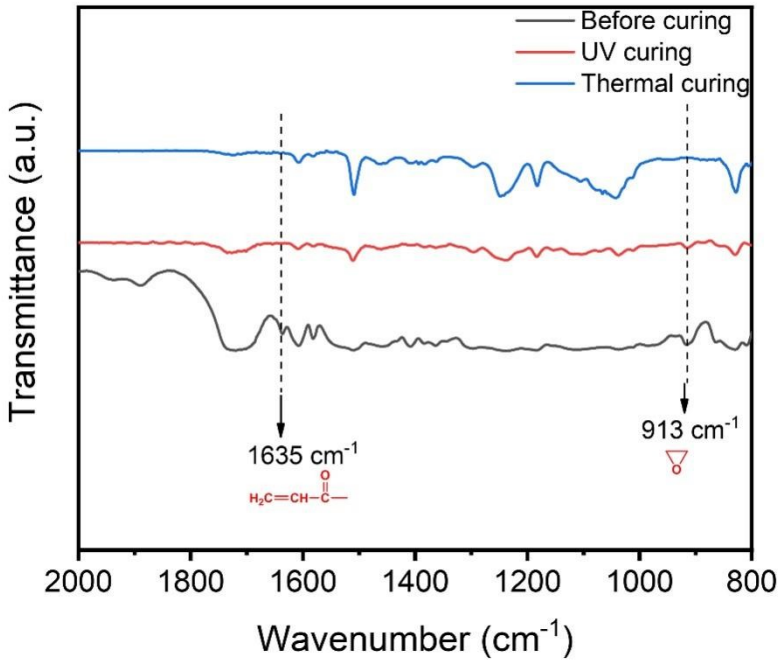

Fig. S8 FTIR spectra of A5-E5 before curing, after UV curing, and after thermal curing

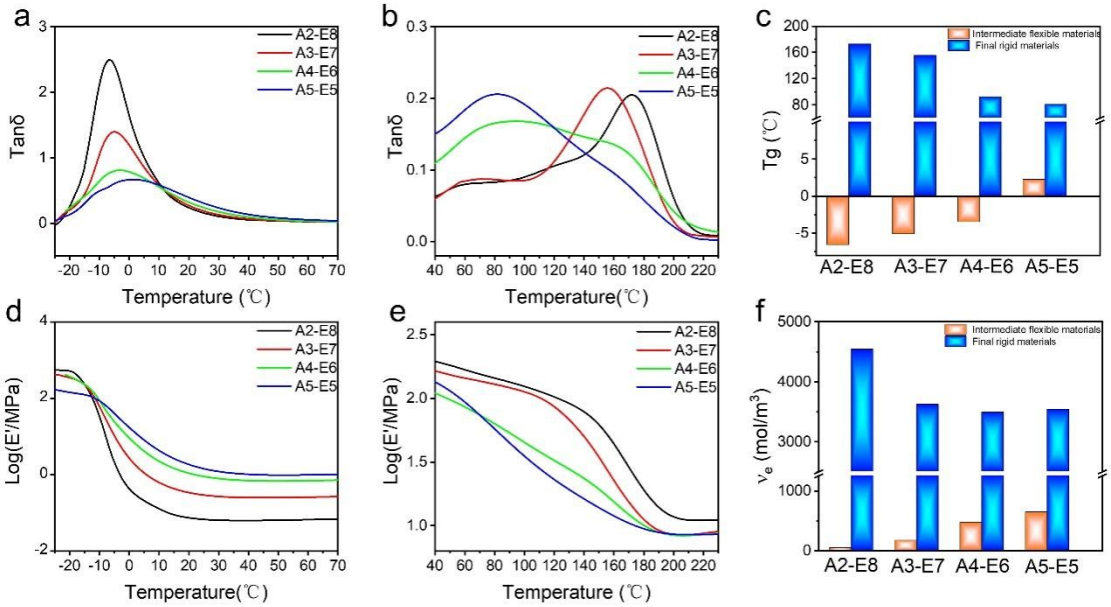

Fig. S9 (a) tanδ-T images of flexible intermediate materials in each system; (b) tanδ-T images of rigid final materials in each system; (c) Comparison of Tg of flexible materials and rigid materials; (d) Log$E^{'}$-T images of flexible intermediate materials in each system; (e) Log$E^{'}$-T images of rigid final materials in each system; (f) Comparison of crosslink density ν_e of flexible materials and rigid materials

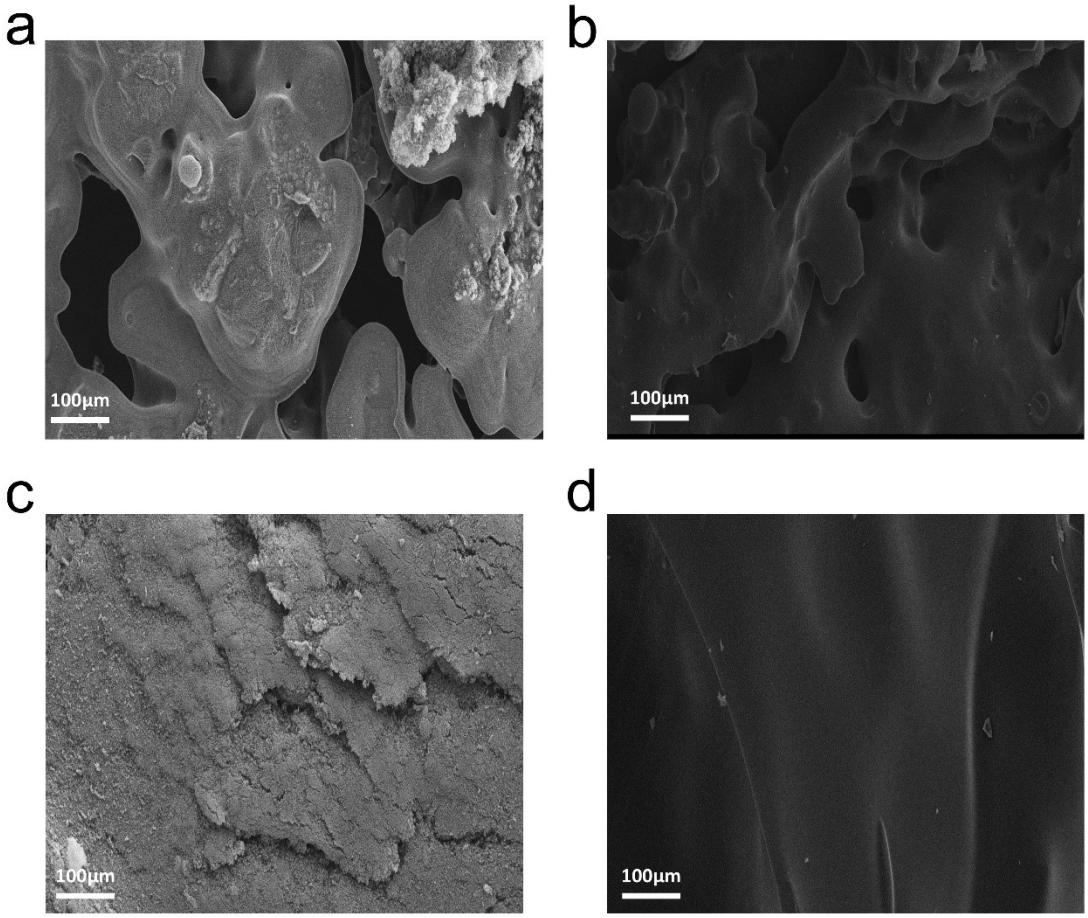

Fig.S10 (a)SEM image of the external surface of the residual carbon of the A2-M8 two-stage material after burning; (b) SEM image of the internal structure; (c) SEM image of the external surface of the residual carbon of the A2-E8 two-stage material after burning; (d) SEM image of the internal structure.