Supporting Information

γ Ray Driven Degradation in Robust Epoxy Thermosets

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Methods

Synthesis of γ-ray-responsive amine curing agents PIAD and PADA. The curing agents can be synthesized by aldimine condensation. A mixture of p-aminoacetophenone (5.05 g, 29 mmol), isophthalic dihydrazide (11.75 g, 87 mmol) and acetic acid (1 mL, catalyst) were stirred in water (500 mL) at 60 ºC for 6 h. The obtained powder was collected by filtration, washed with ethanol, and dried in a vacuum oven to give PIAD as a yellowish powder (91% yield, m.p.: 240 ºC). PADA (95% yield, m.p.: 220 ºC), a white powder, was obtained by the same synthetic method as that of PIAD by using adipic dihydrazide instead of isophthalic dihydrazide. The synthetic routes were illustrated in Figs. S1.

^{1}H NMR (400 MHz, DMSO-d_6, ppm, PIAD) δ: 10.70 (s, 2H), 8.34 (s, 1H), 8.16 – 7.88 (m, 2H), 7.60 (d, 4H), 7.36 (s, 1H), 6.86 – 6.35 (m, 4H), 5.54 (s, 4H), 2.25 (d, 6H).^{13}C NMR (100 MHz, DMSO-d_6, ppm, PIAD) δ: 163.34, 158.13, 151.01, 134.82, 130.88, 128.94, 128.32, 127.47, 125.43, 113.63, 14.77 ppm.

^{1}H NMR (400 MHz, DMSO-d_6, ppm, PADA) δ: 10.29 – 9.96 (m, 2H), 7.48 (t,4H), 6.54 (d, 4H), 5.41 (d, 4H), 2.65 (s, 1H), 2.30 (s, 1H), 2.13 (d, 6H), 1.63 (s, 4H).^{13}C NMR (100 MHz, DMSO-d_6, ppm, PADA) δ =175.08, 169.02, 154.14 – 146.70 (m), 127.74, 125.97, 113.68, 33.64, 26.83–23.51 (m), 13.83 ppm.

Preparation of γ-ray-degradable epoxy resins EP-PIAD and EP-PADA. DGEBA and the curing agents (PIAD, PADA, IPADH, AADH and DDM, respectively) were mixed according to the stoichiometric ratio of hydrogen on the amino groups and the epoxy groups of 1:1. Afterwards, the resulting viscous homogeneous liquid was poured into a metallic mold. EP-PIAD, EP-PADA and EP-DDM were prepared in an oven at 100 ºC for 2 h and postcured at 150 ºC for 2 h. The control samples EP-IPADH and EP-AADH were prepared in an oven at 160 ºC for 3 h.

In addition, a radical scavenger THQ was added to the epoxy thermosets to reduce the uncontrolled recombination and cross-linking of radicals. The added amount of THQ was 3 wt% of DGEBA. The curing process of the epoxy resins containing THQ (EP-PIAD-THQ or EP-PADA-THQ) was exactly the same as that of epoxy samples without THQ.

Mechanism of the bond cleavage using the model compound. BP was selected as a model compound to study the mechanism of γ-ray-induced degradation, which was attributed to the structural similarity between BP and γ-ray-responsive curing agents. The BP methanol solution (20 g/L, 30 mL) was irradiated at a dose rate of 20 kGy/h at room temperature. The total doses were 10 kGy, 20 kGy and 30 kGy, respectively. The degradation products were characterized by gas chromatography-mass spectrometry (GC-MS). ^{60}Co γ-ray irradiation facility (Technical Physics Institute of Heilongjiang Academy of Science) was used as an irradiation resource.

Characterization of γ-ray-induced degradation behaviors of epoxy resins. The cured epoxy resins (70 mg) were immersed in 5 mL of DMSO (no stirring was applied) and irradiated at room temperature with a dose rate of 0.67 kGy/h. The total irradiation doses of EP-PIAD and EP-PADA were 10 kGy, 20 kGy, 30 kGy and 40 kGy, respectively. In particular, the maximum irradiation doses of epoxy resins containing THQ were 30 kGy, and the maximum doses of EP-IPADH, EP-AADH and EP-DDM were 300 kGy. The degradation ratio was calculated using Equation (1).

$$\text{Degradation ratio (\%)} = \frac{m_d - m_0}{m_0} \times 100\% \quad (1)$$

where m_0 and m_d are the mass of the polymeric networks before and after degradation, respectively.

For dry state, the cured epoxy resins (dumbbell shape) were directly irradiated at room temperature with a dose rate of 0.67 kGy/h. The total doses of EP-PIAD and EP-PADA were 200 kGy, 300 kGy and 500 kGy, respectively. To directly demonstrate the degradation process of the thermosets in dry state, the irradiated samples (70 mg) were then immersed in DMSO (5 mL) at room temperature for 48 h to remove the degraded oligomers. The degradation ratio was calculated using Equation (1). ^{60}Co γ-ray irradiation facility (CNNC Isotope&Radiation (Changchun) Technology Co. Ltd.) was used as an irradiation resource.

Bond dissociation energy calculation. Density functional theory (DFT) calculations were performed using Gaussian Program. Geometry optimizations and frequency calculations were at B3P86/6-311G (d,p) level and all stationary points were characterized as minima on the basis of normal vibrational mode analysis. Solvent effect was estimated using SMD method with DMSO. Bond dissociation energy was calculated using following equation:

$$BDE_{A-B} = E_A + E_B - E_{A-B}.$$

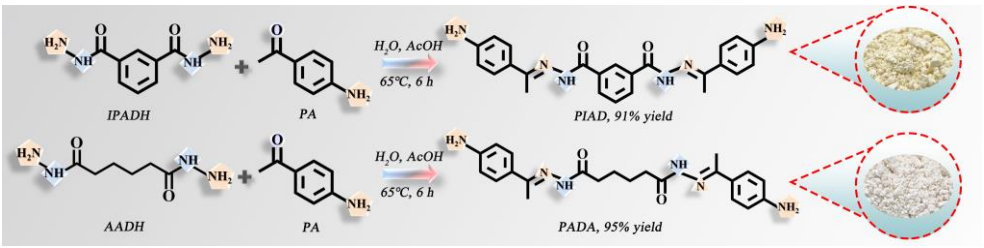
Preparation of carbon fiber reinforced composites CF-PIAD. PIAD (2.188 g) was added to a small plastic cup followed by DMSO (5 mL) and the resulting solution was a bit viscous and yellow in color. Then, DGEBA was poured into the small plastic cup with gentle mixing and the solution was stirred for 5 min at 80 °C. Three piece of plain-weave carbon fiber (5×5 cm) was added to the mould, and the mixed solution was allowed to poured into the mould. The resulting uncured composite was first heat precured and removed solvents for 2 h at 110 °C, followed by 2 h at 160 °C under 10 MPa pressure.

Recycling of the composites CF-PIAD. CF-PIAD (1.1 g, 35 wt% PIAD) was added to a plastic bottle with 10 mL DMSO solvent for γ-ray irradiation. The dose rate of irradiation was also 0.67 kGy/h. During degradation, CF cloths were taken out from the bottle after different doses, cleaned sequentially with acetone, dried at 50 °C for 2 h, and then performed analysis. ^{60}Co γ-ray irradiation facility (CNNC Isotope&Radiation (Changchun) Technology Co. Ltd.) was used as an irradiation resource.

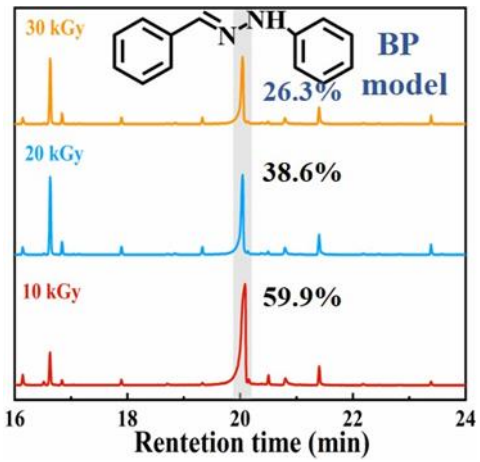
Materials. p-aminoacetophenone (PA), isophthalic dihydrazide (IPADH), adipic dihydrazide (AADH), 4,4-diaminodiphenylmethane (DDM), acetic acid, benzaldehyde phenylhydrazone (BP), benzaldehyde, methyl benzoate, benzophenone, benzaldehyde dimethyl acetal, N-benzylideneaniline and methylhydroquinone (THQ) were purchased from Aladdin-reagent Co., China. Epoxy resin (DGEBA, 0.51 of epoxy value) was supplied from Fenghuang Chemistry Co. Ltd. China. Dimethyl sulfoxide (DMSO) and other organic solvents were obtained from Sinopharm Chemical Reagent Co., Ltd., China.

Characterization. Fourier transform infrared spectra (FT-IR, Bruker, Tensor 27), ^{1}H and ^{13}C NMR (Bruker, AVF400, 400 MHz) were used to characterize the chemical structure of the curing agents and epoxy resins. Thermogravimetric analysis (TGA) was performed with a thermogravimetric analyzer (Netzsch STA449C) from 30 to 600 °C in Ar at a heating rate of 10 °C/min. Dynamic mechanical analysis (DMA) was carried out with a 01Db-metravib-DMA25 apparatus under the N_2 using a stretching mode. Glass transition temperature (Tg) was examined by heating the samples from 25 °C to 220 °C at a heating rate of 5 °C min^{-1}. Differential scanning calorimetry (DSC) was measured via a Mettler-Toledo Star 1 apparatus under a nitrogen atmosphere. The mechanical property of the cured epoxy samples was characterized via an Instron 5567 Electric Universal Testing Machine (Instron, America) at a cross-head speed of 2 mm/min. UV-accelerated aging tests of the epoxy resins were irradiated in an UV-accelerated aging box with the UV intensity of 800

W/m^2 at 50 °C. Hygrothermal aging tests of the epoxy resins were tested at a humidity level of 90% and a temperature of 60 °C. The mechanical samples of the composites with dimensions of 20 mm × 5 mm × 0.3 mm were measured. The degradation products of the model compound were analyzed on Gas chromatography-mass spectroscopy (Thermo DSQ-EI mass spectrometer). Scanning electron microscopy (SEM, SUPRA 55 SAPPHIRE Instrument) were used to investigate morphologies of epoxy resins, composites and the recycled carbon fibers at different irradiation doses. Raman spectra (Renishaw, England) and X-ray photoelectron spectroscopic (XPS, Thermo Scientiflc K-Alpha) was used to determine the changes of chemical structure of the recycled carbon fibers. Tensile properties of the recycled carbon fibers were tested according to ASTM D3379-75 standard on a Instron5500 R universal material testing machine at 1 cm min^{-1} loading speed and a valid gauge length of 2 cm. The test results were averaged from at least 50 pieces of carbon fiber and then were analyzed by the Weibull statistical method.

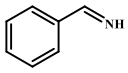
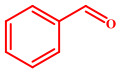


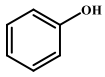
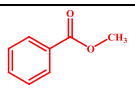
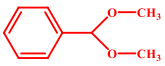
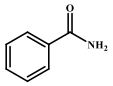
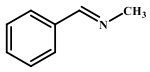
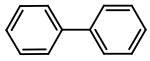
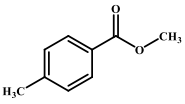
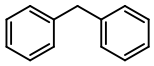
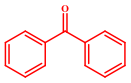
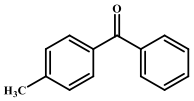
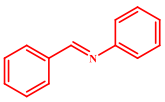
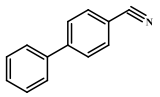
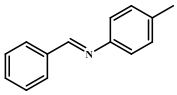
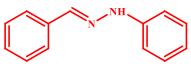
Figs. S1. Synthetic route of γ-ray-responsive curing agents PIAD and PADA.

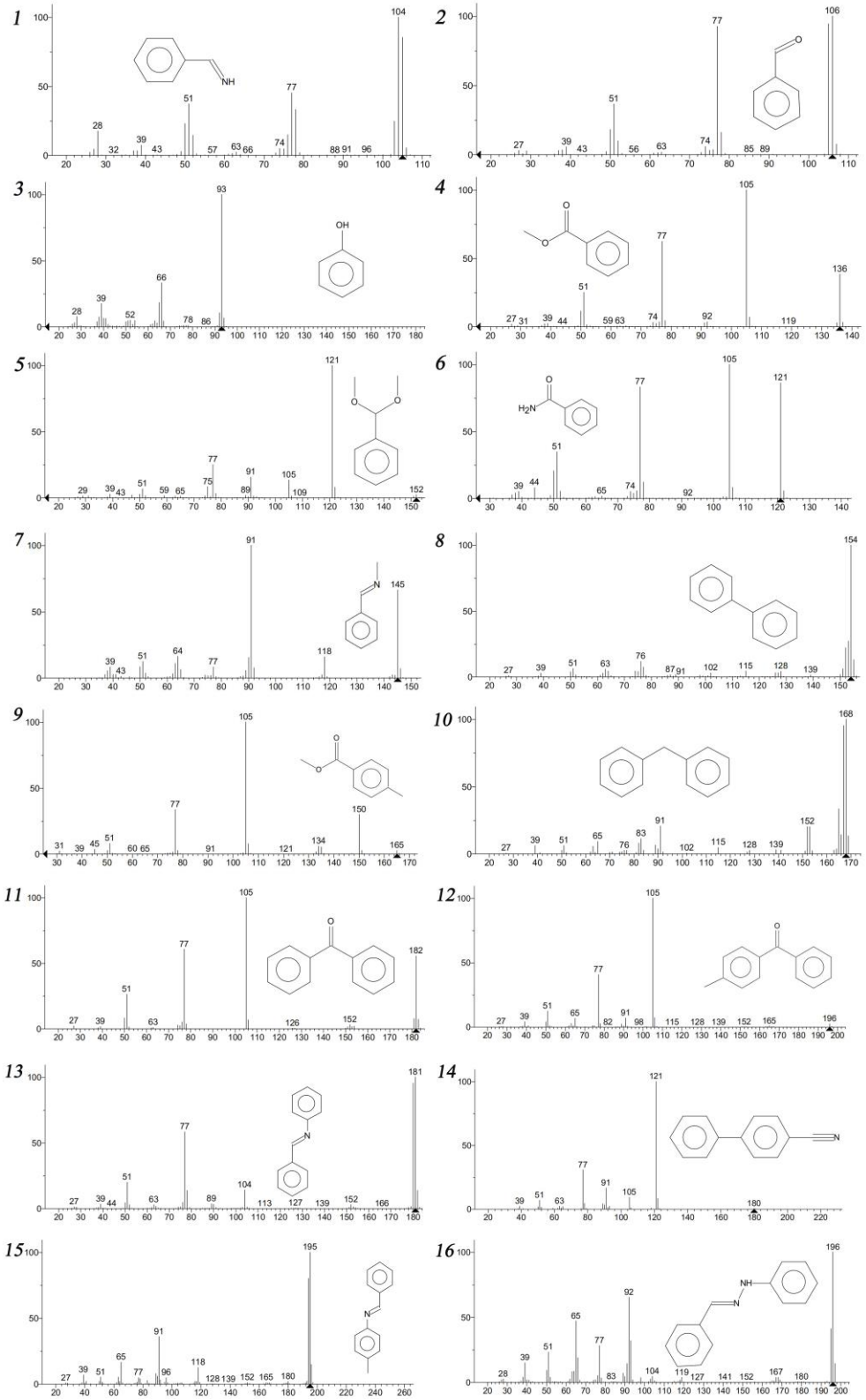


Figs. S2. Representative gas chromatography of BP at a dose of 10, 20 and 30 kGy, respectively.

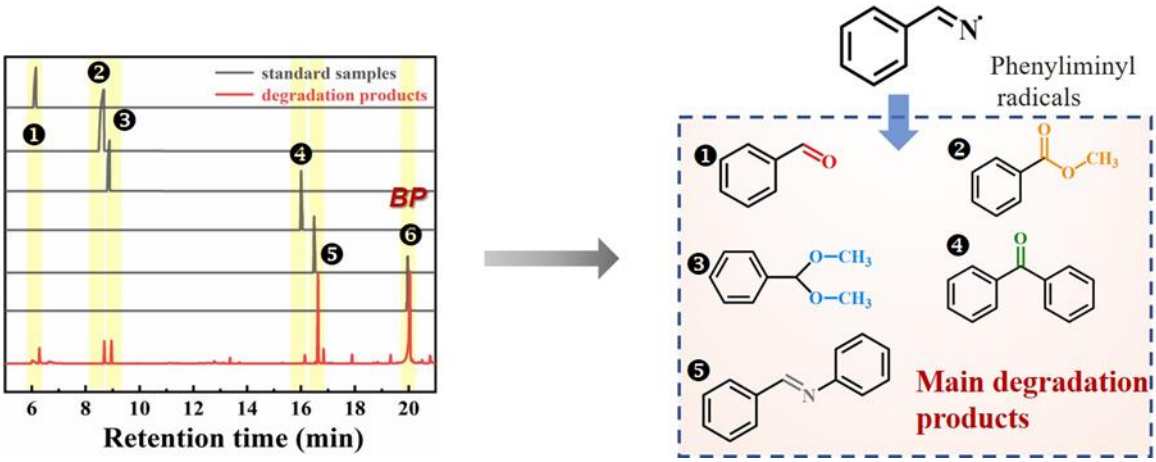
Table S1. The retention time, content, chemical structure of BP degradation products at a dose of 20 kGy.

	R.T (min)	% of total	Chemical structure		R.T (min)	% of total	Chemical structure
1	6.032	2.397%		2	6.284	3.607%	

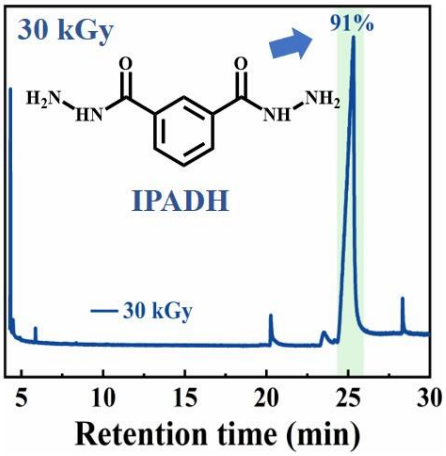
3	6.641	1.231%		4	8.697	4.466%	
5	8.958	4.049%		6	12.232	0.905%	
7	12.772	0.906%		8	13.016	0.123%	
9	13.363	1.141%		10	13.713	0.362%	
11	16.151	1.829%		12	16.526	0.315%	
13	16.639	20.705%		14	17.902	1.730%	
15	19.330	1.729%		16	20.044	38.639%	



Figs. S3. GC-MS of BP degradation products at a dose of 20 kGy.



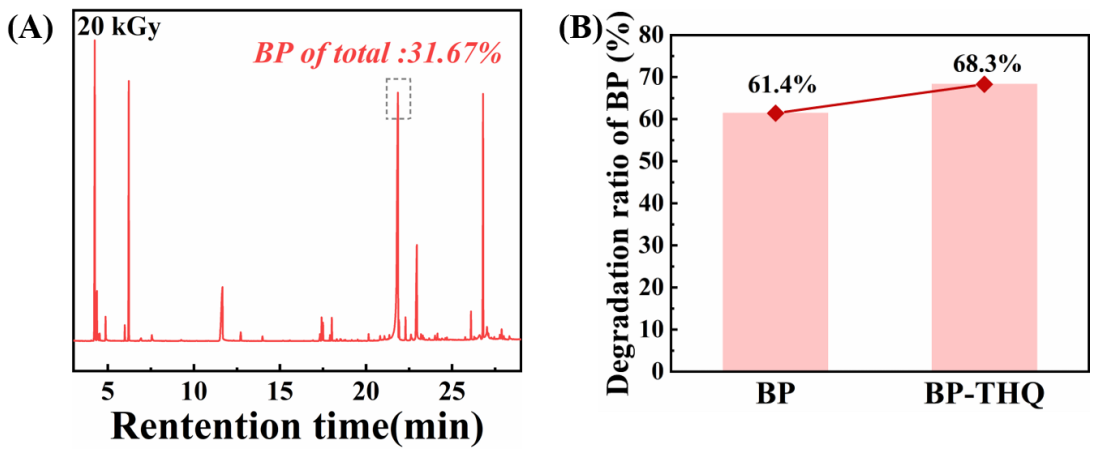
Figs. S4. GC analysis of several standard samples (pure compounds provided by Aladdin-reagent Co., China). The main products of BP at a dose of 20 kGy were then analyzed by comparing the retention time.



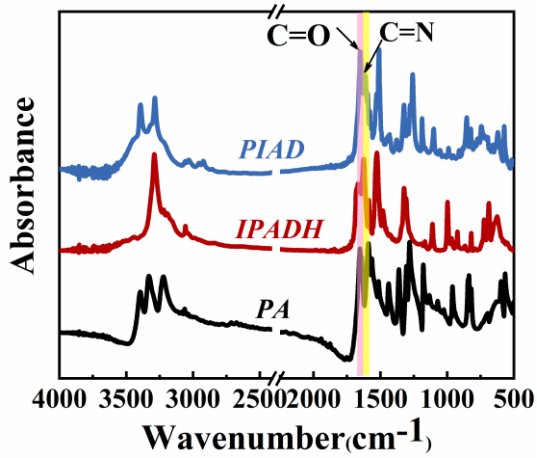
Figs. S5. Gas chromatography of small molecule IPADH at a dose of 30 kGy.

Bond dissociation energy (kcal mol^{-1})	
C-C	113.3
N-N	53.3
C-N	90.5

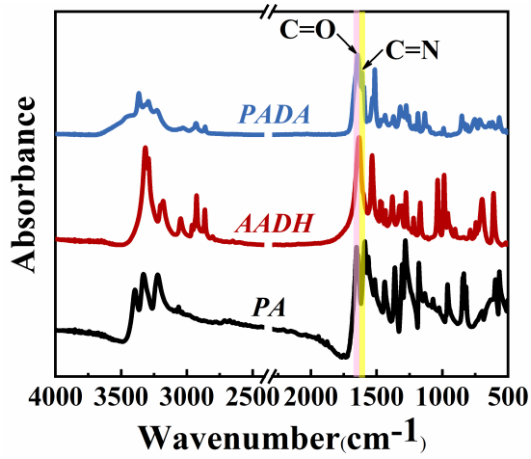
Figs. S6. Bond dissociation energy of C-C, C-N and N-N bond for model compound BP.



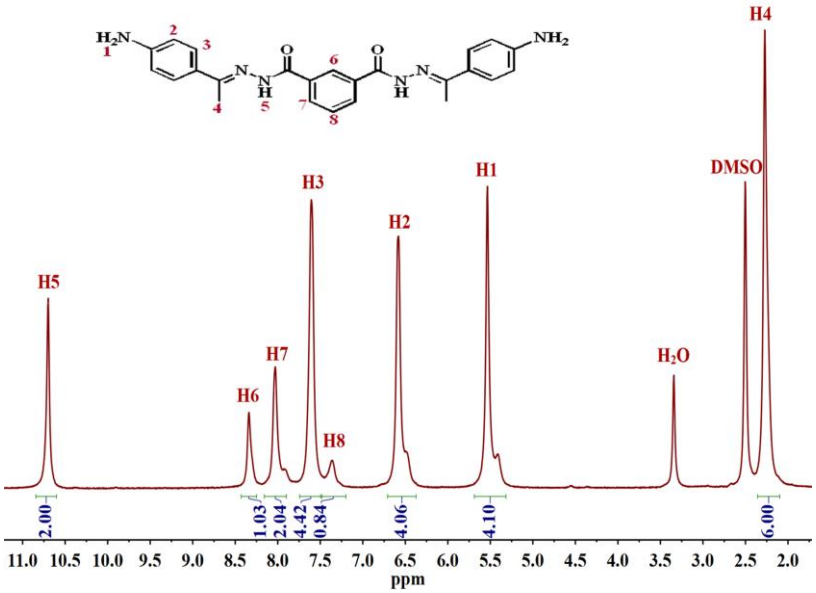
Figs. S7. (A) Representative gas chromatography of the BP-THQ mixed solution at a dose of 20 kGy. (B) The comparison of BP content (20 g/L, 30 mL) of BP solution and BP-THQ solution at a dose of 20 kGy.



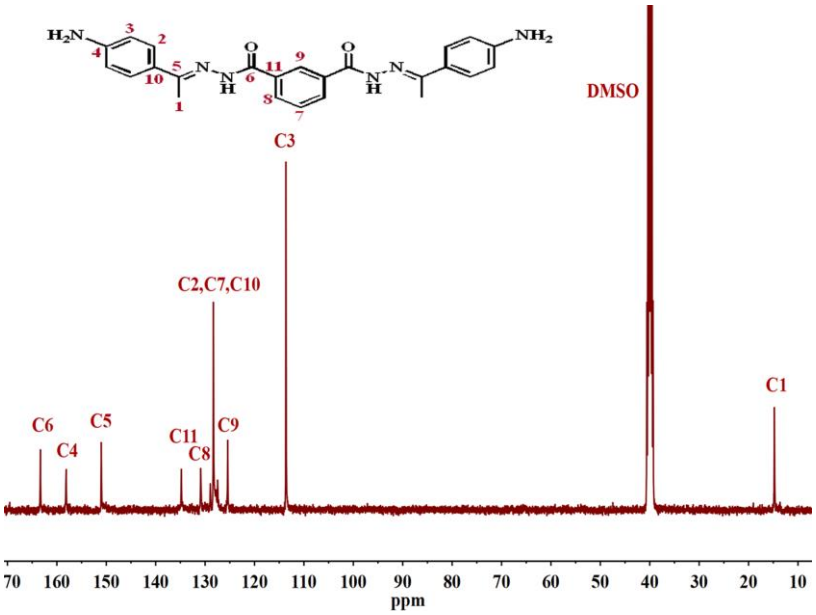
Figs. S8. FT-IR spectra of γ-ray-responsive curing agent PIAD.



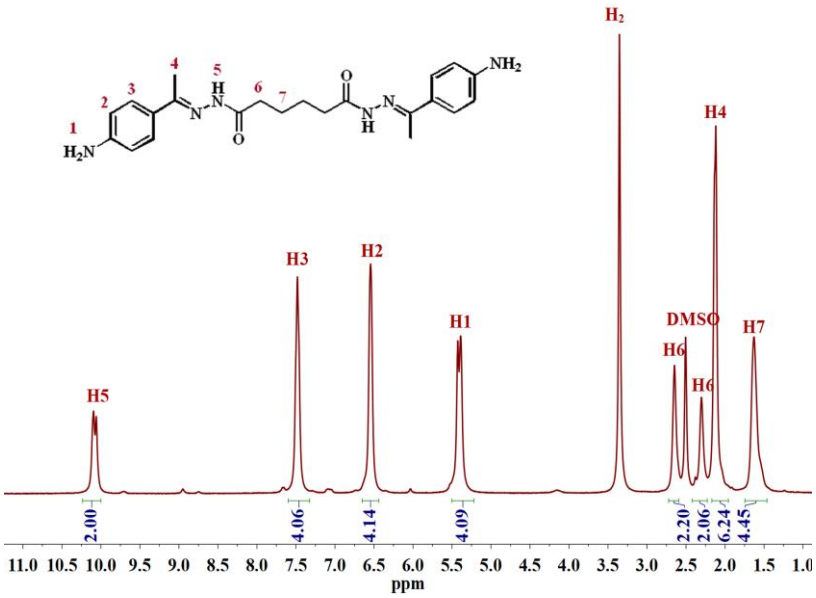
Figs. S9. FT-IR spectra of γ-ray-responsive curing agent PADA.



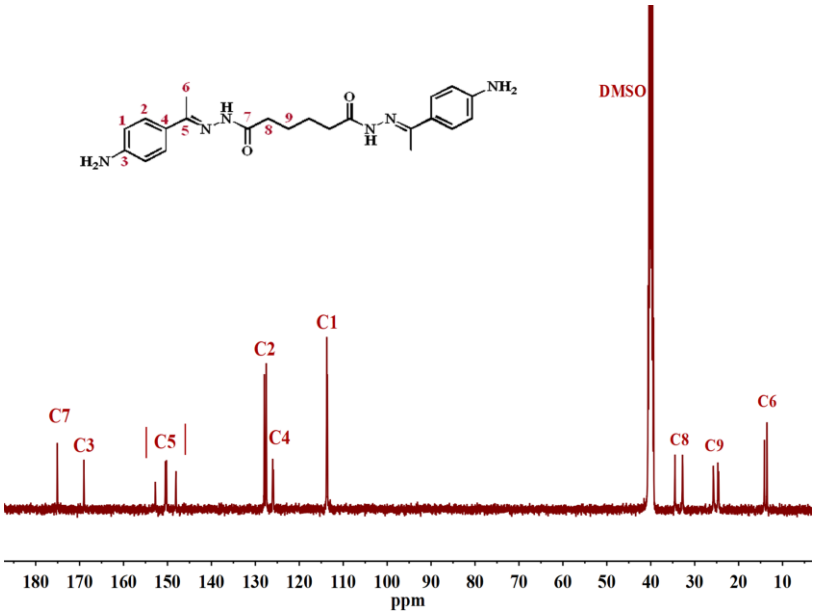
Figs. S10. [1]H NMR spectra of γ-ray-responsive curing agent PIAD.



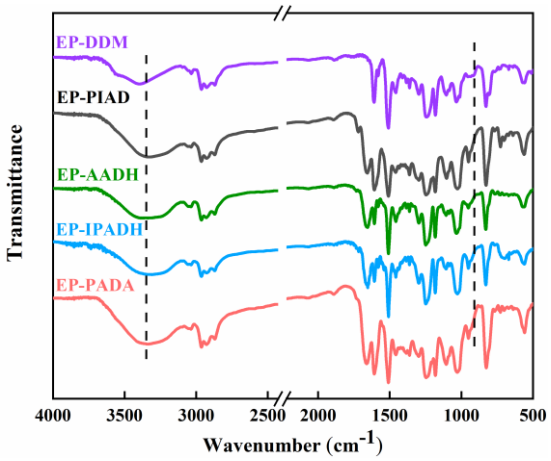
Figs. S11. [13]C NMR spectra of γ-ray-responsive curing agent PIAD.



Figs. S12. [1]H NMR spectra of γ-ray-responsive curing agent PADA.



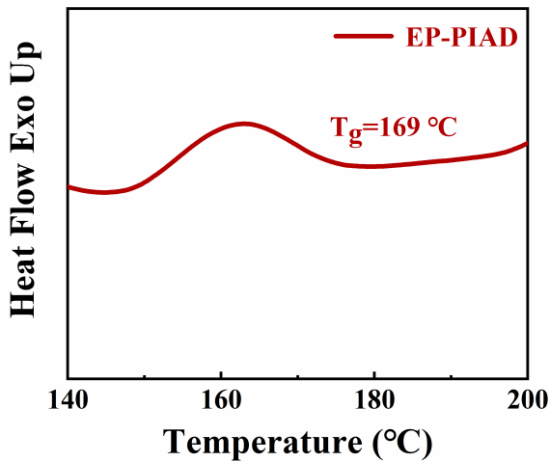
Figs. S13. [13]C NMR spectra of γ-ray-responsive curing agent PADA.



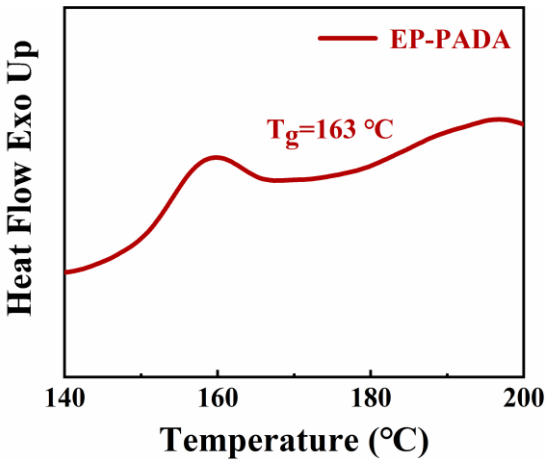
Figs. S14. FT-IR spectra of the several cured epoxy resins.

Table S2. The mechanical properties, thermal stabilities, glass transition temperature (T_g) of all epoxy thermosets.

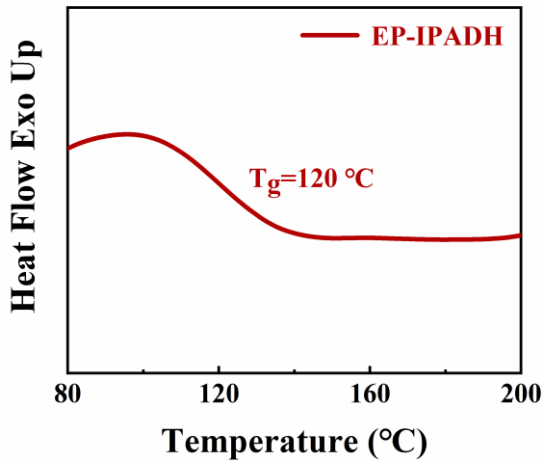
Sample	Tensile stress (MPa)	Young's modulus (MPa)	Elongation at break (%)	T_g		$T_{d5\%}$	$T_{d30\%}$
				DSC	DMA		
EP-PIAD	79±5	2742±302	5.6±0.4	169	180	335	387
EP-PADA	76±6	2292±295	6.5±0.2	163	180	318	383
EP-IPADH	69±8	1840±276	4.6±0.6	120	132	285	355
EP-AADH	68±6	1664±204	4.7±0.5	121	138	284	353
EP-DDM	75±3	2052±281	6.2±0.4	156	154	382	400
HexFlow RTM6	75	-	-	215		300	-



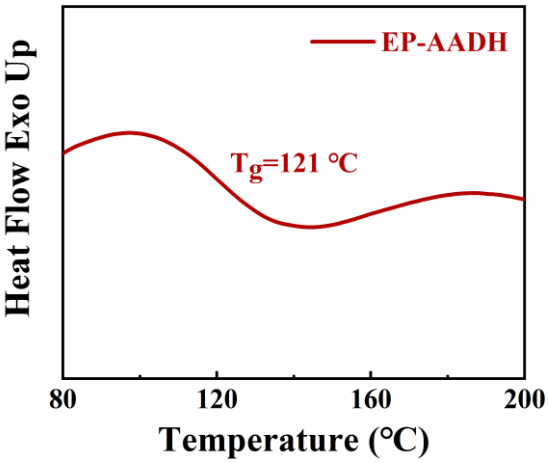
Figs. S15. DSC curve of the cured epoxy resins EP-PIAD.



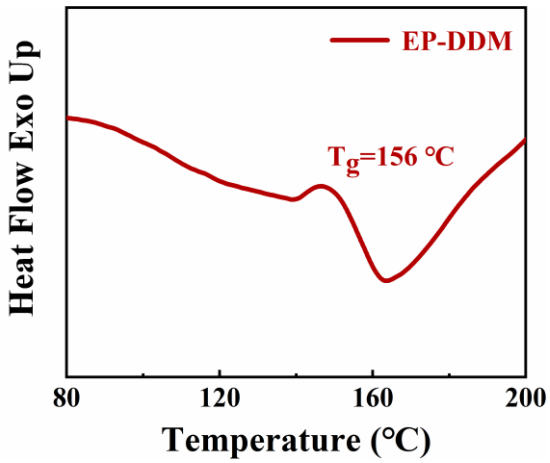
Figs. S16. DSC curve of the cured epoxy resins EP-PIAD.



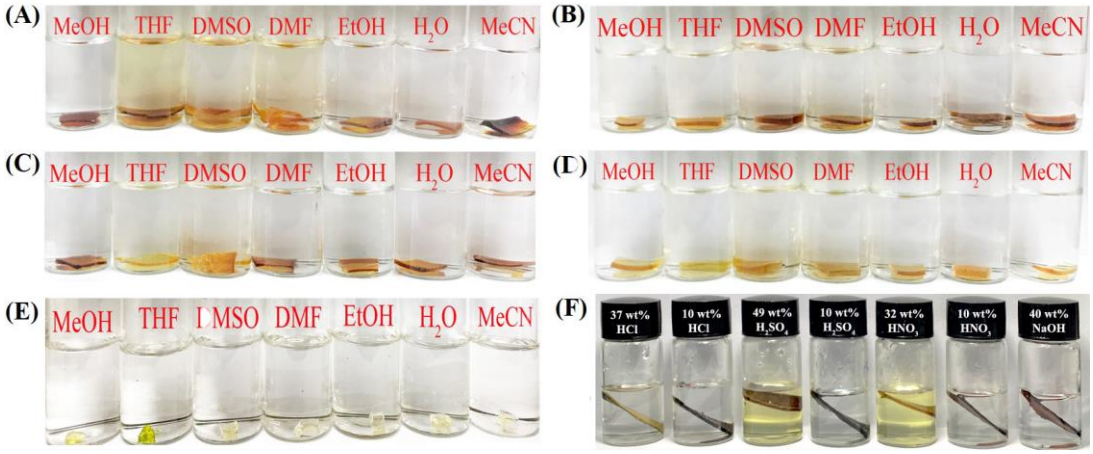
Figs. S17. DSC curve of the cured epoxy resins EP-PIAD.



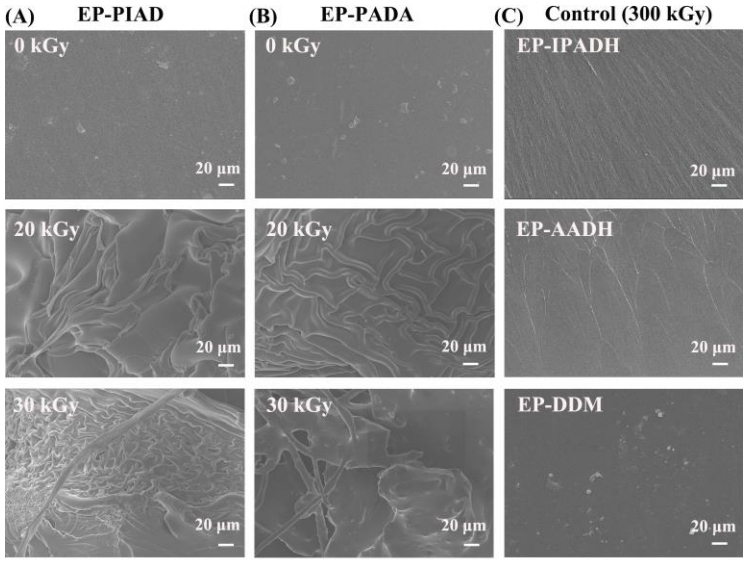
Figs. S18. DSC curve of the cured epoxy resins EP-PIAD.



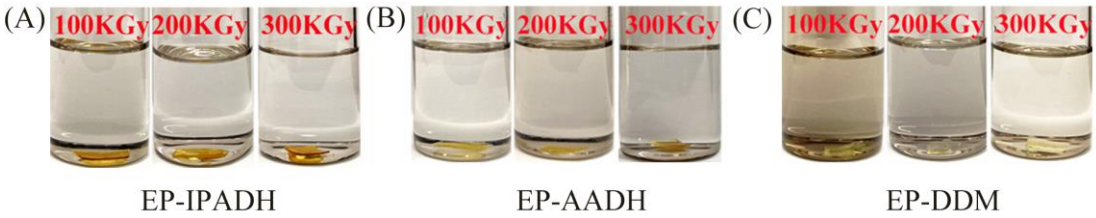
Figs. S19. DSC curve of the cured epoxy resins EP-PIAD.



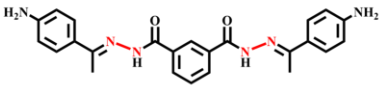
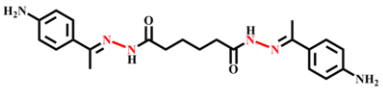
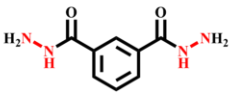
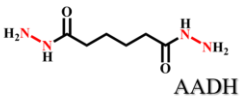
Figs. S20. Solvent resistance of all epoxy thermosets in different solvents at 60 °C for 3 days. (A) EP-PIAD (B) EP-IPADH (C) EP-PADA (D) EP-AADH (E) EP-DDM. (F) Photographs of EP-PIAD in different media for 3 days at room temperature.



Figs. S21. SEM analysis of degradation process for all the epoxy thermosets in DMSO solution. (A) SEM images of EP-PIAD with different irradiation dose. (B) SEM images of EP-PADA with different irradiation dose. (C) SEM images of the control (EP-IPADH, EP-AADH and EP-DDM) at a dose of 300 kGy.



Figs. S22. Photographs of the epoxy resins of the control groups in DMSO media after exposure to γ ray (100~300 kGy).

N-N bond dissociation energy	In the solvent free system (kcal mol^{-1})	In the DMSO solvent (kcal mol^{-1})
 PIAD	64.5	61.6
 PADA	58.3	57
 IPADH	69.2	70.8
 AADH	73.7	74.4

Figs. S23. N-N bond dissociation energy of PIAD, PADA, IPADH and AADH by DFT analysis.

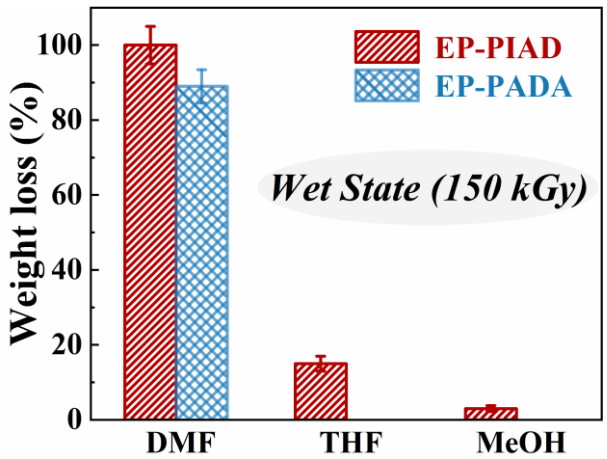
Table S3. The swelling ratio of the samples to various solvents at 60 °C for 3 days.

Samples	DMSO	DMF	THF	Methanol
EP-PIAD	64.2%	54.0%	52.0%	8.2%
EP-PADA	60.6%	49.1%	50.8%	7.6%
EP-IPADH	46.1%	31.6%	45.9%	2.3%
EP-AADH	51.2%	32.4%	37.3%	1.8%
EP-DDM	52.7%	31.9%	40.1%	6.5%

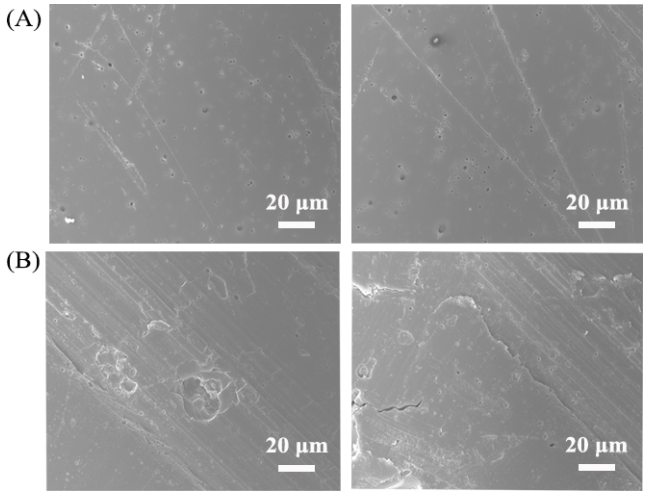
The swelling ratio of the cured resins was calculated based on Equation (1):

$$\text{Swelling ratio (\%)} = \frac{m_s - m_0}{m_0} \times 100\% \quad (1)$$

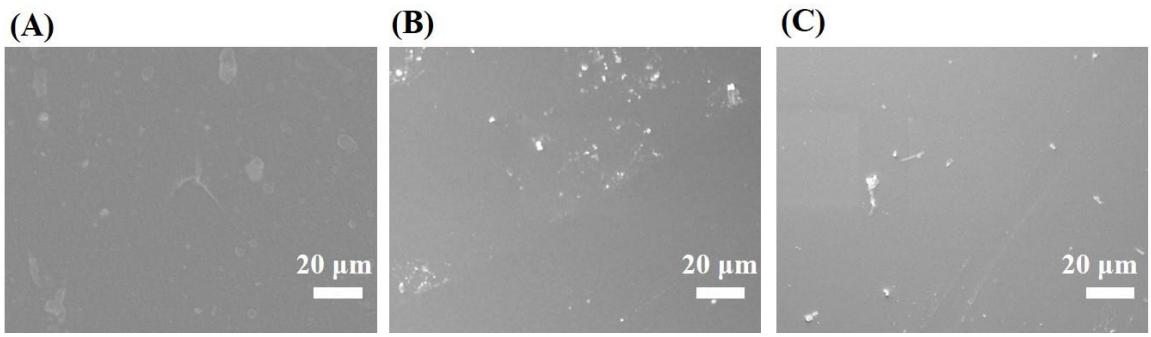
where m_0 is the mass of the epoxy samples before swelling, m_s is the mass of the epoxy samples at swelling equilibrium.



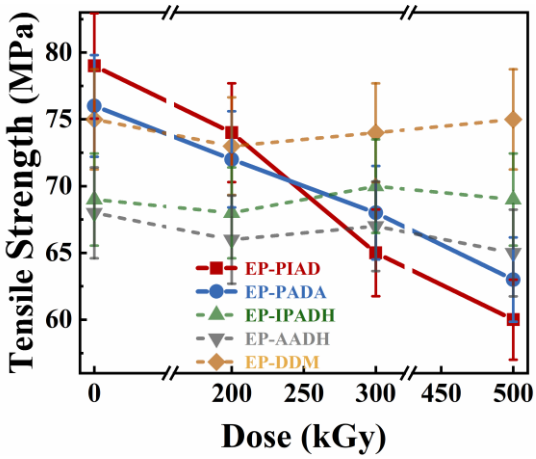
Figs. S24. Analysis of degradation process for the epoxy thermosets EP-PIAD and EP-PADA. After a dose of 150 kGy in other solvents, the resins were taken out and immersed in DMSO for 48 h.



Figs. S25. SEM images of degradation process for EP-PIAD and EP-PADA in dry state (solvent free). After a dose of 300 kGy in solvent free, the resins were immersed in DMSO for 48 h and were tested for SEM. (A) EP-PIAD, (B) EP-PADA.



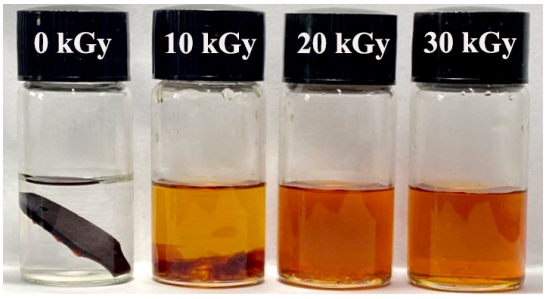
Figs. S26. SEM images of the control groups in dry state after a dose of 500 kGy. (A) EP-IPADH (B) EP-AADH (C) EP-DDM.



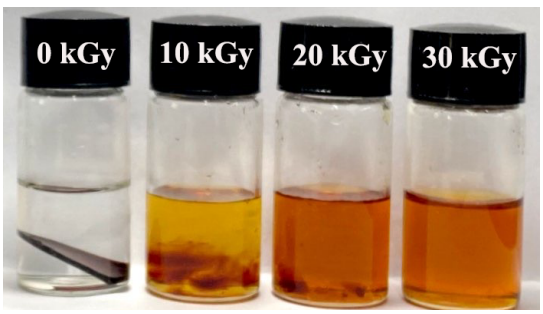
Figs. S27. The variation of the tensile strength of the epoxy thermosets in dry state with irradiation dose ranging from 0 to 500 kGy.

Table S4. The mechanical properties of EP-PIAD and EP-PADA with various irradiation doses in the solvent free system.

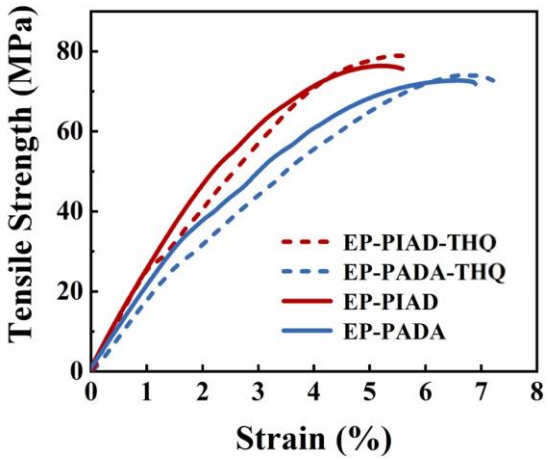
EP-PIAD	Tensile stress (MPa)	Young's modulus (MPa)	Elongation at break (%)
Original sample	79±5	2742±302	5.6±0.4
200 kGy	73±2	2676±290	4.0±0.3
300 kGy	69±4	2309±336	3.6±0.1
500 kGy	63±6	2076±310	2.9±0.4
EP-PADA	**Tensile stress (MPa)**	**Young's modulus (MPa)**	**Elongation at break (%)**
Original sample	76±6	2292±295	5.7±0.2
200 kGy	70±3	1986±259	4.4±0.3
300 kGy	65±5	1745±226	3.5±0.3
500 kGy	60±6	1672±340	2.8±0.2



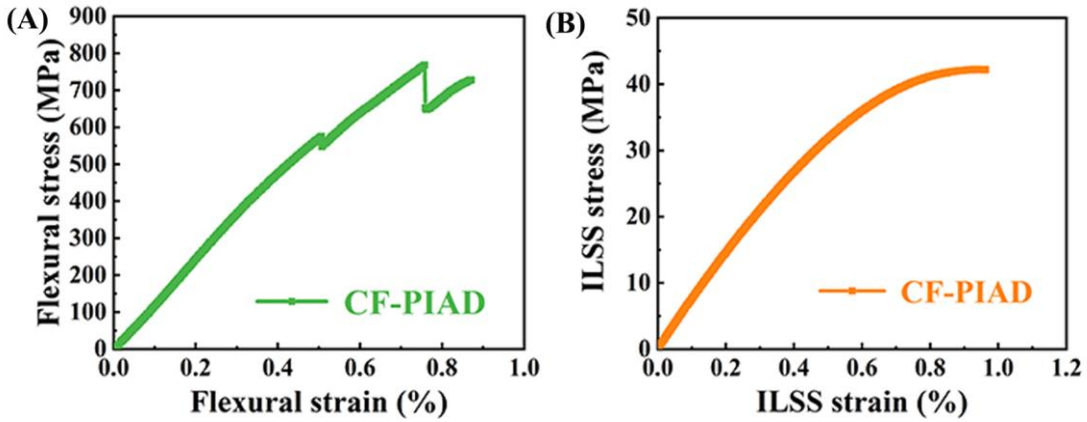
Figs. S28. Photographs of the epoxy resins EP-PIAD-THQ in DMSO media before (0 kGy) and after exposure to γ ray (10~30 kGy).



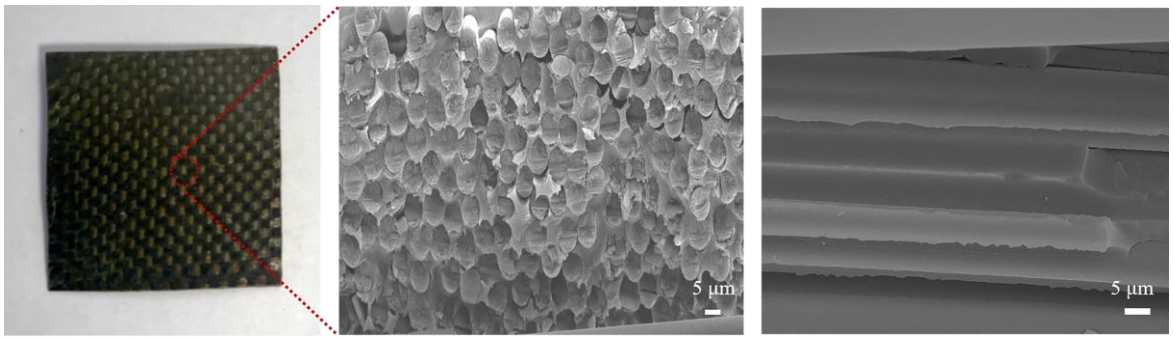
Figs. S29. Photographs of the epoxy resins EP-PADA-THQ in DMSO media before (0 kGy) and after exposure to γ ray (10~30 kGy).



Figs. S30. Representative tensile strength–strain curves of EP-PIAD-THQ and EP-PADA-THQ.

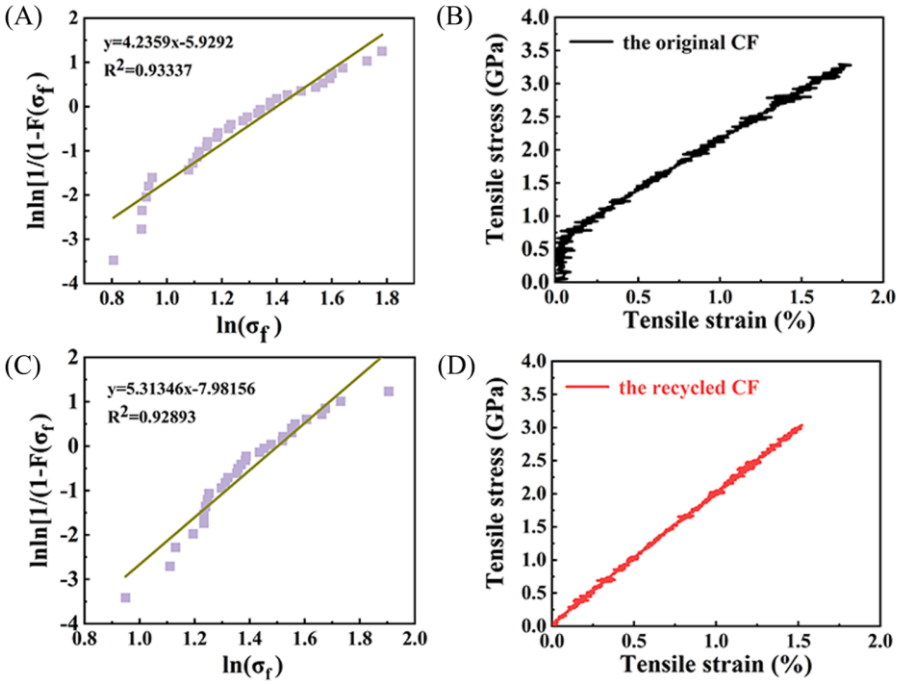


Figs. S31. (A) The representative flexural stress–strain curve of the composites CF-PIAD. (B) The representative interlaminar shear stress–strain curve of the composites CF-PIAD.



Figs. S32. Photographs and cross-cut SEM images of the composites CF-PIAD.

Figs. S33. Photographs and SEM images of the recycled CF at different irradiation doses.



Figs. S34. The Weibull distribution of tensile strength and representative monofilament tensile stress-strain curves of (A) the recycled CF and (B) the original CF.