

Supporting Information for

Cleavage of C-N Bonds in carbon fiber/epoxy resin composites†

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Experimental Section

Preparation of epoxy resin (EP), and carbon fiber/epoxy resin (CF/EP) composites.

EP was bisphenol-A diglycidyl ether (DGEBA) cured with 4,4-methylene dimethyl cyclohexylamine, which is the most representative and widely used epoxy resin. The detailed preparation of EP is as follows: DGEBA was cured with cyclohexylamine with a weight ratio of 100:35 at 80°C for 1h, followed by vacuum degassing and heating at 160°C for 8h. The chemical structure of bisphenol-A diglycidyl ether, 4,4-methylene dimethyl cyclohexylamine, and EP are provided in the Figure S1 in the Supporting Information.

EP was used as the matrix for the preparation of CF/EP composites. CF/EP composites were moulded by using the VARTM process.

Decomposition of EP and CF/EP composites.

The decomposition of EP and CF/EP composites was tested in a Teflon-lined autoclave with a content of 50ml. In each test run, a 30ml of zinc chloride solution was added. After the decomposition of EP, the curing agent part in EP was dissolved in the ZnCl₂ solution, while the remaining decomposed products of EP were solid, which were above the aqueous ZnCl₂ solution and on the wall of the autoclave. In the cases of CF/EP composites, CFs was below the aqueous ZnCl₂ solution. CFs was collected and washed by acetone for three times. The solid decomposed products of EP, which floated on the top of the reaction solution, were collected, followed by a pretreatment process. Specifically, the solid decomposed products of EP were washed with distilled water repeatedly and then dissolved in acetone. The saturated Na₂CO₃ aqueous solution was then added to eliminate the ZnCl₂ in the decomposed products. This process was repeated for several time until the ZnCl₂ was totally eliminated. After filtration and evaporation, the solid inclusion-free and Zn-free degradation products of EP were obtained. These solid decomposed products of EP weight more than 90wt% of the virgin EP, and they can be directly recycled as the curing agent for preparation of EP. Hence, EP can be recycled with a yield of more than 90 wt% by using concentrated ZnCl₂ solution.

Preparation of epoxy resins using recycled EP as curing agent.

The inclusion-free and Zn-free degradation products of EP obtained after the decomposition were directly recycled as the curing agent, and were mixed with fresh 4,4-methylene dimethyl cyclohexylamine with a weight ratio ranging from 0 to 20wt%. The curing agent composed of recycled EP and fresh 4,4-methylene dimethyl cyclohexylamine was mixed with DGEBA with a weight ratio of 35:100 to make new cured epoxy resins at 80°C for 6h, followed by vacuum degassing and heating at 160°C for 8h.

Characterization methods

GPC analysis was performed on an UltiMate3000 Gel Permeation Chromatography with a mobile phase of tetrahydrofuran at a flow rate of 1ml/min. FT-IR characterization was carried out on an EQUINOX-55 spectrometer. The relative contents of C, H, O, Zn and N in original EP, swollen EP, and solid degradation products of EP were analysed by a vario EL CUBE elemental analyser. Particularly, ICP analysis was carried out both on the solid decomposed products of EP collected directly after the degradation, and those after pretreatment (detailed in the above **Decomposition of EP and CF/EP composites**). The content of zinc was detected by a Thermo iCAP 6300 inductively coupled plasma atomic emission spectrometer. The surface structures of recycled CFs and CFs without sizing were characterized by an XploRA Raman spectrometer. The compositions of solid decomposed products of EP were analyzed by NMR and GC. NMR analysis was carried out on a Bruker AVANCE III 400 MHz

spectrometer operating at 100-MHz ^{13}C frequency. The XPS analysis was tested by AXIS ULTRA DLD X-ray photoelectron spectroscopy. The carbon fibers surface was studied by a JEOL JSM-7001Felectron microscopy. The single-fiber tension strength was measured in an LLy-06E equipment. The crosshead speed of the MTS material testing system was 0.5 mm/min. The impact strength of the recycled cured epoxy resins (using recycled epoxy resin as the curing agent) was evaluated by a XJ charpy impact testing machine.

Figure S1. The chemical structures of DGEBA, curing agent, and EP.

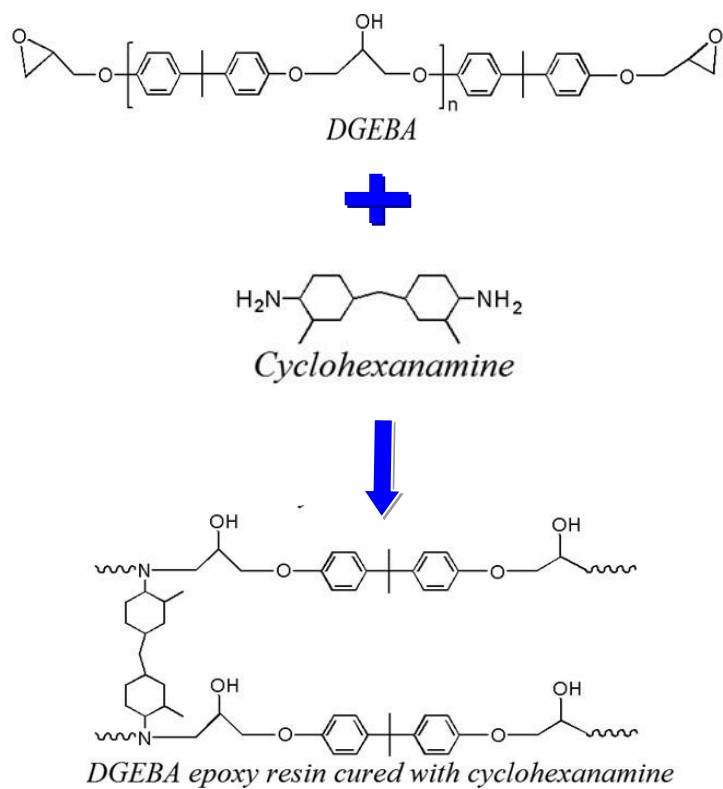


Figure S2. The degradation product distributions of EP.

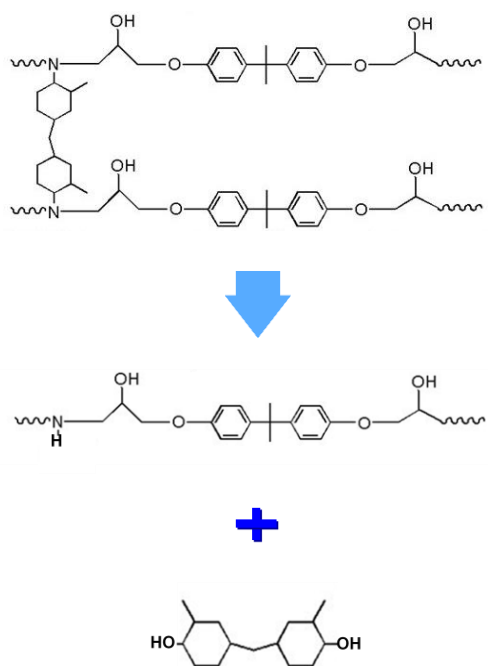


Figure S3. The average molecular weight of the degradation products of EP (10x10x3 mm) analyzed by GPC after degradation in the 60wt% zinc chloride solution at 220°C for (a) 6 hours, (b) 12 hours, (c) 24 hours, and (d) 48 hours.

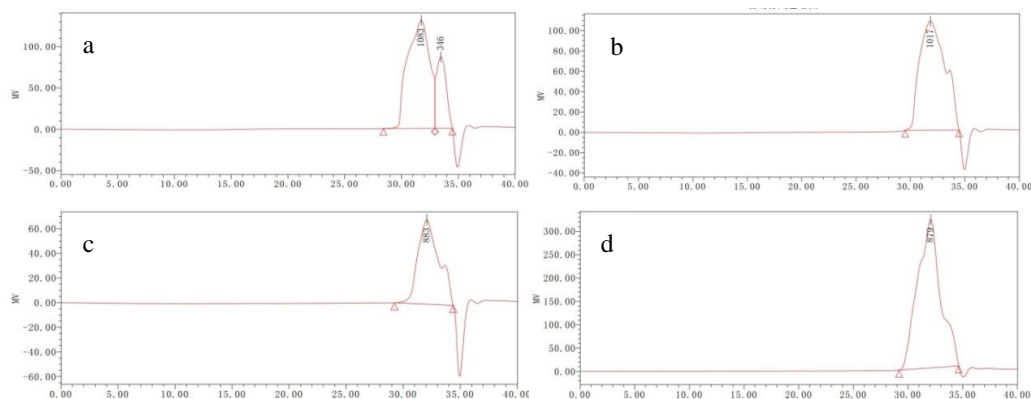
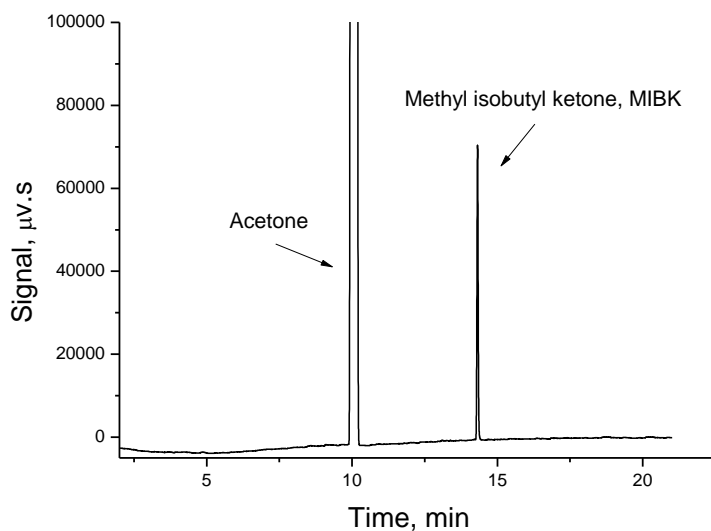
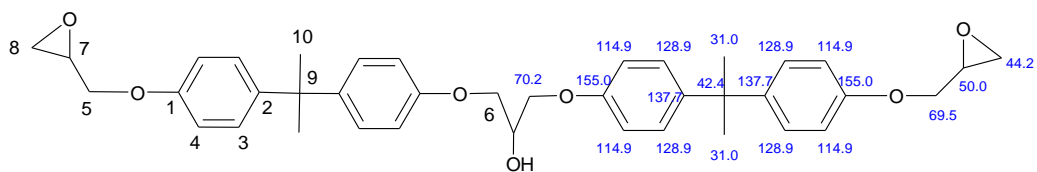


Figure S4. The GC graph of solid decomposed products of EP.



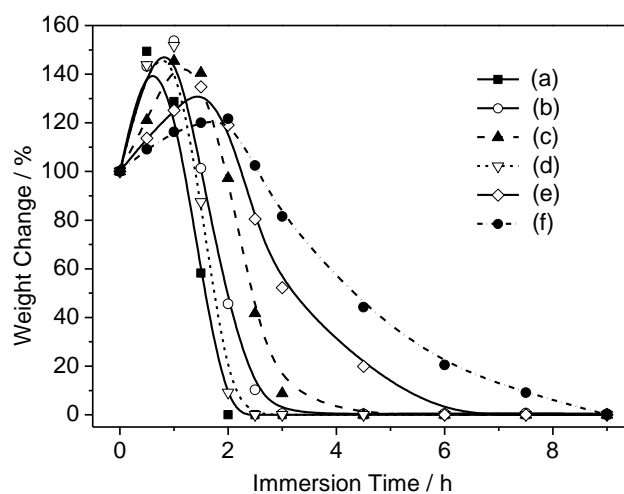
0.1 g of the solid decomposed products of EP was dissolved in 50 ml acetone, then 0.01 ml methyl isobutyl ketone (MIBK) was added as a internal standard. As can be seen in the Figure S5, GC is agile and capable of detecting the trace amount of MIBK. No peaks were detected expect for the peaks that represent for acetone and MIBK. Therefore, no small volatile molecules existed in the solid decomposed products of EP.

Figure S5. The representations of signal 1 to signal 10 in NMR graph of BGEBA.



Signals 1 to 10 in the NMR graph correspond to 1 to 10 atom sites in bisphenol A molecule. Specifically, signals 1, 2, 3 and 4 are corresponding to the four carbon atoms in the benzene ring of bisphenol A, signals 5 and 6 represent the carbon atoms in the $-\text{CH}_2-$ groups that connect to the oxygen atoms, 7 and 8 signals correspond to the two carbon atoms in the epoxy group of bisphenol A, and signals 9 and 10 represent the quaternary carbon and the carbon in the $-\text{CH}_3$ group, respectively. The degradation of EP for 9 hours caused the disappearance of signals 7 and 8, indicating the breakdown of the epoxy group in the bisphenol A.

Figure S6. The weight changes of CF/EP composites with a size of (a) $10 \times 5 \times 3 \text{ mm}^3$; (b) $10 \times 10 \times 3 \text{ mm}^3$ and (c) $10 \times 10 \times 6 \text{ mm}^3$ and EPs with a size of (d) $10 \times 10 \times 3 \text{ mm}^3$; (e) 23.5 mm^3 and (f) $0.01\text{-}0.087 \text{ mm}^3$. Reaction conditions: 30 ml of 60 wt% ZnCl_2 aqueous solution, $220 \text{ }^\circ\text{C}$.



The initial mass increase of CF/EP composites was caused by the swelling of EP. Both swelling and degradation rates were faster for samples with smaller sizes. It is deduced that EP degradation is a liquid-solid reaction and its reaction rate is affected by mass transfer rate. To verify this hypothesis, decomposition of EPs with different sizes were performed (Figure S5d-S5f in ESI). Smaller EPs decomposed more rapidly. A faster degradation of EP in CF/EP composites than EP alone with the same size further proves this hypothesis, as more pores exist among layers of CF/EP composites. These pores enlarge the contact area of EP with IC Zn^{2+} ions.

Figure S7. Raman spectra of (a) Virgin CFs; (b) CFs treated in water at 220°C for 3 hours; and Recovered CFs after recycling at 220°C for 3 hours in (c) 40wt%, (d) 50wt% and (e) 60wt% zinc chloride aqueous solution.

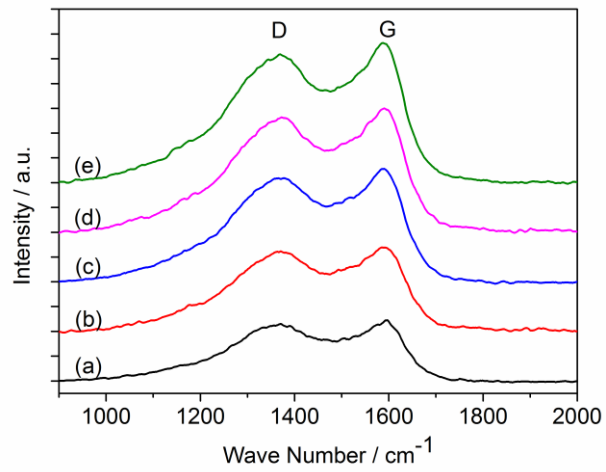


Figure S8. SEM images of (a) virgin CFs, recovered CFs after decomposition in 60 wt% ZnCl_2 solution for 3 h at (b) 220 °C and (c) 210 °C, and (d) recovered CFs after decomposition in 50 wt% ZnCl_2 solution for 3 h at 200 °C.

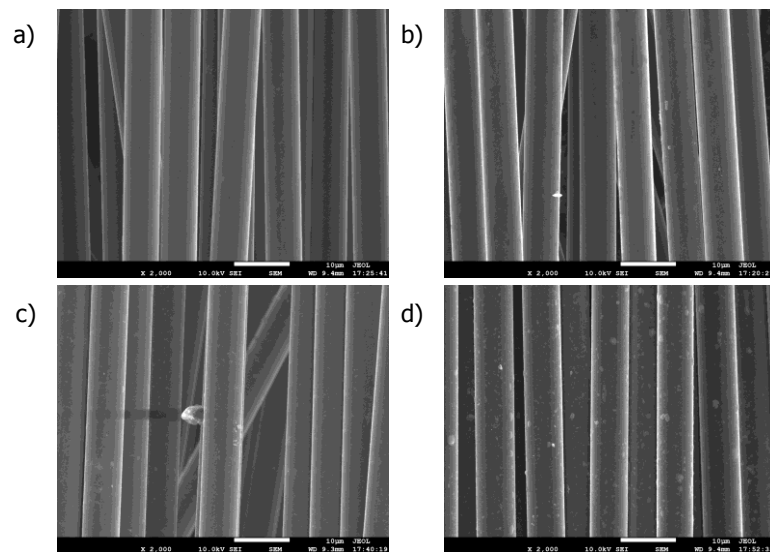


Figure S9. Tensile strengths of recovered CFs after recycling for 3 hours.

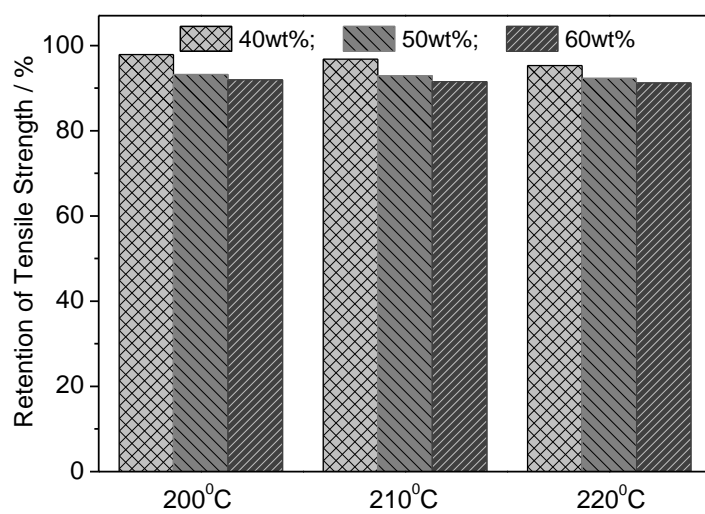


Figure S10. The XPS spectra of virgin CFs without sizing and recoveredCFs. (a) Virgin CFs; and (b) recovered CFs after recycling at 200°C for 3 hours in 60wt% zinc chloride aqueous solution.

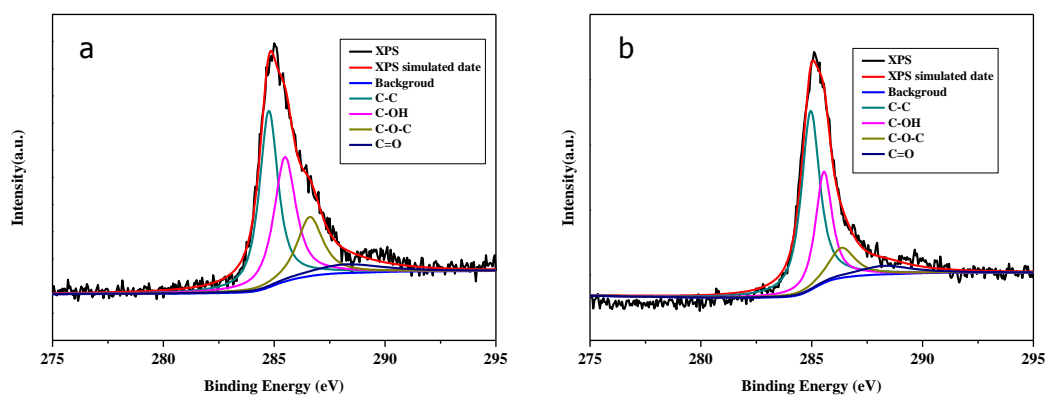


Figure S11. The reuse of (a) 60wt%, (b) 50wt% and (c) 40wt% zinc chloride aqueous solution. Reaction condition: 30ml of zinc chloride aqueous solution, 220°C, 9h, the reactant was EP (10x10x3 mm).

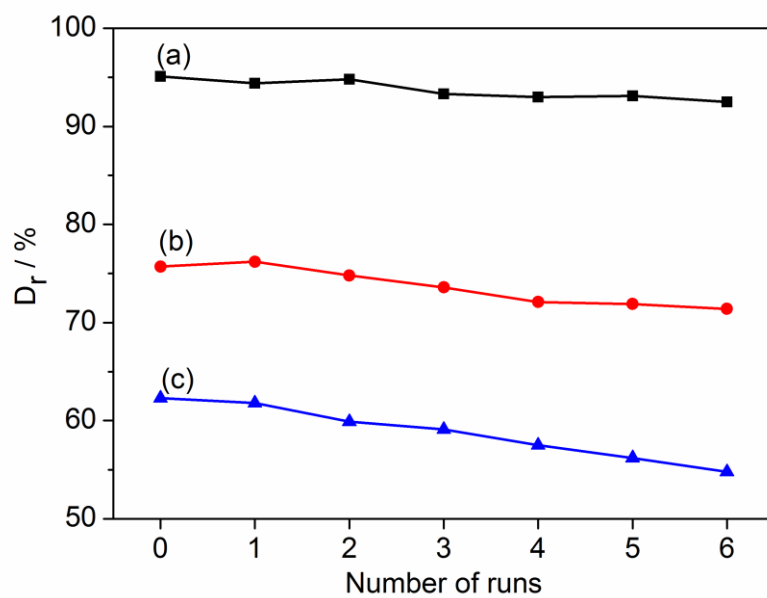


Table S1 The decomposition of several amines in concentrated ZnCl₂ solution

Reactant	Conversion, mol%	Yield of isopropanol, mol%
triethylamine	32	-
N, N-dimethyl isopropyl amine	100	65

Reaction conditions: 0.1g of reactant, 10 ml of 60wt% ZnCl₂ solution, 200 °C, 1h

Table S2 The tensile modulus of virgin and recycled carbon fibers

Entry	ZnCl ₂ Concentration, wt%	The tensile modulus, Gpa ^[a]	Deviation, σ
1 ^[b]	-	234	0.08
2	40	240	0.12
3	50	208	0.19
4	60	236	0.15

Reaction condition in each run: 10 ml of ZnCl₂ solution, 2 g of CF, 200 °C, 3 h; ^[a] The value was calculated by averaging the values of twenty CFs; ^[b] Original CF without treatment in ZnCl₂ solution.

Table S3a The surface elemental distributions of CFs without sizing and recycled CFs

Sample	C%	O%	N%
Recycled CFs ^[a]	76.25	22.99	0.76
CFs without sizing	75.84	21.94	2.22

^[a] CFs after recycling in 60 wt% ZnCl₂ solution at 200°C for 3 hours.

Table S3b The surface oxygen-containing groups of CFs without sizing and recycled CFs

Sample	Distributions of surface groups, %			
	C-C	C-OH	C-O-C	C=O
Recycled CFs ^[a]	51.57	28.85	12.51	7.07
CFs without sizing	45.52	26.28	24.03	4.17

^[a] CFs after recycling in 60 wt% ZnCl₂ solution at 200°C for 3 hours .

Table S4. The effect of weight content of recycled EP in curing agent on the impact strength of EP.

Content of recycled EP in curing agent, wt%	0	5	10	15	20
Impact strength of EP, KJ/m^2	11.49	11.47	11.01	9.97	8.85

Table S5 The weight ratios of various elements determined by ICP

Sample	C	H	O	Zn
Fresh ZnCl ₂ solution	-	0.042	0.356	0.289
ZnCl ₂ solution after recycling for 6 times ^[a]	0.004	0.041	0.360	0.287
The solid decomposed products of EP	0.59	0.072	0.125	0.001

^[a] Reaction condition in each run: 30ml of zinc chloride aqueous solution, 220°C, 9h, 60 wt% ZnCl₂ solution.