A Promising Strategy for Chemical Recycling of Carbon Fiber /Thermoset Composites: Self-accelerating Decomposition in a Mild Oxidative System

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1. Experimental Section

The composites were manufactured in our lab using a vacuum assisted resin infusion (VARI) process. The resin used in our experiment is JR-236 EP with the epoxide value of 0.54-0.57, and curing agent is acyclic amine JH-239 obtained from Changshu Jiafa chemical Co., Ltd., China. The commercially available non-crimp fabric was provided by Changzhou Hongfa Zongheng Advanced Materials Technology Co. Ltd., China. The used CF is T-700 12K from Japan Toray with a diameter of 6-7 μm. The resin and curing agent were mixed at a 100:30 weight ratio and then heated and degassed for 15min. The above mixture was soaked through the carbon fiber layers and cured at 70 ºC for 2h, and then 110 ºC for 2h.

The CF/EP composites were cut into slices of ca. 10×10×2.5 mm^3 before pretreatment. The acetic acid, 30% H_2O_2 solution and acetone were purchased from Sinopharm chemical reagent company and used without further purification. All solvents are A.R. grade. The composites sheets were put into a three-necked flask with 25 ml acetic acid at refluxing temperature of 120 ºC for 30 min. The treated composites were washed with acetone for several times then dried in vacuum at 105 ºC for over 12 h.

About 0.2 g pretreated CF/EP composites, 0~15 ml H_2O_2 and 0~15 ml acetone according to a needed ratio were put into a stainless 100 ml autoclave without stirring. The hermetic autoclave was heated at 50~120 ºC for 30 min. After the reaction, the products were filtered and then the solid CFs were separated and washed with acetone for several times, then dried in vacuum at 100 ºC for over 24 h.

The decomposition ratio (D_r) of the composites was calculated according to the amount of solid composition after treatment using the following formula:

$$D\mathrm{r} = \frac{W_1 - W_2}{W_0}$$

Where W_1 represents the mass of composites before decomposition, W_2 represents the mass of solide residue after decomposition, and W_0 represents the mass of epoxy resin in the composites before decomposition which was determined by using TGA. The results are based on the assumption that the EP is dispersed in the composites uniformly and can be degraded absolutely by heating to 800 ºC at a heating rate of 10 ºC/min under N_2 atmosphere. At the same time the CF can not be damaged during TGA test.

Thermal gravimetric analysis (TGA) experiments were performed on a Mettler Toledo TGA/DSC1 Analyzer. About 5 mg specimens were heated from 25 ºC to 800 ºC at a heating rate of 10 ºC/min under N_2 atmosphere (50 ml/min). The weight of all samples at 800 ºC was used to calculate the $D_{\text{r-tg}}$.

The surface microstructure of the CFs was examined by Vecco dimension 3100V scanning probe microscope on the Atomic Force Microscope (AFM) mode. The samples for Scanning electron microscope (SEM) were sputter-coated with a conductive layer of platinum, and then their surface morphologies were observed by a Hitachi S-4800 scanning electron microscopy with an 8 kV accelerated voltage.

Raman spectra were recorded on a Renishaw RM1000 Raman spectrograph. The laser power measured at the samples was below 10.0 mW for 514 nm radiation. The scanning wavenumber range was 100 cm^{-1} to 3200 cm^{-1}. An

AXIS UTLTRADLD Multifunctional X-ray Photoelectron Spectroscope (XPS) was employed to measure concentration of elements on the surface of the samples.

The single fiber tensile property of the CFs was tested by Donghua university XQ-1/XD-1 single fiber tester. Because the recovered CF was short and disordered, the samples can not be tested according to the standard method. The strength of CF was determined as following. Single filament was selected from T700 12k with a length about 2.5 cm. The distance between two clamps was 2 cm. The stretching speed was 20 mm/min. At least 10 filaments were tested for each sample.

Due to the JR-236 EP is a commercially resin containing 70 wt% diglycidyl ester of bisphenol A (DEBA) and 30 wt% diglycidyl ester of bisphenol F (DEBF). To simplify the experiments of mechanism analysis, the NEPL-127 epoxy resin with 100 wt% DEBA is used with the epoxide value of 0.54-0.57, and curing agent is diethylenetriamine as shown in Scheme S1. Coating on the carbon fiber fabrics, the curing of epoxy resin of network structure was conducted at 120 ºC for 5 h. The mass ratio of NEPL-127 to diethylenetriamine was 100: 11.5. The network structure compound was decomposed in mixed solution of acetone and H_2O_2 at 120 ºC for 30 min. The decomposed liquid component was dehydrated by anhydrous magnesium sulfate and then was evaporated by rotary evaporator. The products were solved in methanol for gas chromatograph-mass spectrometer (GC-MS, QP2010) analysis, using a DB-5MS column (30m× 0.25mm×0.25μm).

2. TATP characterization

Figure S1 shows GC-MS patterns of the crystal separated from the mixed solution of H_2O_2 (30%) and acetone. The prob of the component at 3.78 min is 96.9 with TATP, and its melting point is 93-95 ºC. The C/H mole ratio is about 0.5 the same as TATP testing by element analysis. Figure S2 and S3 shows ^{1}H and ^{13}C NMR spectra of the crystal, respectively. According to the ^{13}C NMR, there are only two kinds of carbon and some strong electron withdrawing groups appear at 107 ppm. While from ^{1}H NMR, only a strong peak at 1.362 ppm is found. The peaks at 3.3 ppm and 2.5 ppm correspond to the H from water and DMSO, respectively. The results indicate that the component is TATP clearly. All the results indicate the formation of TATP during the decomposition reaction. Thus the de-polymerization may be accelerated in the mixed solution of H_2O_2 (30%) and acetone.

3. Surface morphology and structure of the recovered CFs

Surface morphology of the recovered CFs was examined by AFM as shown in Figure S4. The surface of recovered fiber is as smooth as the virgin CF. Few grooves or furrows are observed on the surface of the recovered CFs. The results reveal that there is little destruction on the surface of the CFs in the process of recycling.

The surface elements were observed by XPS as shown in Figure S5. Carbon (BE=285eV) and oxygen (BE=532eV) are apparently detected on the surface of CFs. The surface element atomic concentration of different specimens obtained from XPS spectra are listed in Table S1. The atomic concentration of C 1s and O 1s are obviously different between the virgin and recovered CFs. The O/C ratios of the recovered CFs are a little higher than that of virgin one. It is suggested that the CFs is oxidized by the H_2O_2 during the process of recycling. The CFs has different O/C ratios under different reaction conditions. The reaction temperature also has influence on the O/C ratios of the CFs. As shown in Table S1, O/C ratio of recovered CFs was 0.202 when the composites were treated at 80 ºC for 30 min ($V_{acetone}/V_{H2O2}=0.5$). When the temperature reaches to 90 ºC, the O/C ratio of recovered CFs is increased to 0.217. The O/C ratio of recovered CFs is 0.220 at the temperature of 100 ºC. It is indicated that at a higher temperature the CFs suffer more oxidation.

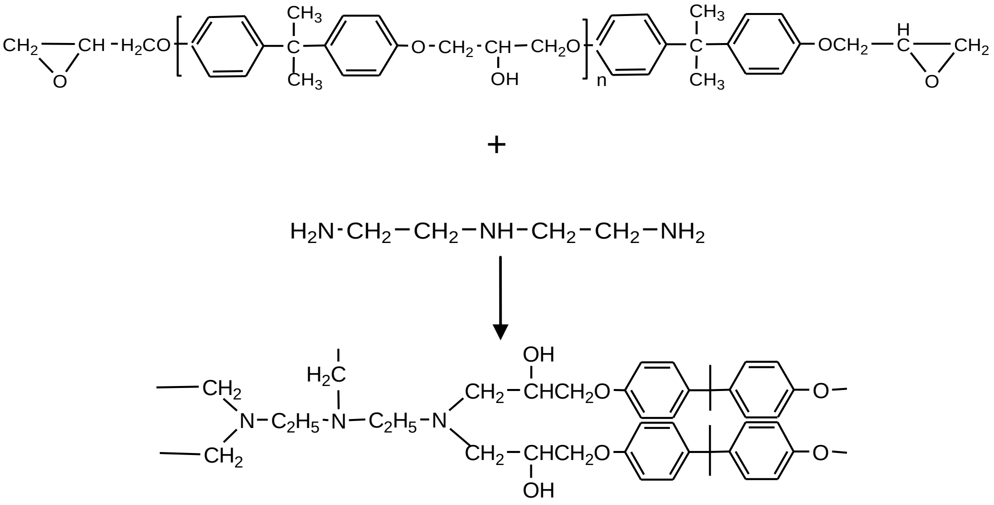
4. Decomposition mechanism of epoxy resin

The decomposition of the epoxy was studied by using GC-MS. The TGA of the cured DEBA epoxy is shown in Figure S6. The DEBA is cured by diethylenetriamine as shown in Scheme S1. From the TGA curve, the decomposition temperature of the DEBA epoxy with network structure is about 330 ºC, which is higher than that of the commercial products. In addition, the EP content in DEBA composites is higher than the commercial products. It is suggested that the epoxy resins are cured entirely. The decomposition products soluble in methanol for the GC patterns are shown in Figure 4 and the decomposition mechanism is listed in Scheme S2.

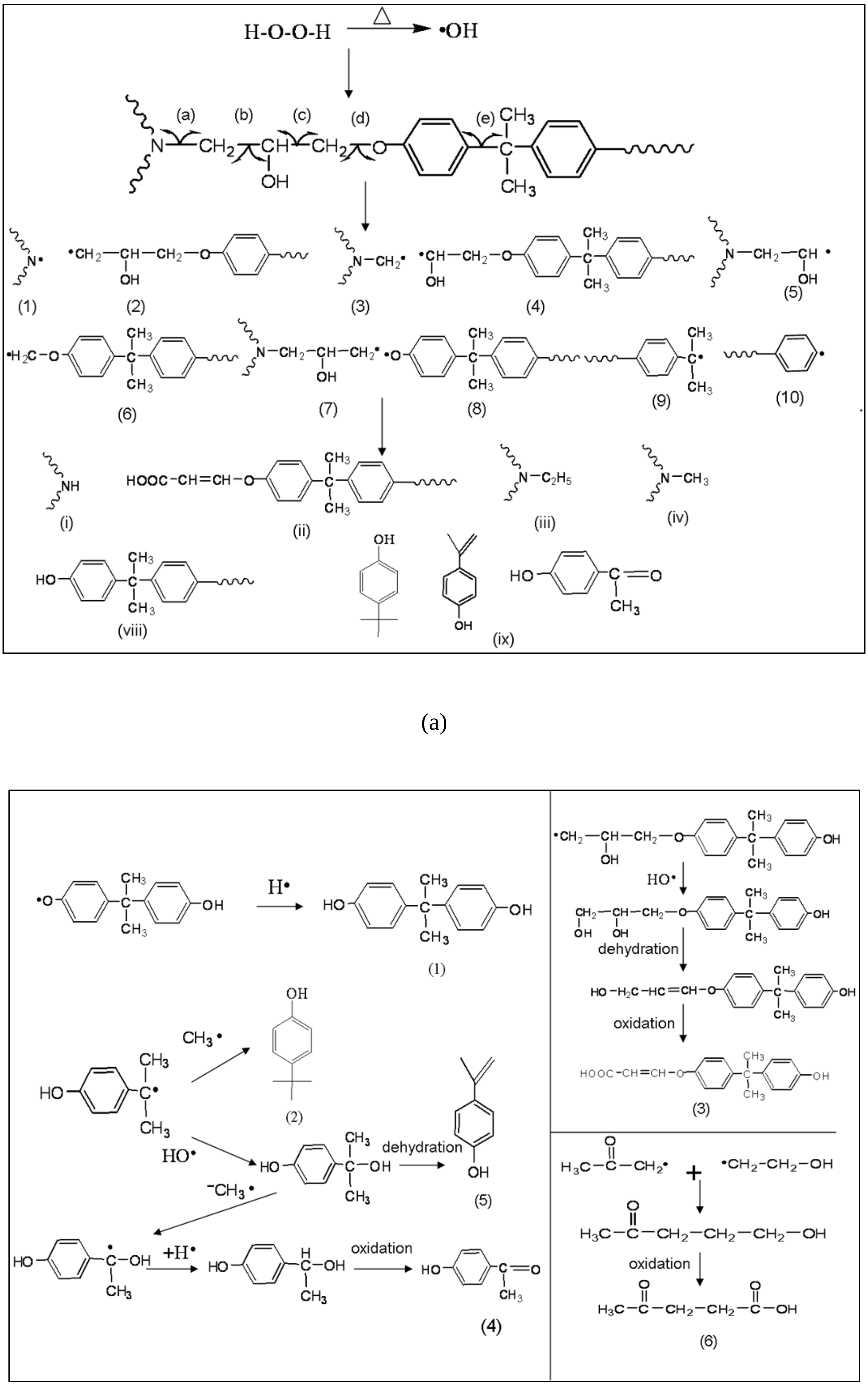
H_2O_2 is a green oxidant for organic chemical reaction. The mechanism of oxidation is different in different environment, such as ionic or free-radical mechanisms and so on. According to the possible reaction between acetone and H_2O_2 and the GC-MS results, free-radical mechanism is considered to be dominated under the reaction conditions. The oxidant system and the resin structure is complicated, thus other types of scission may exist. Scheme S2 shows a possible mechanism of the decomposition reaction of epoxy resin in the mixed acetone and H_2O_2. The main components are bisphenol A, its carboxylic derivatives and derivatives of phenol. The H_2O_2 is cracked into hydroxyl radicals by heat which is superior to other oxidant. Through the scissions of carbon-nitrogen (a), carbon-carbon (b, c and e) and carbon-oxygen (d), the curing epoxy resin are polarized and break into new free radicals (1-10). Free radical (1-10) captured groups or radicals to form the corresponding decomposed products (i-ix). The mechanisms of the product 1-6 are shown in Scheme S2 b). It is not found any nitrogenous organic compounds in GC-MS spectrum. Maybe the nitrogenous organic compounds are formed with low boiling point during the decomposition reaction which is volatilized during the process of extracting. It indirectly reveals that the scission of carbon-nitrogen is also the main scission. Besides bisphenol A and its derivatives, the derivatives of phenol are also generated during the decomposition of epoxy because carbon-carbon (e) is also cracked in the decomposition reactions. The scission of Carbon (benzene ring)-carbon (isopropyl) was another main scission way besides the scission of carbon-oxygen and carbon-nitrogen. All the results suggest that the mechanism of epoxy with network structure is so complex that it can not be illustrated by simple experiment. Many effort need to be done in the following work.

Table S1 Main atomic concentration of different specimens obtained from XPS spectra

Sample			O (%)	C (%)	O/C
T（℃)	t（min）	$V_{Acetone}/V_{H2O2}$			
	VF		12.65	84.48	0.150
80	30	1:2	16.06	79.61	0.202
90	30	1:2	17.03	78.61	0.217
100	30	1:2	17.44	79.38	0.220



Scheme S1 Chemical structure of epoxy resin, curing agent and cured resin



(a)

(b)

Scheme S2. Processing of the decomposition of CF/DEBA-EP composites in the acetone/H_2O_2 mixed solution

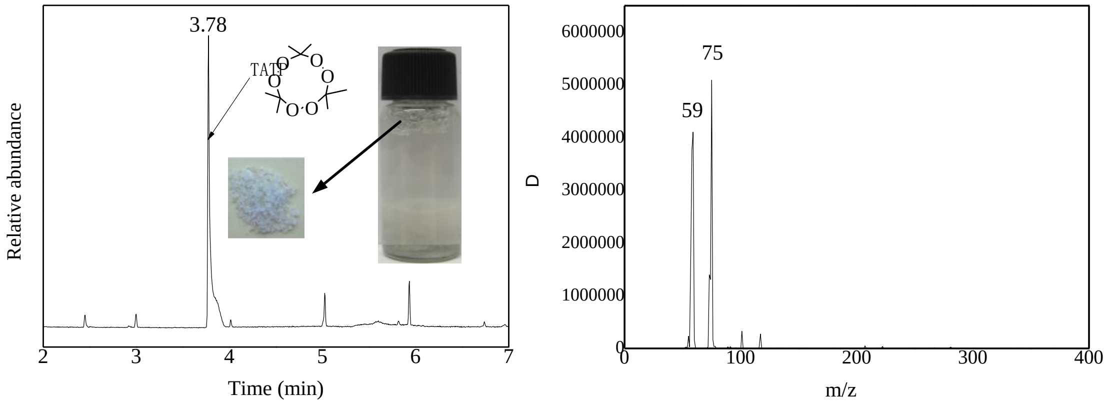


Figure S1 GC-MS patterns of the separated products from mixed solution of H_2O_2 and acetone a) GC b) MS at 3.78 min

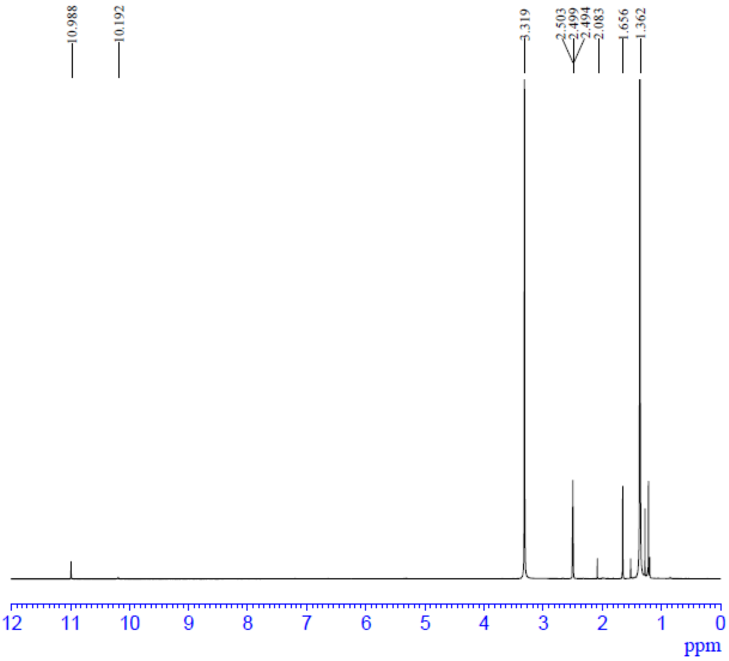


Figure S2 ^{1}H NMR spectra of the separated products from mixed solution of H_2O_2 and acetone (Solvent DMSO-d_6)

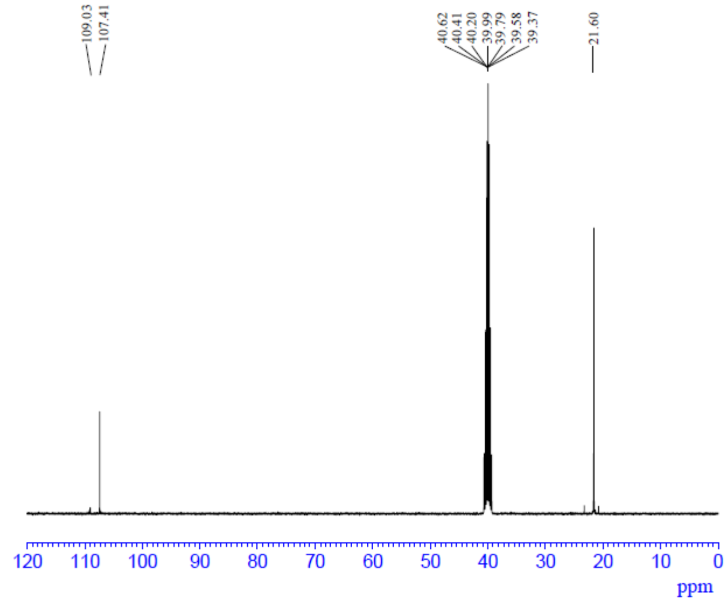
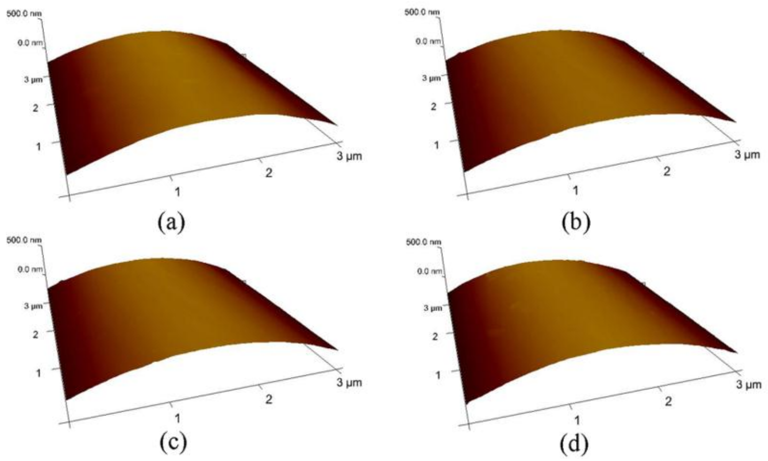


Figure S3 ^{13}C NMR spectra of the separated products from mixed solution of H_2O_2 and acetone (Solvent DMSO-d_6)



(a) (b) (c) (d)

Figure S4 AFM micrograph of different CFs: (a) virgin CFs; (b-d) recycled CFs obtained from the composites treated at 80 ºC, 100 ºC and 120 ºC for 30 min, respectively.

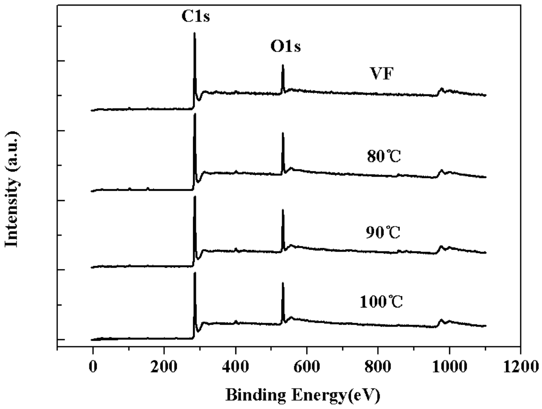


Figure S5 XPS spectra of different CFs obtained from different reaction temperature

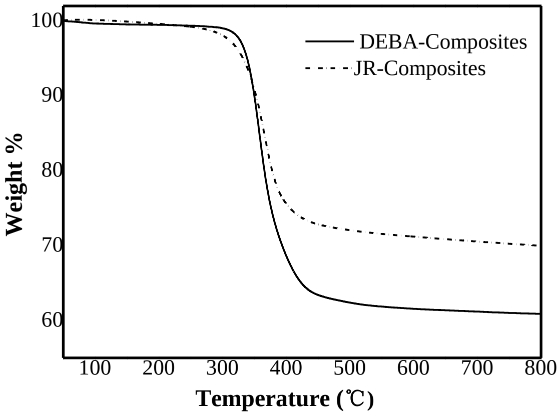


Figure S6 TGA analysis of composites with DEBA and diethylenetriamine and JR-236 epoxy resin