

# Recycling of Carbon Fiber-reinforced Epoxy Resin-based Composites Using a Benzyl Alcohol/Alkaline System

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**Abstract:** High-efficiency recycling of carbon fiber-reinforced epoxy resin-based composites is difficult because of their three-dimensional network structure. In this article, a benzyl alcohol/alkaline system was used to recycle carbon fiber-reinforced epoxy resin-based composites cured by an anhydride. The degradation rate, mechanical properties and degradation mechanism of the recycled carbon fiber were determined by gas chromatography-mass spectrometry, Fourier transform infrared spectroscopy, liquid chromatography-mass spectrometry, scanning electron microscope and X-ray photoelectron spectroscopy. The experimental results indicated that there were two steps in benzyl alcohol/K<sub>3</sub>PO<sub>4</sub> degradation system. The first was transesterification by benzyloxy selective attack to give small-molecule esters. Then the esters were saponified by the alkaline materials. After degradation, the stratification of resin and benzyl alcohol occurred, which was conducive to their separation. The optimal degradation time was 40 min under the weight ratio of alkaline material to benzyl alcohol of 1:10, atmospheric pressure, and temperature of 195 °C and the decomposition efficiency exceeded 90 %. A clean carbon fiber surface was obtained with an oxygen content comparable to that of the original carbon fiber. The tensile strength of the recycled carbon fiber was above 90 % of the original value.

**Keywords:** Carbon fiber-reinforced epoxy resin-based composites, Anhydride curing, Epoxy resin, Recycling, Atmospheric degradation

## Introduction

Carbon fiber-reinforced epoxy resin-based composites have been widely used in various fields such as aerospace, transportation, and construction because of their high specific strength, specific modulus, and corrosion resistance [1,2]. However, a lot of waste carbon fiber-reinforced epoxy resin-based composites are generated, such as leftover materials, defective products, and spent products. These composites cannot be remelted or remolded for recycling or reuse because of the three-dimensional cross-linked network of the epoxy resin even though they contain high-value carbon fiber [3,4]. Therefore, waste from such materials has become a potential environmental issue.

Many methods of recycling carbon fiber-reinforced polymers (CFRPs) have been investigated in recent years, including mechanical [5], thermal [6], and chemical recycling methods [7]. In mechanical recycling, the waste fibers are cut into shorter fibers or ground into a fine powder for secondary use, but it is difficult to obtain recycled fibers with high performance [8,9]. Thermal recycling methods include pyrolysis [10], flow bed [11], and microwave pyrolysis approaches [12]. Such methods easily degrade the resin using high temperature. However, thermal recycling faces the challenges of high energy consumption, gas by-product formation, and poor retention of fiber strength.

Chemical recycling uses chemical reagents to strip carbon fibers from the resin matrix, the recycled fibers of which are more valuable than mechanical recycling. The main

chemical recycling methods are supercritical fluid extraction and solvent degradation. In the supercritical fluid method, the resin is dissolved by a solvent with excellent solubility and mass transfer ability at high temperature and pressure. Water and ethanol are the two most studied reaction media in supercritical fluid extraction [13-15]. Although the mechanical properties of the long fibers recycled by supercritical fluid extraction are good, this technology is still at the laboratory stage because of its strict requirements.

In the solvent degradation method, the special chemical properties of solvents are used to dissolve a resin during heating. Dang *et al.* reported the degradation of epoxy resin cured by amine in 4 M nitric acid solution [16]. The tensile strength of the recycled fiber was more than 90 % of the original value. However, despite the rapid degradation initially, complete degradation took more than 100 h. Lee and co-workers decomposed a CFRP in a mixture of acetone and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) at 60 °C for 30 min to obtain carbon fiber with a clean surface. The recycled fiber retained above 95 % of the original tensile strength [17]. Xu *et al.* decomposed a CFRP in a mixture of H<sub>2</sub>O<sub>2</sub> and dimethylformamide (DMF) at 90 °C. Before decomposition, the epoxy resin composites cured by amines were pre-swelled in acetic acid. The resin degradation rate reached above 90 % [18]. Zhao and colleagues immersed composite waste in dichloromethane to make the resin structure loose and porous, and then degraded the composite waste in DMF using a microwave-assisted approach. The degradation rate of epoxy resin in the CFRP waste at 130 °C for 50 min reached 99 %. However, the large amount of solvent required for CFRP degradation is a drawback of the solvent

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degradation method [19].

In recent years, the development of degradation methods has gradually progressed from simple to more complex, and the value of recycled carbon fibers has increased. In the study of anhydride-cured resin degradation, green systems such as  $\text{ZnCl}_2/\text{water}$  [20,21],  $\text{ZnCl}_2/\text{ethanol}$  [22], and  $\text{AlCl}_3/\text{acetic acid}$  [23,24] have been used. However, almost all reactions had to be performed at temperatures above  $200\text{ }^\circ\text{C}$ . These degradation reactions were usually conducted at temperatures higher than the glass transition temperature of the resin so that the mobility of chain segments was increased [19]. Tomoko *et al.* used a benzyl alcohol/ $\text{K}_3\text{PO}_4$  system to depolymerize an unsaturated polyester resin. The recycled glass fibers retained high mechanical properties. However, relatively harsh subcritical conditions were required [25].

The objective of this paper is to explore a degradation system with a green solution and conventional alkaline material to recycle carbon fiber-reinforced epoxy resin-based composites cured by anhydride at atmospheric pressure. Nontoxic benzyl alcohol is used as both the solvent and reactant in the transesterification reaction. Two different alkaline materials,  $\text{NaOH}$  and  $\text{K}_3\text{PO}_4$ , are used as catalysts in the system. We systematically analyze the degradation mechanism of the system along with the time dependence of degradation efficiency and the physical and chemical properties of the recycled fibers. Our results lay a foundation to select suitable reactants and conditions to degrade epoxy resin and epoxy-carbon fiber composites cured by anhydride.

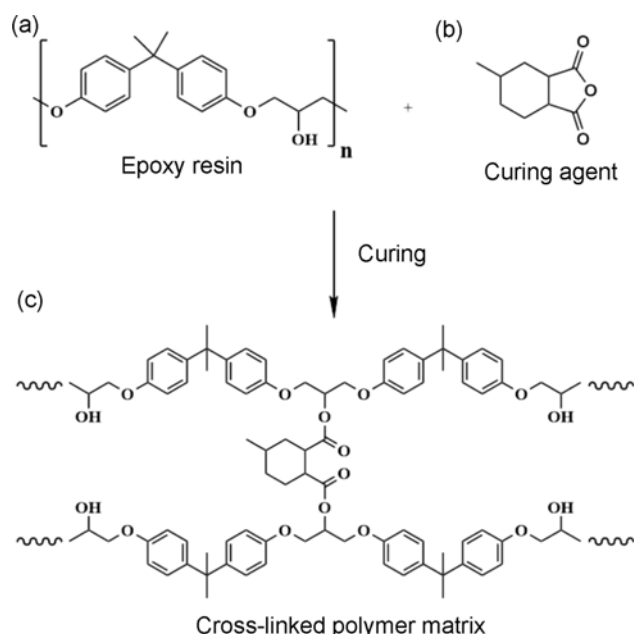
## Experimental

### Materials and Preparation of CFRP

The matrix resin was bisphenol-A epoxy resin (EDK-R05, Fushun Xinrui Catalyst Co. Ltd., China). Methylhexahydrophthalic anhydride (MHHPA) (EDK-X52, Fushun Xinrui Catalyst Co. Ltd.) was used as a curing agent. Carbon fiber was synthesized in the laboratory [26]. Resin, curing agent, and acetone were mixed at room temperature with a weight ratio of 100:84.5:13. The mixture was soaked through carbon fiber bundles and then cured at  $130\text{ }^\circ\text{C}$  for 2.5 h. The resin content of the composite sample was 45 wt% according to GB/T 3855-2005. The molecular structures of epoxy resin, curing agent, and the curing system are shown in Figure 1. Although Figure 1 only shows the curing agent hexahydro-4-methylphthalic as a representation, the actual curing agent was a mixture of anhydrides [27].

### Recycling Process

Degradation reactions were carried out in a 250 ml three-necked flask equipped with a reflux condenser and thermometer. Experiments were performed at a constant temperature of  $195\text{ }^\circ\text{C}$ . Typically,  $\text{NaOH}$  or  $\text{K}_3\text{PO}_4$  and benzyl alcohol were mixed with a weight ratio of 1:10, and



**Figure 1.** Molecular structures of (a) bisphenol-A epoxy resin, (b) hexahydro-4-methylphthalic anhydride, and (c) the curing system.

the volume of benzyl alcohol was 120 ml. Some composite bars ( $55\text{ mm}\times 12\text{ mm}\times 4\text{ mm}$ ) with a total mass of 15 g were charged into the reactor.

After degradation reaction, the solid products including fibers and insoluble materials were separated from liquid products by filtration. The recycled fibers were washed alternately with water and acetone three times in an ultrasonic bath. After cleaning, the fibers were dried in an oven until their mass was constant.

The degradation rate of epoxy resin in the composites was calculated from the rate of mass change according to the following formula:

$$\eta(\text{wt}\%) = \frac{M_1 - M_2}{45\% \times M_1}$$

where  $M_1$  is the weight of the composite before reaction and  $M_2$  is the weight of the dried recycled carbon fiber.

### Characterization

Surface structures were explored using scanning electron microscopy (SEM; Hitachi S-4700, Japan) with an acceleration voltage of 200 kV and magnification of  $13,000\times$  or  $15,000\times$ . The monofilament diameter was measured by an optical microscope (Olympus BX51, Japan). Monofilament tensile strength was measured at room temperature using a universal test machine (YG001A, Taicang Textile Instrument Co. Ltd., China) at a crosshead speed of 10 mm/min, as specified in ASTM-D3379. For each sample, the tensile strength of 30 monofilaments was tested and the average value was used.

The ratio of carbon to oxygen on the surface of the origin and the recycled carbon fiber was analyzed by X-ray photoelectron spectroscopy (XPS; Thermo Fisher Escalab-250, USA). Spectra were collected in a fixed-analyzer transmission mode. High-resolution scans of carbon and oxygen were collected with a pass energy of 30 eV. Before testing, the origin and recycled carbon fiber was pre-washed according to Jiang *et al.* [28].

The components of liquid-phase products from CFRP degradation was determined by Gas chromatography connected with inert XL Mass Selective Detector (GC-MS; Agilent 6890N, USA). The column was an Agilent capillary column (DB-5, 30 mm×0.25 mm, 0.25  $\mu$ m). Helium (purity 99.999 %) was used as a carrier gas at a flow rate of 1.0 ml/min. The initial column temperature was 50 °C for 2 min, and then the temperature was increased linearly to 250 °C at a rate of 8 °C/min. The temperature was held at the upper temperature for 7 min. All MS analyses were conducted in scan mode (mass range of 40-450amu) with the electron impact ionization (EI) of 70 eV.

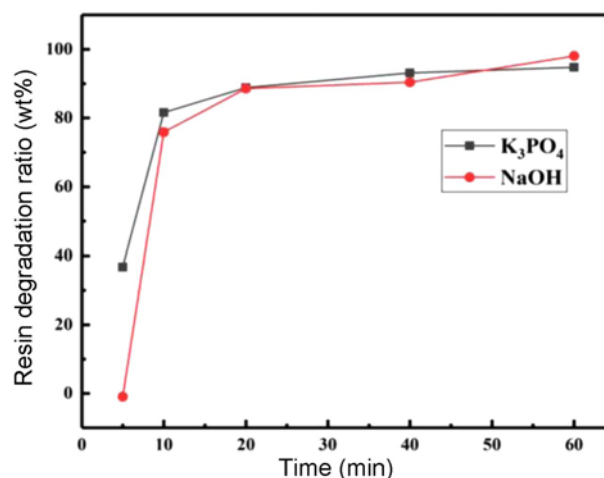
The chemical structures of the liquid products and insoluble products were determined by Fourier transform infrared (FT-IR) spectroscopy (Thermo Fisher, Nicolet 5700, USA). The software OMNIC version 8.2 was used for spectra acquisition. The spectra were recorded in absorbance mode with 32 scans at a resolution of 4  $\text{cm}^{-1}$  in the range of 400-4000  $\text{cm}^{-1}$ .

The composition and molecular weight of the insoluble products dissolved in deionized water were analyzed by LC-MS using a Waters Acquity UPLC liquid chromatograph (USA) coupled with a Waters Xevo G2 QTOF mass spectrometer. An Agilent Zorbax SB-C<sub>18</sub> column (2.1 mm×150 mm, 1.8  $\mu$ m) was used for the separation at 40 °C. Mixed solutions of water and acetonitrile with gradient concentration were used as the mobile phase. At cumulative processing times of 3.5, 3.5-6, 6-8, 8-10, and 10-12 min, the volume content of acetonitrile in the mobile phase was 5 %, 40 %, 70 %, 100 %, and 5 %, respectively. The flow rate was maintained 0.3 ml/min and the injection sample volume was 10  $\mu$ l. The eluate was injected from the high-performance liquid chromatograph (HPLC) directly into the mass spectrometer with negative electrospray ionization. Masslynx v4.1 software was used for data analysis. The MS scan range was 50-2000 amu. Nitrogen with a flow rate of 800 L/h was used as the desolvation gas. The cone gas flow rate was set at 20 L/h. Desolvation was performed at 400 °C. The source temperature was set at 100 °C. The voltages of the capillary, sample cone, and extraction cone were 2.2 kV, 30 V, and 4 V, respectively. The dwell time was 0.15 s.

## Results and Discussion

### Chemical Degradation of CFRP

Experiments were performed using decomposition times



**Figure 2.** Resin degradation rates as a function of time for systems with different alkaline catalysts.

of 5, 10, 20, 40, and 60 min at 195 °C. The weight ratio of alkaline material to benzyl alcohol was 1:10. The relationship between resin degradation rate and time for the degradation systems with the two different alkaline materials is shown in Figure 2. The degradation rate of the composites increased with the reaction duration and reached more than 90 % after reaction for about 40 min. When the degradation time exceeded 40 min, the influence of time on degradation rate was small. Considering economy and energy consumption, the optimum degradation time of the current systems was determined to be 40 min.

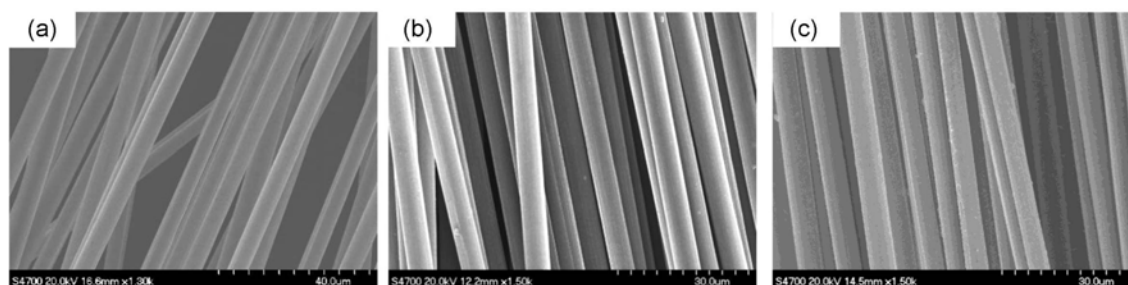
### Characterization of the Recycled Carbon Fiber

After obtaining a good degradation rate, the surface morphology and mechanical property of recycled fibers were detected, in order to deeply compare the surface structure and performance of recycled carbon fiber.

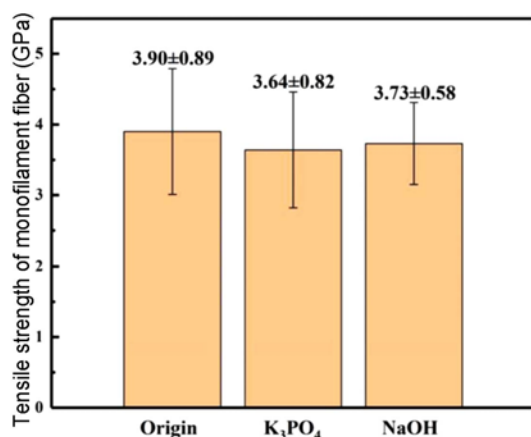
The surface morphology of the recycled carbon fiber was observed by SEM, as shown in Figure 3. Both the original and recycled carbon fiber samples were clean and no holes were found on the surface of the recycled carbon fiber. Although some small white spots of residual epoxy resin were observed on the surface of some recycled carbon fibers. These results imply that the carbon fiber was not damaged dramatically during the treatment process and the resin was almost completely degraded.

Recycled carbon fiber samples from the benzyl alcohol/NaOH and K<sub>3</sub>PO<sub>4</sub> systems degraded at 195 °C for 40 min were selected for monofilament tensile strength testing and compared with the performance of the original carbon fiber.

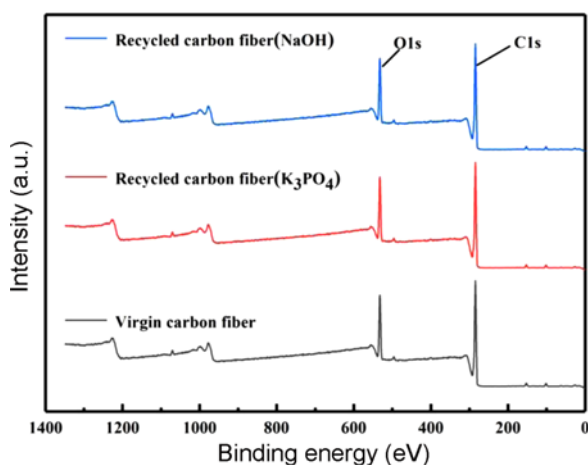
The results of the monofilament tensile strength test are shown in Figure 4. For the fibers treated using the K<sub>3</sub>PO<sub>4</sub> and NaOH catalyst systems, the monofilament tensile strength was 3.64 and 3.73 GPa, respectively, which were 93.3 % and 95.6 % that of the original carbon fibers,



**Figure 3.** SEM images showing the surface morphology of (a) original carbon fibers, and carbon fibers treated using the (b)  $K_3PO_4$  catalytic system, and (c) NaOH catalytic system.



**Figure 4.** Tensile strength of monofilament of the original and recycled carbon fiber samples.



**Figure 5.** XPS profiles of different carbon fiber surfaces.

**Table 1.** Compositions of the original and recycled carbon fiber surfaces

Content of elementary	C (%)	O (%)	O/C
Original carbon fiber	81.67	18.33	0.224
Recycled carbon fiber ( $K_3PO_4$ )	80.72	19.28	0.239
Recycled carbon fiber (NaOH)	79.02	20.98	0.266

respectively. Thus, the strength retention was high for carbon fiber treated using both degradation systems.

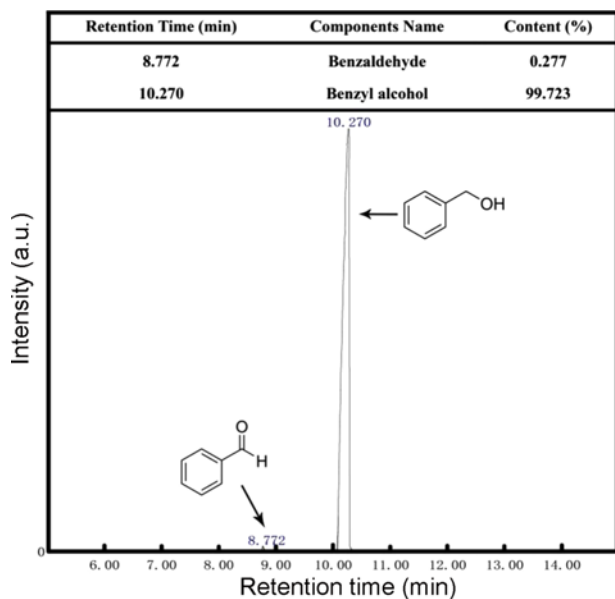
The surface C and O contents of the recycled and original carbon fiber samples were evaluated by XPS. The survey spectra contained are two main peaks originating from C (297.7 eV) and O (544.2 eV). The spectra are shown in Figure 5 and data are listed in Table 1. The content of O on the surface of the recycled carbon fibers increased slightly compared with that of the original carbon fibers because of the small amount of residual resin. The O/C ratios on the surface of the carbon fiber samples before and after degradation were comparable.

### Degradation Mechanism

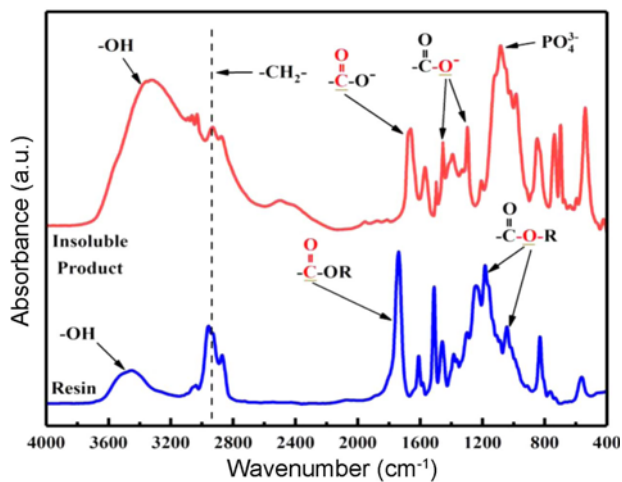
The recycled carbon fibers showed good morphology and mechanical properties. Therefore, the degradation products of benzyl alcohol/ $K_3PO_4$  system were deeply analyzed to explore the degradation mechanism. The degradation products included liquid products and solid products except recycled carbon fibers, so they were tested separately.

The supernatants of degradation reactions performed for 40 min in benzyl alcohol/ $K_3PO_4$  system were analyzed by GC-MS. Figure 6 shows that the benzyl alcohol dominated the supernatants, accounting for more than 99 %, with trace amounts of benzaldehyde. According to the detection of the raw benzyl alcohol solvent, the benzaldehyde was mainly introduced by the synthesis of benzyl alcohol. And the subsequent heating under atmosphere also caused trace oxidation. The Figure 6 reveals that the composition of the solution was almost unchanged after the degradation reaction. Therefore, to further investigate the mechanism of degradation, the insoluble materials isolated by filtration were analyzed.

The insoluble solid products obtained after the degradation reaction from the benzyl alcohol/ $K_3PO_4$  system were analyzed by FT-IR. The FT-IR spectra of the insoluble degradation products and pure resin are shown in Figure 7. The peak at  $2958\text{ cm}^{-1}$  corresponded to methylene ( $CH_2$ ) aromatic and aliphatic stretching vibrations. Slight changes of peak height and position were observed, indicating that degradation barely induced some changes of the resin main



**Figure 6.** GC spectrum of supernatants as reaction performed for 40 min in benzyl alcohol/ $K_3PO_4$  system.



**Figure 7.** FT-IR spectra of the pure resin and insoluble degradation product in benzyl alcohol/ $K_3PO_4$  system.

chain. The peak at  $3200\text{--}3600\text{ cm}^{-1}$  was attributed to hydroxyl (-OH) stretching vibrations. The width of this peak broadened for the insoluble products, indicating that the content of -OH increased after degradation. Meanwhile, the peak position shifted to lower wavenumber, implying that the content of hydrogen bonds increased, which further evidences an increase of -OH content.

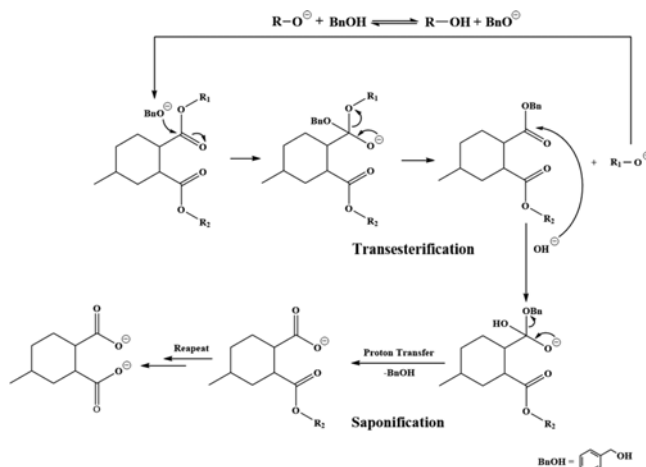
For the pure resin, the peak at  $1746\text{ cm}^{-1}$  was assigned to the C=O stretching vibration and the absorption peaks at  $1042$ ,  $1187$ , and  $1237\text{ cm}^{-1}$  were assigned to the C-O-C stretching vibrations of the ester bonds in the epoxy resin structure. Unlike the pure resin, some degradation products

were adsorbed by the alkaline materials, which affected the vibrations of some functional groups. The characteristic C=O stretching vibration of the insoluble product appeared at  $1660\text{ cm}^{-1}$ , which was shifted to lower wavenumber than that of the pure resin ( $1746\text{ cm}^{-1}$ ), indicating that there were a lot of hydrogen bonds in the insoluble product. The peaks at  $1452$  and  $1295\text{ cm}^{-1}$  were consistent with the C-O<sup>-</sup> stretching vibrations of carboxylate groups, which indicated that the structure of the insoluble product was different to that of the pure resin. A phosphate peak was observed at  $1087\text{ cm}^{-1}$ , which indicated the presence of  $K_3PO_4$ .

The FT-IR spectroscopy results indicated that when the three-dimensional network structure of the resin was destroyed, there were slight changes of the main chain. In addition, the degradation product contained numerous hydrogen bonds, which implied that chemical reactions mainly occurred at active points, i.e., cross-linked ester bonds. That is, the ester groups in the resin were converted into carboxyl and hydroxyl groups during degradation.

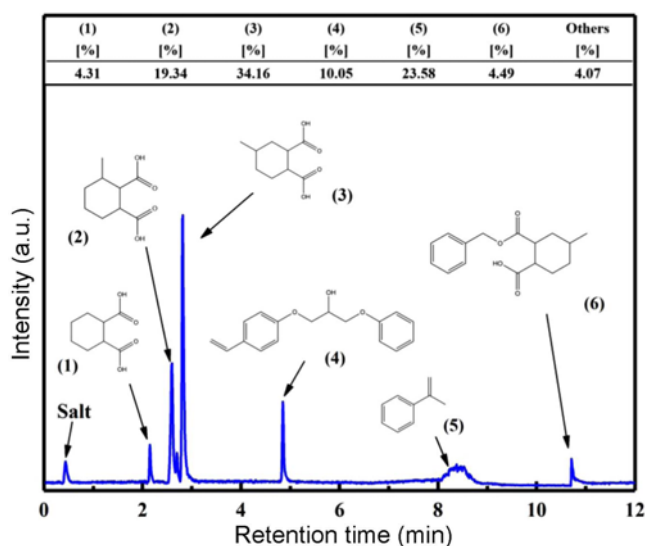
Based on the FT-IR spectra, the degradation mechanism of the resin was considered to involve a complex process of transesterification and hydrolysis. After the resin was swelled by benzyl alcohol, transesterification occurred first by the attack of benzyloxy to form a tetrahedral intermediate structure. The intermediate then disassembled into an alcohol anion and benzyl alcohol ester. The anion went on to react with benzyl alcohol to form a benzyloxy and the benzyl alcohol ester was hydrolyzed by the alkaline system. The detailed degradation reaction process is illustrated in Figure 8.

LC-MS was used to further analyze the structure of the insoluble solid products in the benzyl alcohol/ $K_3PO_4$  system, and the results are shown in Figure 9. The main components were dicarboxylic acid **1**, **2** and **3**, which had a total content exceeding 50 %. The results indicated the scission of carbon-



**Figure 8.** Degradation reaction of the benzyl alcohol/ $K_3PO_4$  system.





**Figure 9.** LC pattern of the degradation products of epoxy resin in benzyl alcohol/ $K_3PO_4$  system.

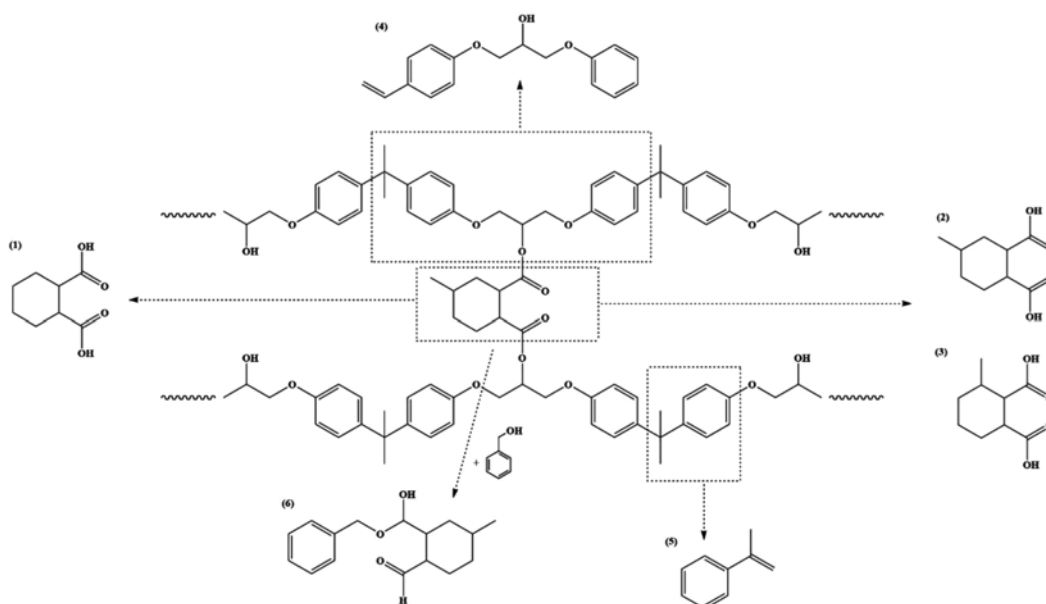
oxygen bonds. Product **6** was generated by intermolecular reaction with dicarboxylic acid and benzyl alcohol, further demonstrating that benzyl alcohol acted as not only a solvent but also a nucleophilic reactant. However, because the system underwent transesterification first and then irreversible hydrolysis under alkaline conditions, the content of **6** was lower than those of dicarboxylic acid **1**, **2**, and **3** in the system. A few other scissions also occurred, including carbon-carbon bond cleavages from the linear molecular chain, generating products such as **4** and **5**.

According to the analysis of LC-MS data and considering

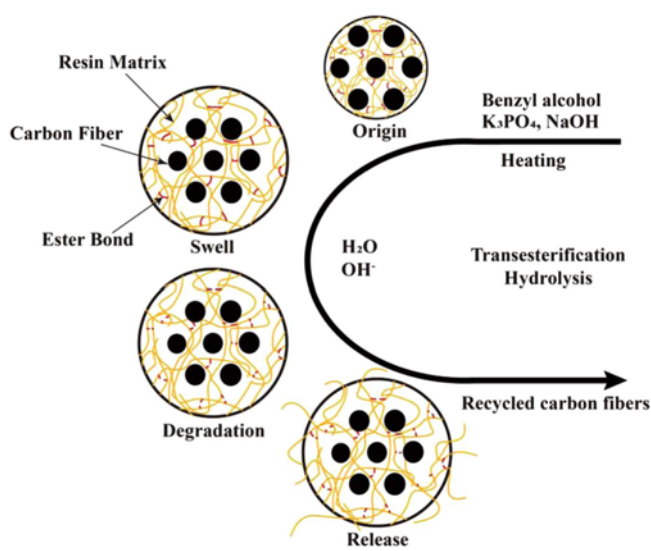
the molecular structure of the cured resin, the relationship between the structure of the cured resin and its degraded molecular products was obtained, as shown in Figure 10. The curing agent linked two different long-chain molecules, with ester bonds at the cross-linked points. Most of the degradation products originated from the fracture of ester bonds. After transesterification and hydrolysis, most of the curing agent was in the form of a dicarboxylic acid salt and the resin was released. The content of both carboxylate and hydroxyl groups increased, which was consistent with the FT-IR spectroscopy results.

We propose that the degradation process in the benzyl alcohol/alkaline material system involved four steps: 1) The solvent medium diffused toward the surface of the composite; 2) Swelling occurred through the movement of solvent; 3) The benzyloxy anion nucleophile attacked the ester bond to break the resin network; 4) The degradation products diffused toward the fluid bulk. A schematic diagram of the process is shown in Figure 11. The large circle in Figure 11 is a section of the composite, which contains aligned carbon fibers. The long curved lines represent the long chains of the resin network, which are cross-linked by short lines that represent ester bonds.

In the degradation process of the carbon fiber-reinforced epoxy resin-based composites, benzyl alcohol played two roles. On the one hand, as a solvent, it swelled the resin and provided a reaction environment for the system. On the other hand, it behaved as the donor of the benzyloxy nucleophilic group that participated in transesterification. For the resin, because of the scission of C-O bonds in the cross-linked epoxy resin system, the curing agent was converted into a dicarboxylic acid salt, which was adsorbed by the alkaline



**Figure 10.** Molecular structures of cured resin degradation products in the benzyl alcohol/ $K_3PO_4$  system.



**Figure 11.** The degradation process of carbon fiber-reinforced epoxy resin-based composite in the benzyl alcohol/alkaline system.

material rather than dissolving in the solvent. Our FT-IR results implied that the degraded linear resin macromolecules also did not dissolve in benzyl alcohol solution but settled under it. That is, the resin and benzyl alcohol and formed layers, which facilitated the separation of solvents after the degradation. Meanwhile, the recycled carbon fibers mixed with the insoluble materials were easily isolated by washing with water or conventional solvents.

### Conclusion

We demonstrated an effective method to recycle carbon fiber-reinforced composites using a benzyl alcohol/alkaline material system. The degradation of the cured resin involved a complex process of transesterification and hydrolysis in benzyl alcohol/ $K_3PO_4$  degradation system. Nucleophilic attack of the ester bond of the resin by benzyloxy played an important role in resin degradation. One of the degradation products was dicarboxylic acid salt, which was produced by the fracture of the C-O bond of ester groups. The dicarboxylic acid salt was adsorbed by the alkaline catalyst. The degraded linear resin sank under the benzyl alcohol, which was beneficial for the separation of benzyl alcohol. The fibers were easily isolated through simple processing for recycling and the liquid products were very pure which can be reused many times. The optimal degradation time was 40 min under the weight ratio of alkaline material to benzyl alcohol of 1:10, atmospheric pressure, temperature of 195 °C, and the decomposition efficiency exceeded 90 %. The O content on the surface of the recycled carbon fiber was comparable to that of the original carbon fiber. The monofilament tensile strength of the recycled carbon fiber retained above 90 % of that of the original carbon fiber. The

developed process does not require additional organic solvent or pressure, which makes it attractive for industrial application.

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