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RESEARCH PAPER

# Recycling of carbon fibers in epoxy resin composites using supercritical 1-propanol

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**Abstract:** The effects of degradation temperature, reaction time and additive on the efficiency of the recovery of carbon fibers from their epoxy resin composites by supercritical 1-propanol were investigated. The recycled carbon fibers were characterized using SEM, TGA, XPS, contact angle measurements and single fiber tensile strength tests. Results indicated that the rate of decomposition of the resin increased, but the mechanical properties of the recycled fibers decreased slightly with temperature. The decomposition rate of the resin and tensile strength of the recycled carbon fibers decreased with reaction time. 1 wt% of KOH additive in 1-propanol improved the recovery efficiency significantly. When the KOH concentration was increased beyond 1 wt% there was no obvious increase in the decomposition rate and the mechanical properties of the recycled fibers became worse. There were slight changes in the surface chemistry of the recycled carbon fibers and their contact angle with epoxy resin. Supercritical 1-propanol is an excellent recycling technology for carbon fibers in epoxy resin composites.

**Key Words:** Carbon fiber; Recycling; Supercritical 1-propanol; Epoxy; Composites

## 1 Introduction

Carbon fiber reinforced polymer composites (CFRP) have been extensively used as load-bearing structural materials in aerospace and automotive sectors as well as many industrial, consumer, and sports goods owing to an interesting combination of low weight, high strength and excellent corrosion resistance [1]. However, disposing of the composites will be a problem when the CFRP reach their service lives [2]. Both landfill and incineration of epoxy based CFRP wastes are not optimal since these will cause environmental pollution from the chemicals released after polymers are degraded [3].

Therefore, researchers and engineers around the world made much effort to develop various recycling technologies [4-7] such as mechanical grinding [8], pyrolysis [9], oxidation in a fluidized bed [10], and chemical treatment [11, 12]. Mechanical grinding through crushing and milling is relatively cheap and simple, but it only reclaim short milled fibers with poor mechanical properties, which could only be used as filler in reinforced materials [13, 14]. Pyrolysis is a commercially applied technology in which the epoxy resin is thermally burned away in an oxygen deficient combustion process [15]. In addition, pyrolysis and oxidation in a fluidized bed is also investigated, in which waste material is fluidized by high-temperature gas passing through from beneath the bed, resulting in gradual separation of its constituents [16, 17]. For example, Yip [18] recycled carbon fibers with the fluidized bed method, which retained 75% of their tensile strength. However, these methods can lead to fiber shortening, some degradation of fiber properties, or both. Various chemical recycling methods are developed to preserve the strength and the stiffness of the original carbon fibers [19,20]. For instance, Bai [21] used supercritical water to recycle carbon fibers from carbon fiber reinforced epoxy resin composites at 30 ± 1 MPa and 440 ± 10 °C. On the other hand, supercritical alcohols represent an alternative for supercritical water because not only are the critical conditions less extreme but also the solubility of polar and high molecular weight solutes in supercritical alcohols is high. Therefore, Jiang [22, 23] used supercritical 1-propanol in a semi-continuous flow reactor to recycle carbon fibers, and unexpectedly found that the tensile strength and modulus of the recycled carbon fibers were almost the same as the virgin carbon fibers. Although much progress has been made in these methods for recycling CFRP waste, there is still some issues needing further investigation, such as the effects of degradation temperature, reaction time and additive on the recovery of carbon fibers with clean surface and high retention of both mechanical properties and fiber length.

The objective of this paper was to evaluate the effects of degradation temperature, reaction time and additive on the

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properties of the recycled carbon fibers using supercritical 1-propanol in a stirred batch reactor. The carbon fiber reinforced epoxy resin composites were placed in a sample holder made of stainless steel mesh. The direct contact between stripped carbon fibers and rotating blades was avoided, while the high mass transfer rate in the stirred batch reactor was guaranteed at the same time. The morphology, the tensile strength and surface chemical properties of the recycled carbon fibers were characterized from representative composites.

## 2 Experimental

### 2.1 Materials

The commercial epoxy resin (tetraglycidyl 4,4′-diaminodiphenylmethane, TGDDM) and curing agent (4,4′-diaminodiphenylsulfone, DDS) were supplied by Shanghai Research Institute of Synthetic Resins and Sinopharm Chemical Reagent Co., Ltd, respectively. The chemical structures of the epoxy resin, curing agent and cured resin were reported in our previous investigation [24]. The reaction medium in this experiment was 1-propanol. Carbon fiber reinforced epoxy resin composites and the virgin carbon fibers were produced in National Engineering Laboratory for Carbon Fiber Technology, Institute of Coal Chemistry, Chinese Academy of Sciences. The average diameter of carbon fibers was about 7 μm, and tensile strength was about 3.53 GPa according to the standard of GB/T 26749. Carbon fiber reinforced epoxy resin composites were manufactured through autoclave processing. In a typical process, 8 layers of the carbon fiber fabric were pressed in a mold with the epoxy resin system containing TGDDM and DDS to form a composite, which was heated at 130 $^{o}$C for 1 hour before it was cured at 180 $^{o}$C for 4 hours. After curing, the composite sample was cut into bars ( 50 mm × 10 mm × 2 mm) for recycling experiments.

### 2.2 Recycling of carbon fibers

The recycling was conducted in a stainless steel batch reactor. The temperature was controlled by a PID controller. The composite samples were inserted into a sample holder made of stainless steel mesh. In order to enhance the mass transfer rate, mechanical stirring was used and stirring speed was set at 200 r/min. Potassium hydroxide (KOH) was used as an additive. The recycling of carbon fiber reinforced epoxy resin composites was performed under supercritical conditions at different temperatures for different times with or without KOH additive. After the supercritical treatment, epoxy resin was decomposed, the recycled carbon fibers were removed from the sample holder, cleaned in an ultrasonic bath of acetone for 30 min, rinsed with fresh acetone several times at room temperature and dried in an oven at 80 $^{o}$C for 24 h before characterization.

### 2.3 Removal of sizing agent on the as-received carbon fibers

Several bundles of the as-received carbon fibers were refluxed in butanone for one day to remove sizing agent. After refluxing, the fibers were rinsed 3 times with fresh acetone and dried in an oven at 80 $^{o}$C for 24 h before use.

### 2.4 Morphology

Field emission scanning electron images for carbon fibers were taken using a LEO 1530VP microscope with an accelerating voltage of 10 keV. Samples of virgin and recycled fibers were all tested using a thermogravimetric analyzer (NETZSCH STA 409 PC/PG, Germany) to analyze resin content and the thermal stability of the fibers. Each sample was heated at 10 $^{o}$C min$^{-1}$ in argon up to a maximum temperature of 900 $^{o}$C. Single fiber tensile test was conducted with a LLY-06E tensile testing machine (Laizhou electron Instrument Co. Ltd. China). Filaments were bonded to a standard card frame with epoxy resin. The length of the fibers was 25 mm and the cross-head speed of the tensile testing machine was set to 0.5 mm·min$^{-1}$. At least 40 filaments were tested to give an average result. The tensile test gave a load, $P$ as a function of extension. The diameter of the single carbon fiber, $D$ was measured using a scanning electron microscope. After each tensile test, the single fiber was carefully collected for the diameter measurement by SEM. Tensile stress $\sigma$ was calculated as follows:

$$\sigma=4P/(\pi D^2) \quad (1)$$

The fiber surface compositions and surface functional groups were analyzed by XPS (PHI Quantera SXM, Japan), operated at ultrahigh vacuum about 6.7 × 10$^{-8}$ Torr with an excitation from an Al K$\alpha$ as a single anode source. The flood gun was an $Ar^+$ scanner with an energy about 2 eV and the binding energy of C 1s (284.6 eV) was used as a reference. The contact angle between carbon fiber and epoxy resin (diglycidyl ether of bisphenol A, DGEBA) were statistically measured using the Image-Proplus 6.0 software from the images taken using an optical microscope (YS100, Nikon, Japan) equipped with a camera (A620, Canon, Japan).

## 3 Results and discussion

### 3.1 Resin content

The epoxy resin content in the composites was determined by thermogravimetric analysis (TGA). As shown in Fig.1b, the epoxy resin in the composites was carbonized completely under the inert atmosphere at 515 $^{o}$C, and the mass fraction of the residual carbonized products remained 77.6% (Fig.1c). The residue contained carbon fiber and coke from the epoxy resin. Almost no weight loss is observed for the carbon