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Decomposition of waste carbon fiber reinforced epoxy resin composites in molten potassium hydroxide

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ABSTRACT

Recycling of carbon fiber reinforced epoxy resin composites has been investigated using molten potassium hydroxide as reaction media. The epoxy resin in composites was decomposed at temperatures ranged from 285 to 330 °C. The recovered carbon fibers were characterized by SEM, XPS and single fiber tensile test. More than 95% of the tensile strength of the virgin carbon fibers was retained. The surface C–OH decreased and COOH increased with increasing temperature. The decomposition products of epoxy resin in KOH was separated and analyzed by FTIR and MALDI-TOF. A possible mechanism for the decomposition of epoxy resin is proposed. The real-world CFRP wastes containing various contaminants such as thermoplastics, paints, sealants and glass fibers were also decomposed in the molten KOH.

1. Introduction

Carbon fiber reinforced polymers (CFRPs) have been extensively used in the aerospace, automobile and sports industries due to their outstanding mechanical properties, low weight and corrosion resistance. In 2012, the global nameplate capacity of carbon fiber was 111,785 tonnes and will rise to 156,845 tonnes by 2016 [1]. However, an increasing amount of waste CFRP generates including expired prepregs, manufacturing cut-offs, testing materials and end-of-life materials [2]. The high carbon fiber price, rising landfill costs, legislation implementation, and environmental pressure require the recycle of the valuable carbon fibers from CFRP waste.

The developed methods for reclamation of carbon fibers from waste thermoset composites can be divided into two categories according to that if the reactive solvent is used or not. The first type is thermal processing including pyrolysis [3–5], fluidized bed process [6–8] and microwave treatments [9]. Pyrolysis, in which the resin matrix is decomposed into small organic compounds at 400–700 °C in an inert atmosphere and carbon fibers are recovered, is the only commercial-scale carbon fiber recycling operation in the world. Char always forms and the extra oxidation step is needed to remove it. Adherent Technologies, Inc. uses a vacuum pyrolysis process for recycling of CFRP waste to reduce the char [10]. Akonda et al. [4] recycled the carbon fibers without visible surface flaws at 500 °C for 10 min in air. The recycled carbon fibers retained 85% of the tensile strength and 93% of modulus of the virgin fibers. Meyer et al. found that the fiber surface was covered with a layer of pyrolytic carbon during pyrolysis process at 700 °C, leading to the increase of the contact resistance between the fibers and the decrease of the adhesion to a new matrix [5]. The fluidized bed process (450–550 °C) is tolerant of mixed and contaminated CRFP waste but the mechanical properties suffer significant degradation [11].

The second type is sovolysis process, which used supercritical/subcritical fluids [12–18], nitric acid [19,20], and alcohols at atmospheric pressure [21–23] as solvent to depolymerize epoxy resin. The research group at the University of Nottingham investigated several supercritical fluids and found that supercritical propanol was an appropriate reaction medium for recycling CFRP [12–14]. Recycled carbon fibers with virtually no mechanical degradation were obtained and degradation products

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from epoxy resin can be recovered [14]. Several other research groups used sub- and supercritical water as reaction medium and various additives such as acid [15], base [16], salt [17] and oxygen [18] were added into reaction system to accelerate the decomposition rate of epoxy resin. However, the high pressure nature of autoclave brings the problem of processing speed and cost control. Some solvents operating at atmospheric pressure have been used as reactive medium to reduce the recycling cost and manipulative steps. Gersifi et al. depolymerized epoxide-amine/anhydride hardened resin in diethylene glycols, using titanium n-butoxide as catalyst in relatively mild conditions [21,22]. The solvolytic cleavage of ether and ester bond was identified for the amine and anhydride cured epoxy resin, respectively. Tomoko et al. [23] separated undamaged fibers in diethyleneglycol monomethylethter and benzyl alcohol with a catalyst (potassium phosphate) under their subcritical state at 190–350 °C for 1–8 h. Such recycling process can be carried out in a standard reactor. The disadvantage of these methods is all the composites and contaminants cannot be treated. In addition, the treatment time is too long. So, to explore a new reaction system which operated under mild conditions and tolerated contaminants is necessary to establish a commercially viable recycling process.

There are still some barriers in recycling the real-world CFRP waste. The real-world CFRP waste commonly consists of various contaminants such as thermoplastic, paint, sealants and glass fiber. The glass fibers in hybrid fiber reinforced epoxy resin composites are especially difficult to remove because of the inorganic nature similar to carbon fiber. The composite contains a thermally stable aromatic resin system such as epoxy novolac resin or 4,4'-diaminodiphenylmethane cured epoxy resin, which is hard to be degraded. In the same time, the mechanical properties should be retained as much as possible during removal of resin from fibers under mild reaction conditions.

A molten KOH process has been developed to recycle CFRP. Molten alkali or salt is solid at standard temperature and pressure but turns into liquid at elevated temperature. In fact, molten alkali or salt is a class of ionic liquids. Molten alkali or molten salt can be operated at low pressure and high temperature due to its non-volatility property. Kamimura et al. have successfully decomposed waste fiber-reinforced unsaturated polyester in ionic liquids by microwave irradiation, and the decomposition reaction could be achieved within several minutes [24]. Flandinet et al. dissolved glasses, oxides and destructed plastics present in waste electrical and electronic equipments without oxidizing the valuable metals using specifically molten KOH–NaOH eutectic at 300 °C for 1 h [25]. Here, the molten KOH at temperatures between 285 and 330 °C was used as reaction medium to decompose CFRP. The effects of reaction parameters on the decomposition reaction, and properties of the recycled carbon fibers and the degradation products of epoxy resin were also examined.

2. Material and methods

2.1. Materials and reagents

Plain weave PAN-based carbon fiber fabrics (T300, 3k) were purchased from Toray Industries, Inc. The mixed matrix resin used was diglycidyl ether of bisphenol A (DGEBA) provided by Wuxi Lanxing Co., Ltd. (China) and epoxy novolac resin (EPN) obtained from Shanghai Resin Factory Co., Ltd. 1-cyanoethyl-2-ethyl-4-methylimidazole (2E4MZ-CN), which was purchased from Shikoku Chemicals Corporation, was chosen as the curing agent. CFRP bicycle wastes were supplied by Anai bicycle factory. Potassium hydroxide (85% purity) was supplied by Beijing Chemical Works and was used without further treatment.

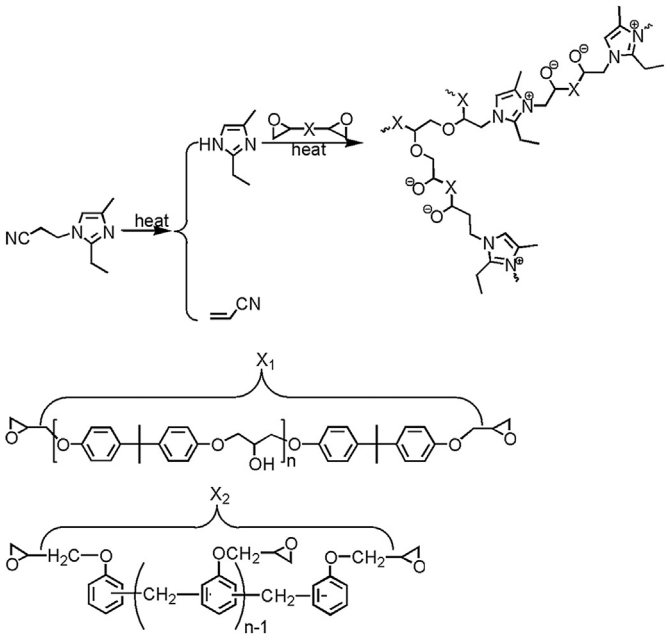
2.2. Preparation of carbon fiber reinforced epoxy resin composites

CFRP sheets were prepared in the laboratory using vacuum bagging technique. The DGEBA, EPN and 2E4MZ-CN were mixed at a 70:30:5 weight ratios and then heated and degassed for 15 min. The above mixture was soaked through the carbon fiber layers under vacuum and cured at 80 °C for 2 h and then 150 °C for 4 h. Fiber content in composites was determined according to the standard method ISO-14127. The mass of a test specimen was determined before and after digestion of the resin with concentrated nitric acid at 120 °C for 90 min. The fiber content in the obtained composite was 63.64 wt%. Scheme 1 shows the process of the matrix of CFRP being formed.

2.3. Decomposition of CFRP in molten KOH

The diagram of the decomposition experiment was shown in Fig. 1. The obtained CFRP sheets were cut into pieces of 10 mm × 45 mm × 1.5 mm. The decomposition reaction was conducted in a cylindrical stainless steel reactor which heated in a salt bath of sodium nitrate, sodium nitrite and potassium nitrate mixture. Potassium hydroxide was put into the reactor and heated to a molten state. The CFRPs were enwrapped in nickel screen and then fed into the molten KOH. The reactor was flushed with pure nitrogen with a flow rate of 20 mL/min. After a period of reaction, the fibers were taken out together with the nickel screen. After cooling, the recycled carbon fibers were collected, washed with distilled water for three times and dried in vacuum at 80 °C for 12 h.

Fig. 2 presents the separation of decomposition products of epoxy resin. The mixture was dissolved in distilled water when the reaction temperature decreased to 80 °C, and then was neutralized with hydrochloric acid and filtered. The resulting solution was extracted by dichloromethane. Dichloromethane solution was concentrated and dried in vacuum and soluble fraction in dichloromethane was obtained. Water solution was concentrated, dried in vacuum and light yellow powder was obtained. The powder was washed with ethanol and soluble fraction in ethanol was obtained. The recovered solid were conducted to Soxhlet extraction and the soluble and insoluble components in acetone



Scheme 1. Reaction paths of the matrix network curing.