



# Recycling of carbon fiber reinforced plastic containing amine-cured epoxy resin using supercritical and subcritical fluids



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## ABSTRACT

Chemical recycling of carbon fiber reinforced plastic (CFRP) containing an amine-cured epoxy as the matrix resin was investigated with a process using supercritical alcohols or ketones as solvents. Amine-cured epoxy resin was decomposed by a supercritical solvent (methanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, *tert*-butanol, acetone, or methyl ethyl ketone) at 320 °C in the reaction time range 6–120 min. The decomposition rate depended on the solvent, and super- and subcritical acetone were ultimately selected as optimal for rapidly degrading the matrix resin. The decomposition rate of the epoxy resin using supercritical acetone was expressed by a surface reaction and shrinking core model. The recovered carbon fibers from the CFRP retained the shape of the plain fabric sheets and their tensile strength reduction was negligible.

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## 1. Introduction

Much attention has been paid recently to the recycling of waste plastics because of concerns for the environment and resource conservation. Among plastics, carbon fiber reinforced plastic (CFRP) has excellent properties, including low density, high strength, and high corrosion resistance. It is widely used in many products such as the airfoils of airplanes, and sports and recreational goods, including tennis rackets and fishing rods. However, for CFRP waste, recycling can be difficult because it contains thermosetting plastics such as epoxy resin. Currently, most CFRP waste is deposited in landfills, which are limited in area and have high associated costs. The greatest benefit of CFRP recycling is the recovery of the most valuable part of the composite, the carbon fiber materials. Understanding the decomposition behavior of the epoxy resin in CFRPs will be

important for establishing appropriate recycling techniques for the recovery of the carbon fiber component.

The recycling of CFRP via the decomposition of the epoxy resin has been investigated [1] through methods such as hydrogenolysis [2], nitric acid degradation [3], and glycolysis [4]. The most important steps are the decomposition or dissolution of the polymer component in the CFRP and the recovery of undamaged carbon fibers.

Supercritical and subcritical fluid techniques for plastics recycling have been widely investigated. In such studies, water [5–19] or alcohols [20–32] have been used as solvents for the decomposition of the plastics. The recycling of CFRPs using supercritical and subcritical fluids has also been investigated [33–35]. The treatment of CFRPs or epoxy resins with supercritical and subcritical water without a catalyst [36,37], with a catalyst [38–40] or oxidant [37,40,41], or with CO<sub>2</sub>-expanded water [42] has been reported. Supercritical alcohol has also gained much attention as a solvent for the degradation of plastics because it can selectively decompose specific chemical bonds such as those in esters, thus allowing the alcohol to dissolve the products. The decomposition of the epoxy resin in CFRPs has been studied using supercritical 1-propanol at 450 °C and above 5 MPa [43] and at 310 °C and 5.2 MPa without

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a catalyst [44], and the addition of KOH was found to promote the Guerbet reaction of 1-propanol [45]. Okajima et al. [46] investigated the treatment of a CFRP using supercritical methanol at 270–350 °C and 8–10 MPa. In this case, the bridge structure of the anhydride-cured epoxy resin was decomposed selectively and the recovered resin had a chemical structure similar to that of the epoxy resin before decomposition; this was accomplished by using a semi-flow-type experimental setup at 270–285 °C and 8 MPa. Pinëro-Hernanz et al. [47] investigated the effect of four different solvents on the decomposition of an epoxy resin. They reported that the decomposition ratio of an amine-cured epoxy resin in CFRP was higher when acetone was used than when methanol, ethanol, and 1-propanol were used at temperatures of 300, 375, and 450 °C over 15 min. Additionally, a supercritical 1-propanol-alkali solution was found sufficient to degrade more than 95% of the resin in less than 15 min. However, the optimum conditions for the decomposition of the epoxy resin using supercritical acetone were not discussed.

In this study, the effect of solvents on the uncatalyzed decomposition of an amine-cured epoxy resin were investigated and the optimum solvent under various reaction conditions (temperature, pressure, and reaction time) were determined. Eight solvents tested were methanol, ethanol, 1-propanol, 1-butanol, 2-butanol, *tert*-butanol, acetone, and methyl ethyl ketone. Reaction kinetics were analyzed using the optimum solvent. Finally, the amine-cured epoxy resin in the CFRP was decomposed via the optimized process and the carbon fiber was recovered using a semi-flow-type bench plant. The tensile strength of the recovered carbon fiber was measured and compared with that of virgin carbon fiber.

## 2. Materials and methods

### 2.1. Materials

Glycidyl end-capped poly(bisphenol A-co-epichlorohydrin) (Aldrich, weight-average molecular weight, 355) was used as the raw material for the thermosetting epoxy resin, where the degree of polymerization was 0 or 1. Tetraethylenepentamine (Aldrich, technical grade) was used as the curing agent. Torayca cloth CO6343, which was made from T300–3000 carbon fibers (Toray Industries, Inc.), was used as the reinforcement. Guaranteed grades of methanol, ethanol, 1-propanol, 1-butanol, 2-butanol, *tert*-butanol, and methyl ethyl ketone (>99.8% purity), as well as acetone (>99.5% purity), were used as decomposition solvents (Wako Pure Chemicals Co.).

The resin and curing agents were mixed at a weight ratio of 10:1.4. To prepare the amine-cured epoxy resin, the mixture was heated at 80 °C for 60 min. The cured resin was crushed into grain-sized pieces that were about 3 mm in diameter with a crusher, and the grains obtained were used for the experiments. The glass transition temperatures  $T_g$  of the cured resins were measured with a DTG-60A thermal analyzer (Shimadzu Co.). The amine-cured epoxy resin was heated at 20 °C/min from 30 to 1000 °C without a hold time in an air flow of 100 mL/min. Weight loss from the cured epoxy resin was observed in the range 300–445 °C. A reference value for the  $T_g$  of a bisphenol-A-type epoxy resin cured with imidazole was 183 °C [48]. Furthermore, the weight of the bisphenol-A-type epoxy resin and 3-methylbenzo[*b*]oxirene-2-ol cured with 3-(2-ethyl-4-methyl-1*H*-epoxy imidazol-1-yl)propanenitrile decreased near 400–475 °C [47].

The CFRP, which contained eight carbon fiber cloths, was manufactured using the hand lay-up method. The carbon fiber cloths were laminated in a mold. The epoxy resin was then impregnated into the carbon fiber cloths and cured at 80 °C for 60 min. The content of the carbon fiber was 52 wt%. After curing, the CFRP plate was cut into rectangular pieces, 200 mm × 45 mm × 3 mm in size, which

were used in the semi-flow-type reactor for the recycling experiments. The weight contents of the carbon fiber and epoxy resin in the CFRP were determined by combustion methods based on JIS K 7075 [49].

### 2.2. Batch-type reactor

The solvolysis of the amine-cured epoxy resin with supercritical fluids was carried out in a batch-type setup. The reactor consisted of a tube composed of type-316 stainless steel, with an outer diameter of 12.7 mm, a thickness of 2.1 mm, a length of 150 mm, and an inner volume of 8.9 cm<sup>3</sup>. The reaction pressure was calculated from the reaction temperature, the inner volume of the reactor, and the loaded weight of solvent by using the equation of state for a pure solvent [50]. The ratios of the solvent volumes to the epoxy resin loaded in the reactor are shown in Table 1.

Predetermined weights of the epoxy resin and solvent were loaded into the reactor. For experiments examining the effects of solvent and temperature, 0.1 g of epoxy resin was loaded, whereas in those concerned with reaction pressures, 0.087 g of epoxy resin was loaded. Then, both sides of the reactor were sealed with Swagelok caps and the reactor was heated in a salt bath to effect epoxy resin decomposition. After a certain reaction time had passed, the reactor was removed from the salt bath and cooled in water to stop the reaction as quickly as possible. For safety, the reactor was cooled in water for 15 min, although only 1 min was required to cool the material in the reactor to room temperature. Solvent-soluble products and residual thermosetting epoxy resin were recovered from the reactor with a solvent. For example, when the epoxy resin was decomposed by supercritical acetone, the decomposition product was recovered from the reactor with acetone. The product and residue were separated into liquid and solid components by filtration. The residual epoxy resin was weighed precisely using an electronic balance after drying it for half a day in an oven at 60 °C.

### 2.3. Semi-flow-type bench plant

The recovery of carbon fiber from the CFRP using supercritical acetone was carried out in a semi-flow-type bench plant as shown in Fig. S1 (the devices were made by the Taiatsu Techno Co.). The reactor, made of type-316 stainless steel, had an inner diameter of 100 mm, a thickness of 10 mm, a length of 600 mm, and an inner volume of 4712 cm<sup>3</sup>. In this study, a predetermined weight of CFRP was loaded into the reactor and acetone was used as a solvent for the treatment of the CFRP. Further details about this apparatus can be found in an earlier study [46]. The flow rate of acetone was 20 mL/min under standard laboratory atmospheric conditions.

### 2.4. Product analysis

The tensile strength of the recovered carbon fiber was measured with a tensile testing machine (Autograph AGS-5kNG, Shimadzu Co.) following methods based on JIS R7606 [51]. Briefly, a single carbon fiber was glued onto a paper frame using cyanoacrylate adhesive; the gauge length was set to 25 mm. The single fiber was then loaded at a rate of 1 mm/min until the fiber failed. During testing, the loading forces versus displacement data were logged on a computer. This type of measurement was performed for at least 30 fibers.

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