



Chemical recycling of carbon fiber reinforced plastic using supercritical methanol



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ABSTRACT

Advanced chemical recycling of carbon fiber reinforced plastic (CFRP) was developed using supercritical methanol. In this method, the thermosetting epoxy resin in CFRP was converted to a thermoplastic resin by the selective decomposition of the bridged structure by supercritical methanol at 270 °C and 8 MPa for 90 min and the resin dissolved in supercritical methanol. On the other hand, the carbon fiber was fully recovered from CFRP without the plastic component and it had no thermal damage. The bridged structure in the epoxy resin could be formed again by adding a cross-linker to the recovered thermoplastic resin and the thermosetting resin was reproduced. This was the first attempt on the recycling of thermosetting epoxy resin. However, in order to maintain the strength of the recycled epoxy resin to that of virgin epoxy resin, the proper ratio of the recovered thermoplastic resin to virgin epoxy resin was determined. The recovered carbon fiber from CFRP maintained the shape of the plain fabric and the reduction of the tensile strength was less than 9% compared with the virgin one. The recovered carbon fiber could be used to make a recycled CFRP with epoxy resin and cross-linker, the strength of which was close to that of virgin CFRP.

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1. Introduction

Recently much attention has been paid to the recycling of waste plastics from the viewpoint of environmental protection and conservation of resources. Carbon fiber-reinforced plastic (CFRP) has excellent properties, including low density, high strength and high corrosion resistance. The material is widely used in many fields such as for the airfoils of airplanes, bodies of rockets and artificial satellites, and sports and recreational goods such as tennis rackets and fishing rods. CFRP has been receiving increasing attention, particularly in the automobile industry because it helps to reduce the weight of the car and improve mileage. However, the huge amount of waste CFRP generated is difficult to recycle because it contains refractory thermosetting plastics such as epoxy resin. Currently most CFRP waste goes to landfill, for which area is limited and the cost is high. Therefore the development of advanced recycling techniques for CFRP is urgently required.

Several methods for recycling of CFRP have been investigated. The most important step is the decomposition or dissolution of the polymer component in CFRP and the recovery of undamaged carbon fiber. Hydrogenolysis was examined in partially hydrogenated aromatic solvents such as tetralin and 9,10-dihydroanthracene at 320–420 °C for 1–5 h, where hydrogenated aromatics were served as hydrogen donor solvents [1]. 8 M nitric acid solution at 90 °C was used to decompose epoxy resin to a mixture of nitrated compounds for 20–100 h [2]. El Gersifi et al. reported that the glycolysis of epoxy resin with a titanium(IV) *n*-butoxide catalyst produced esterdiols and tetra-alcohols, and the reaction proceeded through an alcoholysis/transesterification reaction mechanism [3].

Super/subcritical fluid techniques have been widely investigated [4]. Supercritical or subcritical water is a potential medium for the recycling of plastics because it is harmless, inexpensive, and highly reactive with organic materials. Okajima et al. studied the treatment of CFRP in sub/supercritical water in the presence of an alkaline catalyst at 300–400 °C and 20 MPa [5]. The polymer component was decomposed to small molecules, and the decomposition products could be washed off the carbon fiber using an organic solvent such as acetone. The tensile strength of the

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recovered carbon fiber was about 15% lower than that of the virgin fiber and the number of functional groups containing oxygen atoms on the surface of the recovered carbon fiber decreased. Bai et al. reported that carbon fiber in CFRP could be recovered in oxygen in supercritical water [6]. The recovered carbon fiber had a higher tensile strength than the virgin fiber when the decomposition rate was above 85% at 30 ± 1 MPa and 440 ± 10 °C for 30 ± 5 min. The tensile strength of the recovered carbon fiber, however, decreased rapidly as the decomposition rate exceeded 96.5% owing to excessive oxidation of the recovered carbon fiber. Liu et al. investigated the synergistic effect of phenol and potassium hydroxide for the recovery of carbon fiber from CFRP in subcritical water [7]. The tensile strength of the recovered carbon fiber did not decrease and the concentrations of various oxygenated functional groups on the carbon fiber surface showed little change. However, large amounts of phenol and potassium hydroxide were required for the decomposition of the epoxy resin. Furthermore several research groups have studied the decomposition of other thermosetting matrix resins with bridged structures, such as cross-linked unsaturated polyester [8–10] and phenol resin [11], to small molecules.

Supercritical or subcritical alcohols have gained much attention as decomposition solvents for plastics because they can selectively decompose specific bonds such as ester and urethane bonds, thus allowing the alcohols to dissolve the products [12–22]. Furthermore alcohols are easy to handle because they have a lower critical temperature and pressure than water. Therefore supercritical or subcritical alcohols have been sometimes used to decompose thermosetting resins. Cross-linked unsaturated polyester in glass fiber-reinforced plastic (GFRP) was completely decomposed using supercritical methanol [23], subcritical dimonomethylether and subcritical benzyl alcohol [24]. Silane-cross-linked polyethylene [25,26] and phenol resin [27] were decomposed by supercritical methanol with a decomposition efficiency of almost 100%. The decomposition of epoxy resin in CFRP was investigated using supercritical *n*-propanol at 450 °C and above 5 MPa [28] and at 310 °C and 5.2 MPa [29]. However, only the molecular weights of the decomposition products were measured and the chemical structures of the products were not clarified in these literatures. Amine-curing epoxy resin in CFRP has been decomposed using several kinds of supercritical alcohols and acetone [30]. The molecular weights and functional groups were analyzed but the chemical structures of the products were not. This was because there were many kinds of the decomposition products by the pyrolysis and it was difficult to determine the chemical structure of each product. Furthermore the reuse of the recovered carbon fiber and the decomposition products of the polymer component were hardly investigated in the previous studies.

In order to establish a complete recycling technique of CFRP, we studied the selective decomposition of the cross-linked structure of the thermosetting epoxy resin in CFRP using supercritical methanol and the reuse of the recovered resin and carbon fiber recycled CFRP. For the recovered thermoplastic resin, the curing of the resin was tried and the strength was examined. For the recovered carbon fiber, the tensile strength and the concentration of oxygenated functional groups on the surface were measured and compared with those of the virgin carbon fiber. Next the recycled CFRP was produced from the recovered carbon fiber and virgin epoxy resin and the possibility of the recycling of CFRP was explored.

2. Experimental

2.1. Batch-type reactor

Fig. 1 shows a batch-type experimental setup for the treatment of CFRP. The reactor was a tube of type-316 stainless steel with

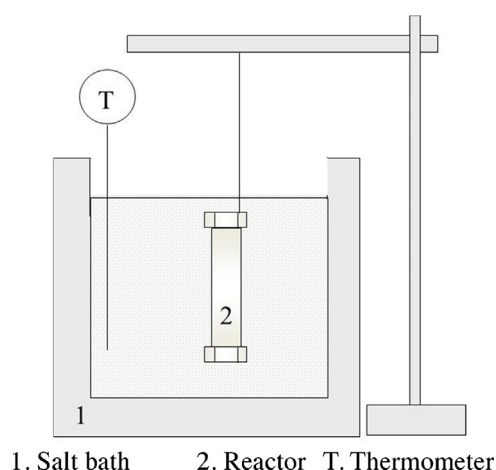


Fig. 1. Batch-type experimental setup.

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 cm³. The whole reactor was immersed in a salt bath. It took approximately 90 s to heat the reactor from room temperature to the maximum reaction temperature of 350 °C. This short period was neglected and the starting point of the reaction time was defined as the time when the reactor was put into the salt bath. Upon reaching thermal equilibrium, the temperature difference between the inside of the reactor and the salt bath was within 2 °C, and thus, the reaction temperature was assumed to be equal to the temperature of the salt bath. The reaction pressure was calculated from the reaction temperature, the inner volume of the reactor, and the loaded weight of methanol using the equation of state for pure methanol [31].

The experimental procedure was as follows. Given weights of CFRP and methanol were loaded into the reactor. Then both sides of the reactor were sealed with Swagelok caps and the reactor was heated in the salt bath to decompose the epoxy resin in CFRP. After a certain reaction time, the reactor was taken out of the salt bath and cooled in water to stop the reaction as quickly as possible. Methanol-soluble products, residual thermosetting epoxy resin and carbon fiber were recovered from the reactor with methanol. They were separated into solid and liquid components by filtration. The recovered carbon fiber with or without the remaining epoxy resin was weighed precisely using an electronic balance after drying it for half a day.

2.2. Semi-flow-type reactor

Fig. 2 shows a semi-flow-type experimental setup made by Taiatsu Techno Co. The reactor was a pressurized cylinder of type-316 stainless steel with an inner diameter of 100 mm, a thickness of 10 mm, a length of 600 mm and an inner volume of 4712 cm³. The reactor was heated using an electric furnace. It took approximately 3 h to heat the reactor from room temperature to the reaction temperature. The reaction temperature was measured at the bottom of the inside of the reactor using a K-type thermocouple. The preheater was a spiral tube of type-316 stainless steel with a length of 2000 mm, an outer diameter of 3.18 mm and an inner volume of approximately 5 cm³. The temperature of the preheater was measured by a K-type thermocouple mounted on its outer wall. The pressure of the reactor and preheater was controlled by a back-pressure regulator to within 1%.

The experimental procedure was as follows. A given weight of CFRP was charged into the reactor, which was then sealed. A given volume of methanol was injected into the reactor using a high-pressure pump. Then the reactor and the preheater were heated to

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