



Mild chemical recycling of aerospace fiber/epoxy composite wastes and utilization of the decomposed resin



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ABSTRACT

Carbon fiber reinforced polymers (CFRPs) with high T_g (>200 °C) are indispensable for aerospace industry where high service temperature is required. Chemical recycling of the matrix polymers for these CFRP composites is more difficult than that of their low T_g analogues. In this work, an efficient approach for mild chemical recycling of CFRP with a T_g of ~ 210 °C was developed using a $ZnCl_2$ /ethanol catalyst system. The high efficiency of $ZnCl_2$ /ethanol was attributed to the strong coordination effect of $ZnCl_2$ with the C–N bonds and the strong swelling ability of ethanol, which worked together to break down the chemical bonds of the cross-linked polymer. Also, mild degradation temperature (<200 °C) imparted little damage to the recovered fibers. The decomposed matrix polymer (DMP) was in the oligomer form and contained multifunctional reactive groups. When DMP was used as a reactive ingredient and added up to 15 wt% to the preparation of new epoxy materials, the resulting cross-linked polymers could still retain the high strength and modulus compared to the neat polymer without addition of DMP.

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1. Introduction

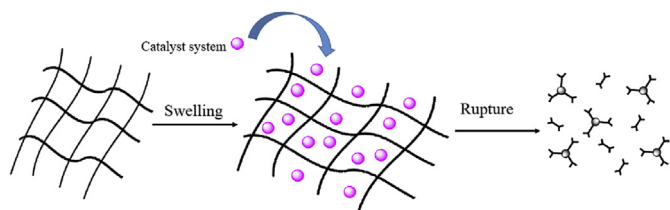
Owing to the high-modulus, high-strength and low-density, CFRP has become a preferred choice of material in the aerospace, sporting goods, automotive and wind energy industries [1–3]. However, the rapid growth of CFRP brings a great environmental and sustainable challenge. The CFRP wastes resulted from product manufacturing and post-service products cannot be recycled as easily as thermoplastics, while disposal in landfills takes no advantage of the residual value but adds burden to waste management [4]. In order to solve this problem, various recycling methods, such as mechanical recycling [5,6], pyrolysis [7], fluidized bed thermal process [8], chemical treatment in near-critical or supercritical water [9,10], have already been explored to recover

carbon fibers and cured resins. However, harsh conditions, such as high temperature (>350 °C) and high reaction pressure, are required for these recycling methods and are energy-intensive. Also, such high recycling temperature likely results in certain damages to the surface of the recovered carbon fibers. More seriously, the decomposed resin at such harsh conditions is often a complex mixture of gaseous, liquid and solid chemicals, making the viable reuse of the recycled chemicals very difficult [11].

In recent years, recycling of CFRP by chemical degradation has become a promising method to claim the residual values for both fibers and chemicals [12]. As shown in Scheme 1, chemical degradation of CFRP usually proceeds in two main stages: first, the cured resin swells in liquid solution and the catalyst permeates into the cross-linked network; second, the chemical bonds of the cured resin are cleaved, forming soluble molecules under the effect of catalysts. It is critical to develop efficient catalytic systems that are capable of permeating into the cured resins and breaking down the chemical bonds of cured resins. Early chemical degradation studies

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Scheme 1. Principle of CFRP degradation using chemical degradation method.

were focused on recycling the CFRP using strong acid [13,14] or strong alkali aqueous solutions [15,16], such as nitric acid and potassium hydroxide solutions. Use of these caustic chemicals poses potential pollution to the environment and easily causes corrosion to equipment, reducing its scalability. Recently, chemical recycling of an aliphatic amine cured bisphenol-A (BPA) epoxy in the $\text{ZnCl}_2/\text{H}_2\text{O}$ solution was performed at $220\text{ }^\circ\text{C}$ [17], which was much lower than the temperatures in most other reports. $\text{K}_2\text{CO}_3/\text{phenol}$ was also found to be an effective catalyst system that can well decompose BPA cured anhydride below $200\text{ }^\circ\text{C}$ [18]. However, to the best of our knowledge, all the reported mild chemical recycling technologies are used to deal with low T_g ($<150\text{ }^\circ\text{C}$) CFRPs. It is important to note that the CFRPs with high T_g ($>200\text{ }^\circ\text{C}$) are widely used in aerospace industry. Due to their stiffer backbone structures and higher crosslink densities, high T_g CFRPs are much more difficult to be recycled compared with their lower T_g analogues. There has not been a report for the degradation of high T_g ($>200\text{ }^\circ\text{C}$) epoxy systems under mild conditions (e.g. low degradation temperature ($<200\text{ }^\circ\text{C}$) and mild catalyst system).

In addition to the reaction severity of CFRP degradation, reuse of the decomposed matrix polymer (DMP) is another challenge to be resolved. The matrix resin under the harsh reaction conditions is decomposed into a complex mixture of small molecules, which show little practical values and may become secondary waste after degradation [19]. Current research on CFRP recycling is mainly focused on the recovery of carbon fibers [20–22], but utilization of the DMP is rarely explored due to the complexity of the decomposed product. Generally, CFRP comprises 30–40 wt% resin materials which are mostly epoxies, bismaleimides and unsaturated polyesters and are much more expensive than traditional thermoplastics [23]. Making utilization of DMP is beneficial to both economic value and environmental protection.

In this work, we introduced an effective chemical recycling method for a waste CFRP of high T_g (Figs. S2 and S3) and high thermal stability (Fig. S4) under mild condition ($<200\text{ }^\circ\text{C}$). The decomposed resin and recovered carbon fiber (CF) were characterized. The decomposed resin was found to be in an oligomer form; when added as a reactive ingredient for preparation of new epoxy, increased in flexural strength, T_g and fracture strain are demonstrated.

2. Experimental section

2.1. Materials

The CFRP waste was obtained from the manufacturing scraps and provided by the Boeing Company, and the main composition of the matrix is amine-cured epoxy. DER331 epoxy resin (DOW Chemical Company, $\text{EEW} = 188.0\text{ g equiv.}^{-1}$) was supplied by EHORN Company. Nadic methyl anhydride (99.4%) was purchased from Electron Microscopy Sciences. Zinc chloride (ZnCl_2), ferric chloride (FeCl_3), magnesium chloride (MgCl_2), aluminium chloride (AlCl_3), phosphotungstic acid (HPW), 2-ethyl-4-methylimidazole (2E4MZ, 99+%, Acros Organics), and all solvents were purchased

from Fisher Scientific. All chemicals were used as received unless otherwise stated.

2.2. Characterizations

Nuclear magnetic resonance (NMR) spectra were recorded on a fully automated Varian 400-MR spectrometer (400 MHz). The sample was dissolved in CDCl_3 and each sample was scanned 16 times. Chemical shifts of ^1H NMR peaks were reported in ppm, and the data was collected from 14 to -2 ppm. Fourier transform infrared spectroscopy (FTIR) spectra were collected on a NICOLET i550 FTIR spectrophotometer. The specimen for FTIR experiment was prepared by grinding the sample (1 mg) and potassium bromide (KBr, 100 mg) powder in a mortar and then compressing the mixture into a disk using a mold. The sample was scanned from 4000 to 400 cm^{-1} with a resolution of 4.0 cm^{-1} for 64 times.

T_g values were measured using a differential scanning calorimeter (DSC 1, Mettler-Toledo, Switzerland). The sample (~ 5 mg) was scanned from 25 to $260\text{ }^\circ\text{C}$ at a heating rate of 10 K min^{-1} under nitrogen atmosphere. Thermal stability was measured using a TGA/DSC 1 thermo-gravimetric analyzer (TGA) and the sample (~ 10 mg) was scanned from 50 to $800\text{ }^\circ\text{C}$ at a heating rate of 10 K min^{-1} under nitrogen or oxygen atmosphere. Dynamic mechanical properties of the epoxy and CFRP composite were measured using a dynamic mechanical analyzer (DMA) (Q800, Thermal Instrument) in the single cantilever mode. The dimensions of the specimen were $35.0\text{ mm} \times 12.8\text{ mm} \times 3.0\text{ mm}$. The frequency was set at 1 Hz and the oscillating amplitude at $15\text{ }\mu\text{m}$. The sample was scanned from 50 to $300\text{ }^\circ\text{C}$ at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$.

Flexural strengths of cured epoxy samples were determined using an Instron 4466 test machine equipped with a 10 KN load cell, and the test procedures was carried out according to the ASTM D790-10 standard. The dimensions of the specimen were $3.2\text{ mm} \times 12.7\text{ mm} \times 125\text{ mm}$. For each sample, at least five specimens were measured. After test, fracture surfaces were coated with gold with a layer thickness of about 3 nm. The gold plated samples were then examined by scanning electron microscopy (FE SEM, Quanta 200F). For observing the surface of conductive carbon fiber, no gold plating was used.

2.3. Decomposition of CFRP

Prior to chemical decomposition, the large CFRP waste board (Fig. S1) were cut into blocks with an average size of $ca. 1\text{ cm} \times 1\text{ cm} \times 1\text{ cm}$ using a power saw.

The degradation reaction was carried out in a 100-mL pressure reactor (Series 4842, Parr Instrument Company). The general procedure (Scheme 2) of the chemical recycling process is described as follows. $\text{ZnCl}_2/\text{ethanol}$ solution and CFRP wastes were directly added into a 100-mL pressure reactor. The amount of $\text{ZnCl}_2/\text{ethanol}$ solution was five times (or higher) that of CFRP wastes by weight to ensure the complete immersion of waste sample in solution. The reaction temperature was raised to a predetermined temperature, and the reaction was continued for several hours (mostly 5 h) at the temperature. The reactor was cooled down naturally to the room temperature. The reaction mixture was filtered and the insoluble was rinsed with acetone for several times. The insoluble part was the carbon fiber and/or some undecomposed resin. The filtration solution was concentrated using a rotary evaporator, and the decomposed matrix polymer (DMP) was precipitated by water. DMP was collected by filtration, washed with saturated Na_2CO_3 aqueous until no ZnCl_2 was detected. Subsequently, the DMP was washed with water and dried in vacuum oven at $70\text{ }^\circ\text{C}$ for 12 h, yielding a brown solid powder. The water solution of the filtration contains mainly (ZnCl_2) and was directly concentrated using rotary

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