

Recycling of Carbon/Epoxy Composites

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ABSTRACT: The recycling of carbon fibers from carbon/epoxy composites was attempted with a solvent method in nitric acid solutions. Gel permeation chromatography and gas chromatography/mass spectrometry showed that the epoxy resin could entirely decompose into low-molecular-weight compounds, and the main components of the dissoluble decomposed compounds were 2,4-dinitrophenol and 2-nitro-4-carboxylphenol. Electron probe microscopy showed no damage to the recycled carbon fibers. The single-fiber tension strength loss of the recycled carbon fibers was 1.1% under the following conditions: a decomposition temperature of 90 °C, a nitric acid solution concentration of 8M,

and a ratio of the sample weight to the nitric acid solution volume of 6 g:100 mL. Through orthogonal experimentation, the recycling conditions for the carbon/epoxy composites were examined. The best combination was a decomposition temperature of 90°C, a nitric acid solution concentration of 8M, and a ratio of the sample weight to the nitric acid solution volume of 4g:100 mL. This method could liquefy raw materials for rocket engine shells reinforced with carbon fibers. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1912–1916, 2004

Key words: composites; fibers; recycling; resins

INTRODUCTION

The aircraft and aerospace industries construct many of their components from high-strength graphite and carbon/epoxy composites. The increased production of carbon/epoxy composites in recent years has greatly increased the amount of waste materials. However, recycling this castoff has been difficult because the epoxy resin in the castoff cannot be melted down and remolded as what is done in the thermoplastic industry. Traditional methods have concentrated largely on disposal in landfill sites. Because of decreasing landfill space and increasing landfill costs, other approaches need to be developed for recycling thermosets.

Work on the recycling of thermoset composites can be divided into three categories. In most cases, thermoset composites are milled into very fine powders and are used as filler materials for polymers.^{1–3} Masatahi⁴ found that using glass-fiber-reinforced epoxy resin boards as fillers for epoxy resin products used as paints and adhesives could yield products with better strength and thermal expansion properties than those made with conventional fillers. For chemical recycling, the polymer is recovered as an organic compound, which may be used as a raw chemical material.⁵ A SMC of glass-fiber polyesters was pyrolyzed by Torres

et al.⁶ The obtained liquid could be used as petrol and fuel oil. Adherent Technologies Inc. has developed a chemical recycling technology that allows the recovery of carbon fibers and also produces a phenolic oil mixture that can be used for the formulation of phenol formaldehyde resins.⁷ Energy recovery means that the caloric content of the polymer matrix is usefully harvested by combustion.⁸ Most existing work on the recycling of thermoset composites emphasizes prepregs, but such technology could not be applied to cured systems.

Dang et al.⁹ found that a bisphenol F epoxy resin cured with 1,8-*p*-menthane diamine could be completely decomposed in a nitric acid solution. The decomposed products were repolymerized with an epoxy resin and a curing agent to prepare a recycled resin. This article reports on this solvent method for recycling carbon fibers from carbon/epoxy composites. The epoxy resin matrix was decomposed in a nitric acid solution at a high temperature, and the carbon fibers were recovered. First, the epoxy resin degradation product's chemical structure and molecular weight were studied, and through orthogonal experimentation, the recycling conditions of the carbon/epoxy composites were examined. Then, the recycled carbon fibers were tested to ascertain what degradation of the properties resulted from the process.

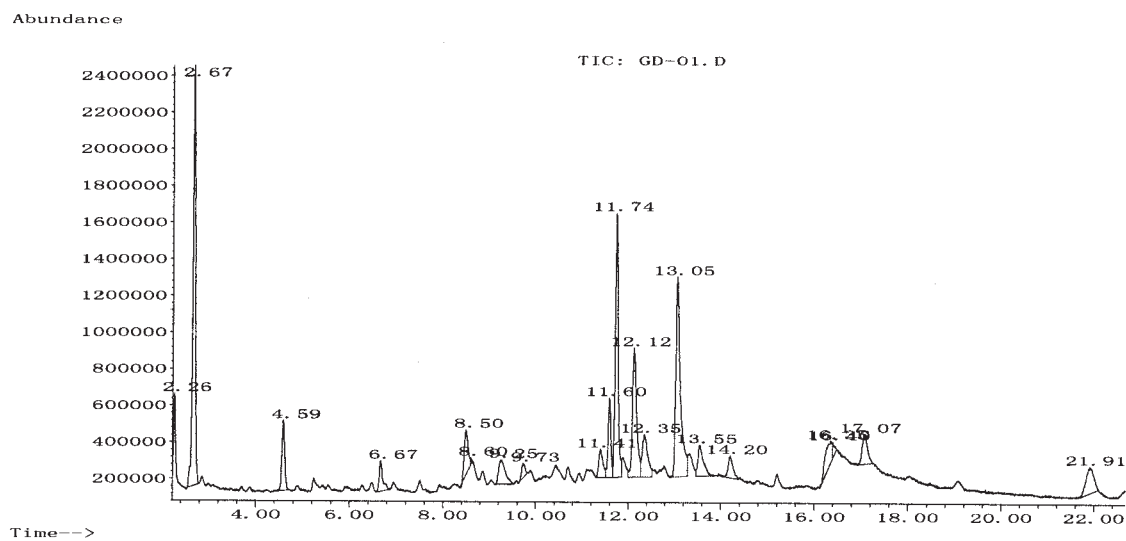
Correspondence to: Y. Liu (liuyy@hit.edu.cn).

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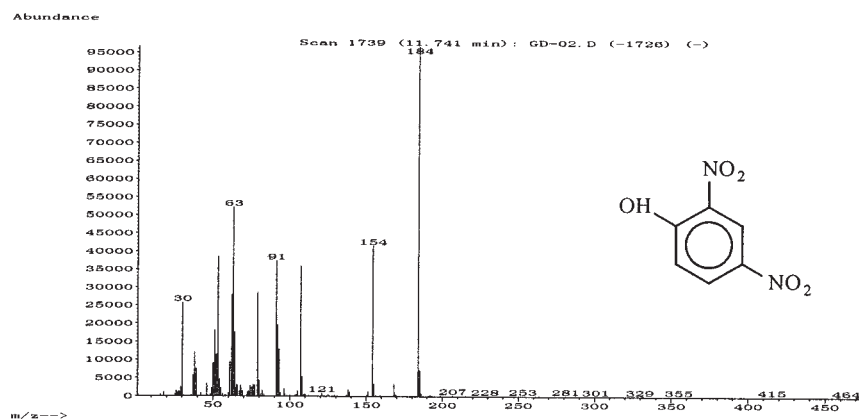
EXPERIMENTAL

Materials and sample preparation

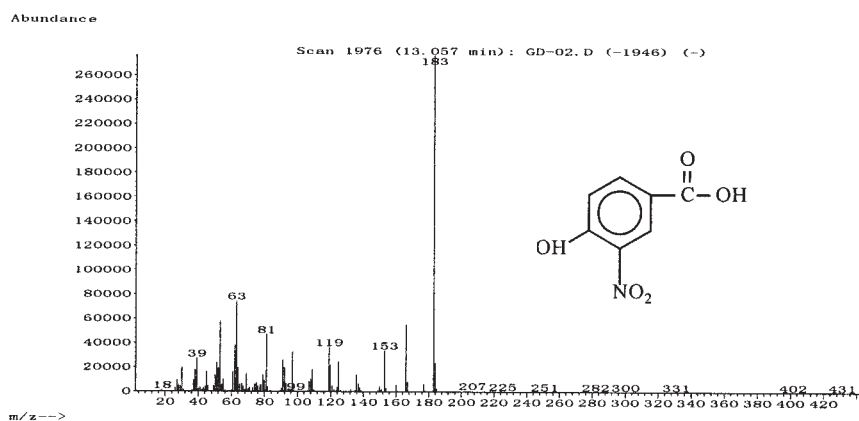
The epoxy composite was fabricated in our laboratory. A bisphenol A epoxy resin and the curing agent IPDA



(a)



(b)



(c)

Figure 1 GC-MS of a dissoluble decomposed substance of EP/IPDA after 9 h of immersion: (a) gas chromatography, (b) mass spectrometry of the 11.741-min peak in gas chromatography, and (c) mass spectrometry of the 13.057-min peak in gas chromatography.

TABLE I
GPC Analysis of the Crystals of a Dissoluble Decomposed Substance After 9 h of Immersion

Peak number	M_n	M_w	M_p	D	Area (%)
P1	3213	3255	3230	1.01	0.85
P2	327	410	495	1.26	80.70
P3	84	93	108	1.11	18.45

were used as the matrix. The carbon fibers were supplied as reinforced fibers in composites by Jilin Carbon Co, Ltd. The epoxy composite, reinforced with 67 wt % carbon fibers, was prepared. The curing conditions were 80°C for 2 h and 150°C for 4 h. The composite was cast into a 200 mm × 6 mm × 2 mm bar.

The technology epoxy composite was supplied by the Harbin Fiber Reinforced Plastics Institute and contained 60 wt % carbon fibers.

Each epoxy resin specimen was placed in a specially designed glass vessel [diameter (D) = 100 mm, length = 300 mm] and then immersed in a 100-mL nitric acid solution. The decomposition temperature was controlled in the water bath.

Measurement of the properties

The decomposed compound of the epoxy resin was analyzed with gas chromatography/mass spectrometry (GC-MS). Gel permeation chromatography (GPC) was conducted on a Waters 150-C ALC/GPC instrument with tetrahydrofuran as the solvent. Polystyrene was used as a calibration standard. The carbon fiber

TABLE II
Level and Factors of Orthogonal Experiments

Factor	T (°C)	C (M)	α (100 g/mL)
Level 1	90	8	6
Level 2	80	6	4
Level 3	70	4	2

surface was observed and imaged with electron probe microscopy with a JEOL JCSA-733 instrument. The single-fiber tension strength was measured as specified in ASTM D 3379. The crosshead speed of the MTS material testing system was 10 mm/min.

RESULTS AND DISCUSSION

Decomposition processing of the epoxy resin

First, an experiment used to examine the decomposition of the epoxy resin under a set of experiment parameters [decomposition temperature (T) = 90°C, nitric acid solution concentration (C) = 8M, and ratio of the sample weight to the nitric acid solution volume (α) = 6 g:100 mL] was carried out. The considered experimental conditions were T , C , and α .

In the beginning of the experiment, a red-brown decomposed compound with a high viscosity could be observed in the bottom of the solution, and the solution became yellow just as in Dang et al.'s experiment.⁹ After 9 h, the original epoxy resin pieces disappeared. The yellow decomposed solution was cooled down after the filtration of the infusibility substance, and a yellow crystal was observed at the bot-

TABLE III
Orthogonal Experiments of Epoxy Composite Decomposition

No.	Level			Results	
	T	C	α	Decomposition time (h)	Strength loss (%)
1	1	1	1	12	1.1
2	1	2	2	22	1.2
3	1	3	3	82	13.4
4	2	1	2	17	3.1
5	2	2	3	95	6.2
6	2	3	1	240	8.0
7	3	1	3	45	9.8
8	3	2	1	250	12.5
9	3	3	2	710	12.7
Decomposition time	I	38.7	24.7	272.3	
	II	117.3	122.3	102.3	
	III	335.0	344.0	116.3	
	R	296.3	319.3	170	
Strength loss	I	5.23	4.67	6.67	
	II	5.77	6.63	6.33	
	III	11.67	11.37	9.67	
	R	6.44	6.70	3.34	



Figure 2 Optical graph of the recycled carbon fibers.

tom. After 6 h of immersion, the crystal was powdery; it became particles after 9 h of immersion and a straw yellow sheet after 20–100 h of immersion.

The dissoluble decomposed substance was analyzed with GC–MS (Fig. 1). The composition of the dissoluble decomposed compounds were complex and included 18 kinds of compounds. The main components were 2,4-dinitrophenol (11.741 min) and 2-nitro-4-carboxylphenol (13.057 min). 2.67 min belonged to acetone. The average molecular weight of the crystal of the dissoluble substance was obtained by GPC (Table I). This showed that the epoxy resin had decomposed into low-molecular-weight compounds. Sulfuric acid and hydrochloric acid were used to recycle the epoxy resin, and the epoxy resin did not decompose. This proved that the oxidation of nitric acid led to broken chemical bonds in the thermoset epoxy resin.

Orthogonal experimentation

The influence of the decomposition conditions on the decomposition of the carbon/epoxy composites was

investigated with orthogonal experimentation. T , C , and α were varied in these experiments (Table II). The results included the entire decomposition time of the epoxy resin and the single-fiber tension strength loss, which was calculated by the division of the decrease value of the single-fiber tension strength of the recycled fiber by the single-fiber tension strength of the original fiber (Table III). Statistical analysis revealed that the significance of the parameters was in the following order: $C > T > \alpha$. Under the optimum conditions, the epoxy resin decomposed rapidly and retained the most fiber strength. The best combination was $T = 90^{\circ}\text{C}$, $C = 8M$, and $\alpha = 4 \text{ g}:100 \text{ mL}$.

The epoxy matrix in the carbon/epoxy composites was completely decomposed in 12 h under a certain set of experimental parameters ($T = 90^{\circ}\text{C}$, $C = 8M$, and $\alpha = 6 \text{ g}:100 \text{ mL}$). Then, the insoluble carbon fibers were separated from the solution and washed with acetone. After they were dried in 60°C , the clean recycled fibers were obtained (Fig. 2). The carbon fiber surface was clean, with very little contamination. No damage could be seen with electron probe microscopy (Fig. 3). The carbon fibers were recovered unharmed. The single-fiber tension strength loss of the recycled carbon fiber was 1.1% for $T = 90^{\circ}\text{C}$, $C = 8M$, and $\alpha = 6 \text{ g}:100 \text{ mL}$. The recycled carbon fiber could be used again. Further work is underway now.

Recycling of the technology epoxy composites

With the aforementioned method, we tried to liquefy a raw material for rocket engine shells reinforced with carbon fibers. The material was cut into $5 \text{ cm} \times 1 \text{ cm}$ pieces so that it could be put into a glass vessel. After only 2.5 h, the resin could be liquefied with a conversion of more than 99 wt % at 90°C and $8M$. After being cleaned with acetone, the carbon fibers were recovered with no contamination.

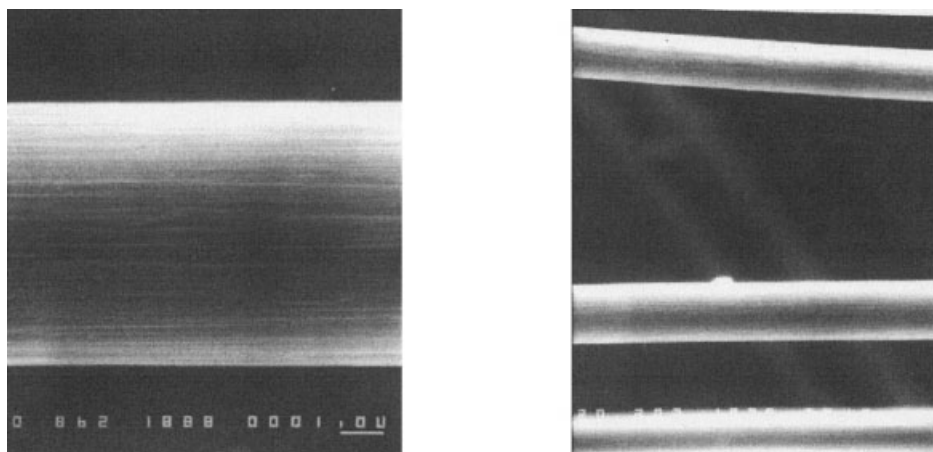


Figure 3 Electron probe micrographs of the recycled carbon fibers.

CONCLUSIONS

The solvent method with a nitric acid solution at 70–90°C was successfully used to recycle carbon fibers from carbon/epoxy composites. The epoxy resin matrix was decomposed into low-molecular-weight compounds, and an insoluble carbon fiber was recovered. Orthogonal experiments revealed that the significance of the parameters was in the following order: $C > T > \alpha$. The best combination was $T = 90^\circ\text{C}$, $C = 8M$, and $\alpha = 4 \text{ g}/100 \text{ mL}$. The recycled carbon fiber was clean and undamaged. The single-fiber tension strength loss of the recycled carbon fiber was 1.1% for $T = 90^\circ\text{C}$, $C = 8M$, and $\alpha = 6 \text{ g}/100 \text{ mL}$. This method was successfully applied to liquefy a raw material for rocket engine shells reinforced with carbon fibers.

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