Journal of Analytical and Applied Pyrolysis 112 (2015) 253–261

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Recycling of carbon fibre reinforced epoxy resin composites under various oxygen concentrations in nitrogen–oxygen atmosphere

Jie Yang[a,b], Jie Liu[b,*], Wenbin Liu[a,*], Jun Wang[a], Tao Tang[b,*]

[a] Polymer Materials Research Center, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China
[b] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

ARTICLE INFO

Article history:
Received 18 August 2014
Received in revised form 20 January 2015
Accepted 21 January 2015
Available online 23 January 2015

Keywords:
Carbon fibre composites
Recycling
Thermal decomposition
Oxygen concentration

ABSTRACT

Pyrolysis is a common method for recycling carbon fibre reinforced polymer composites. However, carbonized residue is preferred to form on fibre surface. Thermal processing in air could eliminate the carbonized residue but the mechanical strength of the inherent fibre tends to be damaged by oxidation. Here, we investigated the influence of the temperature, oxygen concentration in nitrogen and time on the thermal decomposition of carbon fibre reinforced 4,4′-diaminodiphenylmethane cured epoxy resin composite and properties of the recycled carbon fibres. The properties of the recycled carbon fibre were characterized using single tensile test, SEM and XPS. Temperature, oxygen concentration and reaction time appear to be the important factors to tensile strength of the recovered carbon fibres. About 80% of tensile strength and modulus was preserved at optimum conditions. Gas and liquid products from DDM cured epoxy resin were also analysed in nitrogen and 5% O_2–95% N_2.

1. Introduction

Carbon fibre reinforced polymers (CFRPs) are extensively used in the aerospace, military, automobile, and sports industries due to their light and outstanding mechanical properties. With the increasing use of CFRP, an increasing amount of waste generates. The high carbon fibre price, rising landfill costs, legislation implementation, and environmental pressure have motivated to recycle and reuse the high-valued carbon fibre in CFRP waste [1]. The recovered carbon fibre will displace pristine counterparts in some applications when carbon fibre is recycled in an economical way. A lot of energy for producing carbon fibre will be saved from the environmental and economical process.

So far, several ways to recycle the CFRP waste have been investigated. The main recycling methods could be classified into three types, including mechanical recycling [2], sovolysis [3–11] and thermal processing [12–14]. Other recycling methods like microwave treatments have been also studied [15]. Mechanical recycling involves breaking down CFRPs by shredding, crushing, milling, or other mechanical process [2]. This method is not suitable for CFRP waste because the high valuable carbon fibres are wasted. In sovolysis process solvents are used to degrade epoxy resin into soluble fraction and then carbon fibre was recovered. Several solvents, such as tetralin [3], nitric acid [4], supercritical/subcritical alcohols [5–7], and supercritical/subcritical water [8–11] have been used as media for sovolysis of epoxy resin. The mechanical properties of carbon fibre was almost not damaged but it is difficult to scale up for most sovolysis methods.

In the thermal processing process, the polymer matrix was decomposed and carbon fibres were liberated at high temperatures. Thermal processing involves fluidised bed process and pyrolysis [16]. The present commercial-scale carbon fibre recycling operations in the world are all pyrolysis process. ELG Carbon Fibre Ltd., Japan Carbon Fiber Manufactures Association and Matrerials Innovation Technologies all run a pyrolysis plant for recycling CFRP waste [16]. Meyer et. al found that partial oxidation of pyrolytic carbon is possible without seriously damaging the fibres in a semi-industrial pyrolysis plant [17]. López et al. used a combined process of thermolysis and gasification in an air atmosphere to recover a carbon fibre reinforced polybenzoxazine prepreg [18]. The tensile strength of the carbon fibres obtained in thermolysis/gasification process at 500 °C showed around a 28% reduction compared to that of virgin fibre. Ye et al. proposed a combined vacuum pyrolysis and steam thermolysis to recover carbon fibre reinforced epoxy resin composites [19]. The advantage of pyrolysis process is that high mechanical properties of the recycled carbon fibre are retained. However, carbonized residue is preferred to form on fibre surface.

* Corresponding authors. Tel.: +86 431 85262683; fax: +86 431 85262827.
E-mail addresses: liujie@ciac.ac.cn (J. Liu), liuwenbin@hrbeu.edu.cn (W. Liu), ttang@ciac.ac.cn (T. Tang).

http://dx.doi.org/10.1016/j.jaap.2015.01.017
0165-2370/

Thermal processing in air could eliminate the carbonized residue but the inherent fibre is oxidized and the mechanical strength decreases The problem prompted us to raise further questions: Whether we can introduce a small amount of oxygen into inert gas to oxidize the deposited char on the fibre without decreasing significantly the mechanical properties? And if it is possible, how does the oxygen content affect the thermal decomposition behaviour of CFRP and mechanical and surface properties of the recycled carbon fibre?

Herein, a pyrolysis test run was performed on a fixed bed reactor in nitrogen with introduction of small amount of oxygen. The influence of different oxygen concentration in nitrogen on the thermal decomposition of CFRP was studied. Other process parameters including temperature and reaction time were also investigated. The recycled carbon fibre was characterized using SEM, XPS and single-filament tensile tests.

2. Materials and methods

2.1. Preparation of carbon fibre reinforced 4,4′-diaminodiphenylmethane cured epoxy resin composite

Epoxy resin (DGEBA, commercial name: E-51), provided by Wuxi Lanxing Co., Ltd. (China), was used as the matrix resin in this study and 4,4′-diaminodiphenylmethane (DDM), supplied by Sinopharm Chemical Regent Co., Ltd., was used as curing agent. Plain weave PAN-based carbon fibre fabrics were provided by Sinosteel Jilin Carbon Co., Ltd. Vacuum bagging technique was employed to prepare CFRP composites. Mixture of the resin and curing agent at a mass ratio of 100:28 was heated and degassed at 80 °C for 10 min to remove bubbles. Carbon fibre sheets were infiltrated with the resin mixture under vacuum and cured at 80 °C for 2 h followed by a post-curing step at 150 °C for 4 h. Fibre content in composites was determined according to the standard method ISO-14127. The mass of a test specimen is determined before and after digestion of the resin with concentrated nitric acid at 120 °C for 90 min, which does not attack the carbon fibres excessively. The fibre content in the obtained composite was 56.0 wt%. The composite sheets were cut into pieces of 40mm × 10mm × 2 mm.

2.2. Thermal decomposition of CFRP

A fixed bed reactor, as shown in Fig. 1, was used to pyrolyze the CFRP composites. A quartz tube, with a length of 500 mm and an inner diameter of 30 mm, was vertically mounted in an electrical resistance furnace (1.5 kW) and heated to different final temperatures of 550, 600 and 650 °C. A removable porcelain crucible containing the sample (~1 g) was positioned in the centre of the quartz tube. N_2, 5% O_2–95% N_2, 10% O_2–90% N_2 and air with a gas velocity of 600 ml/min were used as reactant gas, respectively. The liquid pyrolysed products were collected using a cold trap and the gas products were collected using a sample bag. The samples were designated as temperture–oxygen concentration–reaction time. For example, 550–5%-60 means the CFRP composite was pyrolyzed at 550 °C for 60 min in 5% O_2–95% N_2. The residue of a sample can be calculated through Eq. (1).

$$\text{Residue } \% = \left(\frac{m_2}{m_1}\right) \times 100\% \quad (1)$$

where m_1 represents the initial mass of composite, m_2 is the residual mass.

2.3. Characterisation

Surface characteristics and diameter of the fibres were determined using a field-emission scanning electron microscope (SEM, XL30, FEI). X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo) was used to examine the surface elemental composition of the carbon fibres. Surface atomic composition analysis and curve-fitting were carried out on commercial thermo scientific avantage software. C1s peak was cuve-fitted using a Shirley type background and Gaussian/Lorentzian line shapes. FWHM was optimized to obtain the curve shape. Thermal gravimetric analyses (TGA) were performed using a thermal analysis instrument (SDTQ 600, TA instruments) from room temperature to 800 °C under nitrogen and air with a heating rate of 10 °C/min. The liquid fraction of pyrolysed products was analysed by gas chromatography–mass spectrometry (GC–MS, AGILENT 5975MSD). The organic gases were analysed by a GC (Kechuang, GC 9800) equipped with a FID, using a KB–Al_2O_3/Na_2SO_4 column (50 m × 0.53 mm ID). The permanent gases (H_2, N_2, CO, O_2, CH_4 and CO_2) were analysed by a GC (Kechuang, GC 9800) equipped with a TCD, using a packed TDX-01 (1 m) and a zeolite 5A column (1.5 m).

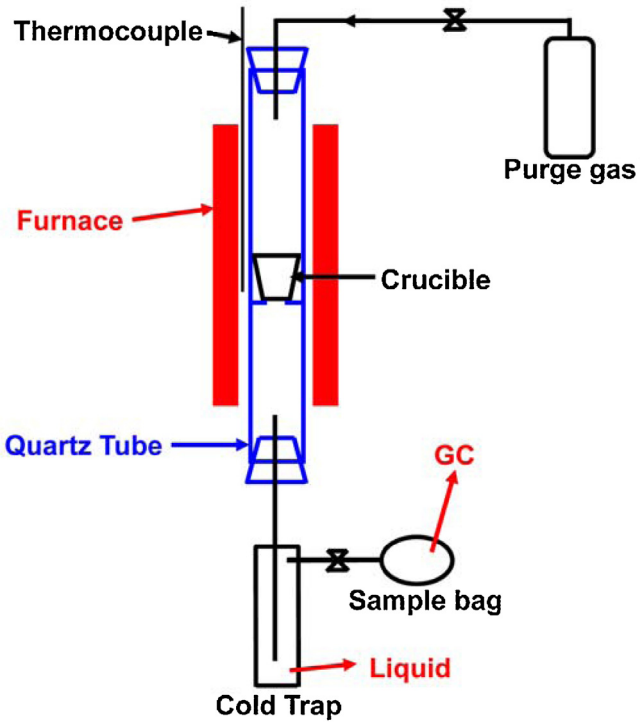

Fig. 1. Schematic diagram of the fixed bed reactor.

Single-filament tensile tests were performed on fibres with clean surface according to the standard ASTM-D3379. Single-filament was bonded to a paper window with an epoxy structural adhesive. After curing at room temperature, the mounting specimen was carefully aligned with the loading axis of an XQ-1A tensile testing machine (Shanghai New Fiber Instrument Co., Ltd.). The gauge length of the fibre was 20 mm and the crosshead speed was set at 1 mm/min. Both sides of the specimen window were cut carefully at the mid-gauge point, to leave the filament suspended between the grips of the testing machine. The carbon fibre was loaded until failure, and the force-displacement curve was recorded. At least 30 filaments were tested for each sample.

There are various defects in the internal or external of carbon fibre. The results of single tensile tests were interpreted by Weibull statistical approach (2) [20,21]:

$$\ln\ln\left[\frac{1}{(1-F(\sigma_f))}\right] = \beta \ln\sigma_f + \ln L - \sigma_0^{\beta} \quad (2)$$