Materials Science and Engineering A 520 (2009) 179–183

Contents lists available at ScienceDirect

Materials Science and Engineering A

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

Recycling of carbon fibre reinforced composites using water in subcritical conditions

Liu Yuyan[*], Shan Guohua, Meng Linghui

Harbin Institute of Technology, No.92 Xidazhi Street, Harbin 150001, China

ARTICLE INFO

Article history:
Received 27 October 2008
Received in revised form 13 May 2009
Accepted 13 May 2009

Keywords:
Composites
Carbon fibre
Epoxy resin
Chemical recycling
Water

ABSTRACT

In this paper, a method of chemical recycling of thermosetting epoxy composite was discussed. Water was used to be reaction medium and the decomposition of carbon fibre reinforced epoxy composites was studied. Experiments were devised in order to identify the significant process parameters that affect fibre reinforced composite recovery potential including temperature, time, catalyst, feedstock, and pressure. Experiments were performed in a batch-type reactor without stirring. Under the condition that the temperature was 260 °C and the ratio of resin and water was 1:5 g/mL, the decomposition rate could reach 100 wt.% and the carbon fibres were obtained. The results from the Scanning Electron Microscopy (SEM) and Atomic Force Microscope (AFM) measurements showed that the fibres were clean and no cracks or defects were found. The average tensile strength of the reclaimed fibres was about 98.2% than that of the virgin fibres.

1. Introduction

Epoxy resins are widely used as adhesives, coatings, encapsulants and also in material area as matrix for high performance fibre reinforced composites. The epoxies may be cured by several types of reactants, along them polyamines are an important class. Once fully cured, the highly cross-linked three-dimensional networks have strong adhesive and thermomechanical properties [1].

Global consumption of carbon fibre composites has increased at an average annual rate of 5.8% from 1997 to 2002. The sector is a particularly dynamic one and as a result of this, carbon fibre reinforced composites (CFRCs) are forecast to grow to a value of $ 13.6 billion by 2010, representing an increase of 37% over 2006 [2].

Therefore, the wastes of such composites have a potential environmental problem since they are generally non-biodegradable and therefore difficult to eliminate by nature. The known recycling processes are mechanical recycling, thermal processing and chemical recycling.

However, they are not fully satisfactory: Mechanical recycling leads to fillers/short fibres mixtures, with poor reinforcing properties. Thermal processing is conducted under high temperature, so clean fibres are produced with a lost in the mechanical properties of the fibres. Chemical recycling is a new and promising route for converting plastic wastes by returning them back to their original constituents, that is, monomers or petrochemical feedstock, and has received a great deal of attention in recent years [3–5].

Pinero Hernanz states that glycolysis or hydrogenolysis could be used to degrade the epoxy resin into its original monomers, and they go on to say that nitric acid solutions at 343–363 K could act as a reactive medium by decomposing bisphenol-F epoxy resins recycling clean carbon fibres [2]. Kubouchi and Tsuda raise an approach to recycle epoxy resin cured with amine using nitric acid as solvent, and renewable resin is obtained with the application of decomposition products, new epoxy resin and curing agents [6–8].

On the other hand, research and development on chemical recycling are a long-range effort. Although considerable advances have been seen in this field in the past decades, chemical recycling is still at the development or pilot plant stage. Among the existing technical difficulties, high cost and low quality of products were still main problems [9,10].

Therefore, chemical recycling technology needs to be improved so that it could be used in a wide range of application and would represent an asset rather than an expensive burden for recovery of recourse and diminution of environment stress. Water can be classed as a green reaction media since they are readily available, cost-effective, and have a low potential toxicity. Thus served as the main solvent decomposes the epoxy matrix and the virgin fibres are released under different decomposition conditions.

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[*] Corresponding author. Tel.: +86 451 86413711; fax: +86 451 86402368.
E-mail address: liuyy@hit.edu.cn (L. Yuyan).

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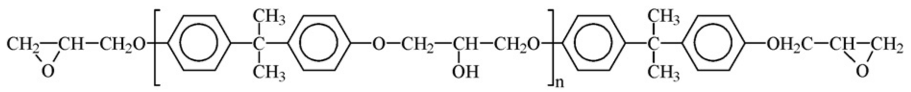
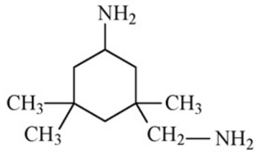
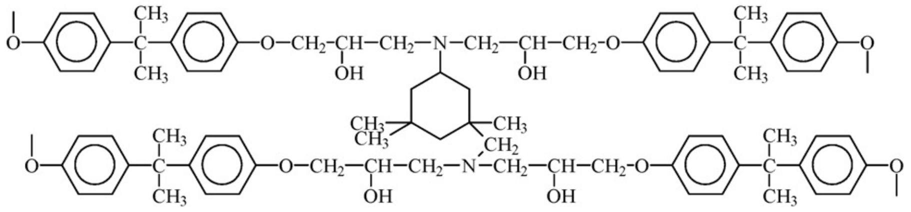
doi:10.1016/j.msea.2009.05.030



Bisphenol A type epoxy resin



IPDA (isophorone diamine)



Bisphenol A type epoxy resin cured with IPDA

Fig. 1. Chemical structures of epoxy resins, curing agent and cured resin.

2. Experimental

2.1. Carbon fibre composite material and decomposition conditions

Experiments were carried out in a batch autoclave without stirring. The apparatus mainly comprised a temperature controller, a removable 30 mm diameter stainless steel reactor (100 mL) connected to a pressure gauge, and a round salt bath furnace to heat the reactor. The decomposition pressure in the reactor could be varied between 1.0 MPa and 40.0 MPa. The carbon fibre reinforced epoxy resin samples were prepared in a laboratory. The bisphenol A type epoxy resin E-44, which has a content of 0.41–0.47 epoxide/100 g resin, and curing agent isophorone diamine (IPDA) were used as a matrix. Fig. 1 shows the chemical structures of E-44 epoxy resin, IPDA and the resin cured with IPDA. The carbon fibre/epoxy resin samples consisted of 60 strands of impregnated fibre laid parallel. They were laid in a mould together. The cure cycle was used as follows: heating from 25 °C to 80 °C for 30 min; holding at 80 °C for 4 h; heating from 80 °C to 150 °C for 30 min; holding at 150 °C for 1 h; then cooling to 25 °C naturally. The samples were then cut into 65 mm × 6 mm × 2 mm pieces and put into the steel reactor with a 1 g resin/5 mL solvent feedstock ratio. They were swelled by solvent using water at different temperature and time. Then after reacting for the fixed time, insoluble composites were removed from the solvent punctually and washed with acetone as well as water.

The decomposition rate of epoxy resin in composites was determined in each experiment by the amount of solid residue using the following formula:

$$\text{decomposition rate (weight\%)} = \left(\frac{\text{weight of composites} - \text{weight of solid residue}}{\text{weight of resin in composites}}\right) \times 100\%$$

2.2. Fibre characterization

Tensile properties and strength loss of the recycled fibres were measured as specified in ASTM-D3379. The crosshead speed of the MTS materials testing system was 10 mm/min. Average tensile strength of precursors and reclaimed fibres under different conditions were obtained. Samples of recycled and virgin fibres were analyzed using a HITACHI S-4700 Scanning Electron Microscope (SEM) to determine the morphology and diameter of the fibres as well as visual signs of residual resin impurities. Surface morphology of the recycled fibres was observed and pictured by a Nanoscope III PIMENSION 3100 Atomic Force Microscope (AFM), and precursors were then analyzed with similar processing.

3. Result and discussions

3.1. Influence of reaction conditions on decomposition rate of samples

In order to study the influence of reaction conditions on the recycling efficiency, a design of experiments approach was used. Tables 1 and 2 show the design of experiments and results. Temperature, reaction time, feedstock ratio and the sulfuric acid catalyst were selected as controlled variables, and pressure was also selected as a controlled variable because of its important influence on decomposition rate, though pressure was determined by the reaction temperature and the initial volume of solvent placed into the reactor.

3.1.1. Reaction temperature

The influence of reaction temperature was investigated under the condition that feedstock ratio was 1 g resin/5 mL solvent and reaction time was 75 min. The decomposition temperature was varied between 250 °C and 290 °C. Table 1 shows the influence of reaction temperature on decomposition rate. It could be observed that the matrix resin was degraded at 250 °C and the decomposition rate was 14.1 wt.%. The decomposition rate rose rapidly as the temperature increased and the matrix of carbon fibre composites could be decomposed completely at 290 °C.

Then the reaction time was continued to be reduced to find much better reaction conditions at 290 °C with feedstock ratio at 1 g resin/5 mL solvent. Finally, under the condition that the tem-