Materials Chemistry and Physics 203 (2018) 293–301

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Mechanical and thermal properties of a room temperature curing epoxy resin and related hemp fibers reinforced composites using a novel in-situ generated curing agent

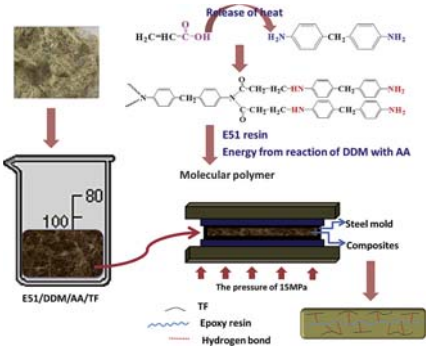
Yi-le Xu, Abdul Qadeer Dayo, Jun Wang*, An-ran Wang, Dan Lv, Abdeldjalil Zegaoui, Mehdi Derradji, Wen-bin Liu**

Research Institute of Composite Materials, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, PR China

HIGHLIGHTS

- An epoxy resin system which can cure at room temperature within 3 h was designed.
- Reaction of AA with DDM released the heat to promote curing reaction of epoxy.
- Rapid prototyping epoxy/TF composites were prepared.
- 213% and 233% enhancement in Young's modulus and impact strength, respectively.
- The thermal stability of the composites was also improved after the addition of TF.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 June 2017
Received in revised form
28 September 2017
Accepted 2 October 2017
Available online 5 October 2017

Keywords:
Self-exothermic hardener
Hemp fibers
Mechanical properties
Thermal properties

ABSTRACT

A novel self-exothermic curing agent, effectively able to cure the diglycidyl ether of bisphenol-A (E51 epoxy resin) at room temperature, has been synthesized by blending 4, 4'-diaminodiphenylmethane (DDM) and acrylic acid (AA). The chemical structure of prepared curing agent was characterized by ^{1}H nuclear magnetic resonance (^{1}H NMR) and Fourier transform infrared (FTIR). The curing behavior of epoxy with synthesized room temperature hardener was studied by differential scanning calorimetry (DSC) and FTIR. Results confirmed that the curing reaction was completed in only 3 h, which can be attributed to the high reactivity of the acryl amide groups with epoxy and high heat release from DDM and AA reaction. The 5 wt% NaOH treated short hemp fibers (TF) were sandwiched in room temperature curing epoxy resin to obtain rapid prototyping high performance composites. The effects of fiber content on the mechanical properties of composites were studied in terms of tensile, flexural, and impact load. The tensile strength of the composites was increased with the increase of the TF content, and the elongation at break was decreased. Compared with the cured neat epoxy resin, an increase of about 233% in impact strength, 52% in flexural modulus, and 213% in Young's modulus were recorded for the cured composite having 7.5 wt% TF content. We used dynamic mechanical analyzer (DMA) and thermogravimetric analysis (TGA) to study the effect of fiber content on the thermal properties of composites. The scanning electron microscope (SEM) revealed excellent adhesion between TF and epoxy resin cured at room temperature.

* Corresponding author.
** Corresponding author.
E-mail addresses: wj6267@sina.com (J. Wang), wjlwb@163.com (W.-b. Liu).

https://doi.org/10.1016/j.matchemphys.2017.10.004
0254-0584/

1. Introduction

Epoxy thermosetting resins have received considerable attention by industries because of their favorable mechanical properties, high adhesive strength, low shrinkage on curing, and excellent resistance against chemicals/weather. These excellent properties increased the application of epoxy resins in the fields of adhesives, packaging for electronic devices, insulation, coatings, composites, flooring, and water proofing [1–4]. Epoxy resins are cured in the presence of a curing agent to form the cross-linking structure. Aliphatic amines have several advantages such as high reaction activity, low melting temperature, low viscosity, and general applicability, the key properties for room temperature cure adhesives and coatings. However, the higher volatility, strong sensitization, quick carbonization in the air, and very strict stoichiometric relation against epoxy are their major disadvantages, which restrict their applications in certain fields [4]. The epoxies cured with aromatic amine hardeners showed excellent properties as compared to the aliphatic amine hardeners, however, high polymerization enthalpy, curing temperature, and melting point are the associated drawbacks of aromatic amine hardeners [5,6]. The most commonly used and reported aromatic amine curing agents include 4,4'-diaminodiphenylmethane (DDM) [7–11], 1,3-diaminobenzene [12,13], and 4,4'-diaminodiphenylsulfone (DDS) [14–19]. Dendrimer hardeners have several advantages over traditional amine-based hardeners like lower toxicity, low volatility, and high compatibility with epoxies [20,21], however, the synthesis of dendrimers is complex [22].

Since the start of 21st century, natural fibers (NF) including hemp, jute, kenaf, sisal, banana, oil palm, flax, etc. have attracted more attention as reinforcements in the polymer material. NF have various advantages of eco-friendly, renewable, low density, cost effective, especially when compared to synthetic fiber. In addition, the NF have the advantages of an easy processability, no skin irritation, high mechanical properties, high aspect ratio (L/D), and high insulating and thermal properties, which broaden their usage in different applications [23–26]. Hemp fibers were reported as fillers for various polymer matrices such as epoxies [27–30], polybenzoxazines [31,32], poly(lactic acid) [33,34], starch acetate [35], and vinyl ester [36].

In the current study, a simple synthesis procedure for room temperature curing agent was designed by using the AA as DDM modifier and the chemical structure of curing agent was analyzed by ^{1}H NMR. The curing behavior of epoxy resin with the prepared self-exothermic hardener was characterized by FTIR and DSC. Moreover, epoxy resins were reinforced using different amounts of alkali treated hemp fibers (TF) and cured by the prepared curing agent. The effects of the fiber content on the mechanical and thermal properties of the prepared composites were analyzed.

2. Experimental

2.1. Materials

The epoxy resin (E51) was kindly provided by Jiangxi Huacui Advanced Materials Co. Ltd. (China). The DDM hardener was purchased from Tianjin Kernel Chemical Reagent Co. Ltd. (China). The acrylic acid (AA) was procured from Shanghai Jingchun Reagent Co. Ltd. (China). Short natural hemp fibers (SHF) were kindly donated by Daqing Branch of Heilongjiang Academy of Sciences, Daqing. Ethanol, cyclohexane and sodium hydroxide (NaOH) were procured from Shanghai Jingchun Reagent Co., Ltd., China.

2.2. Preparation of composites

The SHF were treated by an alkaline treatment process for the good fiber-resin interfacial adhesion. First of all, washing cycle (i.e. with water, ethanol/cyclohexane (1:1, V/V), and water) was performed on the SHF, for the removal of attached physical and chemical impurities. Afterward, the washed SHF were soaked for 6 h under ambient conditions in a sodium hydroxide solution (5 wt %). Then, the fibers were neutralized by washing with water and acetic acid solution (1 wt%), vacuum dried for overnight at 60 °C, and stored in an air tight pot.

The DDM was mixed with E51 epoxy resin at 60 °C and stirred uniformly. Then an appropriate amount of TF was added into the mixture and cooled down to room temperature. Finally, a certain amount of AA (DDM and AA with molar ratio 1:2) was added to the mixture and stirred uniformly. The composite blends were poured into steel molds having the required dimensions for the test specimens and pressed at 15 MPa pressure for 3 h.

2.3. Characterization

The Perkin Elmer Spectrum 100 spectrometer was used to record the FTIR spectra in the range of 4000–450 cm^{-1}. FTIR spectra were obtained at 4 cm^{-1} after averaging four (04) scans by casting a thin film on a KBr plate for samples. ^{1}H NMR spectra were obtained on a Bruker AVANCE-500 NMR spectrometer with tetramethylsilane (TMS) as an internal standard and $CDCl_3$ was used as the solvent. The average number of transients for ^{1}H NMR spectroscopy was 16. DSC was performed under the flow of nitrogen (50 mL/min) on Q200, TA Instruments (USA) at a heating rate of 20 °C/min. The thermal stability of the cured samples was studied from 50 °C to 820 °C under 50 mL/min nitrogen purging. The Q50, TA Instruments (USA), was used at 20 °C/min heating rate. The thermomechanical properties of cured samples were tested on the DMA Q800, TA Instruments (USA). The 30 × 10 × 2 mm^3 rectangular sample was loaded under a nitrogen atmosphere in single cantilever mode at 3 °C/min heating ramp and 1 Hz frequency. The specimen with dimensions 50 × 10 × 2 mm^3 were tested at 1 mm/min crosshead speed on Instron 5569 instrument for tensile and flexural properties. The Izod impact tests were conducted on IT503 impact-resistance, Tinius-Olsen China, whereas ASTM D256-2010 was followed for evaluating impact resistance of composites. SEM micrographs of gold sputtered fracture surfaces were taken on an electron microscope CamScan MX2600FE, Oxford Instruments, UK, at acceleration voltage of 20 kV using secondary electron detector and a working distance about 35 mm.

3. Results and discussion

3.1. Synthesis and characterization of room temperature hardener

The reaction of AA with DDM and curing reaction of epoxy resin with the prepared hardener (AA + DDM) at room temperature are shown in Schemes 1 and 2, respectively. The chemical structures of the neat DDM and the prepared curing agent were characterized by ^{1}H NMR (Fig. 1). The DDM (curve *a*) indicates that the protons of the primary amine at 3.52 ppm(1), the protons of Ar-CH_2-Ar at 3.76 ppm (3), and the protons of phenyl rings at 6.59 and 6.95 ppm (2). After 5 min of mixing of the AA in DDM (curve *b*), the primary amine proton peak at 3.52 ppm disappeared and a new peak attributed the proton acrylamide at 8.51 ppm (1′) was observed. Moreover, the protons of CH_2=CH- in the range of 5.93–6.16 ppm (4′) were also observed. The exothermic reaction of DDM and AA produced acrylamide. The produced acrylamide reacted with DDM via Michael addition reaction [4,37]. After 1.5 h of the AA blending