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Cure behaviors of furfuryl alcohol/epoxy/methyltetrahydrophthalic anhydride and their enhanced mechanical and anti-acid properties of basalt fiber reinforced composites

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ABSTRACT

Catalyzing furfuryl alcohol and epoxy simultaneously with a suitable catalyst plays a key role in the preparation of high-performance blends. Herein, methyltetrahydrophthalic anhydride was utilized to cure furfuryl alcohol/epoxy resins, which reacted with epoxy firstly, then catalyzed the furan reaction and also linked furfuryl alcohol and epoxy. Moreover, partly ring-opened furan further catalyzed the curing reaction of epoxy. The addition content of methyltetrahydrophthalic anhydride affected the curing behaviors of furfuryl alcohol/epoxy blends, and their T_g and char yield at 700 °C reached the maxima of 140 °C and 16.79% respectively as the content increased to 50%. The mechanical and anti-acid properties of basalt fiber-reinforced composites were further studied. The mechanical properties of composites changed identically to those of the matrix did. Furfuryl alcohol improved the acid resistance of composites, probably because furan could be cured in acidic condition and basalt fiber was resistant to acid. All these changes were related to the curing mechanism and crosslinking density of furan/epoxy/methyltetrahydrophthalic anhydride blends.

1. Introduction

Due to environmental and fossil fuel supply concerns, furfuryl alcohol has recently gained wide attention as a sustainable renewable alternative thermoset resin with reduced CO_2 emission in comparison to those of existing petrochemical-based systems [1–7]. Furfuryl alcohol resin has high reactivity, flame and corrosion resistances, and compatibility with other polymers as well as low formaldehyde emission in production, but it cannot be cured without any initiator or catalyst and the mechanical properties are still inferior to those of other thermosetting resins [8–12]. One method to improve the properties of furfuryl alcohol resin is to synthesize new kinds of them. Cho et al. [13] recently reported two furan ring-based diepoxies, both with improved properties. Cooph et al. [14] synthesized epoxy resins containing furan ring then reacted with maleimide, and obtained self-healing materials. Nevertheless, the synthetic method was complex, thereby being limited in practical application. Moreover, the performance of furfuryl alcohol resin can be effectively and facilely boosted by adding epoxy resins. However, furfuryl alcohol/epoxy (FE) blends have seldom been reported [15], probably because the large curing temperature discrepancy leads to severe phase separation that exerts adverse effects on modification [16,17]. Therefore, high-performance FE blends can be fabricated by simultaneously catalyzing furfuryl alcohol and epoxy with a suitable catalyst.

For the catalysis of furfuryl alcohol resin, p-toluene sulfonic acid [18], maleic anhydride [19–22] and ferric chloride hexahydrate [22] have previously been tested, proving that the type and concentration of acidic catalyst affected the curing of furfuryl alcohol resin. A weakly acidic catalyst fails to completely cure furfuryl alcohol. A strong organic acid gives an extremely fast reaction rate, and mild acids, such as maleic anhydride, can cure furfuryl alcohol resin at lower rates [23,24]. On the other hand, amine and maleic anhydride have been successfully used to catalyze epoxy resin [25–28]. Collectively, maleic anhydride may be suitable for the catalysis of both furfuryl alcohol and epoxy. However, the curing mechanism of FE/maleic anhydride remains largely unknown hitherto.

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Additionally, furfuryl alcohol can hardly be used as a matrix for preparing composites because of poor processability and release of small molecules during curing. Nevertheless, it is of great significance to develop furfuryl alcohol-containing composites owing to high cost performance [29,30].

In this study, methyltetrahydrophthalic anhydride was utilized to cure FE resins, aiming to allow simultaneous reaction of furfuryl alcohol resin and epoxy resin and to overcome the processing problem when using furfuryl alcohol as the matrix. The curing mechanism of FE/methyltetrahydrophthalic anhydride blend was clarified. The effects of methyltetrahydrophthalic anhydride content on the thermal properties of blends were investigated. Besides, the improved thermal properties of blends were also analyzed based on the crosslinking density. Basalt fiber-reinforced FE/methyltetrahydrophthalic anhydride composites were prepared successfully, and the corresponding mechanical and anti-acid properties were studied.

2. Experimental section

2.1. Materials

Furfuryl alcohol resins (FA) were received from Shanxi Xinan Foundry Material Co. Ltd, China (purity ≥ 98%, viscosity is 3200 cP at 25 °C). Bisphenol-A epoxy resins E51 (CYD 128, epoxy equivalent 51, viscosity is 2500 mPa s at 40 °C) and the accelerator, tris(dimethylaminomethyl)phenol (DMP-30) (Mw = 265.39, purity ≥ 95%), were purchased from Baling Petrochemical Co. Ltd, China. The catalyst, methyltetrahydrophthalic anhydride (M) (Mw = 166.18, purity ≥ 98%), was obtained from Henan Huicheng Chemical Co. Ltd, China. The structures of molecules used in this paper are showed in Scheme 1. Basalt fiber fabric (areal density: 300 g/m^2; thickness: 320 μm) was acquired from Shanxi Basalt Fiber Technology Co., Ltd., China.

2.2. Preparation of furfuryl alcohol/epoxy/methyl-tetrahydro-phthalic anhydride blends

Appropriate quantities of FA and E51 were placed in a glass container and stirred for 3 min without additional solvent added. The mass ratios of FA and E51 were 1:1. After that, the M and DMP-30 were added with stirring for 10 min until a homogeneous liquid was obtained. Methyl-tetrahydro-phthalic anhydride was blended with FA/E51 in different mass ratios of 30%, 40%, 50% and 60%. DMP-30 was added at 2% of methyl-tetrahydro-phthalic anhydride. Then, the blends were put in a vacuum oven for 1 h to remove bubbles. The blends were denoted as FEMD-30, FEMD-40, FEMD-50 and FEMD-60, where F, E, M and D represents FA, E51, methyl-tetrahydro-phthalic anhydride and DMP-30, respectively. The number indicates the mass ratios of methyl-tetrahydro-phthalic anhydride to FA/E51 blend. In order to comparison, FA/E51 (1:1) blend, furfuryl alcohol and epoxy blended with curing agent (50%) are noted as FE, FMD-50 and EMD-50, separately.

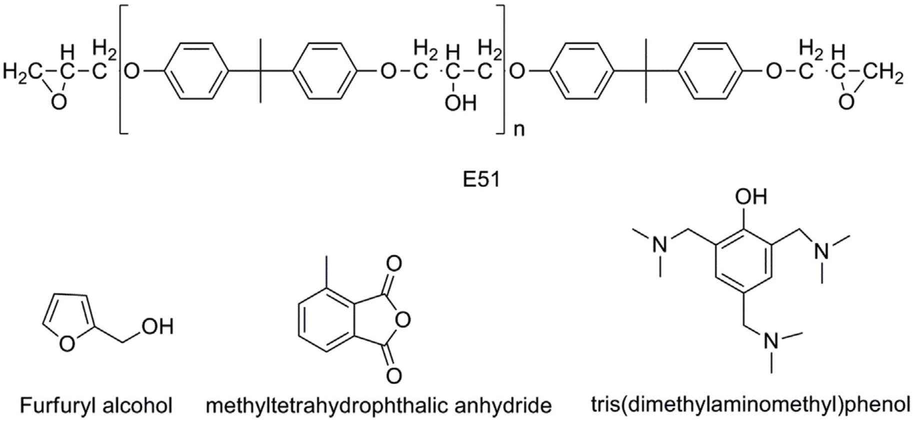
2.3. Preparation of cured resins and basalt fiber reinforced FEMD composites

Firstly, different systems were poured into a preheated metal mold with a silicon coating on the inner surface. Subsequently, the blends were degassed in a vacuum oven for 1 h. Then the blends were cured in a vacuum following a cure profile, that is 80 °C/8 h, 100 °C/2 h, 120 °C/2 h, 140 °C/2 h, 160 °C/2 h, 180 °C/2 h, 200 °C/2 h, 220 °C/2 h.

Basalt fiber fabrics were cut into 30 cm × 30 cm. The FEMD was used to impregnate basalt fiber fabrics by hand layup technique using a roller. The weight ratio of basalt fiber fabrics to FEMD is 1:1. Afterwards, prepregs were compressed with the pressure of 1 MPa in a stainless-steel mold and cured following the procedure of FEMD curing process as showed above. Eventually, the matrix content of composites and fiber volume percentage were calculated and showed in Support information Table S1.

2.4. Characterization

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were recorded on a Nicolet IS50 FTIR spectrometer in a range of 4000 to 500 cm^{-1}. Co-addition of 32 scans was recorded at a resolution of 4 cm^{-1}. Differential scanning calorimetry (DSC) thermogram was carried out with a Mettler-Toledo DSC-1 instrument under a N_2 flow rate of 50 ml min^{-1} at a heating rate of 10 °C·min^{-1} over the temperature range 40–400 °C. The heating rate of 5, 10, 15, and 20 °C/min were used to find the peak temperatures for FEMD-50. Dynamic mechanical analysis (DMA) was performed on a TA Instruments DMA Q800 instrument. The specimen with dimensions of approximately 40 × 10 × 2 mm^3 was tested in three point bend mode from 40 °C to 180 °C with a frequency of 1 Hz, and at a heating rate of 5 °C/min under N_2. Thermogravimetric analysis (TGA) was performed by using a TA Instruments TGA Q50. The cured blends were tested from 40 to 800 °C at a heating rate of 10 °C·min^{-1} under a N_2 flow rate of 50 ml min^{-1}. Mechanical properties of the cured FEMD and composites were measured according to the GB/T2567-2008. Flexural strength and modulus of cured FEMD blends and composites were measured using a testing machine (CMT6104 Electronic Tensile Testing Machine, Shenzhen Sans Measurement Technology Co. Ltd, Shenzhen, China). Five samples were tested to obtain an average. Charpy impact tests of unnotched cast specimens and composites were carried out using a pendulum-type testing machine (XJJD-5, Jinjian, China) in accordance to GB/T2571-1995. Ten parallel samples were tested to obtain an average. Corrosion measurements (based on strength retention) were tested as following



Scheme 1. The structures of molecules.