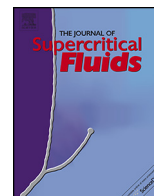




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Insight into the role of potassium hydroxide for accelerating the degradation of anhydride-cured epoxy resin in subcritical methanol

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ABSTRACT

Degradation of methyl-1,2-cyclohexanedicarboxylic anhydride (MeHHPA)-cured epoxy resin in subcritical methanol in the presence of potassium hydroxide (KOH) was studied. The degraded products of epoxy resin were first separated using vacuum distillation, extraction and preparative high-performance liquid chromatography (HPLC) and then characterized by HPLC, electrospray ionization mass spectrometry (ESI-MS), ^1H and ^{13}C nuclear magnetic resonance (NMR). The effects of temperature and KOH on the kinetic behavior of degradation and the product distribution were examined. The temperature for the complete degradation of epoxy resin decreased greatly after adding a small amount of KOH. Transesterification was the dominant mechanism of degradation of epoxy resin. Reaction between KOH and epoxy resin and transesterification mechanism were also proposed. KOH improved the reaction mainly as a catalyst with consumption of methanol but contributed little to the reaction as a reagent. The bending properties of recycled epoxy resin with degraded products obtained at different KOH concentrations were also examined.

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1. Introduction

Epoxy resins are commonly used as the matrix for high-performance fiber-reinforced composites, especially for carbon fiber reinforced composites. However, efficient recycling of waste epoxy resin and its composites poses a challenge because cured epoxy resin cannot be melted or dissolved in solvent. For waste epoxy resin composites, chemical recycling is a promising method because valuable fillers could be recovered. Potential chemical recycling technology for decomposing epoxy resin includes thermal processing and solvolysis [1]. During thermal processes such as pyrolysis [2], thermolysis-gasification [3], and fluidized bed processing [4], epoxy resin is converted into gas and liquid at 400–700 °C to liberate the fibers in the composites. However, char is always produced during thermal decomposition of resin, and the produced gas may be toxic.

Solvolysis, using reactive solvents to cleave chemical bonds in resin, has been considered as a promising recycling method. The reinforced components of the composites and degradation products of resin are both recovered in the solvolysis process. Supercritical/subcritical alcohols have been mostly used as effective reaction media for the solvolysis of thermoplastic and thermoset polymers such as epoxy resin, due to their high solvation

capability and reactivity [5,6]. For example, Pinero-Hernanz et al. compared the capacity of methanol, ethanol, 1-propanol and acetone for decomposition of carbon fiber-reinforced epoxy resin composites in batch and semi-continuous reactor at 200–450 °C, and found that 1-propanol was an efficient solvent for decomposing epoxy resins [7]. Okajima et al. decomposed 1, 2-cyclohexane dicarboxylic anhydride (HHPA)-cured epoxy resin using supercritical methanol without catalyst at 270 °C [8]. The cross-linked ester bond was selectively decomposed without cleaving the main chain of the epoxy resin.

Identification of degraded products and degradation reaction mechanism of epoxy resin is important for reusing these products. Ether and C–C bonds exist in the epoxy resin cured by all types of curing agents. Ester and C–N bonds are cross-linked bonds for the anhydride- and amine-cured epoxy resin, respectively. Appropriate combinations between solvents and catalysts may be crucial to break the chemical bond of cross-linked network. Potassium hydroxide (KOH) has been shown to substantially increase the decomposition rate of epoxy resin in supercritical fluids. Several decomposition mechanisms of cured epoxy resin have been proposed. Jiang et al. demonstrated that thermolysis played a role in the breaking chemical bonds of the amine cured bisphenol A diglycidyl ether-type epoxy resin in supercritical isopropanol, where isopropanol did not act as a reactive solvent [9]. KOH decreased the initial decomposition temperature by 10–30 °C but improved the Guerbet reaction of isopropanol resulting in the products with complex composition. Liu et al. decomposed methyl

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tetrahydrophthalic anhydride (MeTHPA)-cured epoxy resin in subcritical water at 270 °C for 45 min in the presence of KOH or sulfuric acid [10]. KOH promoted the cleavage of ether bonds in the epoxy resin while suppressing the cleavage of ester bonds under the same condition. From the above previous reports, it is clear that the role of KOH in the degradation of epoxy resin in subcritical solvents needs to be further elucidated. On the other hand, epoxy resin was broken into small molecular weight compounds at relatively violent conditions in these studies, including our previous work [11]. The structure of oligomer or higher-weight molecules (molecular weight is higher than that of Bisphenol A) produced at relatively mild reaction conditions are difficult to identify by gas chromatography (GC), gel permeation chromatography (GPC) or mass spectrometry. Gersifi et al. degraded hexahydrophthalic anhydride-cured epoxy resin by the combination of diethyleneglycol and titanium(IV) *n*-butoxide at the boiling point of diethyleneglycol [12]. They proposed a transesterification mechanism for the degradation of anhydride cured epoxy resin according to the nuclear magnetic resonance (NMR) and matrix-assisted laser desorption/ionization time-of flight (MALDI-TOF) results. There were also side reactions such as alcoholysis, but the transesterification reaction did not participate.

Herein, we degraded methyl-1,2-cyclohexanedicarboxylic anhydride (MeHHPA)-cured epoxy resin in subcritical methanol in the presence of KOH at relatively low reaction temperature. The aims of this work were as follows: (1) to specify the degradation mechanism of epoxy resin in subcritical methanol in the presence of KOH via separating and characterizing the degraded products; (2) to examine the effects of KOH on the kinetic behavior of degradation and the product distribution by monitoring the change of mass of the resin and products; (3) to examine the effects of temperature on the kinetic behavior of degradation and the product distribution by monitoring the change of mass of the resin and products; (4) to study the effect of the resultant degradation products on the mechanical properties (bending) of the recycled epoxy resin.

2. Experimental

2.1. Materials

The matrix resin was diglycidyl ether of bisphenol A (DGEBA) with the epoxide value of 0.53 purchased from Sigma-Aldrich. Cured epoxy resin were prepared by mixing the DGEBA, 4-methyl-1,2-cyclohexanedicarboxylic anhydride (MeHHPA, mixture of isomers, 98%, purchased from Alfa Aesa) and *N,N'*-dimethyl benzyl amine (BDMA) at room temperature. The mass ratio of DGEBA/MeHHPA/BDMA was 100/80/1. The epoxy resin was cured in a polytetrafluoroethylene mold (80 × 10 × 4 mm) at 100 °C for 2 h and then at 150 °C for 5 h.

2.2. Degradation of cured epoxy resin

About 5 g of epoxy resin chip, 50 mL of solvent, and 0.018–0.36 mol L⁻¹ of catalyst were introduced into a 100 mL autoclave without stirring. The autoclave was placed in a furnace and heated to the designated temperature under argon. After each reaction, the autoclave was removed and cooled by water. The reaction mixture was filtered, and the solid residue was separated and washed with methanol several times. The weight of the solid residue after drying was used to calculate the yield of eliminated resin.

2.3. Separation of degradation products of epoxy resin

The liquid was concentrated on a rotary evaporator and dried under vacuum for 12 h at 70 °C to remove methanol. The obtained

degradation products were then distilled at 150 °C and 1325 Pa, and methyl-cyclohexane-1,2-dicarboxylic acid dimethyl ester was obtained (from GC-MS results). The remaining residue was dissolved by ethyl acetate and water and separated. Ethyl acetate solution were concentrated and dried in vacuum, and the soluble fraction in ethyl acetate was obtained. The water solution was neutralized with hydrochloric acid and extracted by diethyl ether. Diethyl ether solution was concentrated and dried in vacuum and the soluble fraction in water was obtained.

2.4. Preparation of recycled epoxy resin

The degradation products were mixed with DGEBA epoxy resin and MeHHPA to prepare the recycled resin without BDMA. The mass ratio of DGEBA/degradation products/MeHHPA was 80/20/80. The mixture was heated at 100 °C for 2 h then at 150 °C for 5 h.

2.5. Characterization

Differential scanning calorimetry (DSC) was applied to determine the glass transition temperatures (T_g). The T_g value of neat epoxy was measured as 132.0 °C. The distilled ester and water-soluble fraction were analyzed using a GC-MS (Agilent 5975/6890N), using an HP-5 MS column (30 × 0.25 × 0.25 mm). Soluble fraction in ethyl acetate obtained in methanol at 210 °C for 120 min in the presence of 0.036 mol L⁻¹ of KOH were analyzed by HPLC (Hanbon Sci. & Tech., China) equipped with a UV detector set at 230 nm, using a Double C18 reversed phase column (250 × 4.6 mm, 12 nm pore size, 5 μm particle size). A gradient method was used starting at 60% methanol in water and progressing linearly to 95% methanol over 10–20 min. According to the HPLC results, degradation products were separated on another Hanbon HPLC with a preparative Double C18 reversed phase column (250 mm × 1 cm, 10 μm particle size) equipped with a ultraviolet detector set at 230 nm. Samples (70 mg) were treated, and three single components (Compound 1, 2 and 3) were gained by two exposures to preparative HPLC using a similar gradient method mentioned above. Each fraction was analyzed by HPLC, ESI-MS, ¹H and ¹³C NMR. ¹H NMR spectra were performed on a Bruker AV400 spectrometer using dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) or deuteriochloroform (CDCl₃) as a solvent. ¹³C NMR and ¹³C distortionless enhancement by polarization transfer (DEPT) 135 NMR spectra of compound 1 were performed on a Bruker AV600 spectrometer using CDCl₃ as a solvent. ESI-MS spectra were recorded on Waters Micromass Quattro Premier XE mass spectrometer equipped with an ESI source. The mass spectrometer was operated in the positive ionization mode. The MALDI-TOF spectra of the ethyl acetate soluble extraction were recorded using a Bruker Daltonics Flex Analysis mass spectrometer, and dihydroxybenzoic acid was used as cationization agent. Bending properties were measured on an Instron 1121, at a crosshead speed of 2 mm min⁻¹. The resin bars had a length of 80 mm, a width of 10 mm, and a thickness of 4 mm. All data were the average of five independent measurements; the relative errors for each of the data are reported as well.

3. Results and discussion

3.1. Characterization of the degradation products of MeHHPA-cured epoxy resin in subcritical methanol in the presence of KOH

The degradation of MeHHPA-cured epoxy resin was performed in subcritical methanol in the presence of KOH under different temperatures, KOH concentrations, and time (Fig. 1). As we know, determining the composition of degradation products from epoxy resin will help to clarify the mechanism of the degradation reaction,

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