



Multifunctional deoxybenzoin-based epoxies: Synthesis, mechanical properties, and thermal evaluation



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ABSTRACT

We describe 2,4,4',6-tetrahydroxydeoxybenzoin (THDB) as a multifunctional cross-linker in conjunction with bis-epoxydeoxybenzoin (BEDB), affording new resins that combine excellent physical and mechanical properties with low flammability. The char residue and heat release capacity values of the cross-linked epoxies were measured by thermogravimetric analysis (TGA) and pyrolysis combustion flow calorimetry (PCFC), respectively. Resins fabricated from THDB exhibited low total heat release (13 kJ/g) and high char yields (34%), as well as good mechanical properties, making them suitable candidates for consideration in high performance adhesive applications. The desirable heat release and char yield properties of these structures are realized without the presence of any conventional flame retardant, such as halogenated structures or inorganic fillers that are commonly utilized in commercial materials.

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1. Introduction

Epoxy resins are prominent among thermoset polymers, employed as high performance adhesives, surface coatings, encapsulation matrices, and composites in applications ranging from aerospace transportation to microelectronics packaging [1–3]. Epoxy resins, like many synthetic polymer materials, require low flammability for their safe use. While halogenated flame retardants are common additives that impart low flammability to materials, growing concern and legislation over the potential health and environmental consequences of such additives drives the discovery of new routes to achieve flame retardancy. With respect to epoxy resins, efforts towards non-halogenated materials center on the integration of phosphorus [2–9], boron [10,11], or silicon [12–14] into the cross-linked matrix. We seek to achieve non-flammable resins from purely hydrocarbon systems, without the need for additives of any sort. This requires hydrocarbons that have degradation mechanisms that produce few flammable volatiles, yet that also possess suitable processability and performance characteristics, a challenging combination to achieve. Our prior work showed that numerous low flammability polymer materials can be prepared from deoxybenzoin-containing polymers [15–20], and that bis-hydroxydeoxybenzoin (BHDB) can function as a drop-

in replacement for conventional bis-phenols such as bisphenol A (BPA), including as cross-linked epoxides [16]. For example, we found that bis-epoxydeoxybenzoin (BEDB), though halogen-free, gave cross-linked polymer resins in conjunction with aromatic amines, affording robust adhesives with heat release capacity (HRC) values that were 20–40% lower than conventional BPA-based resins [16].

This paper describes the preparation of an ‘all-deoxybenzoin’ cross-linked resin consisting of the tetrafunctional THDB, with BEDB as the epoxide component. The resulting resins possessed thermal properties similar to, or better than, flame retardant epoxies utilizing halogen or phosphorus-containing additives. Moreover, mechanical measurements, including compression and fracture toughness, were performed to ensure that these materials possess comparable properties to commercial epoxy resins. Lap shear measurements confirmed desirable performance characteristics from these wholly-deoxybenzoin structures.

2. Experimental

All chemicals were purchased from Sigma–Aldrich and used as received unless otherwise noted.

2.1. Characterization

Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker DPX300 or Avance 400 spectrometer. Thermogravimetric analysis (TGA) was performed under nitrogen on a Q500 (TA

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Instruments) at a heating rate of 10 °C/min. Char yields were determined by TGA from the mass residue at 800 °C. Differential scanning calorimetry (DSC) was performed on a Q200 from TA Instruments with a heating rate of 10 °C/min. Specific heat release rate (HRR, W/g), heat release capacity (HRC, J/(g·K)), and total heat release (THR, kJ/g) were measured on a microscale combustion calorimeter (MCC). MCC was conducted over a temperature range of 80–750 °C at a heating rate of 1 °C/s in an 80 cm³/min stream of nitrogen. The anaerobic thermal degradation products in the nitrogen gas stream were mixed with a 20 cm³/min stream of oxygen prior to entering the combustion furnace (900 °C). Heat release is quantified by standard oxygen consumption methods typical to PCFC [21,22]. During the test, HRR is obtained from dQ/dt, at each time interval and by the initial sample mass (~5 mg). The HRC is obtained by dividing the maximum HRR by the heating rate.

2.2. Mechanical testing

2.2.1. Dynamic mechanical analysis (DMA)

Dynamic mechanical properties of film tension specimens were measured on a Q800 machine (TA Instruments) at a single frequency of 1 Hz and a heating rate of 3 °C/min with equilibration at –120 °C. The T_g values were taken as the maxima of the loss moduli (E'').

2.2.2. Compression testing

Compression bullets were formed by cutting cylinders of resin into sections, with height to diameter ratios of 1:1 and diameters of approximately 11 mm. The top and bottom faces of the cylinders were cut parallel to one other, and perpendicular to the sides of the cylinders. The faces were polished to give smooth surfaces. Dimensions for compression testing were measured to the nearest 0.01 mm using calipers. Immediately before compression testing, a surfactant-PTFE film treatment was applied to the top and bottom surfaces of the compression specimens to produce a low friction surface that allows for affine deformation over a large range of strains. The samples are loaded in compression using an Instron 5800 fitted with a 50 kN load cell and controlled using the BlueHill 2 software package. Samples were tested at 20 °C, and a constant true strain rate of 1.0 min⁻¹ (1.67 × 10⁻³ s⁻¹) was maintained during the entire test [23].

2.2.3. Plane-strain fracture toughness

The use of miniature compact tension (mini-CT) specimens for fracture toughness testing of glassy polymers had been reported by Jones and Lee [24], and Hinkley [25]. In our study, 3 mm thick mini-CT specimens with 20 mm width (W) were prepared following ASTM standard D5045 [26]. The thickness (B) satisfied the requirement for achieving plane-strain conditions across the crack front, namely $B \geq 2.5 (K_q/\sigma_y)^2$, where K_q is the measured fracture toughness and σ_y is the yield stress estimated from the compression data [23]. The pre-notches were introduced with a diamond wafering blade. After conditioning the samples at –10 °C for one hour, a sharp pre-crack was generated on each specimen by inserting a fresh razor blade into the pre-notch and tapping lightly with a hammer. Load-displacement curves were recorded by an Instron universal testing machine (Model 4411) at a crosshead speed of 0.5 mm/min at 20 °C. Fracture toughness (K_q) was computed using the following equation:

$$K_q = \frac{P_c f(x)}{BW^{1/2}} \quad (1)$$

where K_q is in units of MPa/m^{1/2}, P_c is the critical load in kN, B and W are in cm. The geometric factor $f(x)$ is a dimensionless power

function in terms of x , which is the ratio of the length of the pre-crack to the width of the specimen (a/W).

$$f(x) = \frac{(2+x)(0.886 + 4.64x - 13.32x^2 + 14.72x^3 - 5.6x^4)}{(1-x)^{3/2}} \quad (2)$$

The term K_q denotes the use of mini-CT samples with a non-standard W/B ratio. Each reported fracture toughness value represents an average of 4–8 measurements.

2.2.4. Lap shear strength

Single joint lap shear strength measurements were performed according to the ASTM D1002 standard [27]. Samples were prepared with bond area of 12.7 mm² using aluminum 2024-T3 (100 mm × 25 mm × 1.60 mm) with inclusion of two 36 AWG wires to maintain constant thickness. The aluminum substrates were roughened with sandpaper and rinsed with hexane and water prior to bonding. Three to seven samples were prepared per formulation. Tests were performed at crosshead speed of 1.3 mm/min on an Instron universal testing machine (Model 4411) at room temperature. The lap shear strength was calculated as the ratio of the load at failure to the overlap bond area.

2.3. Synthesis of 4,4'-bishydroxydeoxybenzoin (BHDB)

4,4'-Bishydroxydeoxybenzoin was prepared following published procedures [16]. Specifically, desoxyanisoin (100 g, 390 mmol) was demethylated with pyridinium hydrochloride (180 g, 156 mmol) by stirring at 200 °C for 5 h. The resulting mixture was poured into water, and a yellow precipitate formed. This precipitate was filtered then recrystallized from acetic acid, to give 68.0 g of BHDB (77% yield). ¹H NMR (DMSO-d₆, ppm): 10.38 (s, OH–Ar–CO), 9.27 (s, OH–Ar–CH₂), 7.89 (d, $J = 7.0$ Hz, 2H, Ar–H), 7.04 (d, $J = 8.5$ Hz, 2H, Ar–H), 6.84 (d, $J = 9.5$ Hz, 2H, Ar–H), 6.68 (d, $J = 8.5$ Hz, Ar–H), 4.10 (s, 2H, Ar–CH₂–CO–Ar). ¹³C NMR (DMSO-d₆, ppm): 196.7, 162.5, 156.4, 131.5, 130.9, 128.3, 126.0, 115.7, 115.6, 43.9.

2.4. Synthesis of the diglycidyl ether of 4,4'-bishydroxydeoxybenzoin (BEDB)

The glycidyl ether of BHDB was prepared generally following published procedures [16]. Specifically, BHDB (68.0 g, 296 mmol) was added to a roundbottom flask with epichlorohydrin (232 mL, 2.96 mol), isopropanol (115 mL) and water (23 mL). A 20% NaOH solution (23.0 g NaOH in 115 mL water) was added dropwise at 65 °C and allowed to react for a total of 1.5 h from the first addition of base. The mixture was cooled and chloroform was added to extract the product. After several washings with water and brine, the organic layer was dried over magnesium sulfate. The solution was poured into hexane, resulting in precipitation of 79.0 g of the final diglycidyl ether product (80% yield). mp 105 °C. ¹H NMR (DMSO-d₆, ppm): 8.01 (d, 2H, $J = 8.0$ Hz, Ar–H), 7.20 (d, 2H, $J = 7.8$ Hz, Ar–H), 6.97 (d, 2H, $J = 7.8$ Hz, Ar–H), 6.90 (d, 2H, $J = 6.9$ Hz, Ar–H), 4.38–4.16 (m, 2H, –O–CH₂–oxirane), 4.16 (s, 2H, Ar–CH₂–CO–Ar), 4.07–3.92 (m, 2H, –O–CH₂–oxirane), 3.45–3.31 (m, 2H, 2(oxirane CH)), 3.01–2.89 (m, 2H, 2(oxirane CH₂)), 2.84–2.74 (m, 2H, 2(oxirane CH₂)). ¹³C NMR (CDCl₃, ppm): 196.5, 162.3, 157.4, 130.9, 130.5, 130.0, 127.5, 114.9, 114.4, 68.9, 66.8, 50.1, 49.9, 44.7, 44.6, 44.4.

2.5. Synthesis of 2,4,4',6 tetrahydroxydeoxybenzoin (THDB)

Tetrahydroxydeoxybenzoin (THDB) was prepared following a reported procedure [28], but at a larger scale. Phloroglucinol

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