Polymer 55 (2014) 4441–4446

Contents lists available at ScienceDirect

Polymer

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

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

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ARTICLE INFO

Article history:
Received 11 March 2014
Received in revised form
11 June 2014
Accepted 13 June 2014
Available online 20 June 2014

Keywords:
Deoxybenzoin
Flame retardant
Mechanical properties

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.

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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http://dx.doi.org/10.1016/j.polymer.2014.06.043
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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 cm^3/min stream of nitrogen. The anaerobic thermal degradation products in the nitrogen gas stream were mixed with a 20 cm^3/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:

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

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).

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

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 mm^2 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). ^{1}H NMR (DMSO-d6, ppm): 10.38 (s, OH–Ar–CO), 9.27 (s, OH–Ar–CH_2), 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–CH_2–CO–Ar). ^{13}C 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. ^{1}H 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–CH_2–oxirane), 4.16 (s, 2H, Ar–CH2–CO–Ar), 4.07–3.92 (m, 2H, –O–CH_2–oxirane), 3.45–3.31(m, 2H, 2(oxirane CH)), 3.01–2.89 (m, 2H, 2(oxirane CH_2)), 2.84–2.74 (m, 2H, 2(oxirane CH_2)). ^{13}C NMR ($CDCl_3$, 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)

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

(39.5 g, 313 mmol), 4-hydroxyphenylacetonitrile (50.0 g, 376 mmol) and anhydrous ethyl ether (200 mL) were added to a roundbottom flask. Under a nitrogen atmosphere at 0 °C, aluminum chloride (5.0 g, 39.3 mmol) was added and the flask was capped quickly. A steady stream of $HCl_{(g)}$, generated by addition of concentrated HCl over calcium chloride, was piped into the flask. The HCl stream flowed for 6 h, yielding a pink precipitate. The precipitate was kept overnight at 0 °C. The precipitate was then filtered and refluxed in water (500 mL) for 2 h. This produced a light red powder that was filtered and dried. The powder was dissolved in acetone and charged with charcoal, filtered, and the solvent removed to afford 42.9 g of pale yellow powder (54% yield). mp 259 °C. ^{1}H NMR (DMSO-d6, ppm): 12.27 (s, 2H,2,6—OH), 10.41 (s, 1H, 4—OH), 9.23 (s, 1H, 4′—OH), 7.02 (d, 2H, $J = 8.1$ Hz, H-2′,6′), 6.68 (d, 2H, $J = 8.1$ Hz, H-3′,5′), 5.82 (s, 2H, H-3,5), 4.21(s, 2H, Ar—CH_2—CO—Ar). ^{13}C NMR (DMSO-d6, ppm): 203.5, 165.2, 164.7, 156.31, 131.0, 126.4, 115.4, 104.1, 95.2, 48.5.

2.6. Preparation of BEDB/THDB resins

Cross-linked resins were prepared in a stoichiometric ratio of BEDB to THDB (2 mol BEDB: 1 mol THDB). As the melting points of the two monomers differ by 150 °C, the higher melting point THDB was solubilized in methanol prior to cross-linking. BEDB was melted at 150 °C and the THDB solution was added slowly while stirring. The resin was quickly poured into a mold and cured overnight at 200 °C. Teflon molds were used for fracture toughness specimens and Surfasil-treated test tubes were used for compression samples. Comparative samples were prepared by reacting the diglycidyl ether of bisphenol A (DGEBA, D.E.R.332, Dow Chemical Company) with stoichiometric amount of polyetheramine (PEA, Jeffamine D230, Huntsman), 4,4′-diaminodiphenylsulfone (DDS, Acros Organic), and THDB (2 glycidyl ether: 1 crosslinker). DGEBA/PEA were cured at 80 °C for 3 h, followed by 3 h at 120 °C, while DGEBA/DDS was cured at 200 °C for 4 h, followed by an additional 2 h at 220 °C. DGEBA/THDB were prepared similarly to the BEDB/THDB resins.

3. Results and discussion

3.1. Synthesis of monomers BEDB and THDB

BEDB was prepared by reacting BHDB with an excess of epichlorohydrin in an aqueous solution of sodium hydroxide, as shown in Fig. 1. The BEDB synthesis is scalable, prepared in our laboratories at about 80 g per batch, and BEDB has proven stable when stored in the laboratory under ambient conditions. THDB was synthesized under Houben—Hoesch conditions (Fig. 1), starting from phloroglucinol and 4-hydroxyphenylacetonitrile. These conditions for synthesizing THDB, known from the natural products literature [28—30], proved scalable to the 40 g level. Using THDB as a multifunctional phenol, and BEDB as the epoxy component, epoxy resins were generated in which the entirety of the polymer resin is composed of monomer units having the inherently non-flammable deoxybenzoin as the aromatic structural unit.

3.2. Thermal properties

We were intrigued to find that the thermal properties of BHDB and THDB, as small molecules, analyzed separately by thermogravimetric analysis (TGA), differed greatly. The TGA curves of Fig. 2 show that BHDB volatilizes completely at ~350 °C, while THDB produces a substantial char residue (~40% at 800 °C). Since BHDB-containing polymers of many varieties exhibit high char yield, we expected that THDB-containing structures would be especially interesting to examine in the capacity of non-flammable polymeric materials.As a multifunctional structure, THDB is well-suited for integration into polymer materials as a cross-linker, tested here in epoxy curing, with subsequent evaluation of mechanical and thermal properties. TGA thermograms of epoxy resins with and without deoxybenzoins in the network are shown in Fig. 3, with clear differences arising from the presence of THDB in the cured material. For example, resins prepared from the diglycidyl ether of BPA (DGEBA) by curing with polyetheramine (PEA) displayed almost no char residue beyond 450 °C. However, replacement of PEA with THDB gave epoxy polymers with a char residue of 22%. Impressively, the all deoxybenzoin cured system, prepared from THDB and BEDB, produced nearly 40% char at 800 °C, approximately 3 times that of a conventional DGEBA/DDS system (char yield ~15%). Such an increase in char yield would be expected to correlate to reduced heat release values, due to fewer escaping volatile components upon thermal degradation of the material. In accord with this expectation, pyrolysis combustion flow calorimetry (PCFC) revealed that the heat release capacity (HRC) and total heat release (THR) values decreased significantly due to the inclusion of deoxybenzoin monomers (defining HRC as the maximum heat released divided by the heating rate). Describing these systems in terms of HRC eliminates the reliance on heating rate that is typical of standard flammability measurements (i.e. heat release rate), rendering it a material dependent property. THR is the total heat of complete combustion of the pyrolysis products per initial mass of the sample. Lower HRC and THR values are thus good indicators of increasing the flame retarding property of the polymer. For instance, by incorporating deoxybenzoin into resins, the HRC of

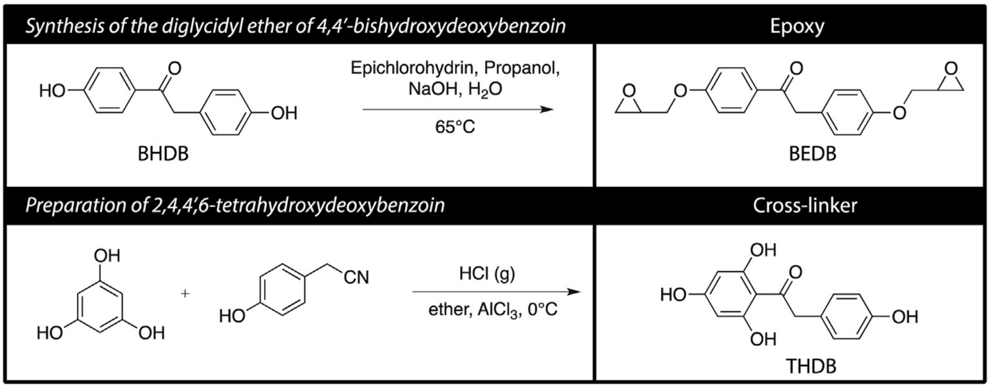

Fig. 1. Synthesis of BEDB (top) and THDB (bottom).

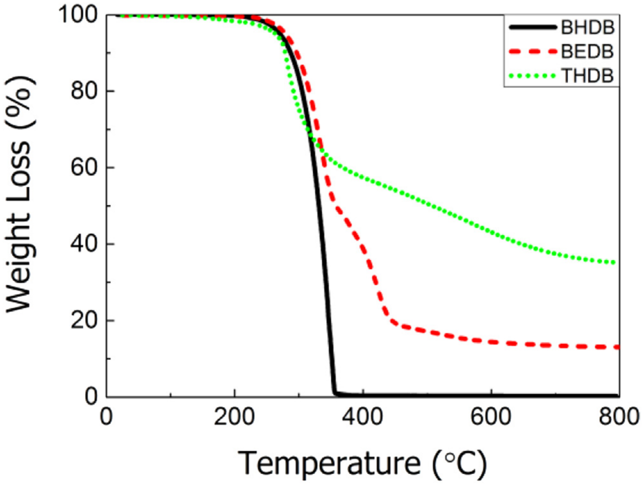

Fig. 2. Thermogravimetric analysis (TGA) curves for BHDB, BEDB, and THDB.

BEDB resins cured with PEA were measured as 480 J/g-K, nearly a 50% reduction from that of DGEBA (850 J/g-K) (see Table 1). Introducing THDB into DGEBA resins led to further reduction in HRC, to 393 J/g-K, confirming 1) the beneficial effect of deoxybenzoin monomers for tempering heat release, and 2) their facile integration into curing chemistry with conventional epoxies. The all-deoxybenzoin cross-linked resins displayed by far the most favorable heat release properties, with THR and HRC values measured as 13 kJ/g and 229 J/g-K, respectively. We note that such values are almost half that of any of the resins we reported previously from BEDB with conventional cross-linking structures: for example, BEDB cross-linked with DDS gave THR and HRC values of 17.2 kJ/g and 420 J/g-K [16]. While we expect that these values could be lowered further by inclusion of halogenated or inorganic flame retardant additives, for the purpose of this study we simply convey the favorable thermal properties of these systems in the absence of additives of any sort.

3.3. Mechanical properties

Cured resin plaques prepared as described above were characterized for their physical and mechanical properties, first employing dynamic mechanical analysis (DMA). The T_g values measured by DMA were similar to those obtained by DSC, showing DGEBA/THDB and BEDB/THDB formulations to be intermediate between the DGEBA/PEA (lowest) and DGEBA/DDS (highest) values. As the DGEBA/PEA and DGEBA/DDS formulations were prepared with stoichiometries intended to give similar average molecular weight between crosslinks, M_c (Table 2), the results illustrate the importance of backbone structure/stiffness in governing T_g in these materials. For example, while the molecular weight between crosslinks of BEDB/THDB is essentially identical to the DGEBA/PEA system (470 g/mol), the higher T_g of the deoxybenzoin system reflects the stiffer aromatic backbone structure of the BEDB/THDB network. Higher T_g of the deoxybenzoin system is also seen relative to the network containing PEA. From a thermal perspective, the BEDB/THDB and DGEBA/THDB formulations fall into a suitable range for numerous applications. Interestingly, DMA results also revealed the storage modulus of the BEDB/THDB network to be ~10% higher than the DGEBA/DDS formulation (Fig. 4a and Table 2), and maintains higher values than the other materials through the entirety of the glassy region. This property is particularly important in fiber reinforced composites, in which the composite compressive strength increases with storage modulus of the resin.

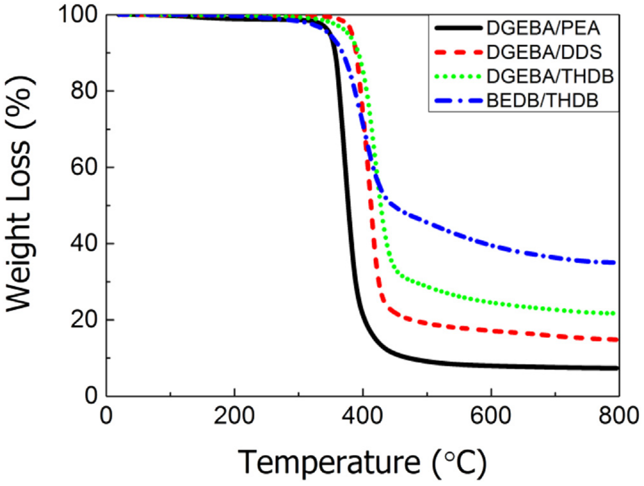

Fig. 3. TGA analysis of THDB-containing resins vs. BPA-based structures.

Table 1
Thermal characteristics of deoxybenzoin based epoxy resins.

Formulation	HRC (J/K-g)	THR (kJ/g)	T_g (°C)	T_d (°C) 5% weight loss	Residue %
DGEBA/PEA	850	29	89	349	7
DGEBA/DDS	510	26	219	383	15
DGEBA/THDB	393	20	164	378	22
BEDB/THDB	229	13	110	322	34

T_g values obtained from DSC. T_d and residue percent from TGA. HRC and THR acquired on MCC.

When comparing the loss moduli of these epoxy formulations (Fig. 4b), the breadth of the beta-transition regime was observed to broaden more substantially for the deoxybenzoin formulations (BEDB/THDB and DGEBA/THDB) relative to the others. The beta transition, combined with T_g values, affect numerous properties including the overall fracture toughness of the networks (*vide infra*).

Compression tests of the resins were conducted to characterize their nonlinear viscoelastic response. Compression testing is advantageous for avoiding premature failure from flaw activation, thereby allowing for post yield characterization. Fig. 5 shows representative plots of the true stress vs. neo-Hookian strain for deoxybenzoin-containing resins and conventional resins, while the elastic modulus, yield stress, rejuvenated stress, and strain hardening modulus are given in Table 2. The elastic moduli for all of these formulations are consistent with the storage moduli values obtained from the DMA tests, with the highest modulus values seen in the BEDB/THDB system. With respect to yield stress, the DGEBA/PEA formulation exhibited the lowest values, with DGEBA/THDB and BEDB/THDB having intermediate values, and the DGEBA/DDS system measuring the highest among the samples examined. This trend is expected, since for glassy amorphous polymers the yield stress scales with T_g for formulations tested at the same temperature and strain rate. However, the plots of Fig. 5 also show that differences in post-yield stress drop were noted among the samples, which can also be seen by comparing the numerical results of yield stress and rejuvenated stress in Table 2. This is important since it is known that a more pronounced post-yield stress drop increases the extent of strain localization that can occur in other stress states and can lead to premature failure in certain circumstances.

Fracture toughness tests assessed the relative toughness of these new deoxybenzoin network formulations; values for fracture

Table 2
Mechanical properties of deoxybenzoin resins.

Resin	M_c g/mol	$T_{g,\text{ DSC}}$ °C	$T_{g,\text{ DMA}}$ °C	Storage modulus GPa	Compressive modulus GPa	Yield stress MPa	Rejuvenated stress MPa	Strain hardening modulus MPa	K_{1c} MPa m$^{0.5}$	G_{1c} (kJ/m^2)
DGEBA/PEA	470	88	92	2.20	2.90	89	70	79	0.82 ± 0.11	0.20 ± 0.004
DGEBA/DDS	474	219	223	1.77	2.61	138	135	162	0.78 ± 0.05	0.20 ± 0.001
DGEBA/THDB	480	164	168	1.46	2.25	112	106	119	0.86 ± 0.15	0.28 ± 0.008
BEDB/THDB	470	108	116	2.41	3.02	129	98	58	0.78 ± 0.14	0.17 ± 0.005

M_c was calculated based on 1:1 stoichiometry between epoxide groups and amine hydrogens, assuming full conversion. A Poisson ratio of 0.4 was used for calculating G_{1c}.

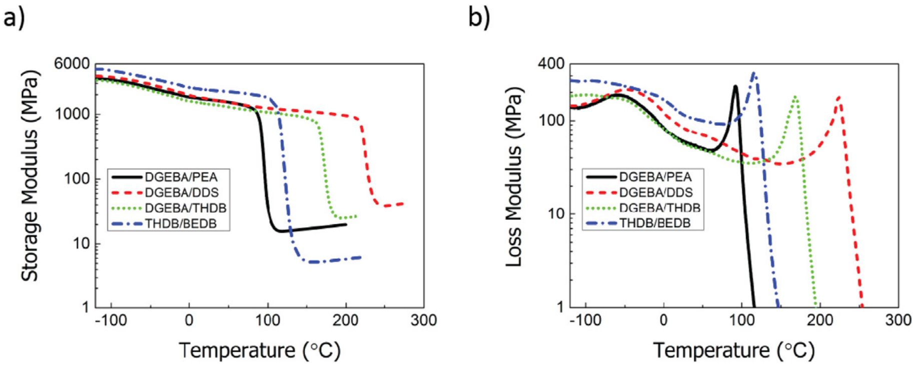

Fig. 4. DMA analysis of resins that contain THDB compared with BPA-based resins. a) Storage modulus and b) Loss modulus as a function of temperature.

toughness and energy release rate are shown in Table 2, while Fig. 6 plots fracture toughness against T_g for each formulation examined. Fracture toughness generally decreases with increasing T_g, since dissipative processes such as yielding and post-yield deformation can occur, and surface area increases during the fracture process. Interestingly, each of the four formulations studied exhibited comparable fracture toughness, despite the significant breadth (spanning 100 °C) of T_g values. This indicates that yield stress is of secondary importance in determining the relative toughness of these formulations, and other post-yield characteristics dominate fracture toughness. Isolating which particular characteristic governs fracture response, and the morphological origins, is beyond the scope of this investigation. Nonetheless, the results show that both the BEDB/THDB and DGEBA/THDB formulations have comparable toughness to commonly used commercial systems with similar crosslink densities.

The utility of these resins as cured adhesives was assessed through ASTM D1002 lap shear evaluation, performed for each of the four resin formulations described above. Aluminum (2024-T3) substrates of 100 mm by 25 mm were prepared by roughening with sandpaper and rinsing with hexane and water. Resins were applied to the surfaces with approximately 13 mm of overlap. Two wires

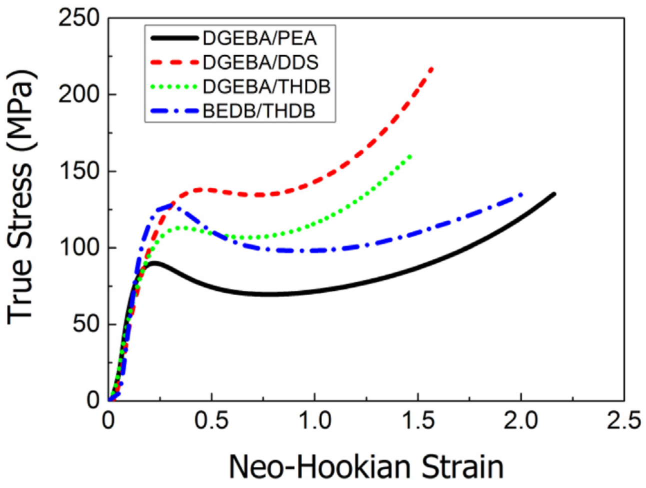

Fig. 5. Compression results of deoxybenzoin (THDB and BEDB) resins relative to conventional BPA-based resins.

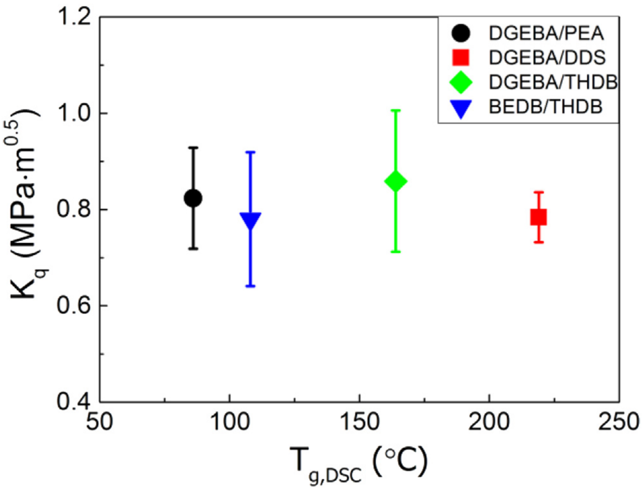

Fig. 6. Fracture toughness values of deoxybenzoin-containing resins vs. conventional BPA-based resins.

Table 3
Lap shear strength values of the THDB and BPA resins.

Resin	Lap shear strength (MPa)
DGEBA/PEA	13.1 ± 1.4
DGEBA/DDS	14.3 ± 1.2
DGEBA/THDB	12.6 ± 2.1
BEDB/THDB	10.1 ± 0.9

were utilized in to maintain a fixed thickness. Binder clips ensured the substrates were aligned and maintained contact during curing. The resins were cured in the oven as per each formulation requirement (e.g. DGEBA/DDS at 180 °C for 4 h, followed by 220 °C for 2 h, see Section 2.6). The substrates were placed in the Instron, and pulled in tension at a crosshead speed of 1.3 mm/min until failure. The lap shear strength values, acquired by dividing the load at failure by the overlap area, are given in Table 3. We were encouraged to find that the resins with THDB give the same order of magnitude lap shear strength values as the resins prepared by crosslinking DGEBA with either PEA or DDS, and are comparable to values for DGEBA resins found in the literature [31–34].

4. Conclusions

Multifunctional deoxybenzoin-containing structures, based on the tetrafunctional THDB and difunctional BEDB were prepared and utilized in curing chemistry. The adhesive materials reported from THDB and BEDB-containing resins proved to have suitable mechanical properties for consideration in a variety of adhesive applications, while the flammability properties of the materials obtained were substantially lower than conventional systems, even in the absence of anti-flammable additives. Evaluation of mechanical properties of these systems revealed a higher elastic modulus for the BEDB/THDB formulation relative to conventional materials, along with good fracture toughness compared to formulations of similar molecular weight between crosslinks. Deoxybenzoin-based materials can thus afford useful epoxy resins that may be suitable for consideration in a variety of adhesive applications.

Acknowledgments

The authors acknowledge the financial support of the Federal Aviation Administration (FAA-09-G-13) and the consortium member companies of the Center for UMass-Industry Research on Polymers (CUMIRP) Cluster group on Flammability. The project utilized the Shared Facilities supported by the Materials Research Science and Engineering Center (MRSEC) on Polymers at UMass Amherst (DMR-0820506).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2014.06.043.

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