Polymer 50 (2009) 767–774

Contents lists available at ScienceDirect

Polymer

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

Deoxybenzoin-based epoxy resins

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A R T I C L E   I N F O

Article history:
Received 11 September 2008
Received in revised form
2 December 2008
Accepted 4 December 2008
Available online 9 December 2008

Keywords:
Deoxybenzoin-based epoxy
Flame resistance
Mechanical properties

A B S T R A C T

The diepoxide of bishydroxydeoxybenzoin, termed BEDB, was prepared and used as a diepoxide in adhesive formulations with various aromatic diamine cross-linkers. These novel epoxy resins were characterized and compared to the properties of bisphenol A (BPA)- and 3,3′,5,5′-tetrabromobisphenol A (TBBA)-based epoxies in terms of their thermal and mechanical properties. Cured formulations were characterized to determine glass transition temperatures by differential scanning calorimetry (DSC). The char residue, heat release capacity, dynamic mechanical properties, fracture toughness, and adhesion strength of the cured resins were investigated by thermogravimetric analysis (TGA), microscale combustion calorimetry, dynamic mechanical analysis (DMA), plain-strain fracture toughness tests, and lap shear tests. The BEDB-based resins exhibited significantly higher fracture toughness and adhesion strength compared to the BPA-epoxy resins, as well as low heat release properties (*i.e.*, lower flammability) despite the absence of halogen.

1. Introduction

Polymers are a mainstay of modern society, used prominently in fabricating textiles, upholstery, construction materials, vehicles (for air, land, and sea travel), and microelectronic devices. The inherent flammability of many polymers poses a significant threat, especially in enclosed or isolated spaces. Fire retardant (FR) additives temper polymer flammability, and brominated organic molecules comprise a large subset of FRs used today. While FR molecules save lives, they also face legislative scrutiny due to health and environmental concerns, particularly related to bioaccumulation (*e.g.* polybrominated diphenyl ether (PBDE) has been detected in umbilical cord serum and breast milk) [1,2]. Legislative action on halogenated FRs has precedent – for example, chlorinated and brominated alkyl phosphates were banned from children's sleepwear in the 1970s, following reports on associated mutagenic and carcinogenic risks [3,4].

The tradeoff between polymer flammability and flame retardant toxicity presents a dilemma that can be addressed, ideally, with new syntheses that avoid halogen altogether [5]. Recently, we described the first use of 4,4′-bishydroxydeoxybenzoin (BHDB) as an A_2 monomer in polycondensation chemistry, and through calorimetric methods identified exceedingly low heat release properties of these BHDB-containing polymers [6,7]. BHDB can be viewed as a drop-in replacement for bisphenol A (BPA), a classic A_2 monomer for polycondensation that has been integrated into a wide range of commercial polymer products. BPA-based polymers, while not nearly as flammable as polyethylene or polystyrene, are moderately flammable and thus used in conjunction with FR additives. Bisphenol C (BPC)-based polymers are attractive for their charring decomposition that insulates the polymer-air interface, and precludes the evolution of gaseous decomposition products required for sustained combustion. However, a general concern over the chlorine content of BPC has slowed (or precluded) commercialization of BPC-containing polymers. We hypothesized that BHDB would possess a similar charring propensity as BPC, dehydrating to form diphenylacetylene units that can aromatize, cross-link, and char [8,9]. Here we introduce the diepoxide (or diglycidyl ether) of BHDB, termed BEDB (meaning **b**is**e**poxy**d**eoxy**b**enzoin), as a novel cross-linker for epoxy adhesive chemistry. We find that BEDB, despite its lack of halogen, gives adhesive materials with low flammability, and also excellent mechanical properties. Moreover, the influence of curing agents on char formation, and the flame-retardancy of the BEDB resins cured with various aromatic diamines are discussed.

2. Experimental

2.1. Materials

The diglycidyl ether of BPA (EBPA, DER332) was obtained from Dow Chemical Co. and used as received. Desoxyanisoin, pyridine

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doi:10.1016/j.polymer.2008.12.009

hydrochloride, epichlorohydrin, and all of the amines used in this work were purchased from Sigma–Aldrich and used without further purification.

2.2. Characterization

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AVANCE 400 NMR spectrometer. In order to investigate the curing behavior and glass transition temperature (T_g) of epoxy resins, differential scanning calorimetry (DSC) was performed on a DuPont DSC 2910 using a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was conducted in a nitrogen atmosphere on a DuPont TGA 2950 using a heating rate of 10 °C/min. Char yields were determined by TGA from the mass of the residue remaining at 850 °C. Specific heat release rate (HRR, W/g), heat release capacity (HRC, J/(g K)), and total heat release (THR, kJ/g) were measured using a pyrolysis combustion flow calorimeter (PCFC) on 3–5 mg samples of cured resins. PCFC experiments were conducted from 100 to 900 °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 are mixed with a 20 cm^3/min stream of oxygen prior to entering the combustion furnace (900 °C). The heat is determined by standard oxygen consumption methods. During the test, HRR is obtained by dividing dQ/dt, at each time interval, by the initial sample mass, and HRC is obtained by dividing the maximum value of HRR by the heating rate in the test. To ensure reproducibility, three-to-five sample runs were conducted for each cured resin.

2.3. Mechanical properties

Dynamic mechanical analysis (DMA) was performed with a TA Instrument DMA 2980, using specimens of 20 mm length, 5 mm width, and ~0.7 mm thickness. The storage modulus (E') and tan δ were determined at a programmed heating rate of 3 °C/min from room temperature to 270 °C at a frequency of 1 Hz. The materials were tested during a second heating to determine if further curing had taken place. Compact tension (CT) specimens having dimensions of approximately ($2.5 \times 2.4 \times 0.5$) cm were tested following ASTM D 5045-99 protocol. The specimens were pre-cracked with a Leco VC-50 diamond saw and a razor blade, and tested at a crosshead speed of 0.5 mm/min on an Instron 4411 equipped with a 0.1 kN (10 kg) load cell. The value of the crack length/width (a/W) of specimens is approximately 0.5. Three-to-five specimens of each resin formulation were tested at room temperature. Lap shear testing was carried out by following ASTM D 1002. Lap shear specimens having a bond area of 12.7 mm^2 were made using two 2024-T3 aluminum panels. Bond line thickness was controlled by the inclusion of short lengths of 0.127 mm diameter wire. Tests were conducted at a crosshead speed of 50 mm/min on an Instron tensile test machine. For reproducibility, three-to-five specimens of each formulation were tested (each at room temperature).

2.4. Synthesis of 4,4′-bishydroxydeoxybenzoin (BHDB)

4,4′-Bishydroxydeoxybenzoin (BHDB) was prepared by demethylation of desoxyanisoin, according to the literature [6,7]. Desoxyanisoin (50 g, 195.1 mmol) and pyridine hydrochloride (90.2 g, 780.5 mmol) were added to a round-bottom flask equipped with a condenser. The mixture was refluxed for 5 h at 200 °C, cooled to room temperature, and poured into water. The precipitate was filtered and recrystallized from acetic acid to give 38 g (85% yield) of the desired product. ^{1}H NMR (DMSO-d_6, ppm): 10.35 (s, 1H, *H*O–Ar–CO), 9.28 (s, 1H, *H*O–Ar–CH$_2$), 7.91 (d, 2H, Ar–*H*), 7.05 (d, 2H, Ar–*H*), 6.84 (d, 2H, Ar–*H*), 6.68 (d, 2H, Ar–*H*), 4.09 (s, 2H, Ar–CO–C*H*$_2$–Ar).

2.5. Synthesis of the diepoxide (diglycidyl ether) of 4,4′-bishydroxydeoxybenzoin (BEDB)

Epichlorohydrin (50 g, 540 mmol), BHDB (12.4 g, 54.3 mmol), 2-propanol (26.9 g, 45 mmol), and water (4.3 g) were added to a round-bottom flask and stirred at 65 °C. A 20% aqueous sodium hydroxide solution (19.5 g) was added dropwise over 45 min, and stirring was continued for 30 min. The mixture was cooled to room temperature, and chloroform (200 mL) was added. The organic layer was washed extensively with water, and the combined organic extract was dried over magnesium sulfate. Solvents were removed by rotary evaporation, and the residue was dissolved in chloroform, then precipitated into hexanes to give 14.8 g (80% yield) of BEDB as a white solid. ^{1}H NMR (CDCl$_3$, ppm): 7.99 (d, 2H, Ar–*H*), 7.18 (d, 2H, Ar–*H*), 6.91 (d, 2H, Ar–*H*), 6.88 (d, 2H, Ar–*H*), 4.32–4.17 (m, 2H, 2(–O–C*H*$_2$–oxirane)), 4.17 (s, 2H, Ar–CO–C*H*$_2$–Ar), 4.01–3.92 (m, 2H, 2(–O–C*H*$_2$–oxirane)), 3.39–3.32 (m, 2H, 2(oxirane C*H*)), 2.94–2.88 (m, 2H, 2(oxirane C*H*$_2$)), 2.78–2.74 (m, 2H, 2(oxirane C*H*$_2$)). ^{13}C NMR (CDCl$_3$, ppm): 196.5, 162.3, 157.4, 130.9, 130.5, 130.0, 127.5, 114.8, 114.4, 68.9, 68.8, 50.2, 49.9, 44.7, 44.6, 44.4. HRMS-FAB m/z $[M+H]^+$ calcd. 340.1311; found 340.1293.

2.6. Synthesis of the diepoxide (diglycidyl ether) of 3,3′,5,5′-tetrabromobisphenol A (ETBBA) [10]

ETBBA was prepared in a similar manner as BEDB, using TBBA (24.9 g) instead of BHDB. This gave ETBBA (25.4 g, 85%). ^{1}H NMR (CDCl$_3$, ppm): 7.30 (s, 4H, Ar–*H*), 4.21–4.18 (q, 2H, 2(–O–C*H*$_2$–oxirane)), 4.09–4.05 (q, 2H, 2(–O–C*H*$_2$–oxirane)), 3.51–3.46 (m, 2H, 2(oxirane C*H*)), 2.92–2.90 (t, 2H, 2(oxirane C*H*$_2$)), 2.75–2.74 (q, 2H, 2(oxirane C*H*$_2$)), 1.60 (s, 6H, Ar–C(C*H*$_3$)$_2$–Ar).

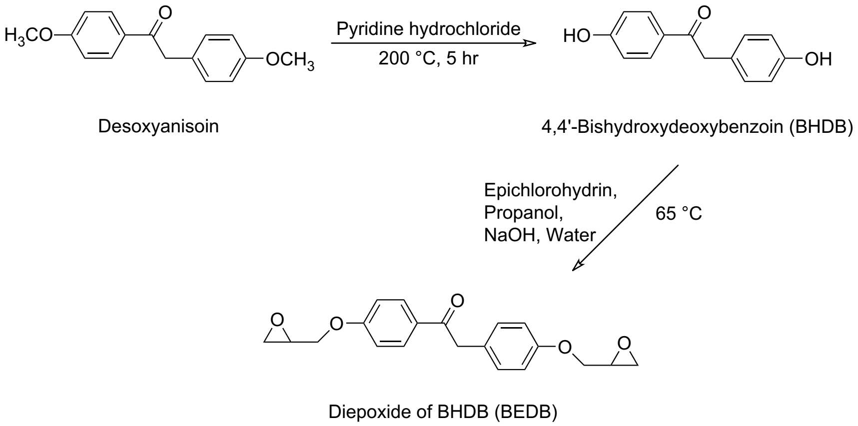
2.7. Preparation of cured resins

Samples for TGA, PCFC, and DMA were prepared by mixing the diepoxides with a stoichiometric equivalent of curing agent at 60–130 °C. The homogeneous mixtures were cured for 2 h at 130–180 °C, followed by a 2 h post-cure at 180–200 °C in a Teflon mold. Mixing and curing temperatures were optimized by considering the glass transition temperature and gelation rate of each formulation.

3. Results and discussion

3.1. Synthesis of BEDB

BEDB, the diepoxide (or diglycidyl ether) of BHDB, was prepared by reacting BHDB with epichlorohydrin under basic conditions, as shown in Scheme 1. BEDB was obtained as a white solid in 80% yield, with a distinctly higher melting point (125–130 °C) than the BPA version (43–47 °C). Nuclear magnetic resonance (NMR) spectroscopy confirmed the intended structure, as seen for example in the proton spectrum showing a singlet at 4.17 ppm for the methylene group adjacent to the ketone, and characteristic glycidyl ether resonances at 4.25, 3.95, and 2.76 ppm. BEDB was then used as the electrophilic difunctional monomer in curing reactions with multifunctional nucleophiles, including 4,4′-diaminodiphenyl sulfone (4,4′-DDS), 4,4′-diaminodiphenyl methane (4,4′-DDM), and *meta*-phenylene diamine (*m*-PDA).



Scheme 1.

3.2. Thermal properties of cured BEDB resins

BEDB, EBPA, and ETBBA epoxy formulations were prepared using 4,4′-DDS, 4,4′-DDM, and *m*-PDA as the curing agents (Table 1). Homogeneous formulations were prepared by mixing the liquid-phase epoxides with the amines at 60–130 °C. In the DSC instrument, the mixtures were heated to fully cure the formulation (*i.e.*, when no further increase in the heat of reaction was seen), and the reported glass transition temperatures were taken from the second heating curves of the fully cured samples (following quenching with liquid nitrogen). Several interesting characteristics were noted in the cured resins. The BEDB-based resins consistently gave the lowest T_g values, which might be due to the absence of the steric bulk between the phenyl groups of BPA and TBBA. In addition, those cured with DDS had the highest T_g values, possibly due to a combination of the polarity and rigidity of the sulfonyl groups in the DDS-containing networks.

With the exception of the ETBBA resins, the initial degradation temperatures (T_{di}) of the formulations were near or above the mid-300 °C range. It is known that the presence of bromine reduces the thermal stability of amine-cured epoxy resins, and TBBA resins specifically are destabilized by the formation of HBr, and instability of the cyclohexadienone structure produced in the initial step of thermal decomposition [11,12].

3.3. Heat release properties of cured BEDB-based resins

Pyrolysis combustion flow calorimetry (PCFC), an oxygen consumption technique, measures 1) total heat release (THR), *i.e.*, the heat of complete combustion of the pyrolysis gas per unit initial mass of a material, 2) heat release capacity (HRC), *i.e.*, the maximum heat release rate divided by the constant heating rate, and 3) T_{max}, *i.e.*, the sample temperature at maximum heat release rate. While an ideal predictor of flammability would be the heat release rate, this depends on the sample heating rate, making quantification difficult. HRC eliminates this uncertainty, more reliably predicting polymer flammability as an inherent material property). PCFC is now recognized as a convenient analytical tool for analyzing small scale (milligram) samples of combustible materials [13,14], and is used here to characterize the cured epoxy resins. In addition, thermogravimetric analysis (TGA) was conducted, also on the cured materials, to evaluate char yields. By both measures (PCFC and TGA), BEDB-based resins are quite promising materials. For example, the BEDB/*m*-PDA revealed a HRC of 390 J/(g K), approximately half of that obtained for conventional EBPA/*m*-PDA resin (HRC of 760 J/(g K)). Char yields of the BEDB-based epoxies were at least twice that of the BPA versions, increasing from about 12% for BPA-based adhesives to 25–30% for BEDB-based resins.

The BEDB- and TBBA-based resins showed much lower HRC and THR relative to the BPA-based resins. Halogen-containing polymers usually produce high levels of incomplete combustion products, and non-combustible gas, which contribute to gas phase combustion inhibition. In spite of halogen-free compounds, the BEDB-based resins exhibit significantly lower HRC and THR than those of the BPA resins. This is because that the effective char formation at

Table 1
Thermal properties of epoxy formulations.

Formulation	Thermal property			Heat release	
	T_g (°C)[a]	T_{di} (°C)[b]	Residue[c] (%)	HRC (J/(g K))	THR (kJ/g)
EBPA/4,4′-DDS	198	385	12	513 ± 10	25.3 ± 0.2
BEDB/4,4′-DDS	181	377	30	420 ± 14	17.2 ± 0.2
ETBBA/4,4′-DDS	213	304	23	443 ± 11	4.8 ± 0.2
EBPA/4,4′-DDM	179	372	16	737 ± 24	25.8 ± 0.6
BEDB/4,4′-DDM	145	354	35	439 ± 7	17.6 ± 0.2
ETBBA/4,4′-DDM	192	274	24	308 ± 14	4.5 ± 0.2
EBPA/*m*-PDA	176	367	14	761 ± 23	25.8 ± 0.6
BEDB/*m*-PDA	144	340	29	391 ± 40	19.7 ± 0.8
ETBBA/*m*-PDA	177	263	23	238 ± 3	5.0 ± 0.2

[a] T_gs were obtained from DSC.

[b] 5 wt% loss temperature on TGA.

[c] Char residues were obtained from TGA at 850 °C in nitrogen (heating rate 10 °C/min).

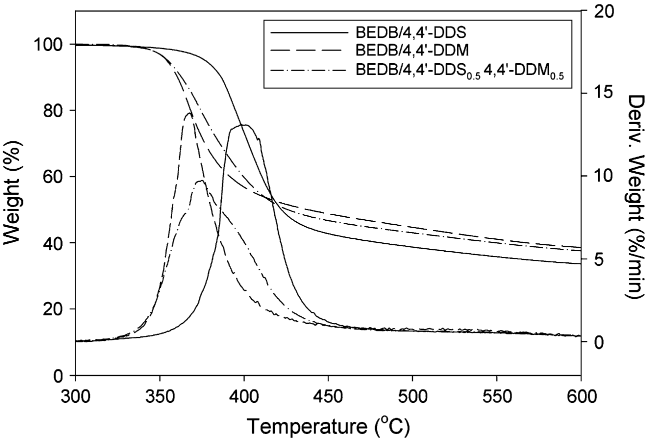


Fig. 1. TGA thermograms of BEDB resins cured with 4,4′-DDS, 4,4′-DDM, and a mixture of 4,4′-DDS and 4,4′-DDM.

Table 2
Thermal properties and flammability of the resins cured with mixed amines.

Formulation[a]	Thermal property		Flammability	
	T_g (°C)[b]	Residue[c] (%)	HRC (J/(g K))	THR (kJ/g)
EBPA/4,4′-DDS	198	12	513 ± 10	25.3 ± 0.2
EBPA/4,4′-$DDS_{0.8}$ 4,4′-$DDM_{0.2}$	196	14	454 ± 30	24.9 ± 0.4
EBPA/4,4′-$DDS_{0.5}$ 4,4′-$DDM_{0.5}$	185	15	577 ± 28	25.4 ± 0.2
EBPA/4,4′-$DDS_{0.2}$ 4,4′-$DDM_{0.8}$	178	16	693 ± 21	26.2 ± 0.4
EBPA/4,4′-DDM	179	16	737 ± 24	26.8 ± 0.4
BEDB/4,4′-DDS	181	30	420 ± 14	17.2 ± 0.2
BEDB/4,4′-$DDS_{0.8}$ 4,4′-$DDM_{0.2}$	180	33	342 ± 4	17.5 ± 0.5
BEDB/4,4′-$DDS_{0.5}$ 4,4′-$DDM_{0.5}$	173	34	321 ± 10	16.9 ± 0.3
BEDB/4,4′-$DDS_{0.2}$ 4,4′-$DDM_{0.8}$	160	35	378 ± 29	16.9 ± 0.1
BEDB/4,4′-DDM	145	35	439 ± 7	17.6 ± 0.2

[a] Subscripts mean mole fraction of compounds.
[b] T_gs were obtained from DSC.
[c] Char residues were obtained from TGA at 850 °C in nitrogen (heating rate 10 °C/min).

the molecular level is to reduce the amount of combustible products and gas.

3.4. BEDB resins cured with mixtures of diamines

Fig. 1 shows TGA thermograms of BEDB resins cured with 4,4′-DDS, 4,4′-DDM, and a mixture of 4,4′-DDS and 4,4′-DDM. The derivative weight curve of the resin cured with mixed amines is broader and its maximum value is smaller than those of the resins cured with a single amine. Because HRC is directly proportional to $\partial W/\partial T$ and the heat of combustion, this reduction in the maximum value of derivative weight can reduce HRC. To investigate the effects of mixed amines on flammability, amine formulations were prepared for BEDB and EBPA. The results for the formulations are listed in Table 2. In the cured resins with the mixed amines, the T_g increased with the mole fraction of 4,4′-DDS, and the char residue increased with the mole fraction of 4,4′-DDM. The HRC of the BPA-based resin is roughly dependant on the mole fraction of 4,4′-DDS, and is the lowest (454 ± 30 J/(g K)) at 0.8 mol fraction of 4,4′-DDS. However, in case of the BEDB-based resins, the resins cured with the same mole fraction of 4,4′-DDS and 4,4′-DDM has the lowest HRC (321 ± 10 J/(g K)). This tempering of heat release in the cured systems is appealing for future integration of BEDB into materials applications, if mechanical properties are sufficiently comparable to those of materials in use today.

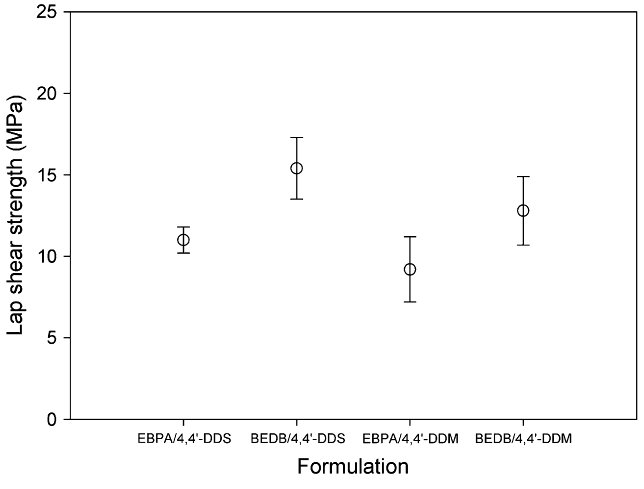


Fig. 2. Lap shear strength of epoxy resins cured with 4,4′-DDS or 4,4′-DDM.

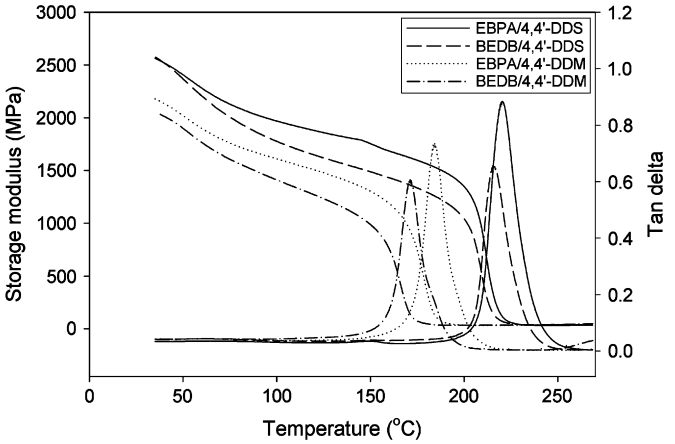


Fig. 3. Plot of storage modulus and tan versus temperature for EBPA/4,4′-DDS, BEDB/4,4′-DDS, EBPA/4,4′-DDM, and BEDB/4,4′-DDM.

Table 3
DMA analysis of the epoxy resins cured with DDS and DDM.

Formulation	T_g (°C)	Height of tan δ	Modulus at 50 °C (MPa)	Modulus at T_g + 40 °C (MPa)
EBPA/4,4′-DDS	220	0.884	2407	34
BEDB/4,4′-DDS	215	0.654	2367	40
EBPA/4,4′-DDM	184	0.736	2020	33
BEDB/4,4′-DDM	171	0.606	1899	36

3.5. Mechanical properties of BEDB-based epoxy resins

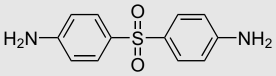
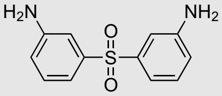
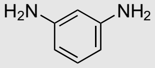
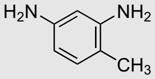
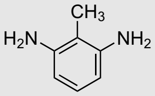
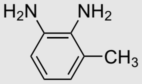
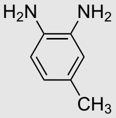
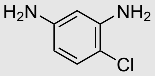
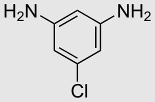
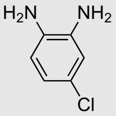
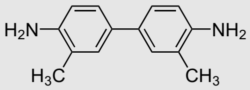
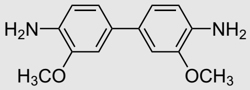
The adhesion strength of cured epoxy resins is derived from several factors, including the hydroxyl groups generated upon curing, the functionality of the components used, and the chemical structures of particular epoxide and curing agent [15]. Lap shear, a characteristic test of bonding shear strength, is indicative of adhesive environmental durability. In accord with the ASTM D 1002 protocol, lap shear tests were performed on the epoxy resins, using three-to-five specimens of four formulations: 1) EBPA/4,4′-DDS; 2) BEDB/4,4′-DDS; 3) EBPA/4,4′-DDM; and 4) BEDB/4,4′-DDM. The results are presented in Fig. 2. The lap shear strengths of BEDB-based resins cured with 4,4′-DDS and 4,4′-DDM were measured as 15.4 MPa and 12.8 MPa, and those of BPA-based resins, also cured with 4,4′-DDS and 4,4′-DDM, were measured as 11.0 MPa and 9.2 MPa, respectively. Both of these cured epoxy resins, using 4,4′-DDS as curing agent, are seen to have slightly higher adhesion strengths than those using 4,4′-DDM, and the strengths of BEDB-based epoxy resins were ~40% greater than the BPA-based resins. The superior adhesive properties of the cured BEDB resins, relative to EBPA analogs, were interesting and unexpected, but clearly indicate that BEDB-based resins have promise from a mechanical standpoint for use in practical adhesive materials.

The elastic modulus at temperatures above T_g (*e.g.* T_g + 40 °C) is valuable for characterizing highly cross-linked epoxies. Cross-link density, typically related to the average molecular weight between

Table 4
Plain-strain fracture toughness of cured resins.

Formulation	K_{IC} (MPa $m^{1/2}$)	G_{IC} (J/m^2)
EBPA/4,4′-DDS	0.76 ± 0.03	222 ± 15
BEDB/4,4′-DDS	1.30 ± 0.03	659 ± 28
EBPA/4,4′-DDM	0.64 ± 0.02	184 ± 16
BEDB/4,4′-DDM	1.06 ± 0.04	553 ± 43

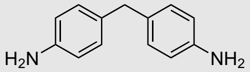
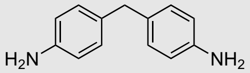
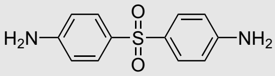
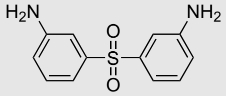
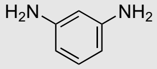
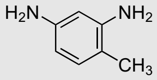
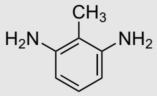
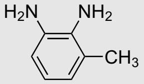
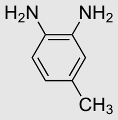
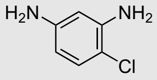
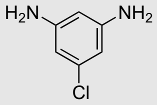
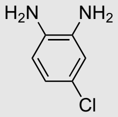
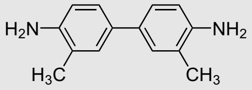
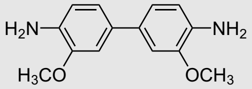
Table 5
Thermal properties of BEDB epoxy resins cured with various diamines.

Formulation	Diamine	T_g (°C)	T_{di} (°C)[a]	$T_{d\ max}$ (°C)[b]	ΔT_d ($T_{d\ max} - T_{di}$)
BEDB/4,4′-DDS		181	377	399	22
BEDB/3,3′-DDS		162	374	390	16
BEDB/*m*-PDA		144	340	352	12
BEDB/2,4-DT		155	341	357	16
BEDB/2,6-DT		153	356	368	12
BEDB/2,3-DT		160	342	357	15
BEDB/3,4-DT		159	337	347	10
BEDB/4-C*m*P		155	295	332	37
BEDB/5-C*m*P		166	332	336	4
BEDB/4-C*o*P		154	348	352	4
BEDB/3,3′-DMB		169	360	374	14
BEDB/3,3′-DMoB		149	344	366	22

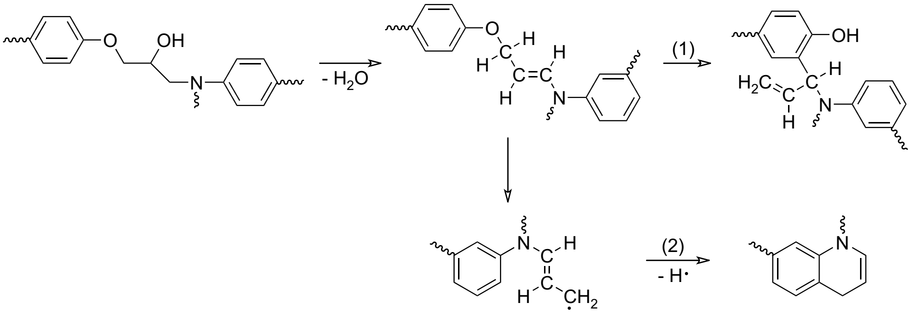
[a] 5 wt% loss temperature on TGA.

[b] Maximum peak temperature of derivative weight curve on TGA.

Table 6
Heat release data for BEDB-based epoxy resins cured with various diamines.

Formulation	Diamine	HRC (J/(g K))	THR (kJ/g)	Residue[a] (%)
EBPA/4,4′-DDM		737 ± 24	26.8 ± 0.4	16
BEDB/4,4′-DDM		439 ± 7	17.6 ± 0.2	35
BEDB/4,4′-DDS		420 ± 14	17.2 ± 0.2	30
BEDB/3,3′-DDS		429 ± 19	17.2 ± 0.1	33
BEDB/*m*-PDA		391 ± 40	19.7 ± 0.8	29
BEDB/2,4-DT		372 ± 36	17.0 ± 0.4	33
BEDB/2,6-DT		530 ± 33	17.9 ± 0.4	32
BEDB/2,3-DT		326 ± 25	20.0 ± 0.3	20
BEDB/3,4-DT		415 ± 6	20.3 ± 0.1	20
BEDB/4-C*m*P		169 ± 13	15.3 ± 0.3	36
BEDB/5-C*m*P		292 ± 17	15.3 ± 0.3	34
BEDB/4-C*o*P		389 ± 22	17.6 ± 0.2	21
BEDB/3,3′-DMB		400 ± 23	17.2 ± 0.1	41
BEDB/3,3′-DMoB		288 ± 7	14.8 ± 0.2	42

[a] Char residues were obtained from TGA at 850 °C in nitrogen (heating rate 10 °C/min).



Scheme 2.

crosslinks (MW_c), is an important factor governing the physical properties of cured resins. According to rubber elasticity theory, the cross-link density of a thermoset resin is proportional to the modulus in the rubbery plateau region [16,17]. Fig. 3 plots storage modulus and tan δ versus temperature for EBPA/4,4′-DDS, BEDB/4,4′-DDS, EBPA/4,4′-DDM, and BEDB/4,4′-DDM, and the results are listed in Table 3. The moduli of BEDB-based epoxy resins at $T_g + 40$ °C are higher than those of EBPAs. Therefore, the cross-link densities of the BEDB resins are higher than for the EBPA case, while T_g values of the EBPA resins are ~5–13 °C higher than those of BEDB resins. In each case, a second run gave data identical to the first, such that no further curing was needed.

To determine the critical stress intensity factor (K_{IC}), and critical strain energy release rate (G_{IC}), compact tension specimens were prepared and tested using the different epoxide starting materials. Plain-strain fracture toughness results are shown in Table 4. The formulations cured with 4,4′-DDS showed slightly higher values than those cured with 4,4′-DDM, and the values of cured BEDB resins represent an increase of 2–3 fold over the cured EBPA resins, regardless of curing agents.

3.6. *Structure/flame-retardancy relationship of BEDB resins*

In an attempt to identify the influence of curing agents on char formation and the flame-retardancy of the cured resins, BEDB was used to prepare epoxy formulations with *ortho*-, *meta*-, and *para*-aromatic diamines which have methyl groups, chlorides, and methoxy groups in different positions. Formulations and thermal properties of epoxy resins prepared with these different diamines are listed in Table 5. In general, resins cured with substituted diamines gave higher T_g values than those prepared using non-substituted *meta*-phenylene diamine (*m*-PDA). This is explained by the more restricted segmental motions of the cured resins possessing the methyl groups and chlorides in a densely cross-linked system. The resin cured with substituted benzidines, the cured resin with methyl substituent exhibited higher T_g values than that of the resin cured with methoxy group. These substituents might lower the rigidity of the material, and decrease the T_g of the benzidine-cured resins. It was reported that the bisphenol A (BPA) based resins cured with *meta*-aromatic diamines have greater thermal stability than the *para*-aromatic diamine cured resins [18]. However, a significant difference was not seen in the BEDB/DDS case. Initial degradation temperatures (T_{di}) of the resins are mid-300 °C range, except for the BEDB/4-C*m*P resin. Unlike other formulations which have a very short interval between $T_{d\ max}$ and T_{di} (ΔT_d), BEDB/4-C*m*P and BEDB/3,3′-DMoB exhibited values of 37 and 22 for ΔT_d, respectively. This high ΔT_d might be related to increasing the flame-retardancy of the resin while exhibiting the same total heat release (THR).

Thermal degradation of cured epoxies, by dehydration to give vinylene ethers, then cyclization and Claisen rearrangement contributes to char formation and thus flame-retardancy [19–23]. The results for char residue and flammability of all formulations are listed in Table 6. As expected from prior studies of BEDB-based polymers, the BEDB-based epoxy formulations showed significantly higher char yields (~30%) than the BPA-based systems (~16%). Resins cured with *meta*-DDS gave char yield about 3% higher than the *para*-DDS cured resin, and the char yields of the *meta*-aromatic diamine cured resins were at least 10% higher than those of the resins cured with *ortho*-aromatic diamine, regardless of substituted groups. These results can be attributed to the effect of the presence and position of substituents on the diamines, where cyclization and subsequent char are favored when an *ortho*-substituent is absent. The effect of cyclization by Claisen rearrangement (Scheme 2), and subsequent charring, has been discussed previously for bisphenol A epoxy resins [19–23]. Moreover, the char residues of the resins cured with substituted diamines were higher than that of non-substituted amine cured resin. The resin cured with the substituted biphenyls, having the greatest aromatic (least aliphatic) character exhibited the highest char yields, over 40%.

The resins cured with chlorinated diamines showed relatively low HRCs, also shown in Table 6. This reduction of HRC can be explained by gas phase combustion inhibition. BEDB/*ortho*-diaminophenylchloride systems exhibited higher HRC and THR than resins cured with chlorinated *meta*-aromatic diamines. The methyl substituted diaminobenzene, BEDB/2,3-diaminotoluene had the lowest value of HRC, but much higher THR than those of the resins cured with *meta*-diaminobenzenes. Again it appears that substituted *meta*-system provides an opportunity for higher flame-retardancy than the *ortho*-case, likely due to more facile intermolecular cyclization reactions during thermal decomposition. Resins cured with substituted biphenyls exhibited higher char residues and flame-retardancy than those cured with DDM, DDS, and *m*-PDA. Specifically, the resin cured with methoxy substituted biphenyl gave HRC and THR significantly lower than the resin cured with the *meta*-diaminophenylchloride.

4. Summary

A novel epoxy molecule, BEDB, was designed, synthesized, and implemented for the preparation of novel epoxy resins. These BEDB resins, though halogen-free, have HRC values that approach the halogenated versions, and that are significantly lower than conventional non-halogenated versions. Various epoxy formulations were prepared and tested. In case of the epoxy resins cured with aromatic amines, the BEDB-based resins had lower T_g than those based on BPA. However, due to the effective char formation of BEDB, the char residues of the BEDB resins (30–35%) were much

higher than those of the EBPA resins (12–16%) and ETBBA resins (23–24%), and the HRC of the EBHDB resins was lower than those of the EBPA resins. When the mixed amine with the same mole fraction of 4,4′-DDS and 4,4′-DDM was used as curing agent, the cured resin based on BEDB exhibited lower HRC than those cured with a single amine. The brominated epoxy materials gave moderately lower HRC values relative to the BEDB materials. This rather small penalty in heat release associated with the absence of halogen bodes well for the future use of BEDB and related molecules in materials for which halogenation is undesirable, and as a component of solutions to the flame retardant dilemma. In addition, the adhesive strength and fracture toughness of BEDB-based resins were significantly higher than those of BPA-based resins. It appears that utilization of the BEDB epoxide can greatly improve flame resistance, as well as enhance the fracture toughness and adhesion of its cured resins.

Acknowledgements

The authors acknowledge the financial support of the Federal Aviation Administration, and the member companies and organizations of the Center for UMass-Industry Research on Polymers that support anti-flammable polymer research, including Boeing, Boltaron Performance Products, Borealis, Hickory Springs, Multina, the National Institute of Standards and Technology, SABIC, Sekisui, Solvay Advanced Polymers, and the US Army.

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