

Dissecondary Amine Synthesis and Its Reaction Kinetics with Epoxy Prepolymers

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ABSTRACT: 3,3'-Diaminodiphenyl sulfone (3,3'-DDS) was reacted with acetaldehyde in the presence of sodium triacetoxo borohydride via reductive amination to yield a 3,3'-DDS based secondary diamine, *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone. Near IR analysis indicated that the 5060 cm^{-1} peak for primary amine ($-\text{NH}_2$) in 3,3'-DDS was absent in the reaction product spectrum. The $-\text{NH}_2$ proton peak at δ 5.66 ppm shifted to δ 6.16 ppm in the product. Methyl and methylene protons of $\text{CH}_3-\text{CH}_2-\text{NH}-\text{Ph}-$ group were observed at δ 3.01 and 1.12 ppm, respectively, in the product. The carbon NMR spectrum of the reaction product showed new peaks at δ 37.46 and 14.47 ppm that further confirmed secondary amine formation. The liquid chromatography coupled mass spectra peaks at 248–250 for 3,3'-DDS and 304 for the reaction product further supported the formation of *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone. A blend of *N,N'*-diethyl-3,3'-

diaminodiphenyl sulfone with diglycidyl ether of bisphenol-A (DGEBA) epoxy prepolymer started reacting at about 110–125°C surpassing an energy barrier of ~ 66 kJ/mol as determined via differential scanning calorimetry analysis. Reaction kinetics were characterized via near IR spectroscopy specific to the reaction between secondary amine and DGEBA epoxy prepolymer. The results confirmed $>97\%$ conversion at a cure protocol of 5 h at 80°C, 5 h at 100°C, 11 h at 125°C, and 6 h at 185°C. *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone-DGEBA thermoplastics displayed tensile and flexural moduli of 3.08 and 2.86 GPa, respectively, and glass transition temperature (T_g) of 120.77°C. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: secondary amine; synthesis; epoxy; DSC; near IR

INTRODUCTION

Multifunctional amines and their derivatives have wide applications such as corrosion inhibitors, antioxidants, stabilizers for cellulose nitrate explosives, protectants against damage from gamma radiation, developers in photography, flotation agents in mining, anti-cling and waterproofing agents for textiles, catalyst and intermediate in organic synthesis, and building blocks in polymers.¹ Because of their varied applications, synthesis of desired amines by an appropriate method is a topic of great research interest. Diaminodiphenylsulfone (DDS) is one of the aromatic amines widely used as a crosslinker in epoxy thermosets for aerospace applications. During cure, the primary amine reacts with an epoxy moiety to form a secondary amine that further reacts with an additional epoxy group to yield a tertiary amine. Often attributed to the tetrafunctionality, DDS produces

mostly brittle, high modulus, high glass transition temperature (T_g) thermosets when cured with low molecular weight, difunctional epoxy oligomers. Under varying cure conditions, different degrees of epoxy conversion result in dissimilar glassy polymeric properties even at the same reactant ratio using a single multifunctional amine. Difference in energy barrier between epoxy-primary amine and epoxy-secondary amine reactions is 10–15 kJ/mol.^{2,3} It is, therefore, very difficult to control an epoxy-amine reaction to synthesize a linear DDS-epoxy polymer as the secondary amine that is formed immediately reacts with the epoxy oligomer. An analogous secondary diamine like *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone is expected to provide additional material design variability and model compounds for structure-property relationship research from molecular to macroscopic material properties. For instance, a diglycidyl ether of bisphenol-A (DGEBA)-based epoxy prepolymer cured with 4,4'-diaminodiphenyl methane has been reported to provide fracture toughness of about 0.75 $\text{MPa m}^{1/2}$.⁴ Linear epoxy thermoplastics synthesized from DGEBA-based epoxy prepolymer and 4,4'-methylene-bis-(*N*-sec-butylaniline) possesses fracture toughness of 3.33 $\text{MPa m}^{1/2}$.⁵ A DGEBA-based epoxy resin and DDS-based epoxy thermoset has fracture toughness 0.51 $\text{MPa m}^{1/2}$.⁶ Bisphenol-A (BPA) has

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been reported as a potential chain extender in DGEBA-based bifunctional epoxy prepolymer and 1,1,1-tris(4-hydroxyphenyl) ethane thermoset system to reduce and vary crosslink density.⁷ We expect the secondary amine of 3,3'-diaminodiphenyl sulfone (3,3'-DDS), i.e., *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone, to function as a potential monomer in the preparation of epoxy-amine thermoplastics and as a chain extender in epoxy-DDS thermosets to controllably reduce crosslink density.

Among the techniques reported for synthesizing secondary amines from primary amines is reductive amination of aldehydes or ketones.^{8–16} This method uses any of a series of reducing agents such as zinc acetic acid,⁸ zinc borohydride-zinc chloride,⁹ zinc borohydride *N*-methyl piperidine,¹⁰ silica gel- $ZnBH_4$,¹¹ sodium borohydride-magnesium perchlorate,¹² dibutyltin chloride hydride,¹³ borane-pyridine,¹⁴ $Ti(OiPr)_4/NaBH_4$,¹⁵ $NaBH_3CN$,¹⁶ *N*-methyl pyrrolidine zinc borohydride,¹⁷ $Cu(PPh_3)_2BH_4$,¹⁸ $Zr[(BH_4)_2(Cl)_2(DABCO)_2]$,¹⁹ and sodium triacetoxy borohydride.²⁰ Pt/C catalyst has also been used for synthesizing secondary amines from primary amines.²¹ In this study, we report the synthesis of the secondary amine, *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone of 3,3'-DDS using sodium triacetoxy borohydride [$NaBH(OAc)_3$] as a reducing agent. $NaBH(OAc)_3$ was chosen because of its remarkable selectivity and mild reducing power that results from the steric and electron withdrawing effects of the three acetoxy groups stabilizing the boron-hydrogen bond.^{20,22} In addition, *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone was reacted with DGEBA based epoxy prepolymer to confirm reaction potential and conditions from the synthesized secondary amine as a building block monomer for increased linearity. The reaction temperatures were chosen using differential scanning calorimetry (DSC) monitored material blends. Singularly, a DSC-based kinetic study of the reaction between an epoxy oligomer and a dissecondary diamine provides only the overall extent of chemical conversion without differentiating and characterizing the individual component reactions.^{23,24} Similarly, studying epoxy cure kinetics via Fourier transform infrared (FTIR) spectroscopy in the mid-infrared range (600–4000 cm^{-1}) is quite complicated due to the abundance of overlapping bands for epoxy-amine systems. On the other hand, several researchers have proved that near infrared (NIR) characterization of epoxy-amine systems is characterized by distinct bands for epoxide, amine, phenyl, and hydroxyl groups.²⁵ Using Lambert-Beer's law, the epoxy and amine concentrations can be accurately determined from their respective band areas.²⁵ DSC and Near IR in combination, confirmed the extent and mechanism of reactions between DGEBA-based epoxy prepolymer and *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone.

EXPERIMENTAL

Materials

3,3'-DDS (98%) was purchased from TCI, America (Portland, OR). $NaBH(OAc)_3$ and dimethylsulfoxide- d_6 were procured from Acros Organics, NJ. Tetrahydrofuran, anhydrous magnesium sulfate, and diethyl ether were purchased from Fisher Scientific, Fair Lawn, NJ. DGEBA-based epoxy prepolymer (Epon® 828) was obtained from Hexion Specialty Chemicals, (Momentive), Stafford, TX. Epon 828 is a liquid prepolymer with an epoxy equivalent weight (EEW) of 185–192 g/eq, viscosity 110–150 Poise at 25°C, and density 1.16 g/mL at 25°C. Before use, the EEW of Epon 828 was determined via ASTM D1652-97 to be 188.72, and its degree of polymerization was calculated from the EEW value to be 0.129. All chemicals were used as received.

Synthesis of *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone

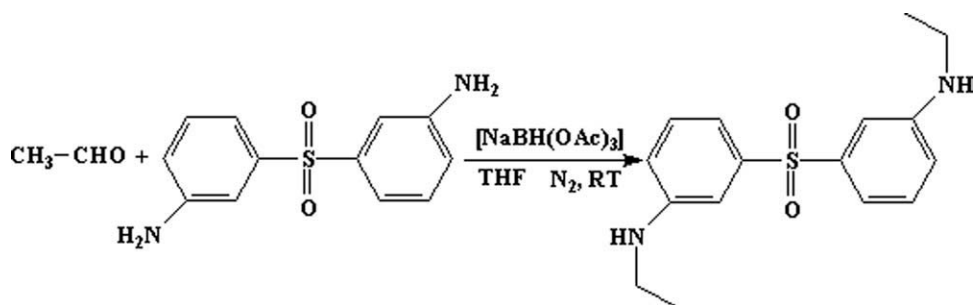
A total of 40 g (0.1579 mol) 3,3'-DDS was dissolved in 700 mL tetrahydrofuran and 15.99 g (0.3631 mol) acetaldehyde was added to it. Immediately, 96.59 g (0.4420 mol) $NaBH(OAc)_3$ was added to the reaction flask under stirring and the reaction was continued for 5 h at ambient. The reactor contents were transferred to a beaker containing aqueous $NaHCO_3$ solution and extracted with ether. The organic layer was washed twice with water. The solvent was removed under reduced pressure without drying the organic phase. The chemical structures and reaction scheme are displayed in Scheme 1.

Fourier transform infrared spectroscopy (Mid FTIR)

FTIR spectra were obtained with a Digilab FTIR spectrometer over a frequency range of 600–4000 cm^{-1} . The samples were analyzed as thin films over sodium chloride disks. The instrument was operated at 32 scans with a resolution of 4 cm^{-1} .

Near IR spectroscopy

Near IR spectra were obtained by Antaris II, FT-NIR Analyzer from Thermo Scientific. Absorption spectra were recorded in the region of 4000–8000 cm^{-1} while operating at 32 scans with a resolution of 4 cm^{-1} using an integrating sphere (via OMNIC version 7.3 software). The sample thickness was maintained constant at 0.15 mm by placing a microscope cover glass between two micro slides. Conversion of epoxy and secondary amine was studied via near IR spectroscopic technique following a cure protocol of 80°C for 5 h, 100°C for 5 h, 125°C for 11 h, 150°C for 3 h, and 185°C for 6 h.



Scheme 1 Synthesis of *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone from 3,3'-DDS.

Nuclear magnetic resonance (NMR) spectroscopy

Proton and carbon spectra were obtained using a Varian Mercury NMR spectrometer operating at a frequency of 300.13 and 75.5 MHz for proton and carbon NMR spectroscopy, respectively. Typical ^1H NMR acquisition parameters were as follows: recycle delay of 1 s, 7.1 μs pulse width corresponding to a 45 degree flip angle, and acquisition time of 2 s. ^{13}C NMR acquisition parameters were: 1 s recycle delay, 7.8 μs pulse width corresponding to 45 degree flip angle, and acquisition time of 1.8 s. All chemical shifts (indicated as δ ppm) were referenced either automatically by the software (VNMR 6.1C) or manually using the resonance frequency of the deuterated solvent (DMSO- d_6).

^1H NMR of 3,3'-DDS (in DMSO- d_6) δ ppm: 7.51 (impurity), 7.19 (1H, t, $J = 7.72$ Hz, meta to both NH_2 and sulfone group), 7.06 (1H, s, ortho to both sulfone and NH_2 group), 6.96 (1H, d, $J = 7.72$ Hz, para to NH_2 group), 6.77 (1H, d, $J = 7.85$ Hz, para to sulfone group), 6.63 (impurity), 6.12 (impurity), 5.66 (2H, s, NH_2), 3.46 (impurity), 2.66 (impurity), and 2.48 (DMSO- d_6).

^1H NMR of *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone (in DMSO- d_6) δ ppm: 7.51 (impurity), 7.24 (1H, t, $J = 8.13$ Hz, meta to both NH and sulfone group), 7.01 (2H, m, $J = 7.63$ Hz, both the ortho positional protons to sulfone group), 6.73 (1H, d, $J = 7.84$ Hz, para to sulfone group), 6.61 (impurity), 6.16 (1H, t, $J = 5.11$ Hz, NH), 5.65 (NH_2 , as impurity from trace amount of unreacted primary amine), 3.58 (THF), 3.42 (impurity), 3.28 (q, diethyl ether), 3.01 (2H, m, $J = 6.99$ Hz, $\text{CH}_3\text{-CH}_2\text{-NH-Ph-}$), 2.48 (DMSO), 1.71 (THF), 1.12 (3H, t, $J = 6.66$ Hz, $\text{CH}_3\text{-CH}_2\text{-NH-Ph-}$), and 1.01 (t, diethyl ether).

^{13}C NMR of 3,3'-DDS (in DMSO- d_6) δ ppm: 150.10 (carbon in phenyl attached to H_2N), 142.54 (carbon attached to sulfone group), 130.45 (carbon meta to both sulfone and NH_2 groups), 118.61 (carbon para to sulfone group), 114.33 (carbon para to NH_2), 111.81 (ortho to both NH_2 and sulfone groups), and 39.93 (DMSO- d_6).

^{13}C NMR of *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone (in DMSO- d_6) δ ppm: 149.91 (carbon in phe-

nyl attached to NH-), 147.95 (impurity), 142.5 (carbon attached to sulfone group), 130.35 (carbon meta to both sulfone and NH- groups), 116.11 (carbon para to sulfone group), 113.85 (carbon ortho to both NH- and sulfone groups), 110.07 (para to NH-), 44.17 (impurity), 39.93 (DMSO- d_6), 37.66 ($\text{CH}_3\text{-CH}_2\text{-NH-Ph-}$), 20.32 (impurity), 14.47 ($\text{CH}_3\text{-CH}_2\text{-NH-Ph-}$), and 12.44 (impurity).

Liquid chromatography coupled mass spectroscopy

The product molar mass was determined using a Varian 500-MS. The liquid chromatography coupled mass spectra (LC-MS) system consisted of an atmospheric pressure chemical ionization (APCI) attachment and a Pursuit XRs Ultra C18 column that was eluted with a 50 : 50 mixture of acetonitrile and tetrahydrofuran at a flow rate of 200 mL/min and 1800 psi pressure.

Cure schedule of *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone with epoxy prepolymer via DSC analysis

Stoichiometric proportions of Epon 828, a DGEBA-based epoxy prepolymer and secondary amine were blended together at 80°C in a scintillation vial under mechanical stirring. The hot mixture was cooled to ambient. DSC analysis was conducted on a DSC Q 2000 from TA Instruments and data were processed via Universal Analysis 2000 software. Reaction temperature range and activation energy were determined for the epoxy-amine reaction from a stoichiometric blend of *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone and DGEBA-based epoxy prepolymer. Approximately 7 mg of the blend was sealed in an aluminum pan and DSC thermal scanning was conducted each at 1.0, 1.5, 2.0, and 2.5°C/min heating rates under nitrogen atmosphere with a temperature range of ambient to 285°C. Reaction samples from each heating rate were subjected to a second cycle DSC analysis to quantify the resulting T_g . Each second cycle DSC scan was performed at 10°C/min heating rate with a temperature sweep of 35–250°C under nitrogen environment. Experiments were

conducted in duplicate and average results have been reported. Kinetic parameters, activation energy of epoxy-amine reaction of DGEBA-based epoxy prepolymer and *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone, were calculated without any assumption on conversion-dependency. In this respect, Kissinger's equation^{26,27} can be used as

$$-\ln\left(\frac{\beta}{T_p^2}\right) = -\ln\left(\frac{AR}{E_K}\right) + \frac{E_K}{RT_p} \quad (1)$$

where β is heating rate, A is pre-exponential factor, R is universal gas constant, E_K is activation energy of the reaction, and T_p is peak temperature at which the reaction rate is maximum. The plot of $-\ln(\beta/T_p^2)$ versus $1/T_p$ generates a straight line from the slope of which activation energy, E_K and from the intercept pre-exponential factor, A can be calculated. Another model-free method, Ozawa-Flynn-Wall²⁸ based on Doyle's approximation was used to evaluate activation energy as

$$\log\beta = \log\left\{\frac{AE_0}{g(\alpha)R}\right\} - c - l\frac{E_0}{RT} \quad (2)$$

where E_0 is activation energy of the reaction, $g(\alpha)$ is conversion dependent function, c and l are couple tabulated coefficients. Commonly, $c = 2.313$ and $l = 0.4567$ if $E_0/RT = 28$ – 50 while $c = 2.000$ and $l = 0.4667$ are used if $E_0/RT = 18$ – 30 . In most of the aromatic diamine and epoxy prepolymer reactions, $E_0/RT = 13$ – 20 , hence, c and l values are different from frequently used ones, i.e., $c = 1.600$ and $l = 0.4880$. For aromatic diamine and DGEBA epoxy reaction, the Ozawa-Flynn-Wall equation can be rewritten as

$$\log\beta = \log\left\{\frac{AE_0}{g(\alpha)R}\right\} - 1.600 - 0.4880\frac{E_0}{RT_p} \quad (3)$$

A plot of $\log\beta$ versus $1/T_p$ yields a straight line. Activation energy (E_0) of the reaction can be determined from the resulting slope. The dependency of activation energy on conversion associated to the reaction of DGEBA-based epoxy prepolymer and *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone was analyzed with the isoconversional method. To evaluate activation energy at each degree of conversion, Friedmann equation²⁹ was used as

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\{f(\alpha)A\} - \frac{E_a}{RT} \quad (4)$$

where E_a is activation energy, $f(\alpha)$ is unknown reaction model. E_a can be calculated from the slope of the straight line from the plot of $\ln(d\alpha/dt)$ versus $1/T$.

Background for determination of concentrations of epoxy and amines

Lambert-Beer's law was used to determine epoxy and amine concentrations from near IR spectra. Lambert-Beer's law is normally expressed as

$$A = \log_{10}\left(\frac{I_0}{I_t}\right) = \epsilon bc \quad (5)$$

where A is the absorbance, I_0 is the intensity of incident radiation, I_t is the intensity of transmitted radiation, ϵ is molar extinction coefficient or molar absorptivity ($\text{L mol}^{-1} \text{cm}^{-1}$), b is the path length of radiation passed through the sample, and c is molar concentration (mol L^{-1}). The molar extinction coefficient is a unique property of each material at a particular frequency and is widely used for quantitative determination.

Measuring the epoxy and amine volume concentrations in an epoxy-amine mixture is a challenging task as some epoxy prepolymers are liquids and amines are either solid or liquid prior to cure. By representing the concentration in terms of mol kg^{-1} , eq. (5) can be simplified (for standard sample thickness or constant path length)²⁴ as

$$A = \alpha C \quad (6)$$

where $\alpha = \epsilon b$, where α is referred to as molar absorptivity (kg mol^{-1}) and C is molar concentration (mol kg^{-1}).

Sample preparation and testing of physical properties of *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone-based epoxy thermoplastics

A calculated amount (stoichiometric) of degassed epoxy monomer, Epon 828, was added to *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone in a 250 mL beaker. The beaker was placed in an oil bath at 100°C and the blend was stirred mechanically to solubilize *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone in epoxy resin. Then, the hot solution was degassed at 100°C for ~ 3 min and cast into preheated (125°C) silicon molds to yield objects with the appropriate dimensions for flexural, tensile, and DMA. The cast samples were subsequently heated for 125°C for 8 h, 150°C for 3 h, and 185°C for 10 h.

Dynamic mechanical analysis was conducted on a DMA Q800 from TA Instruments, in tension mode using free films. The free films (~ 1 mm thick, ~ 5 mm wide) were analyzed at a frequency of 1.0 Hz at a heating rate of $2^\circ\text{C}/\text{min}$ with the DMA set for strain control. DMA data reported are the average of four specimens. The films were monitored for storage modulus and glass transition temperature (T_g) from the $\tan \delta$ maxima.

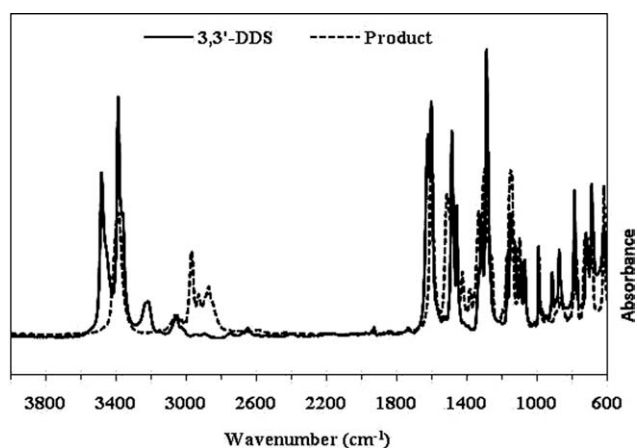


Figure 1 Mid IR spectra of 3,3'-DDS and its reaction product with acetaldehyde.

Tensile properties were measured on a MTS Insight instrument equipped with a load cell of 10 kN (2248.09 lbf). The test was conducted according to ASTM D 638-03. Dumbbell-shaped tensile specimens were prepared with narrow section width ~ 12.5 mm and thickness ~ 3.08 mm. The tests were operated at a crosshead speed of 1.27 mm/min with the aid of an extensometer. Young's modulus was calculated from the slope of the initial linear portion of the stress-strain curve. Average data of five specimens has been reported.

Flexural tests were conducted on a MTS Insight with a 10 kN (2248.09 lbf) load cell and cross-head speed of 5 mm/min. Samples with a thickness of ~ 3.0 mm, width of ~ 13.0 mm, and support span of 16 times the sample thickness were tested according to ASTM D 790. Flexural modulus was calculated from the slope of the initial linear portion of the stress-strain curve. Average result of five specimens has been reported.

The sample T_g was determined on a DSC Q 2000 from TA Instruments and data was processed via Universal Analysis 2000 software. The instrument was operated at a heating rate of 10°C/min in N_2 environment.

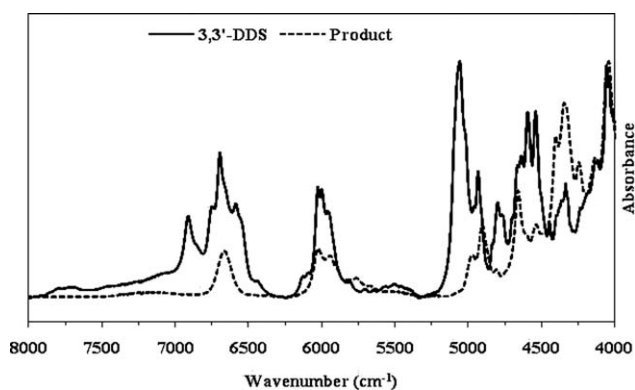


Figure 2 Near IR spectra of 3,3'-DDS and its reaction product with acetaldehyde.

RESULTS AND DISCUSSION

Synthesis of *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone

The Mid IR and near IR spectra of 3,3'-DDS and the product from reaction with acetaldehyde are displayed in Figures 1 and 2, respectively. Mid IR and near IR band assignments of 3,3'-DDS and the reaction product with acetaldehyde are listed in Tables I and II, respectively. Characteristic mid IR bands for 3,3'-DDS are seen at 3485–3227 cm^{-1} for $-NH_2$ stretching, 3066–3053 cm^{-1} for aromatic C–H stretching, 1621–1602 cm^{-1} for $-NH_2$ bending and aromatic C=C stretching, 1485–1456 cm^{-1} for aromatic C=C stretching, 1321 cm^{-1} for C–N stretching, and 1286 and 1149 cm^{-1} for S=O stretching.³⁰ In the NIR spectra of 3,3'-DDS, bands at 6909–6591 cm^{-1} for overtone of $-NH_2$, 6077–5957 cm^{-1} for overtone of aromatic C–H, 5061–4769 cm^{-1} for combination mode of stretching and bending of $-NH_2$, 4665–4641 cm^{-1} combination of aromatic C=C and C–H, and 4598–4535 cm^{-1} combination of C–N stretching and bending of $-NH_2$ were observed.²⁴ When comparing spectral traces in Figure 1, the results are clear that the peaks at 3485–3227 cm^{-1} in 3,3'-DDS merged to a single peak at 3392 cm^{-1} and new bands at 2972–2876 cm^{-1} and 1425–1381 cm^{-1} were

TABLE I
Mid IR and Near IR Band Assignments of 3,3'-DDS

Mid IR		Near IR	
3485-3227	NH_2 (stretching)	6909-6591	NH_2 (overtone)
3066-3053	Aromatic C–H (stretching)	6028-5957	Aromatic C–H (overtone)
1621-1602	Aromatic C=C stretching and NH_2 bending	5061-4769	Combination of NH_2 stretching and bending
1485-1456	Aromatic C=C stretching	4665-4641	Combination of aromatic C–H and C=C stretching
1321	C–N stretching	4598-4535	Combination of C–N and NH_2 stretching
1286	S=O stretching	4404-4000	Combination of aromatic C–H stretching and bending
1168	Aromatic C–H bending		
1149	S=O stretching		
1089-600	Aromatic C–H bending		

TABLE II
Mid IR and Near IR Band Assignments of Reaction Product of Secondary Amine 3,3'-DDS with Acetaldehyde

Mid IR		Near IR	
3392	NH stretching	6670	NH (overtone)
3069	Aromatic C—H stretching	6026-5764	C—H overtone (aromatic, aliphatic)
2972-2876	Aliphatic C—H stretching	4974-4907	Combination of N—H stretching and bending
1602-1512	NH bending and aromatic C=C stretching	4662	Combination of aromatic C—H stretching and C=C stretching
1477	Aromatic C=C stretching	4601-4541	Combination of NH stretching and C—N stretching
1452	Aromatic C=C stretching, and CH ₂ , CH ₃ bending	4404-4000	Combination of C—H stretching and bending
1425-1381	CH ₂ and CH ₃ bending		
1331	C—N stretching		
1295	S=O stretching		
1169	Aromatic C—H bending		
1149	S=O stretching		
1096-600	Aromatic and aliphatic C—H bending		

observed and attributed to the stretching and bending, respectively, by $-\text{CH}_2-$ and $-\text{CH}_3$ groups indicating the formation of the *N*-alkylated amine product. Further observations from Figure 2 reveal multiple bands at $6909\text{--}6591\text{ cm}^{-1}$ in 3,3'-DDS converged to a single band at 6670 cm^{-1} in the reaction product. Additionally, bands at 5060 , 4598 , and 4544 cm^{-1} for primary amine were absent in the reaction product. The absence of primary amine bands at 5060 , 4598 , and 4544 cm^{-1} and the changed peak patterns at $6583\text{--}6755\text{ cm}^{-1}$ are further validation for the formation of secondary amine of 3,3'-DDS, *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone.

The ^1H NMR spectra of acetaldehyde, 3,3'-DDS and the reaction products are shown in Figure 3. Proton peaks at δ 2.10 and 9.64 ppm for $-\text{CH}_3$ and $-\text{CHO}$, respectively, of acetaldehyde were absent in the reaction product, whereas new peaks at δ 1.13 and 3.02 ppm were observed for $-\text{CH}_3\text{--CH}_2\text{--NH-}$ and $-\text{CH}_3\text{--CH}_2\text{--NH-}$, respectively. The Ph--NH_2 proton peak of 3,3'-DDS observed at δ 5.66 ppm was found to be shifted to δ 6.16 ppm (Ph--NH-) in the product spectra confirmed the formation of the secondary amine. Via integration, the ratio of phenyl ring proton to $-\text{NH-}$ proton was determined to be 0.9331, indicating 93.31% conversion. In the ^{13}C

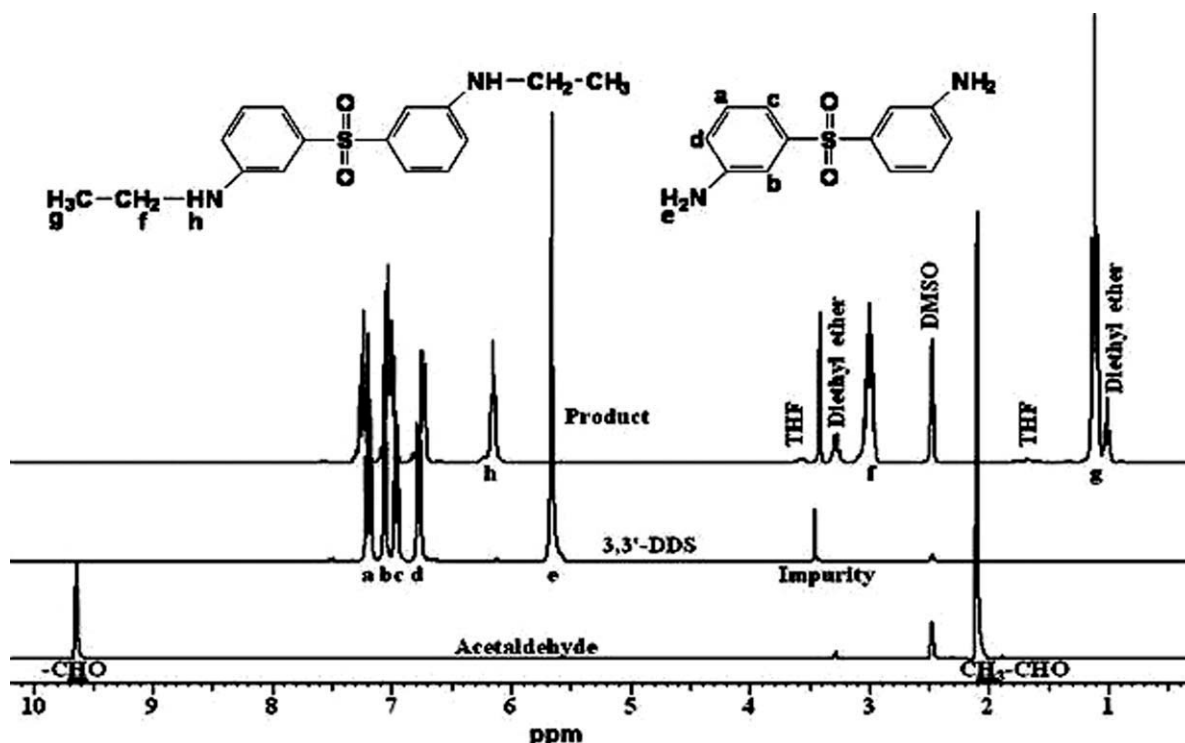


Figure 3 ^1H NMR spectra of 3,3'-DDS and its reaction product with acetaldehyde.

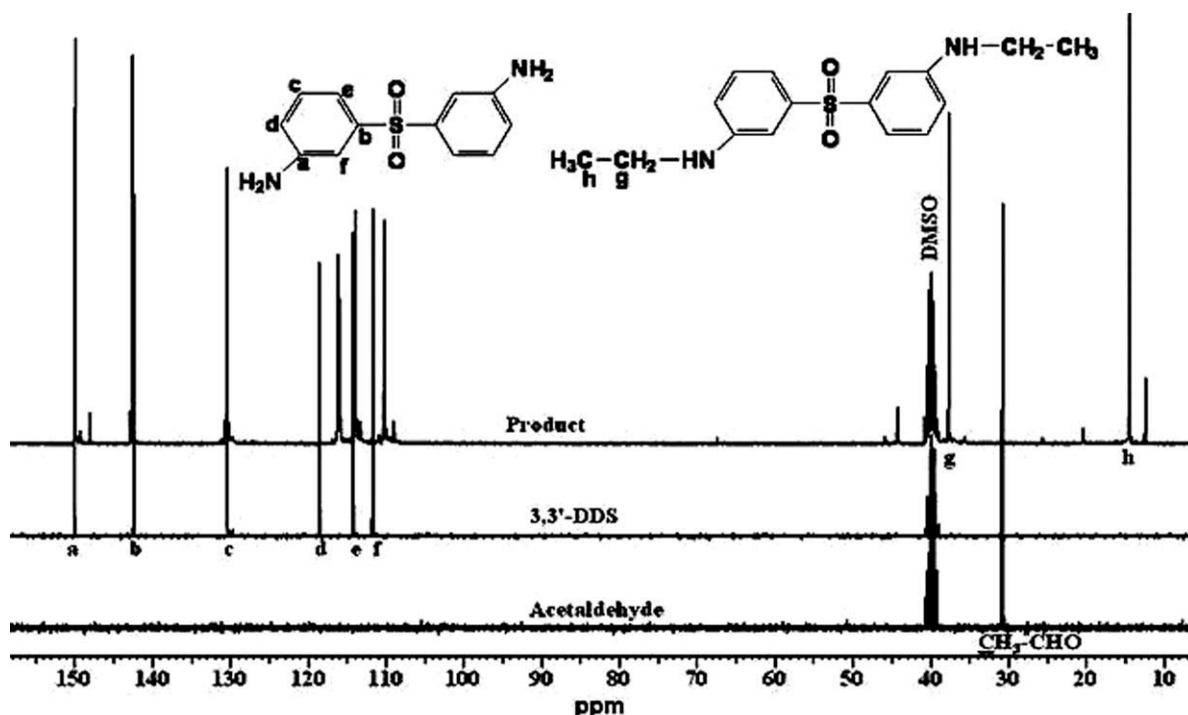


Figure 4 ^{13}C NMR spectra of 3,3'-DDS and its reaction product with acetaldehyde.

NMR spectrum of the product (Fig. 4), signals observed at δ 37.66 and 14.47 ppm are attributed to $-\text{CH}_3-\text{CH}_2-\text{NH}-$ and $-\text{CH}_3-\text{CH}_2-\text{NH}-$ and similarly confirmed secondary amine formation.

The LC-MS spectra of 3,3'-DDS and the resulting reaction product, the secondary diamine, are displayed in Figure 5. The peak at m/z ($M + 2$) of 250 for 3,3'-DDS and 306 ($M + 2$) for the reaction product arise due to bi-protonation and confirmed the formation of the 3,3'-DDS-based secondary diamine. The peaks observed at m/z 608 and 609 in the reaction product spectrum are attributed to the presence of dimer and its protonated form.

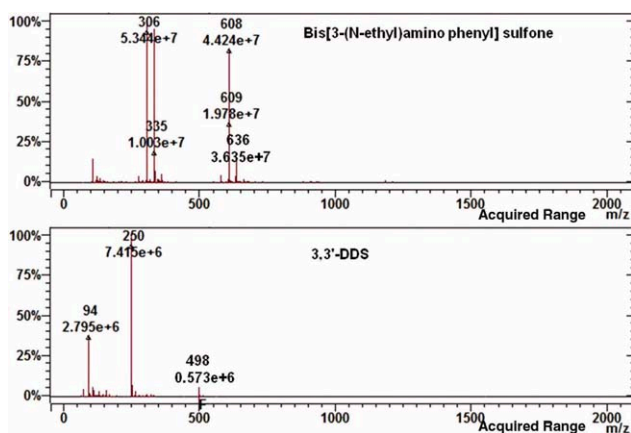


Figure 5 LC-MS spectra of 3,3'-DDS and its reaction product with acetaldehyde. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Curing of *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone with epoxy prepolymer

Dynamic DSC thermal characterization was used to quantify the kinetics for reaction of a stoichiometric blend of DGEBA-based epoxy prepolymer and *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone at four different heating rates (Fig. 6). A single exothermic peak resulted from reactions at each of the four heating rates. DSC analysis quantified, the heat of reaction, (ΔH), initial curing temperature (T_i), peak exothermic temperature (T_p), and reaction end-temperature (T_f) and T_g as determined from the second cycle and were summarized in Table III. It was observed that T_i , T_p , and T_f shift to higher temperatures with

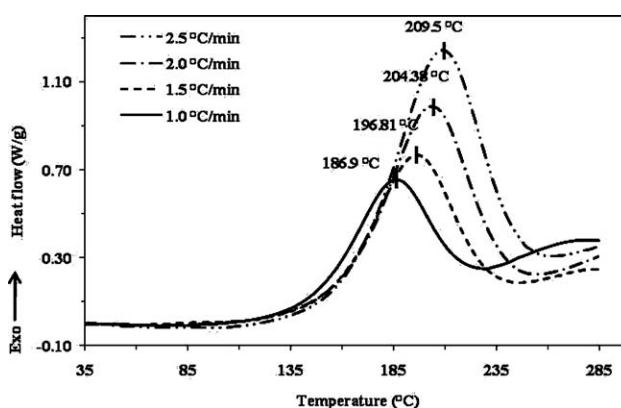


Figure 6 Dynamic DSC scans at different heating rates for DGEBA-based epoxy resin and *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone.

TABLE III
Detail of Dynamic DSC Scan of DGEBA-Based Epoxy Resin and *N,N'*-Diethyl-3,3'-diaminodiphenyl Sulfone

Heating rate (°C/min)	T_i (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)	Time (min)	T_g (°C)
1.0	111.45 ± 1.34	186.36 ± 0.32	224.59 ± 2.70	166.25 ± 8.41	109.01 ± 1.79	103.76 ± 0.19
1.5	115.75 ± 1.34	196.08 ± 1.03	240.66 ± 7.34	168.95 ± 0.64	85.04 ± 8.29	101.57 ± 0.49
2.0	120.00 ± 0.71	203.72 ± 0.93	250.62 ± 7.48	163.40 ± 2.97	66.83 ± 6.24	98.78 ± 0.41
2.5	124.40 ± 1.70	208.87 ± 0.89	260.05 ± 4.73	169.55 ± 3.75	51.57 ± 1.22	97.99 ± 1.37

Glass transition temperature was determined from second cycle at 10°C/min heating rate.

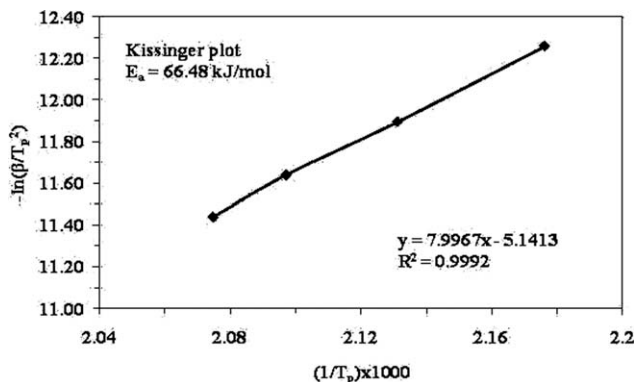


Figure 7 Plot for determination of activation energy using Kissinger equation.

increasing heating rate, whereas ΔH values shifted only 5%. The average T_g of cured samples of all four heating rates is about $100.53 \pm 2.65^\circ\text{C}$. Worth noting, the resulting T_g was consistently lower for samples cured at higher heating rate and higher for sample cured at lower heating rates (amount of time for slowest versus fastest heating systems). These results are attributed to the comparatively longer curing times that correspond to lower heating rates. Plot of $-\ln(\beta/T_p^2)$ versus $1/T$ using Kissinger equation yields a straight line (shown in Fig. 7) with a slope of 7.9967 which corresponds to an activation energy (E_K) of 66.48 kJ/mol. In addition, $\log\beta$ versus $1/T$ plot (shown in Fig. 8) via Ozawa-Flynn-Wall method resulted in comparable activation energy (E_O) of 66.13 kJ/mol. The activation energies for the epoxy-

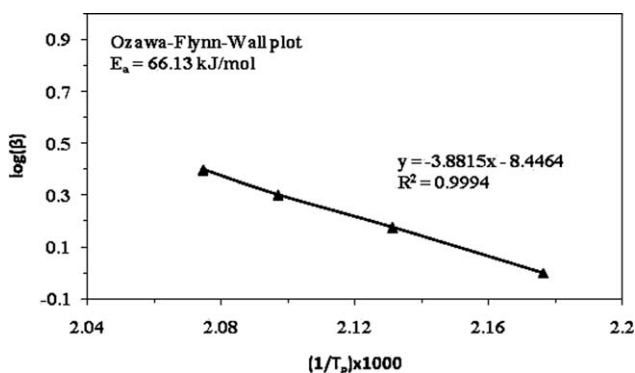


Figure 8 Plot for determination of activation energy using Ozawa-Flynn-Wall equation.

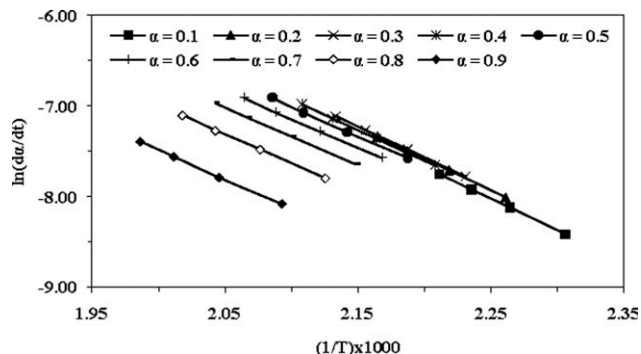


Figure 9 Isoconversional plot (Friedmann equation) at various conversions for DGEBA/*N,N'*-diethyl-3,3'-diaminodiphenyl sulfone.

secondary amine reaction were similar by both calculated methods. Hill et al.³¹ reported activation energy of 69.0 kJ/mol for epoxy-amine reaction from aromatic diamine (DDS) and DGEBA epoxy prepolymer. The change in calculated activation energy across the range of conversion (α from 0.1 to 0.9) for the epoxy-secondary diamine was evaluated by isoconversion analysis via Friedmann method. Friedmann plot, $\ln(d\alpha/dt)$ versus $1/T$ is shown in Figure 9. Activation energy as a function of conversions is displayed in Figure 10. The results clarify that the activation energy for curing decreases initially up to $\sim 60\%$ conversion and then increases for higher degrees of conversion. We attribute the activation energy trend to an autocatalytic effect driven by tertiary amine formation. Additionally, the systems

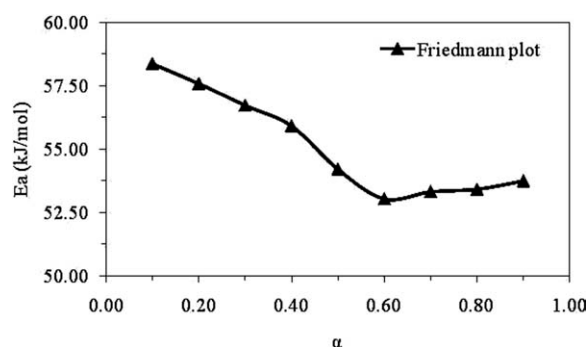


Figure 10 Dependency of activation energy on conversion during reaction of DGEBA epoxy resin and *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone.

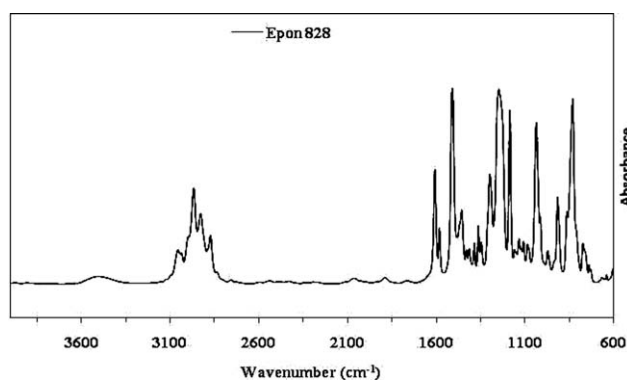


Figure 11 Mid IR spectrum of Epon 828.

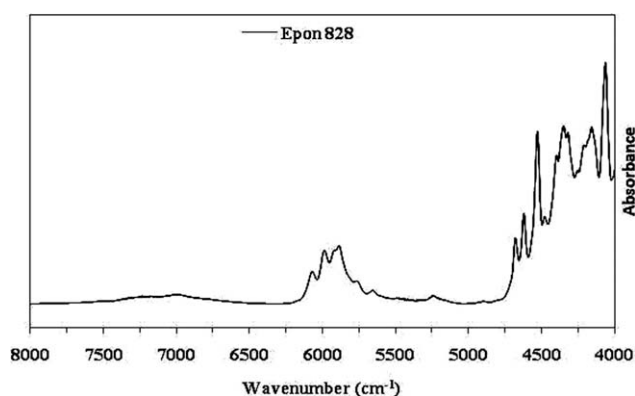


Figure 12 Near IR spectrum of Epon 828.

increase in viscosity at higher degrees of conversion and diffusion limited reactions are attributed to the late increase in activation energy.

Mid IR and near IR spectrum of Epon 828, a DGEBA-based epoxy prepolymer are shown in Figures 11 and 12, respectively, and the band assignments are listed in Table IV. The near IR spectra of Epon 828 confirms a weak absorption at 7001 cm^{-1} due to first overtone of —OH stretching ($\approx 2 \times 3507$).²⁴ The bands detected at 6071 and 4530 cm^{-1} are attributed to the first overtone of terminal $\text{—CH}_2\text{—}$ stretching ($\approx 2 \times 3056$) in combination with the epoxy $\text{—CH}_2\text{—}$ stretching and the epoxy $\text{—CH}_2\text{—}$ deformation ($\approx 3056 + 1456\text{ cm}^{-1}$), respectively.^{24,32–34} The bands at $5989\text{—}5656\text{ cm}^{-1}$ are due to overtones of aromatic C—H ($\approx 2 \times 3037$) and aliphatic C—H ($\approx 2 \times 2968$, 2×2931 , 2×2874 , 2×2834) stretchings.^{24,32} The two spectral bands at 4681 and 4622 cm^{-1} arise from the combination of the aromatic

C—H and C=C stretching ($\approx 3037 + 1607$, $\approx 3037 + 1509$).^{24,34}

Knowing that the phenyl concentration was constant during the reactions, the phenyl band at 4622 cm^{-1} was used as the internal reference to normalize each spectrum and quantify the epoxy and amine concentrations independently and with improved accuracy using Lambert-Beer's law. The amine concentration for the reaction blend was determined using the —NH— band area at 6670 cm^{-1} following

$$A_a = \alpha_a c_a \quad (7)$$

where A_a is —NH— band area at 6670 cm^{-1} , c_a is —NH— concentration (mol kg^{-1}), and α_a is molar absorptivity of —NH— band at 6670 cm^{-1} (determined to be 1.459 kg mol^{-1} from the spectrum of secondary amine of 3,3'-DDS of sample thickness 0.15 mm). The epoxy concentration within the

TABLE IV
Mid IR and Near IR Band Assignment of Epon 828

Mid IR		Near IR	
3507	OH stretching	7001	OH (overtone)
3056, 3037	C—H stretching (aromatic and epoxy)	6071, 5989, 5887, 5761, 5656	C—H overtone (aromatic, epoxy, CH_2 and CH_3)
2968, 2931, 2874, 2834	C—H stretching (CH_2 and CH_3)	4681, 4622	Combination of C—H and C=C stretching
1607, 1581, 1509	Aromatic C=C stretching	4530, 4481	Combination of CH stretching and bending (epoxy)
1456	CH_2 , CH_3 bending and aromatic C=C stretching	4400–4000	Combination of C—H stretching and bending of aromatic, CH_2 and CH_3
1430	CH_2 and CH_3 bending		
1363, 1346	CH_2 bending (epoxy)		
1296	CH_2 bending		
1247	CH_2 bending (epoxy) and C—O stretching		
1184	Aromatic C—H bending		
1132, 1107	C—O stretching		
1085	Aromatic C—H bending		
1035	C—O stretching		
916	C—O stretching (epoxy)		
863–600	CH_2 , CH_3 and aromatic C—H bending		

TABLE V
Initial Concentrations (mol kg⁻¹) of Monomers as well as Functional Groups

Sample	3,3'-DDS	Epon 828	NH	Epoxy	Phenyl
<i>N,N'</i> -diethyl-3,3'-diaminodiphenyl sulfone	1.4745	–	2.9491	–	2.9491
Epon 828	–	1.4746	–	2.9492	3.2979

reaction blend was quantified using the epoxy band area at 4531 cm⁻¹ following

$$A_e = \alpha_e c_e \quad (8)$$

where A_e is epoxy band area at 4531 cm⁻¹, c_e is epoxy concentration (mol kg⁻¹), and α_e is molar absorptivity of the epoxy group at 4531 cm⁻¹ (determined to be 1.626 kg mol⁻¹ from the spectrum of Epon 828 of sample thickness 0.15 mm).

The initial molar concentrations (mol kg⁻¹) of the monomers as well as epoxy and amine groups are calculated and summarized in Table V. The near IR spectra obtained during epoxy-amine cure are displayed in Figure 13. The amine band at 6670 cm⁻¹ and epoxy band at 4531 cm⁻¹ consistently decreased in intensity until the amine and epoxy concentrations were below the detection limits indicating the detectable complete reaction between the amine and epoxy groups. Another supporting factor resulted from the steady increase in intensity of the –OH band at 7005 cm⁻¹ resulting from the secondary hydroxyl formed by the epoxy-amine reaction.

Epoxy-amine reaction of *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone and Epon 828 begins at ~ 110–125°C and exhibits a maximum rate of conversion at ~ 185°C as determined via DSC analysis. The reaction occurs at even lower temperatures, however, at slower rates. To confirm the epoxy secondary amine reaction progress at lower temperatures, another reaction was characterized from heating at 80–100°C. This same lower temperature product was further cured at higher temperatures (125–185°C) to answer whether vitrification limits reduce the maximum possible conversion. Epoxy and amine concentrations were estimated from the near IR spectra during cure (Fig. 14). The data point designated as time –1 h denotes the initial concentration before mixing. The epoxy group did not react with the secondary amine at 80–100°C during mixing and cure. When heated to 125°C, the epoxy group reacted with the secondary amine and resulted in 66.87% conversion in four hours. Extended reactions maintained at 125°C for an additional 7 h (11 h total) resulted in only 83.11% conversion (because of diffusion limited progress). Further curing at 150°C resulted in 89.79%

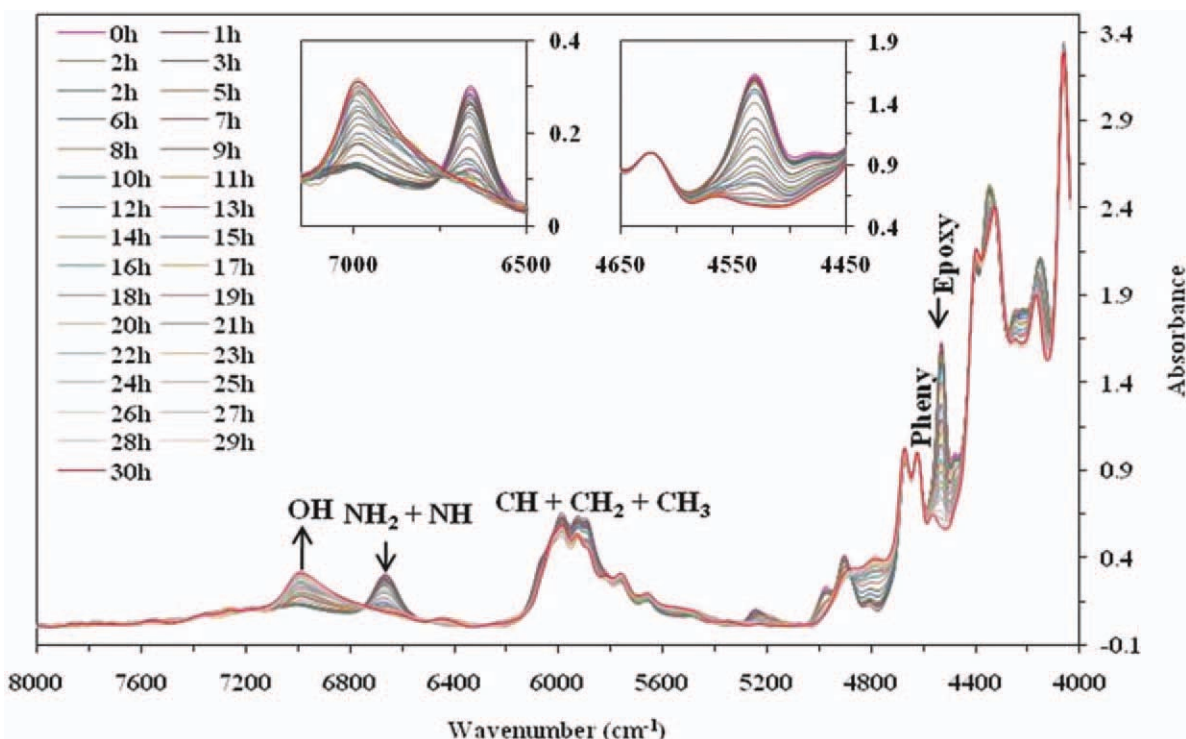


Figure 13 Near IR spectra during cure of Epon 828 with stoichiometric amounts of *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

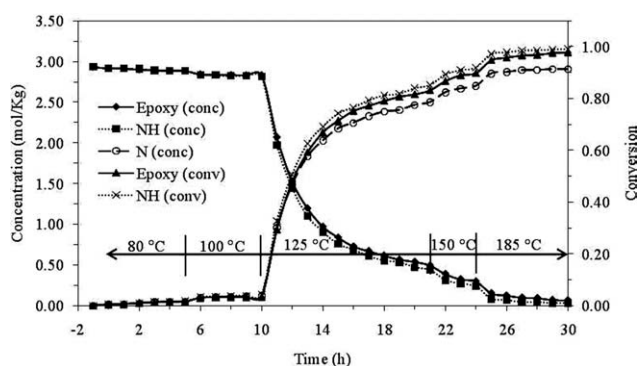


Figure 14 Epoxy and amine concentrations and conversions during cure of Epon 828 with stoichiometric amounts of *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone.

conversion of epoxy after three additional hours (14 h total at two temperatures). Post-curing at 185°C for 1 h yielded 94.74% conversion and extended curing for another additional 5 h resulted in 97.78% epoxy conversion. Important is the fact that the secondary amine conversion curve mirrors the epoxy conversion curve for the same reactions described earlier. The tertiary amine concentration (determined by subtracting the secondary amine concentration at each point in time from its initial concentration) increased progressively during cure and followed the inverse path of epoxy and secondary amine concentrations.

Physical properties of DGEBA epoxy resin and *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone-based thermoplastic polymer are displayed in Table VI. *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone-based epoxy thermoplastic was found to have stiffness in terms of tensile, flexural, and storage moduli of 3.08, 2.86, and 2.85 GPa, respectively, whereas its tensile and flexural strengths were 62.09 and 109.88 MPa, respectively. Polyhydroxy ether of bisphenol-A (PKHH) based thermoplastic possess tensile modulus and strength of ~ 2.60 GPa and ~ 55 MPa, respectively.³⁵ Li and Chung reported a poly ether sulfone (PES)-based thermoplastic having tensile modulus of 2.64 GPa and tensile strength of 45.96

MPa.³⁶ An aromatic secondary diamine and DGEBA-based epoxy thermoplastic has been reported to possess flexural modulus of 2.26 GPa and strength of 66.68 MPa.⁵

The thermal T_g of *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone-based epoxy thermoplastic was determined to be 105.44°C. The mechanical T_g was determined via DMA to be 120.77°C, which is expectedly higher than the thermal T_g . PKHH-based thermoplastics exhibit T_g of ~ 90°C, whereas a thermoplastic formed by reacting a secondary diamine with a DGEBA-based epoxy resin was characterized by a T_g of 78.55°C.^{35,5} 3,3'-DDS cured DGEBA-based epoxy thermoset possessed of mechanical and thermal T_g of 184°C and 173.66°C, respectively.⁵ T_g of *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone-based epoxy thermoplastic is lower than epoxy thermoset with 3,3'-DDS. However, the strength, modulus, and T_g of the *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone-based epoxy polymer are in the range of commercial thermoplastics. It is expected that the secondary amine of 3,3'-DDS, i.e., *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone, will be a viable monomer in the preparation of epoxy-amine thermoplastics and as a chain extender in epoxy-DDS thermosets to controllably reduce crosslink density.

CONCLUSIONS

The secondary diamine of 3,3'-DDS, i.e., *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone, was synthesized successfully by reacting 3,3' DDS with acetaldehyde via reductive amination using sodium triacetoxy borohydride at ambient condition. The reaction product was characterized via analytical techniques such as FTIR, near IR, NMR, and LC-MS to confirm the synthesis of secondary amine from 3,3'-DDS. This in turn supported the fact that the reductive amination path in the presence of $\text{NaBH}(\text{OAc})_3$ is an excellent technique to synthesize secondary amine from 3,3'-DDS. The reaction between the novel secondary amine and a commercial epoxy prepolymer

TABLE VI
Properties of DGEBA Epoxy Resin and *N,N'*-Diethyl-3,3'-diaminodiphenyl sulfone-based Thermoplastic Polymer

Properties		<i>N,N'</i> -diethyl-3,3'-DDS-based thermoplastics	PKHH thermoplastics (Ref. 35)	Poly ether sulfone thermoplastics (Ref. 36)	Secondary amine-based thermoplastics (Ref. 5)	3,3'-DDS thermoset (Ref. 37)
DMA	E' at ambient (GPa)	2.85 ± 0.10	–	–	–	–
	T_g (°C)	120.77 ± 0.96	–	–	–	184
DSC	T_g (°C)	105.44 ± 2.03	~ 90	–	78.55	173.66
Tensile	Strength (MPa)	62.09 ± 7.45	~ 55	~ 45.96	–	–
	Modulus (GPa)	3.08 ± 0.04	~ 2.60	~ 2.64	–	–
Flexural	Strength (MPa)	109.88 ± 11.12	–	–	~ 66.68	–
	Modulus (GPa)	2.86 ± 0.15	–	–	~ 2.26	–

was monitored via DSC and NIR spectroscopy. The epoxy-secondary amine reaction from DGEBA-based epoxy prepolymer and *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone was quantified to begin at 110–125°C with an energy of activation about 66 kJ/mol. Epoxy and amine peak intensities diminished as a function of reaction time/temperature in concert and were confirmed to match the respective, epoxy and amine concentrations using Lambert-Beer's law. *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone-based epoxy thermoplastics possessed tensile and flexural moduli of 3.08 and 2.86 GPa, respectively, with the mechanical T_g of 120.77°C as determined via DMA. *N,N'*-diethyl-3,3'-diaminodiphenyl sulfone can, therefore, function as a potential secondary amine monomer for the synthesis of epoxy-based thermoplastics.

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