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## Thermal and mechanical properties of azomethine functionalized cyanate ester/epoxy blends

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A series of azomethine functionalized diols were synthesized by the condensation reaction of aromatic diamines with 4-hydroxy benzaldehyde. Aromatic diamines with different alkyl chain lengths have been used to prepare the bisphenols. These bisphenols were converted to their corresponding cyanate esters by treating with cyanogen bromide (CNBr) in the presence of triethyl amine (Et<sub>3</sub>N). The curing temperature was measured using differential scanning calorimetry (DSC). The maximum curing temperatures of these cyanate esters are in the range of 203–242 °C. Thermal properties of the cured cyanate esters were studied by using thermogravimetric analysis (TGA). The polymers showed excellent thermal stability ( $T_{5\%}$  was found to be in the range of 358 to 465 °C and  $T_{10\%}$  was found to be in the range of 508 to 525 °C) and the percentage of char yield at 800 °C was found to be in the range of 37.06 to 57.26. The flame retardancy of the cyanate ester resins was evaluated using the limiting oxygen index value which is in the range of 32.32 to 40.40 at 800 °C. Cyanate ester/epoxy blends were prepared and the morphology of the blends were studied by scanning electron microscopy. The mechanical properties and glass transition temperature of cyanate/epoxy ester blends was studied using dynamic mechanical analysis (DMA) and the  $T_g$  was found to increase with increasing cyanate ester content (1 to 5%).

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### 1. Introduction

Cyanate esters are one type of thermosetting resins. On heating or irradiation either in the presence or absence of catalyst, three units of cyanate ester monomer undergo cyclotrimerization to form a symmetric triazine ring with nitrogen and carbon atoms, where the carbon atoms are linked to an ether substituent.<sup>1</sup> The heat resistant character of cured cyanate esters (CE) make them more appealing for use in high thermal applications.<sup>2</sup> The polycyanurates exhibit low dielectric constants and low dissipation factors. This character is well suited for making printed circuit boards in electronic industries.<sup>3–5</sup> Radar transparency, low moisture absorption,<sup>6</sup> very good adhesive character towards metal and high mechanical strength<sup>7–10</sup> make cyanate esters more reliable for high-end applications in aerospace industries. However, the cured CE is inherently brittle in nature and easily undergoes microcracking under service loads. The fracture toughness of cyanate esters can be improved by blending them with thermoplastic tougheners, rubber,<sup>11</sup> organic and inorganic fillers,<sup>6,12</sup> POSS<sup>13–15</sup> and thermosetting resins such as epoxy,<sup>16–20</sup> imides<sup>21–24</sup> and benzoxazines.<sup>25,26</sup>

The commercially available cyanate ester bisphenol A dicyanate ester (BADCY) is widely used in various fields, but further modification is required to enhance its performance properties and reduce the cost of production. The thermooxidative stability and moisture resistance were improved by introducing silicon atoms into BADCY.<sup>6</sup> On the addition of epoxy resin into the BADCY resin, the mechanical and hot-wet properties were improved with concentration ranges of 5 to 30 wt%.<sup>20</sup> Epoxy resins also come under thermosetting resins category and they are widely used for making advanced composites because of their excellent adhesive nature towards metals, chemical resistance and outstanding mechanical properties<sup>27</sup> with superior dimensional stability. They undergo microcracking, which makes them unfit for purpose in high toughness applications (in engineering industries). Another disadvantage of epoxy resins is their moisture absorption.

Azomethine functionalized cyanate esters with shorter alkyl chains were prepared previously.<sup>28,29</sup> In this study, dicyanate esters with azomethine linkages and different alkyl chains with ether linkages were prepared and the effect of the alkyl chain length between two aromatic groups on the thermal stability has been studied. The prepared cyanate esters were blended with epoxy resin in three different weight percentages. Thermal and thermomechanical properties of the CE/epoxy blends were investigated by using thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). The morphology of the system was studied by scanning electron microscopy (SEM) techniques.

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## 2. Experimental procedure

### 2.1. Materials

4-Acetamidophenol was purchased from Aldrich, USA. Acetone, 1,4-dibromo butane, 1,5-dibromo pentane, 1,6-dibromo hexane, potassium carbonate ( $K_2CO_3$ ), cyanogen bromide (CNBr) and 4-hydroxy benzaldehyde were purchased from Sisco Research Laboratories (SRL-India). The diglycidyl ether of bisphenol-A (DGEBA) was purchased from Huntsman (India). Diaminodiphenylmethane (DDM) was purchased from Acros Organics (India). Ethanol and triethylamine ( $Et_3N$ ) were purchased from Merck (India). All other reagents were used as received. Triethylamine and acetone were distilled prior to use.

### 2.2. Measurements

Fourier transform infrared (FT-IR) spectra were recorded in an ABB Bomem MB series FT-IR spectrometer using a KBr pellet.  $^1H$  and  $^{13}C$  nuclear magnetic resonance measurements were carried out with a Bruker AV III spectrometer (500 MHz). Samples were prepared in  $CDCl_3$  or  $DMSO-d_6$  solutions. Melting temperatures were determined with a melting point apparatus, IA 6304, at a heating rate of  $4\text{ }^\circ C\text{ min}^{-1}$ . Differential scanning calorimetric (DSC) analysis for curing studies was carried out using Perkin Elmer DSC 7 model at a heating rate of  $5\text{ }^\circ C\text{ min}^{-1}$  under an air atmosphere using aluminum pans. Thermogravimetric analysis (TGA) was performed using a Perkin Elmer Diamond series model at a heating rate of  $10\text{ }^\circ C\text{ min}^{-1}$  under flowing air in the range of 25–800  $^\circ C$ .

### 2.3. Synthesis of 1,4-bis(4-acetamidophenoxy)butane

4-Acetamidophenol (5.0 g, 0.0330 mol) and 10.26 g of potassium carbonate (0.0742 mol) in 100 mL of acetone were taken in a 250 mL round bottomed flask. To this, 1,4-dibromobutane (3.5708 g, 0.0165 mol) in 50 mL of acetone was added drop wise. The reaction was initiated by adding trace amounts of potassium iodide. Then it was refluxed at 80  $^\circ C$  overnight. The mixture was cooled and poured into water (1000 mL). The white precipitate formed was separated and recrystallized from ethanol.<sup>30</sup> Yield 89%, m.p.: 190  $^\circ C$ . IR (KBr,  $cm^{-1}$ ): 3336 (CONH), 1053 (–C–O–C–), 1675 (C=O), 824 (*p*-substituted aromatic).

### 2.4. Synthesis of 1,4-bis(4-aminophenoxy)butane

1,4-Bis(4-acetamidophenoxy)butane (4.0 g, 0.0112 mol) in 100 mL ethanol was taken in a 250 mL round bottomed flask. To this, 10.0 g of sodium hydroxide (0.25 mol) dissolved in water (35 mL) was added drop wise. After the addition was completed, the mixture was refluxed at 80  $^\circ C$  for 8 h, cooled and poured into crushed ice. The resulting pale brown precipitate was filtered, washed with distilled water twice and recrystallized from ethanol. Yield 93%, m.p.: 140  $^\circ C$ . FT-IR (KBr,  $cm^{-1}$ ): 3395, 3371 (aromatic  $NH_2$ ), 2945 ( $OCH_2$ ), 835 (*p*-substituted aromatic).  $^1H$ -NMR (500 MHz,  $CDCl_3$ , ppm): 3.7 (s, 4H, a ( $Ar-NH_2$ )), 6.6 (d, 4H, b), 7.2 (d, 4H, c), 3.8 (t, 4H, d ( $OCH_2CH_2$ )), 1.8 (m, 4H, e ( $OCH_2CH_2$ )).  $^{13}C$ -NMR ( $CDCl_3$ , ppm):  $C^1$ -139.9,  $C^2$ -115.7,  $C^3$ -

115.2,  $C^4$ -149.3,  $C^5$ -67.9,  $C^6$ -28.8. The other two diamines were prepared in a similar way.

**2.4.1. Synthesis of 1,4-bis[4(4-hydroxyphenylazomethyl)phenoxy]butane.** 1,4-Bis(4-aminophenoxy)butane (2.750 g, 0.01 mol) was taken in a 250 mL round bottomed flask with 100 mL of ethanol and refluxed until it was completely dissolved in ethanol. To this 2.4662 g of 4-hydroxy benzaldehyde (0.0201 mol) in 50 mL of ethanol was added drop wise with constant stirring. The reaction was initiated by adding trace amounts of acetic acid. The mixture was refluxed for a further period of 3 h. The mixture was then cooled and poured into cold water (1.0 L). The resulting yellow precipitate was collected and recrystallized from ethanol. Yield: 91%, m.p.: 83  $^\circ C$ . FT-IR (KBr,  $cm^{-1}$ ): 3380 (OH), 2943 ( $OCH_2$ ), 1680 ( $HC=N$ ), 834 (*p*-substituted aromatic).  $^1H$ -NMR ( $DMSO-d_6$ , ppm): 9.4 (s, 2H, a), 6.9 (d, 4H, b), 7.7 (d, 4H, c), 8.7 (s, 2H, d), 7.1 (d, 4H, e), 6.9 (d, 4H, f), 4.1 (t, 4H, g), 1.9 (m, 4H, h).  $^{13}C$ -NMR (500 MHz,  $DMSO-d_6$ , ppm):  $C^1$ -161.1,  $C^2$ -116.8,  $C^3$ -130.9,  $C^4$ -130.1,  $C^5$ -159.3,  $C^6$ -145.9,  $C^7$ -122.3,  $C^8$ -116.8,  $C^9$ -155.8,  $C^{10}$ -66.3,  $C^{11}$ -27.8.

**2.4.2. 1,5-Bis[4(4-hydroxyphenylazomethyl)phenoxy]pentane.** Yield: 83%, m.p.: 90  $^\circ C$ . FT-IR (KBr,  $cm^{-1}$ ): 3414 (OH), 2945 ( $OCH_2$ ), 1688 ( $HC=N$ ), 836 (*p*-substituted aromatic).  $^1H$ -NMR ( $DMSO-d_6$ , ppm): 9.2 (s, 2H, a), 6.8 (d, 4H, b), 7.8 (d, 4H, c), 8.6 (s, 2H, d), 7.2 (d, 4H, e), 7.0 (d, 4H, f), 4.0 (m, 4H, g), 1.8 (m, 4H, h), 1.8 (m, 2H, i).  $^{13}C$ -NMR (500 MHz,  $DMSO-d_6$ , ppm):  $C^1$ -160.5,  $C^2$ -115.8,  $C^3$ -131.2,  $C^4$ -129.1,  $C^5$ -159.9,  $C^6$ -145.5,  $C^7$ -122.5,  $C^8$ -115.7,  $C^9$ -158.5,  $C^{10}$ -67.3,  $C^{11}$ -29.8,  $C^{12}$ -22.8.

**2.4.3. 1,6-Bis[4(4-hydroxyphenylazomethyl)phenoxy]hexane.** Yield: 91%, m.p.: 109  $^\circ C$ . FT-IR (KBr,  $cm^{-1}$ ): 3342 (OH), 2932 ( $OCH_2$ ), 1676 ( $HC=N$ ) 839 (*p*-substituted aromatic).  $^1H$ -NMR ( $DMSO-d_6$ , ppm): 9.2 (s, 2H, a), 6.9 (d, 4H, b), 7.9 (d, 4H, c), 8.6 (s, 2H, d), 7.2 (d, 4H, e), 6.9 (d, 4H, f), 4.1 (t, 4H, g), 1.7 (m, 4H, h), 1.5 (m, 2H, i).  $^{13}C$ -NMR (500 MHz,  $DMSO-d_6$ , ppm):  $C^1$ -160.8,  $C^2$ -116.1,  $C^3$ -131.1,  $C^4$ -128.9,  $C^5$ -160.1,  $C^6$ -144.8,  $C^7$ -121.5,  $C^8$ -115.9,  $C^9$ -157.8,  $C^{10}$ -68.9,  $C^{11}$ -29.6,  $C^{12}$ -25.8.

### 2.5. Synthesis of cyanate ester monomers

A 250 mL three-necked round bottomed flask, equipped with a magnetic stirring device and a nitrogen inlet, was charged with 3.5 g of the bisphenol (1,4-bis[4(4-hydroxyphenylazomethyl)phenoxy]butane) (0.0114 mol). The flask was maintained at  $-15\text{ }^\circ C$  and then a solution of 2.3 g (0.0228 mol) of CNBr in acetone (50 mL) was added with constant stirring. To this mixture, 3.1 mL (0.0228 mol) of triethyl amine was added drop wise with continuous stirring. After the complete addition of triethyl amine, the reaction mixture was stirred for a further period of 2 h while maintaining the bath temperature at  $-15\text{ }^\circ C$ . The temperature was then raised to room temperature. The mixture was poured into cold distilled water to precipitate the cyanate ester. A light brown product (yield: 91%) was obtained. All other prepared bisphenols were converted into their corresponding dicyanate ester monomers in a similar way.

**2.5.1. 1,4-Bis[4(4-cyanatophenylazomethyl)phenoxy]butane ( $CE_1$ ).** Yield: 91%, m.p.: 91  $^\circ C$ . FT-IR (KBr,  $cm^{-1}$ ): 2198, 2212 (OCN), 2945 ( $OCH_2$ ), 1681 ( $HC=N$ ), 834 (*p*-substituted aromatic).  $^1H$ -NMR ( $DMSO-d_6$ , ppm): 6.9 (d, 4H, a), 7.6 (d, 4H, b),

8.6 (s, 2H, c), 7.1 (d, 4H, d), 6.9 (d, 4H, e), 4.0 (t, 4H, f), 1.9 (m, 4H, g).  $^{13}\text{C-NMR}$  (500 MHz,  $\text{DMSO-}d_6$ , ppm):  $\text{C}^1$ -109.1,  $\text{C}^2$ -156.8,  $\text{C}^3$ -115.9,  $\text{C}^4$ -131.1,  $\text{C}^5$ -135.9,  $\text{C}^6$ -159.9,  $\text{C}^7$ -143.3,  $\text{C}^8$ -122.6,  $\text{C}^9$ -116.8,  $\text{C}^{10}$ -156.3,  $\text{C}^{11}$ -67.8,  $\text{C}^{12}$ -28.7.

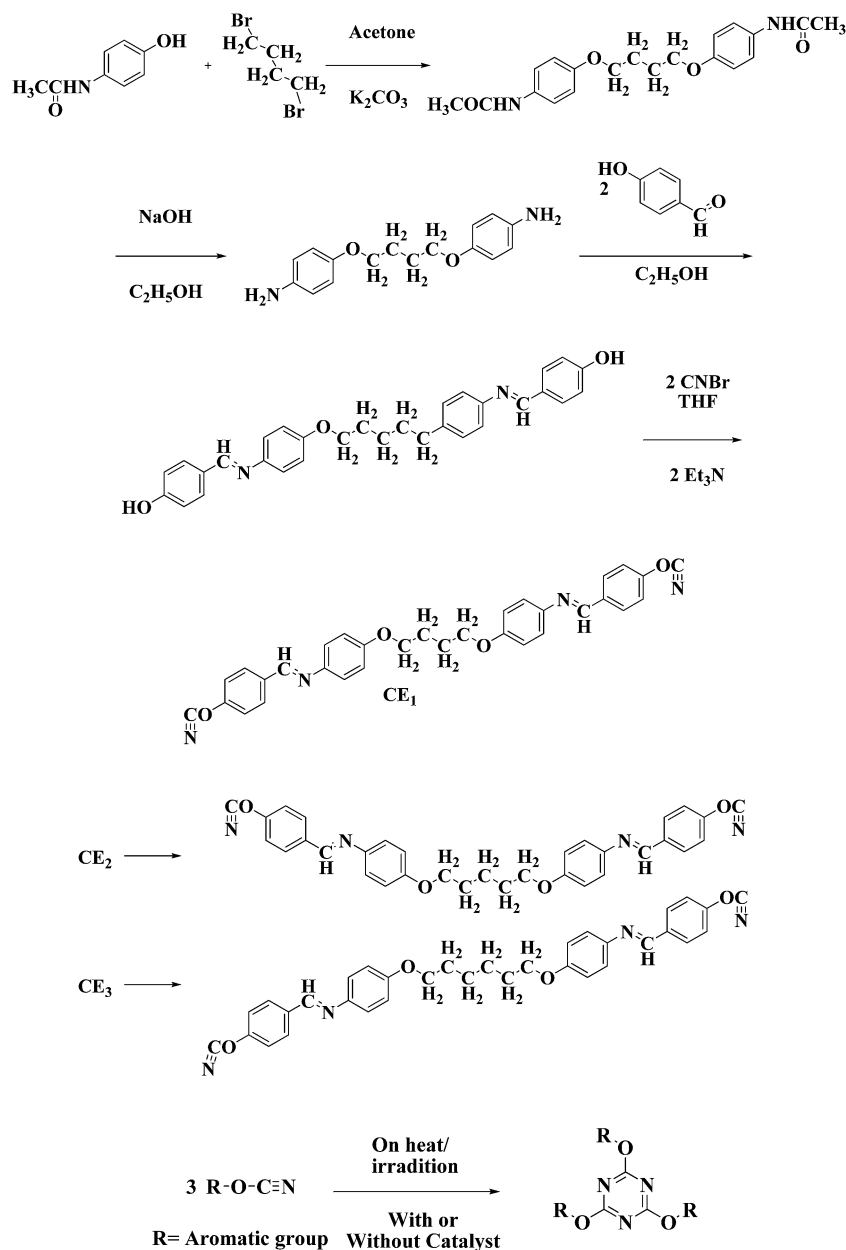
**2.5.2. 1,5-Bis[4(4-cyanatophenylazomethyl)phenoxy]pentane ( $\text{CE}_2$ ).** Yield: 87%, m.p.: 99 °C. FT-IR (KBr,  $\text{cm}^{-1}$ ): 2226, 2240 (OCN), 2942 ( $\text{OCH}_2$ ), 1688 ( $\text{HC}=\text{N}$ ), 835 (*p*-substituted aromatic).  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ , ppm): 7.1 (d, 4H, a), 7.7 (d, 4H, b), 8.7 (s, 2H, c), 7.2 (d, 4H, d), 6.9 (d, 4H, e), 4.1 (t, 4H, f), 1.8 (m, 4H, g), 1.6 (m, 2H, h).  $^{13}\text{C-NMR}$  (500 MHz,  $\text{DMSO-}d_6$ , ppm):  $\text{C}^1$ -109.5,  $\text{C}^2$ -155.8,  $\text{C}^3$ -116.5,  $\text{C}^4$ -131.1,  $\text{C}^5$ -135.8,  $\text{C}^6$ -161.1,  $\text{C}^7$ -144.1,  $\text{C}^8$ -121.9,  $\text{C}^9$ -115.1,  $\text{C}^{10}$ -157.1,  $\text{C}^{11}$ -68.9,  $\text{C}^{12}$ -29.6,  $\text{C}^{13}$ -22.1.

**2.5.3. 1,6-Bis[4(4-cyanatophenylazomethyl)phenoxy]hexane ( $\text{CE}_3$ ).** Yield: 93%, m.p.: 123 °C. FT-IR (KBr,  $\text{cm}^{-1}$ ): 2219, 2242

(OCN), 2938 ( $\text{OCH}_2$ ), 1680 ( $\text{HC}=\text{N}$ ), 838 (*p*-substituted aromatic).  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ , ppm): 7.0 (d, 4H, a), 7.7 (d, 4H, b), 8.7 (s, 2H, c), 7.2 (d, 4H, d), 6.9 (d, 4H, e), 4.0 (t, 4H, f), 1.7 (m, 4H, g), 1.4 (m, 4H, h).  $^{13}\text{C-NMR}$  (500 MHz,  $\text{DMSO-}d_6$ , ppm):  $\text{C}^1$ -109.4,  $\text{C}^2$ -156.3,  $\text{C}^3$ -116.2,  $\text{C}^4$ -131.9,  $\text{C}^5$ -135.1,  $\text{C}^6$ -160.1,  $\text{C}^7$ -143.8,  $\text{C}^8$ -121.8,  $\text{C}^9$ -115.7,  $\text{C}^{10}$ -157.9,  $\text{C}^{11}$ -68.5,  $\text{C}^{12}$ -29.6,  $\text{C}^{13}$ -25.9.

## 2.6. Preparation of cyanate ester/epoxy blends

1 wt% of cyanate ester (0.200 g) was taken with 99 wt% of epoxy resin (19.80 g) (cyanate ester : epoxy = 1 : 99) and stirred at 80 °C until the mixture became homogeneous. 5.346 g (27 g of DDM taken for 100 g epoxy resin) of DDM (a hardener) was added to the homogeneous mixture of cyanate/epoxy resin and



Scheme 1 Synthesis of the dicyanate ester monomers.

the mixture was immediately transferred to the mold and cured at 120 °C for 1 h, 170 °C for 1 h and post cured at 210 °C for 1 h. The same procedure was adopted for the preparation of cyanate/epoxy blends with 3% and 5% of cyanate ester.

### 3. Results and discussion

The synthetic procedure for the preparation of dicyanate esters is presented in Scheme 1. The bisphenol precursors were prepared by the condensation reaction between aromatic aldehydes and a diamine. The structure of the bisphenols was confirmed by FT-IR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$  spectroscopy. The dicyanate esters were prepared from their precursor diols and CNBr in the presence of triethylamine. Fig. 1 shows the FT-IR spectra of the dicyanate esters. The appearance of new bands at around 1680  $\text{cm}^{-1}$  and the disappearance of amine bands (around 3300–3400  $\text{cm}^{-1}$ ) confirmed the formation of the azomethine. The appearance of new bands at 2174–2240  $\text{cm}^{-1}$  and disappearance of the band at 3300–3500  $\text{cm}^{-1}$  due to hydroxyl group in the FT-IR spectrum confirms the conversion of hydroxyl group into a dicyanate ester. The formation of a C–O–C linkage is confirmed by the presence of the band at 1050 to 1070  $\text{cm}^{-1}$ .<sup>30</sup> The signal at 3.7 ppm, due to the amino protons, disappears and a new signal at 8.7 ppm due to azomethine proton is formed indicating the conversion of the amino group to azomethine group. This is further supported by FT-IR spectrum. The strong absorption band due to the amino is missing and a new band is found at 1681  $\text{cm}^{-1}$ .

The conversion of the hydroxyl group to the cyanate ester is confirmed by the disappearance of the hydroxyl proton signal at 9.4 ppm and the appearance of the signal due to the cyanate ester carbon at 109.1 ppm<sup>13</sup> from the NMR spectra (Fig. 2 and 3). The chemical shifts of all the aromatic protons appear in the range of 6.9 to 7.6 ppm. The chemical shift at 4.0 ppm may be attributed to the methylene proton which is attached to

aromatic ring through an oxygen atom. The chemical shift at 1.9 ppm may be assigned to methylene protons which are present in the spacer group between the two aromatic rings. In the  $^{13}\text{C-NMR}$  spectrum, the carbon atoms in the azomethine linkage of the three cyanate esters show chemical shifts in the range of 115–116 ppm. Aromatic carbons appear in the range of 115.8–156.3 ppm. Hence, the proposed structure of the dicyanate ester is confirmed.

#### 3.1. DSC analysis

The cure behavior of the dicyanate esters was studied using differential scanning calorimetry. The DSC curves of the dicyanate esters CE<sub>1</sub>, CE<sub>2</sub> and CE<sub>3</sub> are shown in Fig. 4(a–c) and the data are given in Table 1. The melting points of the dicyanate esters were found to be 91, 102 and 123 °C respectively. The initial ( $T_i$ ) and maximum curing temperatures ( $T_{\text{max}}$ ) were found to be in the range of 143 to 181 °C and 203 to 242 °C respectively. The cyanate ester CE<sub>3</sub> (1,6-bis[4(4-cyanatophenylazomethyl)phenoxy]hexane) shows the peak maximum curing temperature. The end cure temperatures were found to be in the range of 246 to 285 °C. The dicyanate ester CE<sub>1</sub> (1,4-bis[4(4-cyanatophenylazomethyl)phenoxy]butane) showed the highest end cure temperature of 285 °C. The curing temperature of BADCY is found to be at 281 °C<sup>2</sup> and all of the three synthesised cyanate esters were cured at a lower temperature when compared with BADCY. The cyanate ester (CE<sub>1</sub>) with shortest alkyl chain between the aromatic groups was found to cure at the lowest temperature. The glass transition temperatures of the neat cured dicyanate esters decreased with increasing alkyl chain length between the two aromatic groups. No liquid crystallinity was observed for any of the dicyanate esters.

#### 3.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) is the preferred technique for the evaluation of the thermal stability of the polymeric materials. The thermal stability of the cured cyanate esters was evaluated with its 5% weight loss temperature ( $T_{5\%}$ ), 10% weight loss temperatures ( $T_{10\%}$ ) and the char yield at 800 °C. The TGA curves of the various cured cyanate esters are given in Fig. 5 and the data are given in Table 2.  $T_{5\%}$  and  $T_{10\%}$  of all three neat cured cyanate esters were found to be in the range of 358 to 465 °C and 508 to 525 °C respectively. The cured cyanate ester (CE<sub>2</sub>) with an alkyl chain length of five showed the least thermal stability ( $T_{5\%}$  – 358 °C) and lost 40% weight between 520 to 593 °C. The char yield was found to be in the range of 37.06 to 57.26%. From the char yield and LOI values, the cyanate esters (CE<sub>1</sub> and CE<sub>3</sub>) with an even number alkyl chain length between the two aromatic groups were more stable than the dicyanate ester (CE<sub>2</sub>) with an odd number spacer length between the two aromatic groups. The char yield of BADCY is found to be 42.5 at 800 °C,<sup>2</sup> but CE<sub>1</sub> and CE<sub>3</sub> show higher char yields of 57.26 and 48.08 compared to the commercially available dicyanate ester (BADCY). The cured cyanate ester with the shortest alkyl chain length between the two aromatic groups show 5% weight loss at 465 °C. This is greater than that

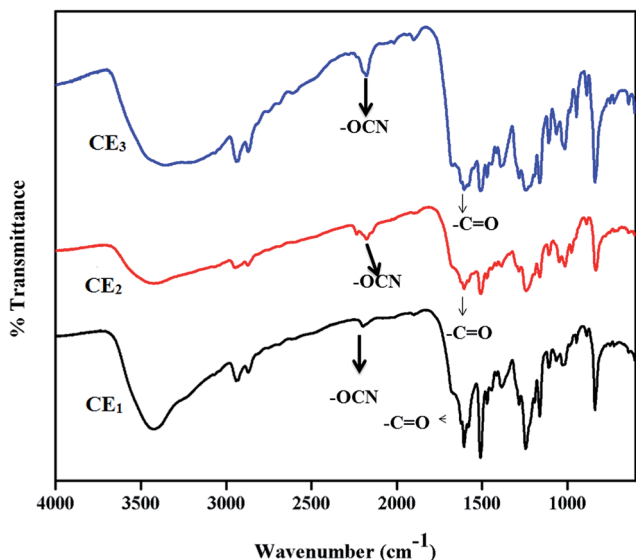


Fig. 1 FT-IR spectrum of the cyanate esters CE<sub>1</sub>, CE<sub>2</sub> and CE<sub>3</sub>.

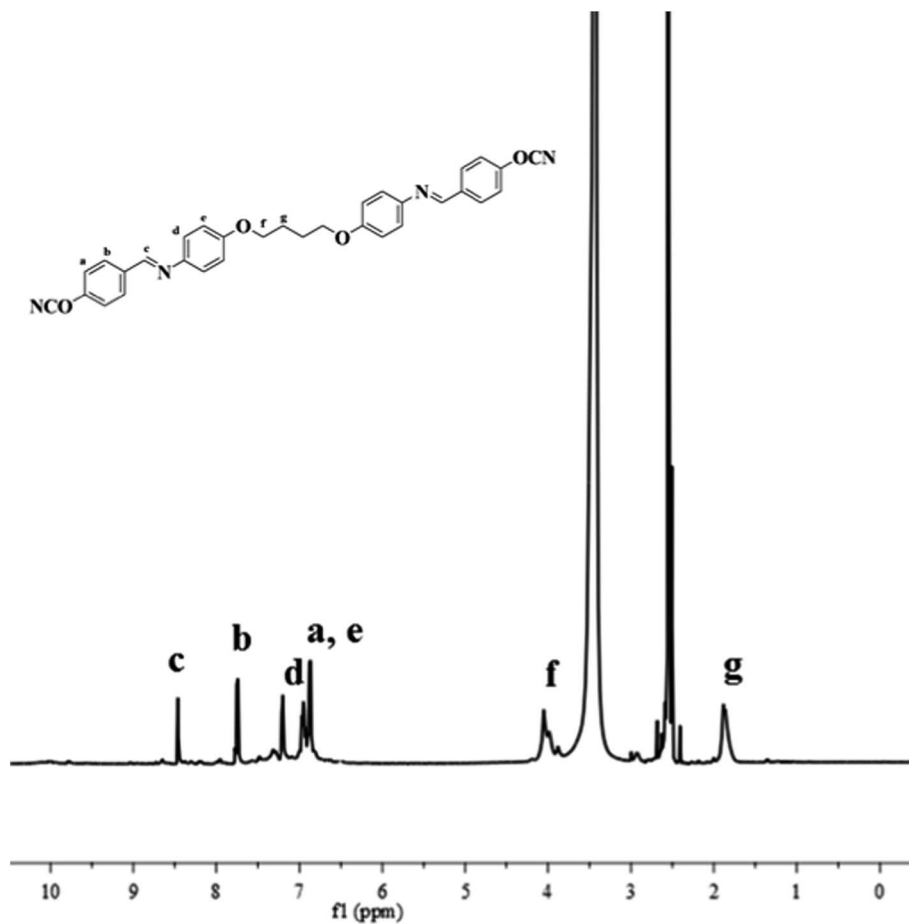


Fig. 2  $^1\text{H}$ -NMR spectrum of the cyanate ester ( $\text{CE}_1$ ).

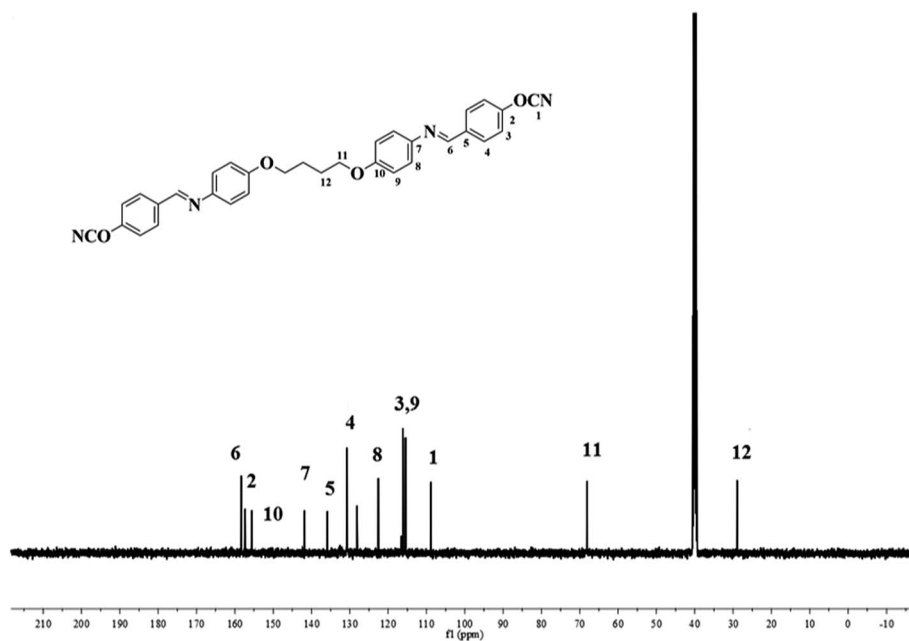


Fig. 3  $^{13}\text{C}$ -NMR spectrum of cyanate ester ( $\text{CE}_2$ ).

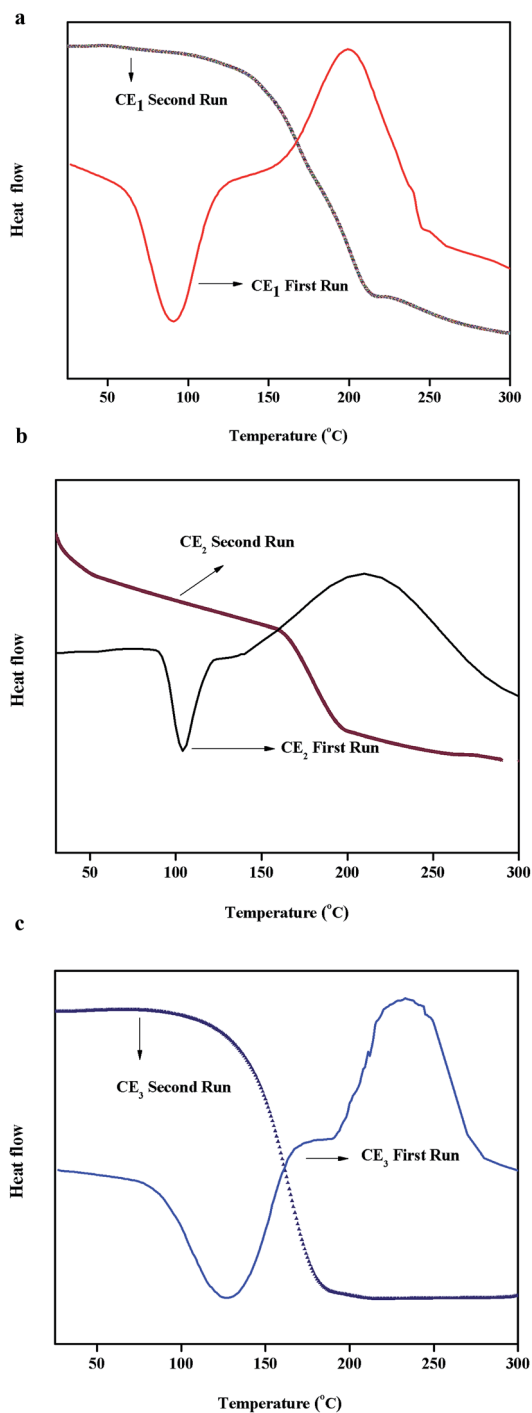


Fig. 4 (a) DSC thermogram data of the cyanate ester CE<sub>1</sub>, (b) DSC thermogram data of the cyanate ester CE<sub>2</sub> and (c) DSC thermogram data of the cyanate ester CE<sub>3</sub>.

Table 1 DSC data of the cyanate esters

Sample code	Melting point (°C)	Onset of cure (°C)	Maximum cure (°C)	End of cure (°C)
CE <sub>1</sub>	91	148	203	285
CE <sub>2</sub>	102	143	216	246
CE <sub>3</sub>	123	181	242	269

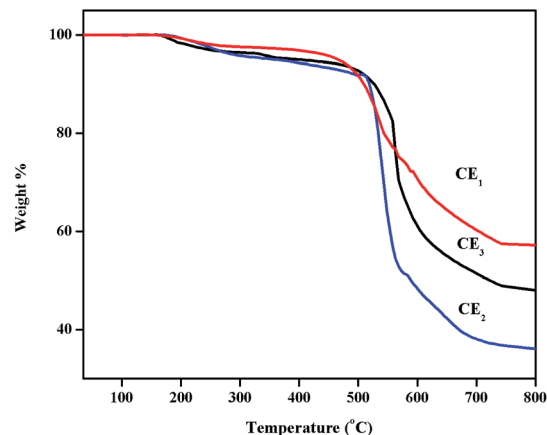


Fig. 5 TGA thermogram data of the cyanate esters.

Table 2 TGA data of the polycyanurates<sup>a</sup>

Sample code	T <sub>5</sub> (°C)	T <sub>10</sub> (°C)	Char yield%	LOI
CE <sub>1</sub>	465	508	57.26	40.40
CE <sub>2</sub>	358	520	37.06	32.32
CE <sub>3</sub>	399	525	48.08	36.73
Neat epoxy	363	369	18.0	24.7
5% CE <sub>1</sub> + 95% epoxy	393	410	31.26	30.00
5% CE <sub>2</sub> + 95% epoxy	378	392	24.11	27.14
5% CE <sub>3</sub> + 95% epoxy	381	395	27.80	28.62

<sup>a</sup> T<sub>5</sub> = 5% weight loss temperature, T<sub>10</sub> = 10% weight loss temperature, LOI = limiting oxygen index.

of other two cured cyanate esters. The 5% weight CE/epoxy blends show 10% (T<sub>10%</sub>) weight loss temperatures in the range of 392–410 °C and char yields in the range of 24.11 to 31.26%. Few reports by other authors that the thermal stability and char yield of cyanate ester/epoxy blends increase with increasing concentration of the cyanate ester in the epoxy blends, which is similar to our case.<sup>13</sup>

### 3.3. SEM analysis

The cross-section (fracture surface) of the CE/epoxy blends was studied by scanning electron microscopy. The fractured surface of the neat CE and CE/epoxy blends was sputtered with gold to deionize the electrons on the surface. Fig. 6(a–c) display the SEM images of the cured neat cyanate ester CE<sub>1</sub>, 1% cyanate ester + 99% epoxy and 5% cyanate ester + 95% epoxy respectively. The SEM images of the fractured surface of CE<sub>2</sub> and CE<sub>3</sub> are given in Fig. 6(d and e) respectively. CE<sub>1</sub> shows a curved hollow structure, CE<sub>2</sub> and CE<sub>3</sub> show a layered structure (on both lower and higher magnification). SEM images Fig. 6(b and c) illustrate the uniform distribution of the cyanate ester in the epoxy blends without any voids. The DMA results show that the toughening of epoxy was affected by adding CE. The neat CE<sub>2</sub> has a similar morphology to the polycyanurate of bisphenol A dicyanate ester.<sup>31</sup>

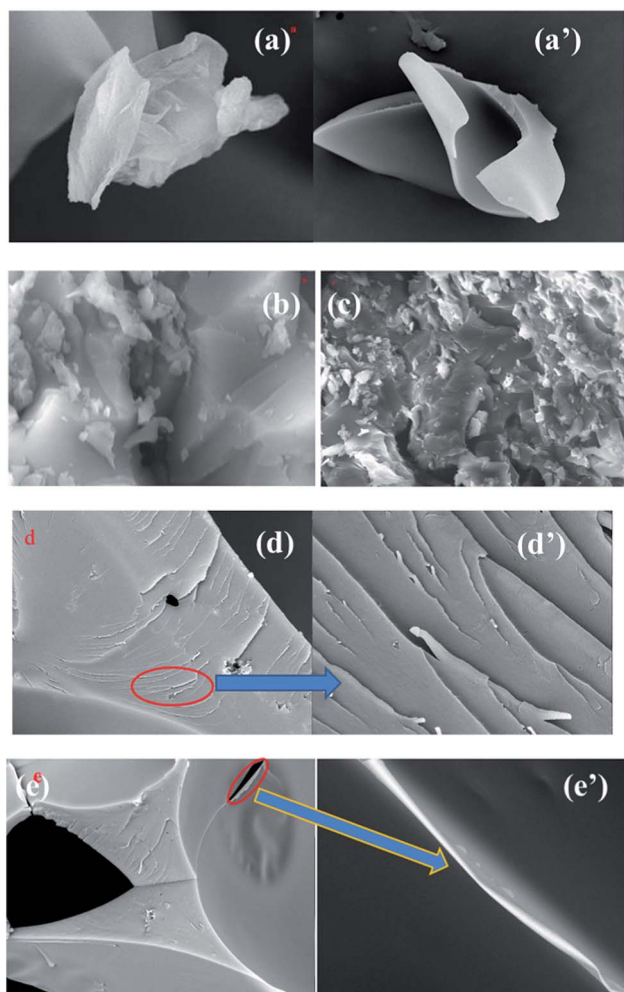


Fig. 6 SEM images of (a) neat cyanate ester  $CE_1$ , (b) 1% cyanate ester  $CE_1$  + 99% epoxy system, (c) 5% cyanate ester  $CE_1$  + 95% epoxy system, (d) neat cyanate ester  $CE_2$  and (e) neat cyanate ester  $CE_3$ .

### 3.4. Dynamic mechanical analysis (DMA)

The dynamic mechanical properties (stress relaxation behavior) were measured for the CE/epoxy blend systems in order to find out the effect of increasing the cyanate ester content. The storage modulus and tan delta of the blend with 5% cyanate ester ( $CE_1$ ,  $CE_2$  and  $CE_3$ ) and 95% epoxy are given in Fig. 7 and 8 respectively. The data obtained from the DMA scans are given in Table 3. The storage modulus of the CE/epoxy blends increases with the increase in the cyanate ester content (from 1 to 5%) except the 1%  $CE_1$ /epoxy blend. The increase in the storage modulus may be due to the increased cross-linking density of the blends as a result of increase in the CE content. The glass transition temperature of the pure epoxy system was found to be 161 °C.<sup>13</sup> In the case of the 1%  $CE_1$  epoxy blend, the glass transition temperature decreased to 158 °C from 161 °C for the neat cured epoxy. However, on further addition of 5%  $CE_1$  to the epoxy resin, the glass transition temperature increased to 180 °C from 161 °C. The glass transition temperature of the blends slightly increased with increase in the cyanate ester content. This observation proves the fact that the co-reaction of cyanate

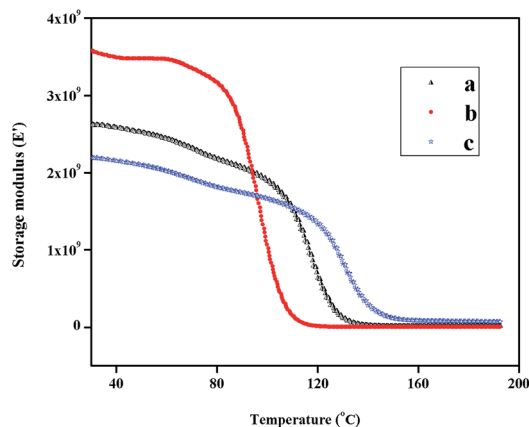


Fig. 7 DMA showing storage modulus ( $E'$ ) of the CE/epoxy blends: (a) 5% of  $CE_1$  + 95% epoxy, (b) 5% of  $CE_2$  + 95% epoxy, (c) 5% of  $CE_3$  + 95% epoxy.

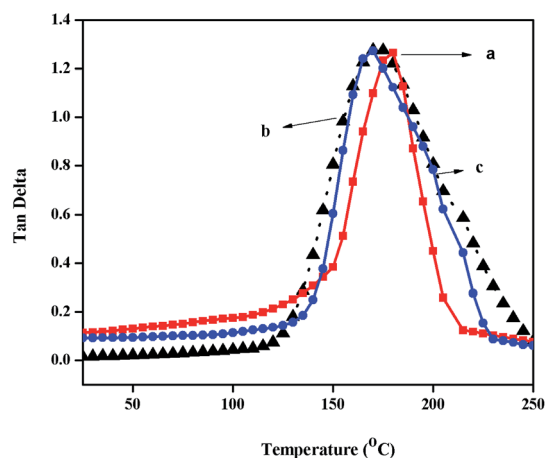


Fig. 8 DMA showing loss modulus of the CE/epoxy blends: (a) 5% of  $CE_1$  + 95% epoxy, (b) 5% of  $CE_2$  + 95% epoxy, (c) 5% of  $CE_3$  + 95% epoxy.

Table 3 Values of the crosslink density of the CE + epoxy blends (from the DMA values)

Sample code	CE%	$E'$ (GPa)	Temp. K (273 + 50)	Crosslink density $\nu_e \times 10^5$ (mol m <sup>-3</sup> )
$CE_1$ + epoxy	5	2.52	323	3.13
$CE_2$ + epoxy	5	3.48	323	4.32
$CE_3$ + epoxy	5	2.09	323	2.59

ester with epoxy resin is almost complete resulting in a homogeneous state<sup>14</sup> and it is the resultant oxazolidinone network<sup>25</sup> which enhances the thermal and mechanical properties of the CE/epoxy blends. However, some authors reported that the addition of POSS-CY to the epoxy resin leads to a decrease in the glass transition temperature from 161 to 155 °C due to the formation of free volume in cyanate/epoxy blend system.<sup>13</sup>

### 3.5. Crosslink density

The crosslink density, or the concentration of network chains ( $\nu_e$ ), is the number of moles of network chains per unit volume

of the cured polymers. The crosslink density of highly cross-linked thermosets can be determined by modulus measurements in the rubbery plateau by using the equation of state for rubber elasticity:<sup>32</sup>

$$\nu_e = E'/3RT$$

where  $E'$  = tensile storage modulus in the rubbery plateau,  $T$  = temperature in K corresponding to the storage modulus value and  $R$  = gas constant.

Table 3 shows the crosslink density for each of the CE/epoxy blends. On addition of cyanate ester to the epoxy resin, the crosslink density increased. The CE<sub>2</sub> epoxy blends showed the highest crosslink density. The storage modulus of CE<sub>2</sub> blends (3.48 GPa), with an odd number alkyl chain length between aromatic groups, is higher than the CE/epoxy blends which have an even number alkyl chain length between the two aromatic groups, CE<sub>1</sub> (2.52 GPa) and CE<sub>3</sub> (2.09 GPa).

### 3.6. Flame retardancy

The resistance towards fire of the CEs and the CE/epoxy blends is expressed in terms of the limiting oxygen index (LOI). LOI may be defined as the minimum fraction of oxygen in a mixture of O<sub>2</sub> and N<sub>2</sub> during a fire. The LOI value should be higher than that of a threshold value (a value of 26) for the polymer to behave as a self-extinguishing material or a self-extinguisher. The LOI value is calculated using Krevelen's equation:<sup>33</sup>

$$\text{LOI} = 17.5 + 0.4(\sigma)$$

where  $\sigma$  is the percentage of char yield. The LOI of the neat CE and CE/epoxy blends were found to be in the range of 32.32 to 40.40 and 27.14 to 30.00 respectively. The cured cyanate ester with the least alkyl space length (CE<sub>1</sub>) showed the highest LOI value and the cyanate ester (CE<sub>2</sub>) with an alkyl chain of five carbons showed the lowest LOI value. The LOI values of all the cured dicyanate esters indicate that they are very good fire retardant materials. From the LOI values, it was found that the cured cyanate ester CE<sub>1</sub>/epoxy blends showed the best flame retardance.

## 4. Conclusions

Dicyanate esters with azomethine linkages were successfully synthesised. The structure of the monomers and precursors were characterized by FT-IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy, which clearly confirmed the molecular structure. The morphology of the cured cyanate ester and CE/epoxy blends revealed the uniform distribution of cyanate ester in the epoxy resin. The cured cyanate ester and BADCY showed the similar morphologies. The DMA studies revealed that the glass transition temperature of the epoxy was increased from 161 to 180 °C and the storage modulus of the epoxy resin increased with increases in cyanate ester content. The crosslink density of the cyanate epoxy blends were calculated from their storage modulus value, which increased (from 3.98 to 4.32 mol m<sup>-3</sup> for CE<sub>2</sub>) with increases in the weight ratio of CE in the blends. TGA

results showed that the char yield values of neat cyanate esters are in the range of 32.32 to 40%. The char yield increased from 18% to 30.0% with increases of CE content in the epoxy blend. This increase in char yield further suggests that the CE/epoxy blends can be used in high flame retardancy applications. The microwave curing and the effect of odd and even alkyl chain length between the two aromatic groups will be studied in future, as CE<sub>1</sub> and CE<sub>3</sub>, which have an even number alkyl chain length between the two aromatic rings, showed better char yield and LOI values compared to CE<sub>2</sub> which has an odd number alkyl chain length between the two aromatic rings.

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