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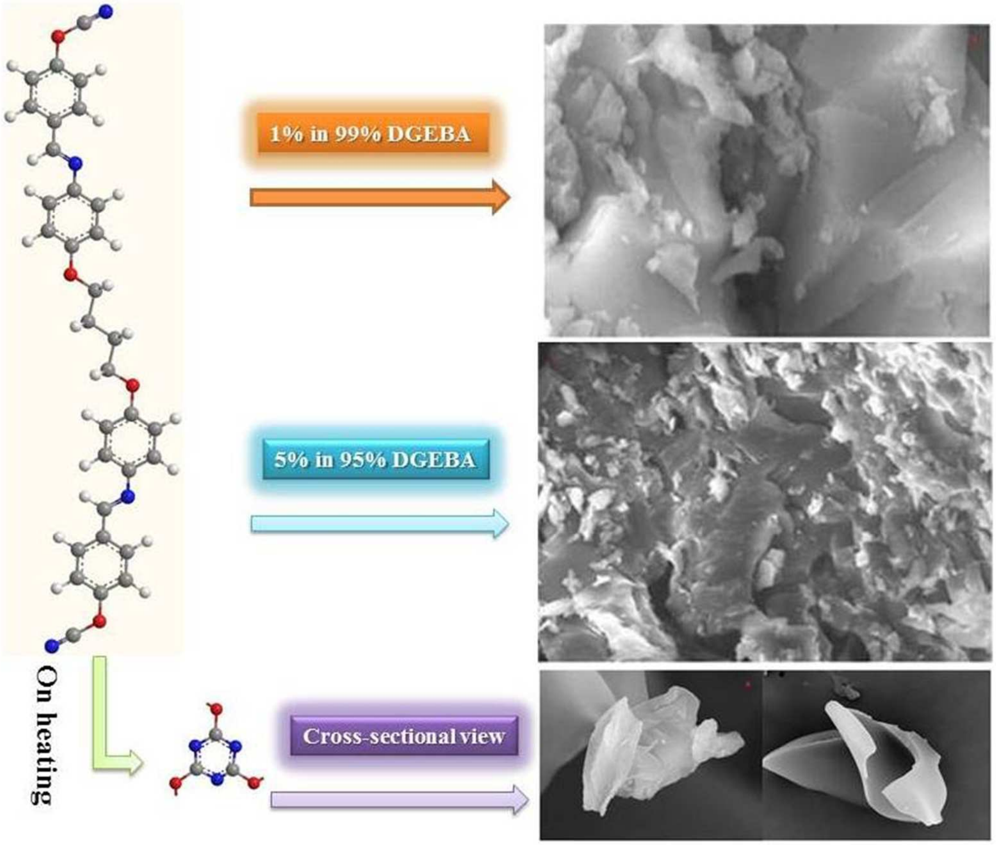

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# Thermal and Mechanical Properties of Azomethine Functionalized Cyanate Ester/Epoxy Blends

C.P. Sakthidharan[§‡], Pudupadi R. Sundararajan[‡] and Muthusami Sarojadevi[§*]

[§] Department of Chemistry, CEG, Anna University, Chennai, India – 600 025

[‡] Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, Canada, K1S 5B6

[*]Corresponding author: msrde2000@yahoo.com

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## Abstract

A series of azomethine functionalized diols were synthesized by 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 (BrCN) in the presence of triethyl amine ($Et_3N$). The curing temperature was measured by using differential scanning calorimetry (DSC). The maximum curing temperature of these cyanate esters are in the range of 203-242 ºC. Thermal properties of the cured cyanate ester were studied by using thermo gravimetric analysis (TGA). The polymers show excellent thermal stability ($T_5$ was found to be in the range of 358 to 465 ºC and $T_{10}$ was found to be in the range of 508 to 525 ºC) and the percentage of char yield at 800 ºC was found to be in the range of 37.06 to 57.26. The flame retardancy of the cyanate ester resins have been evaluated using limiting oxygen index value which is in the range of 32.32 to 40.40 at 800 ºC. Cyanate ester/epoxy blends were prepared and the morphology of the blends was studied by scanning electron microscopy. The mechanical properties and glass transition temperature of cyanate/epoxy ester blends were studied by using dynamic mechanical analysis (DMA) and the $T_g$ was found to increase with increasing cyanate ester content (1 to 5%).

**Keywords**
Azomethine containing cyanate ester-epoxy blends

Thermal and mechanical properties

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## 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 and form symmetric triazine ring with nitrogen and carbon atom in which the carbon atoms are linked with oxygen atom.[1] Heat resistant character of cured cyanate esters (CE) make them more competing in high thermal applications.[2] The polycyanurates exhibit low dielectric constant and low dissipation factor. This character is well suited for making printed circuit boards in electronic industries.[3-5] Radar transparency, low moisture absorption,[6] very good adhesive character towards metal and high mechanical strength[7-10] make cyanate esters more reliable for high end applications in aerospace industries. However, the cured CE is inherently brittle in nature and easily undergoes micro cracking under service loads. The fracture toughness of cyanate esters can be improved by blending with thermoplastic tougheners, rubber,[11] organic and inorganic fillers,[6, 12] POSS[13-15] and thermosetting resins such as epoxy[16-20], imides[21-24] and benzoxazines.[25-26]

Commercially available cyanate ester, Bisphenol A dicyanate ester (BADCY) is being widely used in various fields, but further modification is required to enhance its properties in performance and reduction of cost in production. The thermo oxidative stability and moisture resistance were improved by introducing silicon atom in BADCY.[27] On the addition of epoxy resin into the BADCY resin, mechanical and hot–wet properties were improved when the concentration ranges from 5 to 30 wt %[20]. 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[27] with superior dimensional stability. They undergo micro cracking, which makes them unfit for their requirement for high toughness applications (in engineering industries). Another disadvantage of epoxy resins is their moisture absorption.

Azomethine functionalized cyanate ester with shorter alkyl chain was prepared earlier, [28, 29] in this study, dicyanate esters with azomethine linkages and different alkyl chains with ether linkages were prepared and the effect of alkyl chain length between two aromatic groups on thermal stability has been studied. The prepared cyanate esters were blended with epoxy resin in

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three different weight percentages. Thermal and thermo mechanical properties of the CE/epoxy blends were investigated by using thermo gravimetric analyzer (TGA) and dynamic mechanical analyzer (DMA). The morphology of the system was studied by scanning electron microscopy techniques (SEM).

## 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). Diglycidyl ether of bisphenol-A (DGEBA) was purchased from Huntsman (India). Diaminodiphenylmethane was purchased from Acros Organics (India). Ethanol and triethylamine ($Et_3N$) were purchased from Merck (India). All reagents were used as received. Triethylamine and acetone were distilled prior to use.

### *2.2. Measurement*

Fourier transform infrared (FT-IR) spectra were recorded in ABB Bomem MB series FT-IR spectrometer using 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 $CDCl_3$ and DMSO-$d_6$ solution. Melting temperatures were determined with a melting point apparatus IA 6304 at a heating rate of 4 °C/ min. Differential scanning calorimetric analysis (DSC) for curing studies was carried out using Perkin Elmer DSC 7 model at a heating rate of 5 °C/min under air atmosphere using aluminum pans. Thermo gravimetric analysis (TGA) was performed using a Perkin Elmer Diamond series model at a heating rate of 10 °C/min under flowing air in the range of 25-800 °C.

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

4-acetamidophenol (5.0g, 0.0330mol) and 10.26 g of potassium carbonate (0.0742mol) in 100 mL of acetone were taken in a 250 mL round bottomed flask. To this 1, 4-dibromobutane (3.5708g, 0.0165mol) 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 °C overnight. The mixture was cooled and poured into water (1000 mL). The white precipitate formed was separated and

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recrystallized from ethanol.[30] Yield 89%, M.P.: 190 °C. IR (KBr, $cm^{-1}$): 3336 (CONH), 1053 (-C-O-C-), 1675 (C=O), 824 (p-substituted aromatic).

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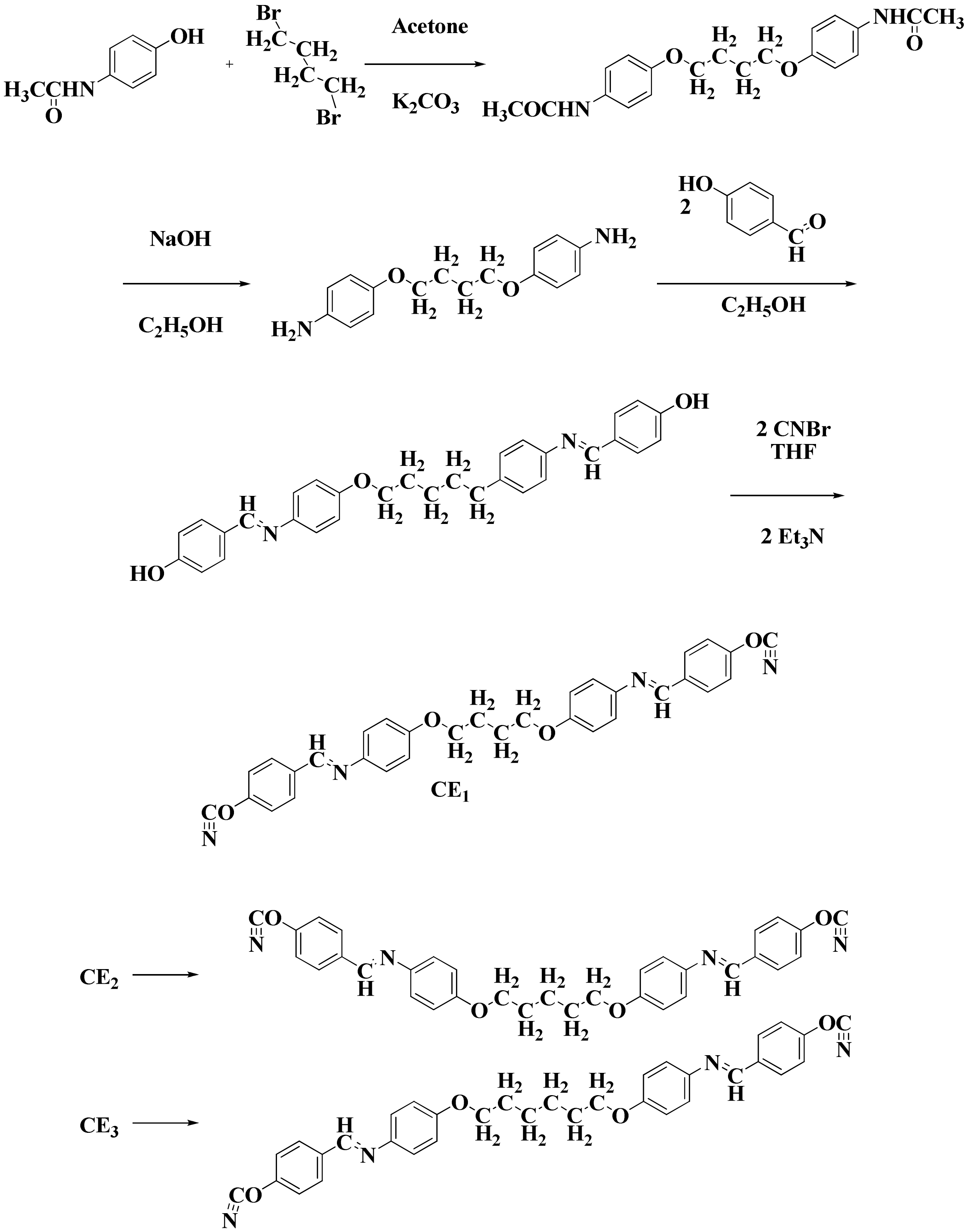

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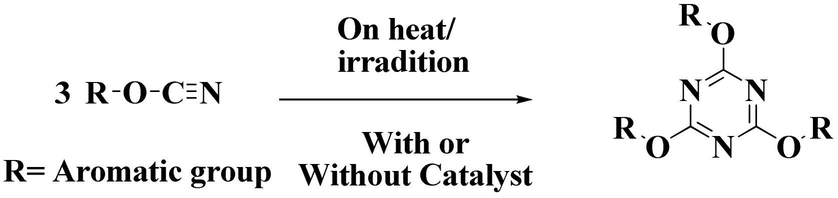

Scheme 1. Synthesis of dicyanate ester monomer

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

1, 4-Bis (4-acetamidophenoxy) butane (4.0g, 0.0112 mol) in 100mL ethanol was taken in a 250 mL round bottomed flask. To this, 10.0g of sodium hydroxide (0.25mol) dissolved in water (35 mL) was added drop wise. After completion of the addition, the mixture was refluxed at 80 °C for 8 hr, 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 °C. FT-IR (KBr, $cm^{-1}$): 3395, 3371 (aromatic $NH_2$), 2945 ($OCH_2$), 835 (p-substituted aromatic). $^{1}$H-NMR (500 MHz, $CDCl_3$, ppm): 3.7 (s, 4H, a (Ar-N$\underline{H_2}$)), 6.6 (d, 4H, b), 7.2 (d, 4H, c), 3.8 (t, 4H, d (OC$\underline{H_2}$$CH_2$)) 1.8 (m, 4H, e ($OCH_2$C$\underline{H_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. Other two diamines were prepared in a similar way.

### *2.5.1. Synthesis of 1, 4-Bis [4(4-hydroxyphenylazomethyl)phenoxy] butane*

1,4-Bis (4-aminophenoxy) butane (2.750g, 0.01 mol) was taken in a 250 mL round bottomed flask with 100 mL of ethanol and refluxed until it gets completely dissolved in ethanol. To this 2.4662g 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 hr. 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 °C. FT-IR (KBr, $cm^{-1}$): 3380 (OH), 2943 ($OCH_2$), 1680 (HC=N), 834 (p-substituted aromatic). $^{1}$H-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.

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### *2.5.2. 1,5-Bis[4(4-hydroxyphenylazomethyl)phenoxy]pentane*

Yield: 83%, M.P.: 90 °C. FT-IR (KBr, cm$^{-1}$): 3414 (OH), 2945 ($OCH_2$), 1688 (HC=N), 836 (p-substituted aromatic). $^1$H-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.

### *2.5.3. 1,6-Bis[4(4-hydroxyphenylazomethyl)phenoxy]hexane*

Yield: 91%, M.P.: 109 °C. FT-IR (KBr, cm$^{-1}$): 3342 (OH), 2932 ($OCH_2$), 1676 (HC=N) 839 (p-substituted aromatic). $^1$H-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.

### *2.6. 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 3.5g of the bisphenol (1,4-Bis[4(4-hydroxyphenylazomethyl)phenoxy]butane) (0.0114mol). The flask was maintained at -15 °C and then a solution of 2.3g (0.0228mol) of CNBr in acetone (50 mL) was added with constant stirring. To this mixture, 3.1 mL (0.0228mol) of triethyl amine was added in drops with continuous stirring. After complete addition of triethyl amine, the reaction mixture was stirred for a further period of 2 hr, while maintaining the bath temperature at -15 °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.

### *2.6.1. 1,4-Bis[4(4-cyanatophenylazomethyl)phenoxy]butane ($CE_1$)*

Yield: 91%, M.P.: 91 °C. FT-IR (KBr, cm$^{-1}$): 2198, 2212 (OCN), 2945 ($OCH_2$), 1681 (HC=N), 834 (p-substituted aromatic). $^1$H-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). $^{13}$C-NMR (500 MHz,

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DMSO-$d_6$, ppm): $C^1$-109.1, $C^2$-156.8, $C^3$-115.9, $C^4$-131.1, $C^5$-135.9, $C^6$-159.9, $C^7$-143.3, $C^8$-122.6, $C^9$-116.8, $C^{10}$-156.3, $C^{11}$-67.8, $C^{12}$-28.7.

### *2.6.2. 1,5-Bis[4(4-cyanatophenylazomethyl)phenoxy]pentane ($CE_2$)*

Yield: 87%, M.P.: 99 °C. FT-IR (KBr, $cm^{-1}$): 2226, 2240 (OCN), 2942 ($OCH_2$), 1688 (HC=N), 835 (p-substituted aromatic). $^1$H-NMR (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). $^{13}$C-NMR (500 MHz, DMSO-$d_6$, ppm): $C^1$-109.5, $C^2$-155.8, $C^3$-116.5, $C^4$-131.1, $C^5$-135.8, $C^6$-161.1, $C^7$-144.1, $C^8$-121.9, $C^9$-115.1, $C^{10}$-157.1, $C^{11}$-68.9, $C^{12}$-29.6, $C^{13}$-22.1.

### *2.6.3. 1,6-Bis[4(4-cyanatophenylazomethyl)phenoxy]hexane ($CE_3$)*

Yield: 93%, M.P.: 123 °C. FT-IR (KBr, $cm^{-1}$): 2219, 2242 (OCN), 2938 ($OCH_2$), 1680 (HC=N), 838 (p-substituted aromatic). $^1$H-NMR (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). $^{13}$C-NMR (500 MHz, DMSO-$d_6$, ppm): $C^1$-109.4, $C^2$-156.3, $C^3$-116.2, $C^4$-131.9, $C^5$-135.1, $C^6$-160.1, $C^7$-143.8, $C^8$-121.8, $C^9$-115.7, $C^{10}$-157.9, $C^{11}$-68.5, $C^{12}$-29.6, $C^{13}$-25.9.

### *2.7. Preparation of cyanate ester /epoxy blends*

1 wt. % of cyanate ester (0.200g) was taken with 99 wt. % of epoxy resin (19.80g) (cyanate ester: epoxy = 1:99) and stirred at 80 °C until the mixture turns homogeneous. 5.346 g (27 g of DDM taken for 100 g epoxy resin) amount of DDM (hardener) was added to the homogeneous mixture of cyanate/epoxy resin and immediately, the mixture was transferred to the mold and cured at 120 °C for 1 hr, 170 °C for 1 hr and post cured at 210 °C for 1 hr. The same procedure was adopted for the preparation of Cyanate ester + epoxy blends with 3% and 5% of cyanate ester.

## *3. Results and Discussion*

The synthetic procedure for the preparation of dicyanate esters are presented in Scheme 1. The bisphenol precursors were prepared by the condensation reaction between aromatic aldehydes and diamine. The structure of the bisphenols was confirmed by FT-IR, $^1$H-NMR, and $^{13}$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 dicyanate esters. The

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appearance of new bands at around 1680 cm$^{-1}$ and disappearance of amine bands (around 3300-3400 cm$^{-1}$) confirmed the formation of azomethine. The appearance of new bands at 2174-2240 cm$^{-1}$ and disappearance of the band at 3300-3500 cm$^{-1}$ due to hydroxyl group in the FT-IR spectrum confirms the conversion of hydroxyl group into dicyanate ester. The formation of -C-O-C linkage is confirmed by the presence of band at 1050 to 1070 cm$^{-1}$. [30] The signal at 3.7ppm 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 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 cyanate ester carbon at 109.1 ppm[13] from the NMR spectra. 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 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 $^{13}$C-NMR spectrum, the carbon atoms in azomethine linkage of the three cyanate esters show the chemical shift 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.

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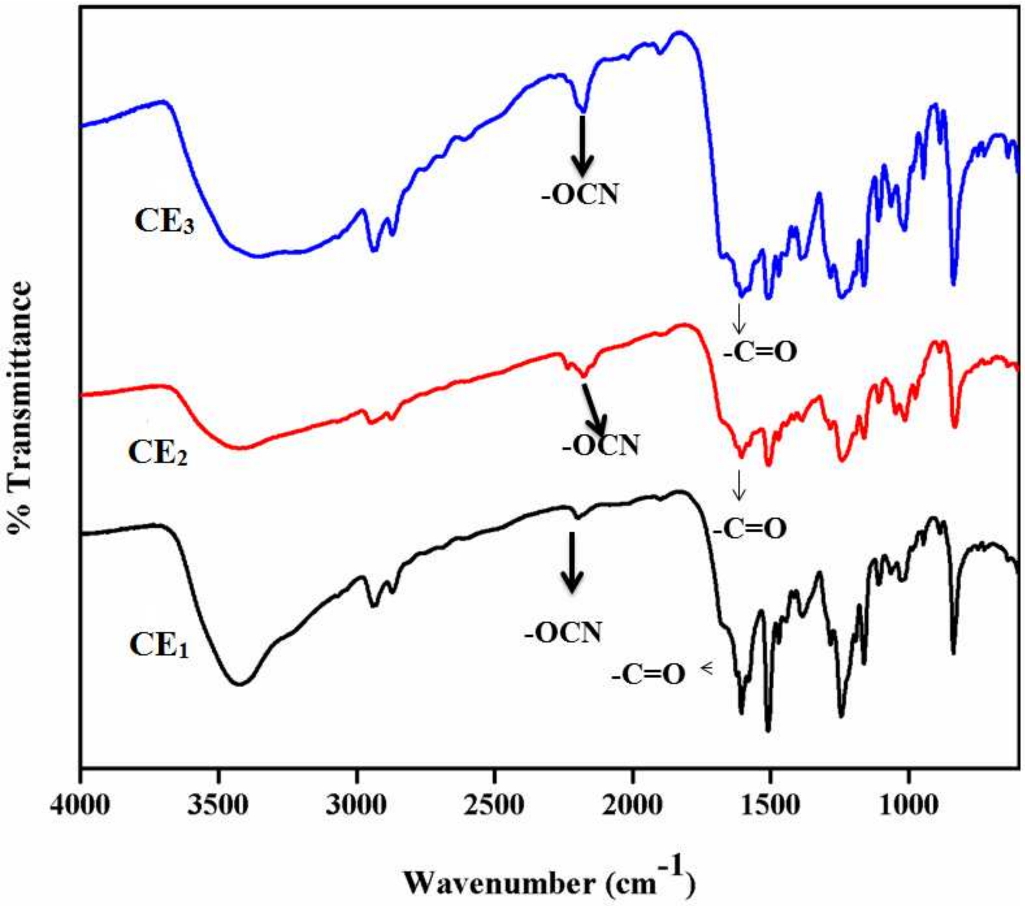

**Figure 1. FT-IR spectrum of cyanate ester $CE_1$, $CE_2$ and $CE_3$.**

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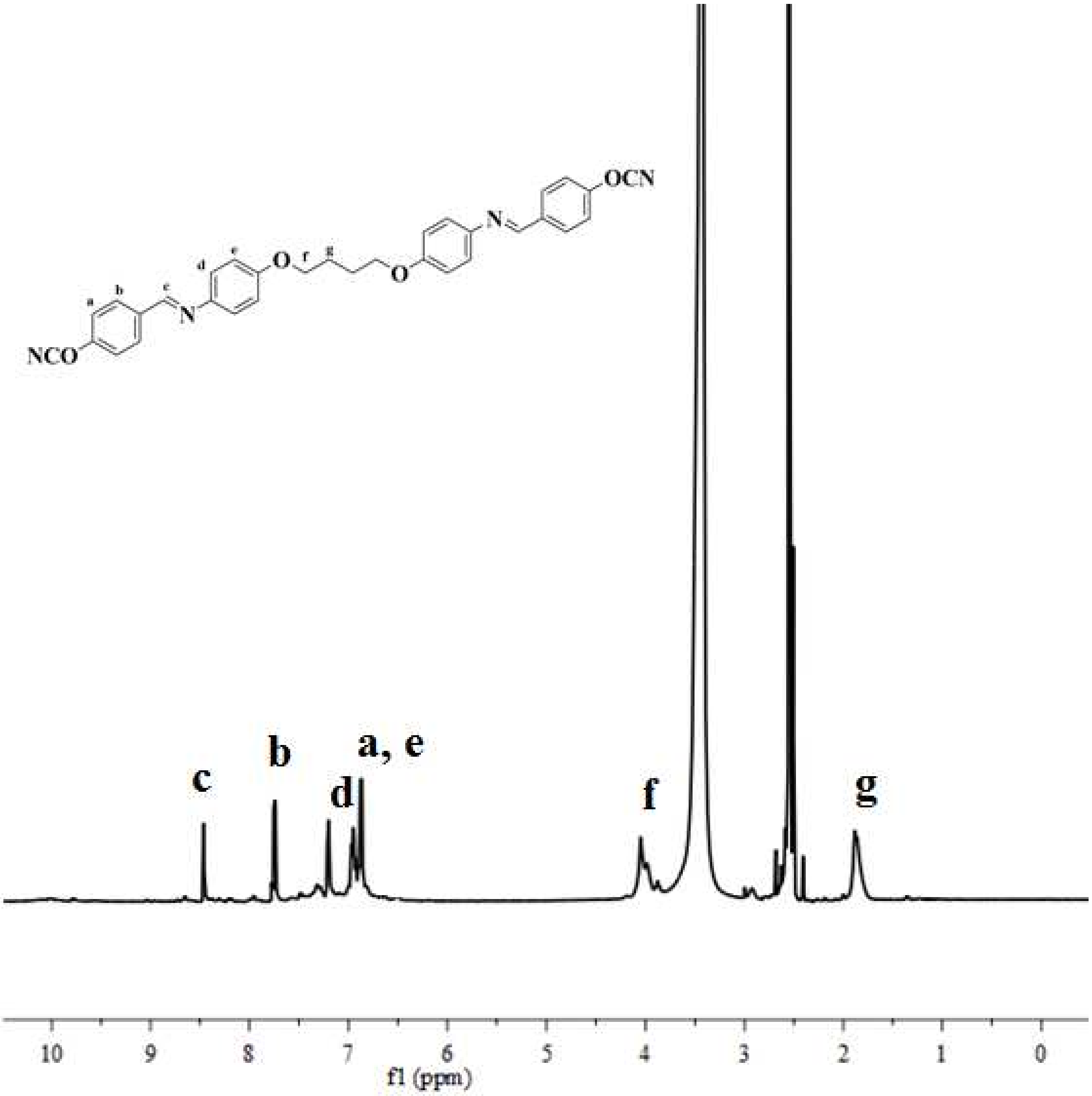

**Figure 2.** $^{1}$H-NMR spectrum of cyanate ester (4,4'-(butane-1,4-diylbis(oxy))bis(N-(4-cyanatobenzylidene)aniline)) (CE$_1$)

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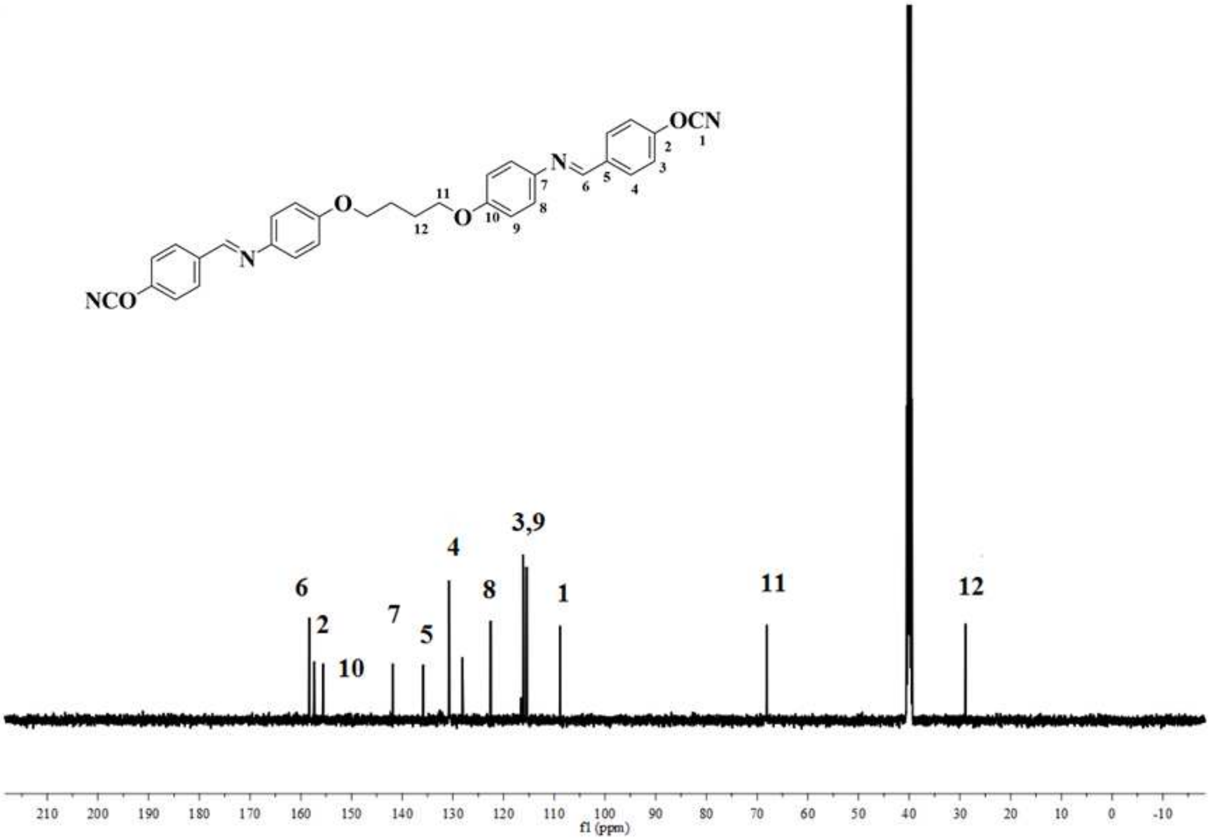

**Figure 3.** $^{13}$**C-NMR spectrum of cyanate ester (4,4'-(butane-1,4-diylbis(oxy))bis(N-(4-cyanatobenzylidene)aniline)) (CE$_1$)**

### *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$_1$, CE$_2$ and CE$_3$ are shown in Fig. 4$_a$, 4$_b$ and 4$_c$ and the data are given in Table 1. The melting points of the dicyanate esters were found to be 91, 99 and 123 $^o$C respectively. The initial (T$_i$) and maximum curing temperatures (T$_{max}$) were found to be in the range of 143 to 181 $^o$C and 202 to 242 $^o$C respectively. The cyanate ester CE$_3$ (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 $^o$C. The dicyanate ester CE$_1$ (1, 4-Bis [4(4-cyanatophenylazomethyl)phenoxy] butane) showed the highest end cure temperature of 285 $^o$C. The curing temperature of BADCY is found to be at 281 $^o$C [2] and all the three synthesised cyanate ester were cured at lower temperature when compared

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with BADCY. The cyanate ester ($CE_1$) with shortest alkyl chain between the aromatic groups was found to cure at the lowest temperature. Glass transition temperature of the neat cured dicyanate ester was decreases with increase the alkyl chain length between two aromatic groups. No liquid crystallinity was observed for all the dicyanate esters.

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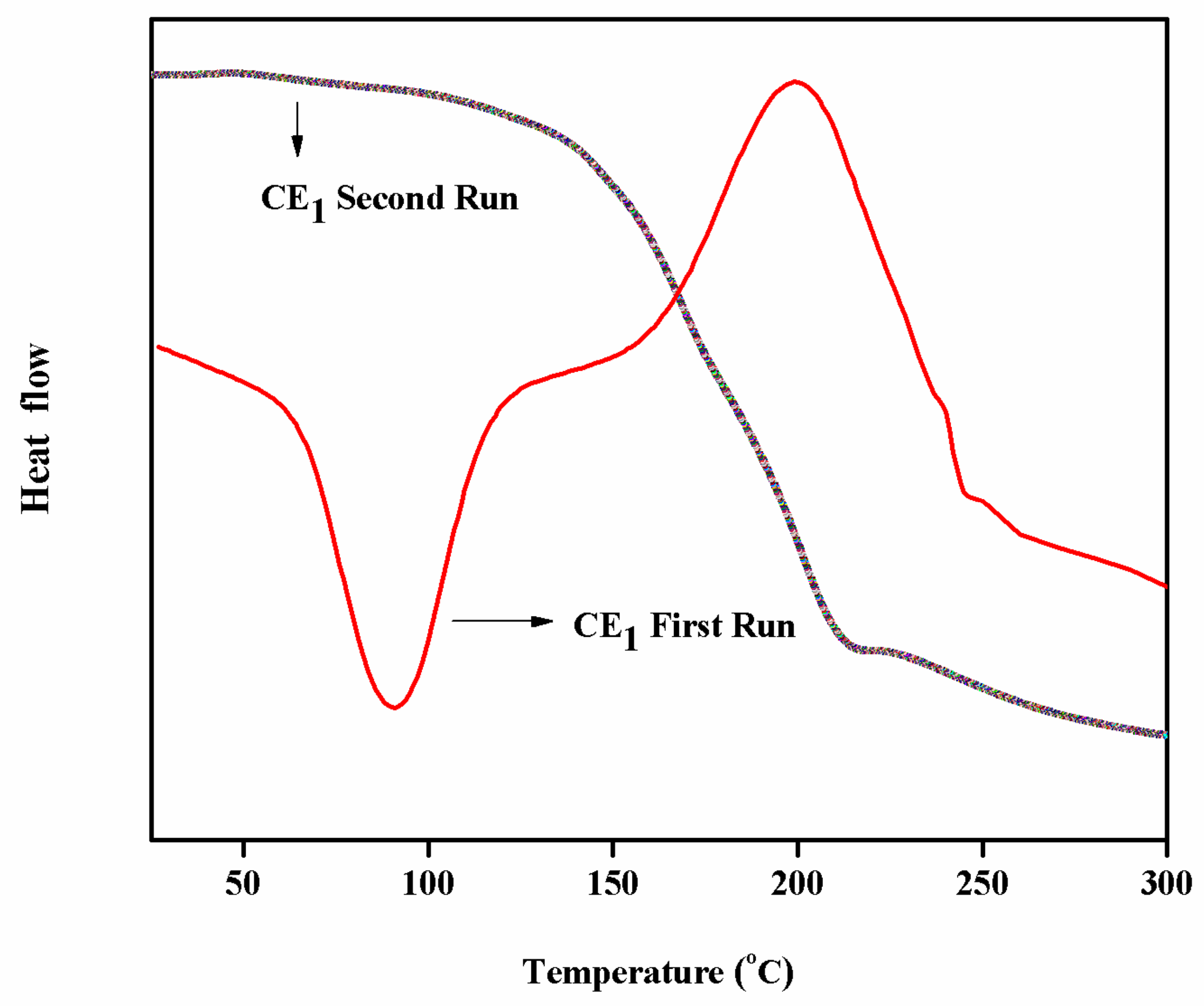

**Figure $4_a$. DSC thermogram data of cyanate ester ($CE_1$)**

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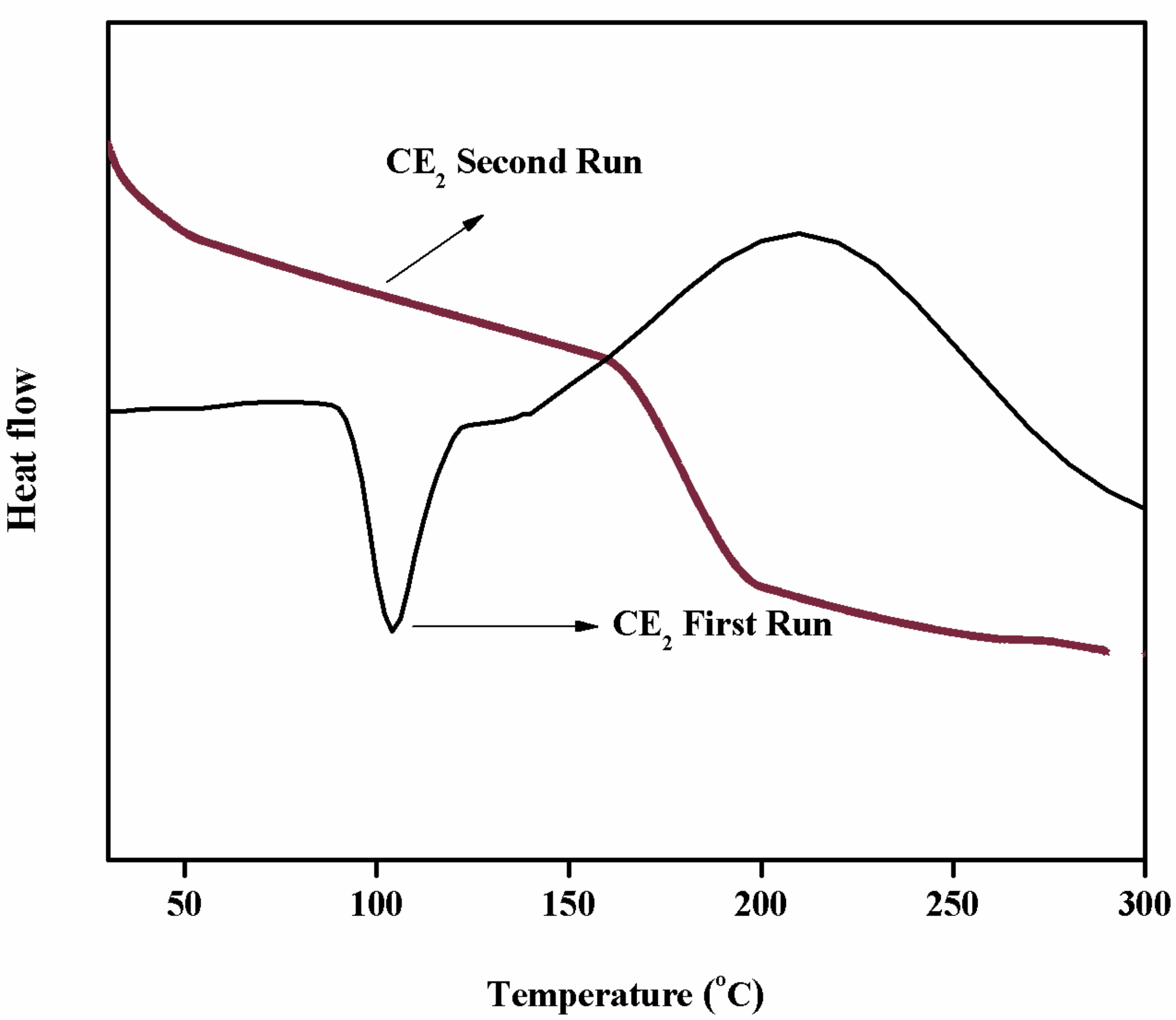

Figure $4_b$. DSC thermogram data of cyanate ester ($CE_2$)

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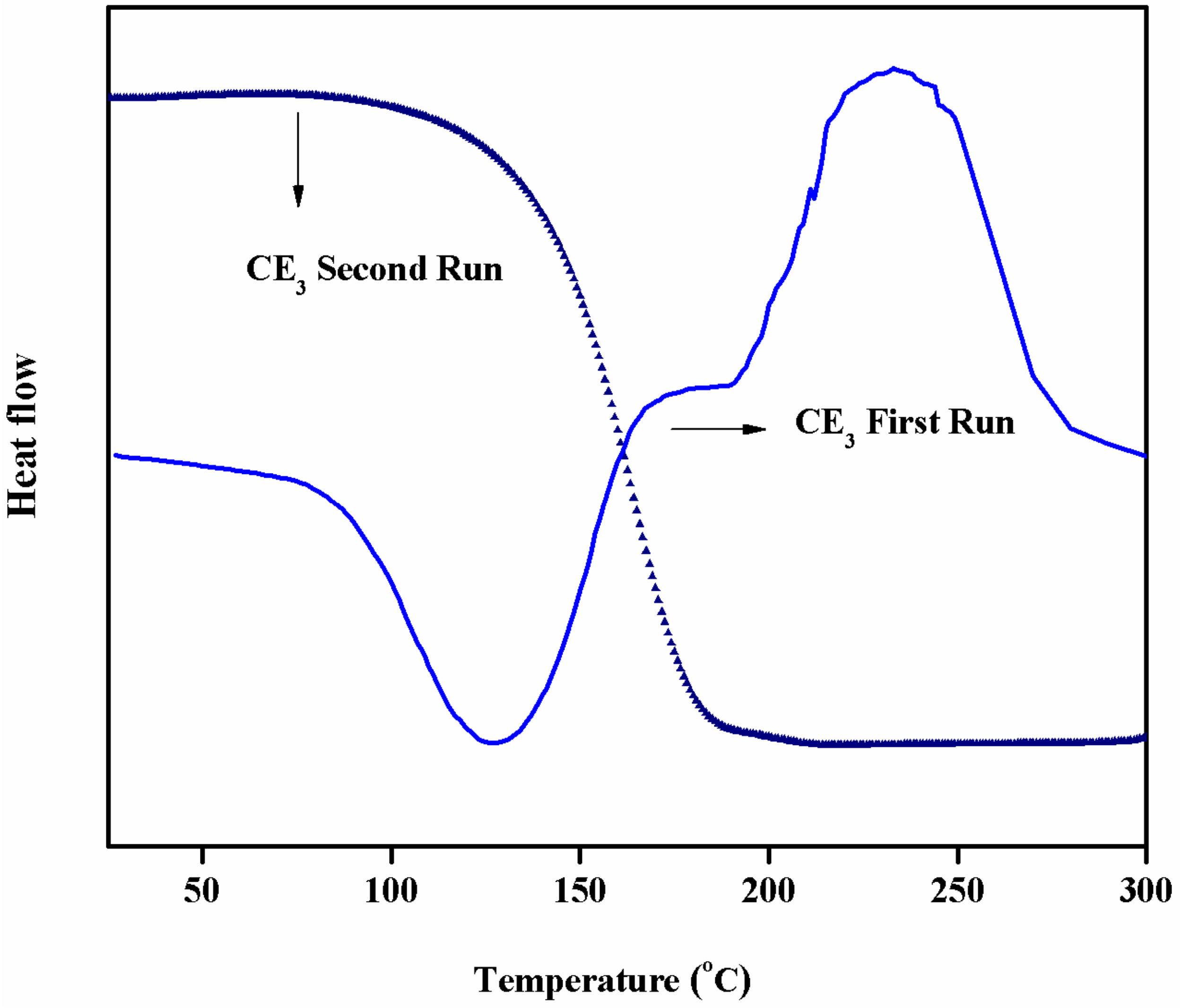

Figure $4_c$. DSC thermogram data of cyanate ester ($CE_3$)

Table 1. DSC data of the cyanate ester

| Sample Code | Melting Point (°C) | Onset of Cure (°C) | Maximum Cure (°C) | End of Cure (°C) |
|---|---|---|---|---|
| $CE_1$ | 91 | 148 | 203 | 285 |
| $CE_2$ | 102 | 143 | 216 | 246 |
| $CE_3$ | 123 | 181 | 242 | 269 |

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### *3.2. Thermogravimetric Analysis*

Thermo gravimetric 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 ($T_{5\%}$), 10% weight loss temperatures ($T_{10\%}$) and the char yield at 800 ºC. The TGA curves of various cured cyanate esters are given in the Fig. 5 and the data are given in Table 2. $T_{5\%}$ and $T_{10\%}$ of all the three neat cured cyanate esters found to be in the range of 358 to 465 ºC and 508 to 525 ºC respectively. The cured cyanate ester ($CE_2$) having alkyl chain length of five shows the least thermal stability ($T_{5\%}$ - 358 ºC) and it lost 40% weight between 520 to 593 ºC. The char yield was found to be in the range of 37.06 to 57.26 %. The cyanate ester having even number ($CE_1$ and $CE_3$) of alkyl chain length between two aromatic groups shows more stable than the dicyanate ester having odd number ($CE_2$) of spacer length between two aromatic groups from char yield and LOI values. Char yield of BADCY is found to be 42.5 at 800 ºC [2], but char yield of $CE_1$ and $CE_3$ show higher char yield of 57.26 and 48.08 compared to commercially available dicyanate ester (BADCY). The cured cyanate ester having least alkyl chain length between two aromatic groups shows 5% weight loss at 465 ºC. This is greater than that of other two cured cyanate ester. The 5 weight % of CE/epoxy blends show the 10% ($T_{10\%}$) weight loss temperature in the range of 392-410 ºC and char yield in the range of 24.11 to 31.26 %. There are also reports by other authors that the thermal stability and char yield of cyanate ester/epoxy blend increases with increase of cyanate ester concentration in epoxy blends which is similar to our case[13].

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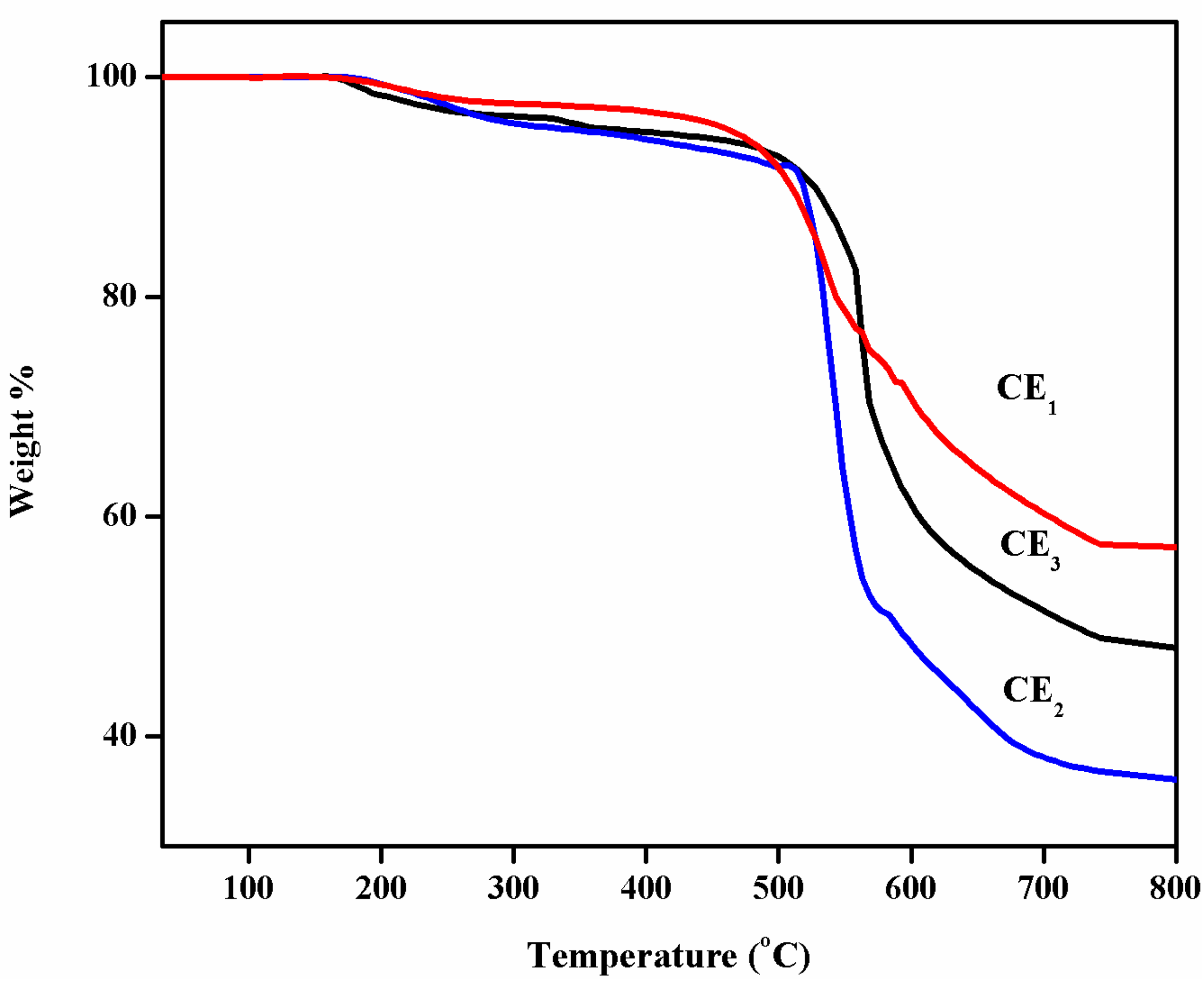

Figure 5. TGA thermogram data of cyanate ester

**Table 2. TGA data of Polycyanurates**

| Sample Code | $T_5$ (°C) | $T_{10}$ (°C) | Char Yield % | LOI |
|---|---|---|---|---|
| $CE_1$ | 465 | 508 | 57.26 | 40.40 |
| $CE_2$ | 358 | 520 | 37.06 | 32.32 |
| $CE_3$ | 399 | 525 | 48.08 | 36.73 |

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| | | | | |
|---|---|---|---|---|
| **Neat Epoxy** | **363** | **369** | **18.0** | **24.7** |
| **5% $CE_1$ + 95% Epoxy** | **393** | **410** | **31.26** | **30.00** |
| **5% $CE_2$ + 95% Epoxy** | **378** | **392** | **24.11** | **27.14** |
| **5% $CE_3$ + 95% Epoxy** | **381** | **395** | **27.80** | **28.62** |

$T_5$ = 5% weight loss temperature

$T_{10}$ = 10% weight loss temperature

LOI = Limiting oxygen index

### *3.3. SEM Analysis*

The cross-section (fracture surface) of CE/epoxy blend 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. Figs. 6 (a, b and c) display the SEM images of cured neat cyanate ester $CE_1$, 1% cyanate ester + 99 % epoxy and 5% cyanate ester + 95 % epoxy respectively. The SEM images of the fractured surface of the $CE_2$ and $CE_3$ are given in figures 6 (d) and (e) respectively. $CE_1$ shows the curved hollow structure, $CE_2$ and $CE_3$ shows layered structure (on both lower and higher magnification). SEM images b and c illustrate the uniform distribution of the cyanate ester in the epoxy blends without any void. The DMA results show that toughening of epoxy was effected by adding CE. The neat $CE_2$ have similar morphology to poly cyanurate of bisphenol A dicyanate ester. [31]

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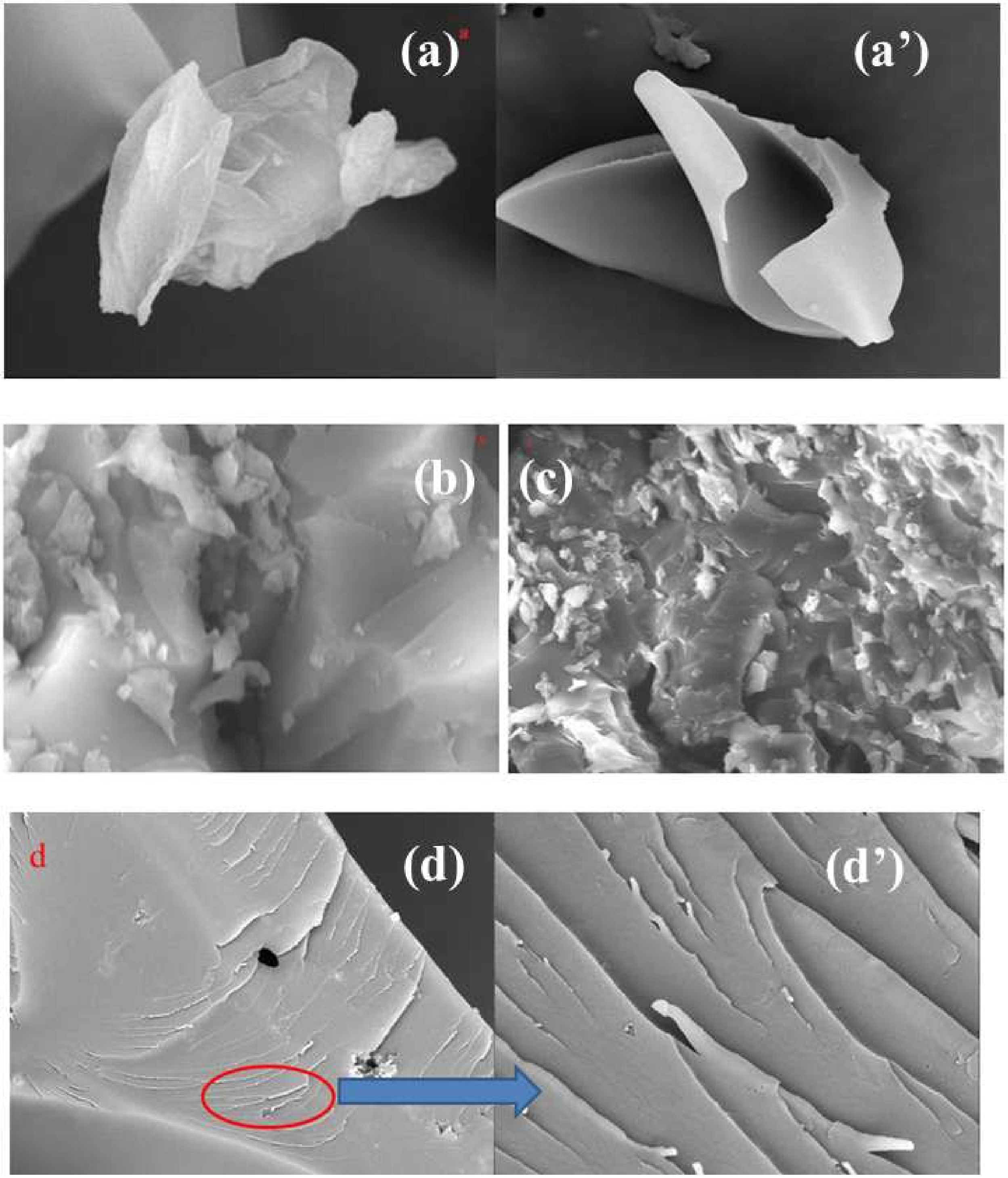

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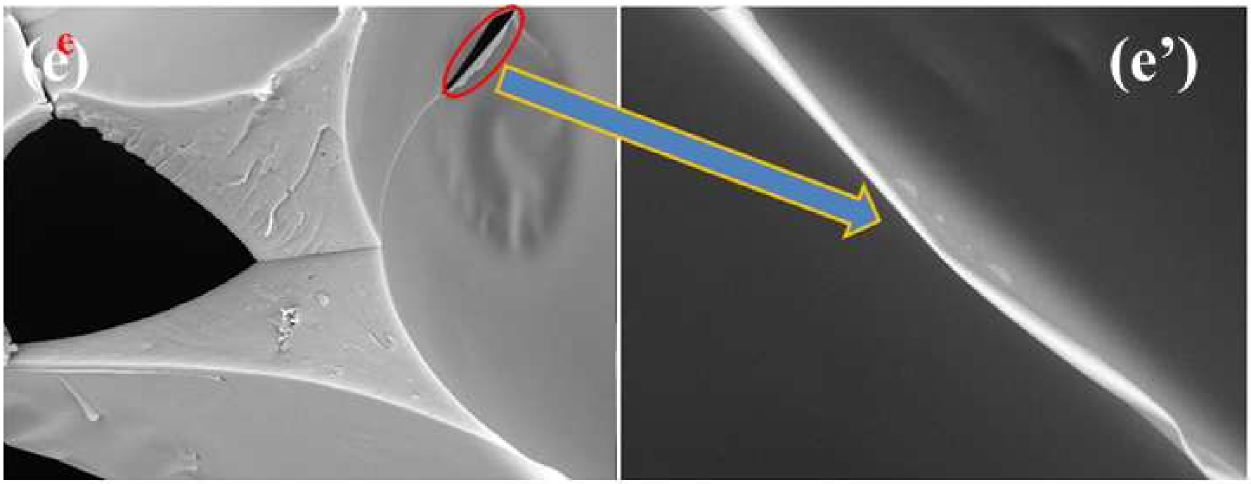

**Figure 6. SEM images of (a) neat cyanate ester CE$_1$, (b) 1% Cyanate ester CE$_1$ + 99 % epoxy sytem and (c) 5% Cyanate ester CE$_1$ + 95 % epoxy sytem, (d) neat cyanate ester CE$_2$ and (e) neat cyanate ester CE$_3$.**

### *3.4. Dynamic Mechanical Analysis (DMA)*

Dynamic mechanical properties (Stress relaxation behavior) were measured for the CE/epoxy blend systems in order to find out the effect of increase of 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 the figures 7 and 8 respectively. The data obtained from DMA scans are furnished in Table 3. Storage modulus of the CE/epoxy blend increases with increase in the cyanate ester content (from 1 to 5% except 1% of CE$_1$/epoxy blend). The increase in storage modulus may be due to the increased cross-linking density of the blends as a result of increase in the CE content. Glass transition temperature of pure epoxy system was found to be 161 $^{o}$C [13]. In the case of 1% CE$_1$ epoxy blend, the glass transition temperature was decreased to 158 $^{o}$C from 161 $^{o}$C for the neat cured epoxy. But on further addition of 5% CE$_1$ to the epoxy resin, the glass transition temperature was increased to 180 $^{o}$C from 161 $^{o}$C. The glass transition temperature of the blends slightly increases with increase in the cyanate ester content. This observation proves the fact that the co-reaction of cyanate ester with epoxy resin is almost complete with homogeneous state [14] and the resultant oxazolidinone network [25] which enhance the thermal and mechanical property of the CE/epoxy blends. But some of the authors reported that the addition of POSS-CY in epoxy resin, leads to a decrease in the glass transition temperature from 161 to 155 due to the formation of the free volume in cyanate/epoxy blend system.[13]

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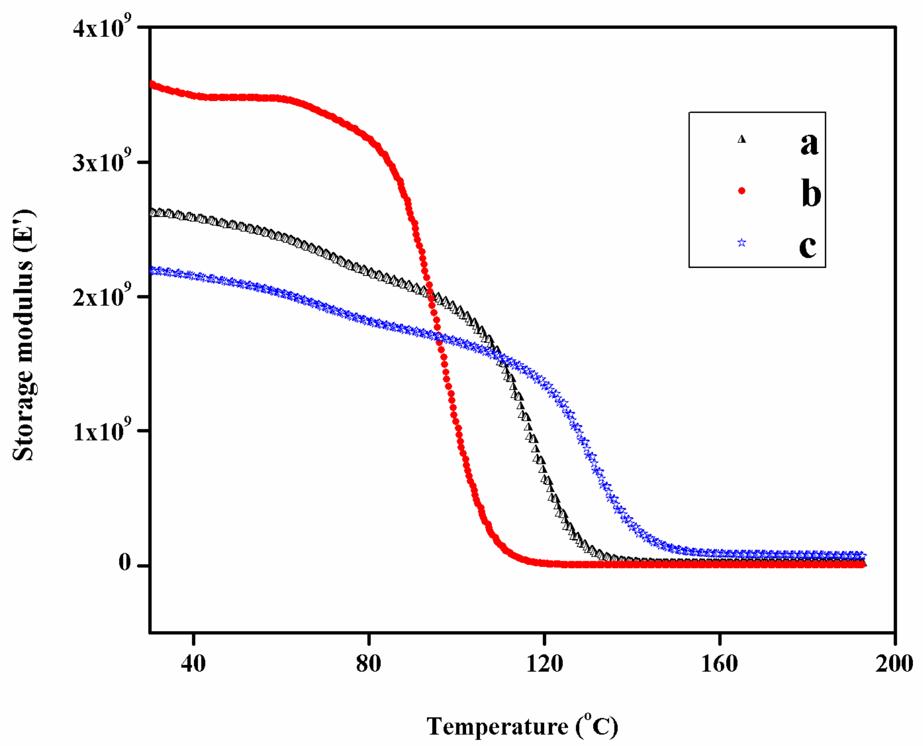

**Figure 7.** **DMA analysis showing storage modulus (*E´*) of the CE/Epoxy blends: a) 5% of $CE_1$ + 95 % epoxy, b) 5% of $CE_2$ + 95 % epoxy, c) 5% of $CE_3$ + 95 % epoxy.**

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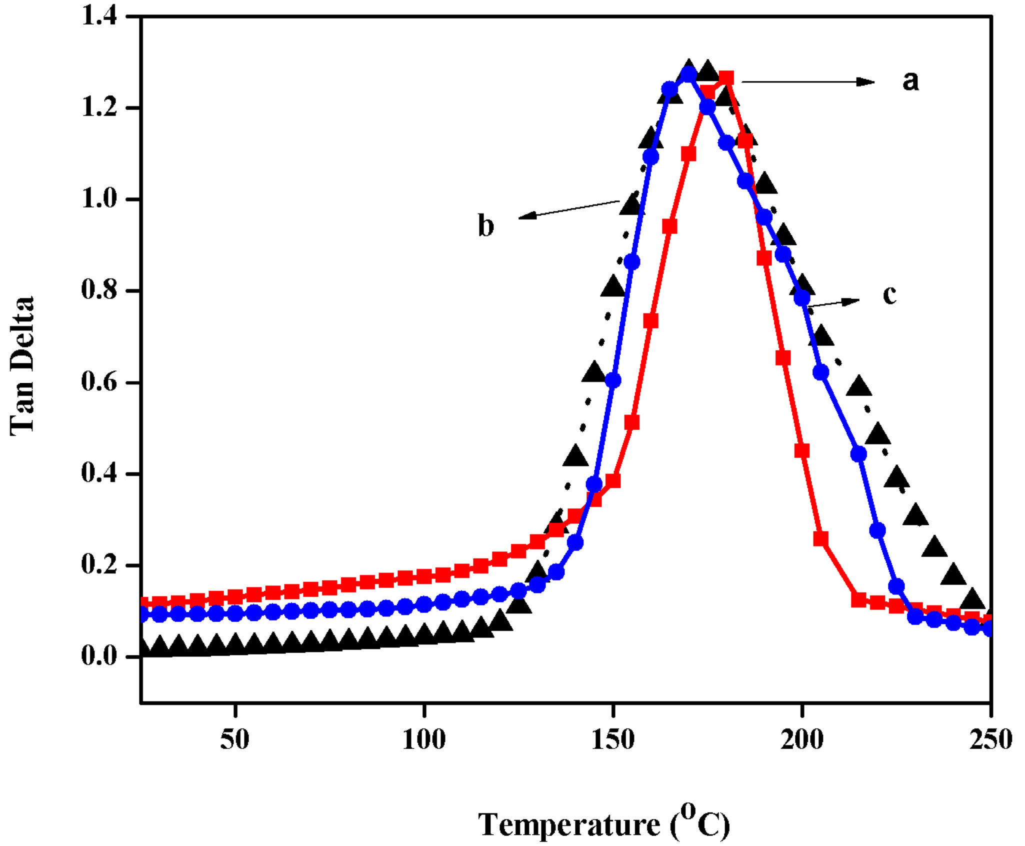

**Figure 8. DMA analysis showing loss modulus of the CE/Epoxy blends: a) 5% of CE$_1$ + 95 % epoxy, b) 5% of CE$_2$ + 95 % epoxy, c) 5% of CE$_3$ + 95 % epoxy.**

### *3.5. Crosslink density*

The crosslink density or concentration of network chain ($\nu_e$), is the number of moles of network chains per unit volume of the cured polymers. Crosslink density of highly crosslinked thermosets can be determined by modulus measurements in the rubbery plateau by using the equation of state for rubber elasticity[32] as

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

where,

E′ = tensile storage modulus in the rubbery plateau

T = temperature in K corresponding to the storage modulus value

R = gas constant

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Table 3 shows the crosslink density of the CE/Epoxy blends. On addition of cyanate ester to the epoxy resin, the cross link density was increased. The $CE_2$ epoxy blends show the highest cross link density. The storage modulus of $CE_2$ blends (3.48 GPa, having odd number of alkyl chain length between aromatic groups) is higher compared to CE/epoxy blends (having even number of alkyl chain length between two aromatic groups) of $CE_1$ (2.52 GPa) and $CE_3$ (2.09 GPa).

**Table 3. Values of crosslink density of CE + Epoxy blends**

**(from DMA values).**

| Sample Code | CE % | E´ (GPa) | Temp k (273+50) | Cross link density $\nu_e \times 10^5$ (mol m$^{-3}$) |
|---|---|---|---|---|
| **$CE_1$ + 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 |

### *3.6. Flame Retardancy*

The resistance towards fire of CEs and CE/epoxy blends are expressed in terms of limiting oxygen index (LOI). LOI may be defined as the minimum fraction of oxygen in a mixture of $O_2$ and $N_2$ during fire. The LOI value should be higher than that of threshold value (value 26) for the polymer to behave as a self-extinguishing material or self-extinguisher. The LOI value is calculated by using Krevelen's equation.[33]

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

where σ 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 least alkyl space length ($CE_1$) shows the highest LOI value and the cyanate ester ($CE_2$) with alkyl chain having five carbons shows the lowest LOI value. The LOI values of all the cured dicyanate esters indicate that they are very good fire retardant materials. From the

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LOI values, it was found that the cured cyanate ester $CE_1$/epoxy blends show the best flame retardance.

## Conclusions

Dicyanate esters with azomethine linkage were successfully synthesised. The structure of the monomers and precursors were characterized by FT-IR, $^1$H-NMR and $^{13}$C-NMR spectroscopy, which clearly confirms the molecular structure. The morphology of the cured cyanate ester and CE/epoxy blends reveal the uniform distribution of cyanate ester in the epoxy resin. The cured cyanate ester and BADCY show the similar morphology. The DMA studies revealed that the glass transition temperature of epoxy was increased from 161 to 180 $^oC$ and storage modulus of the epoxy resin increases with increase in cyanate ester content. The crosslink density of the cyanate epoxy blends are calculated from the storage modulus value, which increases (from 3.98 to 4.32mol/m$^3$ for $CE_2$) with increase in the weight ratio of CE in the blends. TGA results show that the char yield values of neat cyanate esters are in the range of 32.32 to 40%. The char yield increases with increase of CE content in the epoxy blend from 18 % to 30.0 %. 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 (because $CE_1$ and $CE_3$ having even number of alkyl chain length between two aromatic rings showing better char yield and LOI values compared to $CE_2$ which is having odd number of alkyl chain between two aromatic rings.) between the two aromatic groups will be studied in future.

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