

Synthesis, Cure Kinetics, and Thermal Properties of the Bis(3-allyl-2-cyanatophenyl)sulphoxide/BMI Blends

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Received 16 September 2007; accepted 24 April 2008

DOI 10.1002/app.28638

Published online 9 July 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A novel allyl functionalized dicyanate ester resin bearing sulfoxide linkage was synthesized. The monomer was characterized by Fourier Transform Infrared (FT-IR) Spectroscopy, ¹H-, and ¹³C Nuclear Magnetic Resonance (NMR) spectroscopy and elemental analysis. The monomer was blended with bismaleimide (BMI) at various ratios in the absence of catalyst. The cure kinetics of one of the blends was studied using differential scanning calorimetry [nonisothermal] and the kinetic parameters like activation energy (*E*), pre-exponential factor (*A*), and the order of the reaction (*n*) were calculated by Coats-Redfern method and compared with those calculated using the ex-

perimental Borchardt-Daniels method. The thermal stability of the cured dicyanate, BMI, and the blends was studied using thermogravimetric analyzer. The initial weight loss temperature of dicyanate ester is above 380°C with char yield of about 54% at 800°C. Thermal degradation of BMI starts above 463°C with the char yield of about 68%. Inclusion of BMI in cyanate ester increases the thermal stability from 419 to 441°C. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 517–522, 2008

Key words: sulfoxide allyl cyanate; BMI; cure kinetics; differential scanning calorimetry; thermal properties

INTRODUCTION

During the 1990s, aromatic cyanate esters have emerged as a new class of thermosetting resins for use as matrices for advanced composites in both the aerospace and electronics industries (Ref. 1 and references cited there in). Being derived by the cyanation of hydroxyl containing compounds, a variety of backbone structures have been studied.^{2–11} These have in turn imparted varying chemical, mechanical, and electrical properties and glass transition temperature. The chemical structure of the polycyanurate networks dictates the general performance that is observed in subsequent matrix usage. High aromatic content in the monomers and the network formed during cure are responsible for the high *T_g* (enhancing the service temperature in composite applications). They have inherently low smoke generation, good flame retardancy, and low moisture absorption. They have low crosslink density compared with epoxy and BMI and high free volume responsible for good toughness in terms of strain energy release rate and tensile elongation. The balanced dipoles in the cured state and absence of hydrogen bonding functionality are responsible for their low

dielectric properties. The dicyanate monomers melt at low temperatures and hence have good processability. These attributes make cyanates attractive as composite matrices and differentiate them from standard epoxy and BMI resins.

BMIs are probably the most important class of addition polyimides currently in use for advanced material applications, because of their performance-to-cost ratio. However, in common with other addition polyimides, unmodified BMIs suffer from brittleness because of their extensively high crosslink densities.^{12,13} One of the approaches to reduce crosslink density involves designing a material that undergoes crosslinking with the other resins.^{14–16} Allyl functionalized cyanate esters form “linked” interpenetrating networks (LIPNs) with BMI. Hence, in the present study, a new dicyanate monomer containing sulfoxide linkage and allyl functionalities were prepared. This monomer is expected to react with BMI through the allyl functional group and form linked IPNs.

Cure kinetics of the neat cyanate ester resins is extensively available in literature.^{17–24} But for blends, reports on the cure kinetics is scarce. With a view to generate such quantitative informations, a kinetic study of the allyl functionalized dicyanate with BMI is reported. Sulfoxide linked allyl cyanate ester was prepared and characterized. The kinetic parameters of the cure reaction of Cy/BMI blend were calculated (Coats-Redfern) and compared with the experimental method (Borchardt-Daniels).

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Contract grant sponsor: DST and CSIR, New Delhi, India.

Thermal stability of the cyanate ester, BMI, and the blends (all cured resins) are also reported.

EXPERIMENTAL

Materials

2-allyl phenol and thionyl chloride were purchased from Lancaster, Chennai, India. Cyanogen bromide (CNBr) was purchased from Spectrochem, Mumbai, India. Dichloromethane and acetone were purchased from SRL, Mumbai, India. Triethyl amine and anhydrous aluminum chloride were purchased from E-Merck, Mumbai, India. 1,1'-(methylene di-1,4-phenylene bismaleimide) was purchased from Abron organics, Hyderabad, India. Triethyl amine was distilled from CaH₂ and other materials were used as received unless it is stated.

Synthesis of Bis(3-allyl-2-hydroxyphenyl)sulfoxide [BAHS]

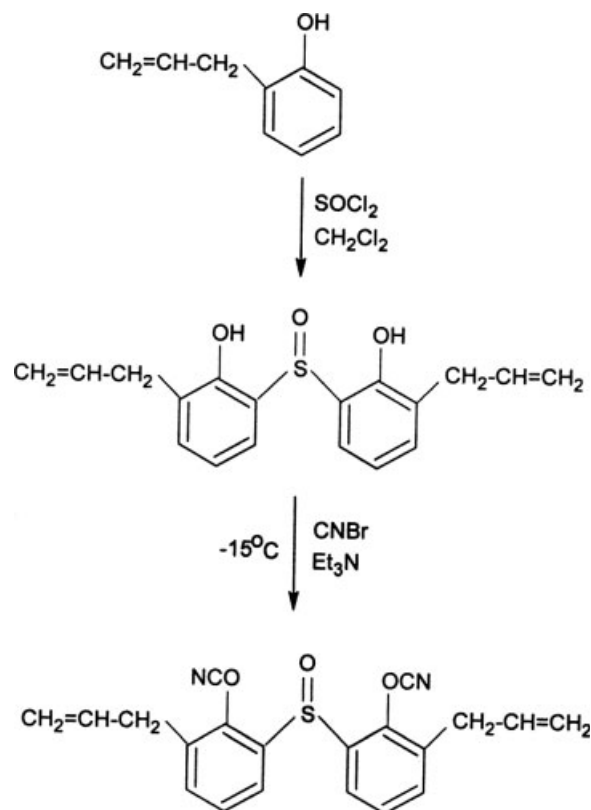
A 250 mL round bottomed flask equipped with addition funnel was charged with anhydrous aluminum chloride (0.03 mol, 4.86 g) and 50 mL of dichloromethane and stirred. The whole set-up was kept in an ice-bath. A 0.06 mol (9 g) of 2-allyl phenol was then added in small portions, and a solution of 5.87 g of thionyl chloride in 10 mL of dichloromethane was added in drops to the mixture over a period of 1 h. After the addition was over, the ice bath was removed and stirring was continued for 4 h. The mixture was allowed to stand overnight and then quenched with ice. The product obtained was extracted with diethyl ether. The ethereal fraction was washed repeatedly with water and solvent was then removed by rotary evaporation. The product was a dark brown liquid (Yield: 90%). The structure of the product was confirmed by FT-IR spectroscopy. The band at 3250–3500 cm⁻¹ may be assigned to O–H stretching. The band at 1640–1645 cm⁻¹ corresponds to C=C stretching vibration of allyl group. The band at 1030–1075 cm⁻¹ due to the S=O stretching vibration confirms the completion of the reaction.

Spot test

The sulfoxide formed a bright blue color solution with concentrated sulfuric acid. The coloration confirms the product formation.

Synthesis of dicyanate ester [Bis(3-allyl-2-cyanatophenyl)sulfoxide] (BACS)

The dicyanate was prepared as shown in Scheme 1. To a three necked 250 mL flask fitted with an overhead stirrer, thermometer, and dropping funnel, was added 75 mL of acetone (dried over fresh 4 Å molecular sieves for 1 day). After cooling to –10°C, 0.04



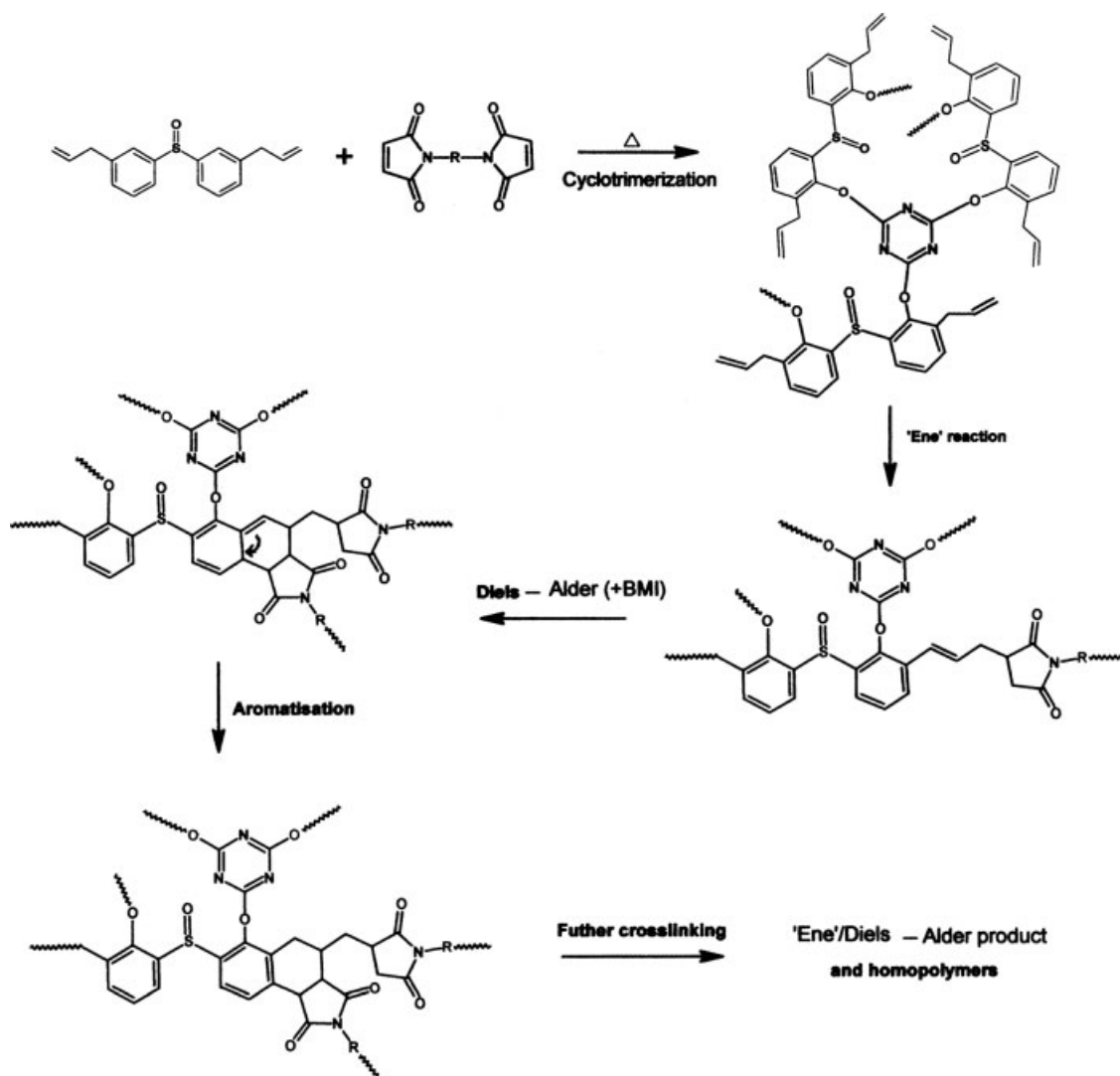
Scheme 1 Synthesis of BACS.

mol (5 g) of CNBr (caution: toxic!) was added and the solution was further cooled to –15°C. A solution of 0.02 mol (7.33 g) of BAHS and 0.02 mol (3.23 mL) of triethyl amine in 25 mL of acetone was prepared, transferred to a dropping funnel, and added drop wise with rapid stirring over a period of 30 min while maintaining a reaction temperature of –15°C. When the mixture had warmed to –2°C, it was rapidly filtered and the white ammonium bromide salt (Et₃N·HBr) was removed. The precipitate was washed further with 25 mL of acetone. The combined cold filtrate and the wash was diluted with 100 mL ice cold CH₂Cl₂, rapidly extracted once with 100 mL of cold distilled water and twice with 100 mL of cold 1% NaCl. The CH₂Cl₂ phase was dried over anhydrous Na₂CO₃. The clear CH₂Cl₂ solution was then distilled to yield a dark brown mass (Yield: 87%).

FT-IR (KBr cm⁻¹): 2236, 2272 (ν_{O-CN}); 1636–1645 (ν_{C=C}); 1030–1075 (ν_{S=O}); disappearance of O–H band at 3400–3500.

¹H NMR (CDCl₃, ppm): 7.03 (2H, d, H_a); 6.82 (2H, t, H_b); 6.73 (2H, d, H_c); 3.25 (4H, d, H_d); 6.03 (2H, m, H_e); 5.25 (4H, m, H_f). ¹³C NMR (CDCl₃, ppm): C₁ 145.1, C₂ 129.2, C₃ 130.9, C₄ 127.2, C₅ 127.8, C₆ 153.6, C₇ 27.3, C₈ 136.7, C₉ 114.6, C₁₀ 109.3.

Elemental Analysis: M.F. C₂₀H₁₆N₂O₃S calculated: C: 65.92, H: 4.43, N: 7.68; Found: C: 65.54, H: 4.54, N: 6.98.



Scheme 2 Proposed reaction mechanism for allyl substituted dicyanate esters and bismaleimides.

Measurements

Fourier transform infrared (FT-IR) spectra of the BAHS and BACS were recorded using a Perkin-Elmer (system 2000 FT-IR) spectrophotometer in the

form of pellet with KBr. ^1H and ^{13}C nuclear magnetic resonance spectrometer measurements were carried out with a Jeol Ex-500 spectrometer (500 MHz). Samples were prepared in CDCl_3 and the spectra were acquired at 298 K using tetramethyl

TABLE I
Cure Characteristics of the Dicyanate

Sample code	Cy : BMI	T_i ($^{\circ}\text{C}$)	T_p ($^{\circ}\text{C}$)	α_p (%)	T_{50} ($^{\circ}\text{C}$)	T_f ($^{\circ}\text{C}$)	ΔH (J/g)
a	100 : 0	T_1 125	T_1 186	52	179	T_1 207	196
		T_2 212	T_2 254	49	258	T_2 292	203
b	25 : 75	185	251	57	238	295	485
c	50 : 50	196	249	59	236	294	511
d	75 : 25	172	252	57	232	291	476
e	0 : 100	165	244	63	226	297	75.9

T_i , temperature of onset of cure; T_p , peak cure temperature; α_p , conversion at peak temperature; T_{50} , temperature corresponding to 50% conversion; T_f , temperature at the end of cure.

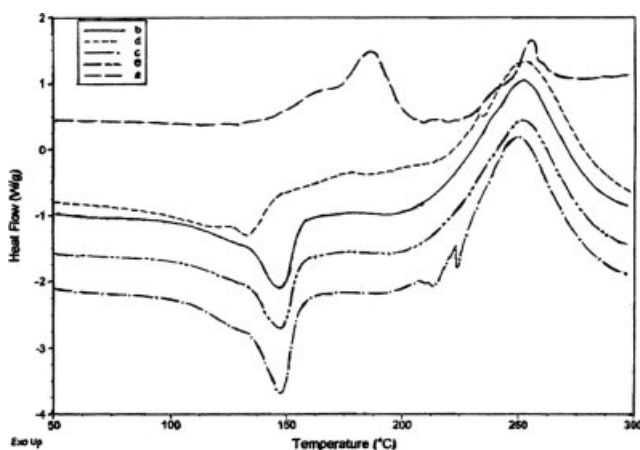


Figure 1 DSC curves of cyanate, BMI, BT resins.

silane (TMS) as the internal standard. Elemental analysis was performed using a Carlo Erbra EA 1108 elemental analyzer. Differential scanning calorimeter studies (DSC) were carried out using TA instruments Q10 model equipment at a heating rate of $10^{\circ}\text{C}/\text{min}$. Measurements were made under flowing N_2 ($60\text{ mm}^3/\text{min}$) using sealed, crimped, aluminum hermetic pans. All the samples were prepared under similar conditions and from the same batch of resin. Borchardt and Daniel method uses the dedicated software (TA Specialty Library) for the determination of kinetic parameters. Coats-Redfern method was used to determine the kinetic parameters theoretically. Thermogravimetric analysis (TGA) was performed using a TA instruments Q600 series at a heating rate of $20^{\circ}\text{C}/\text{min}$ under flowing N_2 between 25°C and 800°C .

RESULTS AND DISCUSSION

Monomer characterizations

The dicyanate ester was prepared from its precursor diol and CNBr in presence of triethyl amine. FTIR was used to confirm the formation of cyanate ester group. The band at 2236 and 2272 cm^{-1} confirms the presence of $-\text{OCN}$ group. The band at 1636 – 1645 cm^{-1} corresponds to $\text{C}=\text{C}$ of the allyl group. The disappearance of $-\text{OH}$ band at 3400 – 3500 cm^{-1} proves the completion of the reaction. In the ^1H NMR the allyl $\text{C}=\text{C}$ protons appear as multiplet at 5.25 – 6.03 ppm . Allyl $-\text{CH}_2$ appears as doublet at 3.25 ppm . Aromatic protons appear in the range of 6.73 – 7.03 ppm . The absence of hydroxyl protons at 4 – 6 ppm proves the formation of the dicyanates. In the ^{13}C NMR the carbon of the cyanate group is found at 109.3 ppm . Aromatic carbons appear in the range of 127.2 – 153.6 ppm . The allyl $=\text{CH}_2$ appears at 114.6 ppm . The signal at 136.7 ppm corresponds to $=\text{CH}-$ of allyl carbon. The signal at 27.3 ppm corresponds to $-\text{CH}_2$ allyl carbon. The calculated

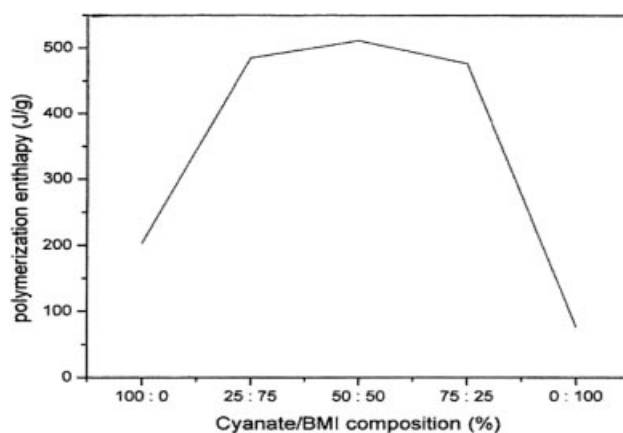
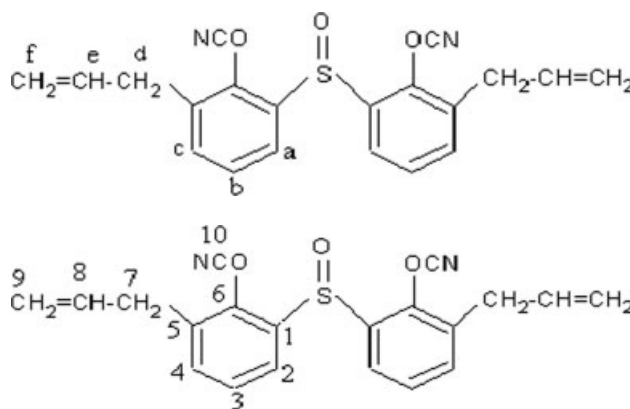


Figure 2 Effect of blend composition on polymerization enthalpy.

and experimental values of elemental analysis data are in good agreement. Hence, the proposed structure of the dicyanate is confirmed.



DSC analysis

Samples for DSC analysis were prepared by solution mixing at various ratios (Table I) of the BACS with

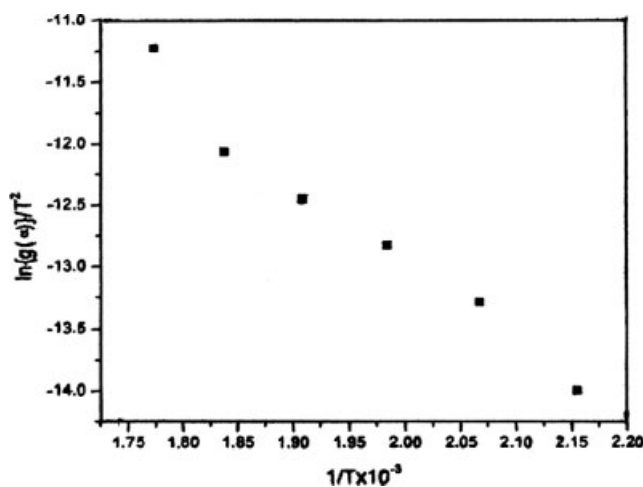


Figure 3 Coats-Redfern plot for determination of n .

TABLE II
Kinetic Parameters for the Sample Code (b)

Kinetic methods	E (KJ/mol)	A (S^{-1})	Value of n
Coats-Redfern (theoretical) Borchardt and Daniels (experimental)	66.5	2.23×10^9	1.00
	77.2	7.8×10^9	1.22

BMI in dichloromethane and the solvent was evaporated. About 10 mg of the dried sample was used for the analysis. The pure allyl cyanate gives two distinct exothermic peaks (Fig. 1). The first exothermic peak may correspond to the polymerization of allyl group and the second exothermic peak corresponds to the polymerization of cyanate functionality. This shows that there is no reaction between the cyanate and the allyl functionality. Scheme 2 shows the proposed reaction mechanism for allyl substituted dicyanate esters and bismaleimides. However, when the BMI was incorporated into the cyanate ester only single exotherm peak was observed. This can be explained by the Diels–Alder/Ene reaction of BMI and the allyl functionalized cyanate ester (Ref. 25 and references cited there in). The ene reaction by which the allyl and maleimide functionalities coreact is also a high temperature reaction and is located within the higher temperature exotherm. The lack of phase separation as confirmed by the single exotherm in the DSC curve indicates that the cyanate ester and BMI react with each other through allyl functionality. The polymerization enthalpy (ΔH) is given in Table I. The ΔH of the curing of BMI is 75.9 J/g. This low ΔH value shows that the product is less stable which may be attributed to its brittleness. For the pure cyanate ester the ΔH is 203 J/g. The increase in ΔH was found to be maximum (485.4 J/g) for 25% cyanate addition in BMI. On further increase in the cyanate content from 25 to 50% only meager increase in ΔH was observed (511 J/g). With 75% cyanate in BMI, the ΔH value was found to be increased to 476 J/g. From these observations, it can be predicted that cyanate/BMI at ratio of 25 : 75 is as stable as cyanate/BMI at a ratio of 75 : 25. This can be exploited for decreasing the brittleness of BMI. Hence, it was proposed to study the kinetics of that composition (cyanate/BMI = 25 : 75) using Coats-Redfern method under single heating rate. Figure 2 shows the effect of blend composition on the polymerization enthalpy.

Cure kinetics

The kinetics of the uncatalyzed cure reaction of cyanate ester has been established to follow second order autocatalytic model²² as

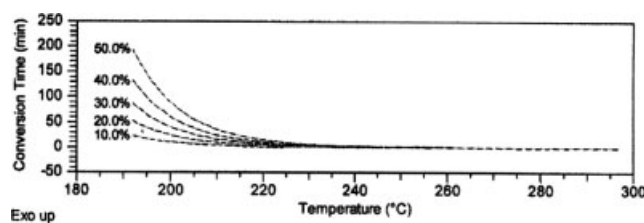


Figure 4 Temperature-conversion profile for the sample code (b).

$$d\alpha/dt = k_1(1 - \alpha)^2 + k_2(1 - \alpha)^2\alpha. \quad (1)$$

However, in some cases, for both catalyzed and uncatalyzed systems an n th order has been found to satisfactorily explain the cure profile.^{17,18} Under nonisothermal conditions, this rate expression takes the form,

$$d\alpha/dT = (A/\phi)e^{-E/RT}(1 - \alpha)^n \quad (2)$$

where α is the fractional conversion at temperature T , at a heating rate ϕ . E is the activation energy and A is the Arrhenius frequency factor. The order of the reaction is n . Several integrated equations^{26–28} have been used for the determination of kinetic parameters using single heating rate. Among them Coats-Redfern equation²⁸ (eq. 3) is used in the present study.

$$\ln\{g(\alpha)/T^2\} = \ln\{(AR/\phi E)(1 - 2RT/E)\} - E/RT \quad (3)$$

where $g(\alpha) = [1 - (1 - \alpha)^{1-n}]/(1 - n)$; when $n = 1$, $g(\alpha) = -\ln(1 - \alpha)$; R is the gas constant. In the above equation, “ n ” is substituted as 0.5, 1.0, 1.5, 2.0, 2.5, and 3. From this $g(\alpha)$ was calculated for every “ n ” value. The order of the reaction was found from the best fit linear plots of $\ln\{g(\alpha)/T^2\}$ against $1/T$ for different values of n . The other kinetic parameters like E and A were determined from the slope and intercept of the plot respectively. The kinetic plot for the determination of n is shown in Figure 3. The order n

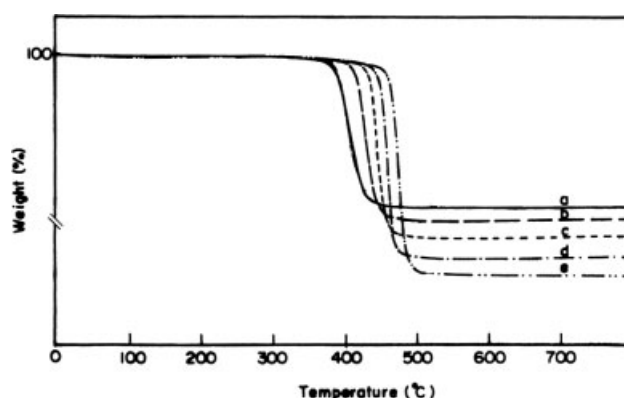


Figure 5 Thermograms of cyanate, BMI, and BT resins.

TABLE III
Thermal Stability of Neat Cyanate, Neat BMI,
and Blends

Sample code	T_i (°C)	T_m (°C)	T_e (°C)	10% Mass loss	Char yield % at 800°C
a	385	434	481	406	54
b	419	451	508	427	61
c	429	456	526	440	64
d	441	468	541	454	65
e	463	481	598	471	68

T_i , temperature of onset of decomposition; T_m , temperature of maximum decomposition; T_e , temperature of end of decomposition.

= 1 was found to be the best fit linear plot. Table II gives the values obtained from the two kinetic methods. The higher E value is kinetically compensated by the higher A value. The temperature-conversion profile obtained by Borchardt and Daniels method is given in Figure 4. The data reveal that a considerable extent of cure takes place in about 200 min at 190°C and that the cure attains near completion in about 3 h at this temperature.

Thermogravimetric analysis

The thermal stability was assessed by TGA. The analysis was carried out between 25 and 800°C in N₂ atmosphere at a heating rate of 20°C/min. The thermograms of cyanate, BMI, and BT resins are presented in Figure 5. The data are given in Table III. The TGA results show single stage decomposition. The onset decomposition temperature of the pure cyanate ($T_i = 385^\circ\text{C}$) has increased to $429 \pm 12^\circ\text{C}$ when it was blended with BMI at various ratios. As the BMI content increases the onset decomposition temperature of the blends also increases. The maximum decomposition temperature for all the blended resins is above 450°C. The 10% mass loss for BT resins starts at 427°C for the sample code "a" with 25 : 75 ratio of cyanate/BMI. The char yield for the BT resins are relatively higher (61–65%). That is the reason for the enhancement in initial decomposition temperature of the BT resin systems than that of pure cyanate (54%).

CONCLUSIONS

A novel allyl dicyanate ester bearing sulfoxide as linking group was prepared and its structure was confirmed by FT-IR, ¹H NMR, ¹³C NMR, and elemental analysis. The dicyanate was blended with BMI at various ratios. The cure behavior of the blend was studied by DSC. The 25 : 75% cyanate/BMI blend shows higher stability and its cure kinetics was studied. The kinetic parameters obtained were

compared with experimental method. The kinetic parameters obtained by both the methods agree well with each other. The cyanate, BMI homopolymers, and the blends exhibit good thermal stability. The maximum decomposition temperature for all the resins is above 450°C. The 25 : 75% cyanate/BMI blend possesses necessary characteristics [relatively high thermal stability (419°C) and polymerization enthalpy (485 J/g) and activation energy 77.2 kJ/mol] for the toughening of BMI with cyanate ester.

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