

Samikannu Rakesh and Muthusamy Sarojadevi

SYNTHESIS AND CHARACTERIZATION OF CYANATE ESTER AND ITS BLENDS WITH BISPHENOL DICYANATE ESTER

*Department of Chemistry, Anna University, Chennai-600 025, India
msrde2000@yahoo.com*

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Abstract. A new keto-ene functionalized 1, 5-bis (4-hydroxyphenyl)penta-1,4-dien-3-one (HPDO) was prepared from *p*-hydroxy benzaldehyde and acetone using boric acid as a catalyst. The prepared bisphenol was converted into 1,5-bis (4-cyanatophenyl) penta-1,4-diene-3-one (CPDO) by reacting with cyanogen bromide (CNBr) in the presence of triethylamine. The synthesized bisphenol and the dicyanate ester were characterized by Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (¹H-NMR and ¹³C-NMR) and elemental analysis (EA) techniques. CPDO was then blended with a commercial bisphenol-A dicyanate ester (BADCy) at different ratios (100:0, 75:25, 50:50, 25:75, 0:100) and the cure characteristics were studied. CPDO was found to be cured at a lower temperature than BADCy. The cyanate ester blends were cured at 373 K (30 min) → 423 K (30 min) → 473 K (60 min) → 523 K (3h). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to study the thermal properties. DSC studies show that the cure (peak) temperature of CPDO with and without a catalyst was found to be 408 K and 466 K respectively. The initial degradation temperature of the cured resins was found to be in the range from 701 K to 705 K. The Limiting Oxygen Index (LOI) value, determined by Van Krevelen's equation, shows that these blends have good flame retardant properties.

Key words: cyanate ester, low curing temperature, thermal property.

1. Introduction

In recent years increasing 'high-tech' applications make ever-increasing demand for materials in both terrestrial and extra terrestrial environments use. High temperature resistant polymers are in great demand for high-speed aircraft structures and as structural components of space vehicles. Cyanate ester (CE) resin systems are currently attracting increasing attention as high-performance thermosetting resins and they can be used as the matrices for high performance composites

because of their superior mechanical properties which are used in the electronic devices, high-temperature adhesive and aerospace industries [1-5]. They have the processability similar to that of epoxy resins and the thermal properties similar to those of phenolic resins. CE resins have their own unique properties such as a good strength, low dielectric constant, radar transparency, low water absorption, and superior metal adhesion [6, 7]. Curing of cyanate esters is catalyzed by heat or a combination of heat and catalyst [8]. The great difference in processing between epoxies and cyanate esters is that the latter ones need relatively high curing temperature. The high curing temperature causes high energy-consumption but what is more important, the resultant resins and composites tend to have higher stress concentration and internal defects and therefore the properties of the resultant composites decline [9-14]. Hence, preparation of cyanate ester having low cure temperature is chosen as the target of the present work and the properties of the prepared cyanate ester with a commercial BADCy as blends have been investigated.

2. Experimental

2.1. Materials

Bisphenol A cyanate resin, BADCy, (4,4'-dicyanato-2,2-diphenylpropane) monomer with the trade name AroCy B10 (99.5 %) was supplied by NaBond Technologies co., Limited, (China). The metal complex cobalt (II) naphthenate, Co (nap)₂, and the co-catalyst nonylphenol, NP, (technical grade) were purchased from Aldrich, USA and used as a catalyst. Acetone, *p*-hydroxybenzaldehyde and cyanogen bromide (CNBr) were purchased from SRL, (India). Triethylamine (Et₃N) was purchased from E-Merck (India). Triethylamine and acetone were distilled prior to use.

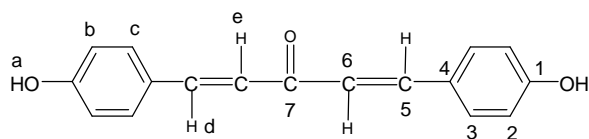
2.2. Measurements

FT-IR (Fourier Transform Infrared Spectroscopy) spectra were obtained using a Perkin Elmer (spectrum-RX1) with a KBr pellet. ¹H-NMR and ¹³C-NMR

spectra were recorded using a Bruker SF-II spectrometer at an operating frequency of 300 MHz. The samples, dissolved in DMSO- d_6 were scanned from 0 to 12 ppm using TMS as an internal reference. Elemental analysis was performed on a Vario micro-cube analyzer. Melting points were determined on an electrothermal melting point apparatus IA 6304 using capillary tubes and are uncorrected. DSC studies were carried out using TA instruments Q10 model equipment. DSC was ranged from room temperature to 623 K at a heating rate of 283 K/min in a flowing nitrogen. Thermogravimetric analysis (TGA) was carried out with TA instruments Q600 model machine at a heating rate of 283 K/min in N_2 atmosphere.

2.3. Synthesis of 1,5-bis (4-hydroxyphenyl)penta-1,4-dien-3-one (HPDO)

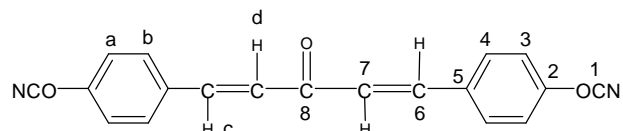
20 ml of concentrated hydrochloric acid was added to a mixture of 7.44 g (0.061 mol) of *p*-hydroxybenzaldehyde and 3.77 g (0.061 mol) of boric acid in a 250 ml round-bottomed flask. The flask was cooled to 273 K. 2.3 ml (0.030 mol) of acetone was added to this mixture dropwise with a vigorous and continued stirring at 273 K for 48 h. Then the mixture was poured into 1 l of cold water. The precipitated product was filtered, washed with distilled water and dried at 343 K for 24 h. Recrystallization from methanol gave light yellow crystals with more than 90 % yield of the main compound [15]. Melting point (mp) was 438 K. IR(KBr): 3452 cm^{-1} (ν_{OH}), 1604 cm^{-1} ($\nu_{C=C}$), 1650 cm^{-1} ($\nu_{C=O}$). 1H -NMR ($CDCl_3$, TMS, ppm): 9.92 (2H, s, H_a); 7.91 (4H, d, H_b); 7.48 (4H, d, H_c), 7.83 (2H, d, H_d); 7.37 (2H, d, H_e). ^{13}C -NMR ($CDCl_3$, TMS, ppm): C_1 - 152.8, C_2 - 115.9, C_3 - 130.2, C_4 - 133.1, C_5 - 140.35, C_6 - 126.2, C_7 - 188.04. Elemental analysis: M.F. $C_{17}H_{14}O_3$ calculated: C: 76.68, H: 5.30, Found: C: 76.52, H: 5.19



2.4. Synthesis of 1,5-bis (4-cyanato phenyl) penta-1,4-dien-3-one (CPDO)

A 250 ml three-necked round bottomed flask equipped with a magnetic stirring device and a nitrogen inlet was loaded with 3.5 g (0.0131 mol) of HPDO. The flask was maintained at 258 K and then 2.7 g (0.026 mol) of CNBr was added while stirring. 3.6 ml (2 mol) of triethylamine was added to this mixture dropwise with a continuous stirring. After complete addition of triethylamine, the reaction mixture was stirred for a period of 2 h at the bath temperature of 258 K. The mixture was

filtered under vacuum to remove the triethylamine. The filtrate was poured into a cold distilled water to precipitate the cyanate ester from the solution. The precipitate was washed with aqueous hydrochloric acid solution until a neutral one. A light yellow product (yield 87 %) was obtained. Mp. 444 K. IR (KBr): 2277 and 2238 cm^{-1} (ν_{OCN}), 1594 cm^{-1} ($\nu_{C=C}$), 1655 cm^{-1} ($\nu_{C=O}$). 1H -NMR ($CDCl_3$, TMS, ppm): 7.91 (4H, d, H_a); 7.48 (4H, d, H_b); 7.83 (2H, d, H_c); 7.38 (2H, d, H_d). ^{13}C -NMR ($CDCl_3$, TMS, ppm): C_1 -108.2, C_2 -153.4, C_3 -116.1, C_4 -130.9, C_5 -133.7, C_6 -140.9, C_7 -126.5, C_8 -188.3). Elemental analysis: M.F. $C_{19}H_{12}N_2O_3$ calculated: C: 72.15, H: 3.82, N:8.82, Found: C: 72.06, H: 3.71, N: 8.70.



3. Results and Discussion

3.1. Spectral Characterization

HPDO was prepared from *p*-hydroxybenzaldehyde and acetone in the presence of a boric acid (Scheme 1). HPDO was analyzed by FT-IR. The formation of a new band at 1580 cm^{-1} corresponds to the alkene group (C=C). The absence of an aldehydic band at 1725 cm^{-1} confirms the completion of the reaction. Fig.1 shows the FT-IR spectrum of HPDO. The dicyanate ester was prepared from its precursor diol and CNBr in the presence of triethylamine. FT-IR was used to confirm the formation of the cyanate ester group. Fig.2 shows the FT-IR spectrum of CPDO. The bands at 2238 and 2277 cm^{-1} confirm the presence of -OCN group. The absorptions due to alkene (C=C) and keto (C=O) groups were obtained at 1655 and 1594 cm^{-1} respectively. The disappearance of -OH band at 3400–3500 cm^{-1} proves the completion of the reaction. Fig. 3 shows the FT-IR spectrum of polycyanurate. Trimerization of the cyanate groups can be easily monitored by the disappearance of the band at 2200–2300 cm^{-1} due to the stretching vibration of -OCN in the IR spectrum and the appearance of new absorptions at 1594 and 1358 cm^{-1} for N-C=N and N-C-O stretching vibrations respectively. In the 1H -NMR spectrum of the dicyanate (Fig. 4) the CH=C proton adjacent to aromatic ring appears as the doublet at 7.83 ppm and C=CH proton adjacent to carbonyl group appears as the doublet at 7.33 ppm. Aromatic protons appear in the range of 7.54–7.98 ppm. The absence of hydroxyl protons at 8.5–10 ppm proves the formation of the dicyanates. In the ^{13}C -NMR (Fig. 5) spectrum the carbon of the cyanate group is found at 108.23 ppm. Aromatic carbons appear in the range of 116.1–153.4 ppm. The C=C carbon signal

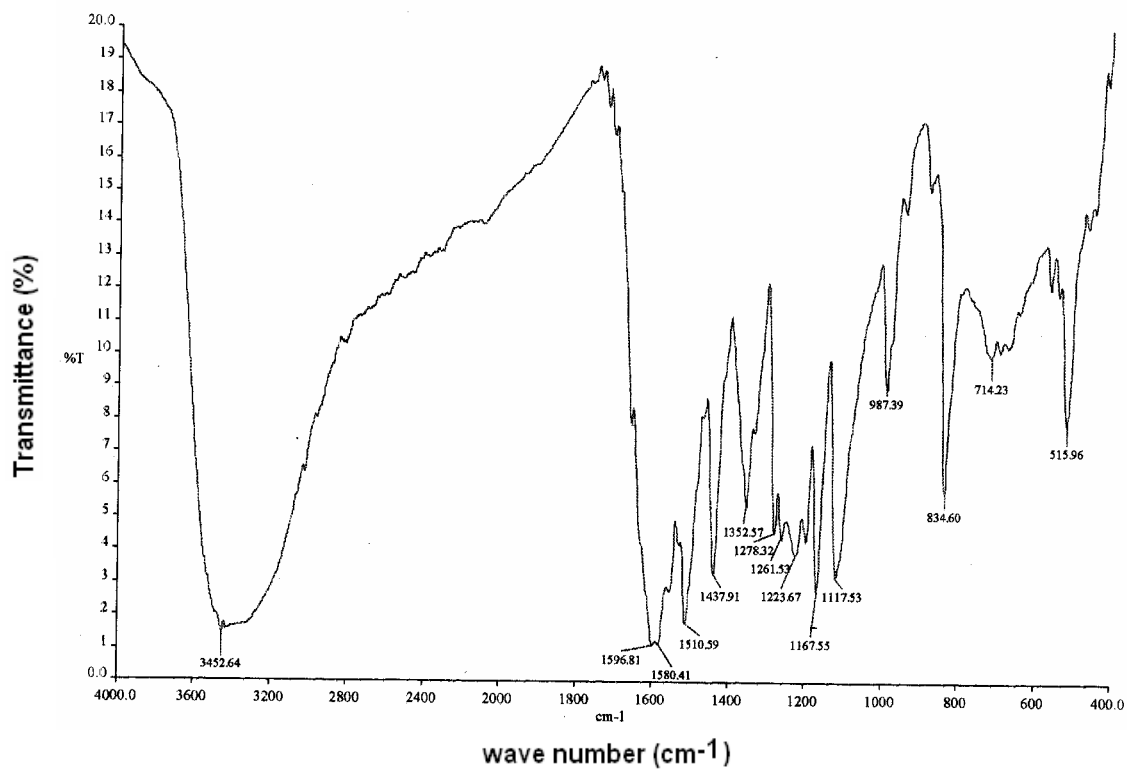


Fig.1. FT-IR spectrum of HPDO

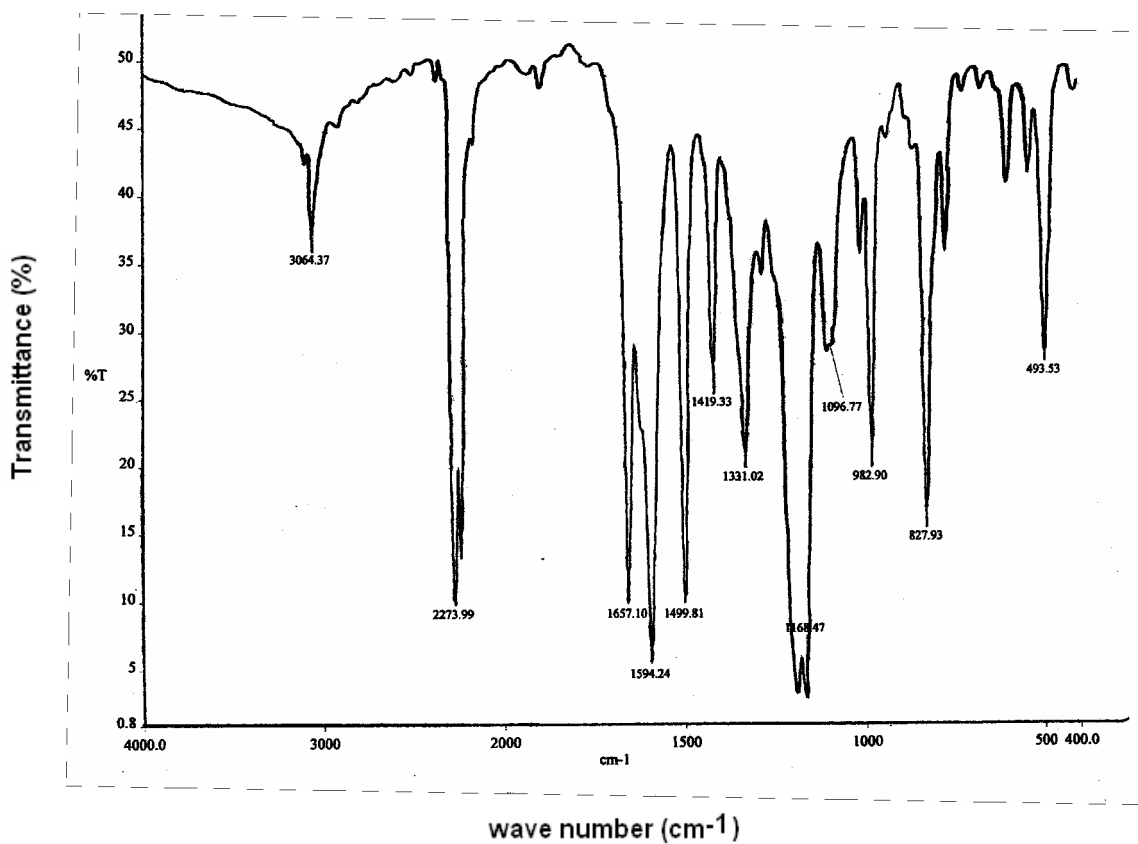
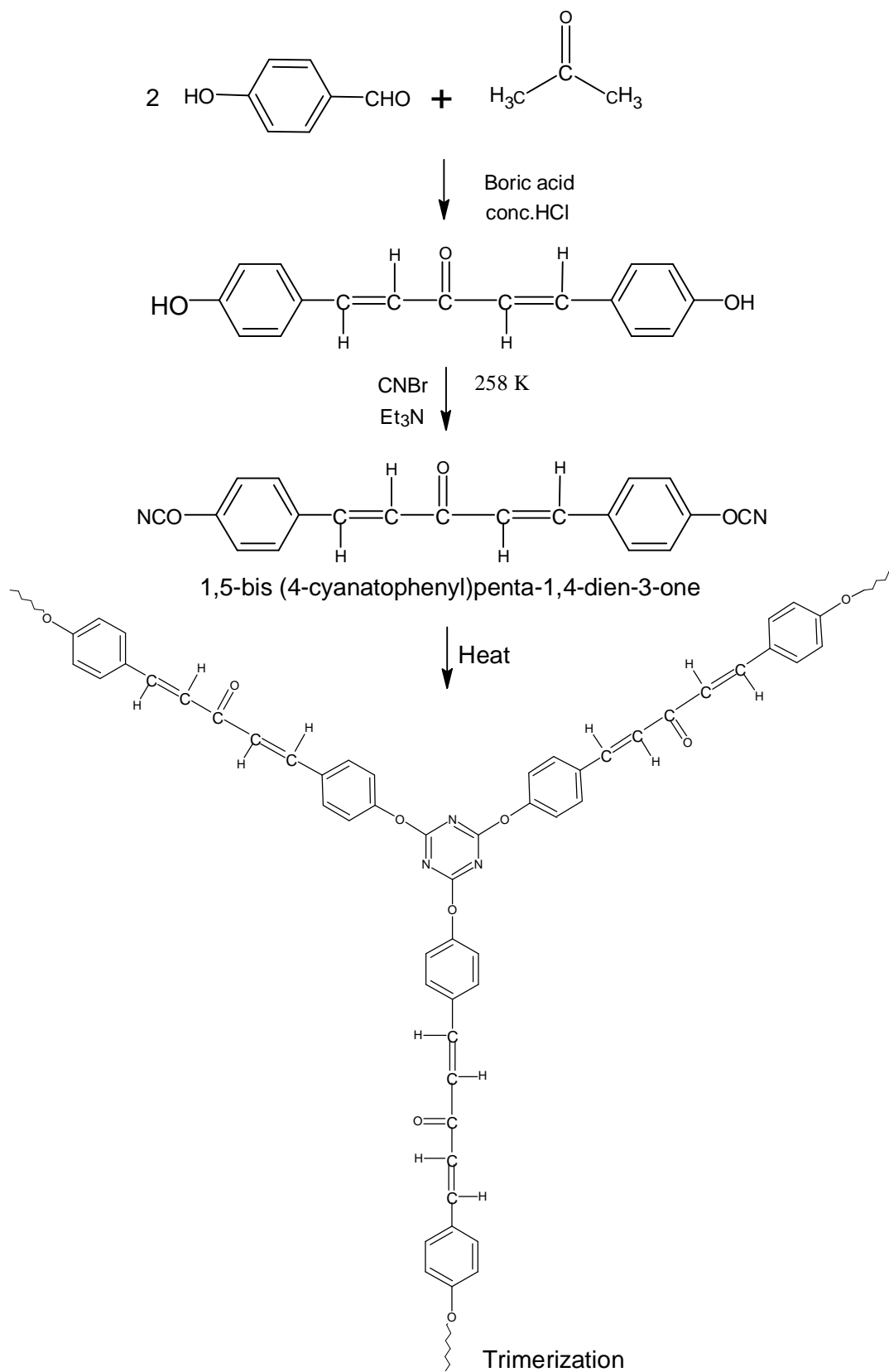


Fig. 2. FT-IR spectrum of CPDO

**Scheme 1.** Synthesis of cyanate ester (CPDO)

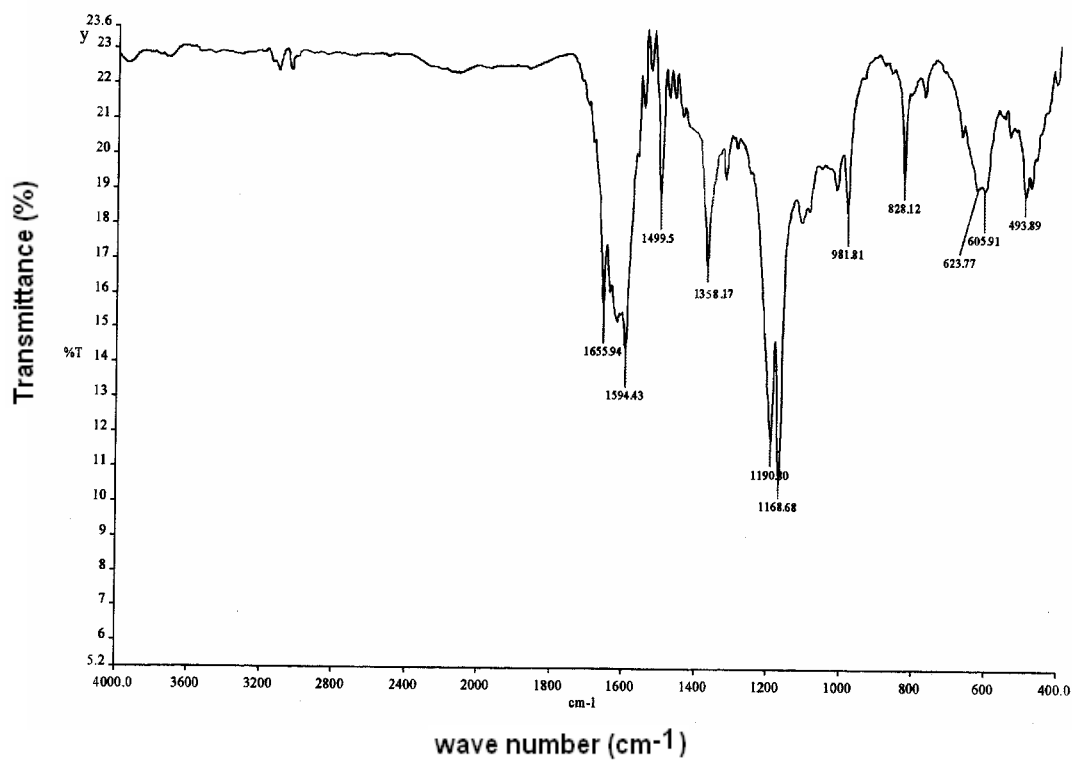


Fig. 3. FT-IR spectrum of cured CPDO

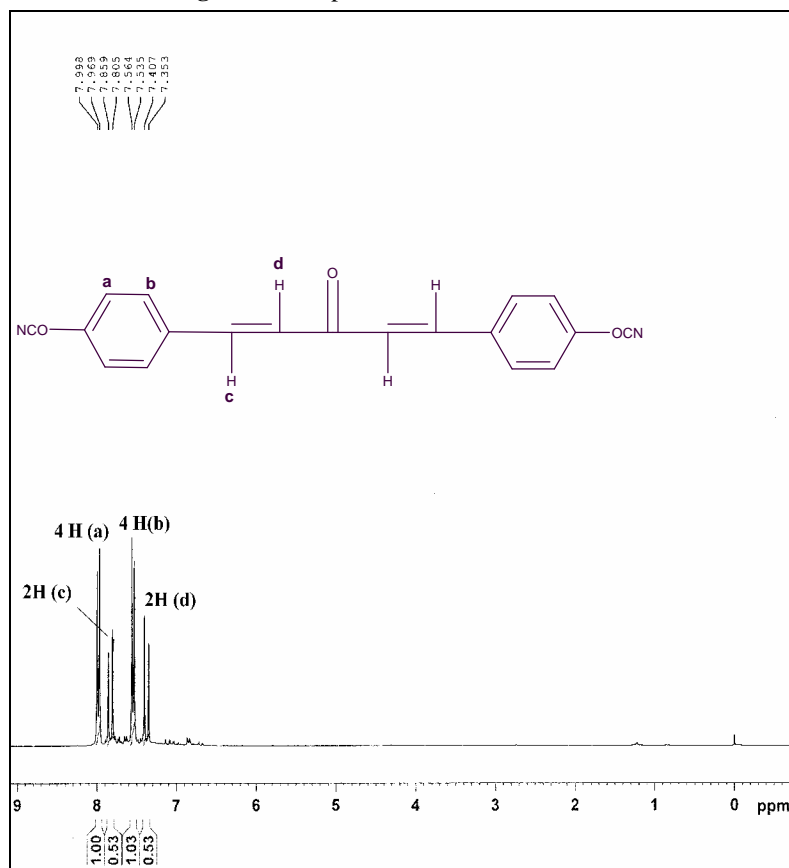


Fig. 4. ¹H-NMR spectrum of CPDO

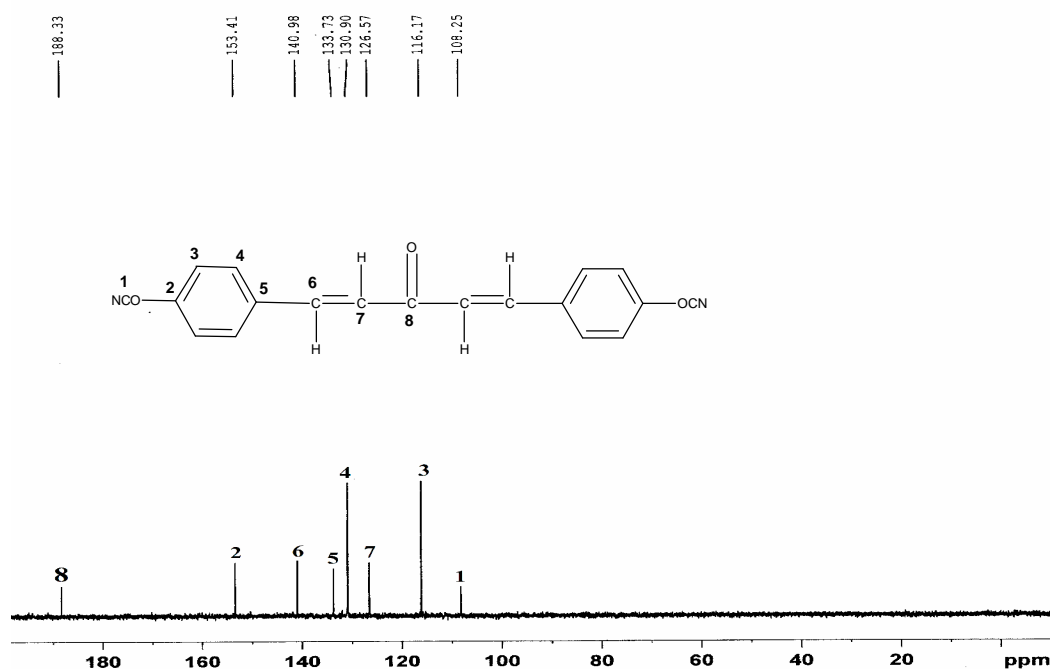


Fig. 5. ^{13}C -NMR spectrum of CPDO

adjacent to aromatic ring appears at 140.98 ppm and C=C carbon signal adjacent to the carbonyl group appears at 126.5 ppm. The signal at 188.33 ppm corresponds to the carbonyl carbon (C=O). The calculated and experimental values of elemental analysis data are in good agreement. Hence, the proposed structure of the dicyanate ester is confirmed.

3.2. DSC Analysis

DSC analysis was carried out to study the cure behaviours of CPDO with and without a catalyst, BADCy and its blends (without a catalyst) respectively, at a heating rate of $283\text{ K}\cdot\text{min}^{-1}$ (Fig. 6). Samples for the DSC analysis were prepared by the solution mixing at various ratios of CPDO with BADCy in dichloromethane and the solvent was evaporated. About 8 mg of the dried sample was used for the analysis. The DSC thermogram of the CPDO monomer shows a typical sharp curing exotherm with a peak (T_p) located at 466 K attributed to trimerization of the cyanate group. The endotherm that corresponds to the melting was observed at 444 K. The initial curing temperature (T_i) at 445 K indicates to an uncontrollable curing window [due to the simultaneous melting (at 444 K) and onset of curing (at 445 K)]. In the case of BADCy, the melting of BADCy was observed as an endotherm at 357 K and it started curing at 496 K with the peak exotherm appearing at 548 K, providing a controllable curing window. This controllable curing window implies the easiness/control over processing. The more the temperature gap between the initial and peak curing, the

easier it is for keeping and curing the material at a low temperature with a good control over processing. But the higher initial cure temperature of 496 K outweighs the reasonable controllable curing window for BADCy. But in all blend compositions, the endotherm corresponding to the melting was observed around 347–357 K. The blend ratios are shown in Table 1. While blending BADCy with CPDO, the T_i got reduced to 414 K and the T_p was shifted to a lower temperature of 456 K. The processing of a thermosetting polymer is always carried out at or near the T_p . It is preferred to process a thermosetting polymer at lower temperatures to avoid void formation. If the polymer is processed at a higher temperature, due to a sudden increase in exothermicity (release of heat) hot spots can be formed. This eventually leads to the formation of voids. As far as the processing is concerned, the peak curing temperature is the primary concern. In this respect, the processing of BADCy was improved significantly by blending with CPDO. The T_p of the blend decreased to 456–504 K in comparison to that of BADCy (548 K). Moreover, the final cure temperature (T_c) of the blend was found to be in the range of 493–549 K compared to that of BADCy (593 K). BADCy has a wide cure window, the melting point of BADCy is 357 K. But its cure initiation appears at a very high temperature of 496.5 K. On the other hand CPDO has a lower cure temperature (444 K). However it has a high melting point. Hence, the cure window is small. It can be seen from the results obtained after blending CPDO with BADCy at various ratios, the high cure initiation of BADCy decreases to 419 K. Further, the high melting point of CPDO also decreases to 348 K.

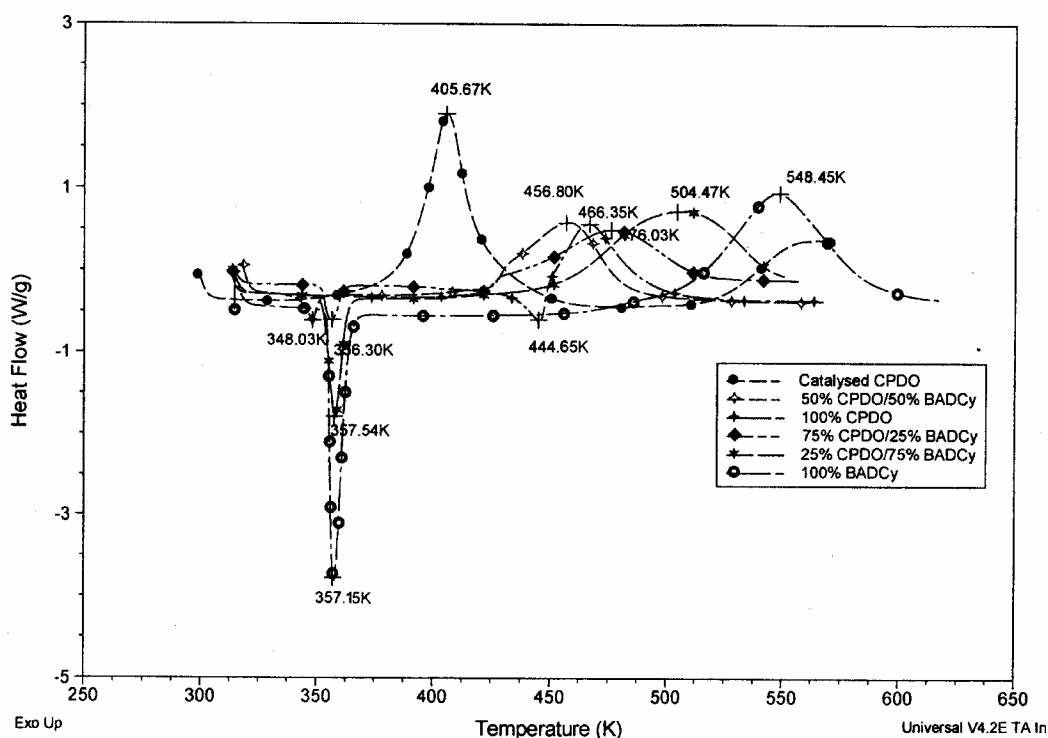


Fig. 6. DSC curves for CPDO, BADCy and CPDO/BADCy blends

Table 1

DSC data for CPDO/BADCy blends

Compositions with CPDO:BADCy ratio, %	T_i , K	T_p , K	T_e , K
100:0	445	466.3	509.4
75:25	420.1	476.1	521.7
50:50	419.8	456.8	493.4
25:75	450.2	504.4	549.6
0:100	496.5	548.4	593.1
Catalysed CPDO	347.6	405.5	463.5

T_i – initial cure temperature; T_p – cure peak temperature; T_e – end peak temperature; Cobalt naphthenate and nonyl phenol (mass ratio is 4:25:100) is a catalyst.

Table 2

TGA data for CPDO/BADCy blends

Composition with CPDO:BADCy ratio, %	Sample code	T_o , K	T_{10} , K	Char yield, %	LOI value
100:0	a	701.1	702.7	68	44.7
75:25	b	702.0	703.4	66	43.9
50:50	c	703.5	704.3	62	42.3
25:75	d	704.3	705.1	58	40.7
0:100	e	705.4	706.0	55	39.5

T_o – onset decomposition temperature; T_{10} – 10 % weight loss temperature; LOI – limiting oxygen index

Thus, the controllable cure window can be achieved after blending these two cyanate esters. From the BADCy point of view, the processing characteristics of the blend are improved. Hence, by making a blend of these resins, the initial and peak curing temperatures are lowered in comparison to BADCy resins or in other words, the processing is facilitated. When CPDO was cured with the catalyst (cobalt naphthenate catalyst and nonylphenol as a cocatalyst in weight percent ratio 4:25) the peak temperature was found to be shifted to a still further lower value (from 466 K to 405 K), than for the neat CPDO.

3.3. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is the most favoured technique for the rapid evaluation of the thermal stability of polymeric materials. It is especially useful in comparing the thermal stabilities of various polymers. The relative thermal stability of cured aryl dicyanate esters was compared with the temperature of 10 % weight loss (T_{10}) and percentage of char yield at 1073 K. This prepared dicyanate ester was then blended with a commercial bisphenol-A dicyanate ester (BADCy) at different ratios (100:0, 75:25, 50:50, 25:75, 0:100) and cured. The cured blends of different compositions of the present study were subjected to TGA in a nitrogen atmosphere and thermograms are shown in Fig. 7. It can be seen from TGA that all formulations are stable towards heat in nitrogen up to temperatures greater than 673 K, and may be used for elevated temperature service applications [16]. The TGA data for cured resins at various ratios of CPDO/BADCy are listed in Table 1. The cured resins of CPDO/

BADCy at various ratios exhibited 10 % weight loss temperature (T_{10}) ranging between 702–709 K in nitrogen and the anaerobic char yields at 1073 K ranging between 55–68 %. The thermal stability of cured resins slightly increases with the increase of BADCy content, which may occur due to the higher crosslink density compared to CPDO. It can be also observed that the char residue of formulations is increased and a thermal stability is decreased slightly with increasing CPDO content in the blend (704.3–702.0 K). Among the prepared cyanate ester blends, the initial degradation temperature is comparatively lower for CPDO. This may be due to more aliphatic linkages in CPDO compared to blend systems and neat BADCy network.

The char yield at 1073 K shows some variations according to different blend ratios. The flame retardancy of the cured cyanate ester resins was evaluated from their limiting oxygen index (*LOI*) value. The *LOI* values of the polymer systems should be above the threshold value of 26, to render self-extinguishing value and for their qualification in many applications requiring good flame resistance [17]. The *LOI* value was calculated by using Krevelen's equation [18].

$$LOI = 17.5 + 0.4\sigma$$

where σ is the percentage of a char yield. *LOI* was found to be in the range of 39.5–44.7. The char formation at the polymer surface reduces flammability by acting as a barrier (principally carbonaceous) to inhibit gaseous products from diffusing to the flame and to shield the polymer surface. Thus, the developed cyanurate can be considered as a better flame retardant material.

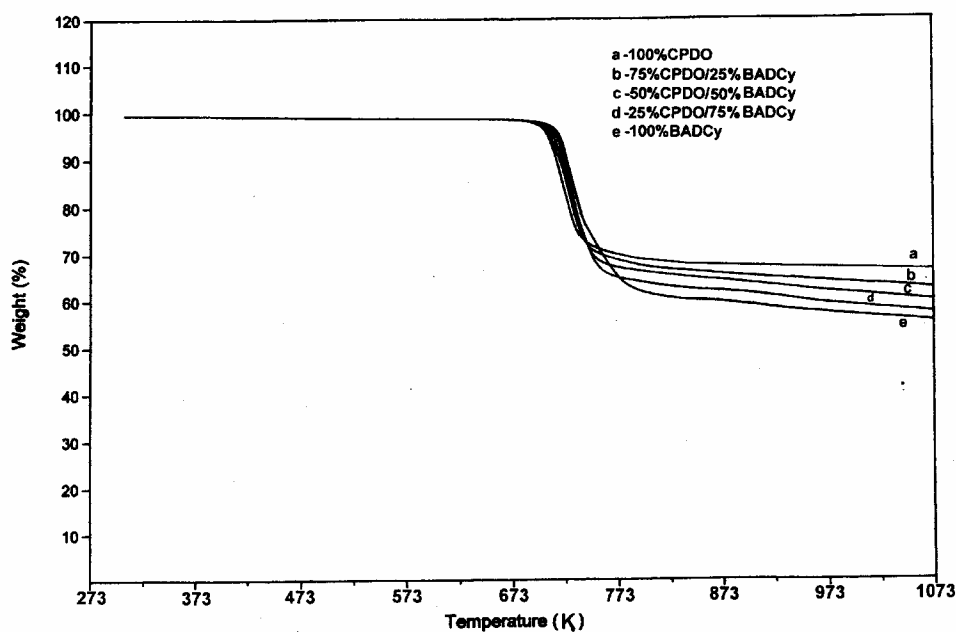


Fig. 7. Thermogram of CPDO, BADCy and CPDO/BADCy blends

4. Conclusions

The present article deals with investigations of synthesis, characterization, curing and thermal properties of blends of CPDO with BADCy resin. CPDO/BADCy blend manifested an apparent single cure profile. BADCy cure was accelerated by CPDO. Thus, the processing temperature was lowered after blending. The thermal stability of the blends was significantly improved over that of CPDO. The results showed that the blending resulted in easier processing and marginal decrease in a thermal stability compared to BADCy.

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СИНТЕЗ І ХАРАКТЕРИСТИКА ЕСТЕРУ ЦІАНАТУ ТА ЙОГО СУМІШЕЙ З БІСФЕНОЛЬНИМ ЕСТЕРОМ ДІЦІАНАТУ

Анотація. На основі *n*-гідроксибензальдегіду і ацетону, з використанням борної кислоти як каталізатора, отриманий новий функціональний кето-ен 1,5-біс (4-гідроксифеніл) пента-1,4-дієн-3-он. Одержаний бісфенол внаслідок його реакції з ціананідом брому (CNBr) у присутності триетиламіну перетворено в 1,5-біс (4-ціанато-феніл) пента-1,4-дієн-3-он (ЦФД). Структура синтезованих продуктів підтверджена Фур'є-спектроскопією, ядерним магнітним резонансом та елементним аналізом. Приготовлено суміші ЦФД з промисловим бісфенольним естером діціанату при різних співвідношеннях компонентів (100:0, 75:25, 50:50, 25:75, 0:100) та вивчені їх структуруючі характеристики за різних умов. Термічні властивості структурованих сумішей вивчені диференційною скануючою калориметрією та з використанням термогравіметричного аналізу.

Ключові слова: естер ціанату, структуровання при низькій температурі, термічні властивості.