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SYNTHESIS AND CHARACTERIZATION OF A NOVEL CYANATE ESTER CONTAINING DIMETHYL BENZENE LINKAGE

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A novel cyanate ester, dimethyl benzene cyanate ester (DMBCY), containing dimethyl benzene linkage, was synthesized from dimethyl benzene, methyl alcohol, formalin, and C1CN by a low-cost procedure. The resin was characterized by Fourier transform-infrared spectroscopy (FT-IR) and mass spectra (MS). The resin was cured with catalysts and studied by DSC. The thermal properties of the cured DMBCY were studied using DMA and TGA, and moisture absorption property was determined for the cured resin as well as its dielectric properties, flexural strength, and flexural modulus. The cured resin exhibited low dielectric constant (2.85), dissipation factor (2×10^{-4}), and moisture absorption (0.43% after 48 h in 100°C).

Keywords: Cure; Cyanate ester; Dielectric constant; Dissipation factor; Thermal properties

INTRODUCTION

In 1960, reaction of alkoxide species with cyanogens chloride was successful when ortho-substituted phenols were employed, and the first ortho-alkylated aryl cyanate was isolated.^[1] In 1963, Farbenfabriken Bayer AG patented a method that was successful with mono- and polyphenols and with a number of partially halogenated aliphatic hydroxyl compounds.^[2,3] Furthermore, it could be carried out on an industrial scale. As a matter of fact, it was the only synthetic method having commercial importance for preparation of high-temperature thermosetting resins between a cyanogen halide and a phenol in the presence of a base.^[4] Reports on the use of cyanate ester resins and related applications are scanty. Practically all the literature pertaining to their trials for potential aerospace applications conclude that this system with its many attractive features is able to replace the epoxies in composites for specific applications.

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Cyanate esters (CEs) are well-known thermosetting resins. They are useful as adhesives and as coatings for substrates. They are also useful for the preparation of advanced composites and electrical laminates. CEs are remarkable in that they polymerize via a cyclotrimerization reaction to form a cyanurate network with a high degree of efficiency; the use of metallic or amine catalysts can reportedly achieve conversions higher than 98%.^[4–6] CEs possess good heat resistance, hardness, electrical properties, dimensional stability, corrosion resistance, and chemical resistance.^[7–9] These properties are further tunable through backbone structure and by blending with other polymer systems.^[10–15] However, the synthesis of new monomers has come to a stage of stagnation and the present attention is on evolving new formulations and processing techniques. Because of its undisputed superiority over conventional matrixes, it is of great importance to keep watch on developments in this area. Our aim is to design and synthesize a novel oligomeric cyanate ester resin containing hydrophobic alkyl and aromatics backbone, as shown in Figure 1. The resin can be cured by heating, and it is expected to possess good dielectric properties and low moisture absorption.

In this work, the novel cyanate ester resin dimethyl benzene cyanate (DMBCY) was synthesized. Its structure was confirmed by IR and electrical impedance (EI) spectra. Thermal properties of the cured resin were evaluated by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and other methods. This article will discuss the synthesis, polymerization, thermal behavior, mechanical properties, moisture absorption, and dielectric property of DMBCY and its cured resin.

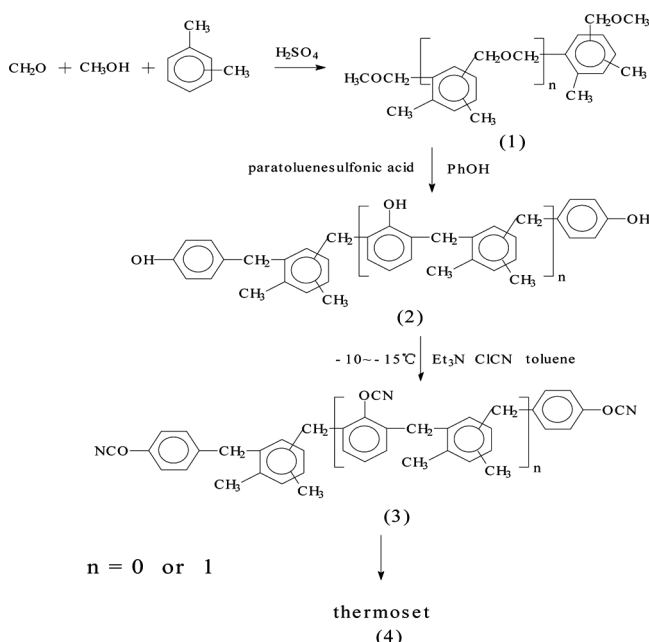


Figure 1. Synthesis of DMBCY.

EXPERIMENTAL SECTION

Materials

CICN was supplied by Shanghai Huifeng Technical & Business Co. Ltd. Phenol, toluene, dimethyl benzene, formalin, and methanol (Sinopharm Chemical Reagent Co. Ltd) were used as received. Paratoluenesulfonic acid and triethylamine were purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd. All solvents were commercial products (LC grade) and used without further purification

Synthesis of Oligomer 1: Dimethyl Benzene-Methyl Aldehyde Resin (DMBMA)

First, 90 g of formalin was placed in a three-necked 500 mL round-bottom flask equipped with a mechanical stirrer, a constant funnel, and a condenser. Then 117.6 g (1.2 mol) concentrated sulfuric acid was added dropwise from the dropping funnel. Finally, 38.4 g (1.2 mol) methyl alcohol and 42.4 g (0.4 mol) dimethyl benzene were added, and the reaction mixture was stirred at 60–70°C. After one hour, the temperature of the mixture was gradually raised to 78–80°C for an additional 6 h. A pale-yellow solution was obtained and allowed to cool to room temperature. After this the upper layer was successively separated, washed with 10% Na₂SO₄ and twice with 60–70°C water. The excess water and dimethyl benzene were evaporated by steam distillation method. The residue was the expected to be the product and was characterized by IR (cm⁻¹): 2920 (–CH₃), 2850 (–CH₂–), 1501 (aromatic), 1451 (aromatic), 1616 (aromatic), 1099 (aliphatic ether); and MS m/z (relative intensity %): 194, 342 (M⁺, 100).

Synthesis of Oligomer 2: Phenol-Dimethyl Benzene Methyl Aldehyde Novolac (PDMBMA)

To a mixture of 74 g phenol and 74 g DMBMA was added 0.68 g paratoluenesulfonic acid catalyst, maintaining the temperature at 70°C. Without the temperature control system, the temperature of the reaction mixture increased to 120°C spontaneously. Then another 0.68 g of paratoluenesulfonic acid catalyst was added to the mixture, and the distillation proceeded for one hour. Then, 10% aqueous solution of sodium hydroxide was added to the resulting reaction mixture to neutralize it. The resulting oil layer was separated and washed by hot water to remove the excess phenol and salt. Then the organic phase was distilled to remove water, and a deep-brown solid PDMBMA was obtained. IR (cm⁻¹): 3504 (O–H), 1505 (aromatic), 1451 (aromatic), 1610 (aromatic), 2917 (–CH₂–), 2863 (–CH₃); MS m/z (relative intensity %): 318, 542 (M⁺, 100).

Synthesis of Oligomer 3: Dimethyl Benzene Cyanate Ester (DMBCY)

To a 500 mL capacity flask was added 14 g of cyanogen chloride and 100 mL of toluene. The mixture was cooled to –15°C ~ –10°C. Then 50 g PDMBMN, 25 g triethyl amine, and 150 mL toluene were added dropwise to the flask. The addition was completed in 1 h with the temperature being held at –15°C ~ –10°C, and

maintained for 2 h more. After the reaction was completed, the solution was kept at room temperature. The solution was then mixed with 300 mL 5% aqueous solution of NaHCO_3 by vigorous stirring for 5 min. The organic layer was separated, washed with 280 mL 3% aqueous solution of H_2SO_4 and then with water. After evaporation the brown resin, DMBCY, was obtained. IR (cm^{-1}): 2918 ($-\text{CH}_2-$), 2864 ($-\text{CH}_3$), 1500 (aromatic), 1451 (aromatic), 1600 (aromatic), 2270 ($-\text{C}\equiv\text{N}$); MS m/z (relative intensity %): 368, 617 (M^+ , 100).

Polymerization

Castings were prepared from the resin as follows: to DMBCY heated to 80°C was added 200 ppm cobalt acetylacetonate and 3% nonyl phenol, wherein said ppm and % were based on the weight of cyanate ester. The resin-catalyst blend was well mixed, then degassed under vacuum. The degassed material was poured into a pre-heated mold, the internal surfaces of which were treated with silicon oil as a mold release agent. The mold was placed in an oven and the resin was then cured by heating at 120°C for 2 h, plus 2 h at 150°C , 4 h at 180°C , 2 h at 200°C , and 2 h at 220°C . The physical properties of the castings were determined after the heating period.

Measurements

Fourier transform-infrared spectra were recorded on a Nicolet Magna 550 with KBr pellets. Spectra in the optical range of $400\text{--}4000\text{ cm}^{-1}$ were obtained by averaging 16 scans at a resolution of 4 cm^{-1} . Differential scanning calorimetric (DSC) analysis was obtained from samples of about 5–10 mg using a Universal V2.3 TA Instruments 2910 modulated system. The heating rate was $10^\circ\text{C}/\text{min}$ at a flow rate of nitrogen $15\text{ cm}^3/\text{min}$. DMA was carried out with a TA DMA 2980 Dynamic Mechanical Analyzer. The storage modulus E' and $\tan\delta$ were determined as the sample was subjected to temperature scan mode at a programmed heating rate of $10^\circ\text{C}/\text{min}$ from ambient to 350°C at a fixed frequency of 1 Hz and an amplitude of $10\text{ }\mu\text{m}$. A sample 15 mm in length, 10 mm in width, and approximately 1.5 mm in thickness was used. The test method was performed by three-point bending mode with a tension ratio at 110%. The thermogravimetric analysis (TGA) was measured using a Mettler TGA/SDTA 851 analyzer with a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen and from 25° to 800°C . The mechanical properties of the cured resins were determined by a SANS universal machine (GB/T9341-2000). The moisture absorption was calculated as percent weight gain $= (W/W_0 - 1) \times 100\%$, where W is the weight of a sample after being placed in 100°C water for 12, 24, and 48 h, and W_0 is the weight of the sample before being placed in water. Dielectric measurements were performed with a Novocontrol Concept 40 measurement system at room temperature by a parallel plate mode at 1 Hz.

RESULTS AND DISCUSSION

DMBCY was obtained as viscous brown oil at room temperature and was soluble in polar organic solvents such as diethyl ether, acetone, dichloromethane, and dimethyl formamide (DMF). Upon heating to 80°C , the viscosity had been

substantially reduced and resulted in a liquid resin with enhanced processability compared to current commercially available solid CE resins. Thermal curing of the DMBCY with catalysts resulted in a cross-linked thermoset 4. The reactions for the formation of the DMBM, PDMBMN, and DMBCY were monitored by infrared spectroscopy and the results are shown in Figure 2. When comparing the spectra of PDMBMN and DMBCY, the most notable feature is the absence of the OH peak at around 3504 cm^{-1} and the appearance of new peaks at around 2270 cm^{-1} , characteristic of the $-\text{OCN}$ group. When there was no visible hydroxyl peak, the formation of the CE resin, DMBCY, from the hydroxyl terminated PDMBMN was considered complete.

Cyanate ester resins were polymerized by a cyclotrimerization reaction to create a uniformly cross-linked polytriazine network with no secondary reactions. It was known that pure cyanate ester resin does not undergo polymerization, even at high temperature.^[16,17] Therefore, the reaction was believed to be catalyzed by a trace amount of active hydrogen-containing compounds and transition metal chelates. Shimp^[18,19] discovered that metal salts mixed with nonyl phenol provide an effective liquid catalyst system for the formation of thermoset networks. In our case, nonyl phenol and cobalt acetylacetonate were used to control the temperature at which the cure exotherm occurred.

The polymerization reactions of neat DMBCY and in the presence of catalysts system were studied by DSC analysis. Figure 3 shows DSC thermograms of DMBCY (plot A) and with catalysts system (plot B) from 50°C to 400°C at heating rate of $10^\circ\text{C}/\text{min}$. We observed during the neat cure of resin an exotherm beginning at $\sim 180^\circ\text{C}$ and ending at $\sim 356^\circ\text{C}$. In the case of incorporating cobalt acetylacetonate and nonyl phenol, the cure exotherm began at around 142°C and ended at around 323°C . These plots show that the beginning of the cure exotherm can be shifted lower

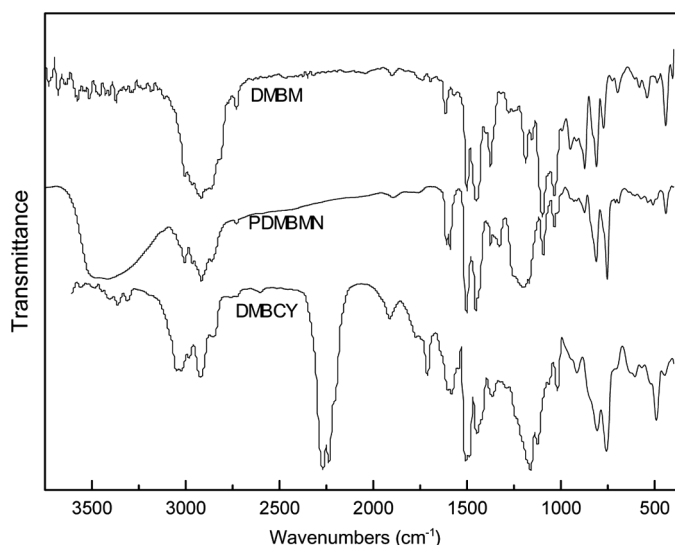


Figure 2. IR spectra of DMBM, PDMBMN, and DMBCY.

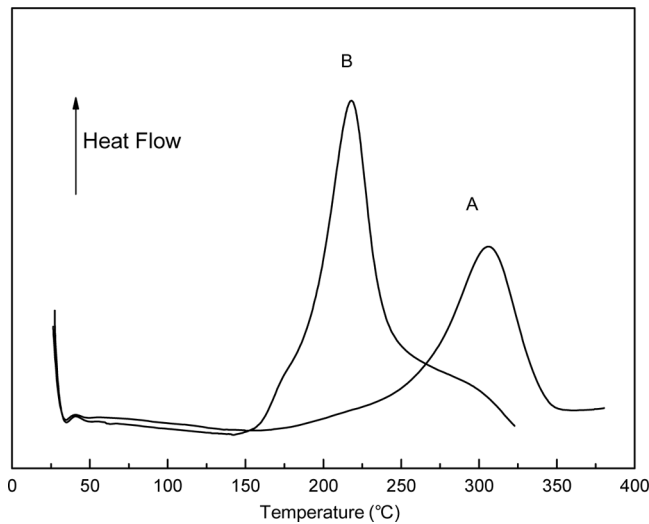


Figure 3. DSC thermograms of DMBCY cured neat (A) and with catalysts system (B).

by incorporating cobalt acetylacetonate/nonyl phenol. This was attributed to the reaction of the cyanate ester groups with the catalysts.

Dynamic mechanical analysis (DMA) is a useful tool for determining the stiffness and mechanical damping of a cyclically deformed material as a function of temperature. Figure 4 shows the temperature dependences of the storage modulus and loss tangent ($\tan\delta$) for thermoset 4 obtained by curing DMBCY in the presence of catalysts system. The storage modulus at room temperature was 3542 MPa. Upon heating to 190°C, the sample showed a sharp reduction in the modulus. The large

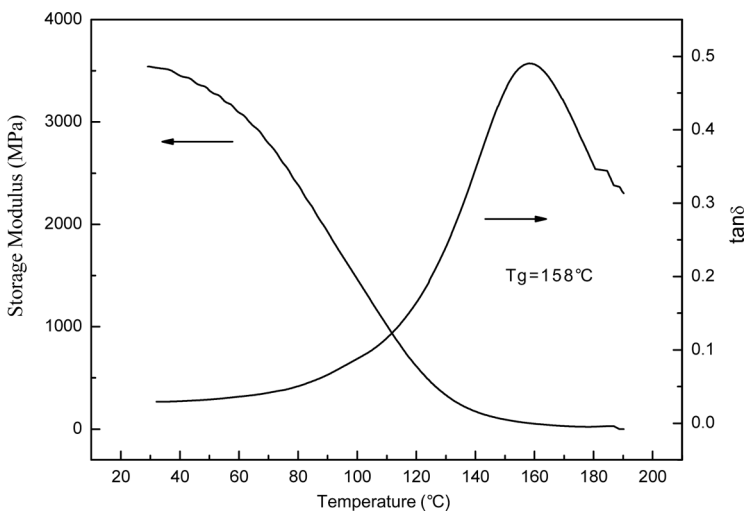


Figure 4. Storage modulus and damping factor ($\tan\delta$) for DMBCY cured with catalysts system.

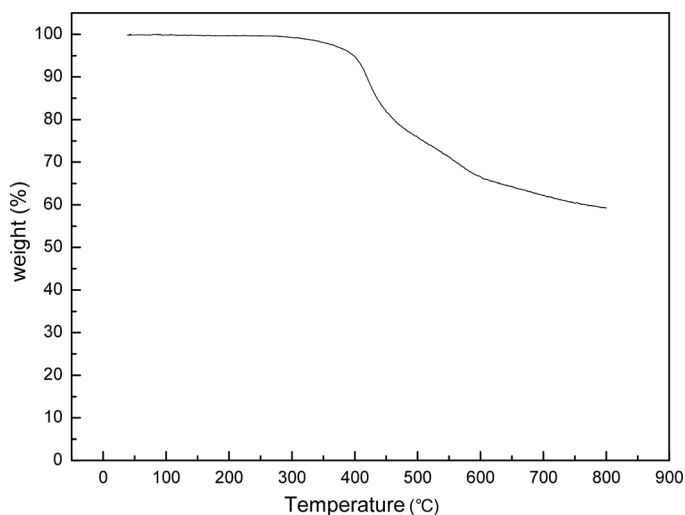


Figure 5. TGA thermogram of DMBCY cured with catalysts system.

decrease transition in the storage modulus appeared between 75°C and 124°C. The T_g value for thermoset 4 was assigned to the peak of the $\tan\delta$ plot, which was situated at approximately 158°C.

Cyanate ester resins are well known for their good thermal stability due to their aromatic ring and triazine ring. The thermal stability of the cured DMBCY with catalysts system was determined by TGA measurement, as shown in Figure 5. The sample exhibited residual weight of 95% at 397°C and overall char yield of 62% at 700°C and 59% at 800°C in nitrogen atmosphere. The thermal stability of the cured DMBCY with catalysts system was higher than that of the highly cross-linked bisphenol A dicyanate ester, which exhibited a residual weight of 40% at 700°C.^[20]

Mechanical properties are important properties of a matrix for advanced composites, especially those used as structural materials. DMBCY cured with cobalt acetylacetonate/nonyl phenol system had good mechanical properties, as shown in Table I. The cured DMBCY displayed a flexural strength of 94 MPa and flexural modulus of 4290 MPa. This can be explained by the cured structure of cyclotrimerization and not by by-products of low molecular weight.^[19] Therefore, the cured resin structure in the final product was more compact and had fewer defects.

Another important feature of the cured cyanate ester resin is its limited water absorption and low dielectric properties. The water absorption for the cured

Table I. Properties of cured of DMBCY with cobalt acetylacetonate/nonyl phenol system

Sample	Flexure strength (MPa)	Flexure modulus (GPa)	H ₂ O absorbs at 100°C (%)			Dielectric constant	Dielectric dissipation faction
			12	24	48		
DMBCY cured with catalysts system	94.24	4.29	0.31	0.37	0.43	2.85	2×10^{-4}

DMBCY with catalysts system was approximately 0.31%, 0.37%, and 0.43% after 12, 24, and 48 h, respectively, in boiling water. The dielectric constant of polymeric system results from permanent dipole motions within the system. The cyanate ester resins have a characteristically low dielectric constant due to a low polarity of the central triazine ring. Furthermore, DMBCY contains hydrophobic alkyl and aromatics backbone, which is favorable to reduce the moisture absorption, and, therefore it reduces the dielectric constant and dissipation factor. The dielectric constant and dissipation factor of cured DMBCY with catalysts system at room temperature at 1 MHz were 2.85 and 2×10^{-4} , respectively. The physical properties are listed in Table I.

CONCLUSIONS

A novel cyanate ester resin, DMBCY, was synthesized successfully from dimethyl benzene, methyl alcohol, formalin, and ClCN by a low-cost procedure. At room temperature, the resin was viscous oil and the enhancement in processability and other important physical properties may allow the use of DMBCY in a wide variety of applications, including printed circuit boards and adhesives and as a matrix resin in structural components. DSC was used to examine the cure reaction of the resin, and it was shown that catalysts were useful for lowering the onset temperature. Upon thermal curing of the resin, T_g , mechanical properties, moisture absorption, dielectric, and thermal stability of the resulting thermoset were studied. The most important feature of the cured resin was its excellent dielectric property (dielectric constant was 2.85, dielectric dissipation fraction was 2×10^{-4}) and moisture absorption property (0.43% after 48 h in 100°C water). Optimization of the curing reaction is in progress, and physical property characterization will be discussed in the future.

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