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Synthesis and properties of a liquid oligomeric cyanate ester resin

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Abstract

A multiple aromatic ether-containing cyanate ester resin system with high thermal stability and superb processability has been developed. The oligomeric monomer was prepared via a hydroxyl-terminated intermediate synthesized from a modified Ullmann synthesis with bisphenol A and 1,3-dibromobenzene in the presence of potassium carbonate and a catalytic amount of a copper (I) complex in *N*,*N*-dimethylformamide. The hydroxyl-terminated intermediate was end-capped with the cyanate moiety by reaction with cyanogen bromide and triethylamine in dry acetone resulting in a resinous material at ambient temperatures. The thermo-oxidative and water absorption properties were determined for the new cyanate ester polymer as well as its flexural strength, flexural modulus and Rockwell hardness. Mechanical tests were also conducted on the commercially available 2,2′-bis(4-cyanatophenyl)isopropylidene cyanate ester resin to investigate the effect of introducing an oligomeric spacer between the terminal end groups on the properties of the material.

Keywords: Cyanate ester; Thermoset; High temperature

1. Introduction

Cyanate ester (CE) resins have received considerable attention in the past few years due to their importance as thermosetting resins for use in the electronics, aerospace, and adhesive industries [1–6]. They have the processability of epoxy resins and the thermal properties of phenolic resins. CE resins have their own unique properties such as good strength, low dielectric constants, radar transparency, low water absorption, and superior metal adhesion [7–9]. These properties make them the resin of choice for high performance applications where such properties are required.

CE resins have been proposed for use as the matrix resin in the fabrication of structural composites for civilian aircraft [10]. Even though most commercial CEs possess good flammability and high temperature properties, they are far too brittle to be widely used in structural applications. Many additives have been used to strengthen the resulting CE thermoset including epoxies [3,11,12], polyesters [13] and bismalimides [2,12–14] with varying success. Co-curing the CEs with these polymers can result in non-miscibility, which has both desired and undesired effects on the physical and thermal properties of the polymeric matrix [15,16]. The thermal stability of the CE thermoset is greatly affected by the addition of aliphatic-containing systems.

A CE resin can be cured alone or with the aid of a catalytic amount of a metal salt into a triazine network (Fig. 1) [17–19]. Similar to epoxy resins, CE resins can be cured rapidly and at low temperatures when employing a polymerization catalyst. Unlike the common curing methods for epoxy resins, which employ stoichiometric amounts of catalyst, CE resins can be cured using only a minute amount of polymerization catalyst to facilitate the crosslinking reaction. There is very little outgassing during the polymerization reaction, which allows for easy fabrication of void free composites. The thermal stability of the thermoset is much higher then most epoxy-based systems. As an example, 2,2′-bis(4-cyanatophenyl)isopropylidene (BACY) **1** (Fig. 2) is a widely accepted CE monomer used in the formation of polymers for various applications. BACY can be processed and cured above its melting point (80 °C). The resulting thermoset exhibits good thermal stability (95% weight retention at 430 °C) and a glass transition temperature (T_g) as high as 290 °C when fully cured [3,11]. However, the resulting polymer is somewhat brittle, which limits its use in many applications.

In an attempt to address the toughness of the CE resin upon conversion to the networked system, a synthetic method to incorporate variable length spacer groups between the reactive ends of the CE resin was envisioned [20–25]. Our efforts have

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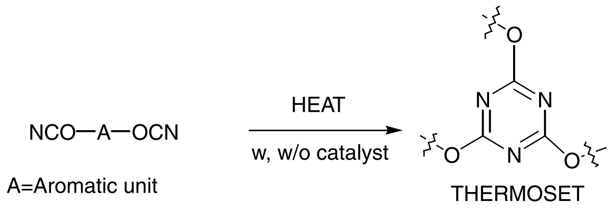


Fig. 1. Triazene network formation.

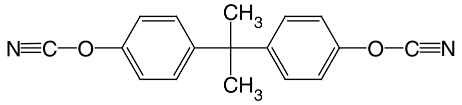


Fig. 2. Structure of 2,2′-bis(4-cyanatophenyl)isopropylidene (BACY) **1**.

resulted in the design and synthesis of a novel oligomeric aryl ether-containing CE resin system by utilizing a modified Ullmann [26–33] reaction. The crosslinking density of the resulting thermoset is reduced, which should enhance desirable physical properties [25]. Utilizing this synthetic method to form oligomeric and not pure compounds, the affinity for the resin to crystallize should be greatly reduced, which should enhance its processability. Additionally, since very thermally stable aryl ether [34,35] linkages are formed during the synthesis of the novel CE monomers, the cured resin system should exhibit excellent thermal and oxidative properties. In this paper, we will discuss the synthesis, polymerization, and the mechanical, thermal and oxidative properties of an oligomeric CE resin system. The physical and mechanical properties will be compared to the parent BACY resin (**1**).

2. Experimental section

All starting materials were of reagent grade and used without further purification. BACY **1** was purchase from Oakwood Chemical. Differential scanning calorimetric (DSC) analysis was performed on a TA Instruments DSC 2920 modulated thermal analyzer at a heating rate of 10 °C min^{-1} and a nitrogen purge of 50 $\text{cm}^3\ \text{min}^{-1}$. The glass transition temperature (T_g) was reported as the temperature centered at the midpoint between the linear baselines of a DSC scan. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q50 at a heating rate of 10 °C min^{-1} under a nitrogen or air purge of 50 $\text{cm}^3\ \text{min}^{-1}$. Infrared (IR) spectra were recorded as films on NaCl plates using a Nicolet Magna FTIR 750 spectrometer. ^{1}H NMR was performed on a Brüker ADVANCE 300 spectrometer.

2.1. Rheometric measurements

A TA Instruments AR-2000 Rheometer, in conjunction with an environmental testing chamber for temperature control and torsion fixtures, was used to monitor the response of samples (50 mm × 13 mm × 2 mm) to oscillatory testing. The measurements were made in nitrogen over the temperature range of ∼40 to 300 °C. A temperature ramp of 3 °C min^{-1} was used to determine the storage modulus and damping factor (tan δ) of the material at a frequency of 1 Hz and a strain of $2.5\times10^{-2}\%$. Normal force control was utilized throughout the tests to keep the samples taut.

2.2. Flexural strength/flexural modulus measurements

A three-point bend test fixture with loading pin and support pins each 6.35 mm (0.25 in.) in diameter was used for the flexure tests. The test fixture was mounted in a screw-driven load frame with an approximately 0.5 kN (100 lb) capacity load cell. Flexural properties of the CE polymers were measured under ambient conditions with a support span/sample thickness ratio of 16:1 and a crosshead displacement speed of 1.27 mm (0.05 in.) min^{-1} following ASTM D790 recommendations.

2.3. Rockwell hardness measurements

The hardness of the CE polymer samples was measured under ambient conditions using the Rockwell M-scale in accordance with ASTM D785 procedures.

2.4. Synthesis of the hydroxyl terminated oligomeric aromatic ether (4)

To a 250 mL, three-necked flask fitted with a thermometer, a Dean–Stark trap with condenser, and a argon inlet were added bisphenol A **2** (10.0 g, 43.8 mmol), 1,3-dibromobenzene **3** (5.16 g, 21.9 mmol), 1,10-phenanthroline (0.350 g, 1.94 mmol), toluene (10 mL) and *N*,*N*-dimethylformamide (DMF) (80 mL). The resulting mixture was degassed thoroughly with argon for 10 min followed by the addition of copper (I) iodide (0.330 g, 1.74 mmol). After filling the Dean–Stark trap with toluene, the mixture was heated to reflux at 135–145 °C for 30 min to 1 h in order to completely dissolve all the starting materials and remove any residual water contained in the solvent. The mixture was cooled to 100 °C and K_2CO_3 (4.50 g, 32.6 mmol) was slowly added in one portion. The resulting mixture was then brought to reflux and heated at 135–145 °C for an additional 2–4 h. The water formed in the reaction was removed by azeotropic distillation. At this time, an additional portion of K_2CO_3 (4.50 g, 32.6 mmol) was added. The mixture was refluxed for an additional 9–12 h until no more water was observed being collected in the Dean–Stark trap. The remaining toluene was then removed by distillation and the reaction mixture was cooled to ambient temperature. Water was then added (300 mL) to the reaction mixture. The slightly basic mixture was made acidic by the addition of 2 M HCl (300 mL) and extracted with ether (2 × 100 mL). The combined ether layers were washed with 2 M HCl (1 × 100 mL) and water (1 × 100 mL) until neutral. Carbon black (2 g) was added and the ether extract was filtered through a short plug of silica gel to remove any insoluble components. The solvent was removed in vacuo and the amber solid was vacuum dried to yield the pure 2:1 hydroxyl terminated oligomer **4** (10.4 g, 91%). IR [cm^{-1}]: ν 3392 (O–H), 3033 (C=CH), 2968 (CH_3), 1591 (aromatic), 1504 (aromatic), 1479 (aromatic), 1363 (CH_3), 1220, 1176, 1125 (C–O), 1013, 968 (C–OH), 831 (aromatic). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21–7.15 (m, aromatic-H), 7.11–7.05 (m, aromatic-H), 6.94–6.88 (m, aromatic-H), 6.76–6.67 (m, aromatic-H), 5.23 (bs, OH), 1.66, 1.64, 1.61 (s, –CH_3).

*2.5. Synthesis of the oligomeric aromatic ether cyanate ester **5***

The oligomer **4** (1.62 g, 3.05 mmol) was transferred to an oven-dried 50 mL three-necked flask fitted with a thermometer. Cyanogen bromide (0.710 g, 6.70 mmol) and dry acetone (10 mL) were added under argon. The resulting mixture was cooled to between -30 and -20 °C and triethylamine (0.95 mL, 0.690 g, 6.82 mmol) dissolved in 1 mL acetone was added drop-wise to keep the temperature of the reaction mixture below -20 °C. After the addition, the reaction was stirred at -20 °C for an additional 1 h resulting in the formation of a voluminous white precipitate of $Et_3N^+Br^-$. The solvent was removed in vacuo. The resulting residue was stirred with 100 mL of a hexane/dichloromethane mixture (1:1). The mixture was then filtered through a short silica plug to remove the $Et_3N^+Br^-$ salt. The solvent was removed in vacuo to yield the cyanate ester-terminated oligomer **5** (1.69 g, 95%) as a pale yellow oil. IR [cm^{-1}]: ν 3060 (C=CH), 2969 (CH_3), 2270 (CN), 2236 (CN), 1591 (aromatic), 1502 (aromatic), 1478 (aromatic), 1365 (CH_3), 1222, 1171 (C–O), 1013, 968 (C–OCN), 833 (aromatic). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31–7.10 (m, aromatic-H), 6.93–6.88 (m, aromatic-H), 6.71–6.65 (m, aromatic-H), 1.67, 1.66, 1.65 (s, –CH_3).

2.6. Polymerization of cyanate ester monomers with copper (II) naphthenate/nonylphenol catalyst system

To the oil of oligomer **5** at 50 °C or the melt of BACY **1** at 85 °C was added 4 phr (parts per hundred parts of resin) of a copper (II) naphthenate dissolved in nonylphenol with stirring to evenly disperse the catalyst. The copper (II) catalyst system was prepared by dissolving 0.62 g of a 77% solution of copper (II) naphthanate in mineral spirits in 6.00 g nonylphenol. The samples were cooled and used in the DSC and TGA studies. After being cured by heating **5** and **1** at 150 °C for 2 h, 200 °C for 8 h and 250 °C for 5 h, the CE polymers **6** and **7** formed as films on the bottom of the TGA pan. TGA analyses of the polymers were then determined on the films from 25 to 1000 °C under either nitrogen or air.

2.7. Mechanical measurement sample preparation

Samples for rheometric measurements were prepared by degassing oligomer **5** or BACY **1** under vacuum at 150 °C for 2 h in a mold with cavity dimensions of 65 mm × 13 mm × 6 mm. The temperature of the mold was reduced to 85 °C and 4 phr of copper (II) naphthenate dissolved in nonylphenol was added with stirring. The resulting mixtures were degassed for an additional 30 min. The samples were placed in an oven and heated at 150 °C for 2 h, 200 °C for 8 h, and 250 °C for 5 h. The cured samples of oligomer **6** and BACY **7** were removed from the mold and sanded to a thickness of approximately 2 mm.

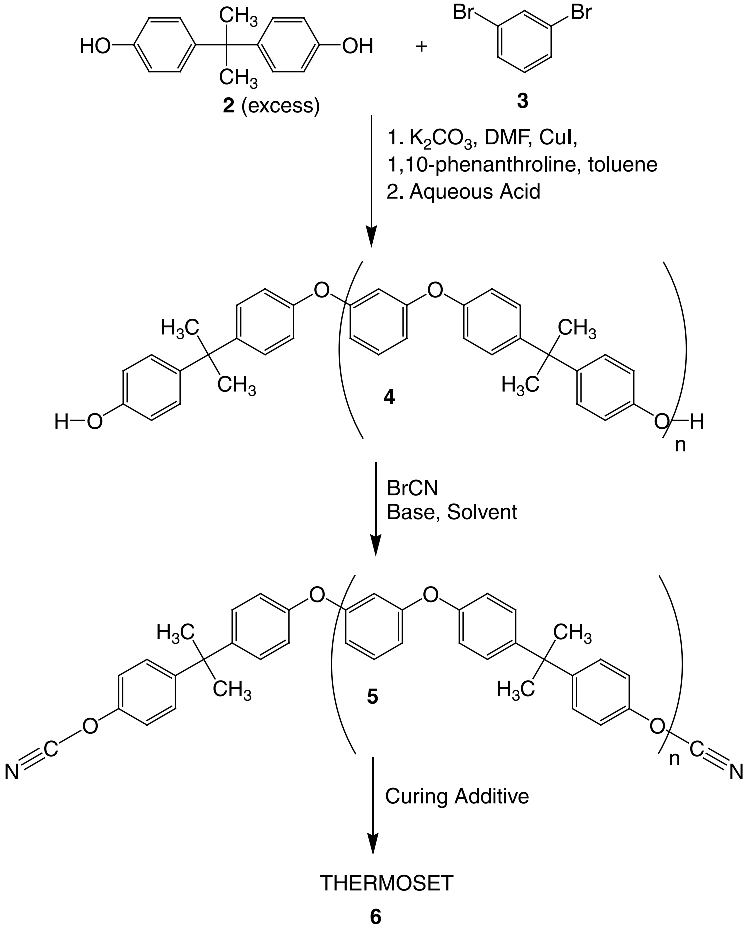
3. Results and discussion

A hydroxyl-terminated oligomeric aromatic ether **4** [24] where $n \approx 1$ was synthesized (Scheme 1) via the reaction between bisphenol A **2**, 1,3-dibromobenzene **3**, an organic solvent soluble copper (I) iodide complex [36–38] generated in situ from copper (I) iodide and 1,10-phenanthroline, and K_2CO_3 in the presence of *N*,*N*-dimethylformamide (DMF) and toluene. About 1.5 equiv. of K_2CO_3 were used in order to shift the reaction equilibrium to the product side in the synthesis of **4**. Water formed as the by-product was removed by azeotropic distillation at 135–145 °C. The hydroxyl-terminated oligomer **4**, which was isolated as an amber solid in 91% yield, was end-capped with the cyanate functionality by reaction with cyanogen bromide in acetone at low temperatures in the presence of triethylamine as the base. The oligomeric CE resin **5** was obtained as a yellow oil in 95% yield and was soluble in polar organic solvents such as diethyl ether, acetone, dichloromethane and DMF.

The reaction to produce CE resin **5** was monitored by infrared spectroscopy. Fig. 3 shows the IR spectra of compounds **4** and **5** (where $n \approx 1$). In compounds **4** and **5**, peaks were observed at 1591 and 1479 cm^{-1} corresponding to the 1,3-aromatic moiety in the oligomeric structure. The most prominent feature of **4** relative to **5** was the disappearance of the hydroxyl stretch at 3392 cm^{-1} and the appearance of the –OCN functionality located at 2270 and 2236 cm^{-1}. Two cyanate ester peaks were observed presumably because of the different length oligomeric species that exist in the mixture.

The incorporation of the aromatic ether spacer between the reactive end units for the neat monomer **5** enhanced its processability relative to BACY **1**. CE resins **5** and **1** exist as an oil and solid, respectively, at ambient temperature. Upon heating to 40 °C, the viscosity of **5** had been reduced to an extent that it could be readily formulated to shaped components without B-staging during the curing process. It appears that composite formulations by cost effective methods such as filament winding and resin transfer molding (RTM) can be performed at temperatures above 50 °C.

Since the ease of processability depended on the rate and temperature at which the resin cures, a metal salt curing additive was employed to allow the polymerization reaction to proceed rapidly and at a low temperature relative to the neat-cured system. Fig. 4 shows the DSC thermograms of the neat-curing of BACY **1** and oligomer **5**. For **1**, we observe an endothermic transition at approximately 80 °C attributed to the melting point and an exothermic transition commencing at around 260 °C and peaking at 295 °C for the conversion to the thermoset **7**. Oligomer **5**, being an oil, exhibits only an exothermic transition for the neat-curing process beginning at approximately 250 °C and peaking at about 310 °C. When 4 phr (parts per hundred parts of resin) of the copper (II) naphthenate/nonylphenol catalyst system was utilized (Fig. 5), **1** showed the melting point transition and an exothermic curing



Scheme 1. Synthesis of CE monomer **5** and thermoset **6**.

transition starting at 85 °C and peaking at 165 °C whereas **5** exhibited a broad exothermic peak commencing at around 80 °C and peaking at about 155 °C. These thermograms indicate that the addition of the copper catalyst lowers the initial curing temperature by about 160 and 180 °C for **1** and **5**, respectively. Moreover, it is apparent that under these curing conditions oligomer **5** has a larger processing window relative to **1**.

Rheometric measurements were performed on samples of the oligomeric **6** and BACY **7** polymers obtained by curing **5** and **1** with 4 phr of the copper (II) naphthenate/nonylphenol catalyst system under identical conditions. Fig. 6 shows a plot of the storage modulus to 300 °C for samples of **6** and **7**. The storage modulus at ambient temperatures for **6** and **7** were 1325 and 1275 MPa, respectively. This indicated a slightly larger storage modulus value for of **6** relative to **7**. Upon heating to 300 °C, both samples showed a sharp reduction in the modulus characteristic of a glass transition temperature (T_g) or a viscoelastic transition to a rubbery state. The T_g values of the CE resins, which corresponded to the midpoint of the sharpest decrease in the modulus curves, were centered at

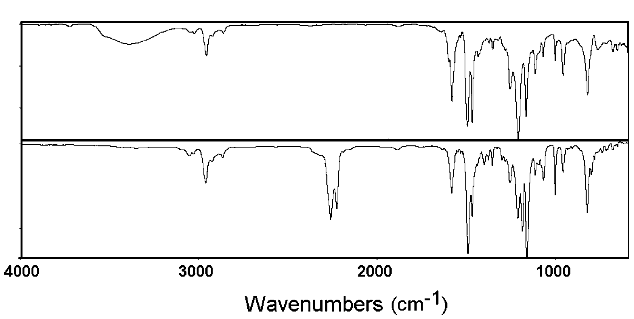


Fig. 3. Comparison of infrared spectra; (top) compound **4**; (bottom) compound **5**.

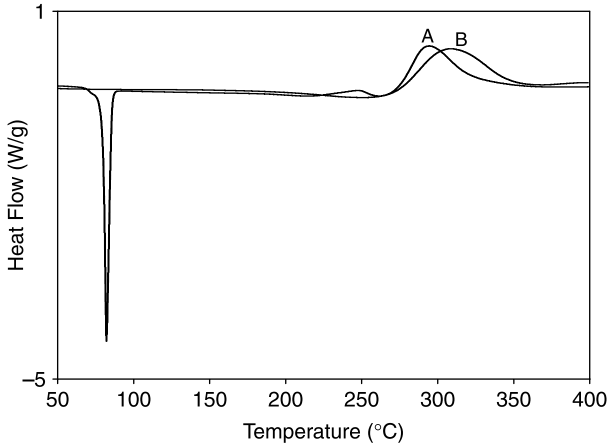


Fig. 4. DSC thermograms for the neat cure of BACY **1** (A) and CE oligomer **5** (B).

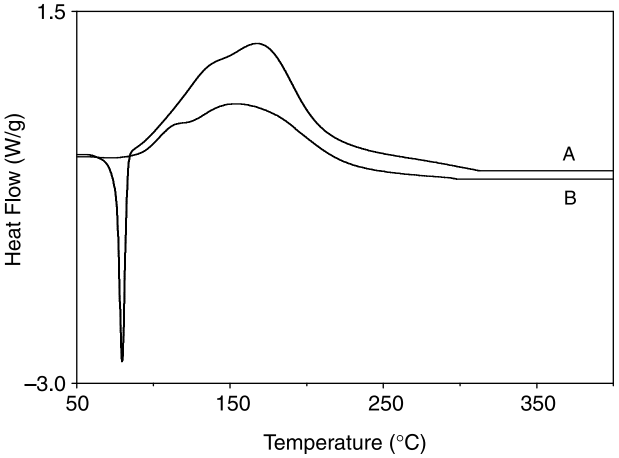


Fig. 5. DSC thermograms of BACY **1** (A) and CE oligomer **5** (B) cured with 4 phr of the copper (II) naphthenate/nonylphenol catalyst system.

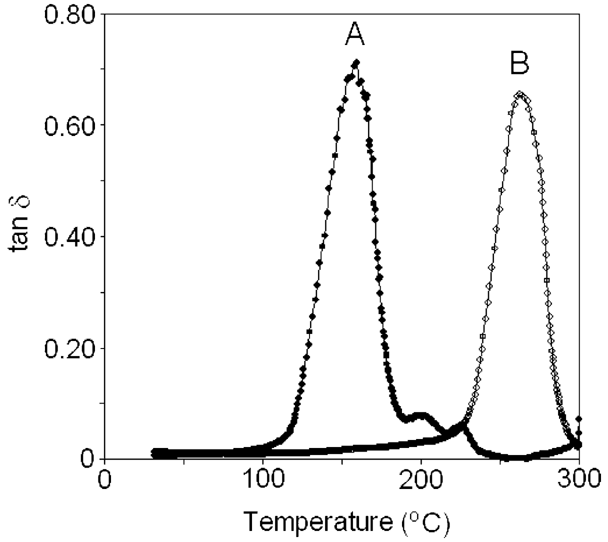


Fig. 7. Damping factor (tan δ) for polymer **6** (A) and **7** (B) cured with 4 phr of the copper (II) naphthenate/nonylphenol catalyst system.

approximately 140 and 255 °C for thermosets **6** and **7**, respectively. Fig. 7 shows the tan δ plots for polymer **6** and **7** cured to 250 °C. The peak maximum in the tan δ plots appeared at a higher temperature for polymer **7** relative to **6** and the peak maximum was near the determined T_g for both systems.

The flexural properties of the CE polymers **6** and **7** were also determined at ambient temperatures under identical conditions. Oligomeric polymer **6** displayed a flexural strength of 124 ± 14 MPa and flexural modulus of 3300 ± 100 MPa. Similarly, polymer **7** exhibited flexural strength and flexural modulus values of 126 ± 17 and 2700 ± 300 MPa, respectively. Based on these data and characteristics of the load-displacement curves, polymer **6** appeared stiffer than **7**. These results indicate that polymer **6** is probably more fully cured relative to **7** under the curing conditions used. Upon maximum heat treatment of 250 °C during the cure cycle, **6** and **7** have T_g values of 140 and 255 °C, respectively. Since, **6** is in the rubbery state at 250 °C, the reactive sites (cyanate esters) can more easily interact to form the network relative to **7**.

The hardness of polymers **6** and **7** was also evaluated and compared. Polymers **6** and **7** exhibited indentation hardness numbers (HR_M) of 97 ± 3 and 117 ± 1, respectively. Since, the higher number corresponds to the harder material, these results revealed that **6** was softer relative to **7**. The hardness number is derived from the plastic flow of a material after the removal of an applied load. It is a measure of the non-recoverable deformation of the material under a compressive stress. These results were not surprising since a reduction of crosslinking density should result in an increase in the plastic flow of a material and thus a decrease in the hardness value.

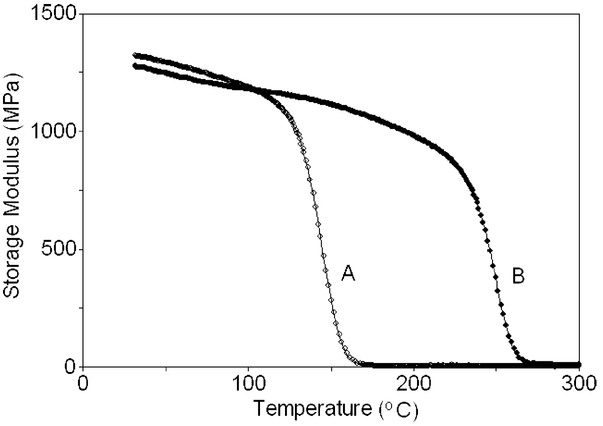


Fig. 6. Storage modulus for polymer **6** (A) and **7** (B) cured with 4 phr of the copper (II) naphthenate/nonylphenol catalyst system.

To verify the T_g values of the cured thermosets obtained by rheometeric studies, DSC analysis was performed on samples of **1** and **5** that had been heated to a maximum temperature of 250 °C in the presence of 4 phr of curing additive. In the case of the copper (II) naphthenate/nonylphenol assisted polymerization of monomer **5**, the T_g of the cured thermoset **6** was located at approximately 140 °C. The T_g did not change significantly and no exothermic peak was observed upon further heating at 275 and 300 °C in 2-h intervals. Additionally, FTIR indicated the presence of triazine ring peaks at around 1580 and 1370 cm^{-1} and the absence of the –OCN peaks at 2270 and 2236 cm^{-1}. Curing **5** in the presence of 8 phr of the copper (II) naphthenate/nonylphenol catalyst system under identical conditions did not change the T_g value. These observations indicated that thermoset **6** formed from CE **5** may be completely cured by post-curing to a maximum temperature of 250 °C for 5 h. The lower T_g value for **6** (140 °C) relative to **7** (255 °C) cured under identical curing conditions was predictable since the crosslinking density was reduced [39]. The T_g values determined by DSC and rheometric analyses were in agreement.

The thermal and oxidative stability of the polymerized products **6** and **7** were determined by TGA analyses (Fig. 8). When cured with 4 phr of the copper (II) naphthenate/nonylphenol catalyst system up to a maximum temperature of 250 °C, **6** shows weight retention of 95, 33 and 32% at 425, 700 and 1000 °C, respectively, upon heating under inert

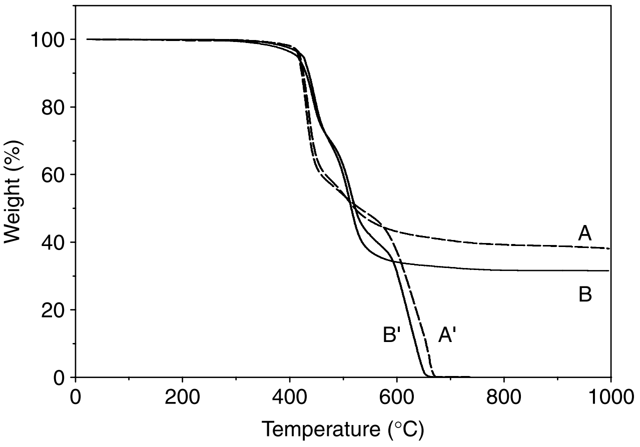


Fig. 8. Thermogravimetric analysis of polymers after catalytic curing: under N_2 polymer **7** (A), polymer **6** (B); air polymer **7** (A′), polymer 6 (B′).

conditions to 1000 °C. The highly crosslinked resin **7** exhibits a weight retention at 420 and 700 °C of 95 and 40%, respectively, and an overall char yield of 38% at 1000 °C [3,11]. The reduced char yield (∼7%) of thermoset **6** relative to **7** could be a result of the lower crosslink density of polymer **6**. When a catalytically-cured sample of polymer **6** was heated to 1000 °C under air, weight retention of 95% was observed at 415 °C with rapid decomposition occurring between 425 and 650 °C. Thermoset **7** showed a similar oxidative stability to 415 °C but exhibited an enhancement in thermo-oxidative properties with catastrophic degradation occurring between 425 and 675 °C.

Another important feature of CE thermosets is their limited water absorption. Fig. 9 shows a plot of the water absorption versus time for a sample of thermoset **6** soaked at 25 and 100 °C in distilled water. The maximum amount of water absorption over the course of 35 days at 25 and 100 °C was approximately 1.2 and 2.2% by weight, respectively. The water uptake appears to level off after approximately 21–30 days depending on the experimental temperature. For the use of polymer **6** in a high humidity or aqueous environment, the limited water absorption is a significant advantage over other high temperature polymers.

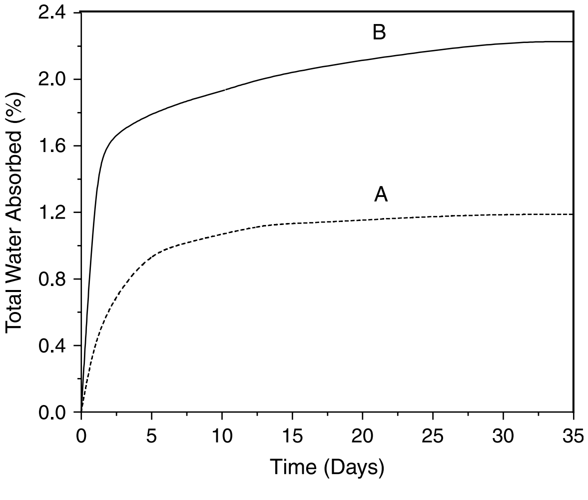


Fig. 9. Plot of the weight of water absorbed over time for thermoset **6** at 25 °C (A) and 100 °C (B).

4. Conclusion

Due to the liquid nature at ambient temperature, oligomeric CE resin **5** could have the potential for a wide variety of applications including printed circuit boards, as an adhesive, and as a matrix resin in structural components. Our synthetic approach permits the design and synthesis of a resin system that can be easily processed into shaped composite components by cost effective techniques such as resin transfer molding (RTM), resin infusion molding, pultrusion, and filament winding at ambient temperatures. Since, the length of the spacer between the terminal –OCN units can be readily controlled by the amount of the reactants used, it may be possible to control the rigidity, crosslinking density, T_g, and other physical properties of the resulting thermoset. When compared to commercially available CE resins, oligomeric resin **5** is a liquid at ambient temperature, has an increased processing window, and exhibits a low curing temperature upon heating in the presence of a copper (II) additive. Additionally, the introduction of the oligomeric spacer into the CE molecule **6** and the corresponding reduction in crosslink density appear to affect both the plastic flow of the material and its elastomeric properties. Polymer **6** also displays good thermo-oxidative properties and shows limited water absorption even at elevated temperatures. The procedure to produce resin **5** can potentially be applicable to a variety of bisphenols and dihaloaromatic compounds.

Acknowledgements

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