



Acceleration of cyanate ester trimerization by dicyanamide RTILs



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ABSTRACT

This work presents dicyanamide-containing ionic liquids as a new initiator system for cyanate ester resins. The cure effect was found in many dicyanamide-containing ionic liquids with diverse cations, and the dicyanamide was found to incorporate directly into the triazine network. The dicyanamide initiator provides an alternative to metal and hydroxyl catalysts, and produces a novel, ionic thermoset polymer. This polymer offers a new range of cure schedules, and opens the door to further research in degradation prevention, ionic thermosets, and nanocomposites.

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1. Introduction

Cyanate esters (CEs) are thermosetting resins with a range of valuable properties for high performance materials applications [1–3]. Notably, a glass transition temperature (T_g) of up to 400 °C promises applications in high temperature composites [4] and as a substrate for hot-solder microelectronics applications. Other significant properties of cyanate ester resins include good fracture toughness, excellent substrate adhesion, low shrinkage, low dielectric loss, and low moisture uptake. For applications in which performance in such areas justifies the additional cost, cyanate esters are a proven replacement for thermosets such as epoxies or maleimides in applications in the aerospace, electronics, and communications industries.

CE monomers polymerize via a unique, ring-forming trimerization. Neglecting side reactions, this reaction is depicted in Fig. 1, after Simon and Gillham [5]. Active hydroxyl donors in concert with coordination-center metal catalysts accelerate cure speed and extent. While nonylphenol is the most commonly added hydroxyl donor [6–8], a wide range of metals are used as synthesis catalysts, including titanium [6], cobalt [7], copper [8], chromium [9,10], iron [11], tin [12], zinc [13], and manganese [14]. Homopolymerization

without added catalysts has also been shown to occur at high temperatures. However, this reaction is still thought to be mediated by trace phenols and metals present in the mixture due to monomer degradation, impurity, or residual from synthesis [15].

Alternative cure systems for cyanate esters are desirable to mitigate the downsides of current catalyst systems. Current cyanate ester systems have practical and environmental downsides. Metal coordination centers, particularly copper, have been shown to accelerate hydrolysis within cured cyanate ester resins, leading to significant network degradation, T_g loss, and blistering [16,17]. Additionally, many hydroxyl donors, particularly the volatile, phenolic-based compounds that are polymer-miscible, such as nonylphenol, have been flagged as toxic to human health and harmful to the environment [18,19].

In this work, we present a family of room temperature ionic liquids (RTILs) that contain a dicyanamide (DCN) anion as an accelerant for cyanate ester cure. RTILs are organic ion pairs that form liquids at room temperature. Their ionic character imparts varied solution and reaction properties. Most notably, RTILs have negligible volatility, allowing for near complete solvent retention during processing. Additionally, the diversity of cation and anion structures combine to form a large library of unique combinations. This large library of compounds with similar structures allows applications engineers to choose ions and pair combinations that specifically optimize relevant properties, including solvent capacity, reaction chemistry, and toxicity.

In recent years, researchers have discovered a number of applications for RTILs in polymer systems, including sorbent

Abbreviations: RTIL, room temperature ionic liquid; CE, cyanate ester; EMIM, 1-ethyl-3-methyl imidazolium; DCN, dicyanamide.

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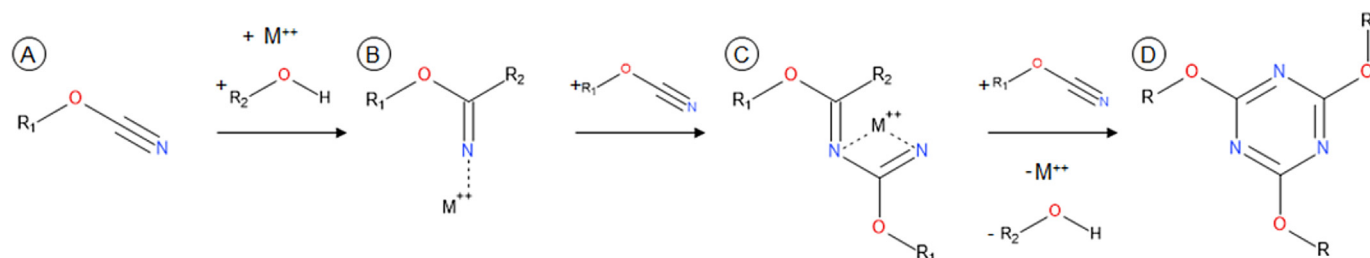


Fig. 1. Cyclotrimerization reaction of a cyanate ester monomer catalyzed by an hydroxyl source and a metal catalyst (M^{++}). The hydroxyl source combines with a cyanate ester monomer (A) to form an imidocarbonate (B). The metal-stabilized imidocarbonate can interact with a second monomer to form a stabilized dimer (C). A third monomer completes the triazine ring (D), and the hydroxyl source and metal catalyst are recycled for further reaction.

polymers, and electroactive polymers. Of particular interest, recent work by our group [20] and others [21–23] has demonstrated the viability of a range of ionic liquids for use in the initiation of polymerization for epoxy resins. In these studies, the cation has been found to be the reactant, and the efficacy of both imidazolium-based [20,21], and phosphonium-based [22,23] cations have been demonstrated. Moreover, our group has shown that RTILs chosen for both solvent interactions and thermoset initiation can create excellent silica [24], graphite nanoplatelet [24], graphite flake [25], and carbon nanotube [24,26,27] nanocomposites with increased processing efficiency.

One motivation for research into RTIL applications is their potentially advantageous environmental impact. The practical non-volatility of RTIL solvents significantly reduces the incidence of contamination and environmental spread. However, RTIL toxicity varies with ionic structure [28]. Current efforts attempt to systematically understand RTIL toxicity and propose new ion pairs which combine low toxicity and biodegradability with the physical properties of the designed compound [29]. Thus, RTILs have the demonstrated potential to reduce toxicity in industrial systems through minimized evaporative loss, but significant additional work must be accomplished before such RTIL systems can be truly considered green processes [30].

The RTIL-based polymer cure system presented here allows for practical replacement of metal and hydroxyl-donating catalysts. This new chemistry allows for the mitigation of the challenges associated with traditional catalyst systems. Additionally, the novel chemistry, processing, and physical properties of RTIL-cured CE systems allows for a range of future applications, including ionic thermosets and nanocomposites.

2. Results and discussion

Differential scanning calorimetry (DSC), Fourier-transform infrared spectroscopy (FTIR), and dynamic mechanical analysis (DMA) were used to characterize the interaction between RTILs and CEs. Calorimetry experiments show the effect of solution composition on cure kinetics, illustrating both the effect of RTIL concentration and cation structure. Isothermal, time-resolved FTIR spectroscopy separately shows the specific interaction between DCN anions and cyanate ester functional groups, the formation of reaction intermediates, the formation of side-products, and the formation of triazine rings. Finally, DMA on cured samples shows the effect of RTIL content on T_g . From these data, a cure mechanism was developed.

Three primary experimental observations led to a hypothesized reaction mechanism. First, RTIL solutions of varying structures and concentrations accelerate cyanate ester cure. Second, the cyanates in the dicyanamide anion were partially then fully reacted. Third, plasticization occurred with increasing RTIL content.

2.1. Cure acceleration

Fig. 2 shows results of a 10 °C/min temperature ramp DSC experiment for 0–9% EMIM-DCN in bisphenol E dicyanate ester (LECY). EMIM-DCN shows a strong effect on cure temperatures. This shift in cure temperature is monotonic with respect to concentration. Even low concentrations (0.5%) showed a marked decrease in kickoff temperature and peak exotherm temperature. This indicates that a range of RTIL concentrations can be used for cure acceleration.

In addition to EMIM-DCN, five other RTILs were tested at equivalent molarities. Fig. 3 depicts their cure DSC curves. All RTILs significantly accelerated cure. 1-(2-hydroxyethyl)-3-methylimidazolium dicyanamide (Fig. 3A) showed the lowest temperature cure, likely due to the hydroxyl-donor on the cation acting as a complementary initiator. A non-dicyanamide RTIL, 1-ethyl-3-methyl imidazolium tetrafluoroborate (BMIM- BF_4 Fig. 3F), also accelerates LECY cure, although the reaction kickoff temperature of BMIM- BF_4 is still significantly higher than for the DCN-containing structures. This indicates that, in addition to the specific cyanamide-cyanate ester interaction reported in this work, the presence of ionic pairs and/or entrained water have a catalytic effect on the cure performance of the CE system.

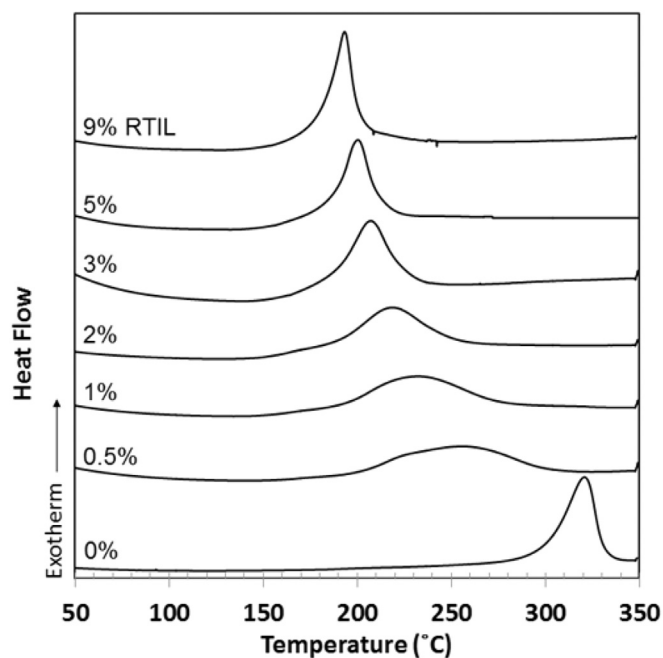


Fig. 2. Calorimetric curves of LECY cured with varying concentrations of EMIM-DCN, from 0 to 9 wt%. An increase in RTIL content causes cure to kick off at lower temperatures.

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