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Room Temperature Ionic Liquids as Thermally Latent Initiators for Polymerization of Epoxy Resins

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Latent curing agents are designed to remain inactive at ambient conditions and to undergo controlled reaction upon exposure to external stimuli, such as elevated temperature or radiation that leads to cure of the resin. The desired inertness increases storage and handling capabilities. Latent curatives have been developed using a variety of hardeners in either multicomponent or one-pot formulations.[1] In particular, the initiation and polymerization of epoxy resins are of commercial interest due to the great versatility in application of these systems. They are used in adhesives, insulation materials, paints, and fiber reinforced composites. Some examples of thermally initiated curing agents are based on nitrogen (amines, imidazole), anhydrides, phenolic derivatives,[1] and metal complexes.[2] One-pot epoxy formulations typically use imidazole[3] or dicyandiamide (Dicy)[4] and exhibit complex initiation and propagation reaction schemes. Dicy is thermally latent because it is a solid at room temperature but melts and dissolves into the epoxy resin at elevated temperatures to initiate polymerization. This need for a phase transformation results in practical drawbacks during manufacture and processing, such as difficulty dispersing the curing agent and inhomogeneous cure. A miscible liquid initiator with a similar range of latent properties would solve these problems and provide significantly improved systems.

Ionic liquids (ILs) have melting points below room temperature, low viscosities, and highly tunable physicochemical properties[5] showing promise in several polymers[6] such as in separation membranes,[7] as solvents,[8] lubricants,[9] porogens or novel composite membranes.[10] There is one communication in the literature wherein the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate has been shown to harden epoxies.[11] However, the degree to which reaction occurs, the mechanism of reaction and resulting mechanical properties remain unclear, and initiation might be through a mechanism similar to $BF_3 \cdot$amine complexes. The following report demonstrates that, out of many ionic liquids tested (see Supporting Information), 1-ethyl-3-methylimidazolium dicyanamide ([emim]$N(CN)_2$) not only can be used to initiate polymerizations of epoxy resins but also can be used in formulations which exhibit excellent miscibility and long-term room temperature latency, in addition to producing a cross-linked structure with good thermomechanical properties once cured.

[emim]$N(CN)_2$ (Solvent Innovation, GmbH) and diglycidyl ether of bisphenol A (EPON-828, $n = 0.13$, molecular weight $= 376$ g mol^{-1}, Miller Stephenson) were used as received. Mixtures of known weight percents of ILs in epoxy resins were prepared at room temperature to obtain homogeneous mixtures. The latency of the mixture at low concentrations of ionic liquid was determined by monitoring the consumption of the epoxy groups using near-infrared spectroscopy (4528 cm^{-1}, epoxide group), following a method discussed in previous work.[12] Figure 1 is a plot of fractional conversion of epoxide groups versus time measured under isothermal conditions. At a concentration of ~3.3 wt % ionic liquid, no apparent conversion of the epoxide group was observed over a period of 1 h at 80 °C. A step increase of the cure temperature to 165 °C caused the reaction to proceed toward completion within 20 min. This behavior demonstrates the thermal latency of the formulation. Figure 1 (inset) shows (a) pure EPON-828 and (b) EPON-828 with 3.5 wt % [emim]$N(CN)_2$ after ~60 days at ambient conditions. Under such conditions, there is no phenomenological evidence to indicate reaction. After complete cure, the result (c) is a highly cross-linked and mechanically strong thermoset which adheres to the bottom of the vial. The results qualitatively indicate that,

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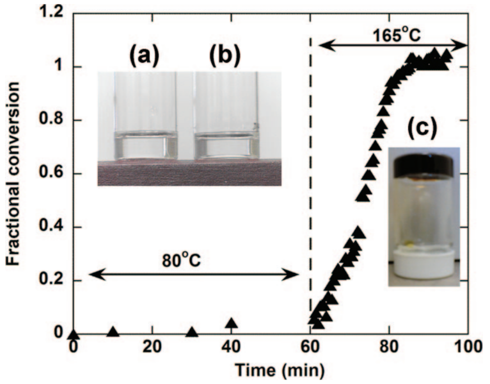

Figure 1. Plot of fractional conversion of epoxide groups versus time showing the 3.3 wt % [emim]N(CN)$_2$-EPON-828 formulation at 80 °C for ~1 h followed by complete cure at 165 °C within 20 min. Inset shows EPON-828 (a) without initiator and (b) with 3.5 wt % [emim]N(CN)$_2$ after 60 days at room temperature showing no apparent changes and (c) after cure at 165 °C for 2 h showing a cross-linked and darkened sample.

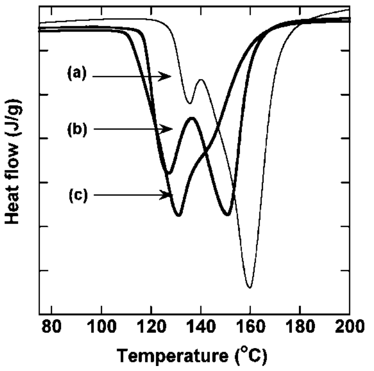

Figure 2. DSC traces of heat flow versus temperature for EPON-828 with (a) 3, (b) 9, and (c) 15 wt % [emim]N(CN)$_2$ heated at 2 °C/min (curves are plotted as exotherm down).

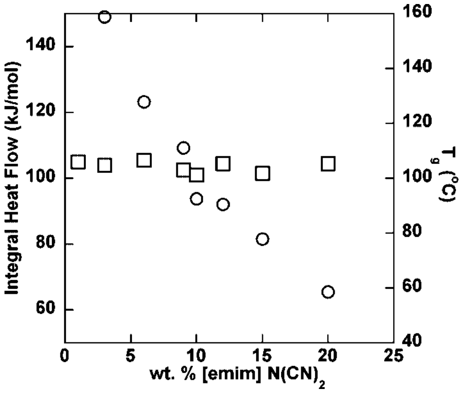

Figure 3. Plot showing (○) T_g and (□) integral heat flow determined from DSC at different [emim]N(CN)$_2$ initiator concentrations.

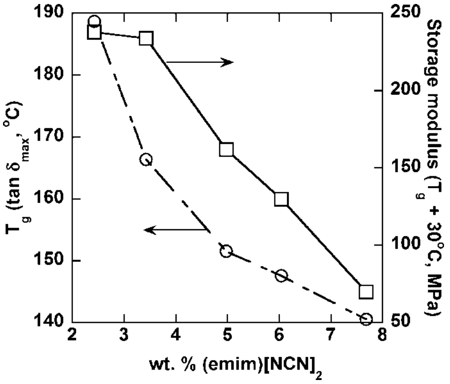

Figure 4. Plot showing the (○) T_g at tan δ maximum and (□) storage modulus at (T_g + 30 °C) as a function of [emim]N(CN)$_2$ initiator concentration evaluated from DMA.

under these conditions, the one-pot formulation consisting of [emim]N(CN)$_2$ and EPON-828 exhibit long-term storage stability.

Scanning differential scanning calorimetric (DSC) analysis of EPON-828 cured using [emim]N(CN)$_2$ provides information regarding differences in cure behavior and glass transition temperatures, T_g, associated with ionic liquid concentration. First scans on these samples were conducted at a ramp rate of 2 °C/min from 0 to 250 °C to determine the heat of reaction (ΔH_R, determined from an integral of the reaction exotherms). Subsequent scans (10 °C/min, 0 to 200 °C) were used to determine T_g, while also confirming the absence of residual reaction.

Figure 2 is a plot of heat flow versus temperature during the first scan of [emim]N(CN)$_2$-EPON-828 mixtures at [emim]N(CN)$_2$ concentrations between 3 and 15 wt %. The plot indicates the presence of a dual reaction exotherm that varies with the concentration of ionic liquid used. An increase of the [emim]N(CN)$_2$ concentration results in a gradual increase of the first reaction exotherm at the expense of the second exotherm, and at 15 wt %, the first exotherm becomes predominant. For an increase in the [emim]N(CN)$_2$ concentration between 3 and 15 wt %, the peak temperature reduces from 160 to 131 °C, and the onset temperature decreases from 130 to 110 °C. We preliminarily suggest that cure might proceed via reactions between the epoxy group and cyanamide, in either its original state[13] or one of its tautomeric forms.[14] Although imidazole and substituted imidazoles are known to polymerize epoxies,[15] the absence of similar reactions in other investigated imidazolium based ionic liquids (see Supporting Information) and the absence of an unsubstituted nitrogen for adduct formation suggests that the cation in itself might not initiate polymerization like an imidazole. However, certain cation/anion combinations could alter reaction behavior such as has been observed for an imidazole/dicyandiamide pair.[15] Such a reaction scheme might suggest a cross-linked network, with imidazolium cations linked to the polymer network through ionic interactions to dicyanamide counterions which are part of the polymer network. Interestingly, the use of 1-butyl-3-methylpyridinium dicyanamide ([bmPy] N(CN)$_2$) as a curing agent results in the initiation of epoxy cure but does not result in similar reaction profiles or reaction enthalpies. Moreover, cured samples have little mechanical stability as they are brittle and powdery. This provides some preliminary clues on the influence of particular cation/anion pairs on the reaction mechanism.

Figure 3 is a plot of integral heat flow and T_g (extrapolated tangent midpoint method) as a function of [emim]N(CN)$_2$ content between 3 and 20 wt %. The overall heat of reaction (per mole of epoxy groups) remains nearly constant at 104 ± 1.7 kJ/mol. A value of 100 kJ/mol appears to agree well with work of other researchers for chain polymerization of DGEBA using imidazole.[16] The plot also indicates a significant depression in the T_g of the cured thermoset, from 158 °C at 3 wt % [emim]N(CN)$_2$ to 58 °C at 20 wt % [emim]N(CN)$_2$. This can be attributed to plasticization of the network structure by the [emim]N(CN)$_2$ and changes in the effective cross-linking density (and molecular weight between cross-links, M_c).

Figure 4 shows a plot of T_g (at tan δ_{max}) and rubbery modulus (storage modulus at T_g + 30 °C) obtained from dynamic

Table 1. Char Yield at 600 °C and Decomposition Temperature, T_d, at 80% Weight Loss at Different [emim]N(CN)$_2$ Initiator Concentrations Compared to Cationically Cured EPON-825[12] and Amine Cured EPON-828[18]

sample	char yield (%)	T_d (°C)
EPON-828 (1 wt %)	2.5	413
EPON-828 (3 wt %)	3.3	413
EPON-828 (9 wt %)	6.1	412
EPON-825 (cationic)	0	414
EPON-828 (amine)	8.0	367
[emim]N(CN)$_2$	20.6	294

mechanical analysis (DMA) on thermosets cured at different [emim]N(CN)$_2$ concentrations (single cantilever, ramp rate: 2 °C/min, frequency: 1 Hz, temperature range: 30−250 °C). The data show that the T_g and rubbery modulus decreases with an increase in [emim]N(CN)$_2$ concentration, suggesting a significant increase of M_c with the ionic liquid content. The formation of a thermosetting network structure in this system is probably dependent on two reactions: the condensation or adduct formation of epoxide groups with [emim]N(CN)$_2$ and subsequent etherification of hydroxyl groups.[17] The increase in M_c with increasing [emim]N(CN)$_2$ concentration could be suggestive of a large number of initiating species being formed at the expense of ether linkages, thus resulting in a lower cross-link density. This hypothesis is also supported by the existence of two reaction exotherms in Figure 2 and the presence of a double peak in the loss modulus from DMA (see Supporting Information).

The values of rubbery moduli are in the range of ~245 MPa to ~65 MPa; although higher than those of amine-cured epoxies,[18] these are consistent with observations on other epoxies cured with ionic liquids[19] and are in the same range as cationically cured epoxies.[20] This suggests that the presence of ionic groups along the polymer backbone may result in an apparent lowering of M_c for such ionic liquid cured epoxies due to physical cross-links associated with ionic interactions. Further studies into the nature of this effect are ongoing.

Table 1 compares thermogravimetric measurements (ramp rate: 10 °C/min, 30−700 °C, N_2 atmosphere) of [emim]N(CN)$_2$ cured EPON-828 compared to an amine cured epoxy (at stoichiometric ratio)[18] and cationically cured epoxy.[12] All samples showed similar degradation profiles (see Supporting Information), and the decomposition temperature at 20% weight loss was 413 °C ± 1 °C for all [emim]N(CN)$_2$ cured samples. The data show that the addition of [emim]N(CN)$_2$ to cure EPON-828 does not result in inferior thermal stabilities when compared to a cationically cured or amine cured epoxy. Comparison of char yields at 600 °C indicates that samples with higher [emim]N(CN)$_2$ concentration have higher char mass, similar to that of an amine cured epoxy, while cationically cured EPON-825 has no measurable char at 600 °C. This result is understandable from the fact that pure [emim]N(CN)$_2$ has a char yield of 21 wt % at 600 °C and could add to the thermal stability of the network structure. In addition, the absence of an appreciable weight loss at the decomposition temperature of [emim]N(CN)$_2$ suggests that most of the ionic liquid has reacted into the network structure.

In summary, this work shows for the first time that [emim]N(CN)$_2$ can be used as a thermally latent curing agent for epoxide group containing monomers. The results indicate that the concentration of [emim]N(CN)$_2$ can be used to influence cure behavior and properties of the resulting polymer network. The ionic liquid appears most likely to be incorporated into the network, perhaps resulting in a cross-linked polymer with bulky counterions. Preliminary work has also shown that [emim]N(CN)$_2$ can be used to cure other multifunctional epoxies. Additionally, on the basis of results to date, it is postulated that slight modification to the ionic liquid's ion pairs should result in control over the latent cure behavior. Further details on the cure mechanism and mechanical properties of IL-initiated epoxy cure are forthcoming.

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Supporting Information Available: List of ionic liquids evaluated using the same cure schedule; storage and loss moduli for [emim]N(CN)$_2$ cured EPON-828; thermal decomposition profiles and the structure of [emim]N(CN)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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