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Rapid Crosslinking of Epoxy Thermosets Induced by Solvate Ionic Liquids

Nishar Hameed, [a,] * *Daniel J. Eyckens,* [b] *Benjamin M. Long,* [c] *Nisa V. Salim,* [a] *Jaworski C. Capricho,* [a] *Linden Servinis,* [b] *Mandy De Souza,* [b] *Magenta D. Perus,* [b] *Russell J. Varley,* [b] *and Luke C. Henderson.* [b,] *

[a] Faculty of Science, Engineering & Technology, Swinburne University of Technology, Hawthorn, VIC 3122 Australia. [b] Institute for Frontier Materials, Deakin University, Waurn Ponds Campus, Geelong, VIC 3216, Australia. [c] School of Health and Life Sciences, Federation University, Mt Helen, VIC 3350, Australia.

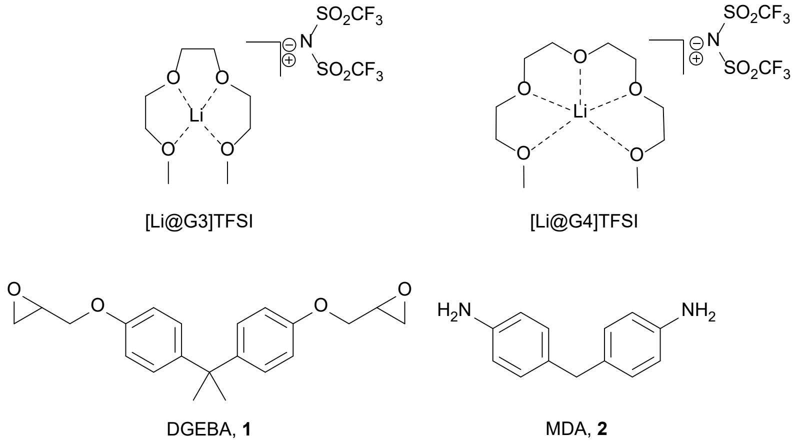
ABSTRACT The high-volume manufacture of fibre reinforced composites faces a huge challenge because long resin curing times put a low ceiling on the total output of parts produced per year. To translate the benefits from using epoxy in large volume production platforms, cure cycle times of less than 1 min must be achieved. In this work, we report solvate ionic liquids (SILs) as simple and efficient rapid curing catalytic additives in epoxy systems. Ultra-fast curing was observed at low levels of 1-5% SILs into epoxy resin, and the cure rate is enhanced up to 26-fold without compromising the mechanical and thermal properties. Further investigations revealed that enhancement in the cure rate is dependent of the type of SILs employed, influenced by the metal centre, the ligands around the metal and the identity of the counter anion. The relative Lewis acidity of each of the active complexes was calculated and the rapid cure effect was attributed to the activation of the epoxide moiety via Lewis acidic nature of the SIL. Making epoxy thermosets rapidly processable enable enormous benefits, finding applications in a whole variety of transformation methods that exists for traditional glass and metals.

Keywords: Rapid cure resin, epoxy, ionic liquids, cross linking, additive manufacturing, Industry 4.0

Introduction

A major limitation with the high volume, rapid manufacture of thermosetting polymer and composite products is their relatively long curing time and high curing temperatures. This induces large costs with respect to energy requirements, capital costs for ovens/autoclaves to be operating in parallel, and frequent maintenance regimens. Compared to thermoplastic polymers, which can be thermoformed, or extruded, in high volume, these limitations must be overcome for thermoset resins to persist as a viable material. Some advances have been made in the development of fast-curing resins,[1,2] though this has mostly been through the design of new chemical systems. This is not optimal as manufacturers have typically optimized a production process specific to the inherent properties of a resin (e.g. viscosity, cure temperature, exotherm, etc.). The use of microwave energy in curing composites has also been shown to induce rapid polymerization in epoxy systems.[2–4] Although an effective approach, process upgrade entails a lot of costs. A much more practical solution to these problems is the use of an additive, which does not affect these physical properties at room temperature but can enhance the rate of cure, or lower the temperature of cure, as required. Thus, offering the best of both situations, high process-ability with ‘on-demand’ curing properties. Ionic liquids (ILs) have been used to modify plastics for some time, with phosphonium and imidazolium derived ILs being employed.[5–7] Typically, macroscopic changes occur due to this modification such as depression in glass transition temperature, increased storage modulus, and plasticization.[8–12] ILs were also reported as suitable curatives of epoxy prepolymer, *in lieu* of amine hardeners[13,14], or in combination with carbon nanoparticles[15] and electrolyte material in battery applications.[16–20] Another class of ionic liquids, known as deep eutectic solvents (DES), were demonstrated to cure epoxy systems at room temperature. However, in the work of Lionetto *et al.*, the use of DES required a chemically functionalized epoxy precursor and the fastest cure time using this system was two weeks at ambient conditions.[21] In contrast, Maka *et al.*, obtained a faster pot life at ambient temperature of two days by direct incorporation of 9 phr DES in a low molecular weight bisphenol-A based epoxy system.[22,23] Significantly, Maka *et al.*, also obtained epoxy/DES formulations that exhibited no viscosity changes for at least 150 days of storage at room temperature.[22] In the recent past, solvate Ionic Liquids (SILs) have been characterized and reported as potential solvents for organic transformations.[24–26] SILs are a relatively new class of ionic liquids consisting of an equimolar mixture of a coordinating solvent with a salt, as in the case of lithium *bis*(trifluoromethanesulfonyl)imide ([Li] [TFSI]) in either tetra- or tri-glyme.[27] The polyether glyme group chelates the lithium ion, thereby 'softening' the hard ion, imparting ionic liquid characteristics. They are relatively cheap, costing approximately $1 per gram at laboratory scale of typically less than a kilogram. It should be noted that the glyme component of the SILs are largely commodity chemicals and are potentially available in significant quantities at a lower price point. Additionally, the use of a lower purity LiTFSI may reduce costs further, though the authors cannot comment on the reproducibility of the properties reported here or elsewhere in this case. A similar 'solvated' lithium derived pseudo-ionic liquid, 5.0 M lithium perchlorate in diethyl ether (5.0 M LPDE) was reported in the late 1990's and 2000's.[28,29] While this solvent was useful as a reaction solvent, it was difficult to process due to the hygroscopic character of both reagents. It has been demonstrated that these glyme-derived SILs are exceedingly useful for electrocyclic reactions,[24] and serve as excellent reaction media for the synthesis of α-aminophosphonates.[26,30] Part of their usefulness is their relatively strong Lewis acidic properties, measured as a Guttmann acceptor number,[31] and thus, can assist in the activation or chemical reactions. Other features of SILs, such as the hydrogen bonding characteristics and polarity are a consequence of this strong Lewis acid character.[32]

This paper reports the use of SILs (Figure 1) as a catalyst to thermoset resins to significantly enhance cure rate and decrease cure temperature as required. This is the first demonstration of using SIL to effect ultrafast curing in epoxy systems with potential for easy adoption in large scale manufacturing. Significant enhancement in curing rate was observed at very low additive amounts (1-5%), with less significant effect on the thermoset's final mechanical or thermal properties. Furthermore, closely related complexes were explored for their catalytic activity, physical properties, as well as their action on other epoxy resin systems.



[Li@G3]TFSI [Li@G4]TFSI

DGEBA, **1** MDA, **2**

Figure 1. Structure of SILs and the epoxy-amine combination used in this study.

Experimental Section

Materials. The epoxy precursor diglycidylether of bisphenol-A (DGEBA) with epoxide equivalent weight of 172–176 and curing agent *4,4'*methylenedianiline (MDA) were purchased from Aldrich Chemicals. RIM935 and its hardener RIMH 936 was obtained from Hexion. RIM935 as a bisphenol A/F based epoxy resin with an epoxide equivalent weight of 155 – 165. Hardener RIMH 936 is a modification of aliphatic and cycloaliphatic amines. Lithium *bis*(trifluoromethanesulfonyl)imide was purchased from Oakwood Chemicals, USA. All other metal salts and ligands were obtained from Sigma.

Preparation of Catalysts. The synthesis of SILs has been reported elsewhere.[33] Briefly, equimolar amounts of metal salt and ligand were combined in a round bottom flask with stirring at room temperature (or heated to 80° C) overnight. To remove residual water observed after long periods of standing, these SILs were dried by heating under vacuum. The resulting mixture was collected and used as is.

For small scale formation of SILs, where neat mixing was not practical, the salts and ethers were taken up in a small volume of water. In cases where the salts or crown ethers were not soluble in water, a small amount (~10%) of ethanol was added to solubilise the reagents and these were heated as described above. The residual solvent and water was removed via heating under reduced pressure.

Preparation of Thermosets. The epoxy/hardener was formulated as per resin system instructions (for DGEBA/MDA and RIM system) with the additive pre-dissolved in the epoxy component (or with the hardener at 80° C for DGEBA/MDA). The mixture was stirred until homogeneous. For DGEBA/MDA systems, the stoichiometric ratio was calculated. The mixture was then poured into pre-heated (100 °C) moulds, cured at 100 °C for 10 hours and then post-cured at 150 °C for 2 hours.

Rheological measurements. Rheological measurements were conducted on a TA Instruments HR-3 Rheometer with parallel plate geometry, using disposable 25 mm aluminium plates. The measurements were performed at a frequency of 1 Hz, a strain of 0.01, and a 0.5 mm gap between the plates. For dynamic rheology, the samples were heated at rate of 2° C /min. The gel point here was calculated from the crossover point of loss modulus and storage modulus values during measurements. The onset point was determined as the temperature point at which curing begins (a rise in viscosity) during isothermal rheological measurements.

For the initial round of rheological measurements (Figure 2 and Table 1), DGEBA/SIL/MDA mixture was stirred at 80 °C until a homogeneous mixture was obtained. The mixture was then immediately transferred to a freezer (-20 °C) to stop from curing and stored for 24 hours before the rheological measurements were taken. For all other samples, the experiment was conducted immediately after the homogenous mixing was achieved at 80 °C.

Thermomechanical measurements. Melting points were determined on SMP3 melting point apparatus.

Differential scanning calorimetry (DSC) experiments were performed using 5–10 mg of the samples under an atmosphere of nitrogen gas with a TA-DSC model Q200 instrument. The samples were first heated to 100 ^{o}C and held at that temperature for 5 min to remove the thermal history. Then, the samples were cooled to 80 ^{o}C at the rate of 20 ^{o}C/min, held for 5 min, and again heated from 80^{o} to 250 ^{o}C at 20 ^{o}C/min (second scan). The *Tg* values were taken as the midpoint of the transition in the second scan of the DSC thermograms.

Thermogravimetric analyses (TGA) were performed on Netzsch STA 409 thermogravimetric analyzer over a temperature range of 25–600 ^{o}C at a heating rate of 10 ^{o}C/min under nitrogen atmosphere.

Dynamic mechanical analysis (DMA) were performed on a dynamic mechanical thermal analyzer (TA Q800, USA) in a single-cantilever mode under liquid nitrogen at a frequency of 1 Hz and a heating rate of 3 °C/min. The specimen dimensions were 30 X 5.0 X 2.0 mm^3. The storage modulus, loss modulus, and tan delta were measured from 25 °C to 250 °C. The *Tg* was taken at the maximum of the tan delta curve in the glass transition region.

The tensile properties of the composites were measured on an Instron 30 kN SD tensile testing machine. The tests were conducted with dumbbell shaped specimens according to ASTM standard D638. At least five specimens were tested to obtain the average values of tensile properties for all the specimens.

Determination of the Gutmann acceptor number: The additive (0.2 mM) was dissolved in a solution of triethylphosphine oxide in Benzene-d_6 (0.067 mM). Phosphorus-31 NMR was conducted on a Bruker Avance 500 MHz spectrometer. A proton decoupled ^{31}P Single pulse experiment was collected and the change in the chemical shift noted ($\delta_{\text{adduct}} - \delta_{\text{triethylphosphine}} = \Delta\delta_{\text{adduct}}$). This was then multiplied by a factor outlined by Gutmann [$\Delta\delta_{\text{adduct}}$ x $1/(\delta_{\text{SbCl5}\leftarrow\text{Et3PO}} - \delta_{\text{triethylphosphine}}) = \Delta\delta_{\text{adduct}}$ x 2.348] to provide the acceptor number.[31] In all cases the sharp peak attributed to the triethylphosphine:additive adduct in the ^{31}P NMR spectra was used in the calculations. The broad undefined peak was attributed to disassociated/hydrated species (NB: a biphasic mixture was isolated after addition of deuterated benzene and was highly likely due to poor solubility of the additives in benzene). For the [Mg@G3]TFSI additive which produced 2 broad peaks with poor signal to noise, one peak was characteristic of the hydrated species previously mentioned and one further downfield was used for estimation of the Gutmann number.

Results and Discussion

Initially, a high additive amount (20% by wt.) was dosed into the bisphenol-A diglycidylether (DGEBA) epoxy resin together with stoichiometric amount of *4,4′*-Methylenedianiline (MDA) curing agent and rheology measurements were carried out to determine any increase in curing rates. Figure S1 showed that addition at 20% by weight of both *bis*(trifluoromethanesulfonyl)imides ([Li@G3]TFSI) and ([Li@G4]TFSI) resulted in substantial reduction in curing onset, specifically to 64 °C and 76 °C, respectively (equivalent to nearly 50% reduction in curing temperature compared to neat epoxy resin). This dramatic decrease in cure temperature has large ramifications on energy consumption and consequently on the cost input of curing these polymers. Following this result, the [Li@G3]TFSI in epoxy/MDA was examined in more detail, and at lower dosages with epoxy (Table S1) to see if, under isothermal conditions, increases in cure rate could be observed. Isothermal rheological experiments at 100 °C of this SIL dosed epoxy (Figure 2) showed significant decrease in cure time. For neat the epoxy/MDA, the curing reaction started after 31 minutes as indicated by the initial viscosity rise (onset) and it is

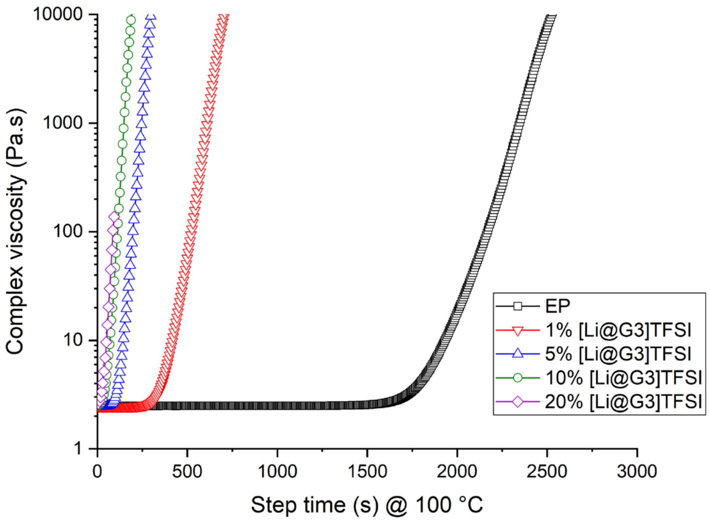


Figure 2. Isothermal rheological profiles of epoxy curing using 1%, 5%, 10%, and 20% of [Li@G3]TFSI additive.

typical for standard DGEBA resin. Upon addition of only 1% [Li@G3]TFSI an 80% reduction in cure time was observed. Further improvements were observed for increasing amounts of [Li@G3]TFSI to 5%, 10%, and 20% of the SIL in epoxy resin. At 20% [Li@G3]TFSI, the onset of curing occurred within 25 seconds, culminating exceptionally rapid cure times. The approximate gel point was also determined from the isothermal rheological profiles in Figure 2 and listed in Table 1. The time where the crossover of the storage modulus and loss modulus (*G’ = G”)* or the point in the curve where *tan δ* is equal to unity is considered as the approximate gel point. Representative curves for the neat epoxy/MDA and with the SIL mixtures showing this cross-over are provided in Figure S2 to Figure S6. Accordingly, for the 20% [Li@G3]TFSI, the approximate gel point occurred in 112 seconds. The cured samples containing various concentrations of SILs were further examined to understand the effect of additives and rapid cure times on the physical material properties. Of immediate interest were properties such as glass transition temperature, storage modulus, thermal decomposition, tensile strength, and Young’s modulus, also listed in Table 1.

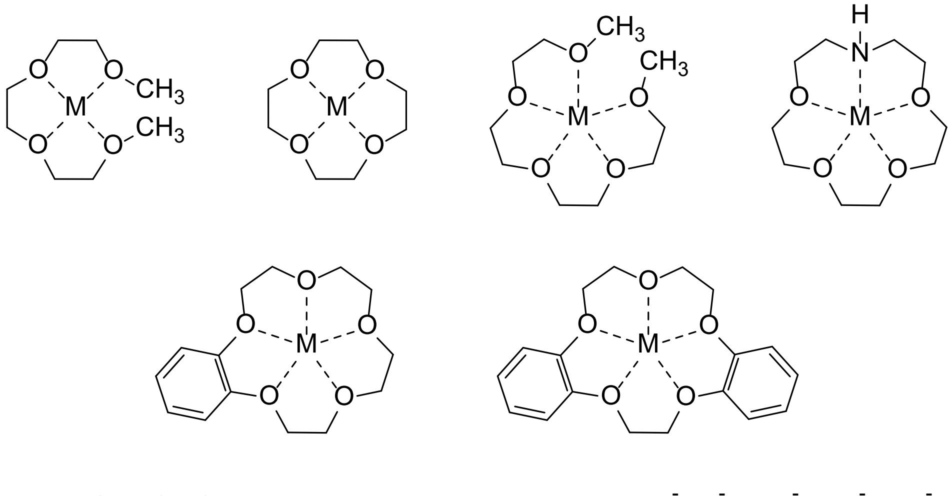
Table 1. Physical properties of rapid cured epoxy/SIL systems

	Gel-Point approx. (sec)	Tg (°C)	Tmax (°C) [a]	Storage Modulus (GPa)	Tensile Strength (MPa)	Young’s Modulus (GPa)
EP	2588	172	404	10.0	75.9±6.5	1.75±0.06
1% [Li@G3]TFSI	724	169	397	10.3	77.4±7.0	1.70±0.07
5% [Li@G3]TFSI	302	160	378	10.7	65.7±5.6	1.83±0.03
10% [Li@G3]TFSI	177	144	371	11.2	57.1±5.0*	1.86±0.04
20% [Li@G3]TFSI	112	122	360	11.3	51.7±6.6*	1.62±0.08

* Denotes statistical difference relative to EP ($P>0.05$)

[a] peak maximum value

The effect of the SIL on these parameters may dictate to what applications these SIL/epoxy systems are viable. As would be expected the *Tg* and degradation onset temperatures both decrease with increasing SIL amount which is attributed to the plasticising effect of SILs. Interestingly, in Figure S7, both increase rate and depression in *Tg* form a linear correlation allowing the 'dialling in' of additive amount to a desired rate, and the corresponding *Tg* loss. Consequently, from Figure S7, rapid cure systems with acceptable allowance for *Tg* change from the neat epoxy precursor may be obtained from less than 5% ionic liquid. At room temperature the storage modulus increases, consistent with the higher SIL loadings as this would encourage a high degree of cross-linking. Though when heated the storage modulus decreases rapidly with increase in SIL content owing to higher proportion of the SIL still being within the polymer. Consequently, the polymer will undergo increasing degrees of plasticisation, thus able to undergo elastic deformation leading to higher modulus at room temperature. When examining tensile strength of these specimens, the only statistically significant changes observed were those for tensile strength, at high SIL loadings of 10% and 20%. Interestingly, the Young's modulus at 20% [Li@G3]TFSI is found to decrease. Residual stresses formed from the high exotherm generated with increasing amount of SIL could have resulted in the observed decrease of Young's modulus. It is important to note that at the lowest SIL loadings of 1% and 5%, there is no statistical difference between the neat polymer and the SIL doped samples, apart from 5- and 16-times faster cure rate, respectively. Generation of high exotherms can result in non-uniform curing. This is counterproductive especially with fibre-reinforced composites because the varying heat of reaction restricts expansion of the fabric, resulting to the creation of waves on the fabric.[34] The effect of residual stress on the initiation of fatigue induced matrix micro-cracking has been investigated by Joosten *et al.*, observing that higher residual stresses results in the formation of macro scale matrix cracking at a lower number of cycles for a given load level.[35] In a complementary work by Agius *et al.*, resin chemistries with very low *coefficient of thermal expansion* were deemed more suitable for high temperature fast cures.[36] Thus, in the design of rapid cure systems, a better understanding of the residual stresses that develop during curing should be given detailed focus.



$M = Li^+, Na^+, K^+, Mg^{2+}$ Counter Ions = $TFSI^-, Cl^-, AcO^-, BF_4^-, PF_6^-$

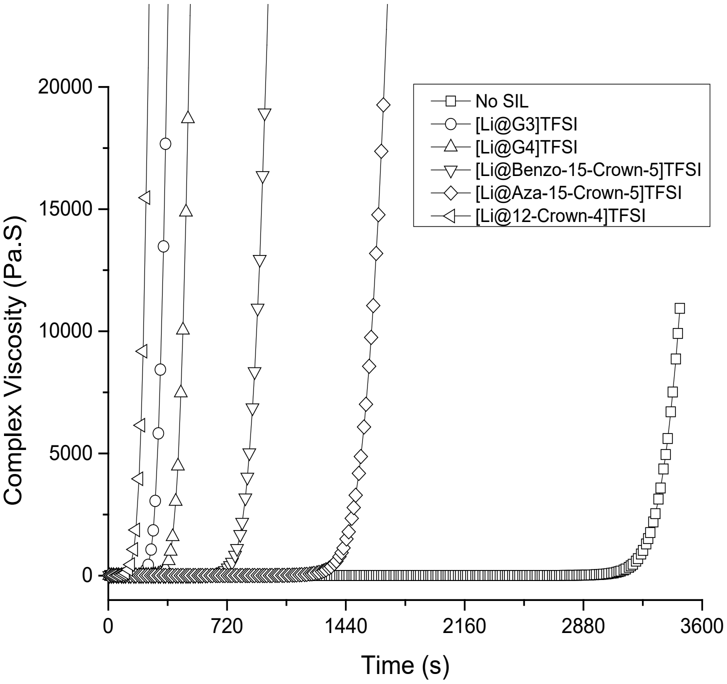
Figure 3. Additional chelate additives explored in this study.

After understanding the effect of TFSI-based additives on the curing rates of epoxy, other closely related complexes were determined and explored for their catalytic ability, physical properties as well as their action on commercially available epoxy resin systems. This included several group I and II cations (Li, Na, K, Mg), and counterions apart from TFSI (Cl, acetate, tetrafluoroborate, hexafluorophosphate) with several glyme-like chelating agents (triglyme, tetraglyme, 12-*crown-4*, benzo-15-*crown-5*, dibenzo-15-*crown-5*, 1-aza-15-*crown-5*), as shown in Figure 3. The above components – anion, cation and chelating agent – were combined and their physical properties investigated as well as their catalytic action on the curing of two commercially available epoxy resin systems. The variations listed in Table S2 were combined to give a cross sectional study of all components. The sodium ions did not produce any notable reaction. Although the remaining combinations produced either a homogenous solid or liquid. For each solid produced, a melting point is also indicated in Table S2. Parallel plate rheology experiments were conducted to screen the complexes for catalytic ability in the curing of epoxy resins. These experiments compare the onset time and gel point of the complexes with a RIM resin system (RIM935 as epoxy component + RIMH936 as hardener) and a DGEBA resin system cured with MDA as hardener. The RIM epoxy system is a commercially available and low viscosity infusion resin system commonly employed in automotive applications where high throughput is of major interest. For this study, the RIM resin system served as the benchmark for rapid-cure thermoset manufacturing owing to its low pot life at high temperatures.

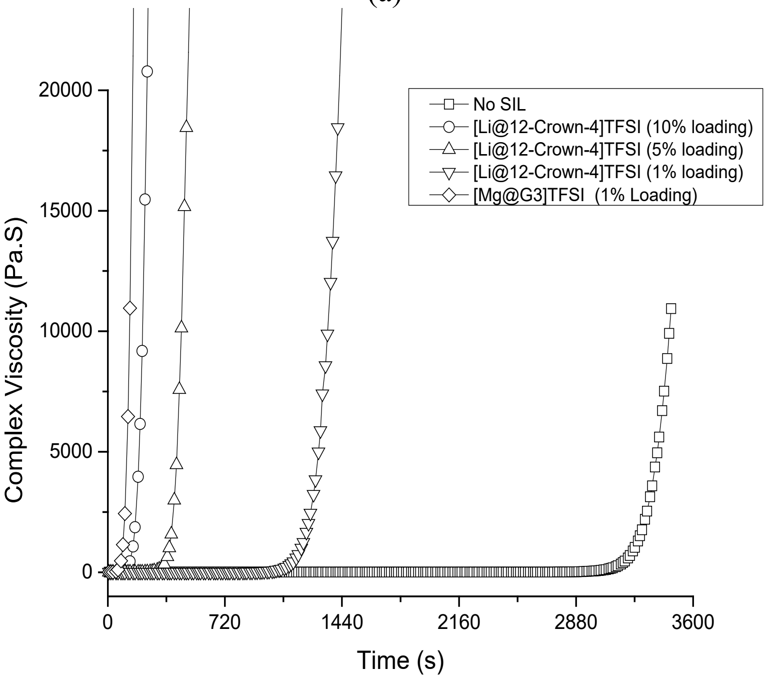
Table 2. Comparison of the effect of the additives on onset points in RIM resin at a 10% wt/wt loading cured at 60 °C.

Additive	Onset Point	Fold Increase
None	4017 s	-
[Li@G4]TFSI	1834 s	2.2 x
[Li@G3]TFSI	1202 s	3.3 ×
[Li@ Dibenzo-18-*c*-*6*]TFSI	Insoluble in epoxy	
[Li@ Benzo-15-*c*-*5*]TFSI	1559 s	2.5 ×
[Li@12-*c*-*4*]TFSI	775 s	5.1 ×
[Li@aza-15-*c*-*5*]TFSI	1733 s	2.3 ×
[Li@G4]Cl	Insoluble in epoxy	
[Li@G3]Cl	Insoluble in epoxy	
[Mg@G3]TFSI	1169 s	3.4 x
[K@G4]PF_6	Insoluble in epoxy	
[K@G3]PF_6	Insoluble in epoxy	

In Table 2, soluble complexes in the RIM resin system all enhanced the onset of curing at 60 °C. However, many of the other complexes were not soluble in the epoxy and thus were not tested. The [Li@12-*c*-*4*]TFSI complex provided the highest rate of enhancement in the RIM resin system (5.1x). While it was noted that [Li@G3]Cl was not soluble in the epoxy resin, the test sample that contained the unsolvated additive cured before a neat sample at room temperature.



(a)



(b)

Figure 4: (a) Complex viscosity of isothermally cured (100 °C) DGEBA + MDA with Lithium chelate complexes; (b) Complex viscosity of isothermally cured (100 °C) DGEBA + MDA with high performing Lithium and Magnesium chelate complexes at different loading levels.

Similarly, the soluble additives were also tested in a DGEBA + MDA system at 100 °C. Comparing the RIM resin system in Table 2 with a DGEBA system (Table S3, with the rheological profiles graphical represented in Figure 4(a)), the rate enhancement for each additive was consistent between resins, with [Li@12-*c*-*4*]TFSI providing the highest rate of enhancement (15x) of the consistent group and the [Li@aza-15-*c*-*5*]TFSI additive affecting the lowest rate enhancement (2.1x). However [Mg@G3]TFSI was exceptional in cure enhancement. In the RIM resin system, the [Mg@G3]TFSI was comparable to the [Li@G3]TFSI in terms of rate enhancement. At 10% loading the [Mg@G3]TFSI cured the DGEBA + MDA resin instantly, in less than 5 seconds of mixing. Due to the high activity of [Li@12-*c*-*4*]TFSI and [Mg@G3]TFSI, these additives were chosen to be used further at lower loadings in the DGEBA system (Figure 4(b)). The [Li@12-*c*-*4*]TFSI was tested at both 5% and 1% additive loadings and both provided lower, but respectable, rate enhancements of 7.6x and 2.4x. Due to the highest reactivity of [Mg@G3]TFSI, it was only able to be tested at 1% and provided a fastest rate enhancement of 26x the rate of the neat resin. As a catalytic additive, [Mg@G3]TFSI outperformed the next best additive with an order of magnitude less material added. As the additives are catalytically active, their ability to cure a neat epoxy without an added hardener was tested. Two samples were prepared, a neat sample of RIM935 and a sample of RIM935 with 10 % wt/wt [Li@G3]TFSI both stored at room temperature for one week. The viscosity of both these samples was determined by parallel plate flow rheometry and there was no discernible difference between the two samples after a week of storage (0.45 Pa.s vs 0.46 Pa.s, respectively). This is a beneficial outcome as the additives could be stored with compatible resin systems without detracting from the usable life of the epoxy.

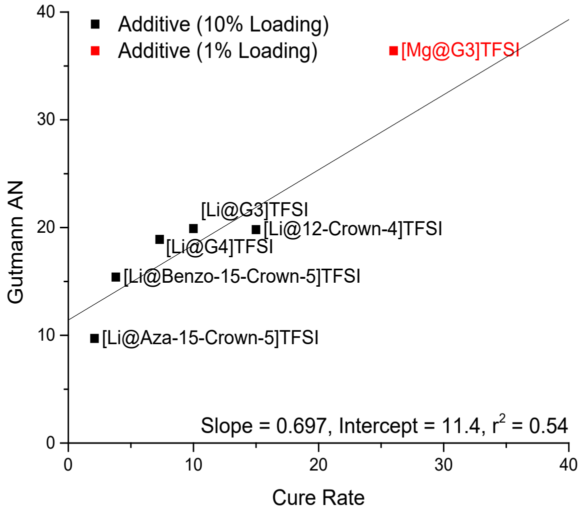


Figure 5: Epoxy cure rate enhancement factor *vs* Gutmann Acceptor number of the additive.

As it is likely that these catalysts proceed *via* a Lewis acid catalysed mechanism,[24] the relative Lewis acidity of each of the active complexes were calculated. The acidity of the complexes was analysed by the Gutmann procedure,[31,37] graphically represented in Figure 5. There was a slight correlation between the acidity of the complexes and the cure rate enhancement. This data suggest that Lewis acidity is one factor that could affect the cure rate. The value for the [Mg@G3]TFSI species, obtained with a poor signal-to-noise ratio, is an estimate only and its relationship to the other values in Figure 5 is skewed because it was only able to be analysed for cure rate enhancement at 1% loading. Di Pietro *et al.*, observed regioselectivity and shorter reaction time for the nucleophilic epoxy ring-opening reaction with methanol and diacetone-D-galactose under [Li@G4]TFSI in their previous work. Furthermore, the presence of non-chelated lithium under otherwise identical conditions have decreased the reaction rate. They speculated that the effect on the reaction rate is related to the higher amount of lithium in the SIL and its strong chelating properties in the epoxy adduct.[38] Contrary to the results obtained by Pietro *et al.*, in this work, both

[Li@G3]TFSI and [Li@G4]TFSI resulted in substantial reduction in curing onset. Arguably, the reaction of epoxy system with SILs involved more complex kinetics.

Conclusion

Solvate ionic liquids (SILs) possess huge potential as rapid cure additives in high technology and high volume (low cost) composite development as they act as accelerators with amine hardeners. As drop-in additives, they can be easily incorporated during thermoset manufacture. In this work, we have successfully synthesized and analyzed the properties of metal chelate complexes that include Group 1 and 2 metals coordinated with ligands consisting of ethers, crown ethers, heteroatom chelates and aromatic backbones; stabilized by either coordinating or non-coordinating counter anions. We also tested their influence in the cure rate of epoxy systems and found out that enhancement in cure rate can be achieved by appropriate selection of the metal center, the type of ligands around the metal and the identity of the counter anions in SILs. We have identified that a magnesium complex has the highest activity, but the activity may affect curing at too high a rate to be useful. [Li@12-*crown-4*]TFSI provides a high and workable rate enhancement. The role of the ionic liquid in epoxy systems have been attributed to participating or enhancing crosslinking events. In this SIL system, there is no suitable nucleophile which can undergo epoxy-ring opening reactions, as the TFSI anion is extremely resonance stabilized and a very poor nucleophile. Indeed, neither the lithium nor the glyme can undergo any form of reaction with epoxy in this system. This was exemplified in the original report of these SILs as reaction media. In that work the dissolution of styrene oxide in neat SIL and heating resulted in isolation of the starting epoxide.[24] Thus, the effect of the SIL has been attributed to the activation of the epoxide moiety *via* Lewis acidic nature of the SIL. This Lewis acidity was inferred from the

Guttmann acceptor numbers (A_N) which we have determined for SILs employed in this work. The general proposed mechanism of this activation is outlined in Figure 6. The coordination of the metal to the epoxide oxygen, we propose, increases the partial charge on the terminal carbon on the oxirane ring, promoting rapid interception with a nucleophile, such as an amine unit present in the hardener. The increasing Lewis acidity of the metal will enhance the polarization of the C-O bond and thus would enhance the catalytic effect. We presume this is the origin of our observations whereby Magnesium ions serve as a more active catalyst than Lithium in the same ligand system.

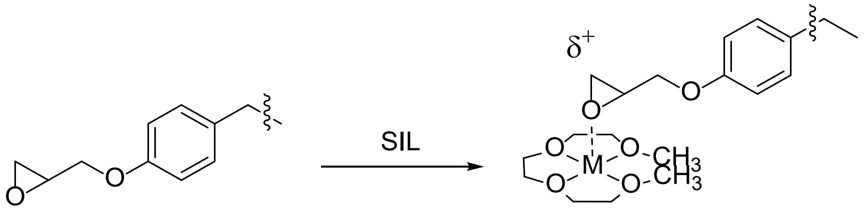


Figure 6. Proposed interaction of the metal atom in the SIL chelate, activating the epoxide moiety via Lewis acids activation.

The unequivocal mechanism of this SIL activation as well as the underlying reaction kinetics on epoxy resins need further exploration. Specific focus should be given on how [Li@G3]TFSI and [Li@G4]TFSI contribute to rapid curing. Moreover, the effect of residual stresses on curing with higher loadings of SILs should be considered when formulating rapid cure systems. Consequently, a rapid curing epoxy will have great interfacial stress due to volume shrinkage and Pressure-Volume-Temperature analyses (PVT) will be insightful. This understanding is necessary for the immediate adoption of this resin system in additive manufacturing.

ASSOCIATED CONTENT

Supporting Information Available:

Dynamic rheology profiles of DGEBA epoxy resin containing 20% of G3TFSI and G4TFSI additives (Figure S1); Isothermal rheological profiles of 1%, 5%, 10%, 20% [Li@G3]TFSI additive (100 °C), showing their cross-over points as the approximate gel-point (Figure S2 to Figure S5) ; Isothermal rheological profiles of neat epoxy/MDA (EP) at 100 °C showing a cross-over point as the approximate gel-point (Figure S6); Linear correlation of ([Li@G3]TFSI) additive amount with fold increase/enhancement in cure rate and with depression of *Tg* (Figure S7)*;* Rheological details using G3TFSI additive at 100 °C (Table S1); Summary of combinations tested and the resulting isolates and melting points (Table S2); Comparison of the effect of the additives on onset points and gel points in DGBEA + MDA resin at a 10% wt/wt loading cured at 100 °C (Table S3); A link to the technical data sheet and typical characteristics of the RIM resin.

AUTHOR INFORMATION

Corresponding Author

* nisharhameed@swin.edu.au; * luke.henderson@deakin.edu.au

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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