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## Investigating the mechanism through which ionic liquids initiate the polymerisation of epoxy resins

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**ABSTRACT:** The mechanism of reaction between 1-ethyl-3-methylimidazolium acetate and the difunctional diglycidyl ether of bisphenol A (DGEBA) is explored using thermal and spectroscopic methods. Investigation of the 1,3-dialkylimidazolium based ionic liquids comprising the common cation (1-ethyl-3-methylimidazolium) and different anions (acetate, diethyl phosphate, dicyanamide or thiocyanate) *via* thermogravimetric analysis revealed 1-ethyl-3-methylimidazolium acetate to be the least thermally stable, both in air and nitrogen, and 1-ethyl-3-methylimidazolium dicyanamide to be the most thermally stable. Dynamic differential scanning calorimetry reveals the formulations comprising DGEBA and ionic liquid where it was revealed that the lowest and highest temperature for the onset of reaction were observed for formulations with 1-ethyl-3-methylimidazolium acetate and 1-ethyl-3-methylimidazolium dicyanamide respectively. 1-Ethyl-3-methylimidazolium acetate was shown, *via* nuclear magnetic resonance (NMR) spectroscopy and residual gas analysis, to degrade at 150 °C to yield dealkylated products including methyl acetate and ethyl acetate as well as 1-methylimidazole and 1-ethylimidazole. The dealkylated imidazole ring is proposed as a route for initiation of the epoxy ring. Adduct formation between 1-ethyl-3-methylimidazolium acetate and benzaldehyde at room temperature was observed leading to the proposal of the generation of a carbene species as a route for initiation of the epoxy ring in formulations with the acetate anion. NMR analysis of formulations comprising 1-ethyl-3-methylimidazolium thiocyanate and epoxy are believed, at room temperature, to initiate *via* reaction of the thiocyanate anion with the epoxy ring.

At elevated temperatures, it is proposed that a second, competing reaction, involving deprotonation of the imidazolium ring, also becomes active. The three proposed reaction pathways, namely the carbene route, the imidazole route and the counter-ion route, are all proposed to occur when an ionic liquid is used to initiate an epoxy resin.

**Keywords:** Epoxy Resins, Ionic Liquids, Imidazoles, Initiators, Polymerisation Mechanism.

## INTRODUCTION

Commercially available epoxy resins debuted in 1947 and were produced by the Devoe-Raynolds Company [1]. However, their origins can be traced back as far as 1909, Prileschajew discovered the epoxide forming reaction between olefins and peroxybenzoic acid [2]. Linear epoxy resins are converted into three-dimensional, crosslinked networks [3,4] which results in them having applications in the engineering industry as a result of their good thermal, mechanical and electrical properties [5,6,7]. They are additionally used as anticorrosive coatings, adhesives and paints due to their corrosion resistance and good adhesion to a wide variety of substrates [8,9]. They are of very high importance in technological applications as they form the continuous phase, which allows many lightweight, tough, composite materials to be bonded together [10]. Epoxy resins are especially interesting due to the wide variety of chemical compounds, which can affect cure [11]. It is possible, upon gaining an appreciation of the chemistry involved, to tailor the level of cross-linking and the temperature at which the reaction is carried out to an individual's specific requirements [12]. The wide variety of curing agents which are available and the different curing conditions mean that it is possible to obtain epoxy resins with many different physical properties such as toughness, chemical resistance [13], mechanical properties which range from extreme flexibility to high strength and hardness, high adhesive strengths, good heat resistance, high tensile, flexural and compressive strength and high electrical resistance [9,11,12,14]. The epoxy, in its uncured form, can take on a variety of appearances ranging from low-viscosity liquids to tacky solids depending on oligomer length, which means the epoxies have application in a wide variety of settings [11].

Imidazoles are very effective curing agents and, when combined with epoxy resins, yield adhesives and coatings with very good mechanical properties. Studies have also shown that epoxy resins cured with imidazoles can have superior physical properties [15] such as better heat resistance [16], lower tensile elongation, a higher modulus and a wider range of cure temperatures compared with amine-cured systems [17,18]. It is for this reason that such materials are added to commercial epoxy resins to catalyse the homopolymerisation of epoxide groups and yield tough thermoset

networks [10,17]. Structurally related imidazolium-based ionic liquids are one of the most studied groups of ionic liquids [19] and are often selected due to the stability of the ring in oxidative and reductive environments, the low viscosity exhibited and the relative ease of synthesis [20]. The general structure of an imidazolium-based ionic liquid is shown in Figure 1.

Whilst various reports have championed the use of imidazolium-based ionic liquids as catalysts for enhancing both the rate of reaction and the yield, other studies are now recognising the benefits of these compounds [20] and few studies in the literature report imidazolium-based ionic liquids as initiators for epoxy resins. Kowalczyk and Spychaj [21] reported that 1-butyl-3-methylimidazolium tetrafluoroborate could be used as an initiator for a commercial epoxy (Epidian 6) and additionally, a formulation comprising the two components could be stored for a period of 6 months at ambient temperature without any change in viscosity. The authors however, did not give any insight into the mechanism of reaction. Rahmathullah *et al.* [22] explored the use of 1-ethyl-3-methylimidazolium dicyanamide as an initiator for epoxy resins and, moreover, determined that it could be used as a latent initiator, which was miscible with another commercial bisphenol A based epoxy (Epon 828, DGEBA) and exhibited long-term stability at room temperature. The stability of the formulation was tracked through monitoring the characteristic epoxy ring absorbance band in near-infrared (NIR) spectroscopy and it was suggested by the authors that the mechanistic route might involve reaction between the cyanamide and epoxy groups and not the nitrogen atoms in the imidazolium cation directly. Maka *et al.* [23] also reported the use of imidazolium-based ionic liquids as initiators for epoxy resins. These included ionic liquids based on both 1-decyl-3-methylimidazolium and 1-butyl-3-methylimidazolium cations with chloride, tetrafluoroborate and dicyanamide anions. It was suggested, in these cases, that thermal decomposition of the ionic liquid could proceed *via* a highly stabilised *N*-heterocyclic carbon structure that, in turn, would result in generation of imidazole or 1-alkyl derivatives. The interaction of the pyridine-type nitrogen atom in the imidazole ring with an epoxy group to form a 1:1 adduct was concluded as the most likely anionic polymerisation route.

Several authors have suggested that thermal decomposition of 1,3-dialkylimidazolium-based ionic liquids yields imidazole and alkylimidazole derivatives that are capable of initiating epoxy resins to undergo anionic polymerisation. The reported ease of carbene formation from certain ionic liquids raise questions with respect to the mechanistic pathway and whether the mechanism is generally applicable to imidazolium-based ionic liquids. The current work seeks to identify the reaction mechanism between DGEBA and 1-ethyl-3-methylimidazolium acetate, 1-ethyl-3-methylimidazolium diethyl phosphate, 1-ethyl-3-methylimidazolium dicyanamide and 1-ethyl-3-

methylimidazolium thiocyanate.

## EXPERIMENTAL

**Materials.** The four ionic liquids (Figure 1) and DGEBA were supplied by BASF. The materials were characterised using  $^1\text{H}$  NMR (in deuterated acetone) and used without further purification (see supplementary data, Figure S1).

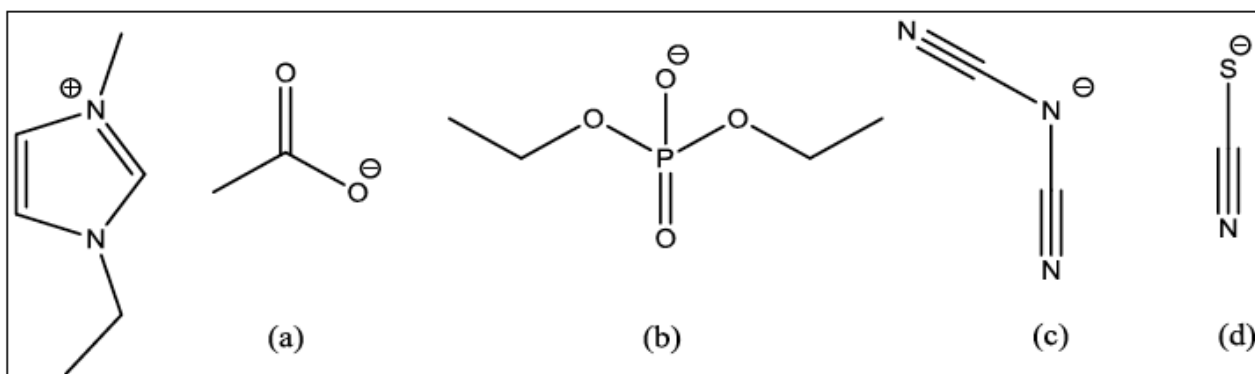


Figure 1. Structures of (a) 1-ethyl-3-methylimidazolium acetate, (b) 1-ethyl-3-methylimidazolium diethyl phosphate, (c) 1-ethyl-3-methylimidazolium dicyanamide, (d) 1-ethyl-3-methylimidazolium thiocyanate. As the cation is common to all, the compounds are referred to by their anions within the text. The samples were cured following the schedules presented in Table 1.

Table 1. Curing schedule for DGEBA formulations containing different initiators in an air circulating oven

Initiator	Cure schedule
1-ethyl-3-methylimidazolium acetate	40 °C (30 min) + 60 °C (30 min) + 80 °C (30 min) + 100 °C (30 min) + 120 °C (30 min) + 140 °C (30 min) + 160 °C (60 min)
1-ethyl-3-methylimidazolium diethyl phosphate	160 °C (60 min) + 180 °C (180 min) + 200 °C (60 min)
1-ethyl-3-methylimidazolium dicyanamide	160 °C (60 min) + 180 °C (180 min) + 200 °C (60 min)
1-ethyl-3-methylimidazolium thiocyanate	40 °C (30 min) + 60 °C (30 min) + 80 °C (30 min) + 100 °C (30 min) + 120 °C (30 min) + 140 °C (30 min)

**Instrumentation.**  $^1\text{H}$  nuclear magnetic resonance (NMR) spectra comprising of 16 scans, conducted on a Bruker 500 MHz NMR spectrometer at room temperature using  $\text{CDCl}_3$  as a solvent

and tetramethylsilane (TMS) as an internal standard.  $^{13}\text{C}$  NMR spectra comprising of 100 scans, conducted on a Bruker 125 MHz nuclear magnetic resonance (NMR) spectrometer at room temperature using  $\text{D}_6\text{-DMSO}$  and  $(\text{CD}_3)_2\text{CO}$  as solvents and tetramethylsilane (TMS) as an internal standard. The samples for analysis (*ca.* 80 mg) were mixed with deuterated solvent (*ca.* 0.6 – 0.7 ml) and transferred to an NMR tube.

Attenuated total reflectance infrared (ATR-IR) spectroscopy was carried out using an Agilent Technologies Cary 600 series Fourier transform infrared spectrometer employing a Golden Gate accessory with a diamond crystal. A background spectrum, consisting of 32 scans, was acquired with the accessory *in situ* before all analyses were performed. The resulting spectrum for each sample was taken from an average of 32 scans, recorded in absorbance mode between 600 and 4000  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ .

Differential scanning calorimetry (DSC) was undertaken using a TA Instruments Q1000 running TA Q Series Advantage software on samples ( $5.0 \pm 0.5$  mg) in hermetically sealed aluminium pans. Experiments were conducted at a heating rate of 10 K/min. from  $-10$  °C to 400 °C (heat/cool/heat) under flowing nitrogen ( $50 \text{ cm}^3/\text{min.}$ ). DGEBA and ionic liquid were combined in a speed mixer pot (100 g) and subjected to two consecutive mixing periods of two minutes at 2000 rpm. The samples were immediately analysed after mixing and the remaining mixture placed in the freezer.

Thermogravimetric analysis (TGA) was performed on a TA Q500 on milled, cured resin samples ( $7 \pm 3$  mg) in a platinum crucible from 20-800 °C at 5 K/min in air and nitrogen ( $60 \text{ cm}^3/\text{min.}$ ).

Residual gas analysis (RGA) was performed using an ESS Ecosys-p residual gas analyser, which was connected to the TGA *via* a plastic capillary tube running from the exhaust pipe of the thermogravimetric analyser to the sample detector in the residual gas analyser. The TGA instrument was programmed in the same manner as described above and the RGA programmed to collect data every 8 seconds. The specific masses of interest were entered directly into the software. Epoxy (DGEBA or PGE) and an ionic liquid were mixed by hand in glass scintillation vials (20 ml) and immediately analysed. The bulk sample was subsequently stored in the freezer for future analyses.

## RESULTS AND DISCUSSION

Several different reaction pathways have been proposed for the initiation reaction with a di-epoxy is proposed to occur *via* a carbene route, an imidazole route or a nucleophilic route (Figure 2), although it is suggested that these reaction pathways are not discrete.

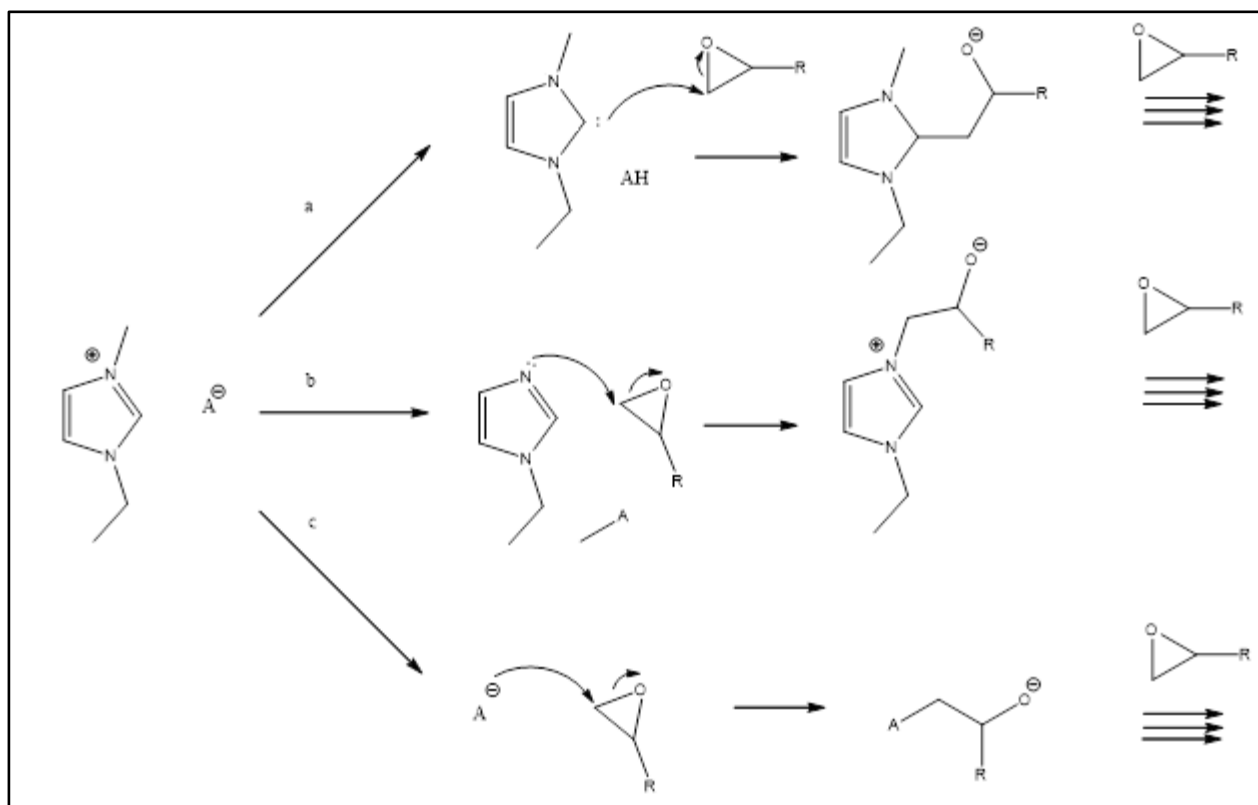


Figure 2. Proposed reaction pathways for initiation of an epoxy polymerization reaction with imidazolium-based ionic liquids *via* a) the ‘carbene route’, b) the ‘imidazole route’ and c) the ‘counter ion’ route.

The carbene species is known to be highly reactive and, as such, would initiate the epoxy ring if generated in sufficient concentration. DSC analysis reveals that a low temperature shoulder peak, present in the thermograms of formulations comprising DGEBA and 1-ethyl-3-methylimidazolium acetate (Figure 3), diminishes over time even when stored at sub-zero temperatures [24]. This implies that generation of a reactive species must still occur in spite of the reduction in temperature and retardation of the reaction in the freezer. The same effect was not observed in formulations containing 1-ethyl-3-methylimidazolium dicyanamide, which indicates that the acetate anion is more reactive towards the epoxy. MacFarlane *et al.* [25] reported the respective  $pK_a$  values (in water) for acetic acid and dicyanoamine as 4.75 and 5.1 respectively, which led Carvalho *et al.* [26] to investigate the use of 1-butyl-3-methylimidazolium dicyanamide for the solvation of  $CO_2$  as it was suggested that absorption of  $CO_2$  could be enhanced when an anion with a higher basicity was employed. Previous work by the same authors [27] had already established that the acetate anion was effective for this purpose. The findings of Carvalho *et al.* however, unveiled surprising results in that the higher  $pK_a$  value of the dicyanamide anion did not result in an increase in  $CO_2$  absorption. This was attributed to the fact that the previously observed enhancement was actually as a result of a Lewis acid/base interaction between the anion and the  $CO_2$ ; a finding also noted by

other research groups [28,29]. Consequently, this led the authors to conclude that, whilst the  $pK_a$  value for the conjugate acid of dicyanamide is indeed greater than that for acetate, meaning that the dicyanamide exhibits a more basic character, it is a markedly weaker Lewis base meaning that the required Lewis acid/base interaction between the  $CO_2$  and dicyanamide is weaker than between  $CO_2$  and a stronger Lewis base [26].

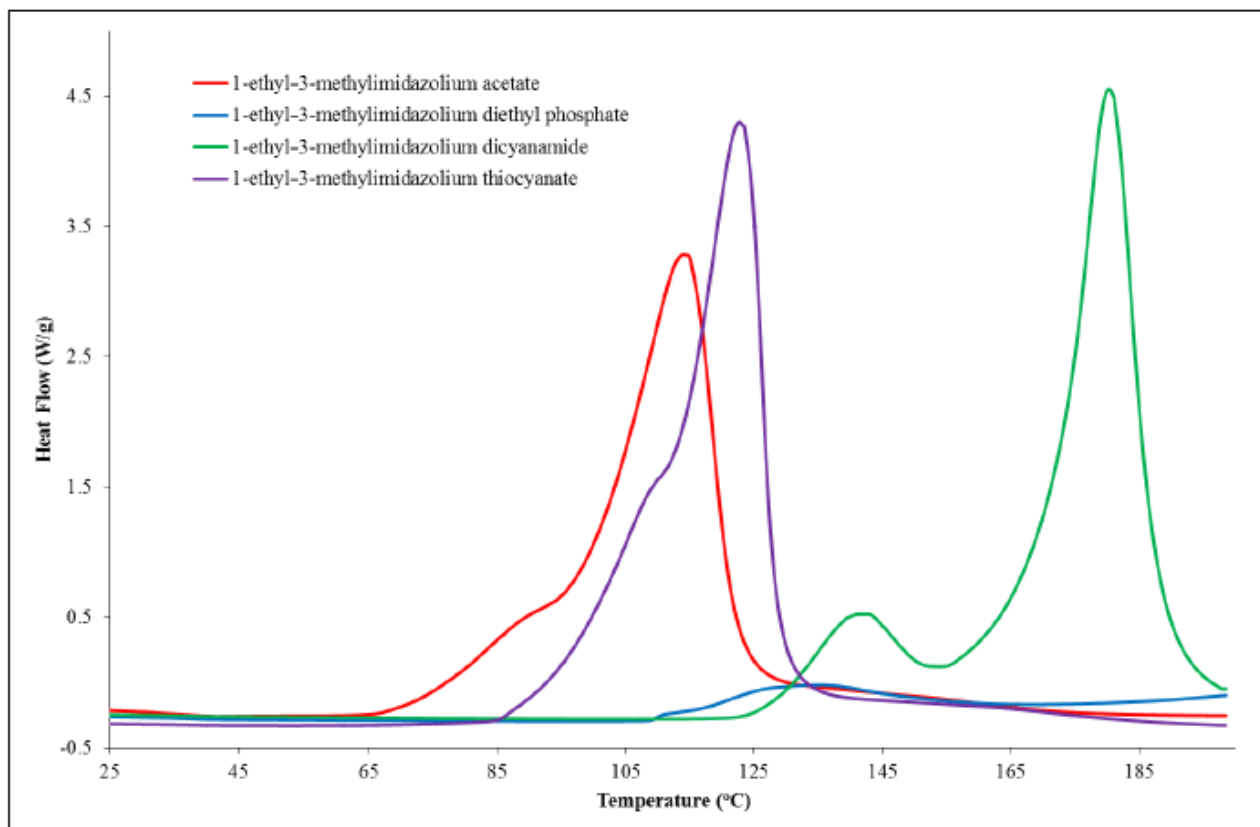


Figure 3. Dynamic DSC data for freshly mixed formulations comprising DGEBA (5 g) and each of the individual ionic liquids (0.25 g)

By extension, this can be applied to the ionic liquid/epoxy formulations. Owing to the higher Lewis base character of the acetate anion compared with the dicyanamide anion, it can be assumed that carbene formation is significantly more likely to occur in the acetate containing formulation; a consequence of which is believed to be the shoulder peak on the main exothermic peak. In addition, Kim *et al.* [28] investigated the solubility of  $CO_2$  in ionic liquids with an increasing number of cyanide groups (*e.g.* 1-ethyl-3-methylimidazolium thiocyanate, 1-ethyl-3-methylimidazolium dicyanamide and 1-ethyl-3-methylimidazolium tricyanomethanide). Owing to the proposed Lewis acid/base interaction between the  $CO_2$  and the anion, it was reported that the solubility was greatest in 1-ethyl-3-methylimidazolium tricyanomethanide as it contained the greatest concentration of a Lewis base species and lowest in 1-ethyl-3-methylimidazolium thiocyanate. In light of the above findings, it is reasonable to present the anions, in terms of



increasing Lewis base character, in the following order: thiocyanate < dicyanamide < acetate. Whilst the reported  $pK_a$  values above are for acetic acid and dicyanoamine in water, it must also be considered whether the ionic liquid exhibits a solvent effect and essentially alters the acid/base properties of certain species. It is unlikely that the acetate anion would be a sufficiently strong Brønsted base to deprotonate the imidazolium ring in classical terms, when considering carbene formation, the solvent effects of the ionic liquid must be examined.

MacFarlane *et al.* [25] employed acid solutes with spectroscopic signatures to compare the magnitude of dissociation in various ionic liquids compared with pure water. The visible spectra of bromocresol purple in water and 1-ethyl-3-methylimidazolium acetate and 1-ethyl-3-methylimidazolium dicyanamide were recorded with significant differences observed. In the case of water, the acid is reported as being approximately 0.2% dissociated whereas in 1-ethyl-3-methylimidazolium acetate, there is only one peak in the visible spectrum which corresponds to the base form, therefore indicating that the acid is fully dissociated. In the case of 1-ethyl-3-methylimidazolium dicyanamide, two peaks were observed in the visible spectrum indicating that the acid is not fully dissociated, but to a greater extent than in pure water. This leads to the conclusion that the strength of the acid is increased when the solvent is an ionic liquid with a basic anion as opposed to pure water. Millán *et al.* [30] also sought to establish a  $pK_a$  scale for *N*-base amines in ionic liquids through use of a cyclic voltammetry method and reported that in all cases the  $pK_a$  values obtained were greater than those obtained in aqueous solution. This supports the theory that carbene formation is possible with 1-ethyl-3-methylimidazolium acetate. Navarro *et al.* [31] reported, using dynamic thermogravimetric analysis at a heating rate of 10 K/min, the onset of thermal decomposition of 1-ethyl-3-methylimidazolium thiocyanate, 1-ethyl-3-methylimidazolium dicyanamide and 1-ethyl-3-methylimidazolium tricyanomethanide to occur at 539 K, 570 K and 616 K respectively. The onset of decomposition for 1-ethyl-3-methylimidazolium acetate was reported to occur at 214 °C (487 K) [32]. A paper by King *et al.* [33] likened TGA data to a crude measure of the reactivity of the ionic liquids and a paper by Maka *et al.* [23] reported a direct correlation between the onset of degradation of the ionic liquid, as measured by TGA, and the reaction of the ionic liquid towards an epoxy monomer and this was examined in more detail here.

**Investigation of the dissociation behaviour of the complexes.** The four initiators were subjected to TGA to assess the stability of the ionic liquid in air and nitrogen as a function of temperature (Figure 4).

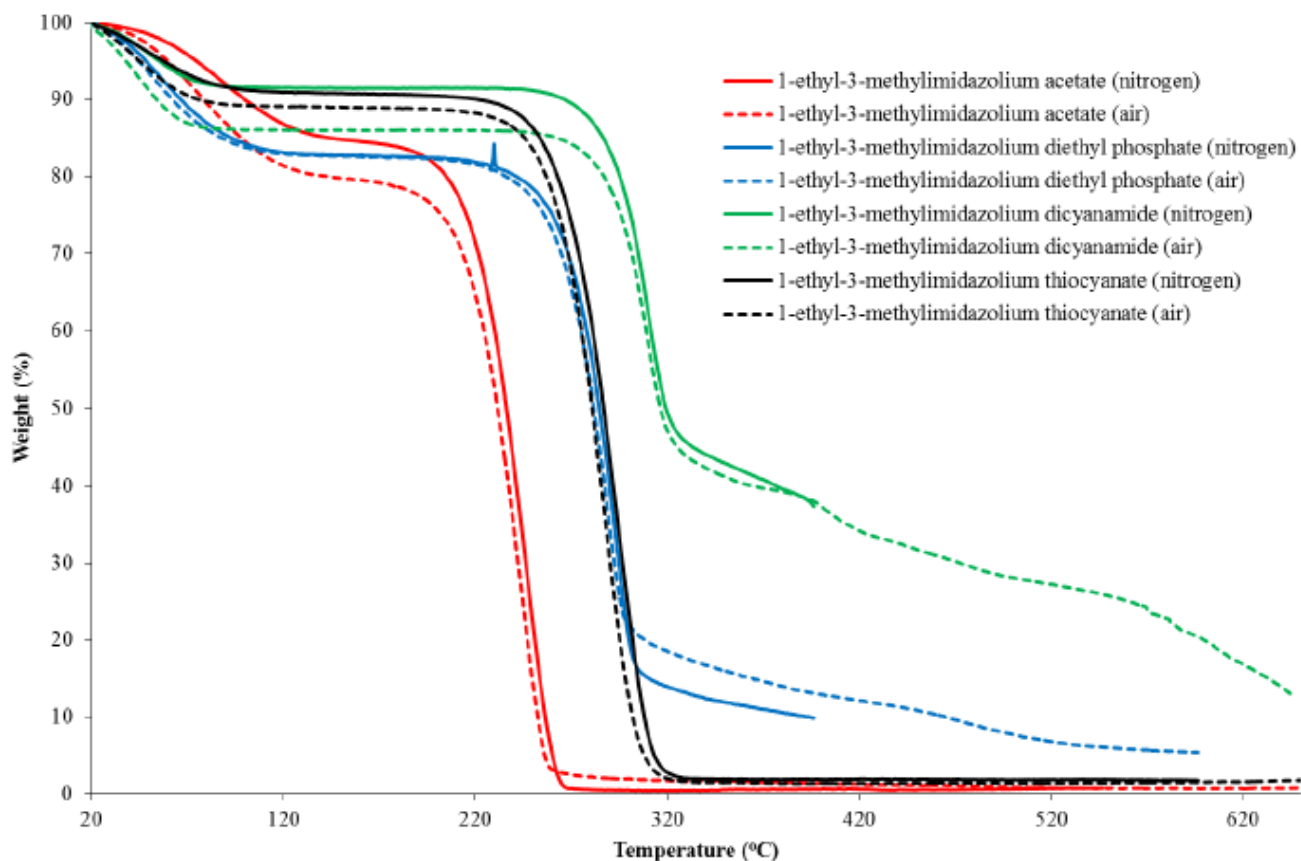


Figure 4. Dynamic TGA data in air (----) and nitrogen (\_\_\_) for the different complexes.

The onset temperatures for the observed weight loss steps are summarised in Table 2. 1-Ethyl-3-methylimidazolium acetate loses mass at the lowest temperature, in both atmospheres, of those compounds studied. Furthermore a significant mass loss (*ca.* 20 wt. %) is observed at 130 °C in air, which is higher than for the other compounds at the same temperature in air, which exhibit mass losses of 17 % (diethyl phosphate), 14 % (dicyanamide) and 11 % (thiocyanate) respectively. 1-Ethyl-3-methylimidazolium acetate has been reported to undergo a 10 % mass loss at 215 °C [34], compared with *ca.* 15 % in this work (Figure 4). Clough *et al.* [32] also reported that the onset of weight loss (measured in triplicate) occurred in a single step at 214 °C for a sample prepared in house and 216 °C for a commercial BASF material. The anomaly of the single step mechanism is explained by the authors having rigorously dried the samples in the TGA oven (heating to 80 °C with a 30-minute isothermal hold and cool to ambient) prior to analysis to remove adventitious moisture. In the same study, the authors reported that the same onset temperature was observed when the experiment was repeated under a compressed air atmosphere, confirming that the degradation does not proceed via a combustion or oxidation step.

Table 2 Dynamic TGA data (10 K/min) for different complexes in different atmospheres.

Sample	1 <sup>st</sup> T <sub>onset</sub> (°C)	1 <sup>st</sup> mass loss (%)	2 <sup>nd</sup> T <sub>onset</sub> (°C)	2 <sup>nd</sup> mass loss (%)	Residual mass (%)
Air atmosphere					
1-ethyl-3-methylimidazolium acetate	20	20	175	79	1
1-ethyl-3-methylimidazolium diethyl phosphate	22	17	205	64 <sup>a</sup>	6 <sup>b</sup>
1-ethyl-3-methylimidazolium dicyanamide	18	14	232	43 <sup>a</sup>	13 <sup>b</sup>
1-ethyl-3-methylimidazolium thiocyanate	21	11	213	87	2
Nitrogen atmosphere					
1-ethyl-3-methylimidazolium acetate	22	15	177	84	1
1-ethyl-3-methylimidazolium diethyl phosphate	19	17	206	67 <sup>a</sup>	10 <sup>b</sup>
1-ethyl-3-methylimidazolium dicyanamide	20	8	245	46 <sup>a</sup>	37 <sup>b</sup>
1-ethyl-3-methylimidazolium thiocyanate	21	9	212	89	2

<sup>a</sup> Subsequent mass loss steps occurred, <sup>b</sup> Degradation was not complete.

It would appear that the nature of the purge gas, namely air or nitrogen, has little or no effect on the degradation profile of the initiators overall when the two are compared and only seems to impact in the early weight loss step where it can be seen that the samples analysed in air degrade (or possibly evaporate) slightly faster than those analysed in nitrogen. The step that accounts of the main mass loss, occurs much earlier for the acetate counter ion than for the other samples and appears to be independent of the purge gas used. TGA data for 1-ethyl-3-methylimidazolium diethyl phosphate and 1-ethyl-3-methylimidazolium dicyanamide reveal a higher number of mass loss stages than observed for the other samples, which probably suggests that the degradation mechanism of those two samples is more complex. This would suggest that the acetate containing ionic liquid should show the highest reactivity towards the epoxy [35,36] and the dicyanamide containing ionic liquid

the lowest. This is consistent with the DSC data collected in this work, but inconsistent with both the proposed order of Lewis base character and the literature reported  $pK_a$  values in water [34].

Ionic liquids have been reported [28,34,35,37,38,39] to degrade *via* dealkylation of the imidazolium ring, which could provide a route for initiation of the epoxy ring *via* a dealkylated nitrogen atom. Consequently, 1-ethyl-3-methylimidazolium acetate was analysed using TGA-RGA and the masses of interest were monitored based on the possible degradation pathways, namely dealkylation and carbene formation (Figure 5).

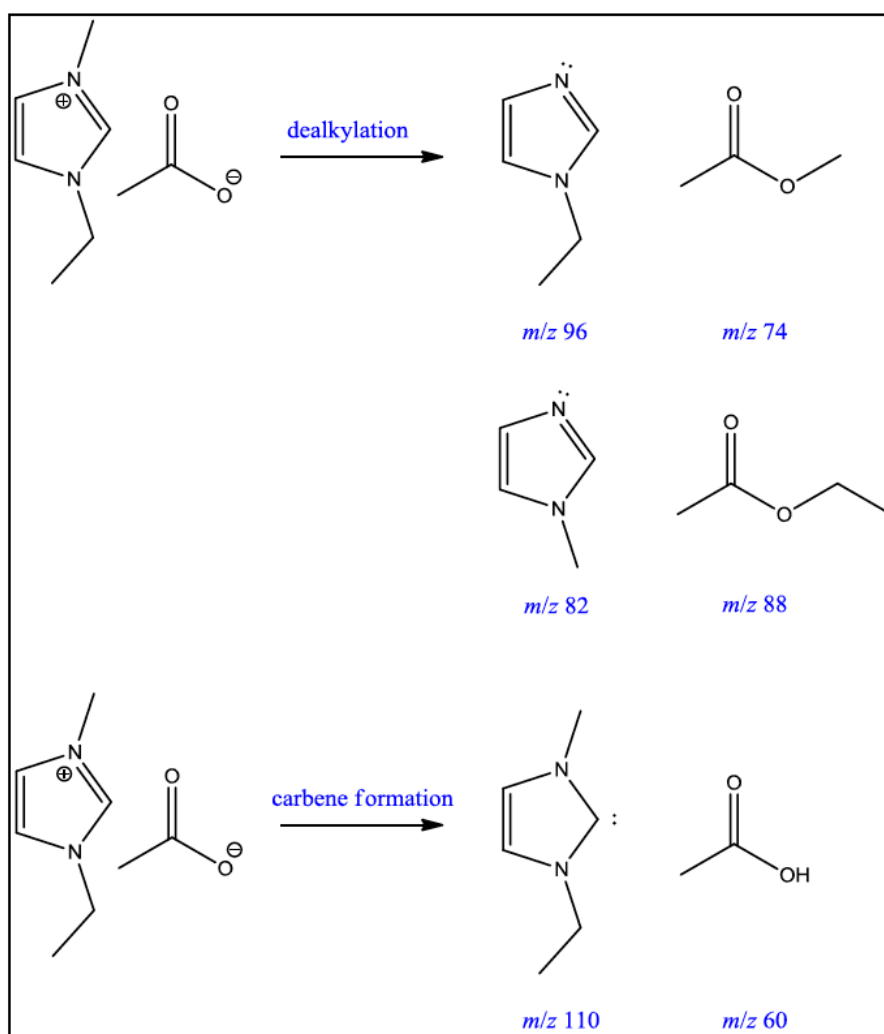


Figure 5. Possible degradation pathways of 1-ethyl-3-methylimidazolium acetate involving dealkylation and carbene formation, showing key fragments.

The TGA-RGA data (Figure 6) show a significant increase in intensity during the isothermal period at 150 °C for a fragment of  $m/z$  74. The latter coincides with the main weight loss observed in the TGA data and the fragment may correspond to methyl acetate, from de-methylation at the nitrogen atom.

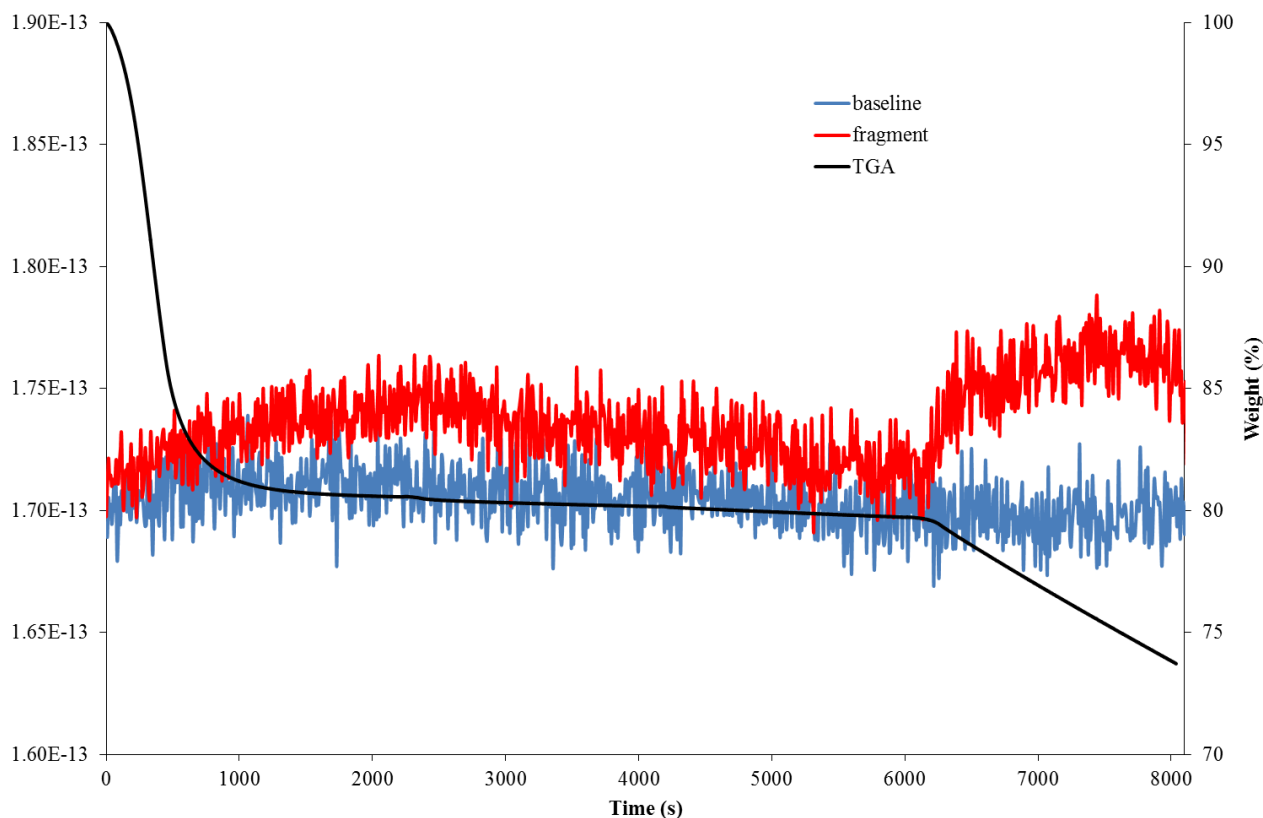


Figure 6. RGA data for 1-ethyl-3-methylimidazolium acetate (scanned for  $m/z$  74) during isothermal TGA experiment (150 °C).

Clough *et al.* [32] conducted a similar experiment involving TGA-MS, employing high purity helium as the carrier gas, and found evidence of the same peak ( $m/z$  74), albeit at considerably greater intensity (from a 20 – 60 mg sample compared with 9 mg in the current study) and at *ca.* 200 °C in dynamic scanning mode, coinciding with the onset of the main mass loss. In the present study, the practical limitations on the sample size meant that no other significant peaks were observed for the other masses of interest, although Clough *et al.* acknowledged that the parent ion may not be seen as a result of fragmentation of the ions due to the harsh conditions used during electron impact mass spectrometry (EI-MS). Consequently, with reference to the National Institute of Standards and Technology Chemistry WebBook [40], it was reported that a peak observed at  $m/z$  59 could be attributed to  $[\text{CH}_3\text{CO}_2]^+$ , a known fragment of methyl acetate, and a small peak at  $m/z$  88 was attributed to ethyl acetate. The presence of a peak at  $m/z$  60 indicated the presence of acetic acid, as neither methyl acetate nor ethyl acetate (nor their respective fragments) are expected to give rise to such a peak [32,40]. It should be noted that no significant peaks corresponding to 1-methylimidazole ( $m/z$  82), 1-ethylimidazole ( $m/z$  96) nor the carbene ( $m/z$  110) were observed, either by Clough *et al.* [32] or in the current work, which would imply that these degradation products are not present in the gas phase.

**Investigation of the dissociation behaviour of the complexes in the liquid state.** Following the foregoing analysis of the solid samples, NMR spectroscopy was employed to observe whether dealkylation could be observed within the ionic liquid. Consequently, samples of ionic liquid (*ca.* 5 g) were heated in open glass scintillation vials on a hot plate to approximately 150 °C. Subsequently a lid was placed on the sample and it was allowed to cool back to room temperature. An aliquot (*ca.* 1 ml) was then placed in a NMR tube (in the absence of deuterated solvent) for analysis. The  $^1\text{H}$  NMR spectra are shown (Figure 7) with assignments where the blue spectrum corresponds to a fresh sample of 1-ethyl-3-methylimidazolium acetate and the red spectrum to the heated ionic liquid; owing to the absence of the deuterated solvent, it was not possible to lock the sample.

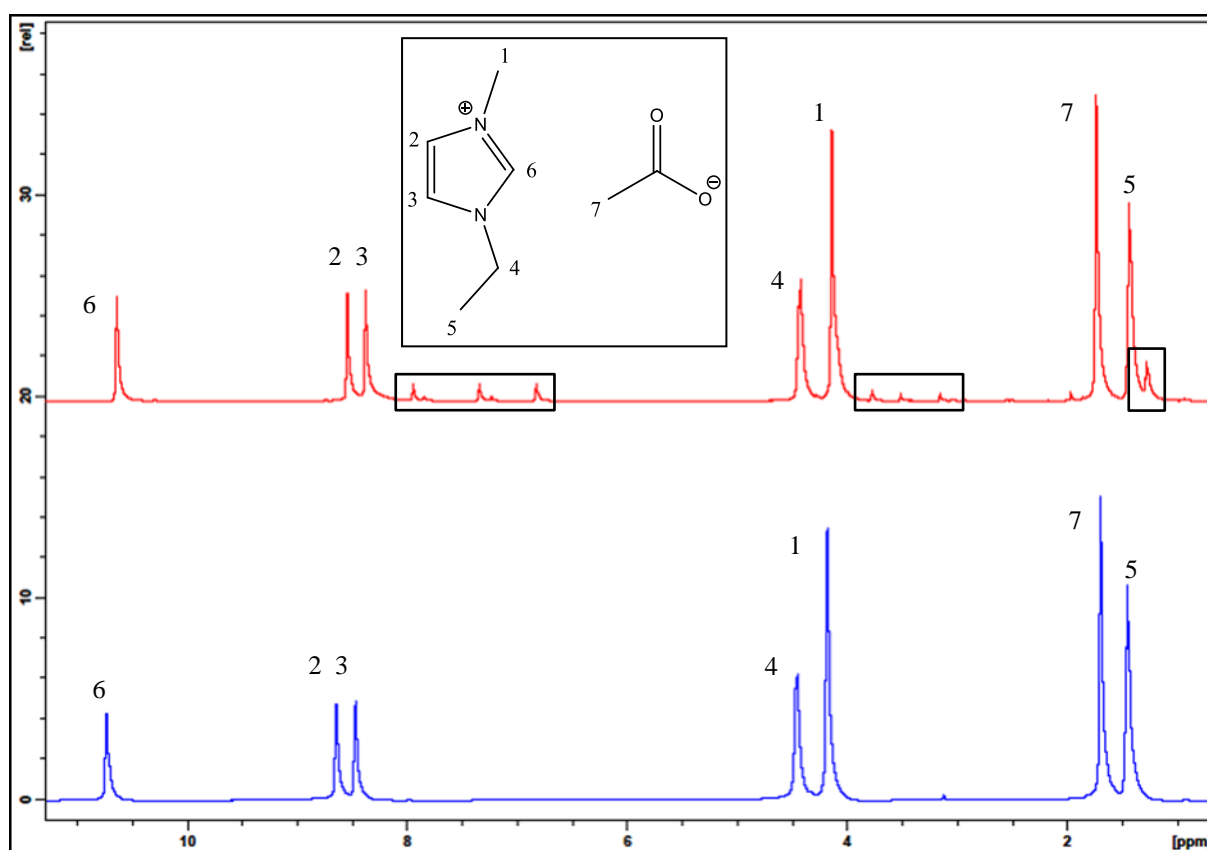
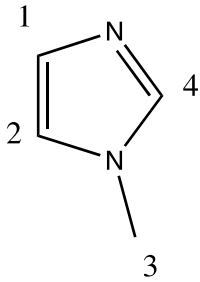
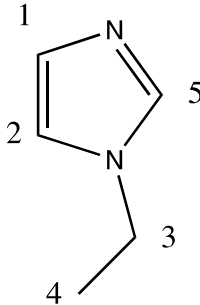


Figure 7.  $^1\text{H}$  NMR spectra (unlocked) for a fresh 1-ethyl-3-methylimidazolium acetate sample (blue) and the sample material following heating to 150 °C (red).

The fresh sample (blue) shows a very similar spectrum to that shown in Supplementary data Fig. S1, which confirms that the inability to lock the sample did not cause any marked shifts in the data. Following heating, all the starting material peaks remain, and there are additional, weaker, peaks that occur in the regions 6.5–8.0 ppm, 3.0–4.0 ppm and 0.5–1.0 ppm. The data from TGA-RGA suggested that certain decomposition products (*e.g.* methyl acetate, ethyl acetate and acetic acid) were present in the sample in gaseous form, but as this sample was heated *ex-situ* on a hot plate,

such volatile decomposition products would not be expected to remain in the mixture. Instead, the products following dealkylation (1-methylimidazole and 1-ethylimidazole) would be expected to remain. The expected chemical shifts are summarised in Table 3.

Table 3  $^1\text{H}$  and  $^{13}\text{C}$  NMR Assignments for 1-methylimidazole and 1-ethylimidazole (from reference [41])

Compound	Proton (Chemical Shift, ppm)	Carbon (Chemical Shift, ppm)
1-methylimidazole 	H <sub>1</sub> (7.011)	C <sub>1</sub> (120.20)
	H <sub>2</sub> (6.863)	C <sub>2</sub> (129.17)
	H <sub>3</sub> (3.641)	C <sub>3</sub> (33.14)
	H <sub>4</sub> (7.385)	C <sub>4</sub> (137.79)
1-ethylimidazole 	H <sub>1</sub> (7.018)	C <sub>1</sub> (118.49)
	H <sub>2</sub> (6.913)	C <sub>2</sub> (129.16)
	H <sub>3</sub> (3.952)	C <sub>3</sub> (41.63)
	H <sub>4</sub> (1.408)	C <sub>4</sub> (16.30)
	H <sub>5</sub> (7.450)	C <sub>5</sub> (136.54)

The peaks at 6.5 – 8.0 ppm exhibit strong similarities to the peaks at 6.9, 7.0 and 7.4 ppm, which correspond to the protons on the imidazole ring in 1-methylimidazole [41]. Additionally, the peaks in the range 3.0 – 4.0 ppm are consistent with the peaks at around 4.0 ppm in 1-ethylimidazole. Finally, the triplet corresponding to the methyl group of the ethyl chain in 1-ethylimidazole may well be observed in Figure 7 at low field (below 1.0 ppm) [41]. Clough *et al.* [32] performed a similar experiment where a sample of 1-ethyl-3-methylimidazolium acetate was heated to 120 °C in a thick-walled, sealed NMR tube and held isothermally for 12 hours. Upon cooling the sample to room temperature, several new peaks were observed in the region 6.10–7.40 ppm, which were attributed to 1-methylimidazole and 1-ethylimidazole. Additionally an observed triplet at 0.69 ppm was assigned to the terminal methyl group of the ethyl chain in 1-ethylimidazole. Interestingly, no new peaks were observed in the spectra which were taken every 30 minutes during the isothermal period at 120 °C; a finding which was rationalised by the fact that the decomposition products may well have been present in the gas phase. The analysis was performed in the absence of a deuterated

solvent, however two samples spiked with a small amount of 1-methylimidazole and 1-ethylimidazole respectively with a D<sub>6</sub>-DMSO capillary insert were run as control experiments to determine the chemical shifts of the ionic liquids and the decomposition products.

<sup>13</sup>C NMR spectra were also obtained (Figure 8) for the samples (*i.e.* fresh and heated 1-ethyl-3-methylimidazolium acetate), but are considered purely qualitatively as they are not of sufficiently high enough resolution to allow a definitive assignment. Nevertheless, it can be seen that, again, there is good agreement between the heated sample spectrum and the literature <sup>13</sup>C NMR spectra of 1-methylimidazole and 1-ethylimidazole [41]. The boxed areas (Figure 8, top) show the new peaks that have emerged in the <sup>13</sup>C NMR spectrum after heating the sample and it can be seen that they are comparable to the three carbon atoms of the imidazole ring in both 1-methylimidazole and 1-ethylimidazole and the two carbon atoms of the ethyl chain in 1-ethylimidazole. The shifts are summarised in Table 3.

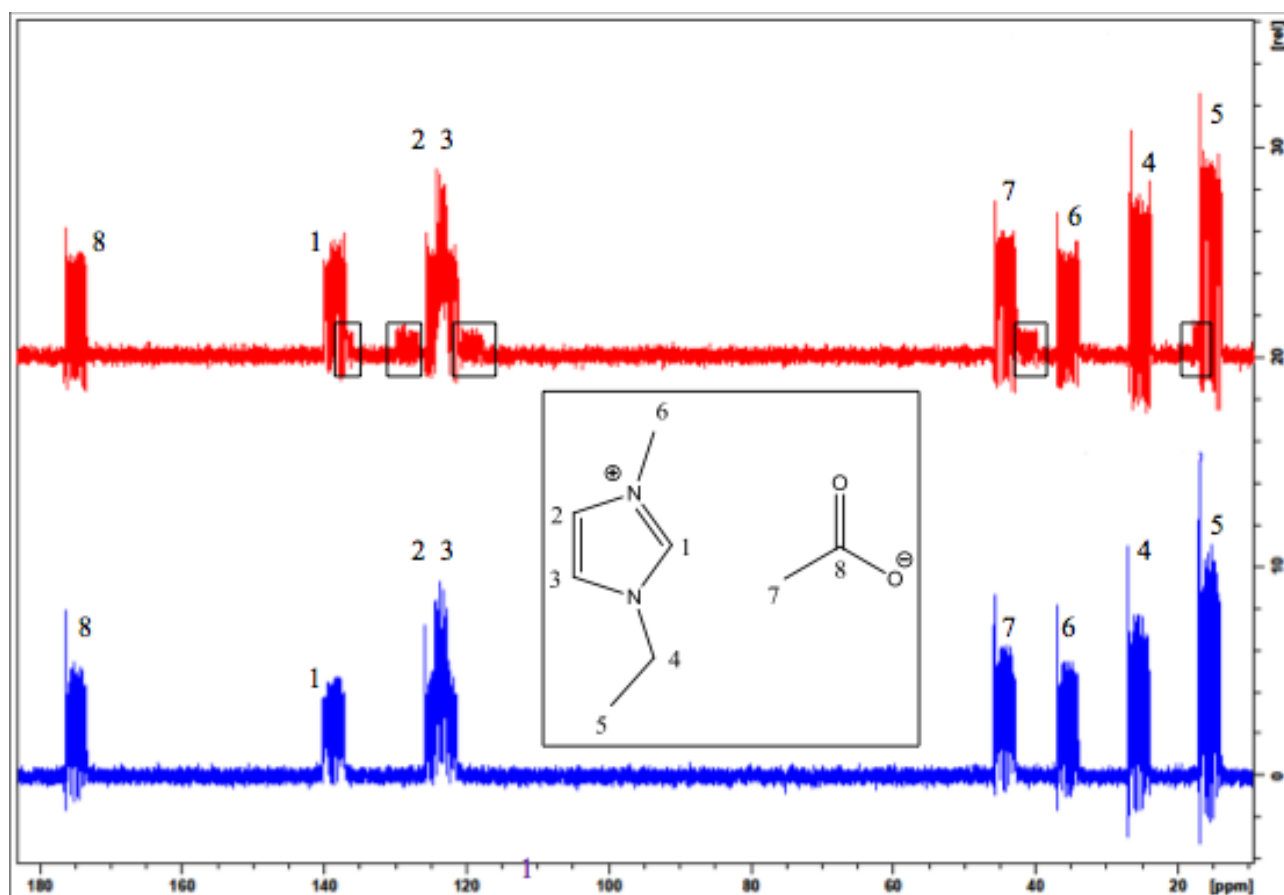


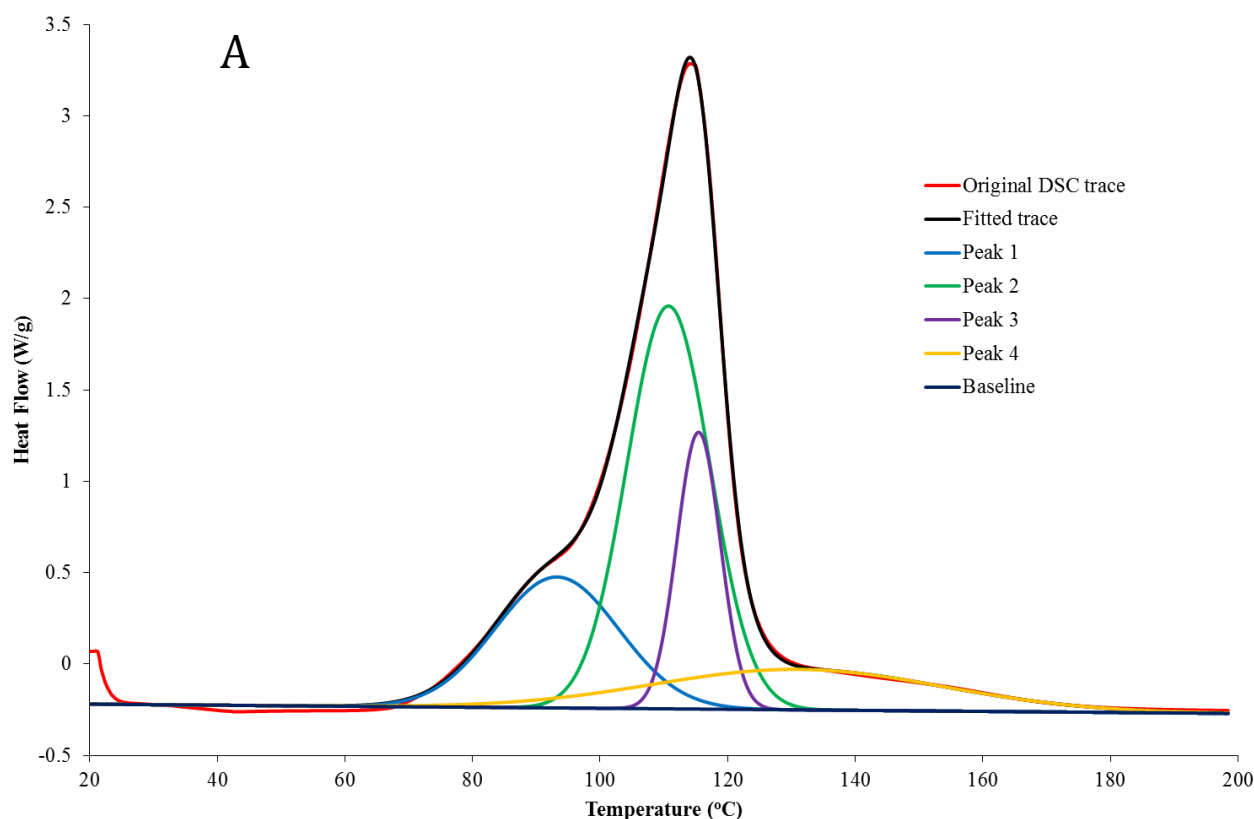
Figure 8. <sup>13</sup>C NMR spectra (unlocked) for a fresh 1-ethyl-3-methylimidazolium acetate sample (blue) and the sample material following heating to 150 °C (red). *N.B.*, the boxed areas show newly appeared peaks following heating.

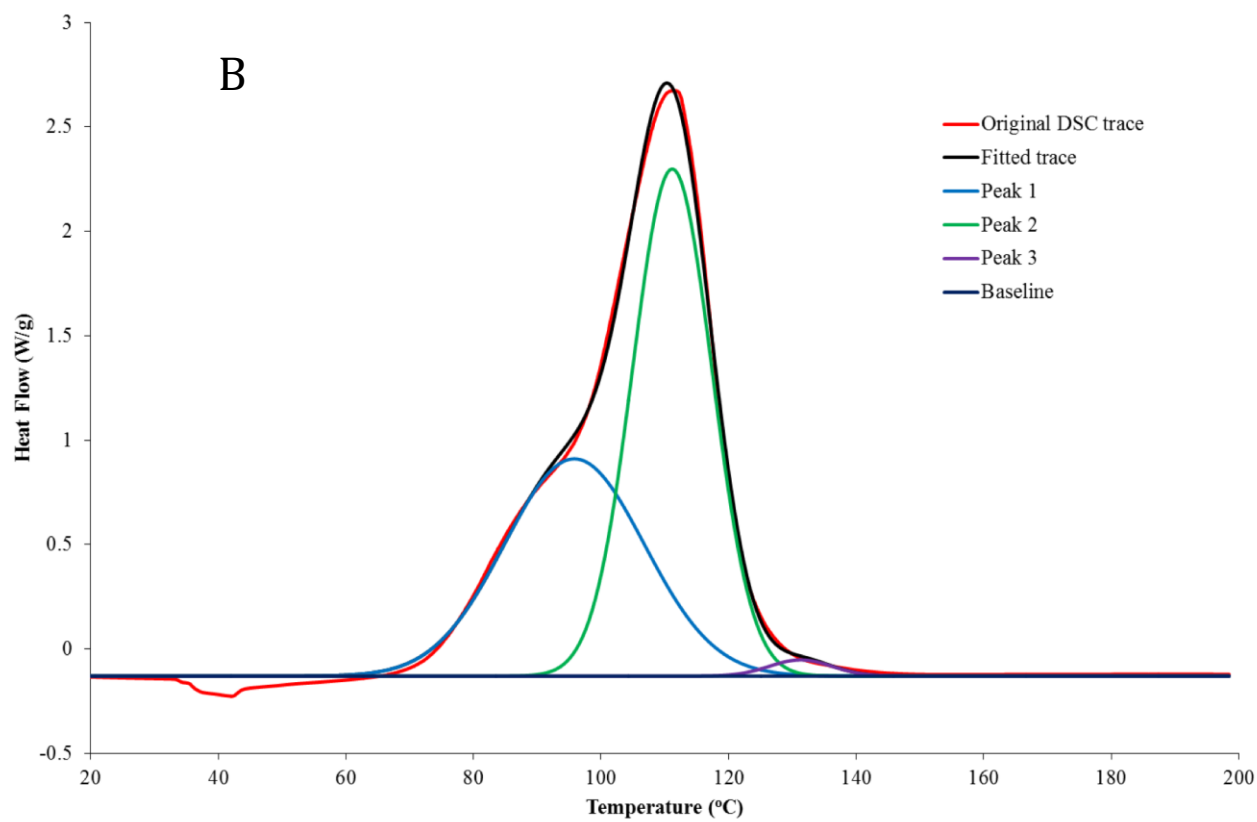


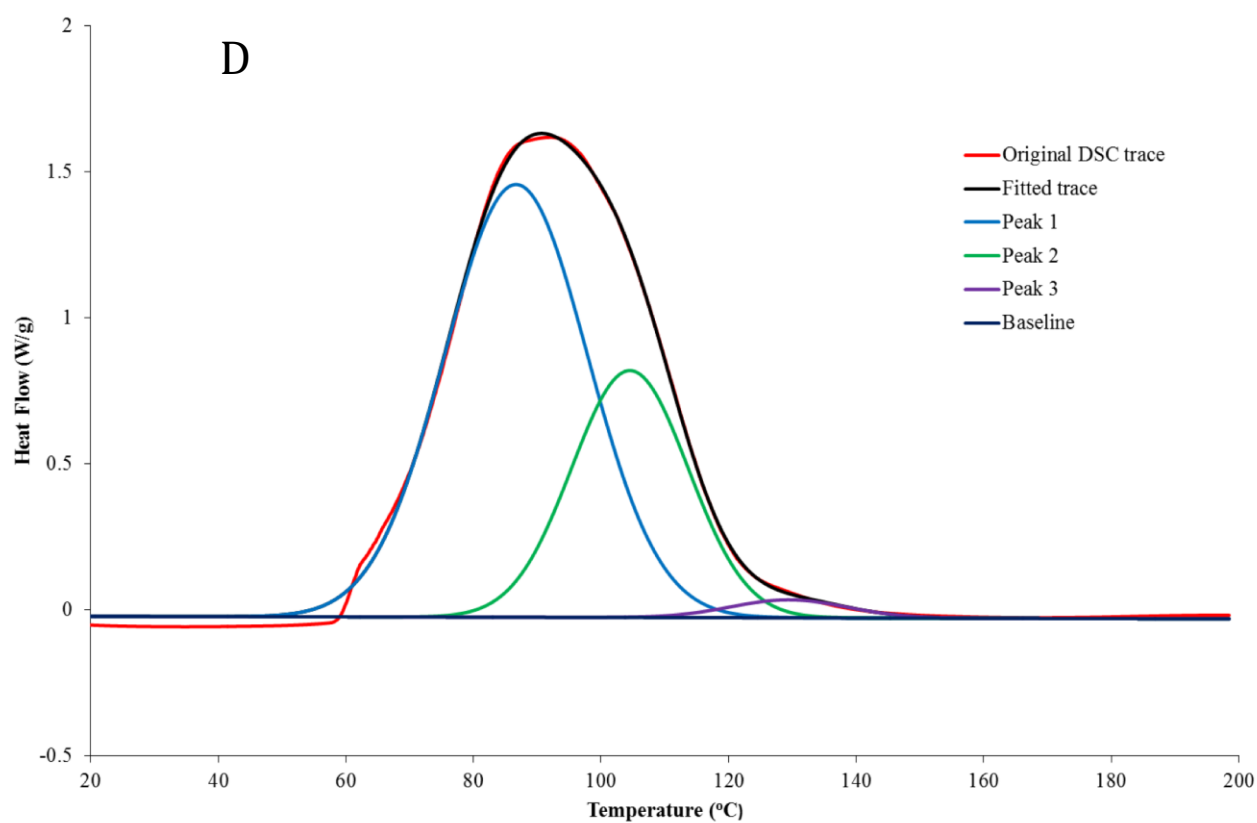
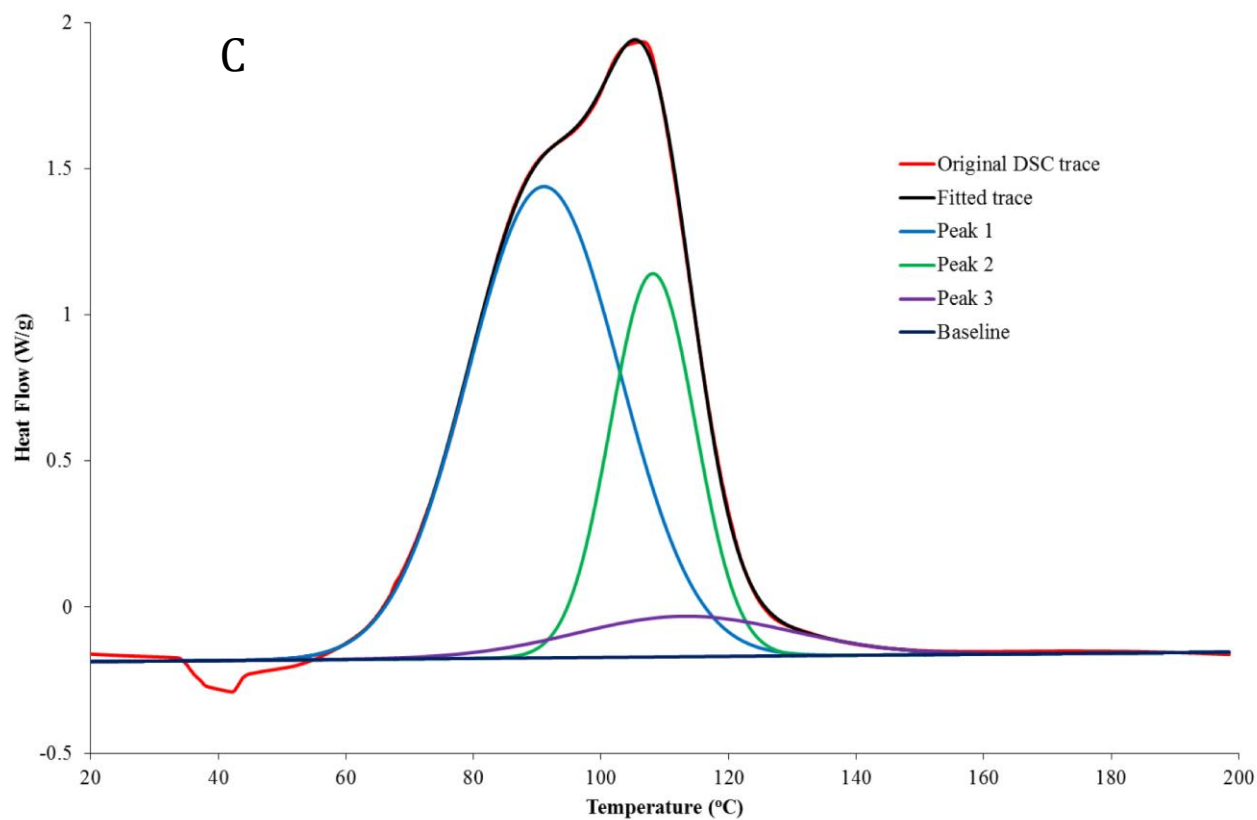
The exposure of dried samples of 1-ethyl-3-methylimidazolium acetate to the atmosphere resulted in an increase in mass due to water absorption, accompanied by a loss of initiating ability as measured by DSC analysis. It was proposed by Cammarata *et al.* [42] that the water molecules preferentially interact with the anion and therefore displace the anion from its location close to the cation. This means that the acetate anion would be unable to abstract the acidic proton, resulting in the carbene formation being prevented. This is reflected in the DSC thermogram where no exothermic reaction is observed to occur. It is proposed that carbene formation is the critical first step for initiation of the epoxy curing mechanism when 1-ethyl-3-methylimidazolium acetate is employed as the initiator.

### Effect of initiator concentration

Samples containing DGEBA (5 g) and various amounts of 1-ethyl-3-methylimidazolium were prepared and subjected to DSC analysis to yield a series of thermograms (Fig. 9). Peak fitting analysis was performed quite successfully using GRAMS software [43] showing that for the lowest level of the ionic liquid (0.25 g) the most complex thermogram could be represented by four individual peaks, each representing a thermal process.







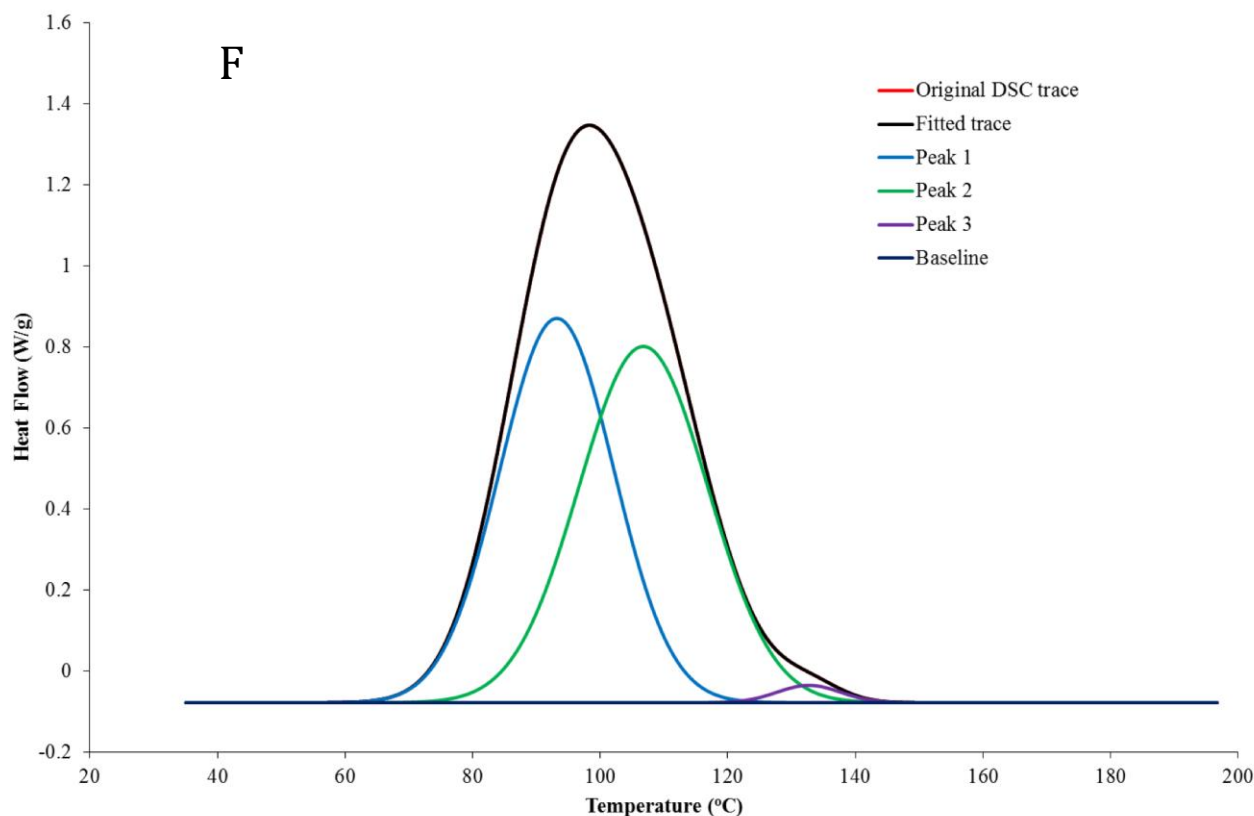


Figure 9. Peak fitting analysis of dynamic DSC data (heat 1) for formulations containing DGEBA (5 g) and 1-ethyl-3-methylimidazolium acetate as a function of loading (A) 0.25 g, (B) 0.50 g, (C) 1.40 g, (D) 2.30 g, (E) 3.30 g, and (F) 4.70 g).

As the amount of ionic liquid is increased, it is apparent that not only does the number of curves required to represent the thermogram reduce to three (implying a simplification in the reaction mechanism), but the increase in the lower temperature peak occurs at the expense of the high temperature peak (confirmed by expansion of the region 130-200 °C). The lowest temperature peak appears to become more prominent as ionic liquid is added, until it becomes the dominant reaction. However, a maximum is reached at 3.30 g, beyond this point the second reaction rises to become of equal intensity to the first process at the highest level of ionic liquid studied here (4.70 g). If this assumption is correct, then this should be reflected in the second heating cycle as a reduction in the glass transition temperature as a result of the reduction in the number of crosslinks formed. This is indeed observed as the resulting data are for formulations including the following quantities of 1-ethyl-3-methylimidazolium acetate: 0.25 g (151 °C), 0.50 g (114 °C) and 1.40 g (53 °C) (Fig. 10).

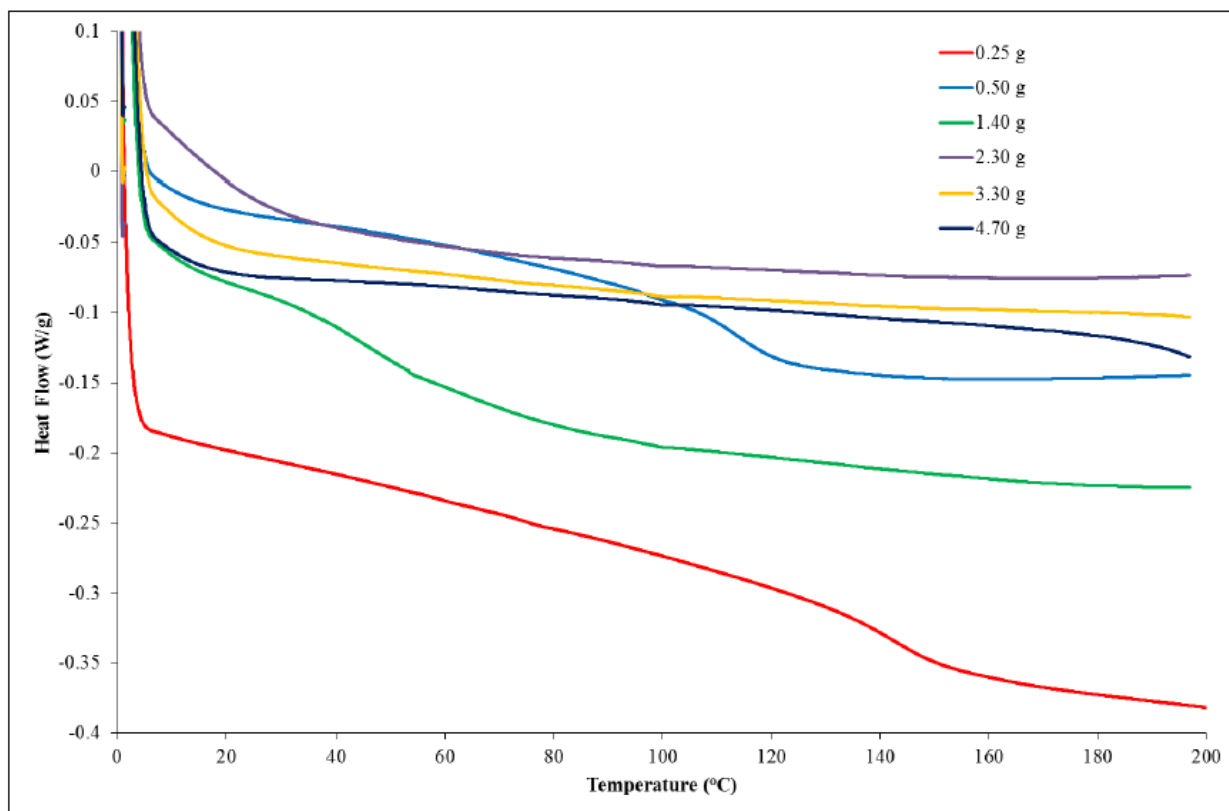


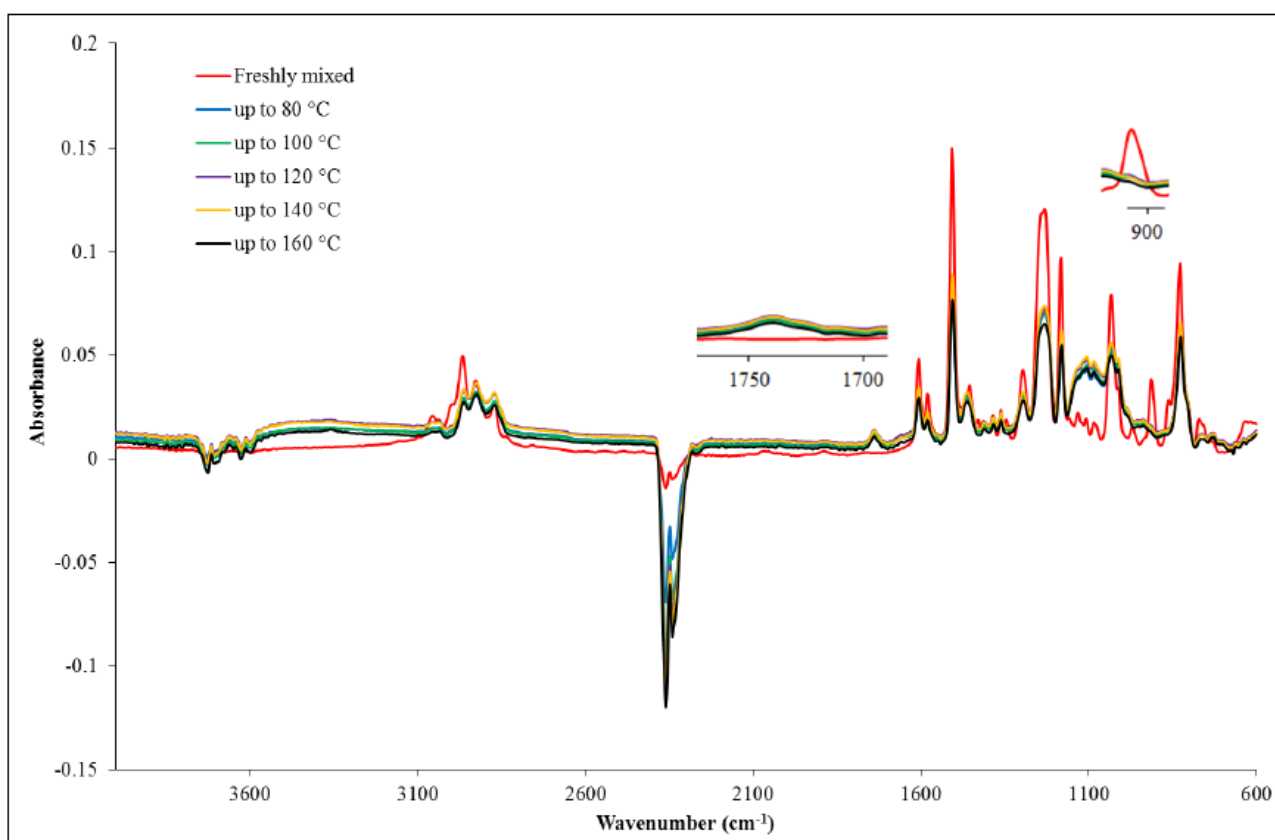
Figure 10. Dynamic DSC data (second heat) for freshly mixed formulations containing DGEBA (5 g) and 1-ethyl-3-methylimidazolium acetate (various contents).

### Spectral analysis of the curing epoxy formulations.

To complement the thermal analysis, both ATR-IR spectroscopy and NMR spectroscopy were employed to provide chemical information. For the ATR-IR analysis, multiple samples were prepared containing DGEBA (20 g) and a selected ionic liquid (1 g), and cured according to the conditions outlined in Table 1; samples being removed after each temperature stage for analysis. In addition, similar formulations were held isothermally at 50 °C and 160 °C in an air circulating oven, with an aliquot of sample being removed at 5 minute intervals for ATR-IR analysis.

**ATR-IR analysis.** Representative ATR-IR spectra for the formulations containing DGEBA (20 g) and 1-ethyl-3-methylimidazolium acetate (1 g) following different cure regimes are shown in Fig. 11—respectively (and the remaining data are supplied as Supplementary information, Figs. S3-S7). The samples containing 1-ethyl-3-methylimidazolium acetate reveal that the absorption band at approximately 912  $\text{cm}^{-1}$ , attributed to the epoxy ring breathing mode [44], is greatly reduced in samples which have been cured according to the programme presented in Table 1, compared with the freshly mixed sample. This finding corresponds well with the DSC data, which reveal that, with the exception of the high temperature peak in the 80 °C sample, there is no residual exotherm

associated observed implying that the consumption of epoxide rings is high. Furthermore, there is are significant increases in the intensity of the spectral bands at *ca.* 1100  $\text{cm}^{-1}$  and 3300  $\text{cm}^{-1}$  characteristic of the ether linkages and hydroxyl bands respectively, resulting from the polyetherification reaction [45]. Soares *et al.* [46] and Omrani *et al.* [47] reported similar observations. The spectra of the samples containing 1-ethyl-3-methylimidazolium thiocyanate and 1-ethyl-3-methylimidazolium diethylphosphate also display similar spectral features at 1100 and 3300  $\text{cm}^{-1}$ , but the latter also reveals that a significant concentration of epoxy rings remain following cure up to 160  $^{\circ}\text{C}$ , which is consistent with the exotherm observed on rescan in the DSC data.



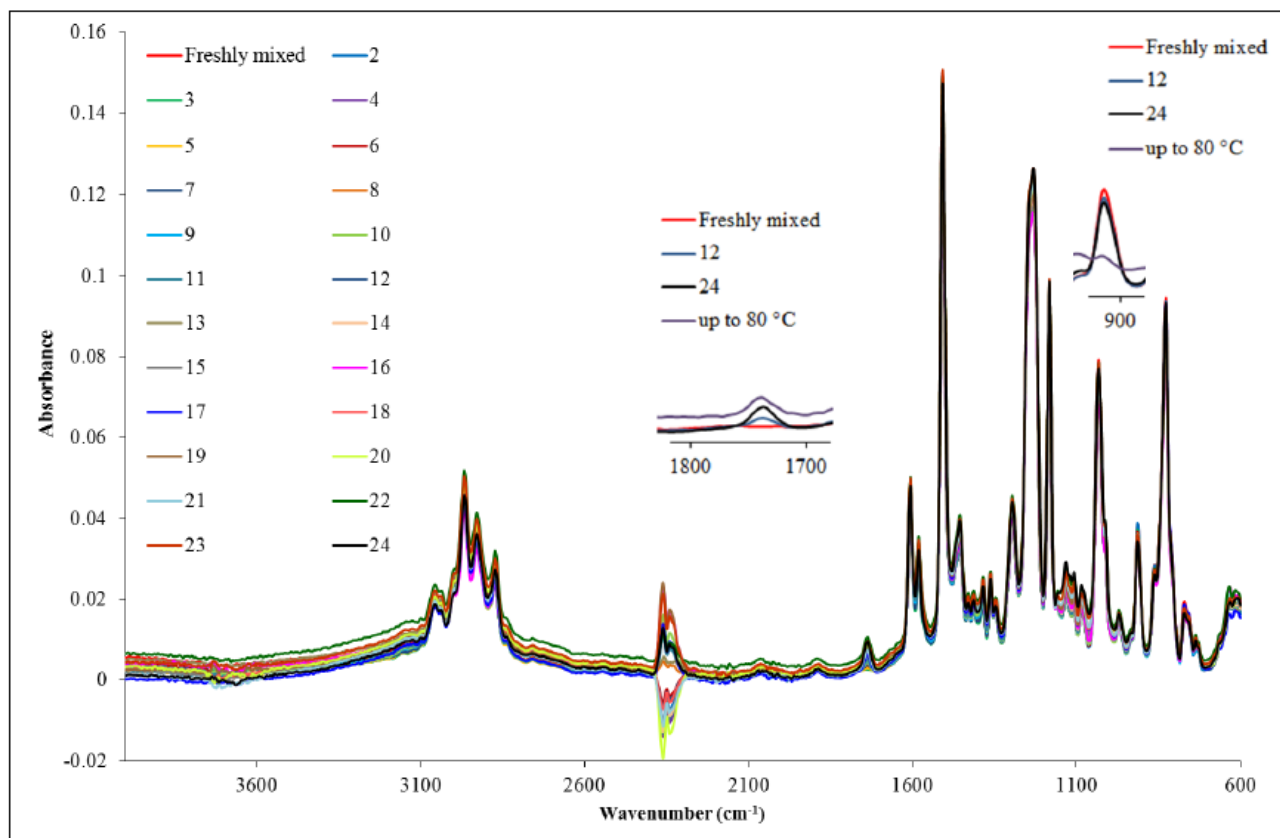


Figure 11. ATR-IR spectra of formulations containing DGEBA (20 g) and 1-ethyl-3-methylimidazolium acetate (1 g) previously cured in an air circulating oven according to the schedule in Table 1 (top) and held isothermally in an air circulating oven at 50 °C (bottom).

In addition, all spectra display a new peak at approximately  $1750\text{ cm}^{-1}$ , which is typical of the carbonyl stretching band [44]. Further spectral analysis was carried out at isothermal temperatures of 50 °C and 160 °C to monitor the disappearance of the epoxy band and the appearance of the carbonyl feature. Soares *et al.* [46] also reported the presence of a similar spectral band when epoxy/4,4'-methylene-bis(3-chloro-2,6-diethylaniline) formulations were initiated with an imidazolium-based ionic liquid, and this was attributed to the degradation of the epoxy as it appeared at elevated temperatures. However, this is unlikely to be the case in the present work, as in all case the band appears over time at relatively low temperatures (*e.g.* 50 °C and 160 °C), significantly lower than the onset of degradation for DGEBA or the ionic liquids. Ricciardi *et al.* [37] proposed that the presence of carbonyl bands was due to a Hofmann elimination reaction, resulting in the formation of an alkene, which could undergo subsequent tautomerisation to form a carbonyl group. Additionally, over the isothermal period, the intensity of the band attributed to the epoxy does not change markedly.

**NMR analysis.** A parallel analysis was performed using NMR spectroscopy, in which samples containing epoxy (20 g) and selected ionic liquids (1-ethyl-3-methylimidazolium acetate and 1-ethyl-3-methylimidazolium acetate) (1 g) were mixed in an aluminium dish and held isothermally at 50 °C in an air circulating oven. An aliquot (*ca.* 80 mg) was taken periodically over the isothermal period and mixed with deuterated acetone (*ca.* 0.7 ml) for analysis using  $^1\text{H}$  NMR spectroscopy. There are many similarities in the spectra: the chemical shift at 11.0 ppm (assigned to the proton bonded to the unsaturated carbon between the nitrogen atoms on the imidazolium ring) diminishes almost immediately on mixing with the epoxy, suggesting that deprotonation occurs rapidly (Fig. 11). This is consistent with the protons becoming more shielded as electron density within the ring increases as a result. Furthermore, the shifts associated with the epoxy ring protons remain broadly unaffected, both in terms of chemical shift and integral value.

Similar observations were made for the corresponding formulation containing 1-ethyl-3-methylimidazolium thiocyanate<sup>1</sup>, although the chemical shift at 9.25 ppm (assigned to the unsaturated proton between the nitrogen atoms on the imidazolium ring) diminishes more slowly,

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<sup>1</sup> *N.B.* owing to molar ratio of the reagents, the shifts corresponding to the ionic liquid are of considerably lower intensity than for DGEBA making it difficult to quantify the observations. This is compounded by the possible change of solubility in acetone from monomer to polymer.



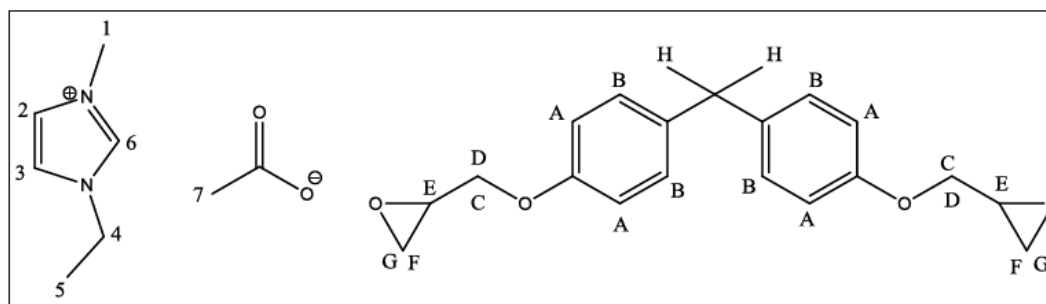
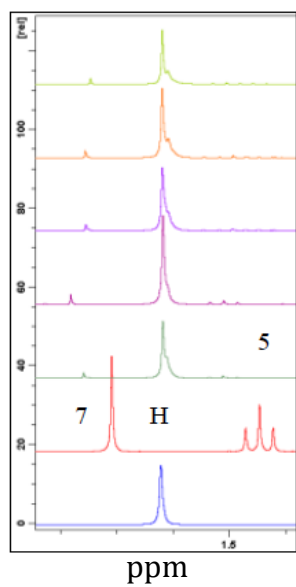
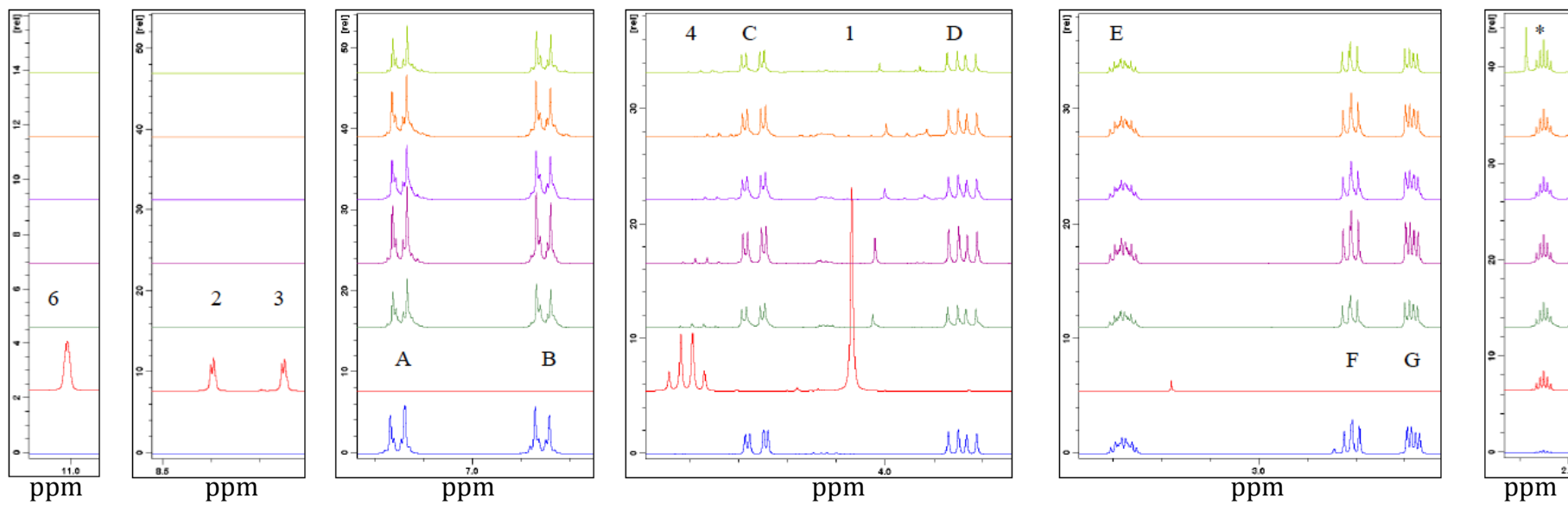


Figure 11. Expanded  $^1\text{H}$  NMR spectra of a formulation containing DGEBA (20 g) and 1-ethyl-3-methylimidazolium acetate (1 g) held isothermally at 50 °C in an air circulating oven.

indicating a slower deprotonation reaction. In addition, the emergence and subsequent disappearance of a new peak at 2.9 ppm is attributed to an intermediate product formed through reaction of the thiocyanate anion with the epoxy ring; presumably with the electrophilic carbon atom on the epoxy ring. This ionic liquid has also been studied by Maka *et al.* [48], who found that it displayed the highest catalytic activity of those studied in the work, with a pot lives of up to a week; the cured epoxies achieved  $T_g$  values of between 138 and 181 °C depending on initiator content.

## CONCLUSIONS

Evidence exists for a number of different reaction pathways and the initiation reaction with a di-epoxy is proposed to occur *via* a carbene route, an imidazole route or a nucleophilic route, although it is suggested that these reaction pathways are not discrete. The anions can be ranked according to the Lewis base character exhibited (*i.e.* the  $pK_a$  value of the conjugate acid formed through abstraction of the acidic proton from the 2- position on the imidazolium ring). A combination of analytical techniques have been applied to explore the nature of the initiation mechanism. DSC and rheological data reveal the reactivity of the anions can be ranked in a similar order and it is proposed that the Lewis base character is the determining factor in whether the reaction will proceed *via* a *N*-heterocyclic carbene and epoxy formulations containing 1-ethyl-3-methylimidazolium acetate will initially proceed *via* this reaction pathway at temperatures below zero. Dealkylation has been observed for 1-ethyl-3-methylimidazolium acetate at temperatures > 150 °C, although the ionic liquids containing diethyl phosphate, dicyanamide or thiocyanate do not appear to undergo dealkylation at this temperature. ATR-IR spectroscopic data suggest that, irrespective of the initiation mechanism, a Hofmann type elimination occurs to yield a carbonyl functional group through tautomerisation of an alkene group.

The  $^1\text{H}$  NMR spectra of epoxy formulations containing 1-ethyl-3-methylimidazolium acetate obtained at an isothermal temperature of 50 °C reveal that the acidic proton on the imidazolium ring diminishes rapidly resulting in carbene formation, although there is no evidence of dealkylation at this temperature. Epoxy formulations containing 1-ethyl-3-methylimidazolium acetate appear to undergo regeneration of the acetate anion to facilitate carbene formation and the ring opening mechanism is believed to initiate when there is a sufficient concentration of carbene species and acetic acid. It is thought that the same mechanism occurs at room temperature albeit more slowly. The  $^1\text{H}$  NMR spectra obtained for formulations comprising a mono-epoxide and 1-ethyl-3-methylimidazolium thiocyanate suggest that the ionic liquid is stable at room temperature (*i.e.*

deprotonation does not occur) and, instead, the reaction proceeds *via* reaction of the counter ion with the epoxy ring. However, if, the formulations are held at 50 °C the deprotonation route also becomes active, leading to two competing reaction pathways.

In summary, the initiation of a commercial epoxy resin using ionic liquid proceeds by a complex mechanism, in which the first step (commencing at *ca.* 60 °C) appears consistent with the deprotonation of the imidazolium ring and subsequent attack of this species on the epoxy carbon. This is particularly fast in the case of 1-ethyl-3-methylimidazolium acetate. The second reaction, attributed to the dealkylation of the imidazolium ring and subsequent attack of this species on the epoxy carbon, commences at around 90 °C, and appears to become more dominant as ionic liquid concentration increases. The third, more sluggish, reaction spanning a wide temperature range might be due to the reported Hofmann elimination reaction, resulting in the formation of an alkene, which could undergo subsequent tautomerisation to form a carbonyl group.

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