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Examining the kinetics of the thermal polymerisation behaviour of epoxy resins initiated with a series of 1-ethyl-3-methylimidazolium based ionic liquids

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ABSTRACT: An epoxy resin based on the difunctional diglycidyl ether of bisphenol A (DGEBA) is reacted thermally in the presence of a series of 1,3-dialkylimidazolium based ionic liquids comprising the common cation (1-ethyl-3-methylimidazolium) and an anion (acetate, dicyanamide, or thiocyanate). Dynamic differential scanning calorimetry was used to analyse the formulations comprising DGEBA and the 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. Cured glass transition temperatures range from 151-175 °C, depending on the anion used. Gelation behaviour is also dependent on the nature of the anion, with the acetate promoting gelation most quickly, whereas the dicyanamide is least reactive. Kinetic analysis of the cure reactions yield consistent results ($R^2 > 0.99$) using the Ozawa method ($E_a = 74-98$ kJ/mol) and are in good agreement with previous studies on imidazoles.

Keywords: Epoxy Resins, Ionic Liquids, Imidazoles, Initiators, Reaction Kinetics.

INTRODUCTION

Epoxy monomers are commonly converted by the application of heat into three-dimensional, crosslinked networks [1,2] which results in their application in the engineering industry as a result

of their good thermal, mechanical and electrical properties [3,4,5]. They also find use as anticorrosive coatings, adhesives and paints due to their corrosion resistance and good adhesion to a wide variety of substrates [6,7], while in many advanced composites, epoxy resins form the continuous phase [8]. The reactivity of the epoxy (oxirane) ring enables the use of a wide variety of chemical compounds to initiate cure [9] and imidazoles catalyse the homopolymerisation of epoxide groups and yield tough thermoset networks [8,12] with attractive physical properties [10] such as heat resistance [11], tensile elongation, a higher modulus and a wider range of cure temperatures compared with amine-cured systems [12,13]. Structurally related imidazolium-based ionic liquids (Figure 1) are one of the most studied groups of ionic liquids [14] 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 [15]. The benefits of ionic liquids (particularly those based on imidazolium ions) as catalysts for enhancing both the rate of reaction and the yield of polymer are becoming increasingly apparent, and a few studies in the literature report imidazolium-based ionic liquids as initiators for epoxy resins, including Kowalczyk and Spychaj [16] (1-butyl-3-methylimidazolium tetrafluoroborate), Rahmathullah *et al.* [17] (1-ethyl-3-methylimidazolium dicyanamide), and Maka *et al.* [18] (1-decyl-3-methylimidazolium and 1-butyl-3-methylimidazolium cations with chloride, tetrafluoroborate and dicyanamide anions). A previous publication [19] has demonstrated that 1-ethyl-3-methylimidazolium acetate undergoes dealkylation 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. At elevated temperatures a second, competing reaction, involving deprotonation of the imidazolium ring, also becomes active. The current work seeks to identify the kinetic parameters associated with these initiation mechanisms.

EXPERIMENTAL

Instrumentation. ^1H nuclear magnetic resonance (NMR) spectra comprising of 16 scans, conducted on a Bruker 300 MHz NMR spectrometer at room temperature. Samples (*ca.* 80 mg) were mixed with D_6 -acetone (0.6 – 0.7 ml) and transferred to an NMR tube for analysis.

Differential scanning calorimetry (DSC) was undertaken using a TA Instruments Q1000 running TA Q Series Advantage software on samples (5.0 ± 0.5 mg) in sealed aluminium pans, with a pinhole to the lid. Experiments were conducted at a heating rate of 10 K/min. from -10 °C to 200 °C (heat/cool/heat) under flowing nitrogen ($50 \text{ cm}^3/\text{min.}$).

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

Dynamic Oscillatory Rheology was performed using an Anton Paar MCR-300 rheometer with a 25 mm peltier plate and disposable aluminium pan set up. The rheometer was operated in oscillation mode and samples were subjected to a temperature ramp from 25 °C to 200 °C at 5 K/minute with the collection of data set to a frequency of 0.2 minutes. The strain was held constant at 0.5 % and the normal force programmed to remain at 0 N. 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.

Gelation measurements were measured using a GELNORM®-RVN Topfzeitmessgeräts instrument operating according to DIN 16945 [20], which defines the pot life as the point at which the sample exhibits a 5% increase in viscosity compared with the starting value. This is calculated by measuring the relative viscosity through the change in power required over time for a spindle probe inserted in the sample to rotate). An aluminum stamper was inserted into the test tube and subsequently affixed to the moving lever within the instrument. The test tube was placed in the furnace and the Ni-Cr-Ni thermocouple placed inside the reacting mixture. The instrument was programmed to heat the furnace to a specified temperature and then begin moving the aluminium stamper up and down. The gel time was recorded at the point at which the test tube was lifted out of the furnace by the stamper (due to an increase in the viscosity) causing the optical line of light to be broken. DGEBA and ionic liquid were combined in a glass beaker (100 ml) and mixed by hand for 120 seconds. A sample (*ca.* 12 g) was subsequently transferred to a glass test tube for analysis.

Materials. The three ionic liquids (1-ethyl-3-methylimidazolium acetate, 1-ethyl-3-methylimidazolium dicyanamide, and 1-ethyl-3-methylimidazolium thiocyanate) and the diglycidyl ether of bisphenol A (DGEBA, BaxxoresTM ER 2200, $\text{ew } 182 \text{ g/mole}$) were supplied by BASF (Fig. 1). The materials were characterised using ^1H NMR (in deuterated acetone) and used without further purification (see supplementary data, Fig. S1 and S2).

Figure 1. Structures of 1-ethyl-3-methylimidazolium (a) acetate, (b) dicyanamide, (c) thiocyanate.

RESULTS AND DISCUSSION

Investigation of cure reactions of the different formulations. Each ionic liquid (0.25 g) was mixed with DGEBA (5 g) in clear glass scintillation vials. Each sample (2-8 mg) was analysed using DSC (a heat-cool-heat cycle from 25 °C to 200 °C at 10 K/min). The enthalpy value associated with the curing reaction (heat 1) and the glass transition temperature range (heat 2) were measured. The thermograms displaying the data obtained during the first heating cycle are shown in Fig. 2, from which it is clear that the anions significantly influence the reaction in terms of onset temperature. All the thermograms, to some extent, suggest that at least two reaction steps occur during the heating cycle (Table 1). This is evidenced by a low temperature shoulder, which occurs on the main peak in the case of 1-ethyl-3-methylimidazolium acetate and 1-ethyl-3-methylimidazolium thiocyanate, or a discrete peak as in the example of 1-ethyl-3-methylimidazolium dicyanamide.

Figure 2 Dynamic DSC data obtained for freshly mixed epoxy formulations containing different ionic liquids based on 1-ethyl-3-methylimidazolium (designated as the corresponding anions).

Table 1 Dynamic DSC for freshly mixed epoxy formulations with different ionic liquids based on 1-ethyl-3-methylimidazolium as a function of counter ion.

Counter ion	First heating scan				Second heating scan		
	T_{onset} (°C)	T_{max} (°C)	T_{end} (°C)	ΔH_p (J/g)	T_{go} (°C)	T_g (°C)	T_{ge} (°C)
Acetate	64	114	187	475	141	151	164
Dicyanamide	122	142, 180	198	474	162	175	184
Thiocyanate	84	121	192	485	152	163	174

Key: T_{onset} = onset of polymerization exotherm, T_{max} = peak maximum of polymerization exotherm, T_{end} = end point of polymerization exotherm, ΔH_p = polymerisation exotherm, T_{go} = onset of glass transition, T_g = midpoint of glass transition, T_{ge} = end of glass transition.

TGA data were acquired (undertaken in nitrogen) for each initiator (Fig. S3). Dynamic oscillatory rheology was employed, alongside a gel timer, to measure the gel point and vitrification point temperature for a series of formulations containing DGEBA (20 g) and each ionic liquid (1 g),

which were mixed together for two consecutive periods of 2 minutes at 2500 rpm. Samples were then immediately analysed, the resulting data are shown in Fig. 3.

Figure 3 Dynamic oscillatory rheology data for freshly mixed formulations comprising DGEBA (20 g) and 1-ethyl-3-methylimidazolium acetate (1 g), 1-ethyl-3-methylimidazolium dicyanamide (1 g) and 1-ethyl-3-methylimidazolium thiocyanate (1 g)

The sample containing 1-ethyl-3-methylimidazolium dicyanamide exhibits the highest gel point temperature whereas the 1-ethyl-3-methylimidazolium acetate containing sample exhibits the lowest which is in agreement with the DSC data (Fig. 2). The initial viscosity of the sample containing 1-ethyl-3-methylimidazolium dicyanamide is considerably lower than for the other two samples, which is expected due to the reported low viscosity of ionic liquids comprising the dicyanamide anion [21]. The vitrification points, which were determined for the acetate and thiocyanate ionic liquids, were shown to differ by approximately 7 K (Table 2).

Table 2 Dynamic oscillatory rheology data for freshly mixed formulations comprising DGEBA (20 g) and different ionic liquids (1 g)

Initiator	Initial viscosity (Pa.s)	Gel point (°C)	Vitrification point (°C)

1-ethyl-3-methylimidazolium acetate	8.47	103	110
1-ethyl-3-methylimidazolium dicyanamide	3.42	165	-
1-ethyl-3-methylimidazolium thiocyanate	7.58	112	117

The vitrification point for the dicyanamide containing sample was not reported as no clear peak was observed in the loss modulus curve. The loss moduli are seen to decrease for all samples in the early stage of the analysis due to the fact that the increase in temperature causes a decrease in viscosity prior to any reaction. Upon initiation of the reaction, both the storage and loss modulus begin to increase until the storage modulus becomes greater than the loss modulus, indicating that the point of gelation has been reached [22]. If the gel point is compared with the DSC data (Fig. 2) where the scan rate is 5 K/min, it can be seen that the gel point occurs after the shoulder or the first peak is completed and at broadly the same temperature as the $T_{\max}$ value of the main exothermic peak.

A sample (12 g) of a DGEBA (20 g) and 1-ethyl-3-methylimidazolium acetate (1 g) formulation was heated to 80 °C in the gel timer instrument. Owing to the exothermic nature of the reaction, the gel point was reached in 4 minutes and a $T_{\max}$ value of 275 °C was recorded at a time of 5 minutes. The sample was removed from the instrument before the end of the post-reaction recording time as a significant amount of smoke was evolved and therefore the $T_{\max}$ temperature could well have increased. The rapid increase in the exothermic enthalpy value was due primarily to the rate at which the sample was heated and the mass of the sample (12 g) which allowed an exotherm to build up quickly within the sample. The samples for DMTA were cured according to the schedules in Table 3.

Table 3. 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 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)
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Formulations comprising DGEBA and 1-ethyl-3-methylimidazolium acetate. The loss modulus data show (Fig. 4, top) that the material undergoes at least two transitions as a function of the temperature ramp. The highest storage modulus value is seen to occur in the sample, which has been cured for the shortest time at the lowest temperature, however the value is seen to decrease rapidly as a function of temperature in a single transition indicating a relatively uniform network. The samples which have reached 140 °C and 160 °C in the curing programme exhibit very similar profiles and are both observed to undergo more pronounced lower temperature *beta* transitions before going through the glass transition temperature at a similar temperature which is indicative of different areas of network formation giving rise to different transitions (as the samples are at different stages in the curing programme). The fact that both the 140 °C sample and the 160 °C sample exhibit very similar curves suggests that the network growth is very similar and does not change markedly during the dwell period at 160 °C. The fact that the 80 °C sample does not exhibit a peak at this temperature, despite reaching 230 °C within the instrument, suggests that the network structure giving rise to the peak at approximately 122 °C develops slowly within the dwell periods and is not achieved during a temperature ramp to 230 °C at 5 K/min. The tan delta curves, shown in Fig. 4, bottom reveal that the 80 °C sample exhibits a considerably higher damping ability than the other samples and a lower glass transition temperature. This implies that the material is not as heavily crosslinked as the other samples, which is expected due to the incomplete cure.

Figure 4 DMTA data for formulations comprising DGEBA (20g) and 1-ethyl-3-methylimidazolium acetate (1 g) previously cured in an air-circulating oven according to the schedule in Table 3. Note symbols denote sample cured up to 80 °C (▲), 140 °C (●), or 160 °C (■).

A DSC scan of the samples that had been cured in the oven revealed that the sample, which had been heated to 80 °C (30 minutes at 40, 60 and 80 °C), still showed an exothermic peak at approximately 150 °C. The samples that had been heated to 140 °C and 160 °C respectively, did not exhibit an exothermic peak during the first heating cycle (Fig. 5).

Figure 5 Dynamic DSC data for 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 3. Note symbols represent freshly mixed (▼) or sample previously heated to 80 °C (▲), 140 °C (●), or 160 °C (■); solid lines represent first heating cycle and dashed lines represent second heat (rescan).

A comparison of the exothermic enthalpy value for a freshly mixed sample (Table 4) with the exothermic enthalpy value for the 80 °C sample revealed that the sample was 95 % cured. As expected, as the heating rate in the DSC experiment is increased, then the peak maximum shifts to a high temperature regime (Fig. 6, the results of other thermal analyses undertaken at a range of heating rates, are given in the supplementary data, Figs. S4 and S5). Additionally, the lower temperature shoulder becomes more dominant as the heating rate increases.

Table 4 Dynamic DSC data for freshly mixed formulations comprising DGEBA (5 g) and different ionic liquids based on 1-ethyl-3-methylimidazolium (0.25 g) as a function of counter ion and heating rate.

Anion	Heating rate (K/min)	Peak maximum, $T_{\max}$ (°C)	Polymerisation enthalpy	
			(J/g)	(kJ/mol epoxy)
acetate ^a	2	91	567	103
	5	105	488	89
	10	115	480	87
	15	121	469	85
	20	128	474	86
Mean				90
dicyanamide	5	167	490	89
	10	180	451	82
	15	187	517	94
	20	189	488	89
Mean				89
thiocyanate ^a	2	99	577	105
	5	112	534	97
	10	123	530	96
	15	129	560	102
	20	134	524	96
Mean				99

Key: ^a data are average of three samples.

Figure 6 Dynamic DSC data for formulations containing DGEBA (20 g) and 1-ethyl-3-methylimidazolium acetate (1 g) at a variety of heating rates.

Kinetics

The good agreement between the DSC analyses performed at different heating rates facilitated determination of the kinetic parameters associated with the polymerisation reaction. Various methods have been proposed, such as Kissinger [23] and Ozawa [24], to determine the kinetic parameters of an epoxy curing reaction. The DSC data were processed using the Ozawa method (eqn 1) and the regression coefficients (R^2 values > 0.99) show good linear fits to the DSC data (Fig. 7 and supplementary Figs. S6 and S7).

$$\ln \beta = \ln \left(\frac{AE_a}{R} \right) - \ln f(\alpha) - 5.331 - 1.052 \left(\frac{E_a}{RT} \right) \quad (1)$$

where A = the Arrhenius pre-exponential factor and f is a constant function.

From this analysis, the activation energies are calculated to be 74 kJ/mol. (acetate), 98 kJ/mol. (dicyanamide), and 77 kJ/mol. (thiocyanate).

Figure 7 Ozawa plot for formulations containing DGEBA (5 g) and 1-ethyl-3-methylimidazolium acetate (0.25 g).

If the DSC data for the three initiators (Fig. 2) are compared with the activation energies, there is also a consistency in that the higher onset temperature (of polymerisation) equates to higher activation energy; in comparison, the samples containing 1-ethyl-3-methylimidazolium thiocyanate display similar activation energies. The kinetic data compare well with data acquired for DGEBA when cured with an adduct of 2-ethyl-4-methylimidazole and phenylglycidylether (PGE-EMI), and also a range of complexes [25]. For example, Brown *et al.* used fused state ^1H NMR spectroscopy to report rate constants for the thermal polymerisation of DGEBA (Epikote 828) and PGE-EMI (3 mol %) at 100 – 125 °C in the absence of solvent. The values for k_1 (relating to attack of the imidazole ring on the epoxy) fell in a range between $5.57 - 8.30 \times 10^{-3} \text{ s}^{-1}$, rising with temperature; k_2 (relating to polyetherification) were $5.00 \times 10^{-6} - 2.00 \times 10^{-5} \text{ s}^{-1}$. For the same reaction, an activation energy of 70 kJ/mol. was calculated for the polyetherification. In a previous study, Buist *et al.* reported values of 45 kJ/mol. (k_1) and 60 kJ/mol. (k_2) for reactions involving DGEBA (MY 750) [26]. Similarly, Heise and Martin [27] reported a study of the reaction of DGEBA and PGE-EMI (5 mol %) for which an activation energy of 88 kJ/mol. was calculated for k_2 .

A series of conversion plots and the corresponding reaction rates are shown in Fig. 8 for the samples containing 1-ethyl-3-methylimidazolium thiocyanate (the other data are given in supplementary form, Fig. S8-S11). In all cases, a higher degree of conversion is obtained at lower temperature when a slower heating rate is used, although when 1-ethyl-3-methylimidazolium

dicyanamide is used the conversion does not follow the same trend as the other initiators, with a second transition observed at a conversion of around 10-20 %, after the first exothermic peak in the thermogram has been completed. This suggests that in this case that the first reaction is critical for the subsequent polymerisation, which is discussed in greater detail elsewhere [19].

Figure 8 Plots of (a) monomer conversion as function of temperature and (b) reaction rate for freshly mixed formulations containing DGEBA (5 g) and 1-ethyl-3-methylimidazolium thiocyanate (0.25 g).

CONCLUSIONS

The addition of around 5 wt % of a series of ionic liquids, based on the 1-ethyl-3-methylimidazolium cation, has a profound influence on the rate of polymerisation of the diglycidylether of bisphenol A (DGEBA). When acetate and thiocyanate anions are incorporated into the ionic liquid formulation, the onset of polymerisation reaction (T_o) occurs at 65 °C and 85 °C respectively. This is explained by an early deprotonation stage, followed by nucleophilic attack on the epoxy ring. The activation energy (E_a) for the reaction initiated with the acetate anion is 74 kJ/mol., compared with $E_a = 77$ kJ/mol. for thiocyanate. The dicyanamide anion displays similar behaviour, albeit much lower reactivity ($E_a = 98$ kJ/mol.), the $T_o = 125$ °C, $T_{gel} = 165$ °C.

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