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Examining the nature of the network formation during epoxy polymerization initiated using ionic liquids

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ABSTRACT: A commercial diglycidyl ether of bisphenol A monomer (BaxxoreTM ER 2200, M_w 182 g/mole) is thermally polymerized in the presence of an ionic liquid, 1-ethyl-3-methylimidazolium acetate at a variety of loadings (5-45 wt %). The loss modulus data for cured samples containing 5 wt % initiator display at least two thermal transitions and the highest storage modulus occurs in the sample that has been cured for the shortest time at the lowest temperature. Samples that are exposed to higher temperatures (140, 150 °C) yield more heterogenous networks, whereas following exposure to a much shorter/lower temperature cure schedule (80 °C) exhibits a considerably higher damping ability than the other samples, coupled with a lower glass transition temperature. Differential scanning calorimetry reveals that the latter sample achieves a conversion of 95 %, while crosslink densities for the DGEBA samples containing 5 wt % and 15 wt % are respectively $9.5 \times 10^{-3} \text{ mol. dm}^{-3}$ and $1.2 \times 10^{-3} \text{ mol. dm}^{-3}$ (when cured to 80 °C) and $2.0 \times 10^{-2} \text{ mol. dm}^{-3}$ and $2.4 \times 10^{-3} \text{ mol. dm}^{-3}$ (when cured to 140 °C).

Keywords: Epoxy Resins, Ionic Liquids, Initiators, Network formation, Physico-mechanical Properties.

INTRODUCTION

Imidazoles are well known for their ability to initiate effectively the homopolymerisation of epoxide groups *via* polyetherification [1,2] to yield tough thermoset networks [3]. The cured epoxy resins that result offer a balance of thermal, mechanical, and electrical properties [4,5,6], making them attractive as adhesives (due to their attraction to a variety of substrates) and coatings (preventing corrosion) [7,8]. Although diamines are among the most widely used curing agents for epoxy resins [9], epoxy networks initiated with imidazoles can offer superior physical properties [10] such as better heat resistance [11], lower tensile elongation, higher modulus, and a wider range of cure temperatures compared with amine-cured systems [12,13]. However, the relatively poor shelf life in one-pot epoxy-imidazole formulations is a real limitation to their wider use and various coordination strategies have been adopted to reduce their reactivity [14]. Ionic liquids are structurally related to imidazoles [15], but by forming imidazolium salts through various counter-ions (*e.g.* acetate, thiocyanate, dicyanamide, or diethylphosphate, *etc.*), their viscosity is reduced [16] facilitating better dispersion within the epoxy along with improved shelf life (*i.e.* the heterocyclic ring is stable in both oxidative and reductive environments) [17,18].

Various studies have demonstrated that imidazolium-based ionic liquids are capable of enhancing both the rate of reaction and the yield of the epoxy network [16,19]. The thermal decomposition of the ionic liquid (*e.g.* based on 1-decyl-3-methylimidazolium and 1-butyl-3-methylimidazolium cations with chloride, tetrafluoroborate and dicyanamide anions as initiators for epoxy resins [20]) has been suggested to proceed *via* a highly stabilised *N*-heterocyclic carbon structure, which would, in turn, generate 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. Our previous work has already offered evidence for the involvement of a carbene in the initiation mechanism [21], but to date little research has been conducted into the structure of the network formed. Consequently, in this present paper, we present data to correlate the thermal reactivity and dynamic mechanical behaviour with the nature of the thermoset network for epoxy resins initiated with a commonly used ionic liquid.

EXPERIMENTAL

Materials.

1-Ethyl-3-methylimidazolium acetate and the diglycidyl ether of bisphenol A (DGEBA, Baxxores™ ER 2200, $\rho = 1.82$ g/mole) were supplied by BASF. The materials were characterised using ^1H nuclear magnetic resonance (NMR) spectroscopy and used without further purification. The 1-ethyl-3-methylimidazolium acetate (IL) and DGEBA were combined in a variety of compositions [IL g/

epoxy resin g] [1 g/20 g] (5 wt %), [3 g/20 g] (15 wt%), [5 g/20 g] (25 wt %), [7 g/20 g] (35 wt%), and [9 g/20 g] (45 wt%) using hand blending or mechanical mixing depending on the moulding method or analysis technique used (see below, Instrumentation). The blends were fully cured using the following schedule: heat to 40 °C (isothermal, 30 minutes) + heat to 60 °C (isothermal, 30 minutes) + heat to 80 °C (isothermal, 30 minutes) + heat to 100 °C (isothermal, 30 minutes) + heat to 120 °C (isothermal, 30 minutes) + heat to 140 °C (isothermal, 30 minutes) + heat to 160 °C (isothermal, 30 minutes). After each isothermal stage, the temperature was increased quickly to the next incremental temperature before another isothermal dwell. DMTA samples were also exposed to shorter variations of this cycle *e.g.* 40 °C (isothermal, 30 minutes) + heat to 60 °C (isothermal, 30 minutes) + heat to 80 °C (isothermal, 30 minutes).

Instrumentation.

Dynamic mechanical thermal analysis (DMTA) data were acquired with a TA Instruments DMA Q800 using a single cantilever clamp requiring sample dimensions of 17.5 mm (L) and up to 15 mm (W) and 5 mm (T). The instrument was programmed to perform a temperature ramp from ambient temperature to 230 °C at 5 K/min at a constant strain of 0.1% and a single frequency of 1 Hz. The tan delta sensitivity and the modulus precision are reported to be 0.0001 and $\pm 1\%$ respectively according to the instrument specification and the data were processed using Universal Analysis 2000 from TA Instruments.

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 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 glass scintillation vials and mixed by hand. The samples were immediately analysed after mixing and the remaining mixture placed in the freezer.

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.

Gelation measurements were measured using a GELNORM®-RVN Topfzeitmessgeräts instrument operating according to DIN 16945 [22], 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. The 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.

RESULTS AND DISCUSSION

Investigating the influence of the cure temperature on network formation.

The DMTA data for the cured samples containing DGEBA (20 g) and ionic liquid [1 g/20 g] are shown as a function of cure schedule in Fig. 1, wherein the loss modulus (Figure 1, top) response displays at least two thermal transitions. The highest storage modulus value is seen to occur in the sample that 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 that had been exposed to 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 similar temperatures. This is indicative of the network containing different structural domains giving rise to different transitions. The similarity in the curves exposed to the higher cure temperatures suggests that the network growth is very similar and does not change markedly during the dwell period at 160 °C.

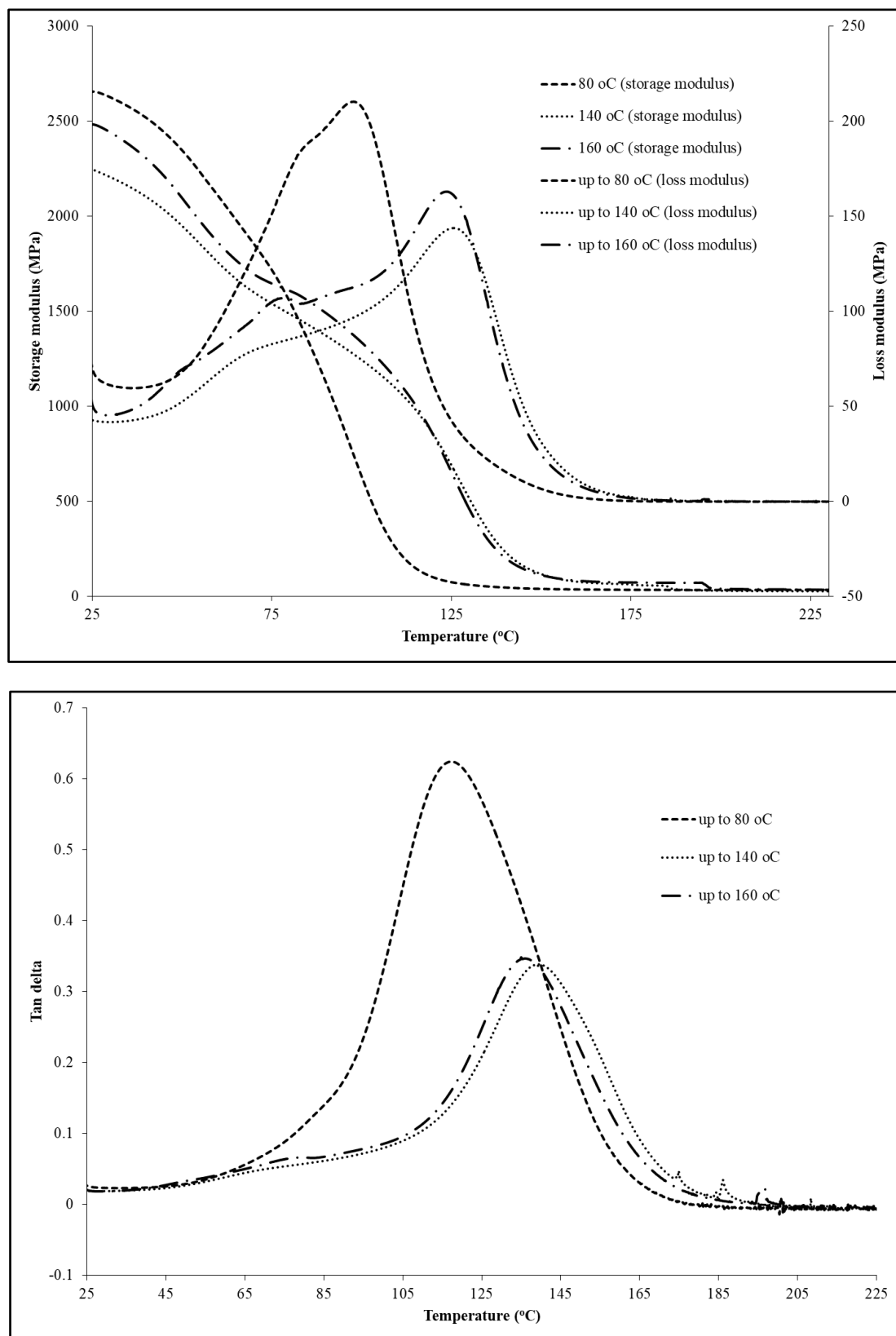


Figure 1. DMTA data for formulations comprising DGEBA (20 g) and 1-ethyl-3-methylimidazolium acetate (1 g) as a function of cure schedule

In contrast, following exposure to the much shorter/lower temperature cure schedule (culminating in a temperature of 80 °C) the partially cured sample does not exhibit a peak at this temperature, despite reaching 230 °C within the instrument, during the analysis. This 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 (Fig. 1, bottom), reveal that the sample exposed to a highest temperature of 80 °C exhibits a considerably higher damping ability than the other samples, coupled with 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. A DSC scan revealed that this sample still showed an exothermic peak at approximately 150 °C, whereas the samples which had been exposed to the higher temperatures (140 °C and 160 °C respectively) did not exhibit an exothermic peak during the first heating cycle (Fig. 2). In our previous publication, using the same DSC experimental conditions, we reported a total enthalpy for a freshly mixed sample of 495.6 J/g (90.2 kJ/mol. epoxy) for the fully cured sample, indicating that the 80 °C sample was 95% cured.

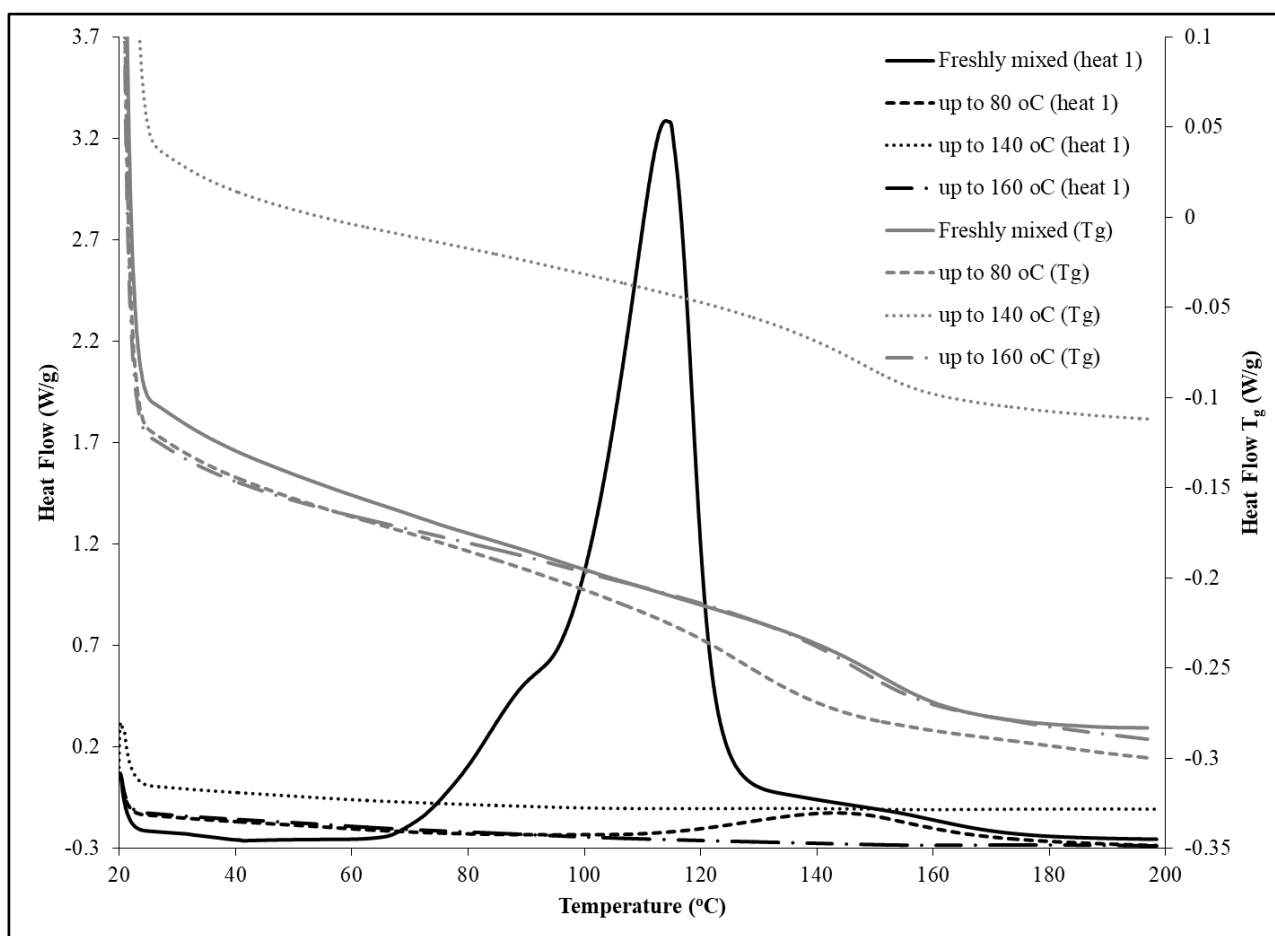


Figure 2: Dynamic DSC data (first heat and rescan) for formulations comprising DGEBA (20 g) and 1-ethyl-3-methylimidazolium acetate (1 g) as a function of cure schedule

Peak fitting analysis, using Grams software (produced by Thermo Scientific), was carried out on the DSC trace for the freshly mixed sample with the results from this analysis shown in Fig. 3, from which it can be seen that the four fitted Gaussian peaks (occurring simultaneously and not discrete reactions) fit the original trace very well. Peak 4, which accounts for the high temperature reaction, is shown to have a T_{\max} value of approximately 135 °C which is lower than the T_{\max} value for the sample which has been cured to a maximum of 80 °C (Fig. 2). The general shapes of the fitted peak and the thermogram are very similar and suggest that the thermal event observed for the sample exposed to a maximum of 80 °C is characteristic of the same process which occurs at approximately 150 °C in a dynamic DSC scan. We have previously attributed this process, on the basis of residual gas analysis [21], to the dealkylation reaction. reaction, and in the same publication examined the thermal stability of not only this ionic liquid (1-ethyl-3-methylimidazolium acetate), but others based on 1-ethyl-3-methylimidazolium diethyl phosphate, 1-ethyl-3-methylimidazolium dicyanamide, and 1-ethyl-3-methylimidazolium thiocyanate. Of these ionic liquids, 1-ethyl-3-methylimidazolium acetate lost mass at the lowest temperature, in both air and nitrogen. Furthermore, a significant mass loss (*ca.* 20 wt. %) was observed at 130 °C in air, which was higher than for the other compounds at the same temperature in air, which exhibited mass losses of 17 % (diethyl phosphate), 14 % (dicyanamide) and 11 % (thiocyanate) respectively.

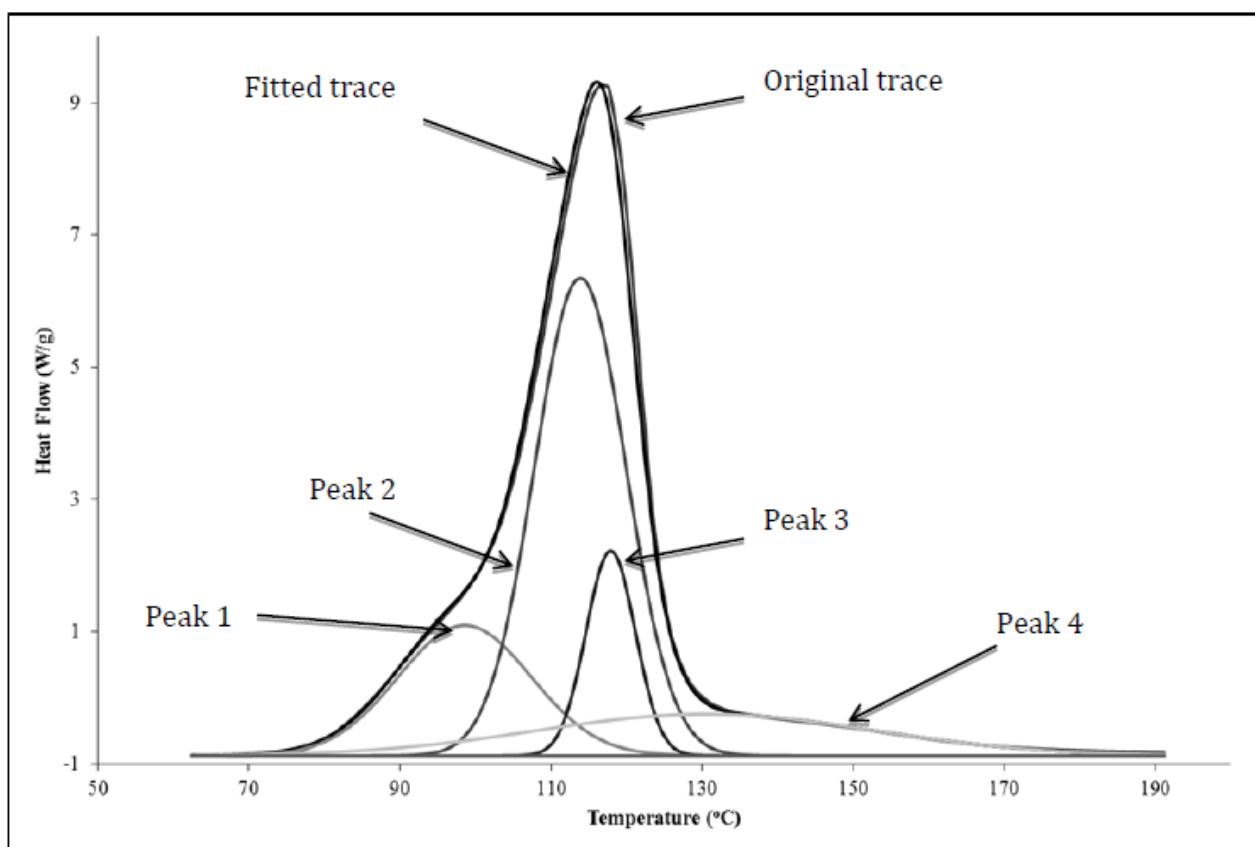


Figure 3. Peak fitting analysis of dynamic DSC data (first heat) for a freshly mixed formulation

comprising DGEBA (5 g) and 1-ethyl-3-methylimidazolium acetate (0.25 g)

A sample, which was heated to 50 °C and subsequently rescanned (Fig. 4), revealed a peak which no longer included a shoulder yet, when compared with the dynamic scan, suggested that the reaction responsible for the main peak had clearly started before the first reaction had been completed. This is also supported by the peak-fitting model (Fig. 3), which suggests that peak 2 occurs at approximately the T_{\max} value of Peak 1 (95 °C).

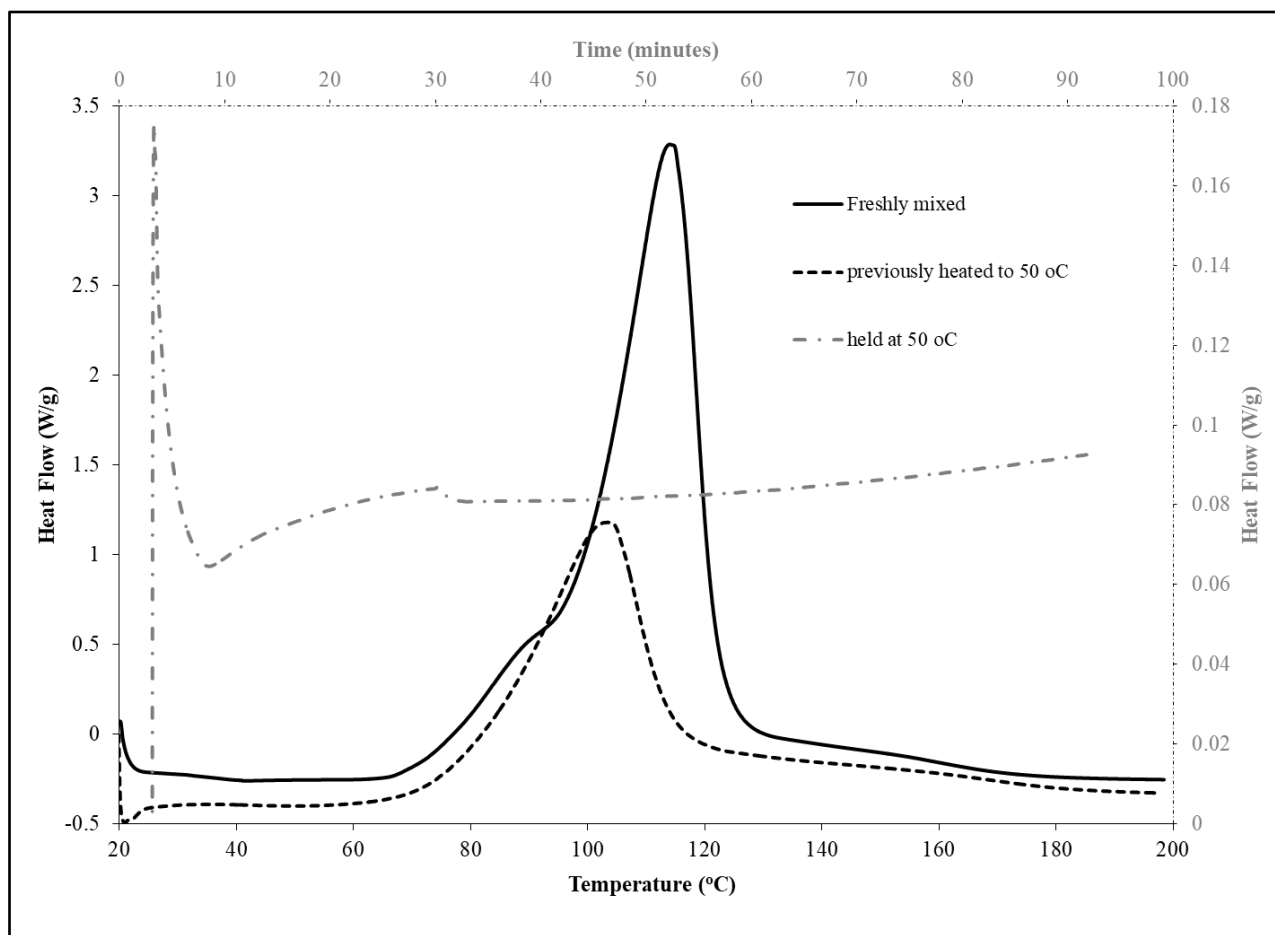


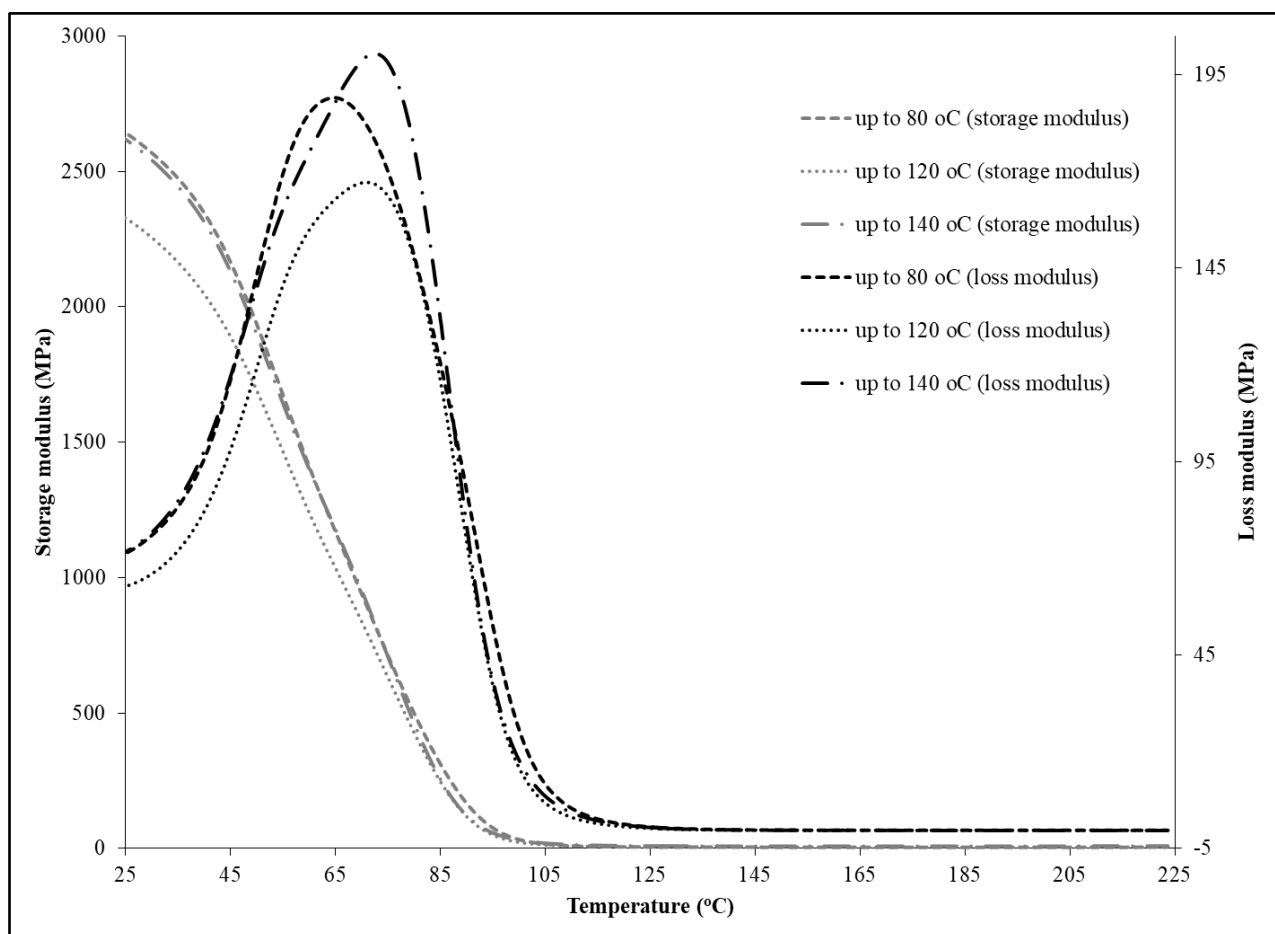
Figure 4: DSC data for samples of DGEBA (5 g) and 1-ethyl-3-methylimidazolium acetate (0.25 g): freshly mixed, previously heated to 50 °C and held isothermally at 50 °C

The observed differences in the storage and loss moduli profiles as a function of cure schedule imply that the high temperature peak observed for the sample cured to a maximum of 80 °C (Fig. 2) has a significant impact on the level of crosslinking observed. This is also supported by the considerably higher damping ability of the sample, which has been cured at a lower temperature (Fig. 1, bottom). This suggests that the dealkylation mechanism involving the acetate anion contributes to a more highly crosslinked system, as evidenced by the increase in glass transition temperature, yet results in

a change in the network properties which can be seen by the lower storage modulus revealed.

Investigating the influence of ionic liquid concentration on network formation.

Samples containing DGEBA (20 g) and a higher loading of 1-ethyl-3-methylimidazolium acetate [3/20 g] were prepared in a similar fashion, cured according to the same schedule, and tested using DMTA (Fig. 5). In contrast with the data obtained using the lower concentration of ionic liquid, the differences between the samples, which have been held at different temperatures for different time periods, are far less marked. For instance, DGEBA samples containing [3 g/20 g] (15 wt %) of 1-ethyl-3-methylimidazolium acetate display a single peak in the loss modulus data, whereas two peaks were observed when [1 g/20 g] (5 wt %) was employed (Fig. 1).



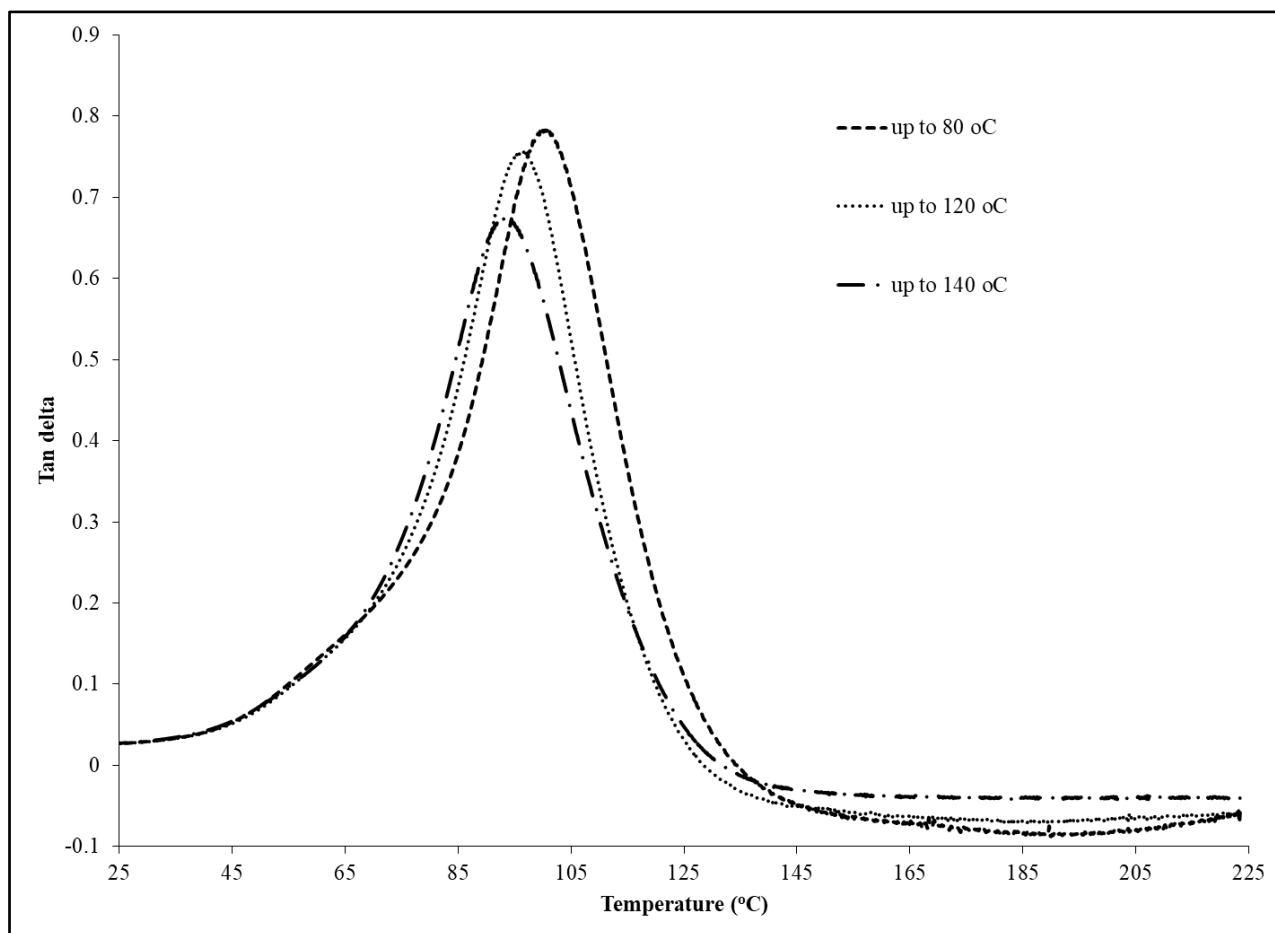
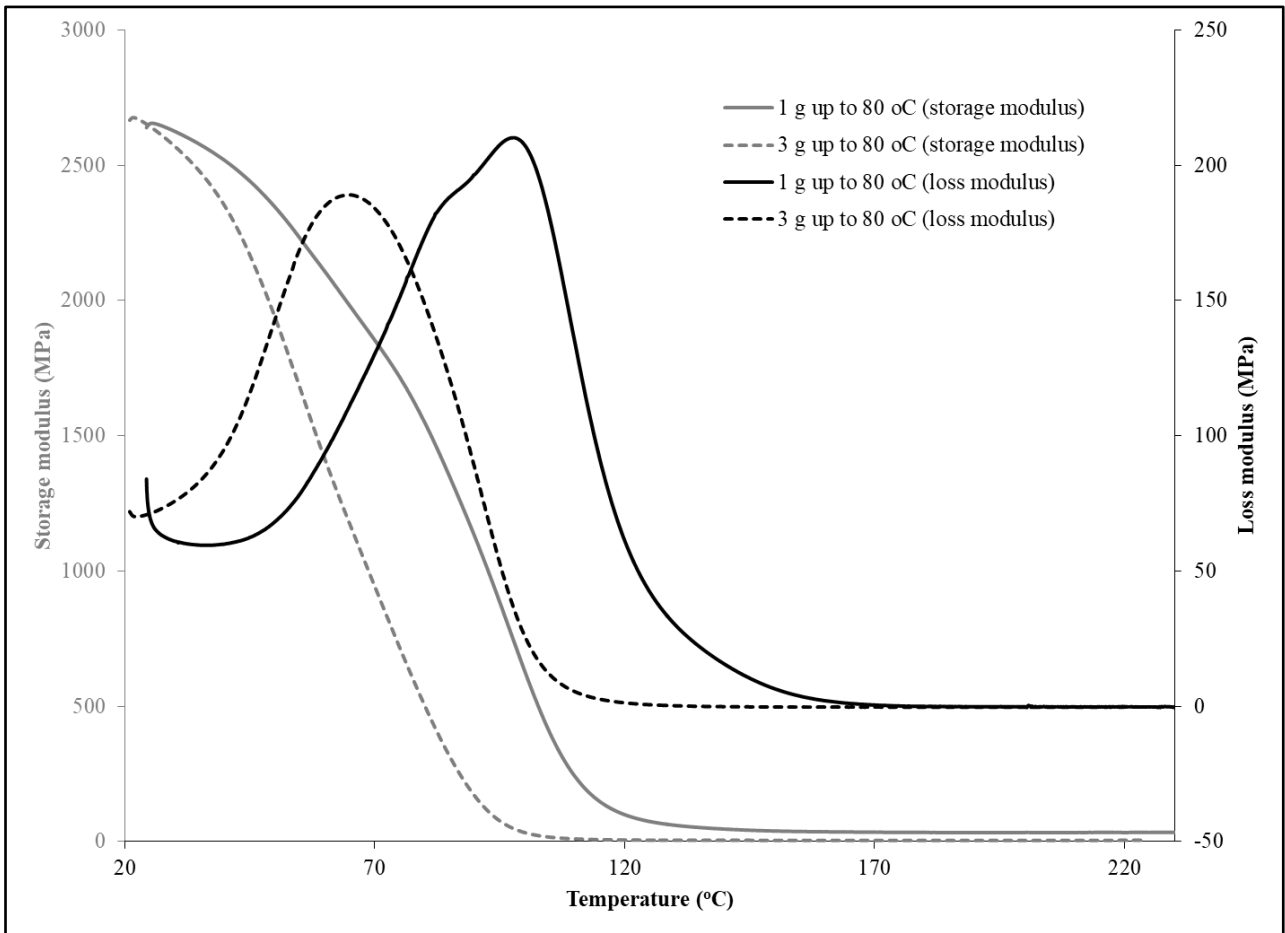


Figure 5. DMTA data for formulations comprising DGEBA (20 g) and 1-ethyl-3-methylimidazolium acetate (3 g) as a function of cure schedule

Comparison of the tan delta values (Fig. 6, bottom) shows that the maximum values occur at higher temperatures when a lower amount of ionic liquid is used, regardless of cure temperature. In contrast if the cure temperatures are compared, it is seen that the DGEBA blend containing 1-ethyl-3-methylimidazolium acetate [1 g/20 g] (5 wt%) yields a higher glass transition value when cured to a final temperature of 140 °C than at 80 °C, whereas the DGEBA blend containing 1-ethyl-3-methylimidazolium acetate [3 g/20 g] (15 wt%) yields a higher glass transition temperature at 80 °C than 140 °C. Samples with a higher amount of ionic liquid exhibit a higher damping ability which is likely to be due to the lower number of crosslinks formed as a consequence of the higher number of initiating species formed. While the temperatures at which the tan delta peak is observed are seen to decrease slightly as the samples progress through the curing schedule, the damping ability exhibited remains broadly the same for all samples, which is consistent with the idea that the network does not change appreciably in spite of the longer reaction time. Hamerton *et al.* reported a similar finding for DGEBA and tetraglycidylaminodiphenyl methane when initiated with 1-imidazole and a series of related coordination complexes with imidazole ligands [23]. Namely, that the nature of the network growth (whether linear growth followed by crosslinking or nucleation growth) is established very quickly at low degrees of conversion and persists regardless of the final cure temperature.



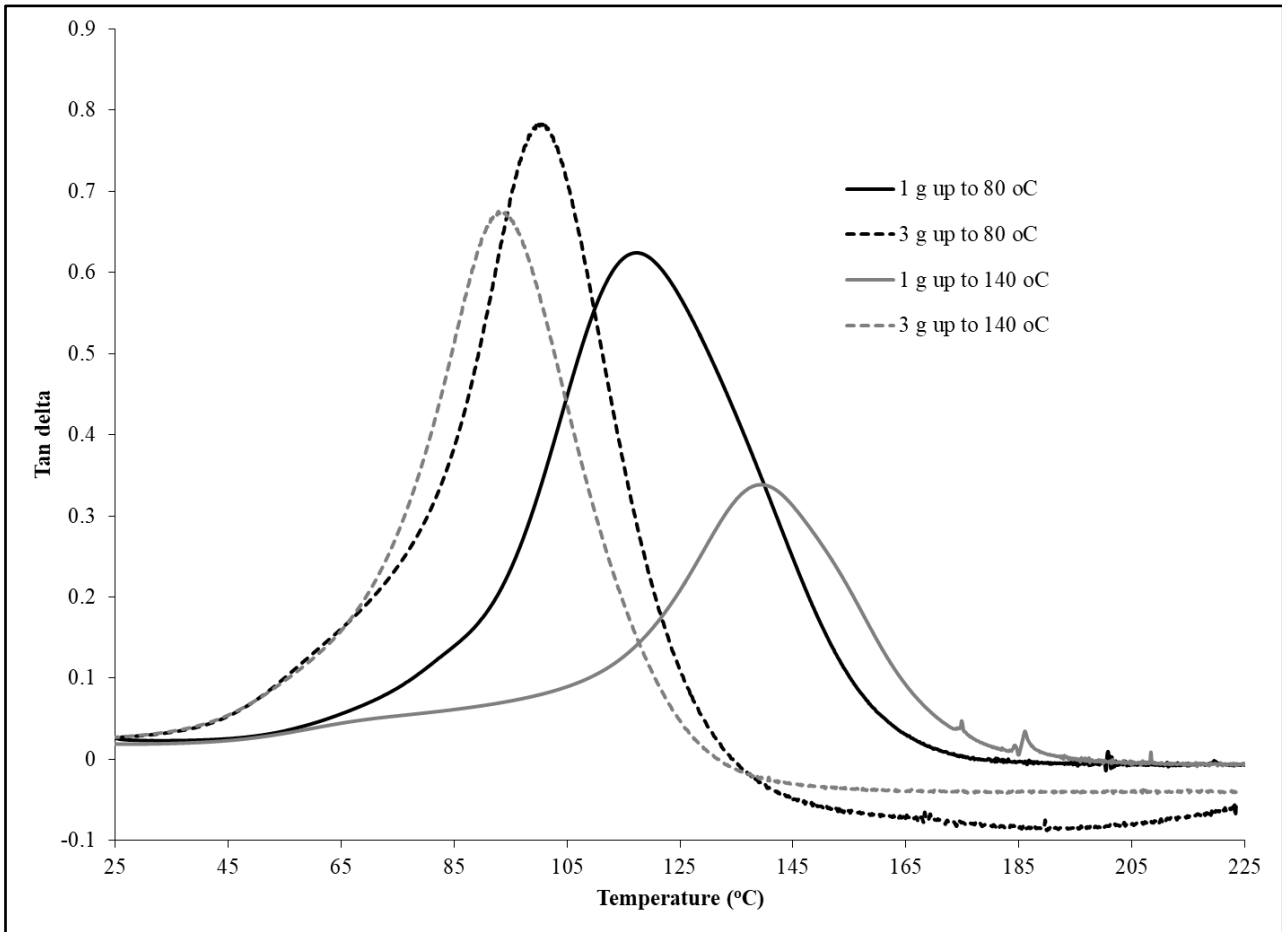


Figure 6. Comparison of DMTA data for formulations comprising DGEBA (20 g) and 1-ethyl-3-methylimidazolium acetate as a function of composition and cure schedule

The determination of the network crosslink density (ν , mol. dm⁻³) is hard to ascertain in an insoluble thermoset polymer. The semi-empirical relationship shown below (equation 1) is more correctly applied to lightly crosslinked elastomers, for which it was originally developed [24], but it has been successfully applied to the examination of polybenzoxazines [25].

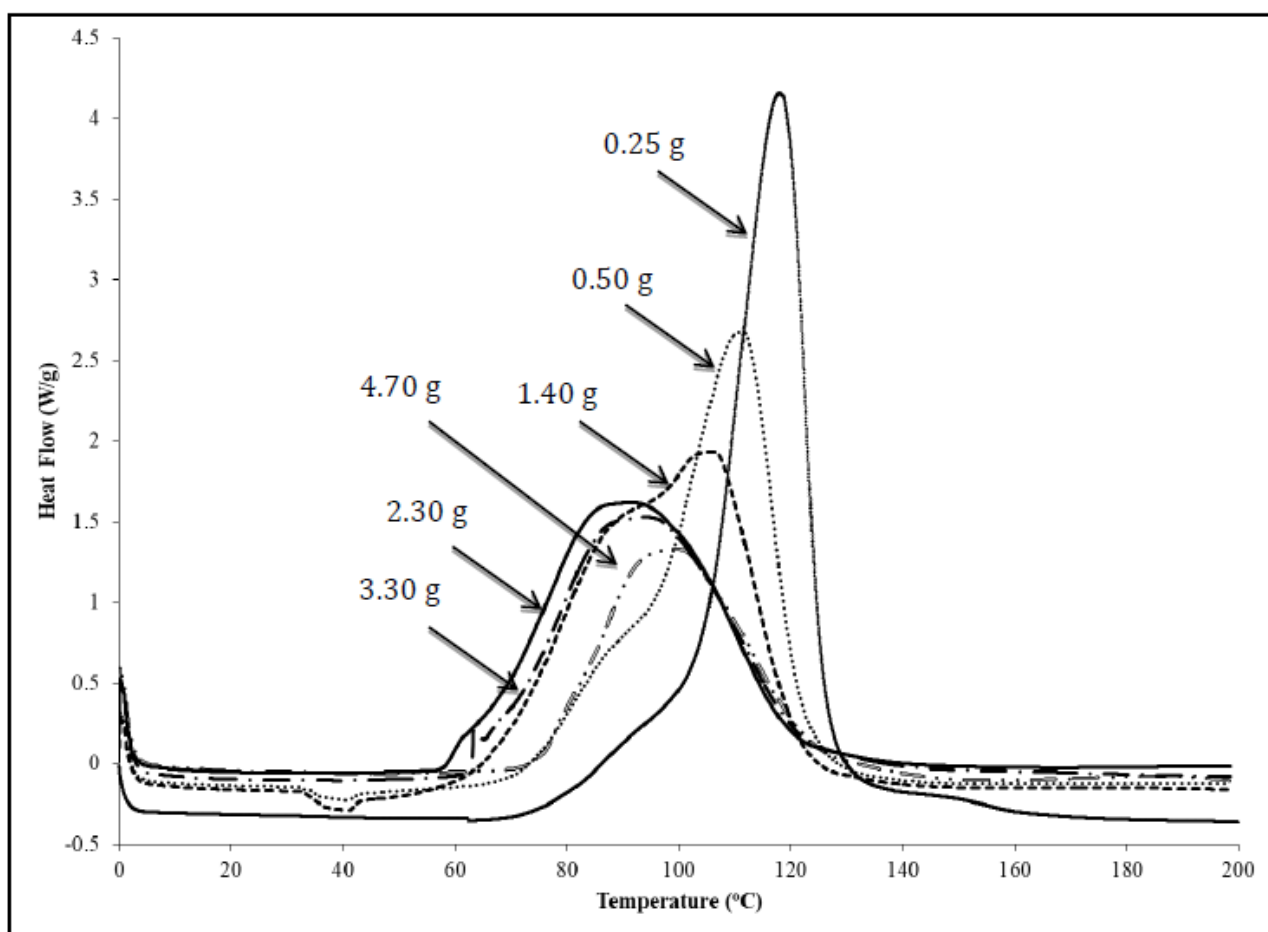
$$\nu = \frac{G_e}{RT_e}$$

...(1)

where G_e = storage modulus (after the sample has reached a plateau) in MPa, $T_e = T_g + 50$ °C (taken from the loss modulus data), and R = universal gas constant (8.314 J mol⁻¹K⁻¹).

While the absolute figures for ν are unlikely to be correct, the trends calculated for a self-consistent series of materials may be informative. In this manner, values for the DGEBA samples containing 1-ethyl-3-methylimidazolium acetate [1 g/20 g] and [3 g/20 g] are determined to be 9.5×10^{-3} mol. dm⁻³ and 1.2×10^{-3} mol. dm⁻³ respectively (cured to 80 °C), and 2.0×10^{-2} mol. dm⁻³ and 2.4×10^{-3} mol. dm⁻³ respectively (cured to 140 °C). These observations correlate well with the DSC data shown

in Fig. 7, which indicate that an increase in the amount of initiator in the blend results in the first peak becoming dominant and the glass transition temperature decreasing (Fig. 7, bottom). The fact that the moduli profiles remain broadly similar (Fig. 5) suggests that network advancement, in terms of formation of crosslinks, does not advance appreciably in spite of the increasing temperature and reaction time. This observation is in agreement with the work of Palmese *et al.*, who reported that, for a series of samples containing various amounts of 1-ethyl-3-methylimidazolium dicyanamide, the observed decrease in the storage modulus and the peak in the loss modulus data occurred at lower temperatures as the amount of ionic liquid increased [18]. This was attributed to a significant increase in the molecular weight between crosslinks as a result of a higher number of initiating species being formed at the expense of ether linkages with the increase in ionic liquid concentration. The team attributed the presence of a double loss modulus peak to competing reactions occurring in the system: the condensation or adduct formation of epoxy groups with 1-ethyl-3-methylimidazolium dicyanamide and the etherification of the hydroxyl groups.



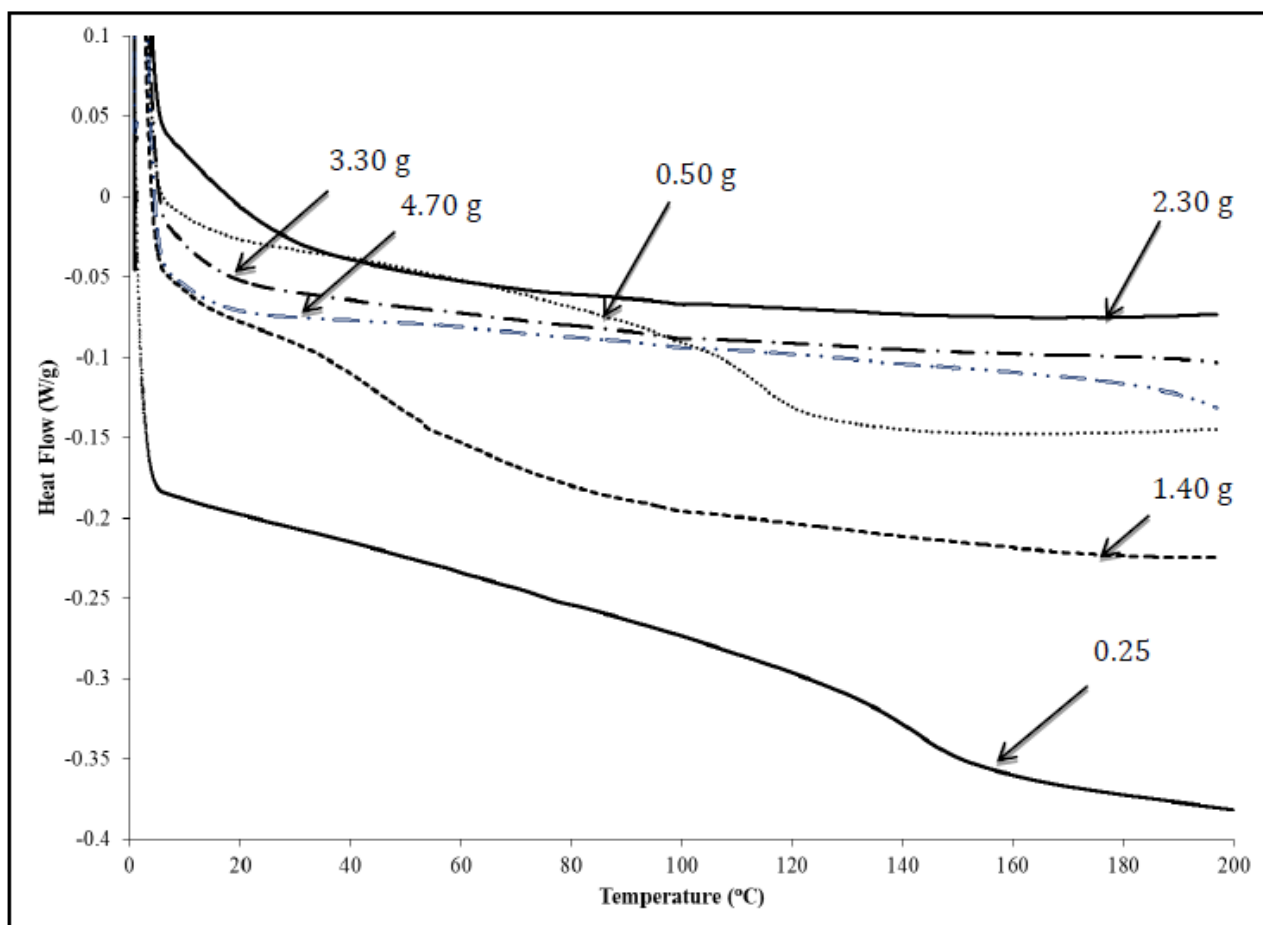


Figure 7. Dynamic DSC data (first heat, top; rescan, bottom) for freshly mixed formulations comprising DGEBA (5 g) and 1-ethyl-3-methylimidazolium acetate as a function of composition

In parallel with the DMTA study, DGEBA samples (20 g) containing different amounts of 1-ethyl-3-methylimidazolium acetate (1-7 g/20 g, 5-30 wt %) were blended in a speed mixer at 2500 rpm for two consecutive periods of two minutes. The samples were subsequently analysed using oscillatory rheology (Table 1).

Table 1 Dynamic oscillatory rheology data for freshly mixed formulations comprising DGEBA (20 g) and 1-ethyl-3-methylimidazolium acetate as a function of composition

| Property | 1-ethyl-3-methylimidazolium acetate, g (wt %) | | | | |
|--------------------------|-----------------------------------------------|-----------|-----------|-----------|-----------|
| | 1/20 (5) | 3/20 (15) | 5/20 (25) | 6/20 (30) | 7/20 (35) |
| Initial viscosity (Pa.s) | 8.47 | 7.14 | 5.05 | 3.46 | 3.46 |
| Gel point (°C) | 103 | 101 | 103 | 112 | 151 |

| | | | | | |
|-----------------------|-----|-----|---|---|---|
| Vitrification point 1 | 110 | 105 | - | - | - |
| Vitrification point 2 | - | 130 | - | - | - |

- not determined

The formulation containing the lowest amount of initiator ([1 g/20 g], 5 wt %) yields a gel point temperature of 103 °C and a single vitrification point temperature of 110 °C. A double peak is observed in the loss modulus data when 3 g of initiator is used (Fig. 8), which is indicative of the sample undergoing some rearrangement at a higher temperature. The second peak of the loss modulus is accompanied by a decrease in the storage modulus. This is supported by the DSC data (Fig. 7, top), which confirm that when the amount of ionic liquid is increased the low temperature shoulder of the exothermic peak increases at the expense of the main peak until it becomes the dominant reaction. This suggests that the double peak in the loss modulus, observed with the [3 g/20 g] sample, may occur as a result of the two reactions effectively reaching parity before the lower temperature reaction becomes dominant. When the initial amount of initiator is increased five-fold (to [5 g/20 g], 25 wt %), the gel point and the vitrification point can no longer be isolated and, after this point, a marked decrease in the loss modulus is observed; a very similar phenomenon is observed when 6 g of the ionic liquid is used to initiate the DGEBA. The correlation between both the DMTA data and DSC data which suggest that the number of initiating species formed increases at the expense of the number of ether linkages, ultimately leading to fewer crosslinks as the amount of ionic liquid is increased.

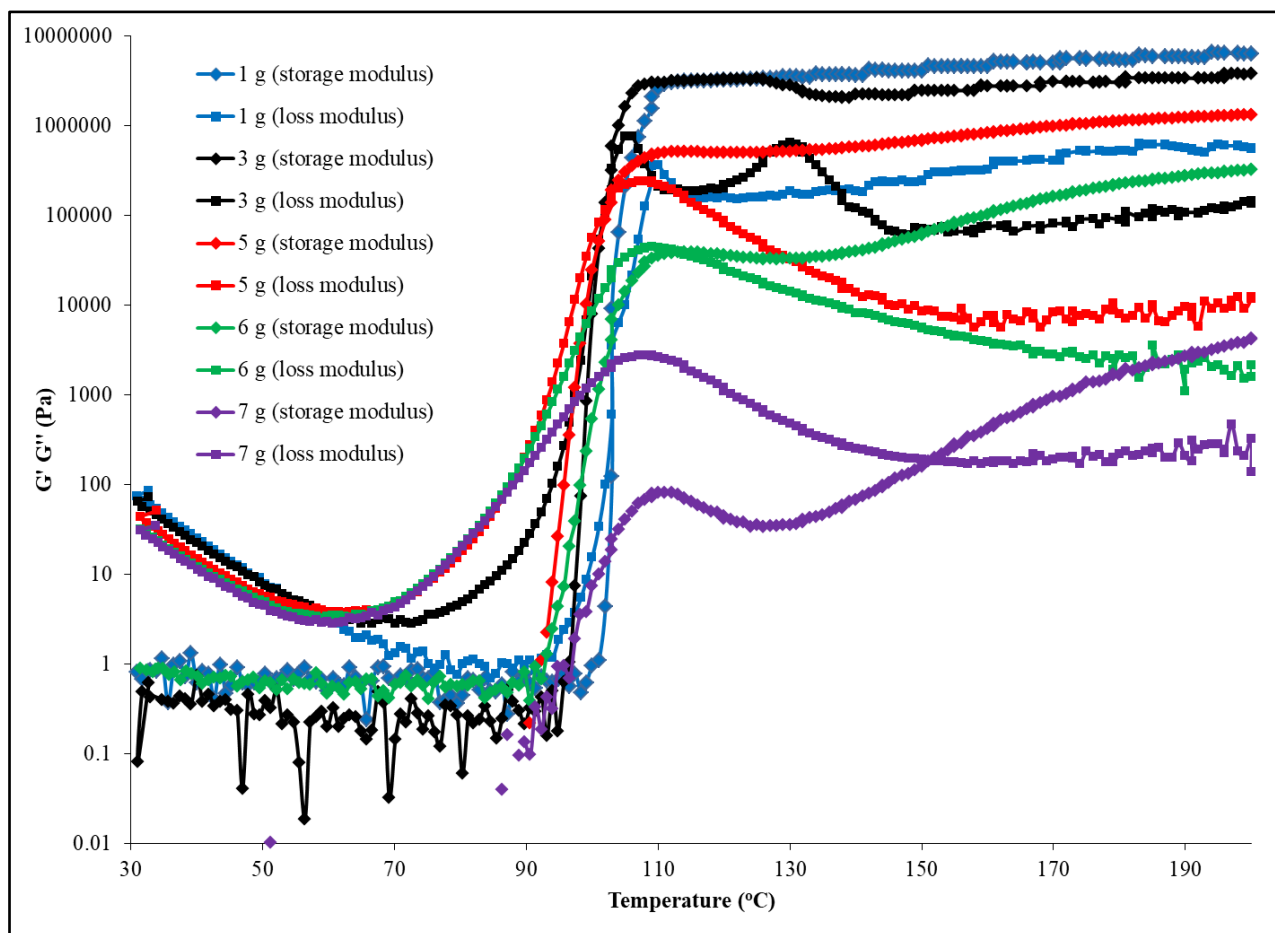


Figure 8. Dynamic oscillatory rheology data for freshly mixed formulations comprising DGEBA (20 g) and 1-ethyl-3-methylimidazolium acetate as a function of composition

Finally, when the highest loading of 1-ethyl-3-methylimidazolium acetate ([7 g/20 g], 35 wt %) is combined with DGEBA, a significantly different rheological profile is observed: the storage modulus and loss modulus values increase, but the crossover point (and hence gelation) does not occur until significantly higher temperatures compared with systems when lower amounts of initiator have been used. The different profiles of the curves suggest that different reaction mechanisms take place as the amount of ionic liquid is increased (Table 2). Measurements of gel time were performed in parallel and the temperature profiles are displayed (Fig. 9) for samples held at 25 °C; all samples exhibit a T_{\max} after approximately 30 - 40 minutes of reaction time and this peak coincides with an observed colour change.

Table 2 Gelation behaviour for formulations comprising DGEBA (20 g) and 1-ethyl-3-methylimidazolium acetate as a function of cure temperature and blend composition.

| Temperature (°C) | Amount, g (wt %) | Gel time (min) | T_{\max} (°C) | Time to T_{\max} (min) |
|------------------|------------------|----------------|-----------------|--------------------------|
|------------------|------------------|----------------|-----------------|--------------------------|

| | | | | |
|----|-----------|-----|-------|----|
| 25 | 3/20 (15) | 161 | 27 | 32 |
| | 5/20 (25) | 139 | 28 | 34 |
| | 7/20 (35) | 116 | 28 | 40 |
| | 9/20 (45) | 135 | 29 | 42 |
| 50 | 1/20 (5) | 94 | 54 | 95 |
| | 3/20 (15) | 5 | >227* | 5 |
| 80 | 1/20 (5) | 4 | >275 | 5 |

* smoke observed therefore measurement stopped

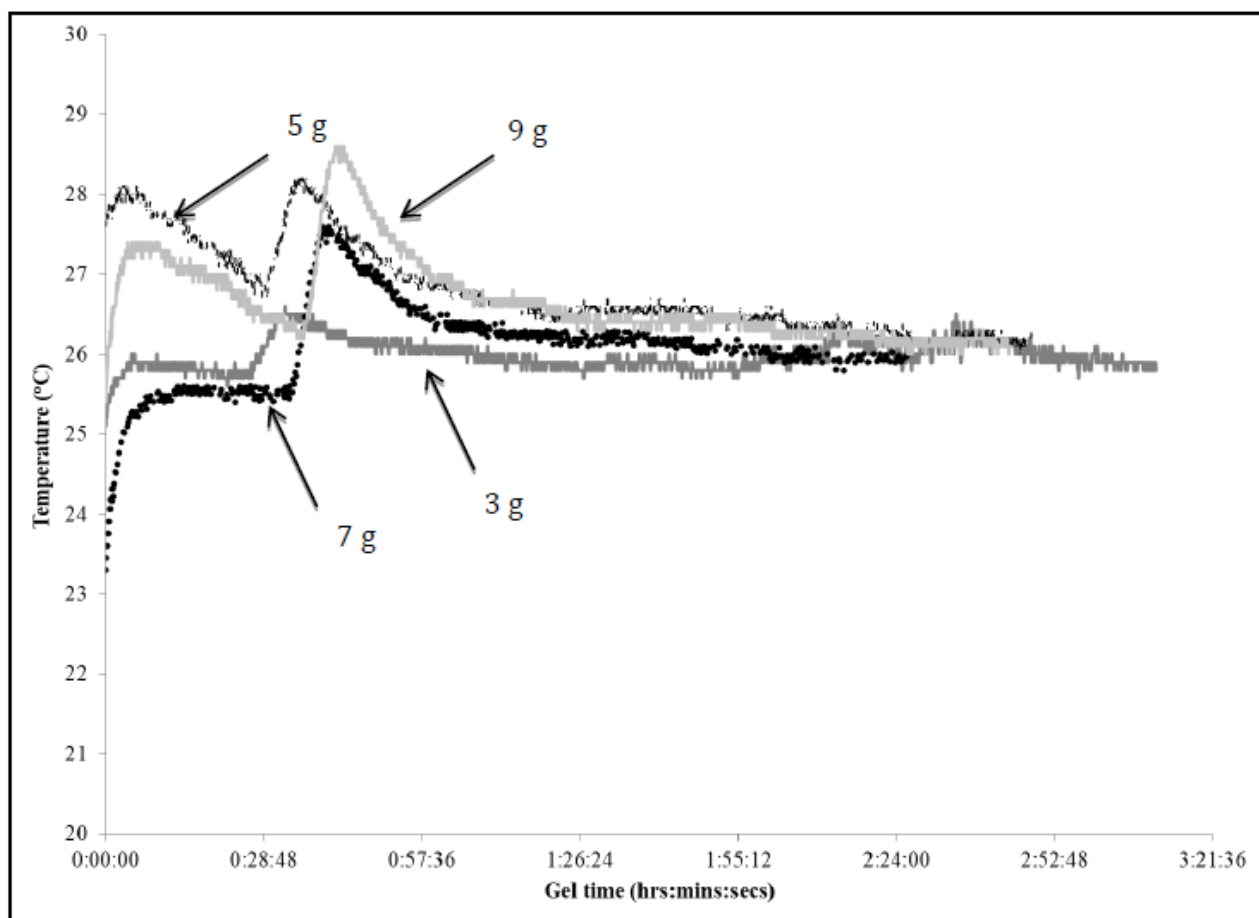


Figure 9: Thermal profile resulting from gel time measurements at 25 °C for formulations comprising DGEBA (20 g) and 1-ethyl-3-methylimidazolium acetate as a function of composition

The gel time initially decreases as the amount of initiator is increased, but increases when [9 g/20 g] (45 wt %) is used. This further supports the observation that the increase in the number of initiating

species promotes oligomer formation and reduces the crosslink density of the material, due to the dominance of the lower temperature reaction (oligomer formation or chain extension). Zhao *et al.* [26] reported that where a large amount of the initiator (6610) was added to commercial di-epoxide (CYD-128), it acted as a reactive diluent, resulted in the crosslinking reaction being hindered.

CONCLUSIONS

The nature of the polyetherification reaction, and the resulting thermoset network, is extremely sensitive to the amount of ionic liquid used to initiate the reaction. Thus, the early stage of reaction (and the path that the ensuing network structure adopts) is governed greatly by the initiator concentration. Rheological analysis shows that an increase in the amount of ionic liquid employed results in a higher gel point temperature and, in cases above [3 g/20 g] (15 wt%), the increase in the number of initiating species occurs at the expense of the crosslinking reaction. This phenomenon is also supported by the dynamic mechanical thermal data which show a lower glass transition temperature (indicative of a lower degree of crosslinking) and a single peak in the loss modulus when higher concentrations of initiator are used, implying the formation of an immature network.

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