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DSC studies of the curing mechanisms and kinetics of DGEBA using imidazole curing agents

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Abstract

The curing mechanisms and kinetics of diglycidyl ether of bisphenol A using 1-methylimidazole (1-MI), 2-methylimidazole (2-MI), 2-phenylimidazole (2-PhI) and 1,2-dimethylimidazole (1,2-DMI) as the curing agents were studied using scanning and isothermal differential scanning calorimetry (DSC). Both scanning and isothermal DSC studies indicated that only 1-MI was an effective curing agent, resulting in a high degree of conversion and high T_g, at relatively low concentrations. In the scanning DSC studies, multiple peaks were observed for the 2-MI and 2-PhI curing systems whereas only a single peak was observed for the 1-MI curing system. These peaks were assigned to adduct formation, etherification (via the alkoxide anion) and to the process of imidazole regeneration. In the isothermal DSC studies, two peaks were observed for all curing systems being attributed to adduct formation and etherification. The differences in curing behaviour of the three imidazole curing agents was discussed in terms of steric versus inductive effects caused by the substituent attached to the imidazole ring located at the 2-position, and of differences in their initiation mechanism.

The curing mechanisms and kinetics of the 1-MI curing system was also investigated in the presence of a salt, tetramethylammonium chloride, hydrochloric acid and water, and were discussed in terms of their effects on adduct formation and on the stability of the propagating alkoxide anion. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxy resin; Curing mechanisms; Curing kinetics

1. Introduction

Epoxy resins are widely utilised in a number of industrial applications. Some of the many uses of epoxy resins can be found in the adhesive, coating, electronic and aerospace industries [1], due to the many excellent mechanical and chemical properties, such as high tensile and compressive strengths, good chemical (and solvent) resistance and high heat distortion temperatures. The superior mechanical and chemical properties possessed by epoxy polymers is a result of the curing process, in which a low molecular weight resin is transformed into an infinite molecular weight polymer with a three-dimensional network structure. This curing process can be initiated by using a wide range of curing agents, such as amines (aliphatic and aromatic), anhydrides, isocyanates and amino formaldehyde resins [2].

Although the cure of epoxy resins, with primary and secondary amines, occurs by a step-growth process, tertiary amines such as imidazoles initiate chain-growth polymerisation. In a study of the polymerisation of the mono-functional epoxy resin, phenyl glycidyl ether (PGE), with 2-ethyl-4-methylimidazole (2,4-EMI, which has both a secondary and a tertiary nitrogen), Farkas and Strohm [3] proposed a two-step initiation mechanism whereby the pyrrole-type nitrogen (–NH–) of 2,4-EMI attacks the terminal carbon of the epoxy functional group of PGE to generate the 2,4-EMI:PGE (1:1) adduct. It was proposed [3] that the 1:1 adduct reacted with a second epoxy group to form the 2,4-EMI:2 PGE (1:2) adduct through the pyridine-type nitrogen (–N=). These adducts were assumed [3] to act as the initiators for the polymerisation of PGE by an etherification reaction in which the reactive alkoxide anion is the propagating species.

In another study, Barton and Shepherd [4] proposed an alternate mechanism in which the formation of the 1:1 adduct is generated through the attack on the epoxy functional group of PGE by the more basic pyridine-type nitrogen of 2,4-EMI (as opposed to that suggested by Farkas and Strohm [3], which involved the pyrrole-type nitrogen). In the second step, the newly generated pyridine-type nitrogen attacks another epoxy group to produce the 1:2 adduct. The

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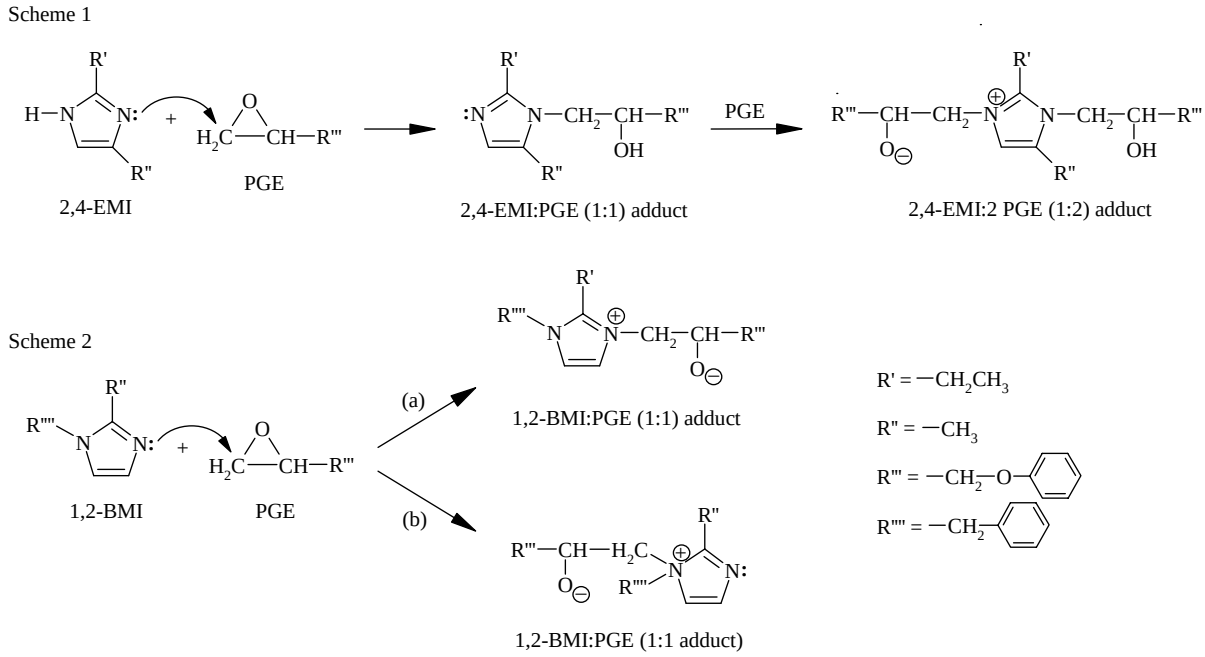


Fig. 1. Proposed mechanisms of adduct formation for the cure of PGE with 2,4-EMI (Scheme 1) and 1,2-BMI (Scheme 2).

mechanism of adduct formation proposed by Barton and Shepherd [4] for the curing reaction between 2,4-EMI and PGE is shown in Fig. 1 (Scheme 1). Evidence for this reaction mechanism was provided through the similar rates of adduct formation observed for both the 1:1 and 1:2 adducts, thus suggesting that both the adduct formation steps involved the same type of amines (i.e. the more basic pyridine-type).

Although the curing mechanism presented in Fig. 1 (Scheme 1) for the cure of epoxy resins with 1,3-unsubstituted imidazoles (i.e. no substitution on the nitrogen atoms) has now been generally accepted, there has been much debate and uncertainty about the curing mechanism of 1-substituted imidazoles. Early studies by Dearlove [5] using 1-substituted imidazoles, such as 1-methylimidazole (1-MI), proposed a similar mechanistic pathway as that

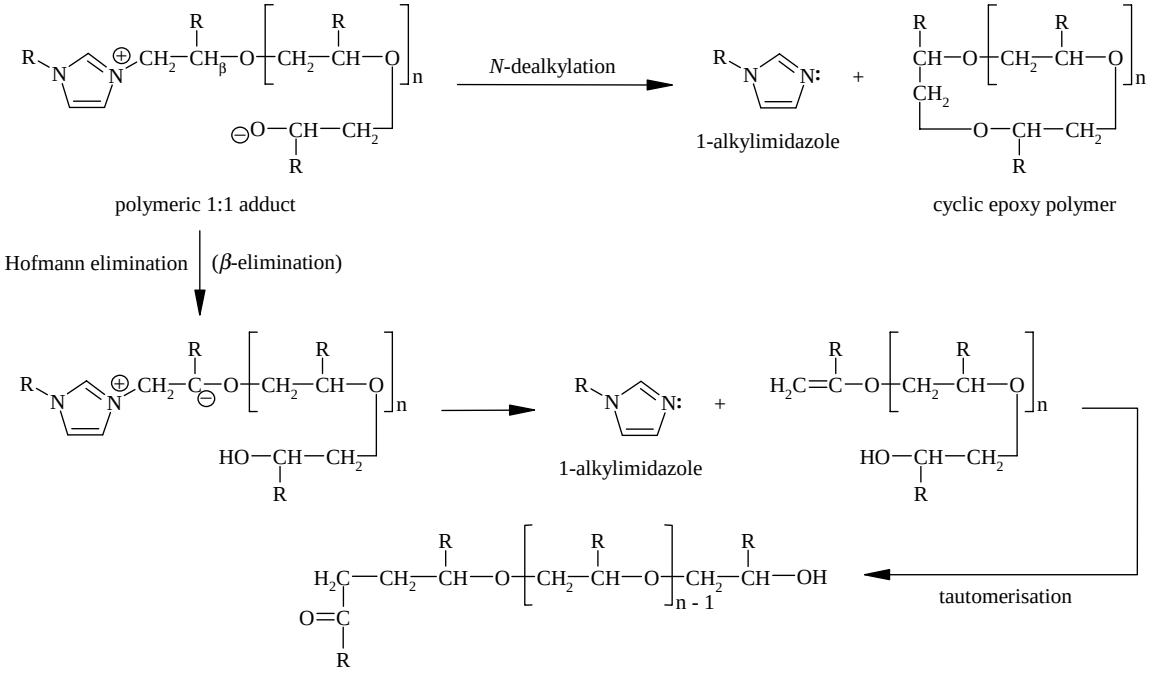
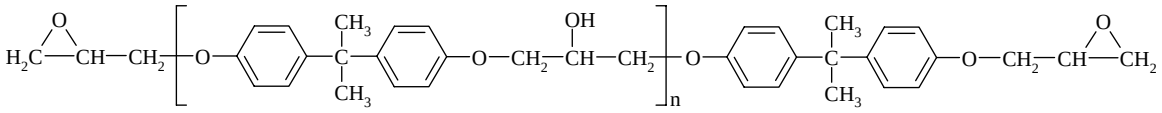
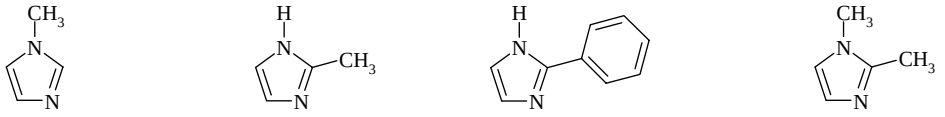


Fig. 2. Proposed mechanisms of imidazole regeneration.



diglycidyl ether of bisphenol A (DGEBA) - n ~ 0.2



1-methylimidazole (1-MI) 2-methylimidazole (2-MI) 2-phenylimidazole (2-PhI) 1,2-dimethylimidazole (1,2-DMI)

Fig. 3. Structures of chemicals used.

shown in Fig. 1 (Scheme 1), with the exception that for 1-substituted imidazoles, the initiating species was the 1:1 adduct (produced via the attack by the pyridine-type nitrogen) and not the 1:2 adduct.

In contrast, Berger and Lohse [6] eluded to the fact that a different reaction mechanism may be involved, noting a small but significant difference in the activation energy (E_a) for the cure of epoxy resins using 2,4-EMI and 1-MI. Further support for an alternate reaction mechanism was provided by Bressers and Goumans [7] who used 1-benzyl-2-methylimidazole (1,2-BMI) as the 1-substituted imidazole. These workers [7] suggested that in addition to the reaction mechanism shown in Fig. 1 (Scheme 2(a)), the lone pair electrons positioned at the 1-substituted nitrogen can also attack the epoxy functional group (Fig. 1, Scheme 2(b)). In an even more extensive study, Ricciardi et al. [8] showed that several reaction products could be obtained from the reaction between PGE and 1-MI. These reaction products thus may lead to several different reaction mechanisms for the cure of epoxy resins using 1-substituted imidazoles as the curing agent.

To further complicate matters, the cure of epoxy resins with imidazoles also exhibits a unique curing behaviour in which the starting imidazole (or the 1:1 adduct) can be regenerated during the curing reaction. Evidence of imidazole regeneration is well documented in the literature [6,8,9] and has now been generally acknowledged. The two main pathways of imidazole regeneration are shown in Fig. 2. The major pathway of imidazole regeneration was suggested [8] to be by *N*-dealkylation of the nitrogen substituents at the 3-position, thus regenerating the 1:1 adduct (or the original imidazole if the curing agent was a 1-substituted imidazole). Another pathway of imidazole regeneration proposed by Ricciardi et al. [8] and Jisova [9] was via a Hofmann reaction involving β-elimination of a hydrogen atom. Evidence for β-elimination was accounted for by the appearance of carbonyl infrared (IR) bands, which from the mechanism presented in Fig. 2, can be obtained by elimination of the β-hydrogen of the adduct or oligomeric epoxy polymer, followed by rearrangement and tautomerisation to produce the carbonyl functional group. The generation of the original imidazole (if 1-substituted) or the 1:1 adduct (if the original imidazole was 1-unsubstituted) by *N*-dealkylation and/or β-elimination may then initiate further polymerisation.

In the present study, the curing behaviour and properties of neat diglycidyl ether of bisphenol A (DGEBA) using 1- and 2-substituted imidazoles were investigated by scanning and isothermal differential scanning calorimetry (DSC) to further elucidate the polymerisation mechanism and the factors controlling the imidazole curing characteristics of DGEBA.

2. Experimental

The structures of the materials used in the present study are shown in Fig. 3. Diglycidyl ether of bisphenol A (DGEBA) (Araldite Algy 9708-1) with an average molecular weight of 381 g/mol was obtained from Ciba-Geigy. 1-Methylimidazole (1-MI, 99%), 2-methylimidazole (2-MI, 99%) and 2-phenylimidazole (2-PhI, 98%) were obtained from Aldrich. Tetramethylammonium chloride (TMAC, 98%) and 1,2-dimethylimidazole (1,2-DMI, 98%) were obtained from Merck. Concentrated hydrochloric acid (HCl) of approximately 10.5 M concentration was obtained from BDH. All chemicals were used as received.

All DSC studies of the curing behaviour were performed with the Perkin–Elmer DSC7 differential scanning calorimeter under a nitrogen atmosphere. High purity indium and zinc were used to calibrate the calorimeter. All samples (≈10 mg) were contained within sealed aluminium DSC pans.

Scanning DSC studies of the cure of DGEBA was performed from 40 to 300°C using 1-MI, 2-MI and 2-PhI as the curing agents at a concentration of 2, 5 and 10 wt%. The heating rate for all scanning runs was 5°C/min. A second scanning run was performed on all cured samples to obtain their glass transition temperature (T_g) by the mid-point method provided by the Perkin–Elmer software.

Isothermal DSC studies of the cure of DGEBA at 80°C was performed with various concentrations of 1-MI (1.1,

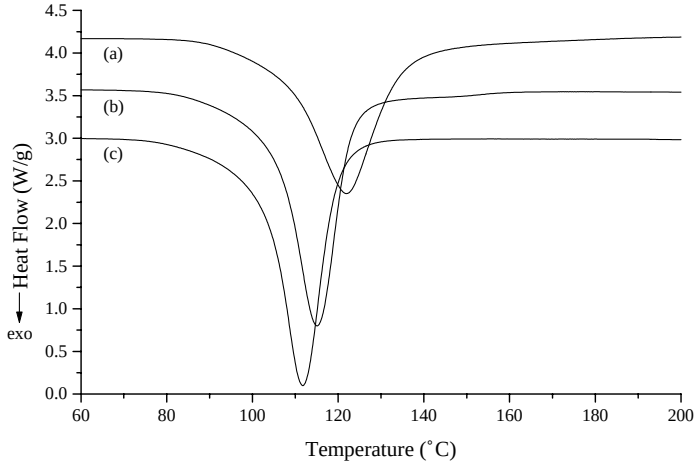


Fig. 4. Scanning DSC of the cure of DGEBA at 5°C/min with 1-MI: (a) 2; (b) 5; and (c) 10 wt%.

3.2, and 4.8 wt%), 2-MI (2.0, 4.6, and 12.5 wt%), 2-PhI (1.3, 2.9, 4.6, and 7.8 wt%) and 1,2-DMI (2 and 5 wt%). A second scanning run at 5°C/min was performed from 40 to 300°C on all isothermally cured samples to obtain full cure. The final T_g was determined by a third scanning run at 5°C/min up to 200°C.

The influence of TMAC (1-MI:TMAC mole ratio = 1:0.93), HCl (1-MI:HCl mole ratio = 1:0.43 and 1:1.05) and deionised water (1-MI:water mole ratio = 1:3.57) on the cure of DGEBA with 2 wt% 1-MI were also performed by scanning DSC. The influence of TMAC (1-MI:TMAC mole ratio = 1:1.14) on the cure of DGEBA with a lower concentration of 1-MI (0.5 wt%) was also performed by scanning DSC.

The degree of thermal cure was followed by monitoring the DSC heat flow as a result of the curing reactions. The heat of reaction (ΔH) was obtained by integrating the DSC exotherm peak area of the heat flow curve. In the scanning DSC studies, ΔH obtained was assumed to represent the total heat of reaction (ΔH_{tot}) due to full cure while in the isothermal DSC studies, a second residual scanning run was performed to achieve full cure. In the latter cases, ΔH_{tot} was obtained by the summation of the heat of reaction generated during the isothermal run (ΔH_{iso}) and the residual heat of reaction generated during the second scanning run (ΔH_{res}).

The activation energy (E_a) was determined by scanning DSC measurements [10] for the cure of DGEBA by 1-MI at a concentration of 2 wt% with heating rates of 2, 5, 10 and 20°C/min.

Table 1
Heat of reaction of DGEBA by scanning cure to 300°C at 5°C/min

Curing agent	Concentration (wt%)	ΔH_{tot} (kJ/mol)	T_g (°C) (after scan)
1-MI	2	97.4	165
1-MI	5	101.8	122
1-MI	10	102.8	85
2-MI	2	26.5	55[a]
2-MI	5	70.4	98[a]
2-MI	10	82.3	118[a]
2-PhI	2	26.0	33[a]
2-PhI	5	80.0	157[a]
2-PhI	10	88.3	135[a]

[a] T_g obtained from these runs were obtained after several scans as no apparent T_g transition was observed after the initial curing scan.

3. Results and discussion

3.1. Scanning DSC studies

Scanning DSC studies of the cure of DGEBA with 1-MI at 2, 5 and 10 wt% are shown in Fig. 4 and the analysis of the data is given in Table 1. Fig. 4 shows that only one exotherm peak was observed at all three concentrations, with the peaks shifting towards lower temperatures due to enhanced reaction rate with increasing imidazole concentration.

Analysis of the heat evolved for the 1-MI curing systems presented in Table 1 indicate that at all three concentrations, complete or near complete cure was obtained with ΔH_{tot} being in the range of about 100 kJ/mol. This value compares very well with values of 99 ± 5 kJ/mol obtained by Vogt [11] for complete chain growth polymerisation of DGEBA using various imidazole curing agents. However, these values differ from that calculated by de Bakker et al. [12] (65 ± 5 kJ/mol) for the etherification side reaction which competes with the condensation reaction of N–H and epoxy groups in the system they studied. As there are no N–H groups in the 1-MI curing system studied here, the values of ΔH_{tot} can be attributed to the etherification reaction. Despite the above differences in ΔH_{tot}, the values obtained in this study for fully cured imidazole/epoxy systems are in agreement with many amine/epoxy condensation systems [13,14], which are generally in the range of 100–118 kJ/mol, as quoted in a review by Rozenberg [15]. The general agreement between the ΔH_{tot} obtained from the

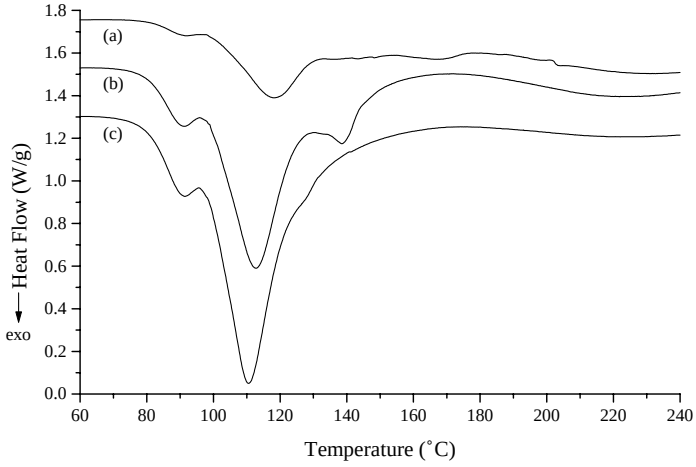


Fig. 5. Scanning DSC of the cure of DGEBA at 5°C/min with 2-MI: (a) 2; (b) 5; and (c) 10 wt%.

cure of epoxy resins using step growth and chain growth curing agents is expected as the heat evolved during the curing reaction involves largely the release of strain energy located within the epoxy functional group.

Scanning DSC studies of the cure of DGEBA with 2-MI and 2-PhI at 2, 5, and 10 wt% are shown in Figs. 5 and 6, respectively. Data analyses of these curing systems are also presented in Table 1. Based on mechanistic studies by Barton and Shepherd [4], the pyrrole-type (N–H) nitrogen in the 2-MI and 2-PhI curing systems does not take part in the formation of the 1:1 or 1:2 adduct, and therefore the values of ΔH_{tot} must again be attributed to the etherification reaction. From the shape of the exotherm shown in Figs. 5 and 6, it is evident that the curing behaviour using 1-unsubstituted imidazole such as 2-MI and 2-PhI are more complex than that of using 1-substituted imidazole such as 1-MI. For the 2-MI and 2-PhI curing systems, multiple exotherm peaks can be observed whereas only one exotherm peak was observed for the 1-MI curing system. It is interesting to note that for the 2-MI and 2-PhI curing systems, a small peak or shoulder was also observed (preceding the dominant exotherm peak which shifts towards lower temperatures with increasing imidazole concentration). Studies by Heise and Martin [16,17] and Vogt [11] working with 1,3-unsubstituted imidazole (2,4-EMI and H-imidazole, respectively), have also observed a lower temperature peak (or shoulder). They attributed this lower temperature peak to the adduct formation steps as shown in Fig. 1 (Scheme 1). Confirmation of this assignment was obtained [16] by noting a gradual increase in the exotherm area of the lower temperature peak (as found in the present work in Figs. 5 and 6) and the simultaneous decrease in that of the main peak on increasing the imidazole concentration (not evident in the present work due to incomplete cure). Vogt [11] arrived at the same conclusion by preparing the 1:1 adduct and noting that its reaction with additional epoxy did not produce the low-temperature “adduct” peak in the DSC exotherm.

For the 2-MI and 2-PhI curing systems shown in Figs. 5 and 6, a third high temperature exotherm peak can also be distinguished, which is particularly noticeable at an

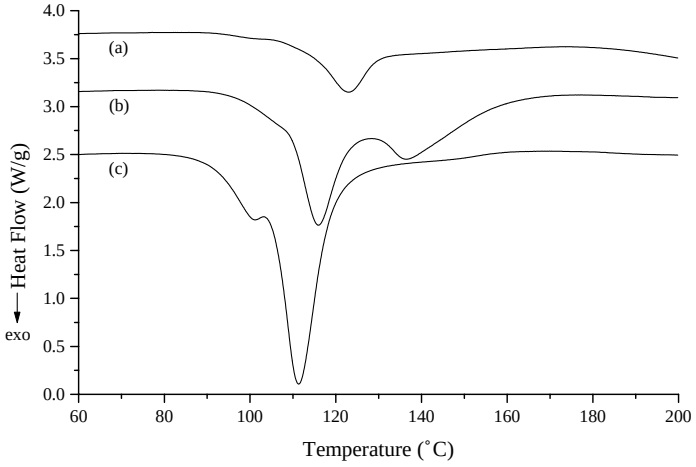


Fig. 6. Scanning DSC of the cure of DGEBA at 5°C/min with 2-PhI: (a) 2; (b) 5; and (c) 10 wt%.

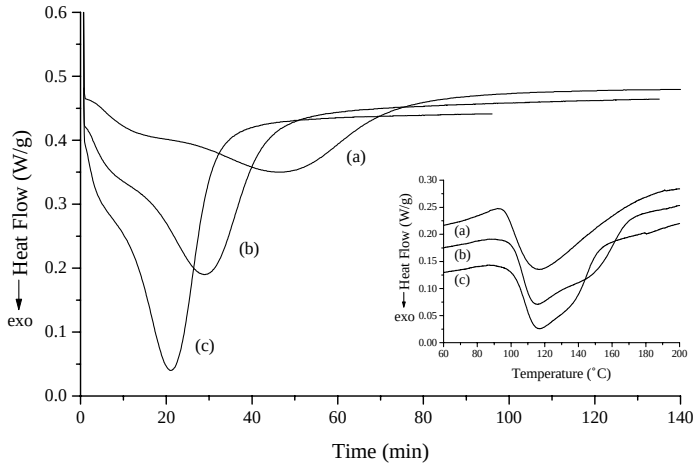


Fig. 7. Isothermal DSC of the cure of DGEBA at 80°C with 1-MI: (a) 1.1; (b) 3.2; and (c) 4.8 wt%. Inset: Scanning DSC of isothermally cured sample at 5°C/min.

imidazole concentration of 5 wt%. Heise and Martin [17] have also observed this behaviour, and have attributed it to epoxy polymerisation via OH-etherification (originating from the 1:2 adduct). Alternatively, the cause of the third peak may also be associated with imidazole regeneration (either by *N*-dealkylation or β-elimination as shown in Fig. 2), which then reinitiates polymerisation. Either of these processes may be accentuated by the lack of complete cure of the epoxy functional groups via the alkoxide anion. Table 1 shows that the 2-MI and 2-PhI curing systems exhibit a relatively low degree of cure compared with the 1-MI curing system. The reason for this poor cure is not clear. The effectiveness of the regenerated imidazole to reinitiate (and sustain) polymerisation will depend on the alkyl substituent as different substituents will exhibit different curing kinetics and behaviour [9]. From Figs. 5 and 6, the magnitude of the third peak seems to pass through a maximum as the concentration of imidazole is raised. This behaviour may be caused by two competing effects. At the lower imidazole concentration, suppression of the third peak may be due to the reduced probability of imidazole regeneration, which is a direct result of a low starting imidazole concentration. At the higher imidazole concentration, the third peak may have been reduced due to the low concentration of epoxy remaining in the system after the second peak (Table 1).

Inspection of the T_gs for the 1-MI curing systems shows that increasing the concentration of 1-MI resulted in a considerable decrease in T_g. It is possible that the significant reduction in T_g observed may be due to the plasticising effect of 1-MI when high concentrations are used. Alternatively, this may be caused by changes in the effective crosslink density. The use of high levels of 1-MI should increase the concentration of initiating species (the 1:1 adduct) and thus reduce the length of each polymerising chain (the kinetic chain length). Since the kinetic chain length resulting from the anionic polymerisation of epoxy resins by imidazole curing agents are generally low [6], a further reduction as the 1-MI concentration is raised could significantly reduce the level of connectivity in the network, lowering the effective crosslink density and thereby resulting in a lower T_g.

In contrast, inspection of the T_gs for the 2-MI curing

Table 2
Heat of reaction of DGEBA by isothermal (80°C) and scanning cure to 300°C at 5°C/min

Curing agent	Concentration (wt%)	ΔH_{iso} (kJ/mol)	ΔH_{res} (kJ/mol)	ΔH_{tot} (kJ/mol)	T_g (°C) (after rescan)
1-MI	1.1	80.1	12.9	93.0	170
1-MI	3.2	97.6	14.8	112.4	133
1-MI	4.8	92.0	11.4	103.4	109
2-MI	2.0	55.8	5.1	60.9	71[a]
2-MI	4.6	70.9	11.0	81.9	159[a]
2-MI	12.5	87.5	9.7	97.2	120
2-PhI	1.3	40.5	30.6	71.1	103[a]
2-PhI	2.9	63.6	20.1	83.7	154
2-PhI	4.6	71.5	13.2	84.7	154
2-PhI	7.8	79.9	14.6	94.5	146
1,2-DMI	2.0	70.3	12.3	82.6	175
1,2-DMI	5.0	72.5	11.8	84.3	145

[a] T_g obtained from these runs were obtained after several scans, no apparent T_g transition was observed after initial curing scan.

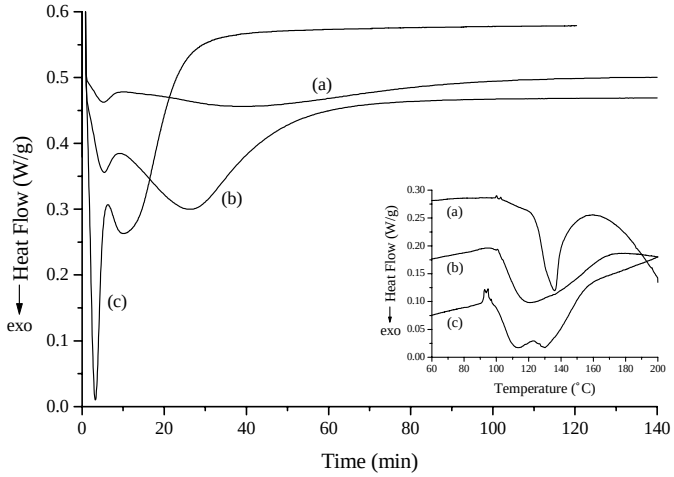


Fig. 8. Isothermal DSC of the cure of DGEBA at 80°C with 2-MI: (a) 2.0; (b) 4.6; and (c) 12.5 wt%. Inset: Scanning DSC of isothermally cured sample at 5°C/min.

system presented in Table 1 shows that increasing the imidazole concentration resulted in a higher T_g which may be explained in terms of a higher degree of cure (as indicated by ΔH_{tot}) which counteracts the plasticisation effect observed for the 1-MI curing system. For the 2-PhI curing system, the T_g was seen to increase and then decrease as the imidazole concentration was raised. The initial increase in T_g may be explained in terms of the substantial increase in the degree of conversion on increasing the imidazole concentration. However, further increases in imidazole concentration resulted in a less significant rise in the degree of cure and a decrease in T_g. The decrease in T_g can once again be explained in terms of the plasticising action of excess imidazole and/or the reduction of the effective cross-link density.

From the results tabulated in Table 1, it can be seen that 1-MI is a more efficient curing agent than 2-MI or 2-PhI as full cure was obtained at low imidazole concentration. In addition, the highest T_g was also obtained with 1-MI as the curing agent and at a low imidazole concentration.

3.2. Isothermal DSC studies

Isothermal DSC studies of the cure of DGEBA at 80°C with 1-MI at various concentrations are shown in Fig. 7 and the analysis of the data is given in Table 2. Fig. 7 shows that two exotherm peaks can now be distinguished whereas only one exotherm peak was observed in the scanning DSC studies. For the 2-MI and 2-PhI curing systems (Figs. 8 and 9, respectively), a similar behaviour was also observed with two exotherm peaks being present. In all cases, the first peak or shoulder can be assigned to the adduct formation steps and the second to the etherification reaction [7]. In all three curing systems, a second scan was performed to achieve "full" thermal cure (inset of Figs. 7–9).

From the results shown in Figs. 7–9, it can be seen that the first peak became more distinct and pronounced for the 2-MI and 2-PhI curing systems as the imidazole concentration is raised, but not for the 1-MI curing system. As all three imidazoles are considered to involve the same pyridine-type nitrogen during the formation of the 1:1 adduct

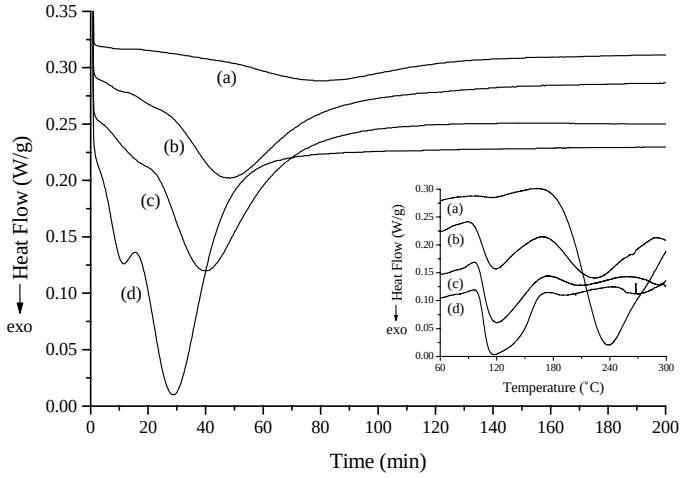


Fig. 9. Isothermal DSC of the cure of DGEBA at 80°C with 2-PhI: (a) 1.3; (b) 2.9; (c) 4.6; and (d) 7.8 wt%. Inset: Scanning DSC of isothermally cured sample at 5°C/min.

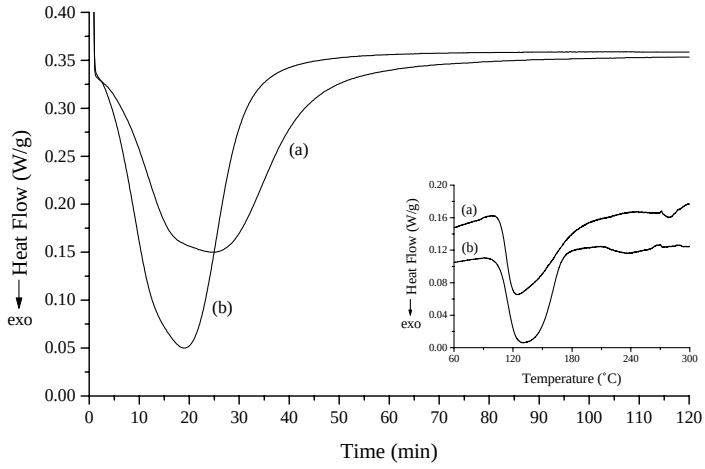


Fig. 10. Isothermal DSC of the cure of DGEBA at 80°C with 1,2-DMI: (a) 2.0; and (b) 5.0 wt%. Inset: Scanning DSC of isothermally cured sample at 5°C/min.

(and for 2-MI and 2-PhI, the 1:2 adduct also), the differences in behaviour must be due to either steric and/or inductive effects caused by the substituent mainly attached at the 2-position. Based on steric considerations, one would expect that the 1-MI curing system would exhibit a more well defined first peak as there is no effective steric barrier (hydrogen substituted at the 2-position), whereas for the 2-MI and 2-PhI curing systems, a much larger methyl and phenyl group is attached at the 2-position, which would have a significant effect on the formation of the 1:1 adduct. As the opposite behaviour was observed, it must be assumed that inductive effects were more dominant over steric effects in determining the curing behaviour. Based on inductive effects, the 2-MI and 2-PhI curing systems are expected to show a well defined first peak as the methyl and phenyl substituent (2-MI and 2-PhI, respectively) located at the 2-position would tend to "push" electrons towards the active nitrogen, thereby enhancing the formation of the 1:1 adduct.

To verify the above rationale, the isothermal cure of a 1,2-disubstituted imidazole, namely 1,2-dimethylimidazole (1,2-DMI), at 2 and 5 wt% was performed and is shown in Fig. 10. Due the inductive effects caused by methyl substitution at the 2-position, the first peak is significantly enhanced, but still not well defined. This behaviour may be characteristic of 1-substituted imidazoles.

Another interesting curing behaviour shown in Figs. 7–10 was that for the 2-MI and 2-PhI curing systems, the rate of adduct formation (first peak) was seen to increase with respect to the rate of etherification (second peak) as the imidazole concentration was raised. In contrast, the 1-MI and 1,2-DMI curing systems exhibited a similar rise in the first and second peaks. The differences in curing behaviour between 1-substituted (1-MI and 1,2-DMI) and 1-unsubstituted (2-MI and 2-PhI) imidazoles can thus be assumed to be related to the differences in the initiation process. From the curing mechanisms shown in Fig. 1, it can be seen that the only difference between 1-substituted and 1-unsubstituted imidazoles is that for the 1-unsubstituted imidazole, the 1:2 adduct is also generated. Therefore, it is reasonable to concluded that the extra reaction step involved in forming the 1:2 adduct is responsible for the enhanced rate of adduct formation, relative to the rate of etherification, as the imidazole is raised.

The results presented in Table 2 show that increasing the imidazole concentration generally increases the degree of isothermal cure, however full cure was not achieved during any of the isothermal runs and as a result the residual heat of reaction (ΔH_{res}) was quite large (particularly for the 2-MI and 2-PhI curing systems at low imidazole concentrations). At the higher imidazole concentration, incomplete cure during the isothermal run was mainly attributed to vitrification (when the T_g equals the curing temperature) where the reaction becomes diffusion controlled [18]. Evidence of vitrification was confirmed by a second, scanning run of the isothermally cured samples (inset of Figs. 7–9). In most cases, a heat capacity step, indicative of a glass transition was observed close to the curing temperature (between 80 and 90°C), and was immediately followed by an exotherm, representing ΔH_{res}. At the lower imidazole concentration, incomplete cure appears to be due to the intrinsic inability of the particular curing system to go to complete reaction, which is in agreement with scanning DSC results where low conversions and low T_gs (<80°C) were obtained for the 2-MI and 2-PhI curing systems at low imidazole concentrations. For most systems, a higher imidazole concentration yielded a higher total heat of reaction (ΔH_{tot}) (equivalent to $\Delta H_{iso} + \Delta H_{res}$), which is in agreement with the scanning DSC results (Table 1). In all cases, ΔH_{tot} obtained for the 1-MI curing system was higher than that obtained for the 2-MI and 2-PhI curing systems, which is also in agreement with the DSC scanning results (Table 1).

Surprisingly, it was observed that ΔH_{iso} and ΔH_{tot} values obtained (Table 2) for the 2-MI and 2-PhI curing systems at low imidazole concentration (2.0 and 1.3 wt%, respectively) was higher than that obtained in the scanning DSC studies (at 2 wt% 2-MI and 2-PhI) shown in Table 1. Intuitively,

Table 3
Heat of reaction of DGEBA with various additives at 2.0 wt% 1-MI by scanning cure to 300°C at 5°C/min

Additive	Mole ratio (1-MI: additive)	ΔH (kJ/mol)	T_g (°C) (after scan)
None	1:0	97.4	165
TMAC	1:0.93	99.6	158
HCl	1:0.43	97.3	141
HCl	1:1.05	96.9	93
Water	1:3.57	98.4	152

one would expect that scanning cure would produce equal or greater extent of reaction than isothermal cure. However, the results presented here suggest that the degree of cure (and therefore, the mechanical and chemical properties) is dependent on the curing conditions employed. Barton et al. [19] have also shown that the curing program is an important parameter in determining both the degree of cure and the final properties of the imidazole cured epoxy. In their isothermal DSC studies, Barton et al. [19] showed that an epoxy which have been cured at a lower temperature exhibited a higher T_g after postcure than those obtained from scanning DSC studies, suggesting that different temperature programs result in different mechanisms of network formation which are due to different extents of inter- and intramolecular reactions. This is supported by the work of Ricciardi et al. [8] and Jisova [9] which shows that when the process of imidazole regeneration occurs, it leads to products (e.g. cyclisation products, Fig. 2) which are not chemically attached to the network. These products not only broaden the molecular weight distribution but can also plasticise the polymer network and depress the T_g. It was proposed above that the process of imidazole regeneration is significant only at high temperatures. This line of reasoning is consistent with the results obtained by Barton et al. [19] in that a lower T_g would be obtained from the scanning studies as the temperatures reached in these runs were higher than those in the isothermal studies, therefore increasing the probability of imidazole regeneration and their resulting plasticising products.

3.3. Activation energy

The activation energy of the cure of DGEBA with 2 wt% 1-MI was determined by the Kissinger [10] method. The value of E_a of 73.3 kJ/mol compares very well with the value of 74.7 kJ/mol obtained by Berger and Lohse [6] using 1-MI as the curing agent for PGE. This comparison, however, should be viewed with caution as the latter value was obtained from isothermal measurements and there may be discrepancies between the values calculated from the two methods. One disadvantage in determining E_a by the scanning methods is that the stages of adduct formation and etherification can not be resolved in such dynamic measurements, and so the E_a obtained represents only an average of the two processes. Heise and Martin [16] have shown that the E_a calculated for adduct formation was consistently lower than that calculated for the etherification reaction.

Table 4
Heat of reaction of DGEBA with TMAC at 0.5 wt% 1-MI by scanning cure to 300°C at 5°C/min

Additive	Mole ratio (1-MI:Additive)	ΔH (kJ/mol)	T_g (°C) (after scan)
None	1:0	34.8	58
TMAC	1:1.14	43.5	74

3.4. Effects of TMAC, HCl, and water

As shown in Fig. 1, the mechanism of polymer growth is believed to be largely due to the etherification reaction involving the propagating alkoxide anion. During the etherification reaction, the quaternary nitrogen cation and alkoxide anion are separated, thus increasing their electrostatic energy and possibly resulting in a propagating species that is less thermodynamically stable unless the charges are balanced by mobile counter-ions. This reduced stability may retard the curing reaction and limit the degree of conversion. The results presented in Table 3 shows that at 2 wt% 1-MI, all curing systems go to complete cure, irrespective of the additives present. However, at 0.5 wt% 1-MI (Table 4), the system failed to go to complete conversion. The work of Berger and Lohse [6] have also observed this concentration dependency behaviour. The cause of this concentration dependency on the degree of conversion may be due to the inability of the propagating species to react with further epoxy functional groups once the charge separation exceeds a certain distance. However, it is predicted that this reaction limit should increase if the reactive alkoxide anion is associated with a mobile counter-ion. To test this theory, the curing kinetics of DGEBA was investigated by the addition of tetramethylammonium chloride (TMAC), to a DGEBA mixture containing 0.5 wt% 1-MI (1-MI:TMAC mole ratio = 1:1.14). This concentration of 1-MI, as noted above and in Table 4, is insufficient to produce a high degree of cure. At this concentration, the heat flow profile presented in Fig. 11 shows two exotherm peaks as opposed to only one at higher concentrations (Fig. 4). The low temperature peak is assigned to adduct formation and chain addition etherification (via the alkoxide anion), while the high temperature peak is assumed to be caused by further polymerisation as a result of imidazole regeneration. Comparison of curves (a) (without TMAC) and (b) (with TMAC) in Fig. 11 shows that the addition of TMAC has no significant effects on the exotherm area of the low-temperature peak and suggests that the presence of the salt does not assist adduct formation or the etherification reaction via the alkoxide anion. From Table 4, the addition of TMAC has the effect of increasing T_g due to the higher degree of conversion obtained. As a comparison, the effects of TMAC at a higher 1-MI concentration (2 wt%) was also investigated and are

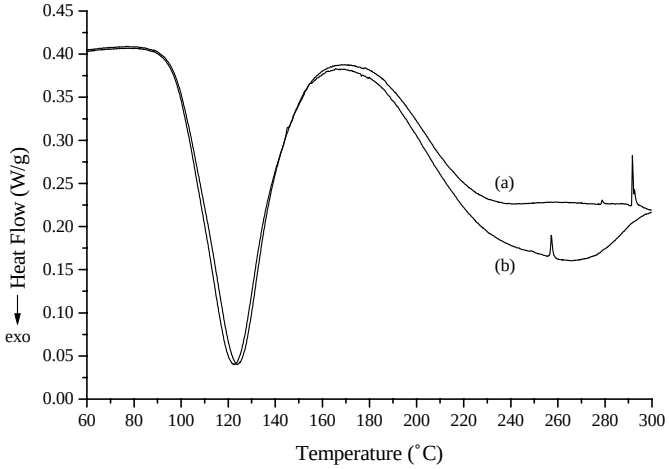


Fig. 11. Scanning DSC of the cure of DGEBA at 5°C/min with (a) 1-MI and (b) 1-MI + TMAC (1-MI:TMAC mole ratio = 1:1.14). The concentration of 1-MI in both samples was 0.5 wt% with respect to DGEBA.

shown in Fig. 12 (curves (a) (without TMAC) and (b) (with TMAC)). No significant effects were noted, except for a broadening of the exotherm peak and a slight decrease in T_g with TMAC present.

The effects of imidazole protonation were also studied to further investigate the initiation mechanism. In this study, HCl solution was added to DGEBA and the mixture initiated with 2 wt% 1-MI (1-MI:HCl mole ratio = 1:1.05). Because 1-MI contains an unsubstituted pyridine-type nitrogen with a lone pair of electrons which are thought [4] to be the locus of adduct formation, the addition of a strong acid should protonate the base preventing its reaction with an epoxy functional group to form the 1:1 adduct. The results of the addition of HCl solution to the DGEBA mixture is shown in Fig. 12 (curve (c)) and can be compared with curve (d) for the cure of DGEBA in the absence of HCl, but in the presence of the same amount of water (~1.5 wt%) as present in the HCl sample. The water curing system (curve (d)) served as a control in separating out the effects of HCl from that of water. The sample containing HCl shows two main exotherm peaks present, one centred around 150°C and the other around 225°C. Other minor exotherm peaks were also observed. Although the precise curing mechanism cannot be accurately determined here, the heat flow profile of curve (c) clearly indicates that the curing reaction was significantly retarded by HCl, presumably because deprotonation of the 1-MI:H^+ species by HCl evolution must occur before adduct formation and etherification can take place.

Interestingly, the addition of HCl does not seem to prevent full conversion, although full conversion was achieved only at higher temperatures. As these temperatures are not normally encountered in practice, an attempt was made to reduce this by decreasing the concentration of HCl to give a 1-MI:HCl mole ratio of 1:0.43. Fig. 12 (curve (e)) shows that decreasing the concentration of HCl has the

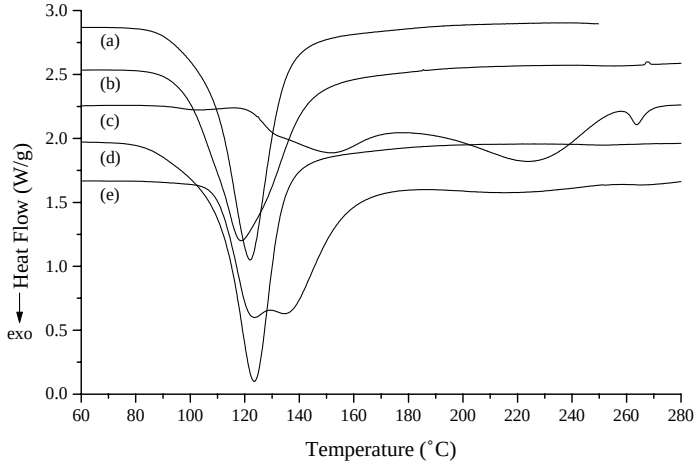


Fig. 12. Scanning DSC of the cure of DGEBA at 5°C/min with (a) 1-MI; (b) 1-MI + TMAC (1-MI:TMAC mole ratio = 1:0.93); (c) 1-MI + HCl (1-MI:HCl mole ratio = 1:1.05); (d) 1-MI + water (1-MI:water mole ratio = 1:3.57); and (e) 1-MI + HCl (1-MI:HCl mole ratio = 1:0.43). The concentration of 1-MI in all samples was 2 wt% with respect to DGEBA.

result of displacing the two exotherm peaks towards lower temperatures. One important observation to note is that the addition of HCl to control the rate of polymerisation can also cause a dramatic decrease in T_g (Table 3). The cause of the large decrease in T_g with excessive HCl is not clear but must be due to the actions of HCl because water alone reduced T_g only slightly (Table 3).

4. Conclusions

Scanning DSC studies show that of the three imidazole curing agents under investigation, only 1-MI had a single peak exotherm resulting in a high degree of conversion of DGEBA at a relatively low concentration (2 wt%). At this concentration, a high T_g of 165°C was obtained. For the 2-MI and 2-PhI curing systems, two or three exotherm peaks were observed depending on the imidazole concentration. The first peak was assigned to adduct formation while the second (major) peak was due to alkoxide initiated polymerisation. In some cases, a third peak was also observed which was attributed to the process of imidazole regeneration.

From the isothermal DSC studies, it was shown that at low imidazole concentration, the degree of cure was generally higher than that obtained in the scanning DSC studies. This result suggests that the curing behaviour, and therefore properties, may be influence by the curing conditions employed (i.e. the temperature program employed). Also, as observed from the shape of the exotherm, there was a distinct difference in the curing behaviour of the 1-substituted and 1-unsubstituted imidazole systems. These differences were rationalised in terms of inductive effects (through the substituent located at the 2-position) and differences in their initiation mechanism.

Scanning DSC studies into the curing mechanism and kinetics of the 1-MI (2 wt%) curing system with the addition of a salt (TMAC) showed that the rate of polymerisation did not increase significantly, and that the overall time (and corresponding temperature) required for complete conversion was essentially the same.

When HCl was added to the 1-MI/DGEBA system, the rate of polymerisation was seen to decrease dramatically, even at low concentrations. In this system, two partially resolved exotherm peaks were observed (compared with only one for the neat 1-MI/DGEBA system). Increasing the HCl concentration resulted in a further decrease in the rate of polymerisation and the presence of multiple exotherm peaks. One undesirable outcome that resulted from this method of cure control was that the T_g was seen to decrease quite considerably with the addition of HCl. In contrast, the addition of water had no significant effect on the rate of polymerisation.

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