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Crosslinking of mixtures of DGEBA with 1,6-dioxaspiro[4,4]nonan-2,7-dione initiated by tertiary amines. Part IV. Effect of hydroxyl groups on initiation and curing kinetics

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ABSTRACT

The anionic homopolymerization of DGEBA epoxy resin and its anionic copolymerization with a bislactone was studied using two alternative tertiary amines, 1-methylimidazole (1MI) and dimethylaminopyridine (DMAP) as initiators. 1MI caused slower cure than DMAP in neat DGEBA and DGEBA-bislactone formulations. Studies of the influence of the hydroxyl concentration in the DGEBA oligomer on its homopolymerization explain descrepancies in the literature regarding the ability of these initiators to produce full cure of the epoxy groups. In contrast, in the copolymerization of DGEBA-bislactone formulations, full cure could be readily achieved with either 1MI or DMAP as initiators, irrespective of the hydroxyl content. FTIR and DSC experiments show that this behaviour is associated with the formation of the carboxylate anion which plays an important part on the curing kinetics and the completion of cure.

1. Introduction

One of the main objectives of our research for the last few years has been the control of shrinkage in epoxy-based crosslinking systems. We have investigated the cationic copolymerization of epoxy resins with expandable monomers such as spiroorthocarbonates (SOCs) [1] and spiroorthoesters (SOEs) [2]. An alternative approach is to form the SOC and SOE structures *in situ*. Thus the cationic copolymerization of epoxides with lactones and bislactones takes place through *in situ* formation of SOE structures and their ring-opening [2–6] (see Scheme 1). In an alternative approach epoxy resin was copolymerized with cyclic carbonates using either anionic or cationic initiators [7,8] to produce spiroorthocarbonates *in situ* during curing which then underwent ring-opening accompanied with volume expansion.

However, bislactones can react with epoxides in a more straightforward manner. It has been reported that, under anionic catalysis, bislactones undergo alternating copolymerization with oxirane rings, resulting in a double ring-opening of the bislactone typical of expandable monomers [9–12]. The proposed curing mechanism consisting of an alternating copolymerization between oxirane rings and bislactones is given in Scheme 2.

Tertiary amines such as imidazoles and 4-(N,N-dimethylamino)pyridine (DMAP) have been reported to be effective anionic initiators for the curing not only of epoxides [13–24] but of lactone- [25,26], bislactone- [17,18,27] or carbonate- [7,28,29] modified epoxy formulations. The anionic copolymerization of bislactones with epoxides has been recently studied by our group, focusing on reaction kinetics [17] and the properties of the final materials [18].

However, anionic polymerization of epoxies often fails to attain full conversion of the reactive groups [16–21]. For example, Ooi et al. [21] observed that when initiated by either 1-methylimidazole (1-MI), 2-methylimidazole, 2-phenylimidazole or 1,2-dimethylimidazole, complete cure of the epoxy groups in a DGEBA oligomer only occurred with 2 parts per hundred (phr) of 1MI. Fernandez et al. [17] observed slightly different curing behaviour because in their study, the complete cure of DGEBA needed 5 phr of 1MI. Related behaviour has been observed for other amine initiators – Fernandez et al. [17] found 5 phr of DMAP was required to attain full epoxy cure, in agreement with the study of Dell'Erba and Williams using DMAP [16]. Likewise, Heise and Martin [19] observed that 4.5 phr of 2,4-ethylmethylimidazole (2,4-EMI) was required for full cure. It has been hypothesized [16,17] that the absence of complete cure at lower concentrations of

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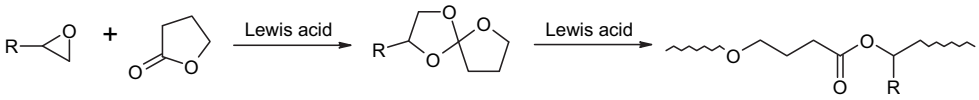


Scheme 1. Formation and subsequent opening of an intermediate SOE by reacting an epoxy monomer with a lactone under acidic catalysis.

initiator is due to the occurrence of termination reactions which deplete the concentration of active species and leads to cessation of the reaction. Interestingly, Fernandez et al. have found [17] that the addition of 1,6-dioxaspiro[4.4]nonan-2,7-dione (s(γBL)) to the DGEBA permitted complete cure with a reduced amount of initiator, and this behaviour was attributed to the partial suppression of termination reactions during the curing process.

It should be noted that previous studies of the final degree of cure of DGEBA using the various amines as anionic initiators was undertaken with DGEBA oligomers of differing molecular weights [16–21], varying from 340 to 381 g/mol. As a result, the fraction of hydroxyl groups per epoxy group ranged from 0 to 0.072 ($n = 0$ to 0.144 in Scheme 3 below) and this may be the cause of some of the disagreements in the literature, such as the concentration of 1MI required to provide complete cure of DGEBA [17,21], as noted above. The present work aims at clarifying the effect of the DGEBA hydroxyl content and the presence of proton donors in general on the curing rate and completion of cure of DGEBA and DGEBA-s(γBL) formulations using 1MI and DMAP as thermal anionic initiators. This work also complements a previous study of the effect of the DGEBA hydroxyl content on the network formation of DGEBA-s(γBL) systems using tertiary amines as initiators [30].

2. Experimental

2.1. Materials

Oligomers of the diglycidylether of bisphenol-A (DGEBA), having different molecular weights (MW = 348 g/mol, 364 g/mol, 381 g/mol), were used as the base resins. 1,6-dioxaspiro[4.4]nonan-2,7-dione (s(γBL)), 1-methylimidazole (1MI) and 4-(N,N-dimethylamino)pyridine (DMAP) from Aldrich were used as anionic initiators without further purification. 1,3-propanediol (C3diol, Merck) was also used as received to investigate the effect of the concentration of hydroxyl groups on the curing behaviour. Scheme 3 shows the structures of the different compounds.

2.2. Preparation of the curing mixtures

Neat DGEBA formulations were prepared by mixing the oligomer and initiator via mechanical stirring. The formulations containing DGEBA and s(γBL) were prepared by first heating DGEBA with the stoichiometric amount of s(γBL) (using a 1:2 molar ratio of DGEBA and bislactone, which is equivalent to an equimolar amount of epoxide groups and bislactone), followed by cooling, addition of the initiator and mechanical stirring. Table 1 shows the notation and composition of the different formulations. The initiator (1MI or DMAP) was used at a concentration of 2 parts per hundred (phr) in the formulations. The formulations have been coded as *X–Y–Z* were *X* is the molecular weight of the DGEBA used, *Y* refers to the initiator and *Z* to the molar ratio between epoxide groups and bislactone units. Formulations with 364 g/mol DGEBA, C3diol and initiator were also prepared (not listed in Table 1).

2.3. DSC

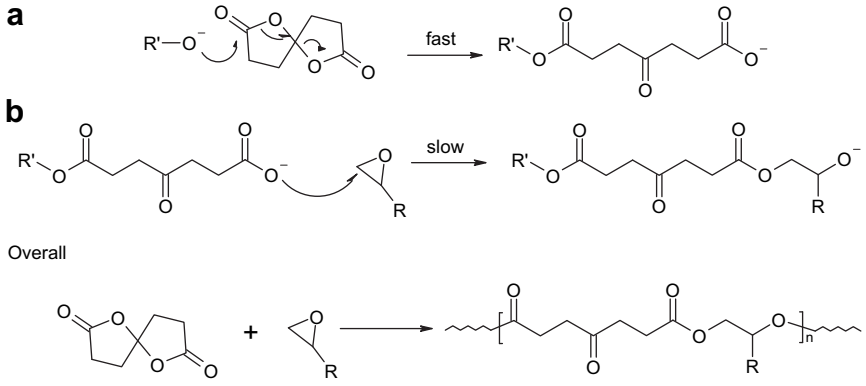
A Perkin Elmer Pyris 1 DSC was used to dynamically cure ca. 10 mg samples of the formulations with DGEBA of molecular weight 348 and 381 g/mol in aluminium pans with pierced lids at 10 °C/min under a dry nitrogen atmosphere. A Mettler DSC822e was also used in dynamic mode at 10 °C/min, to cure ca. 10 mg samples of the formulations with DGEBA ofMW = 364 g/mol in aluminium pans with pierced lids under a nitrogen atmosphere. The degree of cure of the epoxy groups, *x*, was calculated as follows:

$$x = \frac{\Delta h_{\text{total}}}{\Delta h_{\text{ref}}} \tag{1}$$

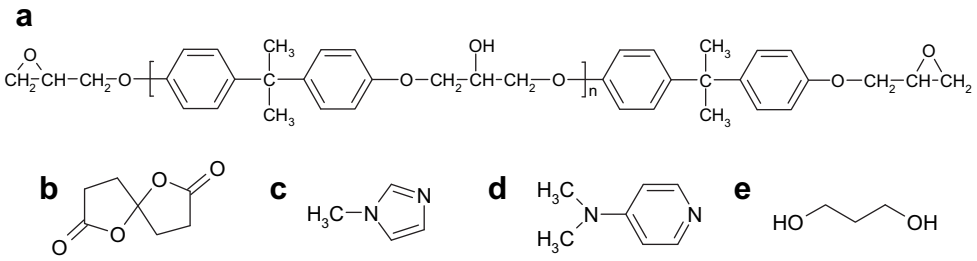
where Δh_{total} and Δh_{ref} are the heat evolved during a dynamic curing and of the theoretical heat of epoxy polymerization (100 kJ/mol [23,31]), respectively. In this calculation, it is assumed that the enthalpy for lactone ring-opening is negligible [4,17].

2.4. FTIR spectroscopy

A Perkin Elmer 1600 Series FTIR spectrometer was used in transmission mode to monitor the isothermal curing of formulations with DGEBA of 348 and 381 g/mol. Individual absorbance spectra were collected at a resolution of 4 cm^{-1}, and eight scans were averaged to give the final spectra. A Bruker Vertex 70 spectrometer was used with an attenuated total reflection accessory with thermal control and a diamond crystal (Golden Gate Heated



Scheme 2. Anionic copolymerization between an epoxide and a spiro bislactone, consisting of (a) ring-opening of the bislactone by attack of an alkoxide anion and (b) ring-opening of the epoxide by attack of the carboxylate anion.



Scheme 3. Chemical structures of (a) DGEBA ($n \approx 0.028$, 0.085 and 0.144 corresponding to molecular weights of 348, 364 and 381 g/mol respectively), (b) s(γBL), (c) 1MI, (d) DMAP and (e) C3diol.

Single Reflection Diamond ATR, Specac-Teknokroma) to monitor the isothermal curing of formulations with DGEBA of 364 g/mol.

In neat DGEBA formulations, the disappearance of the absorbance peak at 915 cm^{-1} (epoxy bending) was used to monitor the epoxy conversion [17]. For the copolymerizations, this peak is obscured by the absorptions arising from the lactone and so the disappearance of the lactone carbonyl absorbance peak at 1795 cm^{-1} (lactone carbonyl) was used to measure the s(γBL) conversion and therefore the epoxy conversion since for stoichiometric formulations, no epoxy homopolymerization occurs [17]. The peak at 1510 cm^{-1} (due to the benzene ring in the DGEBA bisphenol-A backbone), which should not change during the curing process, was chosen as an internal standard [17] to normalize the absorbances of the reactive groups. Conversion was determined by the Beer–Lambert law from the normalized changes of absorbance at 915 cm^{-1} and 1795 cm^{-1}.

$$x_{\text{epoxy}} = 1 - \left(\frac{\overline{A}^t_{915}}{\overline{A}^0_{915}}\right) x_{s(\gamma\text{BL})} = x_{\text{epoxy}} = 1 - \left(\frac{\overline{A}^t_{1795}}{\overline{A}^0_{1795}}\right) \qquad (2)$$

where $\overline{A}^0$ and $\overline{A}^t$ are the normalized absorbance of the reactive group before curing and after reaction time t, respectively.

3. Results

3.1. DGEBA homopolymerization

We have previously reported that 2 phr of 1MI was not sufficient to completely cure DGEBA oligomer with a molecular weight of 364 g/mol [17] but Ooi et al. reported complete cure with an DGEBA oligomer with MW = 381 g/mol [21]. Fig. 1 compares the reaction rate and conversion curves obtained with DSC at 10 °C/min of formulations 348-1MI-1:0, 364-1MI-1:0 and 381-1MI-1:0. Table 2 shows the reaction heat of these formulations (entries 2, 6 and 10). It can be seen that as the molecular weight of the DGEBA oligomer is raised, the reaction rate and the degree of conversion achieved both increase. Taking as a reference a value of 100 kJ/ee [23,31], it can be seen that only formulation 381-1MI-1:0 achieves complete cure. To gain an approximate indication of the magnitude of this effect on the reaction rate, the heat flux at 120 °C (which is on the early stages of polymerization and corresponds to less than 15% conversion) increases from 0.14 to 0.6–1.14 W/g for the systems 348-1MI-1:0, 364-1MI-1:0 and 381-1MI-1:0. As shown in Table 1, two main differences exist between these three formulations. The epoxy to initiator ratio is somewhat lower in the higher molecular weight DGEBA but the difference is only 10% and so is unlikely to be the main effect. On the contrary, the hydroxyl group to initiator ratio increases significantly from 0.33 to 0.95 to 1.15 for the systems 348-1MI-1:0, 364-1MI-1:0 and 381-1MI-1:0, which is well correlated with the reaction rate and thus suggests that the hydroxyl content in the DGEBA oligomer plays a major role on the reaction rate and also the conversion. Addition of C3diol to the neat DGEBA formulations accelerated their cure and even permitted complete cure of the lower molecular weight DGEBA formulations (data omitted for clarity).

According to Rozenberg [23], initiation of epoxy polymerization by tertiary amines requires the presence of a proton donor or electrophilic agent such as a hydroxyl group which forms a complex between the hydroxyl group, the oxygen in the epoxy ring and the tertiary amine. The interaction between the hydroxyl group and the oxygen in the oxirane ring helps to increase the positive charge in the oxirane ring methylene carbons, which then undergoes nucleophilic attack by the lone pair of electrons of the tertiary amine. Thus in the mechanism of Rozenberg [23], an

Table 1
Composition and notation of the systems studied in this work using 2 phr of 1MI or DMAP as initiator and DGEBA oligomers with molecular weights of 348, 364 and 381 g/mol.

Formulation	Sample	n_{DGEBA}:$n_{s(\text{gBL})}$ [a]	eq_{epoxy}:$eq_{s(\text{gBL})}$ [b]	eq_{epoxy}:eq_{init}	eq_{OH} [c]:eq_{init}	eq_{epoxy}:eq_{OH} [c]
1	348-1MI-1:1	1:2	1:1	12.4	0.18	71.0
2	348-1MI-1:0	1:0	1:0	23.6	0.33	71.0
3	348-DMAP-1:1	1:2	1:1	18.5	0.26	71.0
4	348-DMAP-1:0	1:0	1:0	35.1	0.49	71.0
5	364-1MI-1:1	1:2	1:1	12.1	0.51	23.7
6	364-1MI-1:0	1:0	1:0	22.5	0.95	23.7
7	364-DMAP-1:1	1:2	1:1	18.0	0.76	23.7
8	364-DMAP-1:0	1:0	1:0	33.5	1.42	23.7
9	381-1MI-1:1	1:2	1:1	11.8	0.86	13.9
10	381-1MI-1:0	1:0	1:0	21.5	1.55	13.9
11	381-DMAP-1:1	1:2	1:1	17.6	1.27	13.9
12	381-DMAP-1:0	1:0	1:0	32	2.31	13.9

[a] Molar ratio of molecules.
[b] Ratio of equivalents (moles of functional groups).
[c] Calculated from the oligomer molecular weight and its structure.

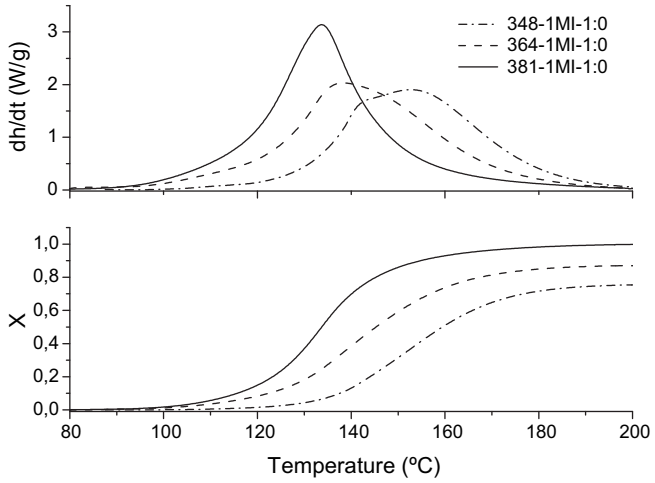


Fig. 1. Reaction rate (dh/dt) and conversion (x) corresponding to the dynamic curing at 10 °C/min of formulations of DGEBA with different molecular weights and 2 phr of 1MI as initiator.

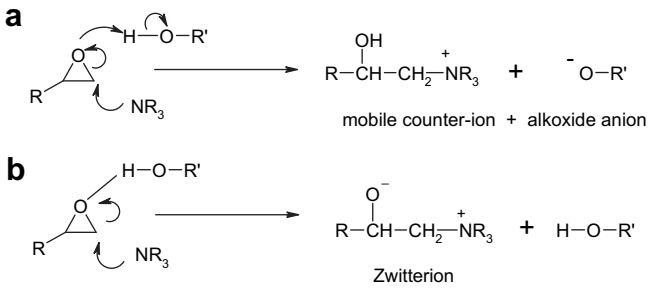
alkoxide and a mobile quaternary ammonium ion are formed between the oxirane and the amine so that the propagating species is an alkoxide arising from the hydroxylic compound (Scheme 4a) and not from the oxirane monomer.

Many other researchers [16,19–21] assume that the initiation mechanism involves formation of a zwitter-ion by interaction between the tertiary amine and the H-bonded oxirane ring (Scheme 4b) and that the subsequent propagation reaction occurs via the alkoxide. This zwitter-ion mechanism was rejected by Rozenberg [23] on the basis of conductivity measurements and the autocatalytic behaviour of the curing process in the absence of proton donors. Whatever the true underlying initiation mechanism, Rozenberg has acknowledged [23] that proton donors promote attack on an oxirane ring by a nucleophile (as indicated in Scheme 4), which does not exclude either of the mechanisms shown in Scheme 4.

Fig. 2 plots the conversion of epoxy groups, measured by FTIR, at 100 °C of the 364-1MI-1:0 formulation and of the 364-1MI-1:0 formulation with 1.18 phr of C3diol added. The curing of these formulations appears to take place in two different stages. The first stage could be associated to the reaction of an epoxy group and 1MI to give rise to an alkoxide anion, in a similar way to the mechanism proposed by Bressers et al. [32] and Ooi et al. [21]. Fig. 2 shows that this first stage reaches up to ca. 0.05 conversion. This value is in fair agreement with the epoxy conversion of 0.044 which would be expected for this formulation if only reaction between 1MI and epoxy groups occurred – this is calculated from the initial initiator to epoxy molar ratio of 0.044 (the inverse of the epoxy:initiator ratio listed in Table 1). After this period, reaction takes place by propagation via the alkoxide anion until the reaction rate slows down due to vitrification [19,20]. Fig. 2 also shows

Table 2
Reaction heat evolved during curing at 10 °C/min of neat DGEBA formulations (as specified in Table 1) in kJ/ee.

Formulation	Sample	Δh (kJ/ee)
2	348-1MI-1:0	75.9
4	348-DMAP-1:0	35.9
6	364-1MI-1:0	87.3
8	364-DMAP-1:0	60.1
10	381-1MI-1:0	101.1
12	381-DMAP-1:0	74.0



Scheme 4. Possible initiation schemes for the anionic curing of epoxides using tertiary amines as initiators.

that while the reaction rate during the first stage is strongly affected by the addition of an extra amount of proton donor such as C3diol due to the catalytic effect on the initiation step, in agreement with the data in Fig. 1, the second stage is virtually unaffected and takes place at a similar rate because this reaction stage is caused by the propagation reaction between the alkoxide anion and the epoxy ring and both are present in similar quantities in the two systems.

Fig. 3 compares the reaction rate and conversion curves obtained with DSC at 10 °C/min of formulations 348-DMAP-1:0, 364-DMAP-1:0 and 381-DMAP-1:0. Table 2 shows the reaction heat for these formulations (see entries 4, 8 and 12). As seen with 1MI, DGEBA oligomers with higher molecular weight (that is, the higher hydroxyl content) cure faster and attain a higher degree of conversion. A comparison of Figs. 1 and 3 shows that curing occurs at a lower temperature with DMAP than with 1MI, which means that DMAP is a stronger nucleophile than 1MI, as reported previously [16,17]. Dell'Erba and Williams [16] have suggested that in comparison with 1MI, the higher nucleophilic activity of DMAP is caused by stabilization of the positive charge not only by resonance within the aromatic ring but also the formation of an additional resonance species, as shown in Scheme 5b. However, and according to the reaction heat values shown in Table 2, the degree of conversion achieved with DMAP is much lower than for 1MI, and the influence of the hydroxyl content on the degree of conversion is also stronger. The low degree of conversion achieved with DMAP was explained by Dell'Erba and Williams [16] by the occurrence of a termination addition reaction between the alkoxide anion and the counter-ion, as seen in Scheme 6.

Fig. 4 illustrates the effect of added hydroxy groups, in the form of C3diol, on the isothermal polymerization of 364-DMAP-1:0 as

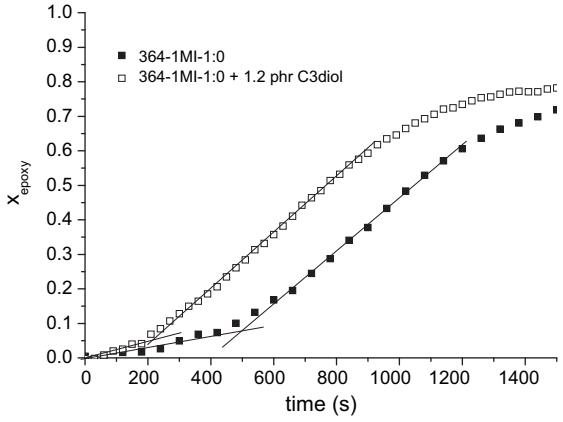


Fig. 2. Conversion of epoxy groups of formulation 364-1MI-1:0 and the same formulation with added 1.2 phr of C3diol during isothermal polymerization at 100 °C.

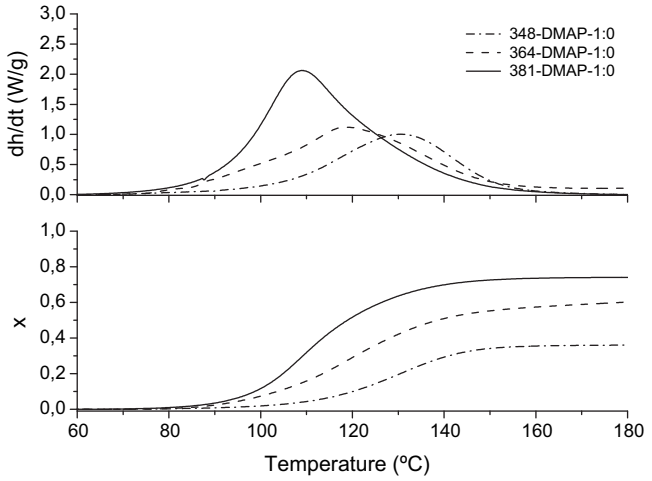
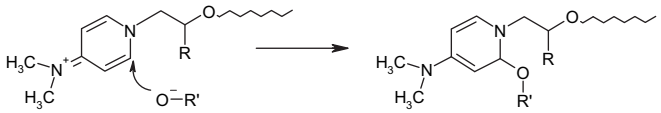


Fig. 3. Reaction rate (dh/dt) and conversion (x) corresponding to the dynamic curing at 10 °C/min of formulations of DGEBA with different molecular weights and 2 phr of DMAP as initiator.

determined by FTIR at two temperatures. As expected, curing at higher temperatures raises the initial polymerization rate. Also, and in agreement with the dynamic DSC data for the cure of DGEBA with DMAP (Fig. 3) or with 1MI (Fig. 1), higher hydroxyl concentration raises the cure rate due to the catalytic effect on the initiation step. C3diol also raises the final conversion of the epoxy groups because the higher concentration of initiating species prevents their premature depletion by side reactions.

For the formulations without added hydroxyl groups (i.e. C3diol), an unusual effect of the isothermal polymerization temperature on the final conversion of DGEBA cured with DMAP is also shown in Fig. 4 – in the absence of C3diol, the final conversion is higher at 100 °C than at 150 °C. In contrast it is usually observed that the conversion of a crosslinked polymer increases with cure temperature [33] because the material is able to polymerize further at the higher temperature before vitrification of the network occurs. More evidence of this unusual behaviour was found in the dynamic curing of 348-DMAP-1:0 and 381-DMAP-1:0 formulations at different heating rates: Fig. 5 shows that the conversion is higher when the scanning rate is lower for both formulations. One explanation for this unusual behaviour has been provided by Barton et al. [13,14] who proposed that the relative importance of the reaction steps during anionic curing of epoxy could be affected by the curing schedule, thus leading to different network development and final material properties. The FTIR spectrum of the curing 364-DMAP-1:0 exhibited a peak at 1650 cm^{-1}. On the basis that this peak was found in the FTIR spectra of 4-(N,N-dimetylamino)pyridinium chloride and 1-cyano-4-(N,N-dimethylamino)pyridinium tetrafluoroborate but was absent from the spectrum of pure DMAP, it was assigned to the structure of the activated DMAP (i.e. the quaternary DMAP ammonium salt). In the samples without C3diol, the absorbance of this peak was higher for the sample cured at 100 °C than for the one cured at 150 °C. The absorbance of this peak was also greater for both samples with C3diol compared with those without C3diol. These observations suggest that the systems cured

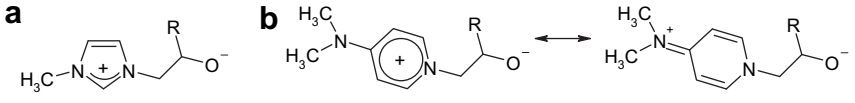


Scheme 6. Proposed termination reaction for DMAP [16].

at lower temperatures or having higher concentrations of hydroxy groups contain more active initiating chains. Thus initiation is favoured at a lower temperature and likewise at a low heating rate [13,14], thus leading to a higher ultimate degree of conversion. Incomplete curing at higher temperatures and higher heating rates can be explained by a combination of a lower initiation rate and the occurrence of the termination reaction shown in Scheme 6. The fact that the reaction is faster at the beginning of curing at higher temperatures (see Fig. 4) in spite of the lower amount of reactive species can be explained by the effect of temperature on the kinetic constant.

A comparison of Figs. 1 and 3 and Figs. 2 and 4 show that curing with 1MI is slower but nevertheless leads to higher degree of conversion than with DMAP. Several authors have reported that imidazoles undergo regeneration during curing [21,22,34], which permits reinitiation of new growing chains. Two main regeneration pathways have been proposed: β-elimination (Scheme 7a) and N-dealkylation (Scheme 7d). According to some authors [21,22], N-dealkylation is the major regeneration pathway but β-elimination has also been reported to take place [22]. Evidence of regeneration via β-elimination has been found for both 1MI (see Fig. 6) and DMAP (data not presented here) in FTIR spectra collected during curing at 100 °C of DGEBA of MW = 348 g/mol. In agreement with the previous observations by Ricciardi et al. [22], small peaks appear at 1660 cm^{-1} and 1730 cm^{-1} corresponding to the vinyl group of the enol ether and the carbonyl group of the ketone, respectively, while the hydroxyl groups band at 3500 cm^{-1} increases in intensity due to conversion of the alkoxide to an alcohol (see Fig. 6). All these signals are in agreement with the β-elimination regeneration pathway shown in Scheme 7a–c (steps b and c have been derived from the work by Perez et al. [35]). We have also observed (data not shown here) that DMAP undergoes regeneration as well, but to a lesser extent than 1MI; the growth of the hydroxyl band is not as important and the small peak around 1660 cm^{-1} overlaps the peak of activated DMAP at 1650 cm^{-1} thus making it almost unnoticeable. Dell'Erba and Williams had previously cited the appearance of a peak at 1642 cm^{-1} as evidence of the regeneration reaction during epoxy cure with DMAP [16] however this peak may be also due to the vinyl groups in the species formed during DMAP termination, as shown in Scheme 6, instead of regeneration.

Thus it can be seen that the curing of DGEBA with tertiary amines is complex and is influenced by a series of factors: (1) the amount of initiator, (2) the content in hydroxylic oligomer of DGEBA, (3) the curing schedule, (4) the ability of the initiator to regenerate the amine initiator and (5) the occurrence of termination reactions. DMAP promotes faster curing than 1MI but the existence of termination reactions and a lower likelihood of regeneration and reinitiation leads to an incomplete curing.



Scheme 5. Active species formed by attack of 1MI (a) and DMAP (b) on an epoxy monomer.

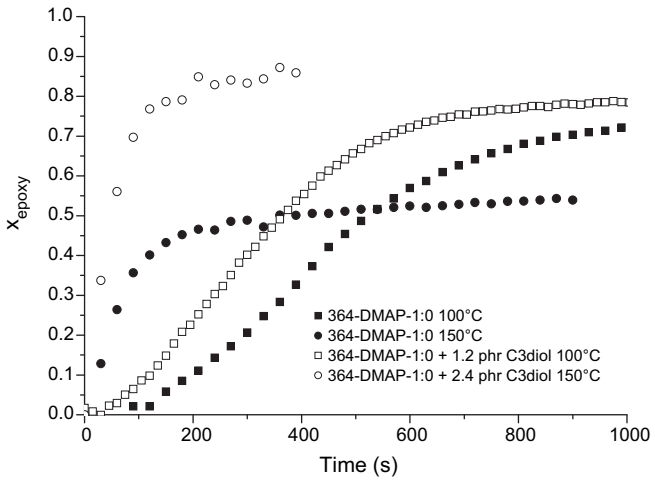


Fig. 4. Conversion of epoxy groups of formulation 364-DMAP-1:0 at 100 and 150 °C and formulation 364-DMAP-1:0 with 1.2 and 2.4 phr of C3diol at 100 °C and 150 °C, respectively.

3.2. DGEBA-s(γBL) copolymerization

The anionic copolymerization of epoxy with bislactone has been investigated by serveral researchers [9–11,15,17,18,36,37]. It was reported that stoichiometric mixtures of DGEBA and s(γBL) could react completely via alternating copolymerization [10,36,37] (see Scheme 2), and recently it was shown that complete cure of both monomers could be achieved with a small amount of either 1MI or DMAP [17,18]. According to the literature [11,36], when the epoxide is in a stoichiometric excess, copolymerization of epoxide and bislactone in bulk can also result in a certain degree of epoxy homopolymerization. Brady and Sikes [9,15] found that during the anionic curing of DGEBA-based formulations containing a stoichiometric deficiency of bislactone, the consumption of s(γBL) took place at the beginning of the reaction. Fernandez et al. [17] confirmed this result but also found that an almost alternating copolymerization occurred between DGEBA and s(γBL) at the beginning of polymerization. In addition [17], epoxy groups could only homopolymerize in epoxy-rich formulations after the s(γBL) was exhausted. It was also proposed [30] that the alternating copolymerization prevailed over DGEBA homopolymerization because the addition reaction of the alkoxide anion to the bislactone (Scheme 2a) is faster than its addition to the oxirane ring.

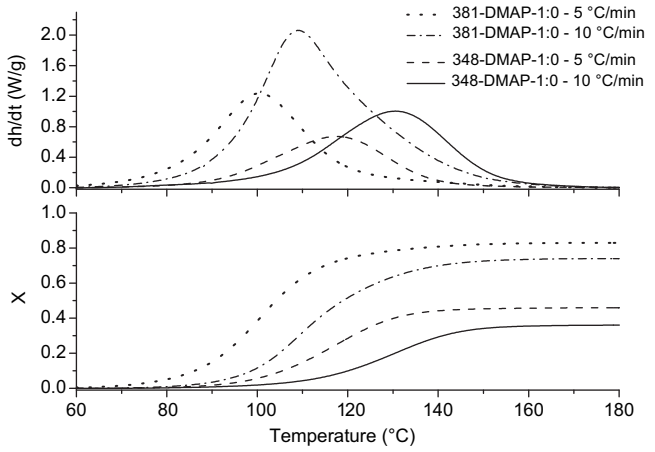


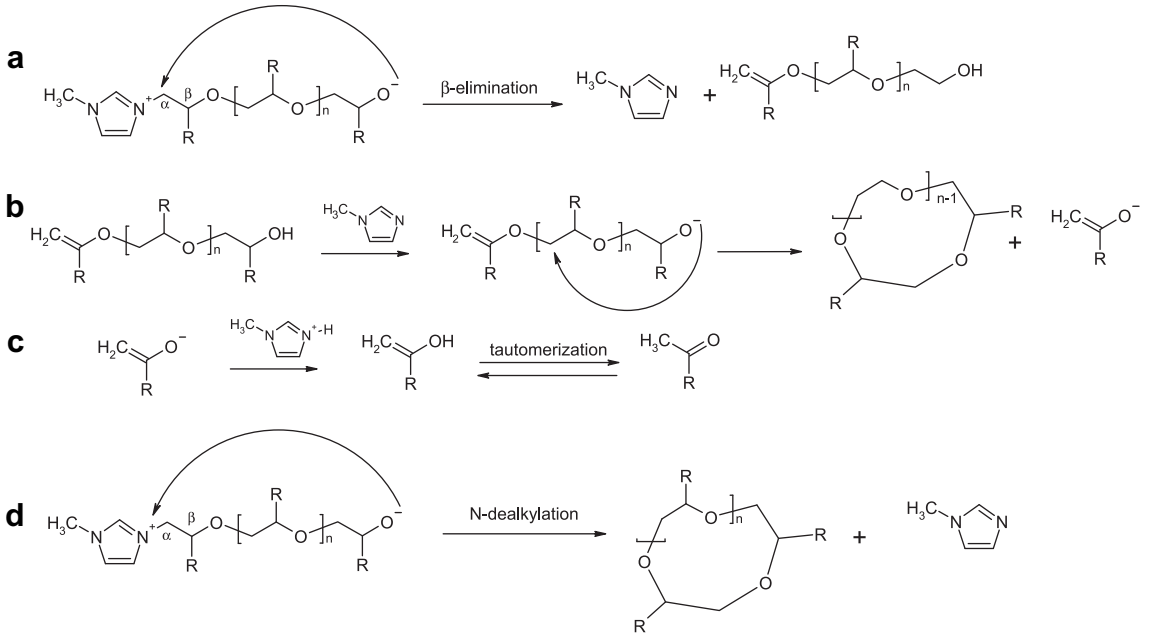
Fig. 5. Reaction rate d*h*/d*t* and conversion *x* corresponding to the dynamic curing at 5 and 10 °C/min of formulations of DGEBA with different molecular weights and 2 phr of DMAP as initiator.

Fig. 7 compares the dynamic curing at 10 °C/min of stoichiometric 1:1 DGEBA-s(γBL) formulations with two different DGEBA oligomers and 2 phr of 1MI or DMAP. Comparison of the data in Fig. 7 with those in Figs. 1 and 3 shows that the peak temperatures during curing of stoichiometric formulations of DGEBA-s(γBL) are higher than those observed for neat DGEBA formulations, which indicates that the reaction rate is lower in the comonomer systems. In agreement with the previously reported data for 364-1MI-1:1 and 364-DMAP-1:1 [17,18], near complete cure was obtained, as were all of the stoichiometric formulations (entries 1, 3, 5, 7, 9 and 11 in Table 1) with 2 phr of either of the initiators. The peak temperature in the dynamic DSC experiment occurs at lower temperaturers for DMAP than for 1MI showing that DMAP is the more efficient initiator, which is in agreement with that discussed above and as reported previously [17] for neat DGEBA formulations. In contrast with that found with neat DGEBA formulations (see Figs. 1 and 3), Fig. 7 reveals that for the DGEBA-s(γBL) copolymerization, there is very little effect of the DGEBA molecular weight and thus the concentration of hydroxyl groups on the reaction rate. The polymerization rate in formulations with 1MI are slightly faster with higher DGEBA hydroxyl content, but formulations with DMAP do not show any effect of hydroxyl groups at all, implying that unlike epoxy homopolymerization, the rate determining step in DGEBA-s(γBL) copolymerization does not involve H-bonding as concluded in our previous work [30].

Fig. 8 shows the variation in epoxy conversion with time during the curing of s(γBL) 364-1MI-1:1 and 364-DMAP-1:1 formulations at 100 °C and compares these with the equivalent formulations containing 1.1 phr C3diol. The DGEBA/s(γBL) stoichiometric formulation with 1MI shows an induction period at the beginning of the curing process that is reduced with the addition of C3diol, as was seen for neat DGEBA formulations with 1MI (see Fig. 2). On the contrary, formulations with DMAP show insignificant induction periods regardless of the presence of the diol and the curing rate is unaffected by the presence of hydroxyl groups, in general agreement with the data in Fig. 7. Due to enhanced initiation, curing of stoichiometric formulations with DMAP is faster than with 1MI with or without added hydroxyl groups, which is consistent with the dynamic DSC thermograms shown in Fig. 7 and our data reported previously [17].

As discussed above and reported previously [17], both dynamic DSC and isothermal FTIR studies show that the reaction rate is much lower in the DGEBA-s(γBL) formulations than for neat DGEBA systems. If Scheme 2 is recalled, ring-opening of s(γBL) by attack of an alkoxide anion during copolymerization leads to the formation of a stable carboxylate anion. Due to its stability and lower nucleophilicity, ring-opening of the epoxide via attack by the carboxylate anion is slow (Scheme 2b), thus reducing the rate of epoxy consumption and controlling the propagation rate. Evidence of the presence of the carboxylate anion during curing of stoichiometric formulations can be found in Fig. 9 which plots FTIR spectra collected during curing at 100 °C of 364-DMAP-1:1 and 364-1MI-1:1 formulations. DGEBA has peaks at 1580 and 1610 cm^{-1} due to double bond stretching of the 1,4-disubstituted benzene ring and Fig. 9 reveals that a shoulder near 1570 cm^{-1} develops on the former peak which corresponds to the carboxylate anion [38].

No increase in the hydroxyl band was observed in the stoichiometric DGEBA-s(γBL) formulations containing either initiator, indicating that regeneration via β-elimination (Scheme 7a) does not takes place at all or only occurs to a lesser extent than for neat DGEBA formulations. The absence of regeneration can be explained by the presence of the carboxylate anion. Due to the fast reaction of the alkoxide anion to give rise to the carboxylate and the slow



Scheme 7. Different initiator regeneration schemes for the anionic polymerization of epoxides using 1MI as initiator. The mechanism for tautomerism of the alkene (shown in b and c) was adapted from [35]. Note that these schemes have been represented as intra-molecular for the sake of simplicity.

reaction of the carboxylate to give rise to alkoxide anion (see Scheme 2), the population of alkoxide anions is much lower in stoichiometric formulations, thus reducing the likelihood of regeneration during the curing process. Accordingly, the likelihood of termination reactions such as the one shown in Scheme 6, is also reduced, thus permitting complete cure with either of the initiators, as reported previously [17].

Fig. 9 shows that the peak at 1650 cm^{-1}, which corresponds to the structure of the DMAP quaternary ammonium species, increases at a similar rate to the carboxylate anion signal. Therefore initiation, that is, formation of the quaternary ammonium species, can also be monitored via the carboxylate anion peak. This is important for 1MI because the 1-methylimidazolium cation peaks overlap other existing peaks in DGEBA-s(γBL) formulations. It can be observed that the growth of the carboxylate peak is faster with DMAP than with 1MI, confirming that initiation is faster with DMAP, as seen for neat DGEBA formulations. Analysis of the FTIR spectra (not shown here) shows that the growth of both the carboxylate and quaternary ammonium peaks for DMAP is faster with added C3diol (as proton donor). Therefore, initiation with DMAP is enhanced by the presence of hydroxyl groups. However, as seen in Fig. 8, there is no induction period with DMAP and the reaction rate in stoichiometric DGEBA-s(γBL) formulations with DMAP is almost unaffected by the presence of C3diol as proton donor. This is caused by the following: (1) the initiation rate is already high because of the high nucleophilicity of DMAP, (2) the

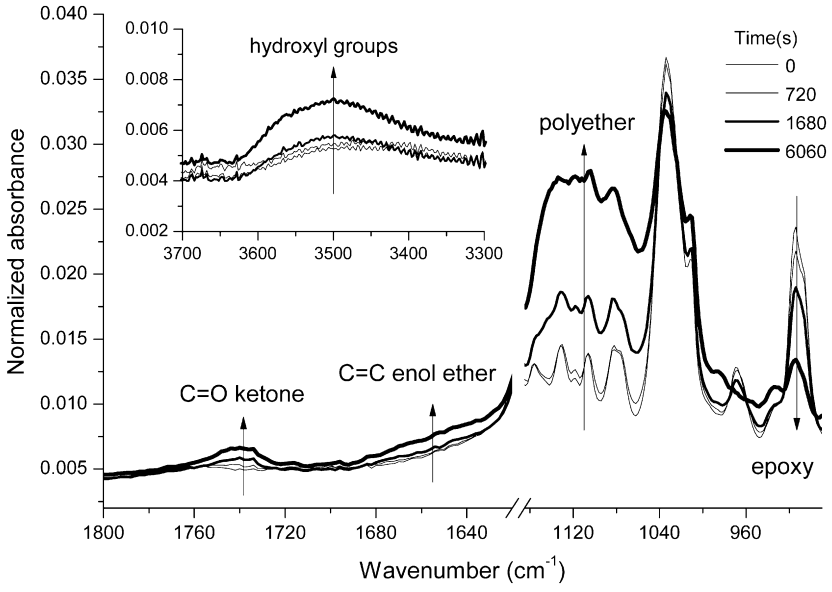


Fig. 6. FTIR spectra collected during isothermal curing of 348 g/mol DGEBA with 2 phr of 1MI at 100 °C.

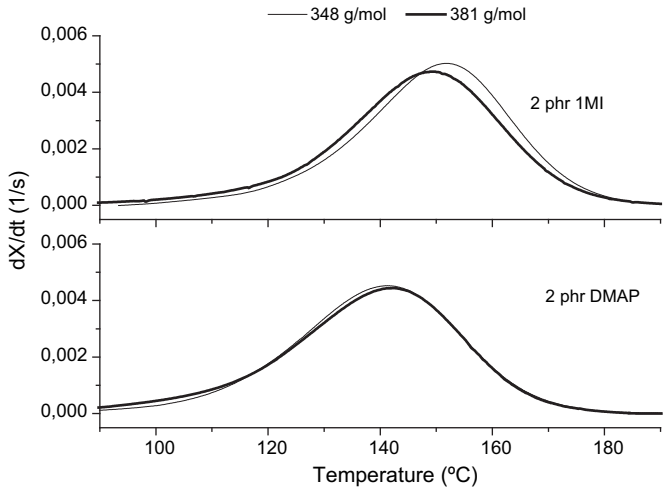


Fig. 7. Reaction rate d*x*/d*t* corresponding to the dynamic curing at 10 °C/min of stoichiometric DGEBA-s(γBL) formulations of DGEBA with different molecular weights and 2 phr of 1MI or DMAP as initiator.

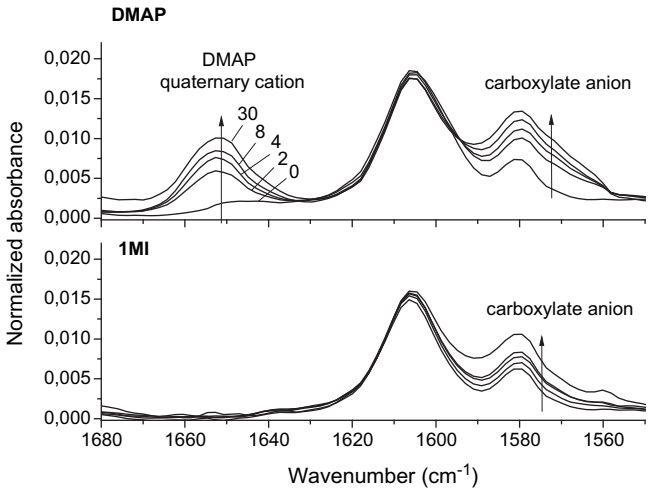


Fig. 9. FTIR spectra collected during isothermal curing at 100 °C of stoichiometric DGEBA-s(γBL) formulation with DGEBA of 364 g/mol and 2 phr of 1MI or DMAP as initiator, showing the formation of carboxylate ions at 1570 cm^{-1} and the quaternary ammonium cation formed from the DMAP initiator species at 1652 cm^{-1}. The numbers indicate the reaction time in minutes (same for both DMAP and 1MI).

potential amount of active species is unaffected by the addition of a small amount of hydroxyl groups, (3) any further increase in initiation rate caused by the presence of hydroxyl groups is offset by the presence of the carboxylate anion, which slows down the curing and controls the reaction rate and (4) this rate-controlling step of the copolymerization process is unaffected by the presence of hydroxyl groups. 1MI is a weaker nucleophile than DMAP and therefore the initiation rate is much lower hence the higher cure temperature in Fig. 7, the induction period and longer curing time in Fig. 8 and the slower growth of carboxylate peaks in Fig. 9. The presence of hydroxyl groups enhances initiation of stoichiometric formulations with 1MI as well, as it can be deduced from the shorter induction period with added C3diol (see Fig. 8). However, once the induction period is complete, the reaction rate is not affected by the presence of hydroxyl groups because a similar amount of active species is formed regardless of the presence of hydroxyl groups and the rate-controlling step is not affected by the presence of hydroxyl groups.

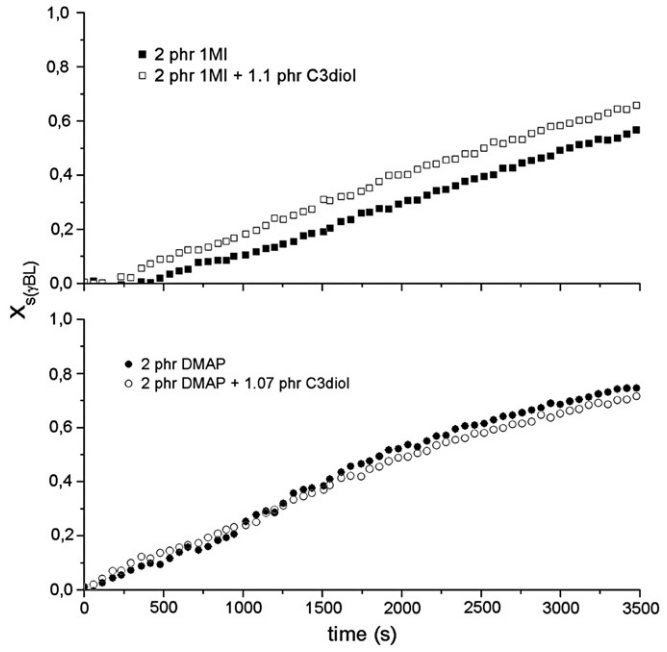
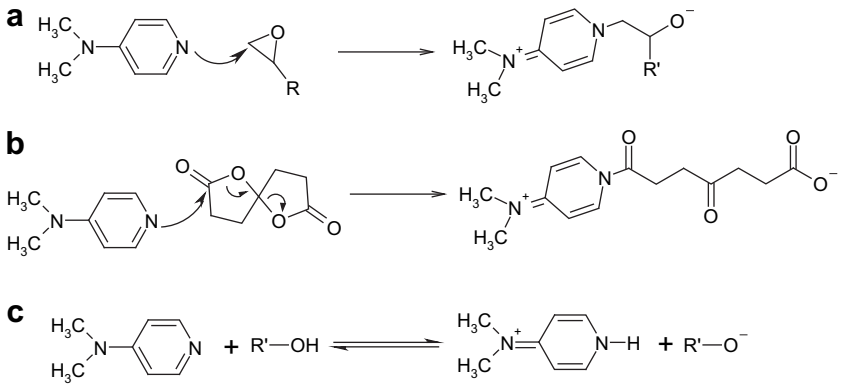


Fig. 8. Conversion of epoxy groups at 100 °C in 364-1MI-1:1 and 364-DMAP-1:1 formulations and the equivalent formulations with ca. 1 phr added C3diol.

The question arises as to whether the DMAP or 1MI initiators prefers to attack the epoxy group, as proposed in Scheme 8a (and implied for epoxy homopolymerization) or the lactone ring in stoichiometric DGEBA-s(γBL) formulations (Scheme 8b). According to Scheme 8b, the opening of s(γBL) would lead to the simultaneous formation of amide, ketone and carboxylate groups and disappearance of the lactone groups. To investigate this issue, a stoichiometric mixture of DMAP and s(γBL) was heated at various temperatures and the FTIR spectrum recorded. After 100 and 150 °C for 1 h, none of the peaks expected of ring-opening of s(γBL) with DMAP could be observed. At 200 °C the reaction proceeded at a very low rate and to a very small extent and only when heated to 220 °C were the characterisitic peaks observed (a ketone group at 1710 cm^{-1}, a tertiary amide at 1643 cm^{-1} and carboxylate signals at 1550 and 1380 cm^{-1}, see [38]). These observations allow us to conclude that initiation of the DGEBA-s(γBL) systems by DMAP does not take place by attack of the tertiary amine on s(γBL) to any significant extent. Similar FTIR studies of the reaction of 1MI with s(γBL) did not reveal any evidence for ring-opening of the lactone by the amine.

Fig. 9 also shows that the carboxylate peak at 1570 cm^{-1} in stoichiometric blends of DGEBA/s(γBL) cured with DMAP is stronger than for 1MI, and a new peak appears at 1560 cm^{-1}. A similar peak at this wavenumber is also found (data not shown here) for neat DGEBA formulations using DMAP as initiator. The FTIR spectrum of the hydrochloride of DMAP (not shown here) exhibits a peak at this wavelength which suggests that this shoulder is related to protonation of DMAP, which could take place by an acid–base equilibrium between hydroxyl compounds and DMAP, as proposed in Scheme 8c. Appearance of protonated tertiary amine is also evident when 1MI was used as initiator (see Fig. 9, lower graph) but its intensity is lower than with DMAP (see Fig. 9, upper graph), which is consistent with its lower basicity and nucleophilicity. This equilibrium leads to the formation of alkoxide anions that can initiate the reaction process. Addition of hydroxyl groups might displace the equilibrium towards protonation of the tertiary amine. A similar acid–base equilibrium also takes place in



Scheme 8. Possible initiation schemes for s(γBL) using DMAP as initiator (a and b) and (c) an acid–base equilibrium between hydroxyl compounds and DMAP.

Scheme 7b–c, which makes possible tautomerization and formation of a methylketone after DMAP regeneration via β-elimination.

4. Conclusions

The anionic homopolymerization of DGEBA has been investigated with the 1MI and DMAP tertiary amines. The polymerization behaviour is complex because it is influenced by several factors – the nature and amount of initiator, the concentration of hydroxyl groups in the DGEBA oligomer, the curing schedule, the ability of the initiator to regenerate the amine initiator and the occurrence of termination reactions. DMAP promotes faster curing than 1MI but the existence of termination reactions and a lower likelihood of regeneration and reinitiation leads to an incomplete curing. The presence of hydroxyl groups in the DGEBA oligomers increases the initiation rate with both 1MI and DMAP and leads to higher conversions because the active propagating species are in higher concentration.

The curing is slowed down when DGEBA is copolymerized with (γBL) due to the presence of the carboxylate anion generated by double ring-opening of s(γBL) in its anionic copolymerization with epoxy groups. The stability of this anion also reduces the likelihood of initiation, amine regeneration and termination reactions, thus permitting complete cure with either of the initiator regardless of the hydroxyl groups content. Initiation of curing of DGEBA-s(γBL) formulations takes place mainly by nucleophilic attack of the tertiary amine on the oxirane ring rather than on s(γBL). DMAP promotes faster reaction of DGEBA-s(γBL) formulations than 1MI because initiation is enhanced by its higher nucleophilicity.

The negative effect of termination reactions on the extent of cure of DGEBA formulations with DMAP can be overcome by the selection of DGEBA oligomers with high concentrations of hydroxyl groups, by increased initiator concentration or by the copolymerization of DGEBA with s(γBL).

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