

# 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 dimethylamino-pyridine (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 discrepancies 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.

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## 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

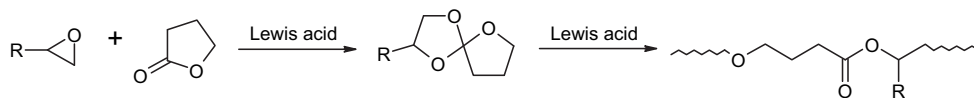
mechanism consisting of an alternating copolymerization between oxirane rings and bislactones is given in Scheme 2.

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*( $\gamma$ BL)) 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*( $\gamma$ BL) 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*( $\gamma$ BL) 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*( $\gamma$ BL)), 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*( $\gamma$ BL) were prepared by first heating DGEBA with the stoichiometric amount of *s*( $\gamma$ BL) (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 where 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

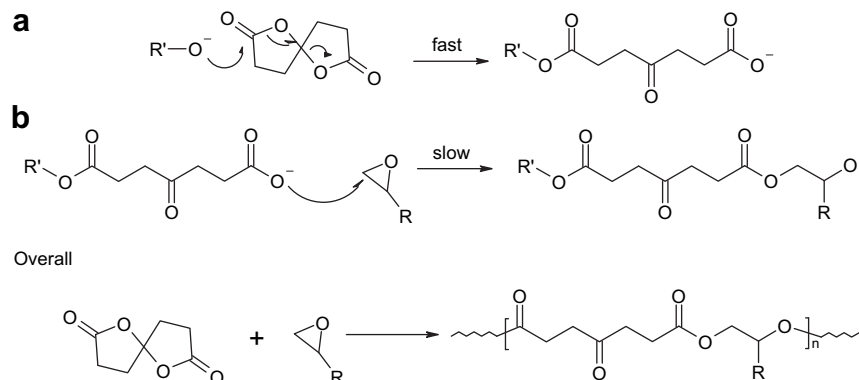
A Perkin Elmer Pyris 1 DSC was used to dynamically cure ca. 10 mg samples of the formulations with DGEBA of molecular weight 348 and 381 g/mol in aluminium pans with pierced lids at 10 °C/min under a dry nitrogen atmosphere. A Mettler DSC822e was also used in dynamic mode at 10 °C/min, to cure ca. 10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

$$x = \frac{\Delta h_{\text{total}}}{\Delta h_{\text{ref}}} \quad (1)$$

where  $\Delta h_{\text{total}}$  and  $\Delta h_{\text{ref}}$  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<sup>-1</sup>, 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.

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