European Polymer Journal 55 (2014) 35–47

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Theoretical modeling of the effect of proton donors and regeneration reactions in the network build-up of epoxy thermosets using tertiary amines as initiators

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ARTICLE INFO

Article history:
Received 18 December 2013
Received in revised form 17 March 2014
Accepted 17 March 2014
Available online 24 March 2014

Keywords:
Epoxy
Tertiary amine
Gelation
Network structure

ABSTRACT

A kinetic-structural model for the curing of epoxy resins with tertiary amines as initiators has been proposed. This model is based on a likely reaction mechanism, which includes the effect of tertiary amine regeneration and the effect of proton donors on the initiation and chain-transfer, and a statistical network build-up methodology based on the independent reactivity of epoxy groups and the random recombination of primary chains. A significant effect of proton donors or impurities is predicted by the model, which can be explained by their likely participation as chain-transfer agents and initiating sites. The occurrence of tertiary amine regeneration has also a profound effect on the curing, but the different regeneration mechanisms have opposite effects and may be counter-balanced. This flexible model is able to explain the curing behavior of different epoxy formulations with tertiary amines as initiator.

1. Introduction

The homopolymerization of epoxides with tertiary amines as anionic initiators has been studied in the past [1–12]. The process is highly complex due to the concurrence of multiple reactions, namely: (1) initiation leading to the formation of an epoxy-tertiary amine adduct alkoxide anion, (2) anionic polyetherification through an alkoxide anion, (3) regeneration of the tertiary amine, which may then restart the homopolymerization sequence and (4) chain-transfer between the alkoxide anions and existing proton donors such as hydroxyl compounds. The complexity of the curing process increases even more if one takes into account the network build-up process. This involves the formation of a variety of n-meric species, macromolecules with an increasing mass and degree of branching as the curing advances. The reactivity of the groups in a chain may depend on the chain size, its topology, the surrounding environment or different levels of substitution effects, among other factors. The occurrence of gelation and vitrification, leads to further topological or mobility restrictions that can have a significant effect on the curing kinetics [13].

Although the epoxy homopolymerization with tertiary amines has been extensively studied [7,9,10,14,15], apparently contradictory results have been reported in the literature concerning the network build-up [10,16]. In some cases, wrong assumptions on the network build-up process have been made [7]. A network build-up method based on the expectation probability, as described by Miller and Macosko [17–19], is used in the present work to model the curing of diglycidyl ether of bisphenol A (DGEBA) thermosetting formulations with tertiary amines as initiators. This method is based on the generation of primary chains or clusters that are later on on randomly recombined in different ways to conform the network structure. Primary chain methods have been used in the past to study

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http://dx.doi.org/10.1016/j.eurpolymj.2014.03.022
0014-3057/

relatively simple chainwise polymerizations [20–22] but can be applied to rather complex copolymerization processes involving substitution effects, chain coupling and chain scission, among other features [23–25]. This method was recently applied, in combination with a relatively simple kinetic model, to the study of the curing of epoxy-anhydride formulations [26]. The effect of proton donors on the curing kinetics and network build-up is taken into account by means of the addition of mono hydroxylic compounds or the increasing hydroxylic oligomer content of DGEBA. Pregel and postgel statistical averages of the primary chain and fragment network build-up methods are calculated and compared with a reference living polymerization kinetic models. The validity and potential applicability of the proposed kinetic and structural model are discussed.

2. Theoretical

2.1. Reaction mechanism

Different initiation mechanisms for the polymerization of epoxy monomers with tertiary amines can be found in the literature [3,4,9]. Although it is commonly assumed that initiation occurs by nucleophilic addition of the tertiary amine to the epoxy ring resulting in a zwitter-ion [1,3,7,9], Scheme 1a, Rozenberg [4] showed that a likely mechanism involved the participation of a proton donor such as a hydroxylic compound, that weakens the oxirane ring strength, resulting eventually in (1) the formation of an alkoxide anion coming from the hydroxylic compound and (2) a tertiary-ammonium counter-cation be with an end hydroxyl group coming from the amine-epoxy addition. According to this mechanism, proton donors become the propagating sites, rather than the epoxy-amine adduct. However, it is also commonly reported that epoxides and imidazoles form adducts [1,7,8], therefore the real initiation mechanism may depend on the type of tertiary amine used for the curing.

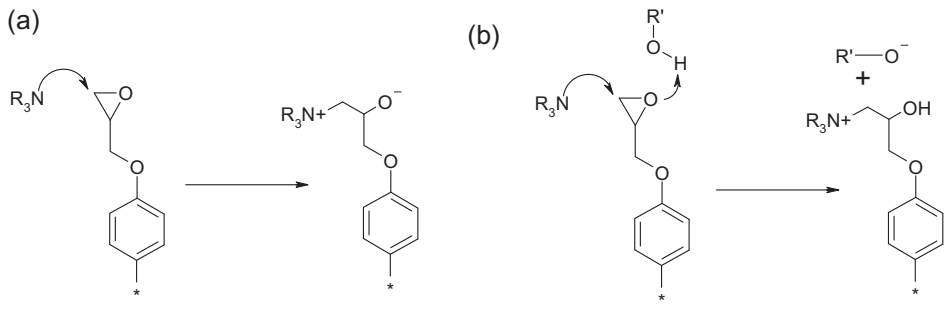
The propagation mechanism, shown in Scheme 2, consists in the ring-opening of an epoxy group by an alkoxide anion.

The regeneration of tertiary amines has been frequently reported in the literature [3,4,9,11,27]. Regeneration may take place by means of two different mechanisms: a β-elimination based on a hydrogen abstraction by an alkoxide anion (Scheme 3a) and a substitution mechanism (Scheme 3b). An important difference between the different tertiary amine regeneration mechanisms is their different effect on the network structure during curing. While elimination simply stops chain growth, thus reducing primary chain length and reducing crosslinking, substitution leads to chain coupling, resulting in an increase in chain length and an increase in crosslinking. In some reports regeneration reactions are considered to be intra-molecular [9], but in the present work it has been assumed that cyclization reactions are negligible and so regeneration is modeled as inter-molecular instead. Matejka et al. [5] reported that initiator regeneration could account for the low molecular weight of the oligomers obtained in the polymerization of N-methylglycidylaniline with tertiary amines or amino alcohols. Short oligomers have also been obtained in the polymerization of phenyl glycidyl ether with different tertiary amines [9]. Although it is acknowledged that the substitution elimination mechanism is a major regeneration mechanism [3,27], evidence of the occurrence of the elimination mechanism is more frequently found [9–11,27]. The formation of hydroxyl groups and vinyl groups during curing has been reported [9,11]. The formation of carbonyl groups has also been reported [11,27] in the literature. Although a rather elaborate mechanism for the presence of carbonyl groups has been recently proposed [11], a more simple mechanism may take place, as illustrated by Scheme 4, if one considers the initiation mechanism proposed by Rozenberg [4] or the occurrence of chain-transfer reactions. However, given the slow intensity of the appearing carbonyl band, this process is considered to take place to a very small extent. The occurrence of termination reactions without regeneration of the tertiary amine, leading to incomplete curing of epoxy resins [9,11], has also been proposed. Chain-transfer reactions between the alkoxide propagating chain and hydroxylic compounds (see Scheme 5) also take place, which has been claimed to have a significant effect on the network build-up during curing [10].

2.2. Kinetic model definition

The above description of the curing mechanisms suggests that, at least, one should consider the following reactions:

– Initiation by zwitter-ion formation without and with the catalysis of hydroxyl groups.



Scheme 1. Initiation mechanisms for the homopolymerization of epoxides with tertiary amines.