Comparative analysis of stochastic network build-up methods for the curing of epoxy–anhydride thermosets

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A B S T R A C T

The network build-up of epoxy–anhydride thermosets has been studied using two different stochastic network build-up methods based on the random combination of primary chains or simple fragments. Explicit expressions for relevant statistic averages in the pregel and postgel states have been derived for both methods. The application of both methods to a living polymerization kinetic model leads to strong divergences in the vicinity of the critical conversion at gelation due to growing differences between the real primary chain distribution and the most probable distribution in the fragment model. However, the application of both methods to an initiator regeneration kinetic model leads to identical results because of the distribution of primary chains throughout the whole curing process is a most probable one.

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1. Introduction

The chainwise polymerization of epoxy thermosets is highly complex due to several factors: (1) the inherent complexity of the curing mechanism, which may include several initiation and termination steps and competitive propagation reactions and (2) the network build-up process, determined by the curing mechanism, which gives rise to a variety of n-meric species, macromolecules with an increasing mass and degree of branching, the occurrence of gelation and vitrification, all of which leading to different topological or mobility restrictions that can have a significant effect on the curing kinetics [1]. Simultaneous chemorheological measurements [2–7], coupled with curing kinetics modeling, also provide significant information on the evolution of viscosity with the conversion, gelation and the build-up of visco-elastic properties of the cross-linked network. However, in order to gain a better understanding of the process, be able to predict the effect of changing formulation composition and processing

conditions, or analyze more complex situations such as reaction-induced phase-separation processes, a more detailed analysis and modeling of curing processes is necessary.

Two stochastic network build-up methods based on the expectation probability, as described by Miller and Macosko [8–10], are used in the present work to study the network build-up during curing of thermosetting formulations using a simple living polymerization kinetic model and a recently developed kinetic model involving initiator regeneration and reinitiation that is capable of describing more accurately the curing process of epoxy–anhydride thermosets [11]. One of the network build-up methods is based on the generation of primary chains or clusters [11–17], and the other is based on the generation of small structural fragments [7,13,18–20]. In both methods it can be assumed that tetrafunctional diepoxide monomers can be splitted up into two independently reacting units [15,16] issuing each a virtual bond. An infinite or finite set of differential equations are used to generate a suitable distribution of primary chains or fragments, respectively. Primary chains and fragments are later on randomly recombined in different ways to conform the network structure, as illustrated in Fig. 1.

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Relevant statistical averages are determined by the random recombination of the disassembled diepoxy units belonging to different primary chains o structural fragments. Stochastic structural models often make use of probability generating functions formalism [16,21], but it is acknowledged this formalism and that based on conditional probabilities [8,10] lead to equivalent results since they are based on the same principles [21]. It can be argued that stochastic methods are not perfect [17]. However, Mikes and Dusek [22] showed that statistical methods and Monte Carlo methods produce similar results for step-wise polymerizations. Khanna and Chanda [23] reported similar predictions before the gel point for fragment-based statistical and Monte Carlo methods. Robbins et al. [24] showed also that the solutions offered by deterministic and stochastic methods are equivalent.

Primary chain methods have been used in the past to study relatively simple chainwise polymerizations [12–14] but can be applied to rather complex copolymerization processes involving substitution effects, chain coupling and chain scission, among other features [15–17]. Fragment methods can be used with confidence to model polycondensation processes [7,8] because of the random nature of step-wise polycondensation reactions. Fragment methods have been successfully used to model the curing of epoxy–phenol resins [25], epoxy–amine condensation followed by epoxy-polyetherification [18,19] and even applied to study chainwise free-radical polymerizations [20]. It is acknowledged that, in principle, the network build-up in chainwise polymerizations is best described using models that take into account the primary chain distribution. However, fragment methods are greatly advantageous because of their simplicity and the lesser amount of calculations required for the modeling of the curing, as will be shown in the theoretical section.

In the present work, the pregel and postgel statistical averages of the primary chain and fragment network build-up methods are compared for a living polymerization and an initiator regeneration models, applied to the curing of epoxy–anhydride thermosets. The validity and applicability of the fragment method in comparison with the primary chain method is discussed.

2. Theoretical

2.1. Kinetic model definition

The curing kinetics and curing mechanism of epoxy–anhydride formulations with tertiary amines is complex, involving a series of competitive initiation, propagation, chain transfer and initiation regeneration steps [6,11,12,14,26–35]. Briefly, the main polymerization mechanism consists in an alternating anionic copolymerization between epoxy and anhydride groups. The occurrence of regeneration reactions and the likely presence of carboxyl groups complicate this simple scheme [11], but the presence of carboxyl groups may not alter the alternating copolymerization character of the curing process [29]. In a previous work [11] it was discussed a novel kinetic model, inspired on the model by Mauri et al. [14], that could be used to describe the curing process and the network build-up of epoxy–anhydride thermosetting formulations. This model, coded as SIM3, was compared with other simple models, in particular a simple living polymerization model coded as SIM1, and was found to describe more accurately both the curing kinetics and some features of the network build-up process [11].

Table 1 shows the reactive species that are considered in this work and their expression in terms of normalized concentration with respect to the initial amount of a
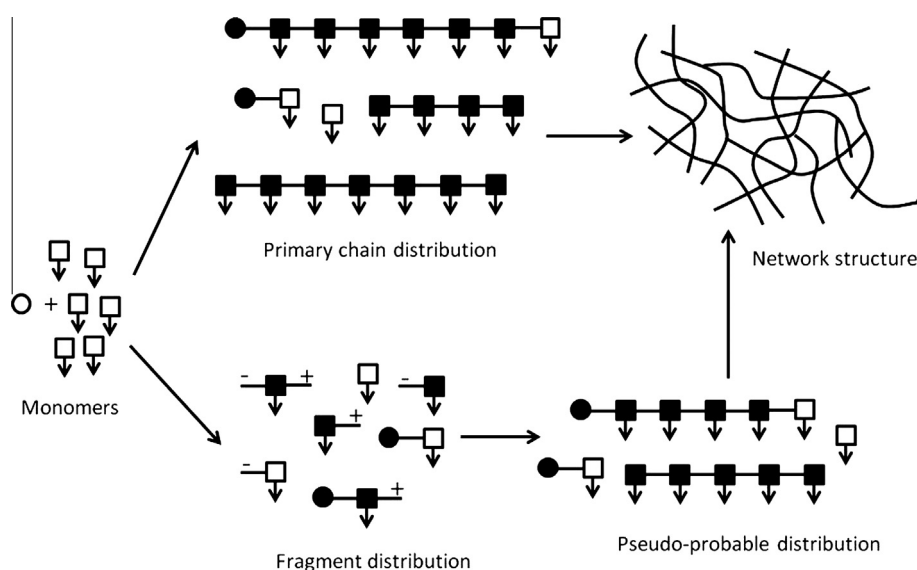

Fig. 1. Illustration of the differences between the primary chain method (above) and fragment method (below) for the network build-up during curing of thermosets.