



# Phenomenological characterization of sequential dual-curing of off-stoichiometric “thiol-epoxy” systems: Towards applicability

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## ABSTRACT

An extensive characterization of a sequential dual-curing system based on off-stoichiometric “thiol-epoxy” mixtures was carried out using thiol compounds of different functionality. The intermediate and final materials obtained after each curing stages at different thiol-epoxy ratios were studied by means of thermomechanical and rheological experiments. The storage and loss modulus and the loss factor  $\tan \delta$  were monitored during the curing process to analyse gelation and network structure build-up. The critical ratio for gelation was determined making use of the ideal Flory-Stockmayer theory and compared with experimental results. Intermediate materials obtained in the vicinity of the theoretical critical ratio did not have the mechanical consistency expected for partially crosslinked materials, did not retain their shape and even experienced undesired flow upon heating to activate the second curing reaction. The rheological results showed that the critical ratio is higher than the predicted value and that a softening during the second curing stage affects the shape-retention at this ratio. From the thermomechanical results, a wide range of intermediate and final materials with different properties and applicability can be obtained by properly choosing the thiol-epoxy ratio: from liquid-like to highly deformable intermediate materials and from moderately crosslinked (deformable) to highly crosslinked (brittle) final materials.

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## 1. Introduction

Crosslinked polymeric materials (thermosets) are used in many application fields because of their excellent thermal and mechanical properties (i.e. aviation, automobile, structures or coatings) [1]. The possibility of forming network structures with tuneable properties and the presence of reversible network relaxation processes make them suitable materials for more demanding applications such as self-healing materials, optical devices or lithographic printing [2,3]. Nowadays, the increasing demand of smart materials with complex shape designs (i.e. aircraft pieces, bio-inspired devices or shape-changing materials [4]), has become a great challenge for thermosets because accurate control of the curing process is necessary to fit the complex processing [5]. The formation of crosslinked network structures is a non-reversible process involving drastic changes in polymer and network structure with tight time-temperature constraints that need to be carefully controlled in order to produce components with required shapes and properties in complex processing scenarios. Recently, a new concept in crosslinking processes based on the sequential combination of two

polymerization processes (dual-curing processing) has come out as an interesting and versatile approach for better controlling of the network structure build-up and properties during processing [6–8].

Dual-curing systems arise from the combination of two compatible and well-controlled polymerization processes taking place simultaneously [9,10] or sequentially [11]. Sequential dual-curing has the advantage of forming an intermediate and stable material after the first polymerization process which is further transformed into the final material after the second polymerization process. This is commonly achieved by combination of polymerization processes triggered by different stimuli, such as UV-light and heat, or else has sufficiently different reaction kinetics. Examples of such processes include photo-curing/thermal-curing click thiol-ene/thiol-epoxy systems [11], aza-Michael addition/free-radical polymerization of amine-acrylate systems [12] and both photo-curing thiol-ene/cationic systems [13].

Click reactions are based on efficiency, versatility and selectivity [14–16], a combination of features that makes them suitable for dual-curing processing [11]. In particular, “thiol-click” reactions are highly interesting because they can react at mild conditions producing radical or anionic species in a controlled and efficient manner by appropriately choosing the catalyst [17–19]. Among them, the thiol-epoxy click reaction, a step-wise reaction mechanism catalysed by tertiary amines, which consists essentially in the nucleophilic attack to the oxirane ring by the thiolate anion, produces functional soft materials with

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excellent mechanical properties (high resistance and elongation at break) that can be useful in a first-stage life as shape-memory polymers (i.e. for size reduction in transport or storage processes) and further transform into new polymeric structures [20–22]. In our previous work [23], a new sequential dual-curing system based on off-stoichiometric thiol-epoxy mixtures with epoxy excess catalysed by tertiary amines was presented. The combination of the thiol-epoxy click reaction followed by the homopolymerization of the epoxy excess produces two-stage materials with tuneable thermomechanical and structural properties with the advantage of a single-pot reaction mechanism. Dual-curing processing is achieved in this case by the kinetics control of both curing reactions: the thiol-epoxy addition takes place rapidly at low temperature while the epoxy homopolymerization remains almost latent due to the slow kinetics at this temperature [24–27]. The intermediate and final material properties depend on the functionality and structure of the thiol and epoxy monomers or oligomers and the thiol-epoxy ratio or epoxy excess in the system. In our previous work [23], the network structure build-up during the thiol-epoxy reaction was analysed from a theoretical point of view assuming ideal step-wise behaviour. The critical ratio  $r_c$  which defines the minimum thiol-epoxy ratio to form a solid-like and therefore conformable material after the first curing stage was also predicted, a parameter that can be of relevance in the processing of complex shapes. Intermediate and stable materials ranging from highly viscous to solid-like and conformable materials can be obtained after the thiol-epoxy polymerization taking place at low temperature (first curing process). Hereafter, through an easy mechanically processing, complex shapes can be achieved which are further fixed by the formation of the new network structure caused by the epoxy homopolymerization taking place at higher temperature (second curing process).

In this work, thiol-epoxy dual-curing systems using thiol compounds of different functionality are studied in order to analyse their processing capabilities and the thermomechanical and physical properties of the multifunctional materials obtained. Mixtures at thiol-epoxy ratios below, close and above the critical ratio,  $r_c$ , were cured and the intermediate and final materials obtained were qualitatively analysed (deformability, consistency, colour, transparency and final shape). Some discrepancies from the theoretical behaviour were found in the processing of materials at the vicinity of  $r_c$ : the intermediate materials showed excessive deformation and even flow upon heating to activate the second curing reaction when they were not supposed to. The dual-curing process was therefore studied by means of rheological analysis in order to relate the viscoelastic behaviour during curing and, in particular, of the intermediate materials, with the observed behaviour. Relevant viscoelastic parameters such as the storage and loss modulus, and the loss factor  $\tan\delta$  were monitored at different frequencies. The experimental results were compared with the behaviour expected from the application of the well-known Flory-Stockmayer theory, for ideal step-wise processes, to the thiol-epoxy reaction occurring in the first curing stage. In addition, the thermomechanical and structural properties of the final materials were analysed by means of DMA and the applicability of all materials formed (intermediate and final materials) were discussed in order to optimise the performance of these multifunctional materials.

## 2. Materials and methodology

The epoxy resin diglycidyl ether of bisphenol A (DGEBA, GY240, Huntsman, Everberg, Belgium) with a molecular weight per epoxy equivalent of 182 g/eq was dried at 80 °C under vacuum during three hours prior to use. The curing agents pentaerythritoltetrakis(3-mercaptopropionate) (S4), with a molecular weight per thiol equivalent unit of 122.17 g/eq and trimethylolpropane tris(3-mercaptopropionate) (S3), with a molecular weight per thiol equivalent unit of 132.85 g/eq (both from Sigma-Aldrich, St. Louis, MO, USA) were used as received

and the catalyst 1-methylimidazole (1MI, Sigma-Aldrich, St. Louis, MO, USA) was used as received.

The mixtures were prepared by mixing the compounds in different thiol-epoxy ratios  $r$  with respect to the epoxy groups. One part per hundred of 1MI of the total mixture (1 phr) was used as catalyst. The mixture was manually stirred in a glass vial and rapidly poured in a Teflon mould. The first curing process was carried out at 50 °C during 3 h to ensure the completion of the thiol-epoxy reaction. Intermediate materials were obtained and the processing of different shapes was carried out using different techniques. Afterwards, the second curing stage was triggered by increasing the temperature up to 120 °C (at 5 °C/min controlled ramp) and maintaining the oven isothermally during 1 h at 120 °C followed by 1 h at 150 °C to ensure the completion of the epoxy homopolymerization. Final materials with different shapes were obtained.

In Fig. 1, the reaction scheme of the first curing process (thiol-epoxy polymerization) and the expected network structure of the intermediate material for a S3-DGEBA formulation is shown. In Fig. 2, the new network structure formed after the second curing stage (homopolymerization of the remaining epoxy) is presented.

### 2.1. Theoretical network build-up parameters

As mentioned in the introduction, one of the main advantages on using sequential dual-curing systems is to get an intermediate solid-like and conformable material. To this end, one approach is to define the thiol-epoxy ratio ensuring the gelation takes place during the first curing stage. The gel point conversion can be calculated, assuming ideal step-growth behaviour for the thiol-epoxy reaction, making use of the well-known theory of Flory-Stockmayer:

$$\alpha_{\text{epoxy, gel}} = \sqrt{\frac{r_{\text{thiol:epoxy}}}{(f_{\text{epoxy}} - 1) \cdot (f_{\text{thiol}} - 1)}} \quad (1)$$

In this expression,  $\alpha_{\text{epoxy, gel}}$  is the conversion of epoxy groups at the gel point,  $f_{\text{epoxy}}$  and  $f_{\text{thiol}}$  are the average functionality of epoxy and thiol monomers and  $r_{\text{thiol:epoxy}}$  is the ratio between thiol and epoxy functional groups. This only produces a valid gel point conversion for values of  $r_{\text{thiol:epoxy}}$  higher than  $r_c$  and lower than  $1/r_c$ , where  $r_c$  is the critical gelation ratio. This parameter can be obtained from the following expression:

$$r_c = \frac{1}{(f_{\text{epoxy}} - 1) \cdot (f_{\text{thiol}} - 1)} \quad (2)$$

In the case of formulations with excess of epoxy groups,  $r_{\text{thiol:epoxy}}$  will be always lower than 1 and therefore only condition for gelation and crosslinking during the first curing stage is that  $r_{\text{thiol:epoxy}} > r_c$ . For lower ratios, the amount of thiol is not sufficient to produce a network during the thiol-epoxy reaction.

### 2.2. Rheological characterization

The dual-curing process was analysed using a rheometer, TA Instruments, New Castle, AR-G2 equipped with an electrical heated plate device (EHP) and parallel plate geometry. Dynamo-mechanical experiments at different frequencies were performed to investigate the evolution of the storage and loss modulus ( $G'$  and  $G''$  respectively) during the curing process. The gel point was determined by the cross-over of the phase angle  $\delta$  at different frequencies. The experimental procedure is defined to simulate the curing procedure in the oven: 3 h at 50 °C with oscillation amplitude of 2% (until  $G'$  has reached a stable plateau) and of 0.5% (until the end of the curing process). Three different frequencies were continuously measured, from 1 to 10 Hz, 2 points per decade in logarithmic scale (1, 3.16 and 10 Hz). Afterwards, the

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