



Time-temperature-transformation (TTT) diagram of a dual-curable off-stoichiometric epoxy-amine system with latent reactivity



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ARTICLE INFO

Keywords:

Epoxy
Diamine
Dual-Curing
Latent base
Thermosets
Time-Temperature-Transformation (TTT) diagram

ABSTRACT

The time-temperature-transformation (TTT) diagram of the curing an off-stoichiometric amine-epoxy formulation with intermediate latent reactivity has been elaborated. The first curing stage is an epoxy-amine polycondensation taking place at low temperatures, while the second curing stage is an anionic homopolymerization of the excess epoxy groups, taking place at high temperatures and catalyzed by a latent base. The curing kinetics of the first and second curing stages have been analyzed separately by integral isoconversional procedures, and the kinetics data has been used to plot the isoconversion lines in the TTT diagram. The relationship between the glass transition temperature (T_g) and conversion has been determined experimentally and theoretically and used to determine the vitrification line in the TTT diagram. The results reflect the clearly different kinetic behaviour of both curing stages and a significant intermediate storage stability, which makes these curing systems highly attractive for multiple stage processing. The shape of the vitrification line also reflects the occurrence of different curing processes with different structure build-up. Safe processing and storage conditions can be easily defined on the basis of the TTT diagram. This is the first time the curing behaviour of dual-curing formulations is illustrated in such a clear and concise way thanks to the TTT diagram.

1. Introduction

Dual-curing, that is, the combination of two different polymerization processes taking place simultaneously or sequentially in a curing process, is a highly advantageous technology for the processing of thermosetting systems [1,2] because of its versatility and flexibility. A significant added value of sequential dual curing is possibility of controlling the curing process sequence and the intermediate and final network structures and properties [3–5]. This has potential application in multi-stage processing of one-pot formulations, where materials can be partially pre-cured before their storage, and with tailored material properties for the final application [4–7]. Processing or assembly and the final properties can be achieved whenever desired by using heat or UV light, depending on formulation chemistry, to initiate the final curing stage. Click-type reactions are commonly used in dual-curing formulations [1], in combination with other click [8,9] or non-click reactions [3,5]. Many dual-curable systems are based on acrylate reactions [2,5], although systems based on epoxy curing chemistries such as off-stoichiometric thiol-epoxy [3] or epoxy-amine [4,10] formulations, or other epoxy systems [11], are also gaining interest in the recent years.

We recently developed a novel off-stoichiometric epoxy-amine system, with excess epoxy groups and latent reactivity in the intermediate state [4]. The first curing reaction was a self-limiting epoxy-amine condensation that takes place at moderate temperatures until exhaustion of reactive amine groups. In the presence of a suitable initiator such as a nucleophilic tertiary amine [10], the excess of epoxy groups can undergo anionic homopolymerization at higher temperatures. However, in this recent work we employed a latent thermal base for the epoxy homopolymerization [4], which ensured at least 7 weeks of storage stability at 30 °C for intermediate materials after the completion of the epoxy-amine reaction. Different materials, coming from a wide range of formulations with different amine-epoxy ratios and tailored intermediate and final properties, were analyzed and characterized, but the curing kinetics of the systems were not analyzed in detail.

The purpose of this paper is to study the curing kinetics of an off-stoichiometric epoxy-amine formulation with a latent thermal base for the activation of the homopolymerization of the epoxy groups in excess. The relationship between glass-transition (T_g) and degree of conversion x is also determined (i.e. the $T_g(x)$ relationship). Gelation is not analyzed but the results from a previous work are used [4]. The results of this analysis are summarized in the conversion-temperature-

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transformation (CTT) diagram [12] and the time-temperature-transformation (TTT) diagram [13–16], which are used to illustrate the main transformations taking place during curing (i.e. gelation and vitrification) and the particular features of this dual-curing system. The CTT and TTT diagrams are also used to illustrate the predictive capabilities of the kinetic modelling employed in this work. The curing kinetics and glass transition temperatures are analyzed using differential scanning calorimetry (DSC). Isoconversional procedures are employed to determine the kinetic parameters, plot the isoconversional and vitrification lines of the TTT diagram and simulate other curing programmes.

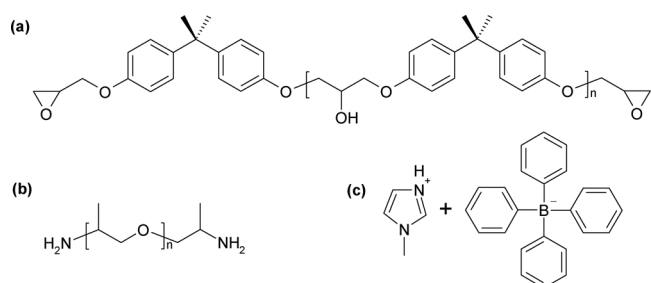
2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA, $M_w = 374$ g/mol or $M_w = 187$ g/ee, Epikote™) (DG hereafter) was kindly supplied by Hexion speciality Chemical B.V. and dried in vacuum before use. All other chemicals and reagents were purchased from Sigma-Aldrich and used as received. Poly(propylene glycol) bis(2-aminopropyl ether) (Jeffamine, $M_w = 400$ g/mol) (JEF hereafter), 1-methylimidazole (1MI) and sodium tetraphenylborate (NaBPh₄) were supplied by Aldrich and used as received. Methanol (MeOH) and chloroform (CHCl₃) were supplied by VWR and were used as received. 1MI-HBPh₄ (BG hereafter) was prepared using the procedure outlined in the literature [17,18]. Firstly, 1MI was solubilized in H₂O slightly acidified with 36% HCl solution (10 mmol in 2,6 mL H₂O and 1 mL HCl). NaBPh₄ was also solubilized in H₂O (11 mmol in 10 mL H₂O) stirred until homogeneous. The two solutions were mixed and the stirring maintained until the white salt formed as precipitate. The salt was filtered, washed thoroughly with distilled water and MeOH, recrystallized from a 4:1 mixture of MeOH and CHCl₃, filtered and dried under mild heat and vacuum. To analyze its purity, its melting point was measured in a DSC thermal scan and was found to be similar to what is reported for other equivalent salts [17,18]. The structures of DG, JEF, and BG are shown in Scheme 1.

2.2. Preparation of the curing mixtures

Samples were prepared in 5 mL vials in 1–2 gr batches using the following procedure: BG was weighed and added to DG and was kept under agitation at 90 °C for 15 min at complete solubilization. The mixture was left to cool down to room temperature after which the required amount of JEF was added, quickly stirred and immediately sent to analysis or sample preparation. DGJEF_0.5BG4 is a formulation in which one half of epoxy equivalents react with amine hydrogens and the other half homopolymerizes in the second curing stage, and 4 wt.% of BG. DGJEF_0.5 is the epoxy-amine formulation with the same excess of epoxy groups but without added initiator. DG_BG4 is the neat DG formulation with 4 wt.% of BG. The details of the composition of the formulations are shown in Table 1.



Scheme 1. Molecular structures of the chemicals used: (a) DGEBA (DG), (b) Jeffamine (JEF) and (c) 1MI-HBPh₄ (BG).

Table 1

Notation and composition of the formulations studied in this work.

Formulation	r^a	DG (wt. %)	JEF (wt. %)	BG (wt. %)	eq_{BG}/ee^b
DGJEF_0.5	0.5	78.9	21.1	0	0
DGJEF_0.5_BG4	0.5	75.7	20.3	4	0.0245
DG_BG4	0	96	0	4	0.0194

^a Ratio between reactive amine hydrogens and epoxy groups.

^b Equivalents of 1MI/Equivalents of epoxy groups.

2.3. Experimental techniques

A Mettler DSC822e equipped with a robotic arm was used. The equipment was calibrated using indium standards. Approximately 10 mg samples were cured in aluminium pans with pierced lids under a nitrogen atmosphere. The DSC was used to study the nonisothermal curing at 10 °C/min up to 300 °C and the isothermal curing at temperatures in the range of 70–100 °C for the first curing process, and 160–190 °C for the second curing process after pre-curing of the samples at 90 °C for 240 min. The degree of cure of the epoxy groups, x , and the reaction rate, dx/dt , were calculated as follows:

$$x = \frac{\Delta h_T}{\Delta h_{total}} \quad x = \frac{\Delta h_t}{\Delta h_{total}} \quad (1)$$

$$\frac{dx}{dt} = \frac{dh/dt}{\Delta h_{total}} \quad (2)$$

where Δh_T and Δh_t are the heat evolved up to a temperature T or time t during a dynamic or isothermal curing experiment, respectively. Δh_{total} is the total heat released during curing and dh/dt is the instantaneous heat flow released.

The glass transition temperature of the uncured formulation T_{g0} was determined in the dynamic curing at 10 °C/min starting at -100 °C. The intermediate glass transition temperature (T_{gini}) of the dual DGJEF_0.5BG4 was determined in a dynamic scan at 10 °C/min after isothermal curing at 90 °C for 240 min. The ultimate glass transition temperature ($T_{g\infty}$) of the fully cured sample (at 180 °C for enough time so as to complete the curing process) was determined after two consecutive dynamic scans at 10 °C/min, the first one to determine the presence of residual heat. The T_g was determined as the midpoint in the heat capacity step during the glass transition. The increase in heat capacity during the glass transition, ΔC_p , was also determined. The DIN method, included in the STARE software by Mettler, was used for these determinations.

The relationship between the degree of conversion and the glass transition temperature, $T_g(x)$, was determined from partially cured samples that were subsequently heated up at 10 °C/min to determine their T_g and the residual heat Δh_{res} , which allowed to determine the degree of conversion as:

$$x = 1 - \frac{\Delta h_{res}}{\Delta h_{total}} \quad (3)$$

3. Theoretical

3.1. Curing kinetics

The isoconversional methodology was used for the determination of the apparent activation energy during the curing process [19]. The basis for this methodology is the assumption that the reaction rate can be expressed as separate functions of conversion x and temperature T as:

$$\frac{dx}{dt} = k(T) \cdot f(x) \quad (4)$$

Where $k(T) = A \cdot \exp(-E/RT)$ is the kinetic constant, A is the

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