



# Analyzing the network formation and curing kinetics of epoxy resins by in situ near-infrared measurements with variable heating rates



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## ABSTRACT

Near-infrared spectroscopy (NIR) turned out to be well suited for analyzing the degree of cure for epoxy systems. In contrast to dynamic scanning calorimetry (DSC), where the released heat of reaction determines the degree of epoxy conversion indirectly, NIR spectroscopy is able to determine the conversion directly by analyzing structural changes. Therefore, a new heatable NIR cell was equipped with an integrated thermocouple, which enables the real sample temperature to be controlled and monitored in situ during epoxy curing. Dynamic scans at different heating rates were used for kinetic modelling, to define kinetic parameters and to predict real curing processes. The kinetic models and their parameters were validated with an isothermal and a more complex multi-step curing scenario. Two available commercial epoxy systems based on DGEBA were used with an anhydride and with an amine hardener. NIR results were compared with DSC data. The simulated conversion predicted with a model fitted on the basis of NIR and DSC dynamic scans showed good agreement with the conversion measured in the isothermal curing validation test. Due to the proven reliability of NIR in measuring the reaction progress of curing, it can be considered a versatile measurement system for in situ monitoring of component production in the automotive, aerospace and wind energy sectors.

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## 1. Introduction

Epoxy resins present amorphous thermosetting materials with excellent mechanical strength and toughness, outstanding chemical, moisture and corrosion resistance and good thermal, adhesive and electrical properties [1]. They have been used as coatings and adhesives, and especially as matrix material in composites combined with glass or carbon fibres [2]. The most important commercial epoxy resin is the linear difunctionalized diglycidyl ether of bisphenol A (DGEBA). Multifunctional hardeners are added to the resin to form a three-dimensional network. Typical hardeners are primary amines [3–5] and anhydrides [6–9]. The hardener type, the hardener concentration and the thermal curing procedure affect the curing process of epoxy resins. Especially the degree of cure has a high impact on the physical, mechanical and electrical properties of epoxy systems [10]. As the curing rate and extent of polymerization are highly dependent on processing conditions

[11], knowledge of curing kinetics is essential to adjust the material properties. During and after reaction, the degree of curing can be determined using indirect and direct methods. Indirect methods are based on rheology [12,13], the velocity of ultrasound [14,15] or the release of reaction heat [5,16]; the last, based on differential scanning calorimetry (DSC) [5,11,16–21], turned out to be an especially reliable method for investigating curing kinetics. However, all of these methods measure a cumulative parameter, which can be affected by local side reactions, gelation, vitrification or temperature changes.

The epoxy conversion can also be measured directly by structural changes using spectroscopic methods like near-infrared (NIR) [4,22–25], mid-infrared (MIR) [26–29] or Raman [30–32] spectroscopy. In the NIR region bands are often difficult to evaluate due to mode coupling and overtones, hence MIR spectroscopy is often preferred to analyze chemical composition. However, particularly for investigating the curing of epoxy resins it turns out that the sharpness and unambiguousness of the characteristic absorption peaks in the NIR are more reliable [4,22,33]. In 1963, Dannenberg et al. pioneered the NIR region for the quantitative analysis of epoxy resins [34]. A comprehensive comparison of NIR and MIR

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spectroscopy evaluated with DSC and size exclusion chromatography (SEC) on epoxy curing was carried out by Poisson et al. in 1996 [4,22], where they demonstrated the comparability of NIR, DSC and SEC to determine the degree of cure, whereas the MIR systematically underestimates the conversion. Pandita et al. [24] could confirm the comparability of NIR and DSC with isothermal experiments. Furthermore, measuring in the NIR rather than the MIR region offers the possibility to measure samples with greater layer thicknesses (up to several millimetres), using low-cost glass cuvettes and materials containing glass fibres, because the glass fibres absorb the infrared irradiation above an excitation wavelength of 5  $\mu\text{m}$ .

A study of kinetic model parameters for epoxy resins can be carried out by means of isothermal or dynamic experiments with variable heating rates. Isothermal experiments at high temperatures are difficult to realize and inadequate due to a lack of information at the beginning of measurement, caused by a fast start of curing and by sample handling. Nevertheless, isothermal experiments are used in the literature almost exclusively to determine kinetic parameters with NIR spectroscopy [35–37]. This is probably due to the absence of a well-controlled heatable NIR cell with adjustable heating rates. Therefore, in this work dynamic NIR measurements with temperatures from 30 °C up to about 250 °C with defined variable heating rates were performed to determine kinetic models. Two commercially available DGEBA epoxy resin systems were investigated in this study. The first system studied, cured with an anhydride curing agent, was Araldite® LY556 HY917 DY 070. The second epoxy system was Epikote™ RIM 135/137, which is cured with an amine curing agent. The experimental results were evaluated with the “Thermokinetics” software by Netzsch. Finally the kinetic models determined were validated and compared with isothermal runs and multi-step curing scenarios.

## 2. Experimental

### 2.1. NIR measurements

The experiments were performed with a new heated NIR Cell from Pike Technologies (Madison, USA) which was modified by RESULTEC analytic equipment (Illerkirchberg, Germany) and used in transmission mode (Fig. 1). This cell was developed for heating samples from room temperature up to 300 °C with a maximum heating rate of 10 K min<sup>-1</sup>. Cuvettes of optical glass (Starna Scientific Limited, Essex, England, type: 1/G/1), of 1 mm layer thickness



Fig. 1. Computer-controlled heatable NIR cell.

were used. The computer-controlled dynamic experiments were carried out using four different heating rates of 1, 3, 5 and 10 K min<sup>-1</sup> from 30 to 250 °C. NIR spectra were recorded using a Nicolet 6700 FT-IR spectrometer (Nicolet Instruments, Offenbach, Germany) equipped with a white light source and a mercury cadmium telluride detector (MCT-A). The measurements were performed within a wavelength range from 4000 to 7500 cm<sup>-1</sup> and with a resolution of 4 cm<sup>-1</sup>, averaging 16 scans. Spectra were recorded continuously with a time interval of 15.6 s per spectrum by OMNIC software (Thermo Fischer Scientific, Karlsruhe, Germany).

For sample preparation about 2–3 g of resin was weighed in a glass vial. Subsequently, calculated amounts of hardener and accelerator (if required) were added and stirred for about 60 s to achieve homogeneity. The mixture was injected with a syringe. A thermocouple was plunged into the resin to enable precise temperature determination. The recording time interval of the spectrometer and the thermocouple were different. Therefore, the temperatures were assigned to spectra by linear regression of the temperature time profiles.

For the validation experiments isothermal curing was performed at 80 °C. The thermocouple was inserted after the desired temperature was reached. The NIR cell was placed in the spectrometer and the experiment was started. A more complex multi-step curing scenario was performed, beginning at 30 °C. Subsequently the sample was heated to 60 °C at a rate of 4 K min<sup>-1</sup>, and this temperature maintained for 10 min. It was further heated to 230 °C at 6 K min<sup>-1</sup>, followed by 10 min at 230 °C. For further evaluations only the sample temperatures from the inserted thermocouple were used.

### 2.2. DSC measurements

A TA Q-2000 DSC from TA Instruments (New Castle, USA) is used to measure the reaction's enthalpy and the glass transition temperature ( $T_g$ ) of the conducted isothermal and dynamic experiments. The attached cooling system RCS90 allows the samples to be cooled down rapidly to -90 °C. Hermetic aluminium pans are used, and samples weighing 6–8 mg are placed in the pans. Several samples are prepared in a single batch and stored at -18 °C in order to interrupt the reaction. The samples are tested with 1, 3, 5 and 10 K min<sup>-1</sup> heating ramps, with the temperature rising from -25 °C (40 K below onset temperature) to 280 °C. The TA Q-2000 was calibrated with indium and sapphire specimens. The heat flow, temperature and time were recorded and used to calculate the degree of conversion and the conversion rate.

### 2.3. Materials

Two kinds of commercial available epoxy systems were used, an amine-cured epoxy system and an anhydride-cured epoxy system. An overview of the trade and IUPAC names, chemical structures and composition of epoxy mixtures is given in Table 1 (all information is taken from material data sheets).

The first resin system investigated was Araldite® LY556, which consists of DGEBA. It was cured with the curing agent HY917, a methyltetrahydrophthalic anhydride (MTHPA). The reaction was accelerated by DY 070, a 1-methylimidazole. They were mixed at a weight ratio of 100:90:2 respectively. The anhydride cured epoxy system was purchased from Ciba Specialty Chemicals Inc.

The other resin, Epikote™ MGS™ RIMR 135 was a mix of DGEBA and the aliphatic epoxy 1,6-hexanediol diglycidyl ether. It was cured with the Epikure™ Curing Agent MGS™ RIM H 137, an aliphatic primary amine mixture of isophorondiamine and alkyletheramine. The weight ratio of resin and hardener was

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