

Effects of thermal history on the polymerisation mechanism and network development in aromatic polybenzoxazines



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ABSTRACT

The effect of heating rate (2, 8 and 15 K min⁻¹) during the initial stages of cure of 2,2-bis(3,4-dihydro-3-phenyl-2H-1,3-benzoxazine)propane is examined. The rate of heating has a marked effect on the observed modulus, measured by DMTA, with the higher heating rate giving rise to an increase in storage modulus of ca. 1000 MPa, although this is not accompanied by an increase in glass transition temperature. The thermal stability of the resulting polybenzoxazines also differs with the slower heating rate giving rise to less thermally stable structures. Data obtained from Raman spectroscopy (when combined with principal components analysis) suggest subtle changes in the mechanism during the early stages of reaction associated C–N–C and C–O moieties, some of which persist following a higher temperature postcure step leading to a crosslinked network with higher aliphatic character.

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1. Introduction

Poly(bis-benzoxazine)s (sometimes simply referred to as polybenzoxazines [1]) are a family of thermosetting polymers that are made up through step growth ring-opening polyaddition from bis-benzoxazine monomers (Fig. 1), which are in turn the products of the Mannich reaction between a bis-phenol, formaldehyde and a primary amine [2]. The monomer–oligomer ratio in the yield can also be influenced by using an excess of formaldehyde and amine during the synthesis; causing the products to form via a different mechanism and resulting in a greater proportion of monomer in the product [3]. This, in turn, affects the properties of the resin before, during and after cure (the presence of oligomers bearing hydroxyl groups in the chain is known to enhance the reactivity of the benzoxazine [4]).

In a previous, unrelated study, we compared the effect of performing dynamic and isothermal cure programmes on commercial epoxy resins initiated with imidazole derivatives [5]. It was found that, contrary to expectation (and conventional wisdom), the influence of the heating programme on the initial reaction and the early stages of network formation was of great importance and persisted throughout the crosslinking process. This led to the finding that, for a given epoxy resin, the measured T_g was not always proportional to measured conversion because the architectural and conforma-

tional structure were more influential. In the present work we conducted a similar examination of the dependence of network growth and architecture on cure conditions. In this paper we present the results of a study into the influence of thermal history on the resulting network formed and its physical properties. The findings have implications for the employment of a cure schedule designed to optimise network development and physical properties.

2. Materials

The monomer, 2,2-bis(3,4-dihydro-3-phenyl-2H-1,3-benzoxazine)propane, based on bisphenol A and aniline (BA-a), (Fig. 2) was used as received (ex Huntsman Advanced Materials, Basel) without further purification having been fully characterised (see Supplementary) and reported in a previous publication [6].

2.1. Cure of polymer samples for thermo-mechanical analyses

The BA-a monomer was first degassed at ca. 100 °C (1 h) and cured in aluminium dishes (55 mm diameter, depth 10 mm) and transferred to a fan-assisted oven set at 90 °C. The samples were allowed to equilibrate before being heated at 2, 8 or 15 K min⁻¹ to 180 °C (2 h isothermal) + heating at 2 K min⁻¹ to 200 °C (2 h isothermal) followed by a gradual cool (3 K min⁻¹) to room temperature. Cured samples were cut to the correct token size for analysis using a diamond saw.

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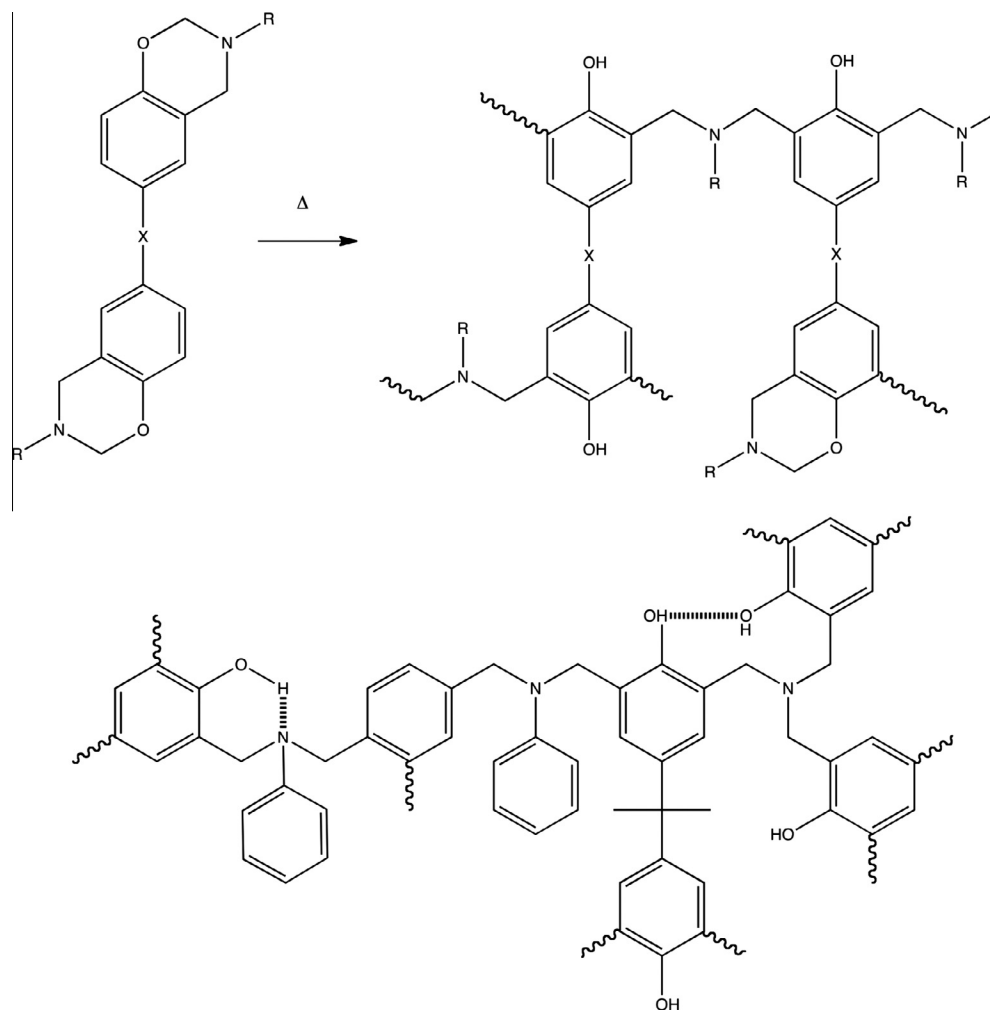


Fig. 1. Polymerisation of bisbenzoxazines through ring opening and crosslinking and representative network.

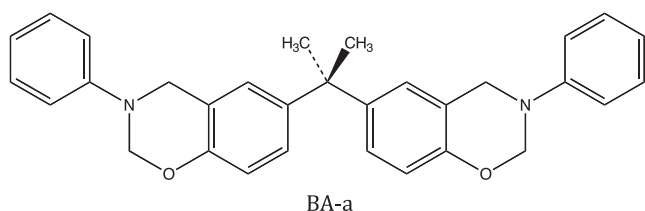


Fig. 2. Bis-benzoxazine monomer structure.

2.2. Instrumentation

Vibrational spectra were obtained using a Perkin–Elmer system 2000 Fourier Transform (FT) NIR-Raman spectrometer operating at 250–500 mW (Nd-YAG laser) and a Perkin–Elmer Fourier Transform infrared (FTIR) system 2000 spectrometer. Samples that were analysed *in situ* during the cure process using Raman spectroscopy employed a heated cell that was ramped from 50 °C to 180 °C (at 2, 8 and 15 K/min) and held isothermally for 120 min (and samples being presented in Durham tubes); spectra being taken at intervals of *ca.* 10 min. For each measurement, 10 spectra were obtained at a resolution of 4 cm⁻¹ and co-added to produce the final spectrum. Samples were post cured at 200 °C (2 h).

In contrast, samples analysed *ex situ*, were first cast from chloroform (GPR) on to pre-pressed KBr disks and the solvent removed in a fan oven (50 °C, 30 min). For each measurement, 16 spectra were

obtained at a resolution of 4 cm⁻¹ and co-added to produce the final spectrum. Chemometrics analysis (PCA) was carried out on the spectral data using The Unscrambler X, v10.1 software (Camo, Oslo).

Dynamic mechanical thermal analysis (DMTA) (in single cantilever mode at a frequency of 1 Hz) was carried out on cured neat resin samples (2 mm × 10 mm × 17 mm) using a TA Instruments TA Q800 operating in static air.

Thermogravimetric analysis (TGA) was performed on a TA Instruments TA Q500 on milled, cured resin samples (5.5 ± 0.5 mg) in a platinum crucible from 20 to 1000 °C at 10 K min⁻¹ in air and nitrogen (40 cm³ min⁻¹).

3. Results and discussion

3.1. Examining the effect of heating rate on network growth and physical and mechanical properties

The starting point for this study was our observation that the polybenzoxazine produced from BA-a, PBA-a, yielded thermomechanical behaviour that differed markedly (triplicate measurements shown in Fig. 3) when the monomer was cured (sample heated to 180 °C, isothermal 2 h + sample heated to 200 °C, isothermal 2 h) at different initial heating rates. Furthermore, although the glass transition temperatures of all three materials were similar (*ca.* 169–173 °C based on the peak maxima values of the loss moduli), the storage modulus varied significantly with

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