

Towards the rational design of polymers using molecular simulation: Predicting the effect of cure schedule on thermo-mechanical properties for a cycloaliphatic amine-cured epoxy resin



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ABSTRACT

We report prediction of selected physical properties (*e.g.* glass transition temperature, moduli and thermal degradation temperature) using molecular dynamics simulations for a difunctional epoxy monomer (the diglycidyl ether of bisphenol A) when cured with *p*-3,3'-dimethylcyclohexylamine to form a dielectric polymer suitable for microelectronic applications. Plots of density *versus* temperature show decreases in density within the same temperature range as experimental values for the thermal degradation and other thermal events determined using *e.g.* dynamic mechanical thermal analysis. Empirical characterisation data for a commercial example of the same polymer are presented to validate the network constructed. Extremely close agreement with empirical data is obtained: the simulated value for the glass transition temperature for the 60 °C cured epoxy resin (simulated conversion $\alpha = 0.70$; experimentally determined $\alpha = 0.67$ using Raman spectroscopy) is *ca.* 70–85 °C, in line with the experimental temperature range of 60–105 °C (peak maximum 85 °C). The simulation is also able to mimic the change in processing temperature: the simulated value for the glass transition temperature for the 130 °C cured epoxy resin (simulated $\alpha = 0.81$; experimentally determined $\alpha = 0.73$ using Raman and $\alpha = 0.85$ using DSC) is *ca.* 105–130 °C, in line with the experimental temperature range of 110–155 °C (peak maximum 128 °C). This offers the possibility of optimising the processing parameters *in silico* to achieve the best final properties, reducing labour- and material-intensive empirical testing.

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1. Introduction

Epoxy resins are one of the most important families of cross-linked, thermosetting polymers [1], which offer a good balance of desirable properties in the neat resin: flexural strength (125 MPa), tensile strength (55 MPa), compressive strength (130 MPa) and impact strength (35–40 MJ/mm²) coupled with a reasonably high glass transition temperature (T_g) of 130 °C [2]. This has led their widespread use in a variety of applications, including advanced composites, adhesives and as high performance dielectrics for microelectronic applications (typical dielectric constants are between 3 and 5 and dissipation factors of 0.002–0.020 at ambient conditions). Polymerization may occur either in the absence or in the presence of curing agents, and in this particular instance a liquid cycloaliphatic diamine is used to facilitate ease of processing with the composite reinforcement (allowing good infiltration) and also rapid, low temperature cure. The cured epoxy also displays good adhesion to a variety of substrates, hardness, chemical inertness and thermal resistance, but the effect of the size of

the polymer network (*i.e.* the conversion) on the final properties can be highly significant. Thus, it is important to be able to predict the likely changes in properties in order that cure conditions might be optimised. This paper is the first to use molecular simulation to predict both glass transition temperatures and thermal stability in diamine-cured epoxy resins as the cure parameters are varied.

Molecular Dynamics (MDs) simulations have been used for a number of decades in the pharmaceutical industry in the search for new lead compounds for drug development and was used to examine the dynamics of biomacromolecules [3] as early as 1977. The application of computational techniques to simulate or predict chemical properties in polymers is a more recent development and although the less complex problem of modelling thermoplastics, such as polystyrene [4], poly(methyl methacrylate) [5], polyethylene oxide [6] and poly(arylene ether sulphone)s [7], is well established. However, the problem of addressing complex network structures is more challenging and, whilst our group has been active in this area since the early 1990s [8–14] and have reviewed the topic [15], it is still an area of research that remains comparatively overlooked. For example, Liao et al. [16] used MD to examine the effect of structural imperfection and stoichiometry on the position of gel point and the nature of the network formed.

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Commonly, the problem of constructing a representative network, containing 'defects' or structural irregularities, limits the accuracy of the simulation produced. A more highly crosslinked, 'perfect' network will almost inevitably yield an overestimate of elastic or mechanical properties, since the thermoset polymer on which it is based will probably only reach a conversion of 80–90% at best following extensive postcure treatment. Recently, Shenogina et al. [17] published MD simulations of epoxy networks and confirmed this observation.

Despite the established use of materials simulation in academia, the materials industry has been somewhat more conservative in its slower adoption of the same techniques despite the undoubted power of the approach. The more widespread availability (as commercial software or freeware) of various polymer-modelling programs, e.g. Gromacs [18], Tripos Sybyl [19] and Materials Studio [20], etc. makes it possible to incorporate these methods in the selection for new candidate polymers for specific applications based on e.g. their physical or mechanical properties. The interactions between the atoms in the MD simulations are based on Newton's laws of motion [21]. Using these classical mechanics to simulate the movement of the polymers under investigation, several physical properties of the polymers can be predicted. These include the volume [22], density [23], T_g [24] and Young's modulus [25], as well as the electronic conduction [26], blend miscibility [27] and thermal stability [28] of polymers.

The aim of this paper is to investigate the prediction of selected physical properties, e.g. the glass (α) transition temperature and the onset of thermal decomposition, of a well-researched, widely published epoxy resin using MD simulations. In order for the simulation to be valid it should reflect as well as possible the real structure and thus the first part of the paper establishes (through thermal and spectroscopic analyses) the nature of the thermoset polymer network. We go onto show that very good agreement can be obtained between empirical thermo-mechanical data at two different cure temperatures. The effect of moisture ingress on the modulus and glass transition temperature, a known Achilles' heel of epoxy polymers, is also addressed in our simulations and will be further developed in a subsequent publication.

2. Experimental section

2.1. Materials

The oligomer, based on DGEBA (eew = 175.5 ± 3.5 g/mol., Hexion) and *p*-3,3'-dimethylcyclohexylamine (Hexion) (Fig. 1) were characterised using Raman and ^1H NMR spectroscopy and used as received.

2.2. Blending and cure of polymer samples for thermo-mechanical analyses

Since both reagents were liquids, the epoxy (10 g) was heated to 50 °C to reduce the viscosity and a measured quantity of diamine (3.4 g) was added and stirred to achieve a one-phase mixture. The sample was then cooled and stored prior to analysis. Samples for DMTA measurements were cured in aluminium dishes (55 mm diameter, depth 10 mm) in a fan-assisted oven: heating from room temperature to 60 °C (4 h isothermal) + heating to 130 °C (3 h isothermal) followed by a gradual cool to room temperature. Cured samples were cut to the correct token size for analysis using a diamond saw.

2.3. Polymer characterisation

Vibrational spectra were obtained using a Perkin–Elmer system 2000 FT-NIR-Raman spectrometer operating at 250 mW (Nd-YAG laser) and a Perkin–Elmer FTIR system 2000 spectrometer. Samples were analysed *in situ* during the cure process using Raman spectroscopy employed a heated cell that was ramped rapidly from room temperature to 60 °C and held isothermally for 4 h; spectra being taken at intervals of ca. 7.5 min. For each measurement, 16 spectra were obtained at a resolution of 4 cm^{-1} and co-added to produce the final spectrum. Samples were post cured at 130 °C (3 h). Chemometrics analysis (PCA) was carried out on the spectral data using the Unscrambler X, v10.1 software (Camo, Oslo).

Differential scanning calorimetry (DSC) was undertaken using a TA Instruments Q1000 running TA Q Series Advantage software on samples (6.0 ± 0.5 mg) in hermetically sealed aluminium pans. Experiments were conducted at a heating rate of 10 K/min from room temperature to 250 °C (heat/cool/heat) under flowing nitrogen ($50 \text{ cm}^3/\text{min}$). The T_g was determined from the midpoint of the inflexion in the heat flow curve during the re-scan (heating) experiment. 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 \times 15 mm \times 35 mm) using a TA Instruments Q800 operating in static air.

For the determination of moisture content, samples of cured epoxy resin (2 mm \times 12 mm \times 30 mm) ± 0.5 mm were conditioned in three chambers each of controlled relative humidity: 33% RH (containing magnesium chloride), 53% RH (containing magnesium nitrate) and 75% RH (containing sodium chloride); each salt solution comprised distilled water. Samples were allowed to equilibrate over approximately 12 months and the moisture content of the cured epoxy resins was determined periodically by measuring the increase in mass. Thermogravimetric analysis (TGA) was

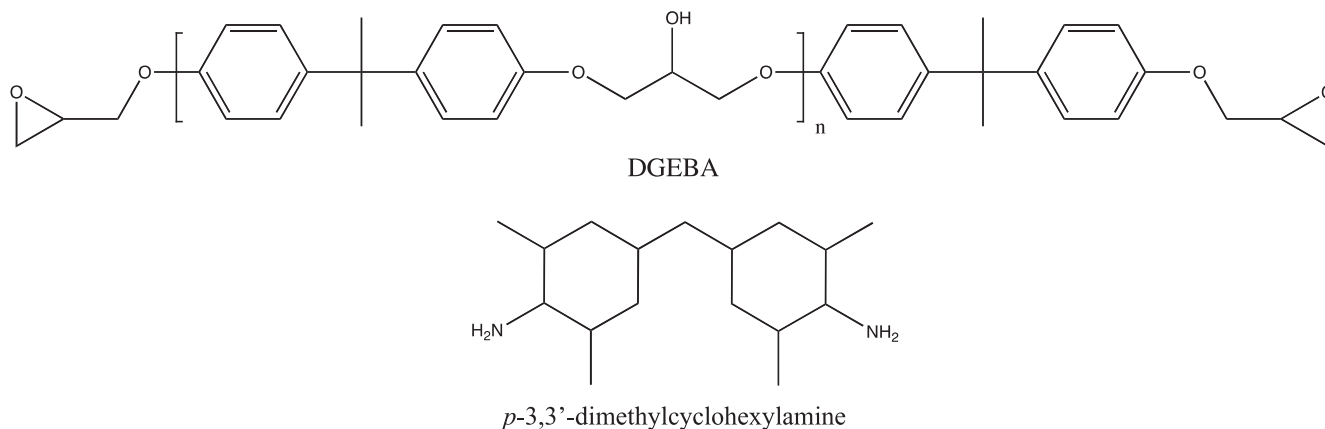


Fig. 1. Structures of the reagents used in this work.

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