



ORIGINAL ARTICLE

Molecular scale cure rate dependence of thermoset matrix polymers



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Abstract This manuscript demonstrates the molecular scale cure rate dependence of di-functional epoxide based thermoset polymers cured with amines. A series of cure heating ramp rates were used to determine the influence of ramp rate on the glass transition temperature (T_g) and sub- T_g transitions and the average free volume hole size in these systems. The networks were comprised of 3,3'-diaminodiphenyl sulfone (33DDS) and diglycidyl ether of bisphenol F (DGEBF) and were cured at ramp rates ranging from 0.5 to 20 °C/min. Differential scanning calorimetry (DSC) and NIR spectroscopy were used to explore the cure ramp rate dependence of the polymer network growth, whereas broadband dielectric spectroscopy (BDS) and free volume hole size measurements were used to interrogate networks' molecular level structural variations upon curing at variable heating ramp rates. It was found that although the T_g of the polymer matrices was similar, the NIR and DSC measurements revealed a strong correlation for how these networks grow in relation to the cure heating ramp rate. The free volume analysis and BDS results for the cured samples suggest differences in the molecular architecture of the matrix polymers due to cure heating rate dependence. © 2015 The Authors. Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Due to a relatively low cost and high thermo-mechanical performance, carbon fiber reinforced polymer composites (CFRPs) typically utilize a thermoset epoxy/amine based polymer (Morgan, 2005). When aromatic amines are used to cross-link the epoxide component high thermal and mechanical performance is often observed (Palmese and McCullough, 1992; Kanchanomai et al., 2005). To realize the high thermo-mechanical performance of these polymers, curing temperatures above 150 °C are often used (Davies et al., 2007; Min et al., 1993; Vyazovkin and Sbirrazzuoli, 1996; Um et al.,

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2002). Furthermore, it is widely reported that the maximum curing temperature of the polymer will significantly impact these properties and is often chemistry specific (Jackson et al., 2011; Zhang et al., 2009; Barton et al., 1998; Guerrero et al., 1996). One of the most common and practical attempts to increase the production speed is to reduce the cycle time for each part, either by increasing the cure heating ramp rate, or allowing a controlled exotherm to cure the part well after removal from an oven.

Despite this drive to drastically increase the cure heating ramp rate, there is little to no published literature about the effect of the ramp rate on the polymer component of the composite. It is commonly believed that as long as an identical extent of cure (conversion) is reached, the polymers must be identical, regardless of heating rate. However, considering the complex kinetics of thermoset matrix polymers it becomes evident that an extent of conversion alone may not provide a clear understanding of the network development during polymer cure (Rosu et al., 2002).

To understand the complex relationships between the cure heating ramp rate, matrix polymer development, and final thermo-mechanical properties, this work will focus on the cure heating rate dependence of a model system for the study of aromatic epoxy/amine thermoset polymers. Differential scanning calorimetry has been used along with near infrared spectroscopy to gain insight into the development of thermoset polymer networks based on diglycidyl ether of bisphenol F and 3,3'-diaminodiphenyl sulfone. Positron annihilation lifetime spectroscopy and broadband dielectric spectroscopy have been used to determine the molecular size scale impact of cure heating ramp rate on the polymers. As a result, we were able to relate the cure heating ramp rate to network architectural formation and report an impact on the molecular level from variations in cure heating ramp rate.

2. Materials and methods

2.1. Materials

The amine (curative) selected for this work was 3,3'-diaminodiphenyl sulfone (33DDS), and was obtained from Royce International. The molecular weight is 248.3 g/mol and the equivalent hydrogen weight (EHW) is 62.08 g/eq. Before use, it was dried overnight in a vacuum oven at 50 °C to remove any residual water present. The epoxide used in this work was the diglycidyl ether of bisphenol-F (DGEBF), obtained as EPON-862 from Hexion Specialty Chemicals. The average molecular weight was 338 g/mol, with an equivalent epoxide weight (EEW) of 169 g/eq. The DGEBF was used as received.

2.2. Thermoset matrix formulation

Matrix polymers were synthesized by adding epoxide (DGEBF) into an Erlenmeyer flask with a vacuum fitting and magnetic stir bar. The epoxide was then heated to 65 °C and vacuum of approximately 10^{-3} torr was applied to remove any air, water, or solvent impurity present in the epoxide. After degassing was complete, vacuum was removed, and amine was added to the reaction vessel. The amount of amine added varied by formulation; however, in all cases, the ratio of epoxide concentration

to active amine hydrogen was maintained at 1:1. In a typical reaction of DGEBF epoxide and 33DDS amine, approximately 70 g epoxide and 26 g amine were used. After the amine was added, the system was vigorously stirred to mix the amine and epoxide components and vacuum was reapplied. After no residual gas evolved from the reaction flask, the temperature is raised from 65 °C to the dissolution temperature of the amine. Upon amine dissolution in the epoxide, the matrix polymer was cast into various geometries for curing. To cure, formulations were heated from 35 to 180 °C at variable ramp rates and held for three hours at 180 °C. Matrix polymers were prepared at the following heating ramp rates: 0.5, 1.0, 2.5, 5.0, 7.5, 10.0, 12.5, 15 and 20 °C/min.

2.3. Differential scanning calorimetry (DSC)

Matrix thermal properties were conducted on a DSC Q200 (TA Instruments). All experiments were calibrated to Indium and Sapphire temperature and enthalpy standards, respectively. Additionally, in all cases, nitrogen was used as the purge gas. Dynamic DSC experiments to determine the exotherm intensity of various cure ramp rates were conducted by placing approximately 30.0 mg of uncured polymer matrix within a hermetically sealed TZero® aluminum DSC pan from 35–180 °C at rates of 1.0, 5.0, 10.0, 15.0, and 20.0 °C/min. In some cases, dynamic and isothermal DSC experiments were conducted consecutively to determine the extent of residual cure and residual exotherm intensity. In these cases, the dynamic experiments were conducted as described above, and the samples were held at 180 °C for three hours to ensure complete cure. Heat/cool/heat (HCH) experiments were also conducted during the analysis to determine glass transition temperature and completeness of cure. The heating and cooling rates for the HCH-DSC experiments were held at 5.0 °C/min with a minimum and maximum temperature of 35 °C and 180 °C.

2.4. Near infrared spectroscopy (NIR)

Near infrared spectra in transmission mode were collected using a Nicolet 6700 FTIR (Thermo Scientific) with variable temperature cell in the range of 4000–8000 cm^{-1} . A white light source with a potassium bromide beam splitter and DTGS potassium bromide detector were used. Samples were prepared by placing, dropwise, B-staged polymer between two glass slides that are separated by a 0.8 mm Teflon® spacer. The samples were then reacted while in a Simplex Scientific Heating Cell. While heating, 32 scans at a 4 cm^{-1} resolution were acquired every 5 min.

2.5. Broadband dielectric spectroscopy (BDS)

Dielectric spectra were collected isothermally using a Novocontrol GmbH Concept 80 Broadband Dielectric Spectrometer over the frequency range 0.1 Hz–3 MHz and temperature range of –80 to 300 °C. Temperature stability was controlled to within ± 0.5 °C. Matrix polymer samples with approximate thickness of 200 μm were prepared by placing uncured polymer on an aluminum panel covered with a Teflon® sheet. An identical panel with Teflon® was placed over the sample. The polymers were cured as described previously. Samples films were kept in a humidity controlled chamber (Model

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