Real-time quantification of network growth of epoxy/diamine thermosets as a function of cure protocol

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ABSTRACT
Traditionally, understanding of thermoset cure has been limited to the analysis of a single degree of cure value obtained via techniques such as dynamic scanning calorimetry. Such analyses limit the scope of understanding of network development during cure. The continued development of rapid cure matrix chemistries necessitates the advancement of analytical techniques capable of quantifying how thermal cure profiles influence crosslinked network architectures throughout cure. In this work, the formation of epoxy/diamine networks was studied, in real time, throughout cure with Fourier Transform Infrared Spectroscopy in the near infrared region (NIR). The NIR technique allows for direct quantification of all functional groups directly involved in the cure of aerospace matrices. This work establishes a means to view a complete picture of the development of epoxy/diamine networks throughout cure, which allows for a more complete understanding of the effect of cure protocol on final network structure.

Introduction
Within the composites industry, there is an inherent drive to expedite part turnover. Increased temperature ramp rates during cure of thermosetting polymer networks is a desirable strategy to reduce cycle time, especially as novel out-of-autoclave technologies continues to push the industry standards [1]. However, the effects of rapid cure rates on epoxy/diamine glassy thermoset networks such as those commonly used as matrices in high performance composite panels are yet to be determined.

While there are many potential effects to consider, when decreasing matrix cure cycle time, this work seeks to understand the effect of varied cure protocols on epoxy-amine network formation during cure. Traditionally, much attention is placed on the final material properties of a cured network and this becomes the only metric to determine the effect of some experimental variable, such as cure protocol. Very little is understood about the state of the network during cure, as the network develops. This is predominantly due to the limited availability to quantify the extent of the epoxy/amine reaction with traditional characterization techniques such as rheology and dynamic scanning calorimetry (DSC).

This work showcases the ability to directly monitor the development of epoxy/diamine networks using real-time Fourier transform infrared spectroscopy (RT-FTIR). With this technique the concentration of specific functional groups can be observed independently throughout cure. This contrasts with the more commonly used DSC heat of reaction technique, which produces one degree of cure value for analysis. RT-FTIR is not only able to quantify the extent of reaction but is also able to distinguish...
the identity of functional groups reacting. This is valuable in epoxy/diamine networks as observing the production and consumption of primary and secondary amines gives insight into the evolution of network morphology in real time. An understanding of the pathway of network formation by this analytical method also has the potential to inform and improve predictive computer modeling [2].

The epoxide prepolymers diglycidyl ether of bisphenol F (DGEBF) and tetraglycidyl-4,4’-diaminodiphenylmethane (TGDDM) were selected because they are representative precursors of standard commercially relevant high glass transition temperature (Tg) glassy epoxy matrices [3, 4]. Both epoxy prepolymers were mixed with the 3,3’-diaminodiphenyl sulfone (33DDS) diamine curative. While the chemical backbone of the two epoxides are similar (as can be observed in Figure 1), the functionality of DGEBF is two and four for TGDDM. It is known for these systems that the network with the higher average functionality (the TGDDM containing system) will theoretically gel earlier in the reaction and have a higher crosslink density in the final cured system [5]. RT-FTIR analysis of these two networks during cure allows for an investigation into the role of average functionality of an epoxy/diamine network during network formation.

Experimentation

Materials preparation

DGEBF (Epon™ Resin 862, Hexion Inc., Houston, TX) with an epoxide equivalent weight (EEW) of 165–173 g/epoxide or TGDDM (Araldite MY721, Huntsman Chemical Company, The Woodlands, TX, EEW: 111–117 g/epoxide) was mixed with solid 33DDS (Royce International, Akron, OH, >99% pure, 4 μm particle size). All networks were formulated using a 1:1 stoichiometric equivalent of epoxide to amine active hydrogen. Samples were physically mixed at low temperatures, careful to avoid premature reaction, forming a slurry. A typical F-33 slurry was prepared by combining 3.58 g of DGEBF and 1.42 g of 33DDS while T-33 slurry required 3.15 g of DGEBF and 1.85 g of 33DDS to make a 5 g batch of each from which the slurry could be taken to make samples for DSC or RT-FTIR experiments.

Differential scanning calorimetry (DSC)

DSC cure studies were performed on the T-33 and F-33 networks in a TA Instruments Q200 DSC. Samples of the slurries (2–6 mg) were placed into hermetically sealed aluminum pans. Two different heating prescriptions were used, one to obtain the total heat of reaction of the uncured specimen (ΔHUC), and another to obtain the heat of reaction of a desired cure profile (ΔHC). The prescription for finding ΔHUC for each ramp rate was a ramp at a set heating rate (10°C/min) from 25 to 300°C. Heat of reaction for each ramp rate was found at a given time point (t) by integrating the exotherm of the various systems up to that time. Degree of cure (DOC) was calculated from DSC data using Equation 1.

\[
\text{DOC}(t) = \frac{\Delta HUC - \Delta HC(t)}{\Delta HUC} \times 100 \quad (1)
\]

Infrared spectroscopy (NIR)

Network formation of the two systems was monitored during 4 different cure protocols. Each sample was cured from 30 to 180°C and held at 180°C for 2 hours. Protocols were differentiated by the ramp rate applied for each system to reach the isotherm which were: 1, 5, 10, and 20°C/min. FTIR in the near infrared range (4000–8000 cm⁻¹, NIR) in transmission mode was used to monitor network formation during each cure prescription studied. The epoxy/diamine slurries were placed in to premade transmission cells composed of two glass cover slides sealed to either side of a steel washer (~1 mm thickness) to provide a constant path length of the sample throughout cure.

Figure 1. Epoxide and diamine curative monomer structures.

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Experimental runs were performed using a Nicolet 6700 FTIR (Thermo Fisher Scientific, Waltham, MA). Samples were heated in a Simplex Scientific HT-32 Heated Transmission Cell. The cell allows for various cure protocols to be performed while simultaneously recording NIR transmission spectra. An average spectrum of 32 scans (4 cm⁻¹ resolution) was collected every 60 seconds to track network formation.

Analysis of the resulting spectra was completed by integrating the peaks which correspond to the presence of the functional groups of interest for the thermosetting reaction; namely, epoxides, primary amines, and secondary amines. Figure 2 shows the near infrared spectrum before cure commences for both F-33 and T-33 (the spectra are vertically shifted for clarity) as well as identifying the peaks monitored in this work. The location and identities of these peaks are well known from the literature [6, 7] wherein epoxide absorbs at 4535 cm⁻¹, primary amine absorbs at 5070 cm⁻¹, and secondary amine absorbs at 6680 cm⁻¹. However, as can be observed in Figure 2, an absorbance peak related to the presence of primary amine is present at the beginning of the reaction in the same location where the secondary amine peak appears during cure. The production and consumption of secondary amine at any point throughout cure were able to be calculated by accounting for the know amount of primary amine consumed at that point (as determined by analysis of the peak at 5070 cm⁻¹) and monitoring the unaccounted-for growth and subsequent reduction of the peak at 6680 cm⁻¹. An internal standard peak, of the nonreactive phenyl group at 4612 cm⁻¹ was monitored as well to normalize results [8, 9]. Baselines were taken as the straight line between the peak bases.

**Results**

The quantifiability of the in situ RT-NIR cure data was validated by comparing the epoxide group conversion data with data derived from DSC. Epoxide conversion calculated from NIR peak integration was compared to a running integral of the cure exotherm of the same networks cured in DSC and show a high degree of agreement which affirms the analysis of functional group concentration during cure (Figure 3). It can be observed that over the course of the isotherm at 180 °C all the samples reach the same conversion for each formulation regardless of ramp rate. DGEBF based systems all reached full conversion while the more crosslinked TGDDM system settled at ~96% conversion for all protocols.

Concentrations of various times of specific functional groups throughout cure of both networks cured with the slowest and fastest ramp rates (1 and 20 °C/min) are shown in Figure 4. Primary amine \( (A') \) is consumed at a faster rate with increasing ramp rate, it is interesting to note that at all ramp rates, the onset of secondary amine \( (A'') \) consumption occurs prior to \( A' \) exhaustion. At each ramp rate the time at which primary amine is exhausted is closely followed by the conversion plateau of epoxide. For both systems and at all ramp rates when primary amine reaches 100% conversion
epoxide conversion has already greatly exceed 50% (between 80 and 90% in all cases). This indicates that both epoxy/diamine networks do not undergo linear growth followed by crosslinking, but rather crosslinking occurs concurrently with molecular weight increase.

It is important to note, as can be seen in all NIR figures, that the final epoxide conversion is comparable regardless of ramp rate for samples of the same formulation (96% for T-33 and 100% for F-33). However, by observing the shape of secondary amine curves in Figure 5 there may be an indication that the pathway of the reaction is different among the two networks. The relatively consistent peak concentration of $A''$ in DGEBF systems indicates a similar network growth pathway independent of cure ramp rate. The TGDDM networks, display a dramatic effect of the ramp rate. The lower maximum of $A''$ concentration observed in the slower cure protocols is not indicative of any undercure relative to the faster cured networks, as indicated by the equivalent final conversion. The lower peak indicates a greater abundance of tertiary amine present in the system earlier in network formation for

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**Figure 4.** Concentration vs. time graphs for epoxide (E), primary amine ($A'$), and secondary amine ($A''$) functional groups for both networks cured with slowest and fastest ramp rates.

![Graphs showing concentration vs. time for F-33 and T-33 at different ramp rates.](image)

**Figure 5.** Secondary amine concentration over time in (a) F-33 and (b) T-33 cured using four different ramp rates.

![Graphs showing secondary amine concentration over time for F-33 and T-33 at different ramp rates.](image)
these slower cured networks. This would result in localized areas of higher crosslink density in the early stage of cure for these systems. The consequence of this different network growth pathway merits further investigation into the effect on final network mechanical properties of networks cured with using these increasing ramp rates.

Conclusions

The development of RT-NIR to monitor network growth of thermosets has the potential to improve the understanding of cure pathways. The results show that, irrespective of ramp rate or crosslinking, the studied networks’ primary and secondary amine react concurrently, and crosslinking occurs at early stages of network growth. However, differences are observed in both networks in the timing and rate of secondary amine production and consumption. This indicates differences in the relative dispersion of crosslink density during different points for cure for networks cured using different cure protocols.

Disclosure statement

No potential conflict of interest was reported by the authors.

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