CURE BEHAVIOR OF A FURAN-BASED EPOXY-AMINE THERMOSETTING SYSTEM FOR LIQUID MOLDING APPLICATIONS

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ABSTRACT

This study investigates the cure behavior of a fully furan-based epoxy-amine network in an effort to help guide the process of preparing composites using vacuum assisted resin transfer molding process (VARTM). The resin system was cured stoichiometrically at room temperature, 60℃ and 80℃. Gelation and vitrification times were obtained using NIR spectroscopy and oscillatory isothermal rheology measurements. A Time-Temperature-Transformation isothermal cure diagram was constructed to summarize these data. The furan-based system possesses a favorable processing window for VARTM. In particular, the viscosity of the system remains below 1000 cp for the first 2.4 h of isothermal room temperature cure, and gelation does not appear to occur at this temperature because it is preceded by vitrification.

1. INTRODUCTION

This work investigates the chemorheological behavior of a novel furan-based epoxy-amine network in an effort to help guide the process of preparing composites using the vacuum assisted resin transfer molding (VARTM) process. Ongoing research shows that furan-based epoxy-amine systems possess excellent mechanical and fire resistance characteristic [1,2,3]. These systems are therefore good candidates for use as matrix materials in fiber reinforced composites. Common epoxy composite resin systems are based on diglycidyl ether of bisphenol A (DGEBA) cured with aromatic or cycloaliphatic diamines. Human health and environmental concerns regarding bisphenol A (BPA) has generated significant interest in the development of BPA free epoxy alternatives[4,5,6]. There is a great diversity of biomass that can serve as feedstock for the generation of alternative epoxy monomers and curing agents with resulting thermoset characteristics suitable for composite applications. Difuran-diamine (DFDA) is a bio-based monomer of interest that has been found to impart good thermomechanical characteristics when used as curing agent in epoxy formulations [1]. In this communication, the reaction behavior of a new furan-based diepoxy (FDE), cured with DFDA was investigated. The reaction behavior was evaluated using near infrared

spectroscopy (NIR) at isothermal cure temperatures including room temperature, 60°C and 80°C. Rheology measurements were conducted under the same isothermal reaction temperatures to assess viscosity and gelation behavior. An preliminary isothermal Time-Temperature-Transformation (TTT) cure diagram was generated to aid the selection of VARTM processing conditions for the FDE-DFDA system.

2. EXPERIMENTATION

2.1 Materials

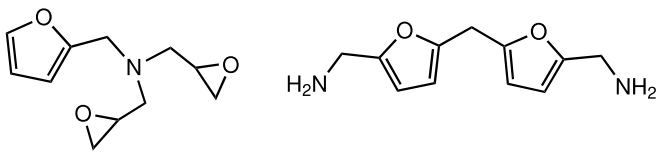
Chemical structures of the bio-based epoxy resin FDE and amine curing agent DFDA used in this study are shown in **Figure 1** Both furan-based resins were synthesized and purified in the laboratory, characterized by H^1NMR. The EEW value of FDE was determined by following ASTM epoxide titration technique, D 1652-97. The titrated value, 105 g/eq, agrees very well with the theoretical value. The DFDA amine curing agent has a theoretical AHEW value of 51.6 g/eq. The FDE/DFDA system was evaluated at stoichiometry using the EEW and AHEW given above.

2.2 Fourier transform infrared (FTIR) spectroscopy

Cure kinetics studies of FDE/DFDA were conducted using A Nexus 6700 FTIR spectrometer (Thermo-Nicolet Corp.) with a CaF2 beam splitter and a DTGS detector. Experiments were conducted in the near infrared (N-IR, 4000-8000 cm-1) at room temperature, 60 °C and 80 °C. Spectra were obtained at regular time intervals using 4 cm^{-1} resolution with 32 scans per spectrum. The epoxy peak of FDE at 4529 cm^{-1} was used to track the epoxy concentration [E] as a function of time.

2.3 Reactivity Study Experimental Setup

Low hydroxyl silica glass tubes with an inside diameter of 1.60 ± 0.05 mm and 65 mm length were employed as sample holders. Samples were prepared by mixing 1.000 gram of FDE and a stoichiometric amount of DFDA. The mixtures were then degassed and injected into the glass tube. A temperature-controlled aluminum sample holder shown schematically in **Figure 2** was used for the N-IR experiments. This device allowed for control of temperature within ± 0.5 °C of the set point temperature. A background scan was conducted before each experiment using the glass tube before filling [10].



a. b.

Figure 1. Chemical structures of (a) FDE, (b)DFDA.

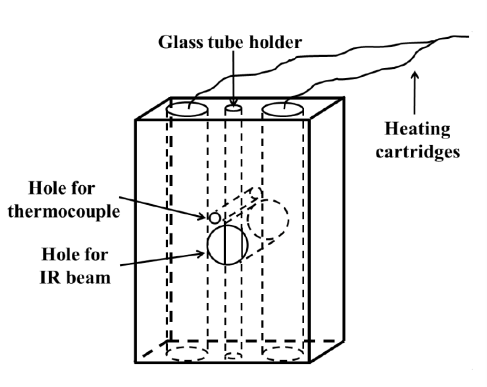


Figure 2. Schematic diagram heated sample holder used for NIR experiments[10].

2.4 Rheological study on curing behaviors at different temperature

Rheology of the curing resin was measured using continuous small amplitude oscillatory shear (SAOS) with a DHR-3 rheometer (TA Instruments, New Castle, DE). Liquid resins were loaded between disposable, aluminum parallel plates with a diameter of 25 mm and gap height of 700 mm. For temperatures other than room-temperature, the plates were heated using Peltier heating to the desired temperature and equilibrated. The sample was then loaded and equilibrated. During curing, a continuous frequency of 1 rad/s and strain amplitude of 1% was applied while maintaining a constant gap. Moduli were measured close to vitrification for most samples. Note that the magnitudes of moduli are artificially high beyond gelation as the sample dimensions are reduced to the point of underfilling the rheometer. At short times, the modulus of the liquid resin is below machine limits.

2.5 Differential Scanning Calorimetry (DSC)

A TA Instruments, Q2000 Differential Scanning Calorimeter (DSC) was used to measure the heat of reaction of FDE/DFDA cured stoichiometrically. FDE/DFDA was heated under inert atmosphere from room temperature to 200 °C at a heating rate of 1 °C/min. The heat of reaction for this system cured stoichiometrically was found to be 560.9 J/g.

3. RESULTS

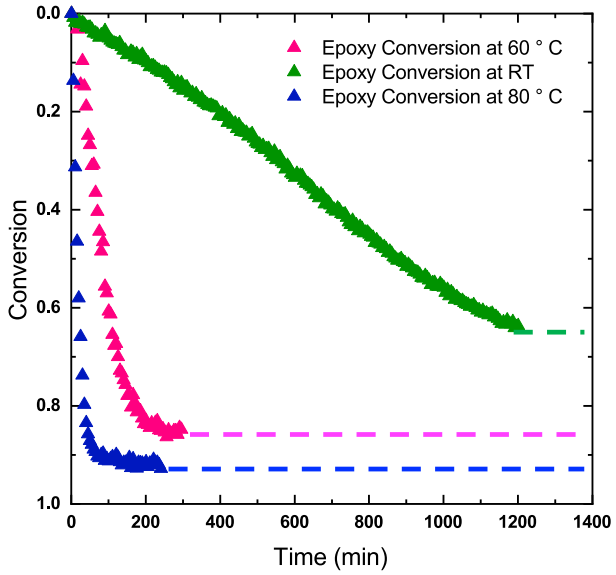


Figure 3. Epoxy conversion vs. time of FDE/DFDA system at room temperature, 60 °C and 80 °C.

Plots of epoxy conversion versus time for the FDE/DFDA cured isothermally at room temperature, 60°C and 80°C are given in **Figure 3**. The plots show typical cure behavior of aliphatic epoxy-amine systems. The reaction proceeds slowly at room temperature and increases significantly as the isothermal cure temperature is increased. The conversion profiles in the early stages of cure exhibit autocatalytic behavior. Moreover, for all temperatures evaluated, the latter stages of cure highlight diffusion limited reaction resulting from vitrification that limits final conversion. The T_g at full conversion of this system is 94°C, as obtained from the loss modulus peak of a DMA (Dynamic mechanical analysis) plot. For the purpose of our analysis, we estimate the time to vitrification by the time point at which conversion ceases to change noticeably. This conversion is also associated with the T_g of the system reaching the isothermal cure temperature ($T_g = T_{cure}$), Times required for the system to vitrify based on isothermal reaction behavior are summarized in **Table 1**. At room temperature, more than 20 hours are required to reach vitrification. Vitrification occurs more quickly at 60 °C and 80 °C (5 hours and 2.76 hours, respectively).

Understanding the chemorheolgical behavior of a resin system is important in order to select appropriate processing conditions. Oscillatory rheology experiments were conducted using the FDE/DFDA system at the same isothermal temperatures employed for the cure studies. **Figure 4** contains data from these experiments in the form of storage modulus and loss modulus plotted as a function of time for the three temperature conditions. The time to gelation is important for defining the processing window of thermosetting resin systems. Once the system gels it cannot be made to flow. For epoxy-amine systems of as given formulation, gelation occurs at a specific value of conversion. The crossover point of loss and storage modulus traces can be used to define the

gel point. Crossover points are clearly identified in the 60°C and 80°C cases. Crossover occurs at 110 min for 60 °C and 36 min for 80°C cure. The room temperature isothermal cure experiment shows the value of the loss modulus grows close to that of the storage modulus but remains lower with the two curves becoming parallel at long times. This behavior suggests that gelation might not occur before vitrification in this case. The conversion versus time data given in **Figure 3** was used to determine gel point conversion associated with the gel times obtained from the rheology experiments. These values are reported in **Table 1** and are 68% and 73% conversion for 60°C and 80°C cure respectively.

Using classical Flory-Stockmayer theory for gelation, the following equation predicts critical conversion at gelation for a system at stoichiometry where $\boldsymbol{f_E}$ is the epoxy molecule functionality and $\boldsymbol{f_A}$ is the amine curing agent functionality.

$$\alpha_{gel} = \frac{1}{[(f_E - 1)(f_A - 1)]^{1/2}}$$

For the system being considered $\boldsymbol{f_E}$ = 2 and $\boldsymbol{f_A}$ = 4 so that the predicted $\boldsymbol{\alpha_{gel}}$ is 57.7%. The predicted value is significantly lower than the measured values. The theory assumes uniform reactivity (i.e. no difference between primary and secondary amine) and no cyclization. Higher reactivity of primary versus secondary amine and cyclization both increase the conversion needed for gelation. In previous work the reactivity ratio of furan systems was found to favor primary epoxy-amine reactions [1,2,10] and it is known that glycidyl amine systems form networks with significant cyclization [12] ; therefore, the higher measured gel conversion is reasonable.

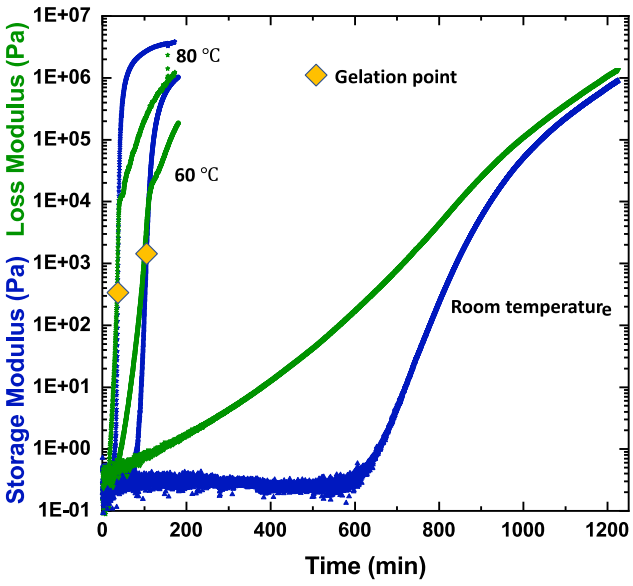


Figure 4. Storage modulus and loss modulus of FDE/DFDA system during curing at room temperature, 60 °C and 80 °C.

Table 1. Summary of gelation time (t_g), gelation conversion (α_g), vitrification time (t_v) and vitrification conversion (α_v) with respect to time for isothermal cure at room temperature, 60 °C and 80 °C.

	t_{gel} (mins)	α_{gel} (%)	t_v (mins)	α_v(%)
Room Temperature	--	-	~1200	64
60 °C	110	68	300	84
80 °C	36	73	166	93

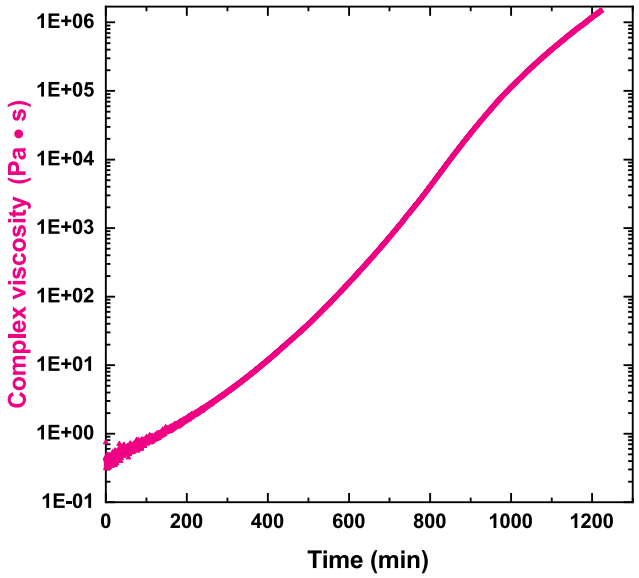


Figure 5. Complex viscosity vs. Time of FDE/DFDA network at room temperature. curing.

The complex viscosity with respect to time at room temperature that was obtained from the rheological study is given in **Figure 5** VARTM requires low viscosity resin systems matrix (100-1000 cp) at the processing temperature. At room temperature the viscosity of FDE/DFDA system reaches 1000 cp 2.4 hours after mixing which provided a usefully long processing window for composite preparation.

4. CONCLUSION

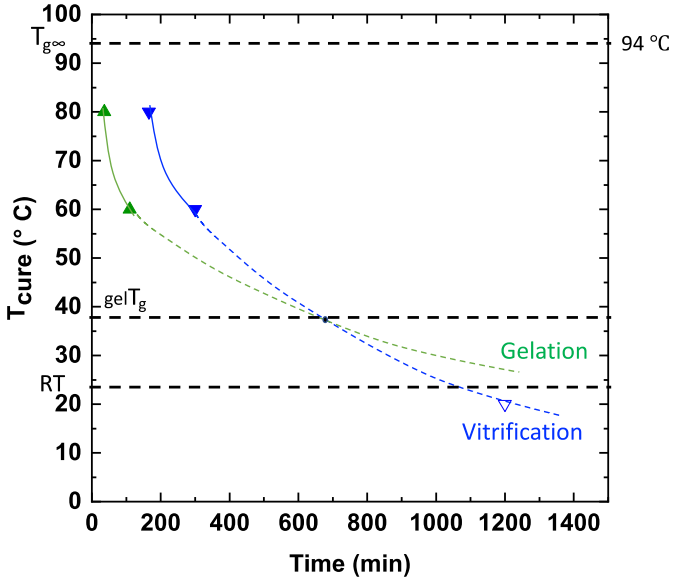


Figure 6. TTT cure diagram of FDE/DFDA system showing gelation (green) and vitrification curves (blue).

Times to vitrification (t_v) determined from isothermal NIR cure experiments at three temperatures as well as times to gelation (t_{gel}) determined from isothermal rheology experiments for the same temperatures are plotted in **Figure 6** to obtain a Time-Temperature-Transformation (TTT) isothermal cure diagram for the FDE/DFDA system. In addition to the gelation and vitrification curves, full cure T_g ($T_{g\infty}$ = 94°C) and an estimate of the isothermal cure temperature at which gelation and vitrification simultaneously ($_{gel}Tg$ ~ 37°C) are shown, $_{gel}Tg$ greater than room temperature indicates a favorable room temperature processing window because gelation will not occur at this cure temperature. This coupled with low room temperature viscosity (< 1000 cp for the first 2.4 h of cure) make the FDE/DFDA system a good choice for VARTM processing.

5. ACKNOWLEDGEMENT

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