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Thermally reversible cross-links in a healable polymer: estimating the quantity, rate of formation, and effect on viscosity

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The conversion behavior of 2MEP4FS, a polymer with thermally reversible Diels-Alder cross-links, is modeled. A processing method is developed to create small, homogeneous prepolymer samples. The glass transition temperature of the prepolymer is estimated using temperature modulated differential scanning calorimetry and equated with the conversion of the polymer. Comparing the measured energy with the literature and computational estimates, the fully cured polymer appears to have a large portion of its moieties unreacted. An autocatalytic model is considered to approximate the reaction rate of 2MEP4FS as a function of conversion and temperature. Outside of the fitted temperature range, the model underpredicts the reaction rates at room temperature and 100 °C. Manual mixing of the monomers is determined to be inadequate to obtain a maximum level of cross-linking. Viscosity measurements made at room temperature and elevated temperatures are correlated with the conversion of the prepolymer.

Keywords: Diels-Alder, cure kinetics, viscosity

1 Introduction

Healable materials have built-in mechanisms for self-repair. When activated, these mechanisms mitigate damage, extending the useful life of the structure or coating. There are several approaches to designing such materials, including embedding healing-agent-filled capsules [1], hollow fibers [2], or vascular networks [3] into a host material, using reversible intermolecular interactions like hydrogen bonding [4,5], or using reversible covalent bonds like the Diels-Alder adduct [6-9] or others [10]. A more detailed survey of the field is given in [11]. In the Diels-Alder (DA) reaction, a diene and dienophile react in a cycloaddition to form a cyclohexene ring. This reaction is thermally reversible; the retro-Diels-Alder (rDA) reaction separates the cyclohexene ring into the original diene and dienophile groups. In a polymer system, using Diels-Alder adducts as cross-linking bonds means the cross-links can be formed, separated, and re-formed. A recent review of the literature on polymers formed by DA reaction between furan and maleimide moieties is given in [12].

Cross-link formation in a traditional highly cross-linked polymer like epoxy generally proceeds in only one direction (increasing). In a DA-based polymer, however, the rDA reaction means the number of cross-links can decrease depending on the thermal and mechanical conditions. Since the thermal and mechanical properties of the polymer are dependent on the number of established cross-linking bonds [13], knowledge of the number of cross-links present at any given time is important for predicting material behavior.

2MEP4FS is one example of a healable polymer with Diels-Alder cross-links. It is formed from the reaction of a tetrauran diene, 4FS, and bismaleimide dienophile, 2MEP. Plaisted et al. [14,15] have extensively tested this polymer. They refer to the tetrauran as '4F', where we use the name '4FS' to distinguish this monomer from the original 4F used by Chen et al. [7], which

has one less ester group due to the synthesis route. Notably, Plaisted and Nemat-Nasser [14] successfully demonstrated complete fracture healing, even obtaining fracture stresses after multiple healings that exceeded the initial, virgin fracture stresses. Since the DA adduct is generally weaker than the surrounding covalent bonds, it is preferentially broken by a propagating crack tip [6]. When the fracture surfaces are brought back together at a temperature below where the rDA reaction occurs, DA adducts are re-established, healing the damage.

One aspect of 2MEP4FS unaddressed by Plaisted is an estimate of the number of DA cross-links present in the fully cured polymer. Here, we seek to make this estimate using DSC thermal measurements with theoretical and empirical approximations. A processing method for producing homogeneous small samples suitable for our experiments is outlined. A model is developed that correlates the measured glass transition temperature (T_g) with the relative number of established Diels-Alder cross-links. A second model is developed for the rate of DA cross-link formation in 2MEP4FS as a function of temperature and the number of established cross-links. Special cases are considered to determine limits on the applicability of the rate model. Finally, the models are applied to mechanical measurements of 2MEP4FS during polymerization to describe the viscosity as a function of cross-linking. In future work, this approach could be used to describe other mechanical and thermal properties as a function of the number of established cross-links.

2 Experimental

2.1 Material synthesis

The bismaleimide 2MEP and tetrafulran 4FS monomers (Fig. 1) were synthesized according to established procedures [7,16]. At room temperature, 2MEP is a solid powder, while 4FS is a viscous liquid. Obtaining a well-mixed final polymer, 2MEP4FS, poses a challenge. Chen et al.

Fig. 1. The tetrafulan and bismaleimide monomers.

[7] used simple mixing to combine two dissimilar monomers before heating to cure the polymer. This approach is evaluated later and found to be insufficient for 2MEP4FS.

Large samples (on the order of grams) can be efficiently produced by separately heating the monomers to melt the 2MEP and reduce the viscosity of 4FS before mixing [14,15,17]. This procedure does not facilitate the preparation of the small samples (on the order of 10 mg) required for differential scanning calorimetry (DSC) thermal measurements. To minimize the initial polymerization before DSC testing, the hot mixture must be quenched, which is challenging when working with relatively large monomer quantities. The unused prepolymer also amounts to wasted material, a significant drawback when monomer production is a time-consuming endeavor. Scaling down the monomer quantities addresses these issues, but quickly and precisely combining and effectively mixing small quantities of hot, low viscosity monomers proved difficult.

For the small samples used here in DSC and viscosity experiments, a polymerization procedure was developed to minimize wasted material, but still enable a precise mixture ratio of monomers. At room temperature, a stoichiometric proportion of 2MEP was added to 4FS in a disposable glass culture tube. The monomers were manually mixed and then placed under high vacuum. While still under vacuum, the culture tube was submerged in a preheated 90 °C silicone

oil bath for 20-35 sec depending on the sample size. The light yellow opaque monomer mixture quickly became transparent as the 2MEP melted and bubbled vigorously as trapped gases were pulled out. Once the contents settled, the culture tube was quenched in liquid nitrogen to slow the polymerization process. After rewarming the culture tube to room temperature in a water bath, the vacuum was broken and the 2MEP4FS prepolymer was ready for testing. At this stage, the prepolymer was a transparent yellow in color and qualitatively similar in viscosity to the starting 4FS monomer. Quantitative viscosity measurements are discussed later.

2.2 Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments DSC 2920. The instrument was configured with a liquid nitrogen cooling accessory and 50 mL/min nitrogen purge gas. All samples were tested in sealed hermetic aluminum pans. Baseline and cell constant calibrations were performed for all heating rates. Temperature and heat capacity calibrations were performed for the modulated DSC experiments using indium and sapphire respectively.

A series of isothermal curing experiments were used for kinetic modeling. Two DSC samples were prepared from a fresh batch of 2MEP4FS prepolymer for each experiment. A total of 4 scans were required to measure the initial T_g , reaction energy during curing, and final T_g . Here, T_g was taken as the inflection point in the reversible part of the heat flow [18].

Scan 1) One sample was immediately tested in the DSC, while the second was stored in liquid nitrogen. Sample 1 was cooled from room temperature to -80 °C over a period of 10 min, the maximum cooling rate capable by the instrument. It was then heated at 3 °C/min with ± 1 °C/min sinusoidal modulation through the glass transition temperature (initial T_g).

Scan 2) Sample 2 was removed from the liquid nitrogen and rapidly heated to room temperature using large aluminum heat sinks. It was quickly loaded into the DSC, cooled to -80 °C, and heated at 30 °C/min to the desired curing temperature. The sample was held isothermally at this temperature for an extended period of time. When the heat flow was deemed to have equilibrated, the sample was cooled to room temperature.

Scan 3) Scan 2 was repeated on sample 2 to establish a baseline heat flow.

Scan 4) Sample 2 was scanned a third time using a 3 °C/min heating rate and ± 1 °C/min sinusoidal modulation from room temperature through the glass transition temperature (final T_g).

Four different curing temperatures were used for kinetic modeling: 60, 70, 80, and 90 °C.

Additional special cases are discussed later.

2.3 Viscometry

A Brookfield HADVII+ viscometer was adapted to turn a custom spindle inside a culture tube containing the prepolymer. The spindle had a hemispherical end and was fabricated from 5/16 inch precision steel rod. A threaded hole was machined into the opposite end, allowing it to be screwed onto the motor shaft of the viscometer. The 10x75 mm borosilicate glass culture tube was mounted in a bracket, which was slid up and into position using a pair of linear bearings riding along precision steel shafts. A ring mounted on one shaft between the bracket and the instrument acted as a stop, enabling the culture tube to be reliably positioned such that the gap around the spindle was estimated to be constant. Nylon set screws secured the culture tube and bracket in position. A picture of the setup and important dimensions are given in Fig. 2. Measurements were made by recording the height of the fluid in the culture tube and the torque

Fig. 2. The modified rotational viscometer system with relevant dimensions. The modifications allow measurements to be made inside the glass culture tube used to produce the 2MEP4FS prepolymer.

required to turn the spindle at the prescribed rotational speed: 200, 105, 10, 5, 1, or 0.1 rev/min. The useful torque range of the instrument was between 10 % and 100 % of the maximum torque, 1.437 mN·m. Since the fluid thickness is small, the torque, T , is related to the dynamic viscosity, η , by assuming a linear variation in Newtonian fluid displacement between the rotating spindle and fixed culture tube:

$$T = \int_0^{R_s+h} \frac{2\pi\eta R(x)^3 \dot{\theta}}{R_t - R_s} dx, \quad (1)$$

where $\dot{\theta}$ is the angular speed (rad/sec), R_s is the radius of the spindle, and R_t is the inner radius of the culture tube. Performing the integration and rearranging yields the estimated viscosity:

$$\eta = \frac{8T(R_t - R_s)}{\dot{\theta}(3\pi^2 R_s^4 + 16\pi h R_s^3)}. \quad (2)$$

Viscosity results from the experimental setup were found to underpredict the true viscosity of a known fluid by ~11 % (Supplemental Material). For our future application of 2MEP4FS as the matrix in laboratory-scale prepreg composite layers, this constitutes a reasonable estimate.

Viscosity measurements were performed at room temperature (22 °C) for neat 4FS and 2MEP4FS prepolymer prepared according to the small-sample procedure. The viscometer setup and measurement method were then modified to test a second prepolymer sample at an elevated temperature. The sample was also prepared according to the small-sample procedure, and a DSC sample was taken to measure the initial T_g . The viscometer spindle and a large oil bath had been preheated to 90 °C. The hot spindle was quickly attached to the viscometer, and the room temperature culture tube was mounted and slid into position. The bottom half of the apparatus was then lowered into the oil bath. A video camera recorded the time, torque, and rotational speed for later analysis. Initially, the sample required the highest rotational speed, 200 rev/min, in order to effectively measure the torque. This speed was periodically stepped down as the polymerization proceeded and the torque would reach 100 %. Once the required torque exceeded the capability of the instrument at the lowest rotational speed, the instrument was turned off and raised out of the bath. The culture tube and spindle were quickly cooled and separated, leaving the 2MEP4FS intact as a thin film inside the culture tube. The height of the polymer was measured, and a small sample was removed for DSC testing to determine final T_g .

3 Results & Analysis

The DSC results for the 2MEP4FS prepolymer samples used for kinetic modeling are summarized in Table 1.

Processing Method	Small	Small	Small	Small	Manual mix monomers	Large	Small
Cure Temp (°C)	60	70	80	90	90	90-95	100
Initial T_g (°C)	-18.03	-17.45	-17.26	-17.36	-23.97	-	-17.83
ΔC_{p0} (mJ/g/°C)	-	-	-	-	332.88	-	-
H_m (kcal/mol DA adducts)	10.31	10.99	11.15	11.65	9.50	-	12.38
Final T_g (°C)	83.71	92.29	95.15	99.85	92.46	101.20	97.68
ΔC_{px} (mJ/g/°C)	-	-	-	-	-	277.60	-

Table 1. DSC experimental results for 2MEP4FS. The first four samples were used to model the reaction and estimate the total heat energy, H_T . The sample prepared by manually mixing the monomers at room temperature (special case 1) is considered the fully uncured case. The sample prepared by rapidly mixing the monomers at an elevated temperature (the large-sample method) is considered the fully cured case. The sample cured at 100 °C is special case 2.

3.1 Conversion rate modeling

The conversion, α , of the polymer describes the level of cross-linking, where $\alpha=0$ indicates no cross-linking bonds are present and $\alpha=1$ is fully cured material with a maximum number of cross-links. Conversion is given as:

$$\alpha = \frac{H_T - H_r}{H_T}, \quad (3)$$

where H_T is the total heat energy of the reaction and H_r is the residual heat energy required to complete the polymerization. The change in conversion over time is then:

$$\frac{d\alpha}{dt} = \frac{-dH_r/dt}{H_T}, \quad (4)$$

where the heat flow rate $-dH_r/dt$ is directly given by the DSC.

In the present study, the heat energy of the reaction for each experiment is determined from the difference between scans 2 and 3. The majority of this energy is given off during the isothermal step of scan 2. The energy released during the temperature ramp step of scan 2 is also accounted for by considering the divergence from linearity of the heat flow as a function of temperature above T_g and relative to scan 3. The only unknown is the total energy of the reaction. Typically, this is determined by heating an uncured sample of material until all exothermic energy has been given off and the heat flow equilibrates [19]. In the present thermally-reversible polymer, this is not a feasible technique as the rDA reaction will consume energy and separate the DA adduct, reducing conversion. Instead, the data are fitted to the DiBenedetto equation to estimate the total energy. The equation uses the properties of fully cured and fully uncured material cases to estimate the glass transition temperature as a function of conversion [19,20]:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda \alpha}{1 - (1 - \lambda) \alpha} \quad (5)$$

The glass transition temperatures T_{g0} and $T_{g\infty}$ are for the fully uncured and cured cases respectively. The parameter λ is the ratio of the change in heat capacity around the glass transition temperature of the fully cured and uncured cases: $\Delta C_{p\infty} / \Delta C_{p0}$. Here, the fully cured case is taken as the polymer prepared using the large sample fabrication method. The large sample had been cured for 5 hours at 90-95 °C and allowed to cool to room temperature over a period of approximately 10 hours before a small piece was broken off for DSC testing. The fully uncured case is assumed to be the monomers after manual mixing, the first step of the small sample fabrication procedure. If the initial T_g for each curing case is assumed to be on the curve given by the DiBenedetto equation (Fig. 3), the final T_g is given by:

$$\alpha_f = \alpha_i - \frac{\Delta H_r}{H_T}, \quad (6)$$

Fig. 3. The DiBenedetto curve was developed considering the fully cured and uncured 2MEP4FS cases. The DSC data from the four curing temperatures (60, 70, 80, 90 °C) are fitted to curve by assuming H_T . The intersection of the tangent lines from $\alpha=0$ and $\alpha=1$ gives the approximate gel point of 2MEP4FS as $\alpha_{gel}=0.545$.

where ΔH_r is the measured change in residual heat energy. A least squares fit of all four curing cases gives an average total heat of polymerization of 12.5 kcal/mol DA adduct.

The estimated DA adduct energy is less than the 23 kcal/mol DA adduct determined by Chen et al. [6] for 3M4F, another thermally reversible polymer. Considering the bonding energies for carbon-carbon single and double bonds, the DA adduct energy is estimated to be 37 kcal/mol (Appendix A). Density functional theory (DFT) calculations of portions of the monomers and 2MEP4FS polymer estimate the adduct energy to be 24-27 kcal/mol (Appendix A). These comparisons suggest a significant number of moieties remain unreacted in the final 2MEP4FS polymer.

The rate of DA cross-link formation (rate of conversion) in 2MEP4FS varies with conversion and temperature. Two models are considered as potential candidates to approximate the kinetics of the reaction: n^{th} order and autocatalytic. An n^{th} order reaction assumes the conversion rate decreases with the concentration of unreacted moieties according to a power law:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n. \quad (7)$$

Conversely, an autocatalytic reaction assumes the products catalyze the reaction, leading to an initial increase, maximum, and then decrease in reaction rate as the unreacted moieties are consumed:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \alpha^m. \quad (8)$$

The parameters n and m are the reaction order, and the rate constant k is assumed to follow the Arrhenius relationship:

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right), \quad (9)$$

where A is a pre-exponential factor, E_a is the activation energy, R is the universal gas constant, and T is the absolute temperature. The two models exhibit significantly different behavior at low conversion: at $\alpha=0$ the n^{th} order model predicts a maximum reaction rate, while the autocatalytic model predicts a reaction rate of zero. Since the present processing methods do not facilitate investigation of the reaction at low conversions, it is unclear from the DSC data which model is more appropriate for 2MEP4FS. Therefore, each model was fit to the DSC experimental results using a least squares method. The autocatalytic model was deemed a better fit across all four curing temperatures ($R^2=0.998$ versus $R^2=0.994$ for the fitted n^{th} order model). A physical mechanism in this reaction that would cause it to behave in an autocatalytic manner is unknown. Park et al. [21] uses an autocatalytic model for the cross-linking of another Diels-Alder-based healable polymer, although a rationale is not given. Here, the fitted autocatalytic model (Fig. 4)

Fig. 4. The conversion rate of 2MEP4FS as a function of conversion and temperature is fitted with the autocatalytic model (solid lines). Increasing the temperature increases the conversion rate of the polymer. Despite starting at similar initial conversions, the samples cured at higher temperatures required more heating time, leading to more conversion during the ramp step and the staggered starts in the data. The first isothermal data points were truncated as the instrument response had not yet stabilized. (Insert) A linear fit of the autocatalytic model rate constants gives the parameters for the Arrhenius relationship (9).

gives a total reaction order for 2MEP4FS ($m=0.35 + n=1.87$) of 2.22. A logarithmic fit of $\ln k$ versus $1/T$ (Fig. 4 insert) gives an activation energy E_a of 55.2 kJ/mol and pre-exponential factor A of 9×10^5 .

3.1.1 Special case 1: manual-mix only

Sample preparation would be greatly simplified if the monomers could be combined at room temperature and fully cured without the intermediate steps of the small-sample processing

procedure. Chen et al. [7] used simple mixing to combine 2MEP and 4F monomers in their study. The effect of this preparation method on the reaction and final conversion of 2MEP4FS was studied using DSC.

A stoichiometric ratio of 2MEP and 4FS monomers was combined in a glass culture tube and hand-mixed vigorously for approximately 5 minutes, at which time the light yellow, opaque mixture was visually homogeneous. High vacuum was briefly applied to remove air trapped during mixing. Two small samples of the mixture were then transferred to aluminum DSC pans, which were subsequently sealed and tested following the previously established procedure with a 90 °C curing temperature.

Comparing the results of the manually mixed sample with the expected behavior given by the DiBenedetto curve, the change in conversion (calculated from the measured energy released during polymerization) is underpredicted given the measured change in T_g . A likely explanation for the missing energy is that it has gone into melting small 2MEP particles that were not fully dissolved in the 4FS. Due to the energy consumed during the reaction, estimating the conversion rate for comparison with the fitted autocatalytic model is problematic. Particularly, the conversion rate is initially determined to be negative as energy is consumed by the sample during the initial portion of the reaction. The final T_g of the manually-mixed 2MEP4FS is 7.4 °C below the final T_g of the 2MEP4FS prepared according to the small-sample procedure. Incomplete mixing of the monomers could lead to the formation of fewer cross-linking bonds in the final polymer. During the small-sample processing procedure, the rapid heating of the monomers melts the 2MEP and lowers the viscosity of the mixture, while the high vacuum leads to violent bubbling as trapped gasses are pulled out. This bubbling likely enhances mixing of the

monomers, leading to a prepolymer that is more homogeneous than that achieved by manual mixing alone.

3.1.2 Special case 2: high temperature cure

Next, we investigate the effect of curing the 2MEP4FS prepolymer at 100 °C, which is near $T_{g\infty}$. Plaisted and Nemat-Nasser cured their 2MEP4FS at this temperature, and subsequently obtained excellent crack healing results, even demonstrating improved resistance to fracture after healing [14]. In the present study, 2MEP4FS prepolymer was prepared according to the standard small-sample processing procedure and tested following the aforementioned DSC method using a 100 °C curing temperature. The conversion rate is observed to be lower than predicted by the fitted autocatalytic model (Fig. 5). The total measured energy also suggests a final conversion of $\alpha=1.05$, meaning there should be more cross-links formed than in the material produced using

Fig. 5. The experimentally measured conversion rate of 2MEP4FS at 100 °C is compared with the rate predicted by the fitted autocatalytic model (solid line).

the large-sample processing method, which had been cured at 90-95 °C. DSC measurements of the 100 °C cured sample give a final conversion of $\alpha=0.98$, indicating there are fewer cross-links after the curing process has completed and the sample has cooled. The retro-Diels-Alder (rDA) reaction offers a possible explanation for these observations. During curing at 100 °C, the DA and rDA reactions may both be occurring, slowing the overall rate of cross-link formation. The literature gives the rDA reaction as starting at 110 °C [7], but this observation was made based on dynamic DSC scans. Assuming the rDA reaction is occurring, increased moiety mobility due to softening of the material at the glass transition temperature and additional thermal energy could lead to more cross-links being formed despite the rDA reaction. Once the material cools, however, the rDA reaction reduces the overall conversion of the sample. This explanation suggests that there is a maximum level of cross-linking for the polymer, and it is below the total number of DA adducts possible.

3.1.3 Special case 3: room temperature cure

After preparation according to the small-sample processing method, the 2MEP4FS prepolymer is at room temperature (22 °C). During previous experiments, the prepolymer spent only a minimal amount of time at this temperature before being cured at an elevated temperature. But, if the prepolymer is subsequently worked with or used elsewhere such as in a composite prepreg, it could spend an extended period of time at room-temperature. We seek to evaluate the rate of cross-link formation at ambient conditions. Since the fitted autocatalytic model predicts a slow rate of conversion at room temperature, measuring the heat flow over an extended period of time using DSC as previously done is not practical. Instead, a series of prepolymer DSC samples were tested after different periods of time at room temperature. By comparing the change in T_g

between samples, an average conversion rate can be estimated and compared with the predicted autocatalytic behavior.

Seven DSC samples were created from one 2MEP4FS prepolymer preparation and tested after nominal periods of 8 min, 30 min, 1 hr, 3 hr, 6 hr, 1 day, and 3 days at room temperature. Since the modulated DSC test requires approximately 1 hour for a complete scan according to the previously established procedure, the 30 min and 1 hr samples were held at room temperature and then stored in liquid nitrogen until the instrument was ready. The DiBenedetto equation (5) is used to translate the observed T_g to conversion, α . The change in conversion between samples gives a series of average conversion rates. These rates are significantly lower than those predicted by the fitted autocatalytic model (Fig. 6). Room temperature is significantly below the temperature range used to fit the autocatalytic model, and the predicted conversion rates are very

Fig. 6. Average conversion rates of 2MEP4FS at room temperature (22 °C) are compared with the rate predicted by the fitted autocatalytic model (solid line).

slow. At 22 °C, there may be insufficient thermal energy to overcome energy barriers to the reaction. Another possibility is the 2MEP monomer is precipitating out of the 4FS. During the small-sample process, the 2MEP is melted and dispersed in the 4FS. But since the material is cooled before significant cross-linking occurs, there are still large quantities of unreacted 2MEP monomers. At room temperature, there could be a crystallization process competing with and inhibiting polymerization.

A visual investigation was conducted using a series of 2MEP4FS polymer films. The first film was prepared following the initial portion of the small-sample processing method, but without quenching. Instead, the hot prepolymer was removed from the culture tube and placed between two nylon films in a preheated 90 °C oven. Two more films were prepared following the entire small-sample processing method, with the room temperature prepolymer distributed between nylon films. The prepolymer was held at room temperature for 5 min and 1 day respectively, before being cured at 90 °C. Observed using cross-polarized light microscopy, the three 2MEP4FS films have bright regions that could be caused by small crystals (Fig. 7). The number of these bright regions increases with the time the prepolymer spent at room temperature before final curing. It was noted that the density of the bright regions did not change as a result of curing.

Fig. 7. Polarized light microscopy images of 2MEP4FS polymer films cured at 90 °C after the prepolymer spent (A) zero time, (B) 5 min, and (C) 24 hr at room temperature.

If the crystals are 2MEP precipitates, the final conversion of the 2MEP4FS polymer may be reduced. A new series of three prepolymer DSC samples were prepared following the small-sample processing method. The samples were held at room temperature for 1 hr, 4 hr, and 1 day respectively before being curing at 90 °C in the DSC. After curing, each sample was scanned to estimate final T_g (scan 4), and the associated conversion was normalized by the conversion obtained for the earlier 90 °C cured sample that had spent minimal time at room temperature. The results show no significant changes, with normalized final conversions of 1.0041, 0.9999, and 1.0004 respectively. The consistent results indicate that time at room temperature does not negatively affect cross-linking in the final, cured 2MEP4FS polymer. Since the low final conversion of the manual-mix only case (special case 1) was attributed to poor mixing of the monomers, the present results suggest the observed crystalline regions are not 2MEP precipitates.

3.2 Application to viscosity measurements

The formation of cross-linking bonds in 2MEP4FS leads to changes in thermal and mechanical properties. In the previous section, the change in glass transition temperature was explored and related to the conversion of the polymer. Using this relationship, 2MEP4FS prepolymer viscosity can be correlated with conversion.

Viscosity is a measure of the resistance to flow of a fluid subjected to mechanical shearing. During polymerization at a constant temperature, the prepolymer will initially have a minimum viscosity. As cross-linking between the monomers proceeds, the average molecular weight and viscosity increase, eventually going to infinity when the material becomes solid. At this gel point, a continuous polymer network has formed. The evolution of viscosity with conversion

and the gel point are important parameters for processing the prepolymer, particularly in composite applications.

There are a number of standard viscosity measurement techniques available. Calibrated funnels or capillary tubes can be used to estimate viscosity based on the movement of the fluid as a function of time [22]. A falling sphere (or rising bubble) viscometer relies on a sphere moving through a fluid at terminal velocity [23]. Stokes law relates this velocity with a drag force, which depends on viscosity. Ghezzi et al. [17] successfully used the falling sphere method to characterize the viscosity of 2MEP4F prepolymer as a function of time and temperature. Rotational viscometers apply an external torque to an object in the fluid to produce angular rotation [24]. The relationship between torque and angular speed is related to the viscosity of the fluid. Rotational viscometers include the cup and bob, cone and plate, and electromagnetically spinning sphere types [25]. Plaisted [15] used a cone and plate viscometer to estimate the initial viscosity of 2MEP4FS prepolymer as 0.112 Pa·s (112 cP) at 90 °C.

In the present work, a cup and bob-type rotational viscometer was modified to make measurements directly inside the production culture tube. This approach offers several benefits. Following the small-sample processing method yields prepolymer at a minimum initial conversion, but the limited quantity of material (< 0.3 mL) precludes most of the aforementioned viscosity methods. The electromagnetically spinning sphere approach is possible but limited to 10 Pa·s [25], which is too low for the present materials at room temperature. Effectively transferring this small quantity of prepolymer to a cone and plate-type viscometer would be challenging.

3.2.1 Room temperature

The 4FS monomer exhibited an average viscosity of 94 Pa·s (940 P), while the initial measurement of 2MEP4FS prepolymer was 345 Pa·s (3450 P). The viscosity of the 2MEP4FS prepolymer was tracked as polymerization proceeded (Fig. 8), until the required torque exceeded the capability of the instrument. Since approximately 10 minutes elapsed between the completion of the small-sample processing method and the first viscosity measurement, an exponential fit of the data gives the initial viscosity of the 2MEP4FS prepolymer as 208 Pa·s (2080 P). This indicates that the combination of the 2MEP and 4FS monomers roughly doubles the viscosity of the 4FS monomer alone at room temperature.

Fig. 8. The viscosity of 2MEP4FS prepolymer as a function of time at room temperature after the conclusion of the small-sample processing method. The exponential fit gives an initial viscosity of 208 Pa·s.

3.2.2 Elevated temperature

Since the 2MEP4FS prepolymer needs to be cured at an elevated temperature to achieve maximum cross-linking, knowledge of the viscosity at such a temperature is useful. The initial and final T_g are used with the DiBenedetto equation and the fitted autocatalytic model to estimate viscosity as a function of conversion (Fig. 9).

Given the initial and final conversions ($\alpha_i=0.075$, $\alpha_f=0.577$) and the observed time between them (7 min), numerical integration of the autocatalytic model gives an average polymerization temperature of 73.1 °C. This is significantly lower than the 90 °C oil bath where the experiment was conducted. The discrepancy can be attributed to a non-constant sample temperature over the

Fig. 9. The viscosity of 2MEP4FS prepolymer measured in a 90 °C oil bath. The dashed line gives the estimated gel point of the polymer as measured by DSC at the conclusion of the viscosity test. The gaps in the data are due to delays waiting for the reading to stabilize after stepping down the rotational rate of the spindle.

course of the test. The spindle had been preheated in an oven, but it had to be taken out and attached to the viscometer prior to sliding the sample into position and lowering the apparatus into the hot bath. The cooling associated with this delay coupled with the sample starting at room temperature likely meant the prepolymer did not approach 90 °C until later in the experiment. The average polymerization temperature is also weighted by conversion rate. Since the maximum conversion rate for any given temperature occurs at low conversions, an initial period of low temperature will disproportionately skew the average temperature down. The viscosity data suggest the temperature was relatively low at the start of the test. The initial viscosity measurement was 0.817 Pa·s (817 cP), which is higher than the 0.112 Pa·s estimated by Plaisted [15]. Decreasing the temperature would increase the viscosity. Thermal expansion effects on the geometry of the experiment are estimated to be small and were not considered in the calculations.

The final conversion, $\alpha_f=0.577$, can be taken as the approximate gel point of the polymer. Another estimate of the gel point is given by the Flory-Stockmayer equation [26]:

$$\alpha_{gel} = \frac{1}{\sqrt{r(f_F-1)(f_M-1)}}, \quad (10)$$

where r is the stoichiometric ratio, f_F is the functionality of furan, and f_M is the functionality of maleimide. This equation gives the gel point for stoichiometric 2MEP4FS as 0.577, which matches the DSC-measured estimate. A third estimate of gelation is given by the intersection of the tangents at $\alpha=0$ and $\alpha=1$ on the DiBenedetto curve (Fig. 3) [27]. This method gives a gel point of $\alpha_{gel}=0.545$. For a true measurement of the gel point, dynamic rheometric analysis should be used to find the point where $\tan\delta$ becomes frequency independent [28].

4 Discussion and conclusions

The conversion and conversion rate models are useful tools for estimating the number of Diels-Alder cross-links in 2MEP4FS as a function of glass transition temperature, time, and sample temperature. Using DSC measurements and the DiBenedetto relationship between T_g and conversion, the total heat energy of the reaction was estimated to be 12.5 kcal/mol DA adduct. Comparing this result with another DA adduct measurement in the literature (23 kcal/mol, [6]), a simple theoretical estimate (37 kcal/mol, Appendix A), and a computational estimate (24-27 kcal/mol, Appendix A) suggests that even at the maximum measured conversion, a significant portion of potential DA adducts are unformed in 2MEP4FS. Based on the computational estimate, only half of the potential DA adducts are established when $\alpha=1$. The energy measured during DSC experiments included the temperature ramp and isothermal portions of the test. It could be argued that these measurements miss the initial energy given off during manual mixing of the monomers. While true, estimating the elapsed time and the initial reaction rate at room temperature suggests the missed energy accounts for less than 1 % conversion.

The conversion rate model was determined by fitting DSC data for 2MEP4FS cured isothermally at temperatures ranging from 60 °C to 90 °C. Assuming an autocatalytic reaction provided a better fit of the data than an n^{th} order model. These two approximations exhibit significantly different behaviors at low conversion levels, but due to the processing method and temperature ramp, this period of the reaction was not captured. Outside of the fitted temperature range, the conversion rate was underpredicted by the model. At room temperature, insufficient thermal energy to overcome energy barriers or other processes like crystallization could be inhibiting polymerization. The time spent at room temperature before curing at an elevated

temperature did not affect the final conversion of the polymer. At 100 °C, the rDA reaction could be separating DA adducts, although this is 10 °C below the estimated onset observed in the literature [6,7]. The rDA reaction would reduce the conversion rate and final conversion of the polymer. The final conversion was found to be highest for 2MEP4FS cured at 90-95 °C.

The small-sample processing method provided an efficient method for effectively mixing small quantities of 2MEP and 4FS monomers, while minimizing the initial conversion. Manual mixing of the monomers was determined to be insufficient to obtain maximum conversion in the final, cured polymer. The developed approach will be useful in future experiments where the 2MEP4FS prepolymer must be manipulated before final curing, such as preparing unidirectional fiber prepreg layers and multilayered healable composites. The small-sample approach conserves monomer supplies, but experiments must be modified to use small quantities of material. Here, a rotational viscometer was adapted to make viscosity measurements on a small quantity of prepolymer. At room temperature, the prepolymer was estimated to have an initial viscosity approximately twice that of neat 4FS. In a hot oil bath, the first viscosity measurement of 2MEP4FS prepolymer was higher than others have estimated, but DSC results and the autocatalytic model indicate the sample had not yet reached the bath temperature. Modifications to the experimental setup or an alternative approach, such as the electromagnetic spinning sphere, could reduce the temperature variability.

Rotational viscometer measurements were made as a function of time and combined with DSC measurements of T_g to estimate viscosity as a function of conversion. The final conversion of the viscosity sample tested at an elevated temperature was taken as the gel point. Since the final viscosity measurement is limited by the torque capability of the instrument, the quantity of prepolymer in the culture tube will influence the end of the experiment. This suggests we have

underpredicted the gel point of 2MEP4FS, even though our estimate agrees reasonably well with estimates determined by other methods. Dynamic rheometric analysis would be useful here for monitoring the complex viscosity during polymerization and obtaining a better determination of the gel point.

The models developed here can be used to characterize additional mechanical properties of 2MEP4FS as a function of conversion. Fracture toughness would be one property of particular interest, given the healing capability of this polymer. Plaisted and Nemat-Nasser [14] studied the fracture and healing behavior of 2MEP4FS, and found that under ideal conditions, samples required more stress to propagate cracks after healing than in their virgin state. The samples had been cured at 100 °C for an extended period of time. In a separate DSC study, Plaisted [15] determines the T_g of his cured 2MEP4FS to be 93 °C. Assuming this polymer has been treated comparably to the polymer used in the fracture study, the data presented in the current work suggest that the conversion of the samples was below the maximum level; they were not fully cured. After fracture, the samples were healed at a temperature of 95 °C, which happens to be the approximate temperature determined to achieve maximum cross-linking in 2MEP4FS. Additionally, if there are a significant number of unreacted functional groups in the polymer sample, there would be a surplus of moieties at the fracture surface available to heal the crack. Hence, the present conversion study offers a rational explanation for the observed increase in fracture resistance. New fracture measurements of 2MEP4FS at different levels of conversion will be considered in future work.

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References

- [1] White SR, Sottos NR, Guebelle PH, Moore JS, Kessler MR, Sriram SR, Brown EN, Viswanathan S. *Nature* 2001;409:794.
- [2] Pang JWC, Bond IP. *Compos Sci Technol* 2005;65:1791.
- [3] Toohey KS, Sottos NR, Lewis JA, Moore JS, White SR. *Nat Mater* 2007;6:581.
- [4] Cordier P, Tournilhac F, Soulié-Ziakovic C, Leibler L. *Nature* 2008;451:977.
- [5] Chen Y, Kushner AM, Williams GA, Guan Z. *Nat Chem* 2012;4:467.
- [6] Chen X, Dam MA, Ono K, Mal A, Shen H, Nutt SR, Sheran K, Wudl F. *Science* 2002;295:1698.
- [7] Chen X, Wudl F, Mal AK, Shen H, Nutt SR. *Macromolecules* 2003;36:1802.
- [8] Wiggins KM, Syrett JA, Haddleton DM, Bielawski CW. *J Am Chem Soc* 2011;133:7180.
- [9] Syrett JA, Mantovani G, Barton WRS, Price D, Haddleton DM. *Polym Chem* 2010;1:102.
- [10] Brantley JN, Wiggins KM, Bielawski CW. *Science* 2011;333:1606.
- [11] Murphy EB, Wudl F. *Prog Polym Sci* 2010;35:223.
- [12] Gandini A. *Prog Polym Sci* 2013;38:1.
- [13] Nielsen LE. *J Macromol Sci-Rev M* 1969;3:69.
- [14] Plaisted TA, Nemat-Nasser S. *Acta Mater* 2007;55:5684.

- [15] Plaisted TA. Multifunctional composites: healing, heating and electromagnetic integration [PhD dissertation]. La Jolla (CA): University of California at San Diego; 2007.
- [16] Weizman H, Nielsen C, Weizman OS, Nemat-Nasser S. J Chem Educ 2011;88:1137.
- [17] Ghezzi F, Smith DR, Starr TN, Perram T, Starr AF, Darlington TK, Baldwin RK, Oldenburg SJ. J Compos Mater 2010;44:1587.
- [18] TA Instruments. DSC 2920: differential scanning calorimeter operator's manual. New Castle (DE): TA Instruments; 1998.
- [19] Sheng X, Akinc M, Kessler MR. J Therm Anal Calorim 2008;93:77.
- [20] Pascault JP, Williams RJJ. J Polym Sci 1990;28:85.
- [21] Park JS, Kim HS, Hahn HT. Compos Sci Technol 2009;69:1082.
- [22] Washburn EW. Phys Rev 1921;17:273.
- [23] ASTM D1343-95. Standard test method for viscosity of cellulose derivatives by ball-drop method. West Conshohocken (PA): ASTM International; 2006.
- [24] ASTM D2983-09. Standard test method for low-temperature viscosity of lubricants measured by Brookfield viscometer. West Conshohocken (PA): ASTM International; 2009.
- [25] Sakai K, Hirano T, Hosoda M. Appl Phys Express 2010;3:016602.
- [26] Flory PJ. Principles of Polymer Chemistry. Ithaca (NY): Cornell University Press; 1953.
- [27] Wingard CD. Thermochim Acta 2000;357-358:293.
- [28] Holly EE, Venkataraman SK, Chambon F, Winter HH. J Non-Newton Fluid 1988;27:17.
- [29] Oxtoby DW, Gillis HP, Campion A. Principles of Modern Chemistry, 7th ed. Belmont (CA): Brooks/Cole Cengage Learning; 2012.
- [30] Singh RK, Tsuneda T. J Comput Chem 2013;34:379.

- [31] Frisch MJ, Trucks GW, Schlegel HB et al. Gaussian 09, Revision C.01. Wallingford (CT): Gaussian Inc; 2009.
- [32] Zhao Y, Truhlar DG. Theor Chem Acc 2008;120:215.
- [33] Schäfer A, Huber C, Ahlrichs R. J Chem Phys 1994;100:5829.

Appendix A: Diels-Alder adduct energy

The energy given off by the formation of a Diels-Alder (DA) adduct can be roughly estimated from bond energies. A carbon-carbon single bond gives off 345 kJ/mol, while a carbon-carbon double bond gives off 612 kJ/mol [29]. The DA reaction converts the three double bonds and one single bond of the diene and dienophile moieties to a cyclohexane ring with one double bond and five single bonds. This process requires 2181 kJ/mol reactants and releases 2337 kJ/mol product, resulting in an exothermic reaction of 156 kJ/mol or 37 kcal/mol DA adduct.

A more precise estimate of the energy released by the formation of the DA adduct can be obtained from computational simulations of the reaction [30]. Thermochemistry calculations for optimized 4FS and 2MEP monomers and the 2MEP4FS adduct were performed by the software package Gaussian09 revision C.01 [31]. The calculations used Density Functional Theory with the M062X meta-GGA hybrid functional [32] and fully optimized contracted triple- ζ basis set from Ahlrichs and co-workers [33]. The difference between the combined enthalpies of the partial monomers before the reaction and the enthalpy of the final DA adduct was taken as the energy released due to the reaction. It has been previously reported that M062X gives thermodynamic quantities with an average error of 2.5 kcal/mol when compared with higher theory levels [30], which makes it a suitable choice for these calculations. Preliminary calculations using a minimal model of the DA reaction confirmed that M062X was better able to

reproduce the MP2 energies than other investigated functionals. For the actual 2MEP4FS calculations, approximations were required in order to avoid excessive computational cost due to the large size of the system. The molecules furthest from the functional groups and DA adduct were assumed to have a minimal effect on the released energy and therefore, only the portions of the monomers near the functional groups were included in the calculations. Atoms were incrementally added to the tethering chains in the preliminary schemes to get to the final schemes shown in Fig. 10. It was observed that increasing the number of atoms to better represent the monomers and polymer increased the calculated energy given off by the DA adduct. This suggests the tethering atoms in each monomer have a significant effect on the frontier molecular orbitals of the functional groups in the reactants and product. The total exothermic energy of the simulated reaction was found to be 24 and 27 kcal/mol DA adduct for the endo- and exo- products respectively.

Fig. 10. The simulated Diels-Alder reaction used to estimate the energy released by the formation of a DA adduct in 2MEP4FS.

Supplementary Material

Viscosity Measurement Validation

Since the Brookfield HADVII+ rotational viscometer was modified to make measurements inside glass culture tubes, the accuracy of the measurements was investigated using corn syrup. The syrup was first tested using a falling sphere technique at room temperature. The same syrup was then tested in the rotational viscometer, and the results were compared.

Falling sphere viscometer

A 25 mL graduated cylinder was filled with corn syrup. The cylinder was backlit and photographed with a Nikon D70 SLR camera externally controlled by an electronic trigger programmed to take a picture every four seconds. A 1/16 inch chrome steel ball bearing was dropped in the center of the cylinder opening and allowed to fall to the bottom of the cylinder. The test was conducted 3 times. Subsequent image analysis was used to determine the velocity of the ball bearing between every two pictures. Assuming no inertial effects ($Re \ll 1$), a modified Stokes equation can be used to related the movement of the ball bearing due to gravity with the opposing drag force due to the viscosity, η :

$$\eta = K \frac{2gr_b^2(\rho_b - \rho_c)}{9s}, \quad (S.1)$$

where g is acceleration due to gravity, ρ_b is the mass density of the ball bearing (7.99 g/cm³), ρ_c is the mass density of the corn syrup (1.40 g/cm³), r_b is the radius of the ball bearing, and s is the measured speed of the ball bearing. Here, the corrective factor, K , accounts for the finite size of the sphere relative to the inner diameter of the cylinder, D (19.11 mm) [23]:

$$K = 1 - 2.104 \left(\frac{2r_b}{D} \right) + 2.09 \left(\frac{2r_b}{D} \right)^3. \quad (S.2)$$

Each test had 10 useful pictures, yielding 9 speeds. The average viscosity of each test is given in Fig. S.1. The average viscosity of all three tests is 5.77 ± 0.15 Pa·s.

Rotational viscometer

Small amounts of corn syrup were transferred from the graduated cylinder to a 10x75 mm borosilicate glass culture tube. Three rotational measurements were performed at three different fluid heights: nominally 10 mm, 15 mm, and 30 mm. For each test, a rotational speed was selected such that the required torque could be measured by the viscometer. Using (2), the viscosity of the corn syrup was estimated (Fig. S.1). The average viscosity of all three fluid levels is 4.92 ± 0.30 Pa·s. The rotational viscometer underpredicts the viscosity measured by the falling sphere method by an average of ~11 %.

Fig. S.1. The results of the falling sphere viscometer and modified rotational viscometer for corn syrup measured at room temperature.

DSC Measurements of 2MEP4FS from Room Temperature Viscosity Test

Two DSC samples were prepared from the 2MEP4FS prepolymer prepared for room temperature viscosity measurements. The samples were taken immediately after completion of the small-sample processing method and tested at time periods coinciding with the beginning and end of viscosity measurements to obtain the T_g of the prepolymer at these points. The glass transition temperature associated with the first sample was correlated with polymer conversion. Using the average conversion rates previously determined at room temperature, the 2MEP4FS viscosity data points were correlated with the conversion. During testing, the second DSC sample was stored near the instrument to maintain a similar sample temperature. The second DSC-measured T_g indicates very good agreement between the predicted and measured conversions (< 0.3 % difference).