



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



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ABSTRACT

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.

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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 Ref. [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 Ref. [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

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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 tetrafulan 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. [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 s 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 10 × 75 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 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

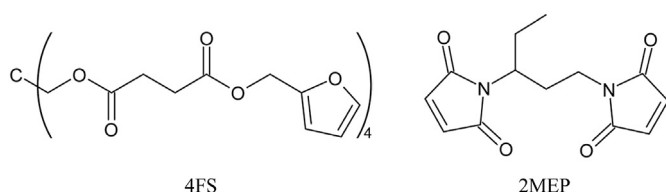


Fig. 1. The tetrafulan and bismaleimide monomers.

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