Concurrent Curing Kinetics of an Anhydride-Cured Epoxy Resin and Polydicyclopentadiene

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ABSTRACT

The development of interpenetrating polymer networks provides a route to create tough materials that maintain high strength and stiffness, suitable for meeting the demands of an off-shore wind turbine environment. This work has focused on a system composed of diglycidyl ether of bisphenol A (DGEBA)-based epoxy resin, contributing high tensile strength and modulus, and polydicyclopentadiene (polyDCPD), which has a higher toughness and impact strength as compared to other thermoset polymers. *In situ* Fourier transform infrared spectroscopy was used to explore the reaction kinetics in neat, diluted and sequentially cured mixtures of epoxy resin and polyDCPD. There were significant differences in the rate of network formation in the two neat systems, as the rate of anhydride curing of the epoxy was extremely slow at the temperatures required for reasonably measurable dicyclopentadiene (DCPD) ring-opening metathesis polymerization. The dissimilar kinetics of these two systems were leveraged in the design of a sequential curing protocol in which the DCPD was first cured in the presence of the epoxy resin components, followed by curing of the epoxy resin at an elevated temperature. The curing kinetics of the macroscopically phase separated domains of the epoxy resin components in the presence of the polyDCPD network behaved as expected for a diluted epoxy resin. These results provide the kinetic basis for future studies to prepare interpenetrating polymer networks which employ thermodynamic control of phase separation such as through the addition of compatibilizing molecules.

INTRODUCTION

Development of off-shore wind energy is a long-term strategy with potential to address large energy demand over the next few decades.⁽¹⁾ The current generations of thermoset polymers and composites are inadequate to address significant challenges facing off-shore wind turbine blades, including a corrosive environment and dynamic stresses, along with the increased capacity, physical size and mass of off-shore wind systems.⁽¹⁻²⁾ Wind turbine blades go through millions of dynamic stress-strain cycles during their lifetime and suffer catastrophic failure of the brittle epoxy material once crack growth is initiated.^(1, 3-6)

The toughness of brittle thermoset materials is often augmented by the use of particulate additives. Toughening can be achieved by the addition of rubber particles⁽⁷⁻⁸⁾ (rubber toughening) or through the addition of nanoscale or colloidal particles such as carbon black,⁽⁹⁾ core-shell particles,⁽¹⁰⁻¹¹⁾ and block copolymers.⁽¹²⁻¹⁷⁾ The addition of the particulate additive increases the energy required for failure by either dissipating the energy locally in the region of crack growth or by increasing the crack length by causing local plastic deformation of the material in the proximity of the inclusion.⁽⁷⁻¹⁸⁾ However, such particle additives often have negative impacts on the thermo-mechanical properties, such as a loss of stiffness due to rubber toughening⁽⁷⁾ or the development of stress-concentrators due to poor dispersion that leads to loss of flexural strength.⁽¹⁹⁻²⁰⁾ The inability to reproducibly create a homogeneous, well-dispersed particle dispersion is often based upon kinetic or processing limitations rather than the thermodynamic behavior of the mixture.

The development of interpenetrating polymer networks (IPNs) provides a route to create tough materials that maintain high strength and stiffness. When appropriately designed as mesoscopically homogeneous mixtures of two crosslinked polymers, IPNs can demonstrate synergistic improvements

in toughness and ultimate properties while exhibiting linear thermo-mechanical properties that scale roughly as the rule of mixtures.⁽²¹⁻²⁴⁾ An IPN in which one network provides toughness and the other network provides strength and stiffness would not suffer from the challenges of traditional particulate composite materials. A significant challenge in the creation of homogeneous IPNs is suppressing macroscopic phase separation of the two networks that is favored as the size of the individual polymers and network grow and the entropic contribution to mixing is diminished. Macroscopically phase separated blends lack the mechanical advantages of homogeneous IPNs and the mechanical properties of such blends can be further diminished should one network cause the system to vitrify and trap unreacted or dangling functional groups of the other.⁽²⁵⁾

Keys to achieving an interpenetrating structure are that the monomers or building blocks of the networks are compatible and, as the network formation occurs, the chains remain compatible or have kinetic / diffusive barriers that prevent them from phase separating. Various strategies for preparing IPNs have been developed over the years, including sequential network formation, simultaneous network formation, latex IPNs, gradient IPNs and semi-IPNs.⁽²⁶⁾ One method to prepare homogenous IPNs is through simultaneous polymerization of the two networks using non-interfering reactions. In this approach, the relatively fast gel times of the two network forming materials must be matched, kinetically trapping the IPNs and inhibiting phase separation.⁽²⁵⁻²⁶⁾ Often, the polymerization reactions of the two components proceed through different types of chemistries, i.e. step-growth and chain-growth, and can result in vastly different kinetic schemes. When the curing kinetics for the two networks differ substantially, the sequential curing of the networks is a more convenient approach to IPN formation.^(25, 27) It is our hypothesis that through the careful tuning of the kinetics of network formation through either simultaneous or sequential curing, IPNs with limited phase separation can be created that possess mechanical properties superior to the neat components.

In this work, we examine the behavior of blends of diglycidyl ether of bisphenol A (DGEBA)-based epoxy resin, contributing high tensile strength and modulus, and polydicyclopentadiene (polyDCPD), which has a higher toughness and impact strength as compared to other thermoset polymers.⁽²⁸⁻³³⁾ The DGEBA is cured with an anhydride and the dicyclopentadiene (DCPD) is cured with a transition metal catalyst via ring opening metathesis polymerization (ROMP). It is important to note that the two systems are not only desirable because of their complementary mechanical properties, but also due to their respective non-interfering thermosetting reactions. Herein, we examine the kinetics of network formation in the neat systems as well as in diluted and sequentially cured, macroscopically phase separated blends. The kinetic insight provided by this study will provide the basis for *future* work focused on the creation of IPNs with superior mechanical properties.

EXPERIMENTAL MATERIALS AND METHODS

Materials

The diglycidyl ether of bisphenol A (DGEBA) was supplied by Dow Chemical in the form of Dow Epoxy Resin (D.E.R.) 331 (the fraction of DGEBA molecules that are pre-polymerized and possess an extra hydroxyl-containing mid-group, $n = 0.15$; structure shown in Scheme 1). Nadic methyl anhydride (NMA, > 95% purity) and dicyclopentadiene (DCPD) with butylated hydroxytoluene as a stabilizer (> 96% purity) were purchased from Sigma Aldrich and used as received. The 2nd generation Grubbs' catalyst (G2) was purchased from Sigma Aldrich and stored under an ultra-pure nitrogen environment. The G2 catalyst was freeze-dried in benzene before use. An epoxy resin catalyst, 2,4,6-Tri(dimethylaminomethyl) phenol, was supplied by Air Products as Ancamine K54 (referred to as K54 in this manuscript) and used as received.

Sample Preparation

Blend nomenclature. Blends are labeled as xxEyyD, where xx corresponds to the wt % of epoxy resin (consisting of DGEBA, NMA, and K54) and yy corresponds to the wt % of DCPD. For example, 90E10D indicates a blend containing 90 wt% epoxy resin and 10 wt% DCPD.

Curing of DCPD. Pure DCPD was cured using a 5000:1 molar ratio of the DCPD monomer to the G2 catalyst. Freeze dried G2 catalyst was added to a 20 mL scintillation vial. DCPD was melted at 30 °C and forcefully injected in the Grubbs' catalyst. The fine particulates of freeze-dried G2 were dissolved by repeatedly drawing the G2/DCPD mixture into the syringe and subsequently re-injecting it into the vial. The sample was then injected into a preheated Fourier transform infrared (FTIR) spectroscopy cell at 30 °C. Spectroscopy measurements began immediately and reaction time during mixing was assumed to be negligible. The start of the reaction, time = 0, was considered to be the start of the spectroscopy measurements. The pure DCPD/G2 mixtures exhibited an induction time of 5-6 minutes. The time to prepare the mixture and inject it into the FTIR cell was approximately 30 sec (or less). Therefore, data collection began well before the end of the induction time and the induction time did not impact the kinetic parameters extracted in this study.

Curing of DGEBA. Pure DGEBA was cured using 95.3 phr (parts per hundred parts by weight of DGEBA resin) of NMA and 1 phr K54. This corresponds to the following concentration of each component: 50.9 wt% of DGEBA, 48.5 wt% of NMA and 0.6 wt% of K54. The mixture components were mixed in a 20 mL scintillation vial using mechanical stirring. The sample was then injected in a preheated FTIR cell at a specified temperature (88, 97, or 106 °C).

DGEBA curing in the presence of unreacted DCPD monomer. DGEBA was cured with NMA and K54 (NMA and K54 were added to the DGEBA at concentrations of 95.3 phr and 1 phr, respectively),

diluted with DCPD. The mixtures contained the following concentrations of DCPD, by weight: 10%, 30%, 50%, and 70%. Sample 90E10D was mixed in a 20 mL scintillation vial using mechanical stirring, while the other samples possessed a low enough viscosity to mix in a 20 mL scintillation vial by vigorously shaking. The sample was then injected in a preheated FTIR cell at 88 °C with the ports capped to avoid DCPD evaporation.

DCPD curing in the presence of unreacted epoxy resin components. DCPD was cured using a 5000:1 molar ratio of the DCPD monomer to the G2 catalyst, diluted with the epoxy resin components (DGEBA, with the addition of 95.3 phr NMA and 1 phr K54). The mixtures contained the following concentrations of the epoxy resin (consisting of DGEBA, NMA and K54), by weight: 10%, 30%, 50%, 70%, and 90%. The freeze dried G2 catalyst was added to a 20 mL scintillation vial. A mixture of the epoxy resin components and DCPD was then forcefully injected in the Grubbs' catalyst. The fine particulates of freeze-dried G2 were dissolved by repeatedly drawing the mixture into the syringe and re-injecting it into the vial. The sample was injected into a preheated FTIR spectroscopy cell at 30 °C. An induction period was not observed in these mixtures. The time to prepare the mixture and inject it into the FTIR cell was approximately 30 sec (or less). The reaction that occurs during this mixing time was negligible (the blends achieved less than 1% conversion during this time), and therefore the error bars on the time axis are smaller than the data points shown on plots of the conversion vs. time data obtained from diluted DCPD blends. For samples used in optical microscopy, K54 was omitted from the sample. Optical microscopy slides were prepared by taking a drop of the reactive mixture and sandwiching it between a glass slide and a glass cover slip. The sample was cured overnight at 30 °C.

Sequentially cured blends. Blends containing the epoxy resin components (DGEBA, 95.3 phr NMA, and 1 phr K54) and DCPD (with G2 catalyst added at a 5000:1 molar ratio of the DCPD monomer to G2) were cured sequentially. The freeze dried G2 catalyst was added to a 20 mL scintillation vial. A

mixture of the epoxy resin components and DCPD was then forcefully injected in the Grubbs' catalyst. The fine particulates of freeze-dried G2 were dissolved by repeatedly drawing the mixture into the syringe and re-injecting it into the vial. The sample was injected into a preheated FTIR cell at 30 °C. The sample was allowed to cure at 30 °C. Once the conversion of the DCPD was unchanged over a period of 30 minutes, the cell was heated to 60 °C for one hour and then heated to a specified temperature (88, 97, or 106 °C) until the conversion of anhydride did not change with time. Reaction that occurred during the transient portion of the temperature step changes (a small fraction of the total reaction time) was not accounted for in the calculation of the final conversion of sequentially cured samples.

Characterization

Optical Microscopy. Optical microscopy was performed on a Leica DM2500 M microscope with a HCX PL FLUOTAR 20X/0.50 BD objective in bright field mode using a mercury lamp. Optical microscopy images were processed using the ImageJ fast Fourier transform (FFT) function. The average domain size (d) was taken to be that at the peak maximum in the intensity versus wavevector plot.

Fourier Transform Infrared (FTIR) Spectroscopy. To explore *in situ* reaction kinetics, a Nicolet 4700 spectrometer from Thermo Scientific was used in transmission mode with a ported heating cell and KBr windows (32 mm diameter, 3 mm thick). The OMNIC Series software was used to follow selected peaks at 4 cm⁻¹ resolution using 32 scans. The heating cell's temperature controller maintained the temperature at the outer edge of the cell and as a result the actual temperature in the center of the windows differed from the set-point value. Controller set points of 35, 70, 100, 110, and 120 °C corresponded to a center temperature of 30, 60, 88, 97, and 106 °C, respectively (measured directly

with a thermocouple). All reported temperature values correspond to the temperature at the center of the cell.

Conversion of reactive moieties as monitored by the corresponding FTIR peaks (here denoted as α) is described by Equation 1, where A_0 is the absorbance at the beginning of the reaction (at time = 0) and A_t is the absorbance at time t.

$$\alpha = \frac{A_0 - A_t}{A_0} \quad (1)$$

REACTION MECHANISMS

Anhydride Curing of DGEBA in the Presence of a Tertiary Amine

The alternating copolymerization of epoxy and anhydride monomers catalyzed by a tertiary amine is commonly assigned the mechanism detailed in Scheme S1 of the *Supporting Information*.⁽³⁴⁻³⁷⁾ The tertiary amine attacks an epoxide group on the DGEBA molecule, creating an alkoxide anion. This alkoxide anion then reacts with an anhydride to form a carboxylate anion as the propagating species. Propagation proceeds as the carboxylate anion reacts with an epoxide group to form a monoester containing an alkoxide anion that can react with another anhydride. While this mechanism has been demonstrated to be the main curing pathway, it neglects the numerous side reactions that can take place and convolute the kinetics, *e.g.*, tertiary amine-catalyzed homopolymerization of the epoxy and ring-opening of the epoxide or anhydride in the presence of hydroxyl groups.⁽³⁷⁻⁴²⁾

Since the reaction proceeds as a strictly alternating polymerization, following either the epoxide or the anhydride conversion will produce an accurate representation of the reaction kinetics. The vibrational spectra of both DGEBA and NMA have been well explored by Antoon and Koenig and we use their work to assign spectral peaks to vibrational modes of the different chemical moieties.⁽⁴³⁾ As the reaction

progresses, the peaks located at 1781 and 1857 cm^{-1} , associated with asymmetric and symmetric stretching of the anhydride respectively, diminish. Ester creation is observed through the appearance of peaks at 1747 cm^{-1} and 1780 cm^{-1} associated with the stretching of the C=O and C-O bonds of the ester, respectively.⁽⁴³⁻⁴⁴⁾ We have chosen to use the peak located at 1857 cm^{-1} , corresponding to the symmetric stretching of the anhydride, to monitor the anhydride conversion, avoiding overlap with the ester creation peak at 1780 cm^{-1} . The peaks located at 1508 cm^{-1} and 1608 cm^{-1} , associated with the C=C stretching within the aromatic rings of DGEBA, remain unaffected by the reaction. Relevant FTIR peak locations and vibrational modes for the uncured and cured epoxy resin are summarized in Table 1.

Table 1: Characteristic vibrational modes and corresponding wavenumbers of uncured and cured epoxy resin

	Vibrational Mode	Wavenumber (cm^{-1})⁽⁴³⁻⁴⁴⁾
Anhydride Monomer	Symmetric stretching of C=O	1857
	Asymmetric stretching of C=O	1781
Epoxy Monomer	Aromatic C=C stretching	1608, 1508
Cured Network	C=O stretching (ester)	1743
	C-O stretching (ester)	1780

Based on the mechanism in Scheme S1 (and the assumption that the reaction with rate constant k_2 is rate-determining), one would expect the rate equation for anhydride to follow the form

$$\frac{d[NMA]}{dt} = k_2[\text{Alkoxide Anion}][NMA] \quad (2)$$

However, it has been experimentally reported that after a brief induction time the DGEBA/NMA reaction, catalyzed by a tertiary amine, follows first order kinetics with respect to the NMA concentration despite the continued increase in the alkoxide anion concentration. This behavior was also observed for this system in ref. ⁽⁴³⁾ and was attributed to a shift in the active center away from the

alkoxide anion.⁽⁴³⁾ While the precise nature of this shift is not fully understood, the consumption of anhydride can be treated as first order over a wide range of conversions.⁽⁴³⁾ Integration of the rate law in Equation 2 results in the expression in Equation 3:

$$\ln(1 - \alpha) = -k_2 t \quad (3)$$

Equation 3 is linear with respect to time (α is the reaction conversion, defined in Equation 1). A plot of $\ln(1-\alpha)$ vs. time yields a straight line if the system is first order and the slope is a measure of k_2 . The activation energy associated with the reaction is calculated by the construction of an Arrhenius plot by plotting $\ln(k_2)$ versus $1/T$.

Ring Opening Metathesis Polymerization of DCPD

The curing of DCPD proceeds via ring-opening metathesis polymerization (ROMP). In the ROMP reaction using Grubbs' catalyst, the driving force is relief of the ring strain on cyclic olefins (Scheme S2 in the *Supporting Information*). The mechanism presented by Grubbs et al. in ref.⁽⁴⁵⁾ proceeds with the dissociation of the tricyclohexylphosphine (Cy_3P) ligand followed by formation of the intermediate with the olefin. For 2nd Generation Grubbs' catalyst (G2), the dissociation of the ligand (Cy_3P) is the rate limiting step and the reassociation of the ligand proceeds at a much slower rate than the formation of the intermediate with the olefin. As a result, it is expected that ROMP follows pseudo-first order kinetics, once equilibrium between the dissociation and reassociation of the ligand is achieved.⁽⁴⁵⁾

As DCPD monomer undergoes ROMP, the original *cis* double bonds of the monomer are broken and an equilibrium creation of new *trans* (majority) and *cis* (minority) double bonds occurs. This new *trans* double bond formation manifests itself in the creation of a new FTIR peak at 974 cm^{-1} corresponding to the out of plane bending of $\text{C}=\text{C}-\text{H}$, while the peak associated with the out-of-plane bending of *cis*

double bonds is found in the 700 cm⁻¹ region.⁽⁴⁶⁾ Table 2 summarizes the explored FTIR peaks for the ROMP of DCPD.

Table 2: Characteristic vibrational modes and corresponding wavenumbers of DCPD monomer and polyDCPD.

	Vibrational Mode	Wavenumber (cm ⁻¹)	Ref.
DCPD Monomer	Out-of-Plane Bending (<i>cis</i>) C=C-H	754, 727	(47-48)
	In-Plane Bending C=C-H	1339	(48-49)
	Molecular Torsion	484	(48)
PolyDCPD	Out-of-Plane Bending (<i>trans</i>) C=C-H	974	(50)
	Out-of-Plane Bending (<i>cis</i>) C=C-H	754,735	¹

Previous studies characterizing the kinetics of the ROMP of DCPD through differential scanning calorimetry (DSC) indicated that the reaction proceeds by an nth order autocatalytic model described by:²

$$\frac{d(\alpha)}{dt} = k_{obs}(1 - \alpha)^n \alpha^m \quad (4)$$

where k_{obs} is the observed rate constant assigned to the conversion of DCPD.^(31, 51) To account for any diffusion control, a diffusional factor, $f(\alpha)$, was applied to the kinetic data [the right-hand side of Equation 4 was multiplied by $f(\alpha)$], where C is a system-dependent constant and α_c is the conversion at the onset of diffusion control.

$$f(\alpha) = \frac{1}{1 + C \exp(\alpha - \alpha_c)} \quad (5)$$

¹ The C-H stretching of olefinic acyclic and cyclic *cis* C=C-H moieties is often assigned to the 700 cm⁻¹ region.^[46] From the spectra shown in Figure 4, it is apparent that there is a new peak that forms at 735 cm⁻¹ upon curing DCPD. Following the discussion in the main text, peak creation also occurs at 754 cm⁻¹ that can be attributed to creation of new olefin species upon curing.

² The temperature dependencies of the exponents in Equation 4 (n and m) were reported in ref. [31]; at 30 °C, n and m were 2.3 and 0.5, respectively. The temperature dependencies of the exponents (n and m) were linearly extrapolated to determine their values at temperatures relevant to this study.

The Arrhenius pre-exponential factor, A , and activation energy, E_a , describing the temperature dependence of k_{obs} were previously determined from DSC for G2 at $T=303.15$ K to be $A = 2.14 \times 10^{18} \text{ min}^{-1}$ and $E_a = 110,750 \text{ J mol}^{-1}$.⁽³¹⁾ The activation energy is dependent on the reaction conversion and increases sharply at high conversions, following ref.⁽³¹⁾. This effect is neglected in our study, as the data are modeled through a limited range of conversions ($\alpha \leq 0.6$), over which isoconversional modeling in ref.⁽³¹⁾ indicated the activation energy was fairly constant.

RESULTS AND DISCUSSION

Blend Morphology through Optical Microscopy

Blends were prepared at 30°C in which DCPD was cured in the presence of the uncured epoxy components (DGEBA and NMA, without addition of the K54 catalyst). The epoxy components were left uncured to improve the contrast of the phase separated morphology. Optical micrographs of blends of various compositions are shown in Figure 1. As the fraction of the epoxy resin components decreased from 90 to 70 percent, the morphology transitioned from discrete to co-continuous domains. For samples that exhibited co-continuous domains, the average domain size was determined from the location of the peak in the Fast Fourier Transform of the image (refer to Figures S1-S2 in the *Supporting Information*). The domain sizes were $3 \mu\text{m}$, $2 \mu\text{m}$ and $4 \mu\text{m}$ for samples 70E30D, 50E50D, and 30E70D, respectively, confirming macroscopic phase separation of the partially cured samples. Interestingly, the macroscopically phase separated (and opaque) blends of polyDCPD and uncured epoxy resin components became transparent once the epoxy resin was cured, likely due to matching of the refractive indices of the epoxy and polyDCPD domains.

Figure 1: Optical micrographs at 20X magnification of blends containing uncured epoxy resin components (DGEBA and NMA) and DCPD cured with G2 at 30 °C, with the following designations: a) 30E70D, b) 50E50D, c) 700E30E and d) 90E10D. Discrete domains are present at high concentrations of the epoxy resin components (i.e. sample 90E10D) and a transition to co-continuous domains was apparent as the weight percent of the epoxy resin components decreased. The scale bar applies to all images.

Reaction Kinetics through FTIR

In situ FTIR was used to explore the reaction kinetics in neat, diluted and sequentially cured epoxy resin and DCPD systems. Raw and processed FTIR data are included for all samples in the *Supporting Information*.

Pure Epoxy Resin Curing Kinetics

A time series of *in situ* FTIR spectra obtained during the curing of DGEBA with NMA and K54 catalyst at 97 °C is shown in Figure 2. Reaction and consumption of NMA is highlighted by the decrease in the absorbance of the peaks associated with the symmetric and asymmetric anhydride stretching, located at 1857 cm^{-1} and 1781 cm^{-1} , respectively. Ester creation, resulting from the curing reactions outlined in Scheme 1, was monitored through the increase in the absorbance of the peak

located at 1747 cm^{-1} , associated with the stretching of the C=O bond. The conversion of the anhydride moieties, evidenced through the evolution of the absorbance of the peak located at 1857 cm^{-1} , was calculated as a function of time at each temperature, employing Equation 1, and shown in Figure 3. The time dependence of the conversion of anhydride was modeled using Equation 3 with the rate constant, k_2 , as a fitting parameter, in the region between 20-70% conversion. At early times (*i.e.*, prior to 20% conversion), creation of the carboxylate anion convolutes the spectra (refer to discussion in the *Supporting Information*) as the concentration of the alkoxide anion continues to change. As a result, the first order kinetic modeling (Equation 3) is not valid at low conversions. At intermediate times (*i.e.* 20-70% conversion), the anhydride consumption follows first order kinetics despite continued increase of the carboxylate anion absorbance, possibly indicating a shift away from the alkoxide anion as an active center.⁽⁴³⁾ At long times (*i.e.* after 70% conversion), the reaction becomes diffusion-controlled and the sample vitrifies or is close to vitrification; the conversion as a function of time deviates from Equation 3. Using the first order rate constants at 88, 97, and $106\text{ }^{\circ}\text{C}$, the activation energy was determined to be $82\text{ kJ mol}^{-1} \pm 10\text{ kJ mol}^{-1}$ which is in good agreement with literature.⁽⁴³⁾

Figure 2: *In situ* FTIR spectra for the curing of DGEBA with NMA and K54 catalyst at $97\text{ }^{\circ}\text{C}$, obtained at times between 0-200 min in 10 min intervals. The absorbances of the peaks located at 1857 cm^{-1} and 1781 cm^{-1} steadily decrease while the 1747 cm^{-1} peak absorbance increases. Conversion was monitored by following the peak absorbance at each time point, employing Equation 1.

Figure 3: Time-dependence of the conversion of anhydride, α , in the curing of DGEBA with NMA and K54 catalyst at 88, 97 and 106 °C. The linear region, denoted by the red lines, was used to extract rate constants at each temperature using Equation 3.

Pure DCPD Curing Kinetics

While DCPD ROMP kinetics have been previously explored using thermal and rheokinetic analysis,^(31, 51-55) there is little literature on the use of spectroscopy to follow the progress of the ROMP reaction.⁽⁵⁶⁻⁵⁹⁾ Figure 4 shows the spectra of DCPD pre- and post-curing at 30 °C. Three candidates are identified to follow the kinetics of ROMP of DCPD due to the lack of overlap with peaks in the epoxy resin spectra and strong peak intensity: 1) the peak located at 1339 cm^{-1} associated with the in-plane bending of the C=C-H moiety, 2) the peaks located at 754 and 727 cm^{-1} associated with the out-of-plane bending of the C=C-H moieties, and 3) the peak located at 484 cm^{-1} associated with the molecular torsion of the DCPD molecule. As observed in Figure 5, the peak located at 1339 cm^{-1} , associated with the in-plane bending of the C=C-H bond, and the peak located at 484 cm^{-1} , associated with molecular torsion, exhibit similar time-dependent changes in their absorbances. The peaks located at 754 and 727 cm^{-1} (associated with the out-of-plane bending of the C=C-H moieties) reside in the fingerprint region, and reaction of either C=C bond is expected to alter their peak locations given the fingerprint region's representation of the entire molecule or large portions of the molecule working in conjunction.⁽⁶⁰⁾ In

addition, the curing reaction results in creation of new *cis* double bonds that have similar vibrational frequencies as the monomer in the 700 cm^{-1} region as evidenced by the development of shoulders off of the peaks at 754 and 727 cm^{-1} (Figure 4 inset). (The creation of *trans* double bonds results in the formation of a new peak at 974 cm^{-1} associated with the out-of-plane bending of the C-H located on a *trans* double bond). For these reasons, it is not expected that the overall conversion can be accurately monitored using the peaks located at 754 and 727 cm^{-1} ; Figure 5 shows that the conversion calculated using the peak at 754 cm^{-1} is an outlier when compared to the results from the other peaks. Given the consistency in the conversion calculated using the peaks located at 484 and 1339 cm^{-1} (associated with molecular torsion and in-plane bending of the C=C-H bond, respectively), and the isolated location of the peak at 484 cm^{-1} , we have chosen to monitor the kinetics of the ROMP of DCPD using the peak located at 484 cm^{-1} .

Figure 4: FTIR spectra of DCPD prior to curing (solid black curve) and after curing at $30\text{ }^{\circ}\text{C}$ for 60 min with G2 catalyst (dashed red curve at 67% conversion). (a) Wavenumbers specifically assigned to *cis* C=C-H modes are highlighted at 1339 and $754/727\text{ cm}^{-1}$ for the in-plane and out-of-plane bending, respectively. The peak at 484 cm^{-1} is assigned to DCPD molecular torsion while the peak at 974 cm^{-1} is associated with *trans* C=C-H out-of-plane stretching.⁽⁴⁷⁻⁴⁸⁾ (b) The 800 to 450 cm^{-1} region of the FTIR spectra is highlighted showing the development of shoulders and broadening of the peaks located around 775 to 700 cm^{-1} that occur during reaction (due to new *cis* creation and peak shifting).

Figure 5: Conversion versus time of select peaks during the ROMP of DCPD at 30 °C with G2 catalyst.

Various kinetics models were applied to the data obtained from curing DCPD at 30 °C (Figure 6). First, the n^{th} order model (Equation 4 with the α^m term dropped) does not capture any relevant features of the data (Figure 6). Application of n^{th} order *autocatalytic* model (Equation 4) using the aforementioned kinetic parameters describes the behavior at low values of α , though it shows deviations at high conversions (Figure 6). Lastly, the n^{th} order autocatalytic model *with diffusional control* (combining Equations 4 and 5), with fitting parameters $C=13.8 \pm 3.9$ and $\alpha_c=0.40 \pm 0.03$, provides the best fit to the data, indicating that the reaction becomes diffusion controlled at moderate conversions. This result is consistent with prior studies by Yang and Lee, who observed distinct behaviors for the ROMP of DCPD using 1st and 2nd generation Grubbs' catalysts (G1 and G2, respectively).⁽³¹⁾ In reactions catalyzed by G1, an n^{th} order model was sufficient to represent the data, whereas an autocatalytic model was required for the ROMP of DCPD using G2.⁽³¹⁾ The authors proposed that the autocatalytic behavior observed for the G2 catalyst may have origins in its longer induction period and increased preference for binding to the norbornene moiety, relative to the G1 catalyst.⁽³¹⁾ We also note that it has been reported in the literature that the dissociation of the ligand occurs more slowly for G2 relative to G1.⁽⁴⁵⁾

Figure 6: Various kinetic models applied to the conversional data obtained from DCPD curing at 30 °C with G2 catalyst. Kinetic parameters such as the order, activation energy, and pre-exponential factor were taken from ref. 6 as described in the text. Diffusional parameters C and α_c were adjusted to provide the best fit to the data.

As shown in Figure 5, the ultimate conversion of the characteristic DCPD peaks remained relatively low, around 60%, resulting in a large portion of free monomer in the system.

Effect of Dilution on the Epoxy Resin Curing Kinetics

The curing kinetics of epoxy resin were characterized in the presence of unreacted DCPD monomer using FTIR spectroscopy. Raw data were processed with the application of Equations 1 and 3 to determine the composition dependence of the rate constant. The volume fraction of epoxy resin components (including DGEBA, NMA, and K54) in the mixture, Φ , was calculated using the known masses of each component and the polymer densities (taken to be 1.16 g cm^{-3} and 0.98 g cm^{-3} for D.E.R. 331 and DCPD, respectively). The first order rate constant is plotted as a function of Φ in Figure 7.

Figure 7: Composition-dependence of the first order rate constant, k , associated with the consumption of anhydride in the curing of DGEBA with NMA and K54 at 88 °C. The red solid line shows a slope of 2 on the log – log plot of k vs Φ predicted by collision theory (Equation 6). Experimental values (black squares) show a strong deviation as the volume fraction moves away from unity.

The solid red line in Figure 7 indicates a slope of 2 on the log-log plot, the composition-dependence of the rate constant that is predicted by collision theory defined in Equation 6 for a reaction between molecules 1 and 2, where N_1 and N_2 are the number of molecules of type 1 and 2, respectively, d_{12} is the distance between molecules 1 and 2 at which the reaction takes place, μ is the reduced mass of the system and k_b is the Boltzmann constant.⁽⁶¹⁾

$$k = A \exp\left(\frac{-E_A}{RT}\right) = N_1 N_2 d_{12}^2 \sqrt{\frac{8k_b T}{\mu}} \exp\left(\frac{-E_A}{RT}\right) \propto \Phi^2 \quad (6)$$

The data in Figure 7 show large deviations from the expected behavior at low volume fractions of epoxy resin (Φ). From Figure 7, it is clear that a linear fit to the rate constants' Φ^2 dependence does well to describe the larger epoxy volume fraction samples but deviation in the positive direction occurs at low epoxy compositions. This behavior may be explained by the transition from a polar (epoxy-rich) environment at high Φ to a non-polar (DCPD-rich) environment at low Φ as well as the change in viscosity as the composition changes. Two competing factors are expected to influence the rate constant as more DCPD is introduced into the system: the dielectric constant of the solvent decreases due to a

decrease in solvent polarity (decreasing the rate constant) and the transition state becomes more stable due to less steric hindrance (increasing the rate constant).⁽⁶¹⁻⁶²⁾ It is also worth noting that the diluted epoxy resin samples were opaque, similar to the optical character of the samples containing cured DCPD in the presence of unreacted epoxy resin (shown in Figure 1). Depending on the conversion required for the onset of phase separation, the kinetics of the diluted blends may be impacted by the presence of a phase separated morphology.

The final conversions of the diluted systems (~92%) were higher than that of the neat system (~85%), which can possibly be attributed the increased mobility of DGEBA and NMA molecules in the presence of the unreacted DCPD monomer.

Effect of Dilution on the DCPD Curing Kinetics

Blends were prepared containing DCPD and G2 catalyst combined with the epoxy resin components (DGEBA, MDA and K54) and cured at 30 °C. The reaction time was limited to ~ 700 min to minimize curing of the epoxy resin. The conversion of DCPD (the sum of the conversion of both cyclic moieties), determined through application of Equation 1 to the peak located at 484 cm⁻¹, was characterized as the DCPD content in the blends varied from 10-100 wt % (Figure 8). The final DCPD conversion was fairly consistent (65-67%) for samples containing 50-90 wt% DCPD, and slightly higher than the final conversion of neat DCPD (61%), possibly attributed to an increase in mobility upon dilution. For the mixtures containing low DCPD concentrations, the final conversion at 30 °C was significantly reduced, 39% and 12% conversion for samples containing 10 and 30 wt% DCPD, respectively. This is most likely due to the combined effects of the reduced concentration of the DCPD monomer and an increase in viscosity at high contents of DGEBA. The viscosities of DGEBA (in the form of D.E.R. 331) and DCPD are 11,000-14,000 cP and 1 cP, respectively, at room temperature.⁽⁶³⁻⁶⁴⁾ Even at low DCPD

conversions, the system may be diffusion-limited at high concentrations of the epoxy resin components. An alternative explanation is that the G2 catalyst may become oxidized in solution at high concentrations of the epoxy resin components.⁽⁶⁵⁾ The small quantity of G2 in a dilute polar solution may result in the decomposition via oxidation before any appreciable reaction can take place. The lower overall conversion at low DCPD compositions is troublesome as the properties of the polyDCPD network may not be fully realized and the large degree of free monomer may simply plasticize the epoxy system, impacting the thermomechanical properties, which is undesirable in composite applications.

Figure 8: Conversion versus time for DCPD cured in the presence of the epoxy resin components (DGEBA, MDA and K54) at 30 °C.

Sequential Curing of the Epoxy Resin and DCPD

The kinetics of the epoxy resin curing in the presence of polyDCPD were explored through a sequential curing protocol. Blends were prepared containing DCPD and G2 catalyst combined with the epoxy resin components (DGEBA, NMA and K54) and cured through the following multi-step process. The blends were injected in a preheated FTIR cell at 30 °C. DCPD was allowed to polymerize at 30 °C until

the ROMP reaction stagnated, the sample was then held at 60 °C for one hour, and the cell was subsequently heated to a desired temperature (88, 97, or 106 °C) to cure the epoxy resin. To account for the thermal expansion of the material and changes in the molar absorptivity with temperature, the absorbance of the symmetric stretching of the anhydride located at 1857 cm^{-1} was normalized with respect to the absorbance of the constant aromatic C=C stretching located at 1508 cm^{-1} . In situations where the absorbance at 1508 cm^{-1} was greater than 2 (i.e. in the spectra at 30 and 60 °C) the peak located at 1608 cm^{-1} , also associated with the C=C stretching in the aromatic ring, served the same purpose for normalization and yielded similar results. The rate constant for the epoxy resin curing was determined through application of Equations 1 and 3. Figure 9 shows the comparison of the first order rate constant for the sequentially cured samples and the diluted epoxy resins at 88 °C. The rate of anhydride consumption remains fairly constant in sequentially cured samples over a wide range of compositions, in stark contrast to the strong composition-dependence observed in the diluted samples (Figure 9).

Figure 9: First order rate constants of anhydride consumption at 88 °C of sequentially cured blends (red open circles) compared to the diluted epoxy resins (black squares). The sequentially cured 90E10D sample was repeated 5 times to determine the sample-to-sample variation; the standard deviation is indicated by the error bar.

The observed deviation from the behavior of the diluted samples is most likely to due to the phase separation of the epoxy resin monomers (or oligomers) and the polyDCPD network. If the epoxy

monomer (or oligomers) phase separate from the polyDCPD during the DCPD curing process, they are free to follow kinetics similar to that of the neat epoxy resin. However, from the conversional data of DCPD it is clear that there are unreacted DCPD molecules present in the system that may contribute to the dilution of epoxy resin. As a result, the kinetics of the sequentially cured systems are not identical to that of the neat epoxy resin.

The final conversion of the anhydride in the sequentially cured blends, after curing at 88 °C, was also measured through application of Equation 1, and is reported in Table S1 of the *Supporting Information*. The final conversions of all sequentially cured blends were comparable to one another, $86 \pm 2 \%$, and similar to that of the neat epoxy resin cured at 88 °C (85%). Interestingly, these values are slightly lower than that of the diluted epoxy resins (refer to Figure S11 of the *Supporting Information*).

The mechanical behavior of select sequentially cured blends was probed through tensile testing. As expected, the mechanical properties of these macroscopically phase separated blends did not offer any advantages over the neat systems.

Temperature-Dependence of the Rate Constant in Neat and Sequentially Cured Systems

The kinetics of curing DGEBA with MDA and K54 were explored at three temperatures: 88, 97, and 106 °C. Figure 10 shows an Arrhenius plot for the neat epoxy resin and sequentially cured blends containing 30-90 wt% epoxy resin. Temperature measurements in the middle of the FTIR windows showed a 1 °C variation from sample-to-sample (the temperature controller measures and controls the temperature at the *edge* of the cell), which is indicated by the x-axis error bars in Figure 10. The standard deviation obtained for blend 90E10D was assumed to be representative of the error associated with the determination of rate constants in the studies performed here. This information was used to calculate the error in the determination of the activation energy (reported in Table 3). It is clear that

over the temperature range of the study, and considering the errors in the measurements of the rate constants and temperature, the activation energy was largely independent of the blend composition and similar to the curing of the pure epoxy resin.

Figure 10: Arrhenius plot of the first order rate constant for the neat epoxy resin (DGEBA cured with NMA and K54) and the following sequentially cured blends: 90E10D, 70E30D, 50E50D, and 30E70D. The x-axis error was calculated using the known variation in temperature at the center of the FTIR cell while the y-axis error was determined through repeating the measurement on the 90E10D sample multiple times at 88 K (2.76 1/K x1000).

Table 3: Activation energy in the neat epoxy resin and sequentially cured blends of varying composition.

Sample	$E_a(\text{kJ mol}^{-1})$	Error in E_a (kJ mol^{-1})
Neat epoxy resin	82	10
90E/10D	87	11
70E/30D	77	10
50E/50D	76	10
30E/70D	91	11

CONCLUSIONS

In situ FTIR was used to explore the reaction kinetics in neat, diluted and sequentially cured epoxy resin and DCPD systems. The curing of the neat epoxy resin (DGEBA cured with NMA and K54 catalyst) exhibited first order kinetics over a broad range of conversions. Neat kinetics of the ROMP of DCPD with G2 catalyst were consistent with an n^{th} order autocatalytic model with diffusional control and became strongly diffusion-controlled at low to moderate conversions. The ultimate conversion of the neat DCPD system was around 60%, indicating the presence of a large quantity of monomer at the end of the reaction. Most importantly, these kinetic studies have shown that there are significant differences in the rate of network formation in these two systems, as the DGEBA/NMA/K54 curing reaction is slow at the temperatures employed for the DCPD ROMP reaction (30-60 °C). Such disparate kinetics are not appropriate for the formation of IPNs through the simultaneous curing of the two networks. Rather, the dissimilar kinetics of these two systems can be leveraged in the design of a sequential curing protocol in which the DCPD is first cured in the presence of the epoxy resin components at low temperatures, followed by curing of the epoxy resin at an elevated temperature.

As an important first step toward the development of a sequential curing protocol, the effect of dilution on the kinetics of each network formation was explored. The kinetics of the diluted epoxy resins (in the presence of unreacted DCPD) showed a strong dependence on composition yet deviated from the expected squared volume fraction dependence. The final conversions of the diluted epoxy resins were higher than that of the neat system presumably because of the possible plasticization of the phase separated epoxy domains with unreacted DCPD monomer. In the case of DCPD curing in the diluted blends, the rate of polyDCPD network formation was strongly influenced by the presence of the unreacted epoxy resin components (DGEBA, NMA and K54 catalyst). As the concentration of DCPD in the blend decreased, the overall conversion drastically diminished presumably due to the reduced

concentration of the DCPD monomer, increased mixture viscosity at high contents of DGEBA providing a kinetic barrier for the DCPD monomer to migrate, and possible catalyst oxidation.

In the sequentially cured blends, the ROMP of DCPD was first performed at 30 °C in the presence of the epoxy resin components, followed by curing of the epoxy resin at an elevated temperature. Blends of the epoxy resin components and DCPD cured with G2 catalyst at 30 °C exhibited micron-scale phase separation (observed through optical microscopy). These macroscopically phase separated domains of the epoxy resin components in the presence of the polyDCPD network behaved to a large extent as expected for a neat epoxy resin. The overall anhydride conversion in the sequentially cured blends was consistent with the neat epoxy resin, regardless of the blend composition, and was not impacted by the presence of unreacted DCPD or the polyDCPD network. The rate constant for anhydride conversion in the sequentially cured blends was independent of the blend composition (in contrast to the behavior of epoxy resins diluted with unreacted DCPD), yet was consistently lower than that of the neat epoxy resin (at a value similar to that of the diluted epoxy resin containing 90 wt% epoxy components and 10 wt% DCPD). The activation energy of the epoxy curing was relatively insensitive to the blend composition, and consistent with the value obtained for the neat epoxy resin, within the error of the measurement.

These studies provide unique insight into routes of forming IPNs containing an epoxy resin and polyDCPD. The differences in the kinetics of the neat systems are likely too great for suppressing macroscopic phase separation by kinetic means alone. We have demonstrated the utility of a sequential curing protocol in which the epoxy resin kinetics are largely unaffected by the presence of the polyDCPD curing reaction. These results can be leveraged in future studies to prepare IPNs which employ thermodynamic means of controlling phase separation such as the addition of compatibilizing molecules.

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REFERENCES

1. Hayman, B.; Wedel-Heinen, J.; Brøndsted, P., Materials Challenges in Present and Future Wind Energy. *MRS Bulletin* **2008**, 33 (04), 343-353.
2. NREL, Large-Scale Offshore Wind Power in the United States. **2010**.
3. Brøndsted, P.; Lilholt, H.; Lystrup, A., Composite Materials for Wind Power Turbine Blades *Annual Review of Materials Research* **2005**, 35 (1), 505-538.
4. Sutherland, H. J.; Mandell, J. F., Effect of Mean Stress on the Damage of Wind Turbine Blades. *Journal of solar energy engineering* **2004**, 126 (4), 1041-1049.
5. Mandell, J. F.; Samborsky, D. D.; Wang, L.; Wahl, N. K., New Fatigue Data for Wind Turbine Blade Materials. *Journal of solar energy engineering* **2003**, 125 (4), 506-514.
6. Samborsky, D. D.; Wilson, T. J.; Mandell, J. F., Comparison of Tensile Fatigue Resistance and Constant Life Diagrams for Several Potential Wind Turbine Blade Laminates. *Journal of solar energy engineering* **2009**, 131 (1), 011006-011006.
7. Kim, D. S.; Cho, K.; Kim, J. K.; Park, C. E., Effects of Particle Size and Rubber Content on Fracture Toughness in Rubber-modified Epoxies. *Polymer Engineering & Science* **1996**, 36 (6), 755-768.
8. Sultan, J. N.; McGarry, F. J., Effect of Rubber Particle Size on Deformation Mechanisms in Glassy Epoxy. *Polymer Engineering & Science* **1973**, 13 (1), 29-34.
9. Kim, B. C.; Park, S. W.; Lee, D. G., Fracture Toughness of the Nano-particle Reinforced Epoxy Composite. *Composite Structures* **2008**, 86 (1-3), 69-77.
10. Sue, H. J.; Meitin, E. I. G.; Pickelman, D. M.; Bott, C. J., Fracture Mechanisms in Rigid Core-shell Particle Modified High Performance Epoxies. *Colloid & Polymer Science* **1996**, 274 (4), 342-349.
11. Day, R. J.; Lovell, P. A.; Wazzan, A. A., Toughened Carbon/Epoxy Composites Made by Using Core/Shell Particles. *Composites Science and Technology* **2001**, 61 (1), 41-56.
12. Liu, J.; Sue, H.-J.; Thompson, Z. J.; Bates, F. S.; Dettloff, M.; Jacob, G.; Verghese, N.; Pham, H., Nanocavitation in Self-Assembled Amphiphilic Block Copolymer-Modified Epoxy. *Macromolecules* **2008**, 41 (20), 7616-7624.
13. Liu, J.; Sue, H.-J.; Thompson, Z. J.; Bates, F. S.; Dettloff, M.; Jacob, G.; Verghese, N.; Pham, H., Strain Rate Effect on Toughening of Nano-sized PEP-PEO Block Copolymer Modified Epoxy. *Acta Materialia* **2009**, 57 (9), 2691-2701.
14. Thompson, Z. J.; Hillmyer, M. A.; Liu, J.; Sue, H.-J.; Dettloff, M.; Bates, F. S., Block Copolymer Toughened Epoxy: Role of Cross-Link Density. *Macromolecules* **2009**, 42 (7), 2333-2335.
15. Liu, J.; Sue, H.-J.; Thompson, Z. J.; Bates, F. S.; Dettloff, M.; Jacob, G.; Verghese, N.; Pham, H., Effect of Crosslink Density on Fracture Behavior of Model Epoxies Containing Block Copolymer Nanoparticles. *Polymer* **2009**, 50 (19), 4683-4689.
16. Liu, J.; Thompson, Z. J.; Sue, H.-J.; Bates, F. S.; Hillmyer, M. A.; Dettloff, M.; Jacob, G.; Verghese, N.; Pham, H., Toughening of Epoxies with Block Copolymer Micelles of Wormlike Morphology. *Macromolecules* **2010**, 43 (17), 7238-7243.
17. Thio, Y. S.; Wu, J.; Bates, F. S., Epoxy Toughening Using Low Molecular Weight Poly(hexylene oxide)-Poly(ethylene oxide) Diblock Copolymers. *Macromolecules* **2006**, 39 (21), 7187-7189.
18. Tang, L.-C.; Zhang, H.; Sprenger, S.; Ye, L.; Zhang, Z., Fracture Mechanisms of Epoxy-based Ternary Composites Filled with Rigid-soft Particles. *Composites Science and Technology* **2012**, 72 (5), 558-565.

19. Bergstrom, J. S.; Boyce, M. C., Mechanical Behaviour of Particle Filled Elastomers. *Rubber Chemistry and Technology* **1999**, 72 (4).
20. Sheng, N.; Boyce, M. C.; Parks, D. M.; Rutledge, G. C.; Abes, J. I.; Cohen, R. E., Multiscale Micromechanical Modeling of Polymer/Clay Nanocomposites and the Effective Clay Particle. *Polymer* **2004**, 45 (2), 487-506.
21. Raymond, M. P.; Bui, V. T., Epoxy/castor oil graft interpenetrating polymer networks. *J. Appl. Polym. Sci.* **1998**, 70 (9), 1649-1659.
22. Lin, S. P.; Han, J. L.; Yeh, J. T.; Chang, F. C.; Hsieh, K. H., Composites of UHMWPE Fiber Reinforced PU/Epoxy Grafted Interpenetrating Polymer Networks. *European Polymer Journal* **2007**, 43 (3), 996-1008.
23. Hourston, D. J.; Schäfer, F.-U., Poly(ether urethane)/poly(ethyl methacrylate) interpenetrating polymer networks: Morphology, phase continuity and mechanical properties as a function of composition. *Polymer* **1996**, 37 (16), 3521-3530.
24. Lin, M.-S.; Liu, C.-C.; Lee, C.-T., Toughened interpenetrating polymer network materials based on unsaturated polyester and epoxy. *Journal of Applied Polymer Science* **1999**, 72 (4), 585-592.
25. Cook, W. D.; Chen, F.; Ooi, S. K.; Moorhoff, C.; Knott, R., Effect of curing order on the curing kinetics and morphology of bisGMA/DGEBA interpenetrating polymer networks. *Polym. Int.* **2006**, 55 (9), 1027-1039.
26. Sperling, L. H.; Mishra, V., The current status of interpenetrating polymer networks. *Polymers for Advanced Technologies* **1996**, 7 (4), 197-208.
27. Sperling, L. H., Interpenetrating networks: an overview. *Interpenetrating Polymer Networks* **1994**, 239, 3-38.
28. Constable, G. S.; Lesser, A. J.; Coughlin, E. B., Morphological and Mechanical Evaluation of Hybrid Organic-Inorganic Thermoset Copolymers of Dicyclopentadiene and Mono- or Tris(norbornenyl)-Substituted Polyhedral Oligomeric Silsesquioxanes. *Macromolecules* **2004**, 37 (4), 1276-1282.
29. Jeong, W.; Kessler, M. R., Toughness Enhancement in ROMP Functionalized Carbon Nanotube/Polydicyclopentadiene Composites. *Chemistry of Materials* **2008**, 20 (22), 7060-7068.
30. Li, H.; Wang, Z.; Wang, Y.; He, B., Ring-opening metathesis polymerization of dicyclopentadiene catalyzed by a polymer-supported tungsten catalyst. *Reactive and Functional Polymers* **1997**, 33 (2-3), 193-200.
31. Yang, G.; Lee, J. K., Curing Kinetics and Mechanical Properties of endo-Dicyclopentadiene Synthesized Using Different Grubbs' Catalysts. *Industrial & Engineering Chemistry Research* **2014**, 53 (8), 3001-3011.
32. Hu, F.; Du, J.; Zheng, Y., Morphological effect of fillers on graphite reinforced polydicyclopentadiene based composites. *Polymer Composites* **2014**, 35 (10), 1918-1925.
33. Kissin, Y. V., Polymers of Higher Olefins. In *Kirk-Othmer Encyclopedia of Chemical Technology*, Online ed.; Seidel, A.; Bickford, M., Eds. John Wiley and Sons, Inc.: Accessed: April 6, 2015.
34. Tanaka, Y.; Kakiuchi, H., Study of Epoxy Compounds. Part VI. Curing Reactions of Epoxy Resin and Acid Anhydride with Amine, Acid, Alcohol, and Phenol as Catalysts. *Journal of Polymer Science Part A: General Papers* **1964**, 2 (8), 3405-3430.
35. Mauri, A. N.; Galego, N.; Riccardi, C. C.; Williams, R. J. J., Kinetic Model for Gelation in the Diepoxide-cyclic Anhydride Copolymerization Initiated by Tertiary Amines. *Macromolecules* **1997**, 30 (6), 1616-1620.

36. Trappe, V.; Burchard, W.; Steinmann, B., Anhydride-cured Epoxies via Chain Reaction. 1. The Phenyl Glycidyl Ether/Phthalic Acid Anhydride System. *Macromolecules* **1991**, *24* (17), 4738-4744.
37. Pham, M.-P.; Pham, B. Q.; Huynh, L. K.; Pham, H. Q.; Marks, M. J.; Truong, T. N., Density Functional Theory Study on Mechanisms of Epoxy-phenol Curing Reaction. *J. Comput. Chem.* **2014**, *35* (22), 1630-1640.
38. Tanaka, Y.; Tomio, M.; Kakiuchi, H., Oligomerization of Substituted Phenyl Glycidyl Ethers with Tertiary Amine. *Journal of Macromolecular Science: Part A - Chemistry* **1967**, *1* (3), 471-491.
39. Luston, J.; Manasek, Z., Co-Polymerization of Epoxides with Cyclic Anhydrides Catalyzed by Tertiary-Amines in the Presence of Proton-Donating Compounds. *Journal of Macromolecular Science-Chemistry* **1979**, *A13* (6), 853-867.
40. Fisch, W.; Hofmann, W.; Koskikallio, J., The Curing Mechanism of Epoxy Resins. *Chemistry & Industry* **1956**, (29), 756-757.
41. Fischer, R., Polyesters from Epoxides and Anhydrides. *Journal of Polymer Science* **1960**, *44* (143), 155-172.
42. Luston, J.; Manasek, Z., Character of Active-Centers in the Co-Polymerization of Epoxides with Cyclic Anhydrides. *Journal of Macromolecular Science-Chemistry* **1978**, *A12* (7), 983-994.
43. Antoon, M. K.; Koenig, J. L., Crosslinking Mechanism of an Anhydride-cured Epoxy Resin as Studied by Fourier Transform Infrared Spectroscopy. *Journal of Polymer Science: Polymer Chemistry Edition* **1981**, *19* (2), 549-570.
44. Mertz, E.; Koenig, J. L., Application of FT-IR and NMR to Epoxy Resins. In *Epoxy Resins and Composites II*, Dušek, K., Ed. Springer Berlin Heidelberg: 1986; pp 73-112.
45. Sanford, M. S.; Ulman, M.; Grubbs, R. H., New Insights into the Mechanism of Ruthenium-Catalyzed Olefin Metathesis Reactions. *Journal of the American Chemical Society* **2001**, *123* (4), 749-750.
46. Coates, J., Interpretation of infrared spectra, a practical approach. *Encyclopedia of analytical chemistry* **2000**.
47. Dall'Asta, G.; Motroni, G.; Manetti, R.; Tosi, C., Homopolymerization of Dicyclopentadiene Induced by Ziegler-Natta Catalysts and by Other Transition Metal Systems. *Makromol. Chem.* **1969**, *130* (1), 153-165.
48. Parker, S. F.; Williams, K. P. J.; Steele, D.; Herman, H., The Vibrational Spectra of Norbornene and Nadic Anhydride. *Physical Chemistry Chemical Physics* **2003**, *5* (8), 1508-1514.
49. Tjahjono, A. M.; Feng, G.; Hermanto, M. W.; Cechao, F.; Garland, M., Combining in situ FTIR spectroscopy, BTEM analysis, bulk density measurements and DFT for two Diels-Alder reactions. A general approach for partial molar volume and reaction volume analyses. *RSC Advances* **2014**, *4* (42), 22194-22204.
50. Abadie, M. J.; Dimonie, M.; Couve, C.; Dragutan, V., New Catalysts for Linear Polydicyclopentadiene Synthesis. *European Polymer Journal* **2000**, *36* (6), 1213-1219.
51. Kessler, M. R.; White, S. R., Cure kinetics of the ring-opening metathesis polymerization of dicyclopentadiene. *Journal of Polymer Science Part A: Polymer Chemistry* **2002**, *40* (14), 2373-2383.
52. Kessler, M.; Larin, G.; Bernklau, N., Cure Characterization and Viscosity Development of Ring-opening Metathesis Polymerized Resins. *Journal of Thermal Analysis and Calorimetry* **2006**, *85* (1), 7-12.
53. Liu, X.; Sheng, X.; Lee, J. K.; Kessler, M. R., Isothermal cure characterization of dicyclopentadiene - The glass transition temperature and conversion. *Journal of Thermal Analysis and Calorimetry* **2007**, *89* (2), 453-457.

54. Mauldin, T. C.; Kessler, M. R., Latent catalytic systems for ring-opening metathesis-based thermosets. *Journal of Thermal Analysis and Calorimetry* **2009**, 96 (3), 705-713.
55. Ng, H.; Manas-Zloczower, I.; Shmorhun, M., Rheokinetic studies for the reaction injection molding of polydicyclopentadiene. *Polymer Engineering & Science* **1994**, 34 (11), 921-928.
56. Barnes, S. E.; Brown, E. C.; Corrigan, N.; Coates, P. D.; Harkin-Jones, E.; Edwards, H. G. M., Raman spectroscopic studies of the cure of dicyclopentadiene (DCPD). *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2005**, 61 (13-14), 2946-2952.
57. Mohite, D. P.; Mahadik-Khanolkar, S.; Luo, H.; Lu, H.; Sotiriou-Leventis, C.; Leventis, N., Polydicyclopentadiene aerogels grafted with PMMA: I. Molecular and interparticle crosslinking. *Soft Matter* **2013**, 9 (5), 1516-1530.
58. Constable, G. S.; Lesser, A. J.; Coughlin, E. B., Ultrasonic spectroscopic evaluation of the ring-opening metathesis polymerization of dicyclopentadiene. *J. Polym. Sci. Pt. B-Polym. Phys.* **2003**, 41 (12), 1323-1333.
59. Rule, J. D.; Moore, J. S., ROMP Reactivity of endo- and exo-Dicyclopentadiene. *Macromolecules* **2002**, 35 (21), 7878-7882.
60. Yadav, L. D. S., *Organic Spectroscopy*. Springer Science & Business Media: 2013; p 334.
61. Vyazovkin, S., On the Phenomenon of Variable Activation Energy for Condensed Phase Reactions. *New Journal of Chemistry* **2000**, 24 (11), 913-917.
62. Reichardt, C.; Welton, T., *Solvents and Solvent Effects in Organic Chemistry*. Fourth, Updated and Enlarged Edition edition ed.; Wiley-VCH: Weinheim, Germany, 2010; p 718.
63. Li, Y.-S.; Li, M.-S.; Chang, F.-C., Kinetics and Curing Mechanism of Epoxy and Boron Trifluoride Monoethyl Amine Complex System. *Journal of Polymer Science Part A: Polymer Chemistry* **1999**, 37 (18), 3614-3624.
64. Gupta, R. K., *Polymer and Composite Rheology, Second Edition*. CRC Press: 2000; p 416.
65. Slugovc, C.; Demel, S.; Riegler, S.; Hobisch, J.; Stelzer, F., Influence of Functional Groups on Ring Opening Metathesis Polymerisation and Polymer Properties. *Journal of Molecular Catalysis A: Chemical* **2004**, 213 (1), 107-113.