Studies of the development of intermolecular networks during the curing of coatings using single-sided nuclear magnetic resonance

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Studies of the development of intermolecular networks during the curing of coatings using single-sided nuclear magnetic resonance

A thesis submitted in partial fulfillment of the requirement for the degree of Bachelor of Science in Chemistry from The College of William and Mary

by

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ABSTRACT

In recent years, the development and accessibility of UV-cured coatings have made them a focus of polymer studies. UV-cured coatings provide a variety of benefits over traditional air-drying coatings. UV-coatings have been studied fairly extensively but many of the techniques used to track curing are destructive. Single-sided nuclear magnetic resonance (NMR) provides an alternative, non-invasive and non-destructive technique for these curing studies. The cross-linking in the coating poly(ethylene glycol) diacrylate (PEGDA) was monitored through two measurements, $T_2$ relaxation and Multiple-Quantum Coherences. These two NMR experiments will provide a picture of the level of molecular network formation during the curing process. $T_2$ relaxation measurements are frequently used to track cross-linking and provide a reliable look at the rigidity of the intermolecular network. Multiple-Quantum Coherences have been used to probe residual dipolar couplings, which are indicative of local orientation and cross-linking. The quantitative cross-linking and local orientation gathered from these experiments can be used to draw conclusions about strength and completeness of the intermolecular networks formed. Cross-checking the results between these two fundamentally different measurements creates a realistic picture of the formation of intermolecular networks in the PEGDA coating.
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1 INTRODUCTION:

1.1 UV-curable coatings:

Coatings are polymers applied to the surface of an object or substrate and are usually applied to protect against damage. There are a variety of applications of coatings, for example, protecting against chemical spills on a lab bench, the prevention of water damage to wood or metal on the hull of a ship or to protect against scratches on a car’s exterior paint. One of the best-known applications of coatings is the protection against the wear of atmosphere on paintings and cultural artifacts over time.

UV-cured coating, or a coating that must undergo an application of ultraviolet light to cure, is becoming more common. There are many benefits to this type of coating relative to other standard air-dried coatings. These benefits include a distinctly shorter drying time for UV-coatings, sometimes complete curing occurs in only seconds whereas air-dried coatings may take hours or days. In addition, the short curing time reduces some negative environmental impacts in the curing process. This is achieved through a reduction—sometimes to nearly zero—in the release of volatile organic compounds (VOC). The problem with VOCs is the health and environmental risks caused by the evaporation from these organic solvents. Standard air-drying coatings have significantly higher VOCs and therefore higher environmental and health impacts than the UV-coatings that are currently being produced. The VOC for UV-cured coatings is close to or exactly zero depending on the product providing an environmentally friendly coating option. A final benefit is a higher standard of coating protection, indicated by a high-level of crosslinking density and consistency.

UV-coatings are consistent in their overall method of network formation, although different coatings undergo these steps in slightly different ways. Intermolecular networks
typically form in three stages; initiation, propagation and termination. Initiation begins the process and occurs when a photoinitiator (PI) is activated using a UV-light source. The photoinitiator is a molecule added to the coating, which when excited by the UV-radiation in the correct range, splits in two and forms a radical. The radical then reacts with the double bond in the coating monomer and the coating becomes a radical. Next is the propagation phase where a strand or network of monomers are attached together through free radical polymerization\textsuperscript{2}. The termination phase comes last when the radicalized acrylate bonds to another radical on the acrylate molecule or with the photoinitiator radical completing the chain.

One of the most problematic parts of this three step reaction for UV-cured coatings is the possibility of the oxygen quenching the reaction whereby the radical on the photoinitiator or acrylate reacts with oxygen causing the network to be incompletely formed\textsuperscript{2}. This can cause weaker molecular networks or inconsistent network formations because the polymer chains are not completely bonded. This is frequently treated by running curing processes under nitrogen instead of air to eliminate the exposure to oxygen.

The coating used in this study is poly(ethylene glycol) diacrylates (PEGDA), an acrylate that can form multiple bonds. The photoinitiator used is 1-hydroxy cyclohexyl phenyl ketone (HCPK). This photoinitiator is active at 254nm. The glass transitions temperature for this coating is 50-52ºC, so our experiments were run at room temperature, well below the glassy state.

![Molecular structures of PEGDA and HCPK](image)

**Figure 1:** (a) The molecular structure of the coating used, poly(ethylene glycol) diacrylates (PEGDA) and (b) the molecular structure of the photoinitiator, 1-hydroxy cyclohexyl phenyl ketone (HCPK).
Initiation:

The initiation phase for PEGDA and HCPK shows the UV light (signified above by $h\nu$) radicalizing the photoinitiator which is then able to attach to the carbon-carbon double bond of the first monomer. The double bond is then replaced by a carbon-carbon single bond on the PEGDA molecule beginning the reaction process.

Figure 2: The initiation phase of the curing of the PEGDA coating, including the radicalization of the photoinitiator and the initial electron attack on the carbon-carbon double bond of the first monomer.
Propagation:

Figure 3: The propagation phase of the curing process with the coating PEGDA, includes the monomer from the initiation phase with the single electron bond with another monomer to form a polymer chain.

The propagation phase consists of the radical moving from the radical on the first coating monomer to the second coating monomer. This is the beginning of a network of polymers, each individual monomer able to act as a new radical to attack the double bond on a free, unbound monomer, beginning to form an intermolecular network.
Termination:

![Diagram](image)

Figure 4: The termination phase of the curing process includes the radical on the polymer network reacting with another polymer network radical or a photoinitiator radical molecule, terminating the reaction.

The termination phase of the reaction is when the polymer chain interacts with either the photoinitiator radical or another polymer chain radical. In the illustration above (Figure 4) it is shown with the polymer interacting with the radicalized photoinitiator, causing the reaction to halt and the curing process to stop.

Above is an example of the process of curing that UV-coatings undergo. The three steps are clearly delineated for the coating PEGDA with the HCPK photoinitiator. The final structure of the curing process described above can vary with the functionality of the coating. Depending on the coating, the cured product can exist as a single strand of cured coating, a branched string or a rigid cross-linked structure of cured coating. PEGDA is a diacrylate meaning it is di-functional\(^3\), therefore there are a total of four possible sites on a PEGDA monomer that could reasonably react with photoinitiator molecules or other PEGDA molecules. The predicted results
of this molecular network formation after curing is a cross-linked structures for PEGDA and is shown in the illustration to the right (Figure 5). This perfectly bonded result would only occur without disruption from oxygen and with complete network formation. Complete network formation does not happen, the structure is usually unable to continue curing after approximately 90% of the carbon-carbon double bonds have been cured. This cross-linked, rigid structure would possess a large amount of local orientation and alignment which can cause spin alignment called residual dipolar couplings and can be studied with NMR. Tracking the amount of cross-linking or local orientation can give insights into the intermolecular networks present in the cured structure of a UV-cured coating.

1.2 Nuclear Magnetic Resonance:

1.2.1 Quantum Mechanics

Nuclear magnetic resonance (NMR) depends on the reaction of nuclear spin and angular momentum in an applied magnetic field ($B_0$). Nuclei intrinsically possess the quantum mechanical property of nuclear spin angular momentum and its associated spin and magnetic quantum numbers. Spin is a quantum number ($I$) that varies with each atom or isotope. For example hydrogen ($^1H$) nuclei and carbon ($^{13}C$) nuclei, both common nuclei studied with NMR, have a spin of $\frac{1}{2}$. In order for nuclei to be studied with NMR the spin associated with it must be a nonzero number. The nonzero spin is required because there must be a spin value in order for
the nuclei to possess a net nuclear spin angular momentum and a magnetic moment. The nuclear spin angular momentum \((I_z)\) is a quantum value dependent on the spin quantum number and the magnetic quantum number \((m)\) that has a quantized magnitude and direction such that:

\[
I_z \text{ (magnitude)} = \sqrt{I(I + 1)}\hbar
\]

where \(\hbar\) is quantized unit value and \(I\) is the spin quantum number. This value of \(I_z\) explains the magnitude that exists along the positive z-axis with quantized values described by:

\[
I_z = m\hbar
\]

where \(m\) are the quantized magnetic quantum numbers equal to \(2I+1\) for values between +\(I\) and – \(I\). For a spin \(\frac{1}{2}\), the values for \(I_z\) can be either +\(\frac{1}{2}\hbar\) or –\(\frac{1}{2}\hbar\).

When nuclei are placed in a magnetic field the direction of the spins align either parallel or antiparallel to the field, because of the nuclear spin angular moment and its quantized relationship to the magnetic quantum number. The alignment of the spin angular momentum creates an energy gap between the negative \(m\) (antiparallel to the field and possessing a higher quantized energy value) and positive \(m\) (parallel to the field and possess a lower quantized energy value), otherwise frequently called spin-down and spin-up, respectively, in the applied magnetic field. This energy difference arises from the angular momentum and the angle between the applied magnetic field and the direction of the spins magnetic moment \((\mu_z)\) because when the field is applied the spins will “move” to either align parallel (spin-up) or anti-parallel (spin-down) with the applied magnetic field.

\[
\mu_z = I_z \gamma
\]
The magnetic momentum associated with the nuclei is based on the spin angular momentum and the gyromagnetic ratio. The gyromagnetic ratio is a constant that differs for each atom, for example, for hydrogen the gyromagnetic ratio ($\gamma$) is $42.576\ \text{MHz T}^{-1}$.

The distance between the energy levels ($\Delta E$) is dependent on the magnitude and direction of the nuclear magnetic moments, the magnitude and direction of the applied magnetic field and the gyromagnetic ratio. The spin magnetic moment and the applied magnetic field then generate the value of the energy (see equation below), which can then be translated to calculate the difference between the quantized energy levels between the spin-up and spin-down states of the magnetic moments.

$$E = - \mu_z B_0 \text{ (along the field direction)}$$
\[ \Delta E = - m\hbar \gamma B_0 \]

The energy levels are populated by nuclei and the population difference can be detected due the movement of nuclei between the populations, between the energy levels. The population difference tends to be the smaller population of nuclei at the higher energy level and the larger population on the lower energy level\(^7\). The strength of the applied magnet field determines the energy distance between the two levels, where a higher power will produce a larger energy level difference and therefore, an easier to detect signal based on the population difference. Furthermore, the stronger the applied magnetic field, the more nuclear magnetic moments are able to align with the field, increasing the population of nuclei and population difference. The more nuclei aligned, the stronger the intensity of the signal for the NMR spectra.

Although these terms are called angular momentum and spin it does not indicate that the nuclei move in a circle because the translation from quantum mechanical properties mentioned here do not have a direct equivalent in classical physics\(^6\).

### 1.2.2 Chemical Shifts, Larmor Frequency and Offset

NMR spectra are able to distinguish between nuclei in slightly different local environments due to chemical shifts. Chemical shifts occur when nuclei experience marginally different \( B_0 \) due to shielding by other nuclei and the slight current that is induced in molecules when placed in an applied magnetic field. This small current causes a small, opposing-in-direction magnetic field, lessening the effect of \( B_0 \). The amount of shielding will cause a different signal for nuclei experiencing different local environments. In order to understand how chemical shift alter the frequency output depending on environment, we will be using a vector model\(^7\).
When in an applied magnetic field, spins are treated as precessing around the positive z-axis. This precession can be disrupted with an applied pulse of radio electromagnetic frequency otherwise known as an RF pulse\textsuperscript{6,8}. When an RF pulse is applied, according to the right-hand rule the magnetization will begin precessing around the z-axis (moving counter-clockwise in the x-y plane), but this is made more complicated due to the chemical shifts adjusting $B_0$ for nuclei depending on the local environment. In order to understand the data it is important to understand that when spins are placed in $B_0$ there is a frequency that describes the rotating frame called the Larmor frequency, denoted as $\omega_0$. The Larmor frequency is dependent upon the strength of the magnetic field and gyromagnetic ratio of the nuclei.

$$\omega_0 = -\gamma B_0$$

Having a positive gyromagnetic ratio means that magnetic moment of the nuclei is parallel to the spin angular momentum of the nuclei, while a negative number would indicate an antiparallel orientation.

When the RF pulse is applied to the nuclei aligned with the applied magnetic field it causes a directional flip into the +x-direction of the coordinate plane. In order for the RF pulse to occur, the Larmor frequency must be resonant to the applied RF frequency. So, for example, with spin magnetization aligned with the $B_0$, a single 90° RF pulse or a $\frac{\pi}{2}$ pulse, of equal frequency to $\omega_0$, will cause the spins to align with the +x-axis and be precessing in the x-y plane around the z-axis. This precession of the spin magnetic moments in a rotating frame around the z-axis causes the precession to then differ in frequency from the Larmor frequency, the difference between these two frequencies is called the offset ($\Omega$).
\[ \Omega = (\omega_0 - \omega) \]

The offset, which is a result of the difference between the frequencies, determines the reduced field, or the field felt by the nuclei in a rotating frame. This reduced field and the field applied with the RF pulse will give an effective magnetic field, which will have its own associate effective frequency. This effective frequency difference is detectable because it is dependent on the spin’s realignment to the applied magnetic field or relaxation following the RF pulse\(^8,9\).

\[ \omega_{\text{eff}} = |\gamma| B_{\text{eff}} \]

Another important type of RF pulse that can be applied is a refocusing pulse. This is done by applying a 180° or \(\pi\)-pulse. This is important because when sampling oftentimes the loss of spin coherence in their precessions based on differences of local environment after time makes collecting data difficult because the signal-to-noise ratio is too low, the refocusing pulse amplifies the signal by flipping the pulse from the \(+x\) axis to the \(-x\) axis and causing the spins to come together and the signal to increase.

### 1.2.3 Inhomogeneous Field NMR

The research done here uses a magnet that produces an inhomogeneous-field and is single-sided. The samples are placed on top of the coil that is surrounded by four magnets with a magnetic field that runs perpendicular to the surface of the magnets. This system set up allows for fewer restrictions on the size and geometry of the sample because samples are easily placed on top of the magnet. The magnetic field produced is inhomogeneous, decreasing in strength as the samples moves away from the coil. This makes it critical to place the sample in the strongest
parts of the applied magnetic field to maximize signal because as the sample moves away from the magnet the strength of the field decreases rapidly.

The process of exciting the spins to precession with a high-powered RF pulse, and then recording the decay signal, in an acquisition time, is a very simple example of an NMR experiment. The creation of this short-lived signal is called the Free Induction Decay (FID)\(^6\). When there is an applied RF pulse, the spins will begin precessing in the x-y plane. With an inhomogeneous-field NMR, the decay of FID happens quickly because the signal is dampened by the \(T_2\) decay (described in the next section) and the FID is lost because immediately after the pulse, the decay of this transient signal happens before end of the RF pulse and the acquisition time is unable to monitor the rate of decay. In order to overcome this barrier, a refocusing pulse must be applied so the detection time is delayed.

Field inhomogeneity with single-sided magnets causes a very large offset. This inhomogeneity causes the effective magnetic field and the effective frequency to be very different from the Larmor frequency and applied magnetic field because there exists a component of the magnetic field perpendicular to \(B_0\)\(^8\).

### 1.2.4 \(T_2\) – spin-spin relaxation

In low-field NMR, relaxation or returning to equilibrium of magnetization of spins is frequently studied. There are two main types of relaxation used, \(T_2\) relaxation and \(T_1\) relaxation. Here the focus is on \(T_2\) relaxation because it provides information about the cross-linking and the intermolecular networks formed. \(T_2\) relaxation, also called spin-spin relaxation or transverse relaxation, must be shorter than the \(T_1\) values on the same sample. Spin-spin relaxation is dependent upon the idea that when spin magnetic moments are precessing after an applied RF
pulse, in the x-y plane, the field inhomogeneity and the local spin environment variation will cause the precession rates to differ slightly between different nuclei. Immediately after the RF pulse is applied the spins should be precessing uniformly, but as the differentiating factors act on the spins they will lose coherence. This is to say, that spins directionally flipped into the x-y plane to precess around the z-axis will initially all precess in unison together. All the spins were simultaneously, flipped into the same +x-direction, so the spins begin precessing from the same spot and rotate in the same direction. Then the spins begin to effect each other rate of precession because of their interacting magnetic moments and over time these interactions cause the rate at which they are precessing to vary slightly. Over time these slight variation in precession rates will cause the spins to be moving inharmoniously around the z-axis, in other words, the spins have lost coherence in their precession. The rate at which these spins lose coherence is called the $T_2$ relaxation.$^6,^8$

$$\frac{S}{S_0} = e^{-\frac{t}{T_2}}$$

$$\ln \frac{S}{S_0} = -\frac{t}{T_2}$$

$S/S_0$ is a normalized signal intensity taken from measurement. $\log(\frac{S}{S_0})$ is proportional to $-t/T_2$, which is the time over the $T_2$ value, the subject of study in spin-spin relaxation.

When using NMR, one way to change the data being collected is to change the pulse sequence, or the change the number, type, direction and the speed of RF pulses and the time between the RF pulses or the evolution time.$^8$ A pulse sequence is a method of varying how the RF pulses affect the spins and variation will determine what physical or chemical property is
being studied. One of the simplest pulse sequences used frequently is the Carr-Purcell-Meiboom-Gill. The CPMG pulse sequence is used to determine the $T_2$ value(s).

![CPMG Pulse Sequence](image)

Figure 7: CPMG pulse sequence that is used to gather $T_2$ relaxation data. It is a single 90° pulse to begin precession in the x-y plane and a series of 180° pulses to repeatedly refocus and form echoes that can be detected$^{11}$.

It is a single 90° followed by a series of refocusing (180°) pulses$^{11}$. In the section above, we mentioned the FID for an inhomogeneous-field NMR was unable to determine the relaxation because the decay happened completely before the end of the RF pulse. CPMG pulses circumvent this problem by using a series of refocusing pulses to form a series of echoes. Echoes are the frequency output signal that composes the NMR data. The decay in intensity of these echoes after the 180° pulse is the loss of coherence that is $T_2$ decay mentioned above. These experiments are simple and short, they typically will only run for five to ten minutes with a single-sided magnet. This ease of use makes them a useful tool in understanding the cross-linking in a substance.

In the case of coatings being studied in this research, a shorter $T_2$ time is an indication of a stronger cross-linking and more curing, this is because the local alignment causes the effect on the spins to magnetically effect surrounding spins more quickly. This causes the rate of decay to
occur more quickly and the $T_2$ relaxation times should be shorter in a stronger cross-linking network. This should correlate to lower levels of cross-linking and less curing to longer $T_2$ relaxation time.

1.2.5 Quantum Mechanical Background for Multiple-Quantum Coherences

When two spins exist in a system, there are a variety of ways they can interact with one another. The spins can be uncoupled, meaning each transition between energy levels happens independent of the other spin, obeying the selection rule of $m$ can only transition $\pm 1$. The two spins can be coupled, for example J-coupling, where the spins can undergo coupled transitions but the transition terms continue to obey this selection rule. Or the spins can undergo multiple-quantum transitions. These are forbidden transitions that break the $\Delta m = \pm 1$ selection rule and can be probed with two-dimensional NMR experiments$^6$.

![Figure 8](image_url)

Figure 8: (a) The allowed transitions possible for coupled spins and (b) multiple-quantum transitions. The direction of spin changes when $\alpha \rightarrow \beta$ or $\beta \rightarrow \alpha$, causing $m$ to change.

The Hamiltonian ($\hat{H}$) for a single spin is dependent on the spin angular momentum, the gyromagnetic ratio and the applied magnetic field, values introduced in the Quantum Mechanics section (1.1) of this paper.
\[ \hat{H} = -\gamma B_0 I_z \]

This equation can be simplified to:

\[ \hat{H} = \omega_0 I_z \]

based on the understanding that the Larmor frequency is equivalent to \(-\gamma B_0\). For two uncoupled spins the Hamiltonian is:

\[ \hat{H} = \omega_{0,1} I_{z,1} + \omega_{0,2} I_{z,2} \]

because in the case of uncoupled spins, the individual spins can simply be treated as linear combinations of eigenvalues.

When dealing with two coupled spins, in this case J-coupled spins, another term must be included in the Hamiltonian that factors in the effects of coupling, as in the effect of the spins on each other.

\[ \hat{H} = \omega_{0,1} I_{z,1} + \omega_{0,2} I_{z,2} + J_{1,2} I_{z,1} I_{z,2} \]

In this equation, the \(J_{1,2}\) term indicates the effect of the coupled nuclei 1 and 2, on each other.

Multiple-quantum transitions create a more complex system that relies on the understanding of a density matrix. A density matrix is a matrix composed of possible density operators, which are a collection of state mixtures or superposition of states\(^{12}\). For pure states, the eigenfunction is a linear combinations of the state mixtures in the density matrix. The density operator (in Dirac notation) is defined by:

\[ \hat{\rho} = |\psi\rangle\langle\psi| \]
where $\psi$ is the time-dependent wavefunction\textsuperscript{13}. The density matrix ($\rho$) can then be constructed from the time-dependent wavefunction linear combination equation and the density operator.

$$
\rho = \begin{bmatrix}
\langle \alpha | \hat{\rho} | \alpha \rangle & \langle \alpha | \hat{\rho} | \beta \rangle \\
\langle \beta | \hat{\rho} | \alpha \rangle & \langle \beta | \hat{\rho} | \beta \rangle
\end{bmatrix} = \begin{bmatrix}
\rho_{11} & \rho_{12} \\
\rho_{21} & \rho_{22}
\end{bmatrix}
$$

The density matrix is able to show the population of the eigenstates for the multiple-quantum coherences. The density matrix can be used in the Time-Dependent Schrödinger Equation (TDSE) to determine eigenstates or energy levels.

### 1.2.6 Multiple Quantum Coherences, Dipolar Couplings ($S_{LM}$) and Dipolar Encoded Longitudinal Magnetization

Multiple quantum coherences (MQ coherences), or the multiple-quantum coupling of two spins, have been used with NMR to explore the dipolar couplings in samples\textsuperscript{14}. MQ coherences are the local alignment of spins in a material, useful in tracking the dipolar couplings and the cross-linking in a system\textsuperscript{15}.

There are two major properties that make studying the dipolar couplings in coatings relevant: spin magnetic moments are directional and spins are coupled with each other. In order for spins to be coupled they must have proximity and local alignment to each other. One important type of coupling is dipolar coupling. This is a coupling of aligned dipole moments of spins. If two spins exist in a network that are locally aligned parallel to each other or antiparallel to each other they will experience dipolar coupling. When a structure has a high rigidity in an cross-linked intermolecular network, there is a higher level of dipolar couplings. This more rigid and cross-linked the material, the more likely the material has a high number of residual dipolar couplings\textsuperscript{16}. 

17
Figure 8: With spins that are not aligned or are far apart the dipolar couplings will not be present. When the spins are spatially aligned the dipolar couplings will exist and are measurable with multiple quantum coherences.

When two spins possess dipolar couplings, there is a collection of multiple-quantum studies that can be done on the spins to determine cross-linking. In the case of this research, the dipolar couplings were studied with a technique called Dipolar Encoded Longitudinal Magnetization. This is a three pulse sequence with an excitation, evolution, and reconversion phase. This pulse sequence is the basis for a range of tests that study MQ coherences such as Double Quantum (DQ) Buildup, Triple Quantum (TQ) Buildup and DELM$^{15-17}$. 
The excitation and reconversion sections are made up of a sequence of 90°, 180°, 90° pulses and the evolution section is a single 180° pulse. The excitation and reconversion sections are spaced out by a value \( \tau \) otherwise called the dipolar encoding periods\(^{17}\). This technique examines the dipolar encoded spins in the longitudinal plane. Longitudinal magnetization indicates that the spins being studied here are not involved in zero, double or multiple quantum coherences. The equation below shows the relationship between residual dipolar couplings \( S_{LM} \) and the frequency output indicated by \( (\bar{\omega}_D)^2 \) for a DELM experiment. The frequency is a measure of energy, which correlates to the strength of the residual dipolar couplings in the coating. It is common in spectroscopy for energy or intensity to be output as a frequency value.

\[
\frac{S_{LM}(\tau_0 + 2\tau)}{S_0} \propto \langle \cos^4 \theta \rangle_\theta + \langle \sin^4 \theta \rangle_\theta \left(1 - \frac{3}{2} (\bar{\omega}_D)^2 \right) \tau^2
\]

This frequency value quantitatively links to the dipolar couplings, indicative of cross-linking and intermolecular networks over the progression of the \( \tau \) value. In this experiment, the values of \( \theta \) is 90° so the \( \cos \) term can be ignored and the \( \sin \) term goes to one leaving the dipolar coupling directly related to the product of \( (\bar{\omega}_D)^2 \) and \( \tau^{16,17} \).
The DELM experiments explained here are complex and three dimensional and take hours to run. The specificity that is established regarding the presence of dipolar-couplings is the payoff from the long run time of the DELM experiments.
2 METHODOLOGY:

2.1 Instrumentation

The UV-curing process was done with a ThorLabs LED UV-lamp (CS2010). The wavelength for this lamp is 254 nm which is middle UV and aligns with the active wavelength for HCPK, the photoinitiator used. The intensity for this lamp was measured with an intensity meter at a distance of 1 inch from the sample and 50% power to be 1.3 mW/cm².

These NMR measurements were done on a PM5 by Magritek, a small, single-sided, low-field magnet (an NMR-MOUSE). This magnet has a coil surrounded by two magnets that are used to create the applied magnetic field. The magnet is placed on a lift that can be moved up or down to guarantee testing in the center of the sample.

2.2 Sample Preparation

The samples of PEGDA (molecular formula illustration shown in the UV-Cure Coating section, Fig.1) were prepared with 1% by weight of the HCPK photoinitiator (Fig.1). The coating and photoinitiator were both bought from Sigma-Aldrich and were used directly without undergoing a purification process. The coating was then placed on a 1 mm glass slide, in a 0.5 cm radius circle, an area slightly smaller than the area of UV-light applied for the curing process. The sample is about 150 μm ± 25μm thick, as determined by the Elcometer 115, a wet film comb. The measurement of the thickness is performed on a standard uncured sample of the PEGDA

The sample was then placed under the UV light for the desired amount of curing, increasing in increments of 10 seconds from zero to 60 seconds. After the curing, the sample was immediately placed on the magnet to begin the experiment. For the PEGDA samples, the effects
of evaporation or drying were ignored because we considered the drying over the experiment
time insignificant relative to the curing process of the coating.

2.3 Experimentation

The study includes two experiments performed on the magnet, the CPMG (or $T_2$
determination) and the DELM (or residual dipolar coupling studies). The experimental
parameters for $T_2$ were adjusted to gather the largest and most dependable amount of information
about the curing process.

For the $T_2$ experiments, there are two major adjustable parameters: the number of scans
and the number of echoes. For sake of consistency, the echo time for these studies was held at a
constant 60 $\mu$s. Echo time is the time between the application of an RF pulse and the peak signal
induced. That is the amount of time between the pulse and the detection of signal. The number of
echoes was adjusted because the longer it takes for the $T_2$ to undergo a complete decay, as the
spins fall completely out of alignment, the more echoes needed in order to see complete decay.
The number of scans determines how many times the experiment is repeated in order to increase
the signal-to-noise ratio. A larger signal-to-noise ratio improves the precision of the experiment
so more scans means a more precise $T_2$ value(s).

The $T_2$ values for zero seconds of curing required a very large number of echoes to see
the entire decay, which is necessary to determine the $T_2$ values. This put a strain on the
mechanical capabilities of the coil and the magnet so a compromise was made, which was
decreasing the number of complex points, making the individual echoes less well defined in
order to keep the number of echoes extremely large.

For the DELM experiments, there are a far greater number of parameters that can be
adjusted. For example, the length of the DELM decay is determined by the minimum and
maximum τ values or the signal-to-noise ratio is determined by the number of scans. Because these experiments are much more complex and include an extra dimension of the τ value (defined in the Multiple Quantum Coherences, Residual Dipolar Couplings and DELM section of the Introduction), the values that can be adjusted include the number of echoes, the number of scans, the number of τ points, the τ minimum and maximum and whether the τ scale is logarithmic or linear. In this experiment, for consistency the number of echoes was left at 64, the number of τ points were 80 and the τ minimum was 0.05 ms and maximum was 4 ms. Over the course of the experiment, the number of scans was increased because, as the coatings cured, the signal-to-noise ratio deteriorated. For the more uncured coatings the values of τ were linearly spaced and as the curing time increased the τ increments were logarithmically spaced in order to acquire the best data.

2.4 Data Processing

Data processing for this project was done exclusively in Matlab (Mathworks, Inc.; Natick, MA). The scripts were provided by Dr. Meldrum and edited for specificity for this problem (see Appendix B for scripts). For the $T_2$ data processing, the values were imported, then underwent echo summing and were run through $T_2$ biexponential fitting script. The $T_2$ values of curing 10 seconds or greater were biexponential in fit and the monoexponential processing scripts proved ineffective in data processing.

The DELM data processing also provided a bit more complexity. The different τ points were summed to a single value of normalized intensity, which was then plotted. The experimenter then must select a range of points that are the initial linear slope, indicative of the dipolar couplings. The range for this varies with each sample, resulting in shorter τ times and
fewer points when the coating has undergone more curing. The slope of this value is then used to indicate the amount of curing that the sample had experienced.

2.5 Raman Studies

As a method to check the ability of the NMR system to accurately track the intermolecular networks development in coatings, a simple Raman experiment was run. Raman is a spectroscopic technique that uses a laser to excite electrons to a high-energy state and detects vibrational transitions from inelastic scattering. The Raman experiment was run on an Advantage Series Raman Spectrometer by DeltaNu. The samples were prepared in the same method but on optically transparent glass for Raman studies. The laser was set on high power and the sample was manually focused, in a goal to elucidate the carbon-carbon double bond stretch at $1636 \text{ cm}^{-1}$ in the Raman spectrum$^1$. 


3 RESULTS & DISCUSSION:

3.1 $T_2$ Results

The $T_2$ data was found to possess a biexponential fit. This means that each individual $T_2$ decay was made up of two separate $T_2$ values and two associated amplitudes. Interestingly, the initial value, the decay for 0 seconds of curing was not found to be biexponential which was the fit best applied to the other values of $T_2$ for the longer (non-zero) curing times. In this case, the no curing study, the decay fit was monoexponential and offset from zero. It is possible the monoexponential fit changed to a biexponential fit because once the curing process is initiated there is an aspect of the $T_2$ decay that develops immediately after the coating is struck by UV-light and decays as the curing process continues. The PEGDA undergoes curing by experiencing a decrease in the number of $\pi$-bonds as the polymer chain forms and this chain elongation could cause the $T_2$ relaxation fit to move from a monoexponential fit to a biexponential fit.

In order to understand the $T_2$ provided values, they will be denoted $T_2 (1)$ and $T_2 (2)$. These two different values vary by approximately two orders of magnitude but both are relevant to understand of the curing process of the PEGDA coatings. Included below are graphs of both the $T_2 (1)$ and $T_2 (2)$ values over the curing times. The errors associated with the values are a 95% confidence interval for the $T_2$ values.
As is apparent in Figure 11 (a) and (b), there is decay in both of the values of $T_2$ over the first 40 seconds, then the values either stay the same or there is a slight rise. This suggests that the majority of the curing process takes place in the first 40 seconds under the intensity and conditions of these $T_2$ experiments. The values of $T_2$ were expected to decrease exponentially
until complete curing. In the cases seen here, there is a linear decrease until the estimated completion of curing.

It is interesting to note that the zero curing $T_2(2)$ value is monoexponential and lower than the 10 second $T_2(2)$. It is possible that the lower value is a result of the monoexponential fit and it would better fit the trend if it were biexponential. This value was found to be repeatable and while it does not fit the trend it is an accurate value of $T_2$. While looking at all the other values there is clear decay, which indicates an increase in the cross-linking.

Finally, it is important to note that the slight rise in values after the 40 second mark is small enough to exist within the error of this experiment and could be the result of several factors including oxygenation making it difficult to reach completion of curing or the effect of the inhomogeneous field on the values of $T_2$ relaxation.

### 3.2 DELM Results

As mentioned earlier, DELM is a more quantitative way to probe the molecular cross-linking directly and to track the intermolecular network development during the curing process. It is able to exclude variations that become present due to the inhomogeneity of the field. This is relevant when dealing with an inhomogeneous field present in the low-field, single-sided magnet. For these values, the experiments were run with the same 10 second intervals of curing.

DELM results are a plot of normalized intensity (the units associated are arbitrary) against $\tau$ values, which were mentioned earlier and provide the waiting time between pulses and the minimum and maximum values of $\tau$ are determined by the researcher. When data is collected the area of interest is the initial linear slope between the normalized intensity and the $\tau^2$ values. The reason it is limited to just this initial linear slope is to avoid the inclusion of relaxation or decay for reasons other than the cross-linking density. This makes understanding where and
when the slope begins and ends more difficult, especially when the results have a significant error. Distinguishing the initial linear slope from other forms of decay is difficult due to the significantly low signal-to-noise ratio. With the coatings that underwent longer curing times it was found that there is a larger error associated with the results and this was found to significantly decrease the signal-to-noise ratio. There was a certain amount of this error that was fixed by increasing the number of scans during the experiment.

In the DELM scans there is an area at the beginning of the experiment when the $\tau$ values were too short for the decay to exist in the smooth decay fashion, although the reasoning for this is unknown at this point. We were unable to find any literature explaining or even mentioning this beginning signal noise. At a later $\tau$ value (this value varied depending on the sample being run) this excessive signal noise stopped and the slope began to look like what the literature DELM images look like, with a clear and fairly neat slope. For this reason, in this study, the initial noise was ignored because it could be in response to the very low $\tau$ times. The literature values for DELM typically start experiments with minimum $\tau$ values at around 0.25ms. This was not possible for our experiment because when the coating experienced a long curing time the linear DELM slope begins at a very short $\tau$ time.

Included here are the DELM graphs for the no cure and 10 second curing. At first glance, it is obvious how much the noise has increased as the coating has undergone just 10 seconds of curing. It is also apparent noise has made that the selection of points more difficult as the coatings cure. It was also noted that because a majority of the decay occurred early in the curing process a shift to a log scale was used for the DELM experiments of greater than 10 second curing.
Figure 12: DELM results for the coating with no cure (a) and 60 seconds of curing (b) measured in normalized intensity vs $\tau^2$ (2). The red line indicates the slope $(\omega_D)^2$ used to calculate the residual dipolar couplings.
The red-line on the $\tau^2$ graphs above indicates the line representing the initial slope referred to earlier. Even visually, there is a clear difference between the no curing coating and the 10 second cured coating and a clear difference between the slopes of the red lines. As the coating cures it becomes more difficult to determine at what point it qualifies as linear $\tau^2$ slopes and it is important to make sure the residuals are randomized and therefore are not entering an area of relaxation. There is no clear reason why the increase in curing would cause a significant increase in the amount of noise and error associated with the slope.

![Slope values for different curing times](image)

Figure 13: The effect the amount of curing has on the slope of the intensity of the DELM signal. As the coating undergoes longer curing times the slope of the initial intensity are steeper and more negative.
The initial slope (also denoted $\tilde{\omega}_0^D$) get significantly steeper as the curing increases, indicative of more residual dipolar couplings in the more cured samples. This is likely an indication that the amount of curing increases as the coating is placed under the UV-light for longer periods. There is literature to suggest that the steeper slope is indicative of a more cross-linked network. It also suggests that as the DELM increases there are more dipolar encoded coupling which is a result of a more rigid local orientation. Dipolar coupling, as mentioned in the introduction, is precisely what the DELM is attempting to quantitatively track through the coating curing process. A more rigid local orientation is a clear indication that there is a cross-linked network because the alignment of molecules is stronger as the molecules are given more inelasticity through bonding to nearby molecules.

Figure 14: The values of the slope at any curing time over the initial curing time (0 seconds of curing), showing the increase in the ratio for the longer curing times.
The decay becomes dramatically steeper in the first 10 seconds (as shown in Figure # above), and continues to dramatically change in the first 40s of curing which corresponds to the results found in the $T_2$ experiments, then continues to cure but in smaller increments. These results are encouraging because they suggest that one could use DELM to more precisely track the dipolar couplings in coatings because the results accurately mirrored the $T_2$ values. This is also interesting because it provides an example to see the precision of the DELM values compared to the $T_2$ values. When the $T_2$ values reach 40 seconds they either stay constant or slightly increase, which does not indicate the coating is continuing to be cured. DELM on the other hand shows a slope decreasing in small increments after the 40 seconds of curing. This is suggestive of a higher level of precision and more accurate tracking of the cross-linking properties of the coatings.

3.3 Raman:

For the Raman studies performed there was difficulty reproducing our NMR results. The peak at 1636 cm$^{-1}$ was present in the uncured sample but in any of the further cured samples (e.g. 10 seconds, 20 seconds) the peak was not present. This suggests that the number of double bonds present after just 10 seconds of curing is low enough that the Raman is unable to detect it. These results differ from what was expected, which was to see the carbon-carbon double bond peak for the first 30-40 seconds of curing mirroring the results of the $T_2$ measurements and the DELM measurements. The peak was expected to decrease as the carbon-carbon double bonds became single bonds in the polymerization of the PEGDA coating. These results vary significantly because they suggest that the coating was fully cured in the first 10 seconds. The difference from the NMR curing results suggests more Raman studies are needed, in order to verify where this significant difference arises from.
Figure 15: The Raman spectra for the no curing (black) coating and the 10 seconds of curing (grey). These two overlaid show a clear loss of the peak at 1636 after just 10 seconds which is indicative of an increased degree of cross-linking.
4 CONCLUSION:

It was discovered through experimentation that it is possible to use $T_2$ and DELM measurements on a single-sided inhomogeneous magnet to track the curing in UV-cured coatings. These results provide an accurate method for measuring the amount of curing in objects that have unusual geometries or shapes using a non-destructive technique. The determination of the curing of coating is useful to determine the strength of an already cured coating or whether the coating applied has reached its maximum cross-linking density.

For the intensity and UV-light used, the PEGDA coating with 1% by weight HCPK were cured to almost completion in about 40 seconds based on experiment. After the 40 second curing time there is still slight curing taking place according the DELM measurements but it is in smaller increments of dipolar couplings over the same amount of time. The value of curing for the $T_2$ stopped showing noticeable curing after the 40 seconds of exposure to UV-light. The disparity between the continuing curing for DELM and no curing for $T_2$ after 40 seconds could be a result of the specificity provided in the DELM measurements. When performing the lengthy DELM experiments the quantitative representation of just the residual dipolar coupling values can be determined giving direct results to the amount of cross-linking developed, which with the shorter $T_2$ values you are unable to get. $T_2$ values also can contain effects from the inhomogeneity of field or other factors besides cross-linking that can cause loss of coherence in the precession of spins. These alternative explanations for relaxation in the $T_2$ experiment makes DELM a more selective and useful method for tracking the curing process of coatings.

The combination of both $T_2$ and DELM results in a full picture approach to tracking the cross-linking in the coatings. It provides both generalized relaxation from the $T_2$ values and a
deeper analysis of the residual dipolar couplings indicative of cross-linking degree from the more complex and longer DELM experiment.
5 MOVING FORWARD:

The experiments performed begin the process of understanding what single-sided NMR can indicate regarding the amount and completion of cross-linking in coatings. Moving forward it would be beneficial to complete a number of other experiments. Potential experiments include running the curing in nitrogen or another anaerobic gas and running the $T_2$ and DELM measurements on other coatings to understand the variety of potential coatings appropriate for this process.

Using anaerobic gases is a critical next step because it will determine how much effect the oxygenation was having on the curing process. The literature suggests that oxygenation has a large effect on the amount of curing that the coating is able to undergo, so to see how the NMR technique changes when oxygenation plays a significantly smaller role in the curing process$^1$. It would be helpful to be able to determine how much of the curing process was being quenched by the exposure to oxygen. Many studies of the problems associated with UV-coatings and oxygen have already been done but ideally we should be able to track the level of curing that is quenched with the combination of $T_2$ and DELM used here.

The Raman studies performed here need further investigation, understanding why the coatings only underwent 10 seconds of curing before peak was no longer visible and why there is a discrepancy between that and the results received from the NMR studies. This is critical to check the validity of the experiments run here because the attempt to repeat the results with Raman proved insufficient.

There also may be a less subjective way to determine the fitting for the initial slope. It would be ideal to move the fitting process from something that can be effected dramatically by
the experimenter to a program that predicts the best fit. This would provide more accuracy and less possibility for experimenter bias.

Another future experiment could be an examination of bifunctional and monofunctional coatings to see whether this process can distinguish between the highly cross-linking bifunctional coatings and the linearly or circularly bonded monofunctional coatings. This would also be used to demonstrate a goal of this research that this process is relevant for understanding which coating would be best cured in different settings. Furthermore, this level of determination would be a very important in supporting the results stated here that the use of DELM and $T_2$ can be used to accurately track the cross-linking during the curing process of coatings.

We would also like to use this technique to take a depth analysis of the coatings during the curing process. It would be helpful to know how quickly the top of the coating cures and how much longer it takes deeper levels of the coating to cure using the DELM and $T_2$ experiments.

This experiment is a first step in using single-sided magnets to studying the curing process of UV-coatings. There are many ways in which the impact of this study could be amplified in order to understand the complexity of this system, and the usefulness of this instrumentation and these techniques.
REFERENCES


APPENDIX A:

$T_2$ Data:

Table 1:

The Effect of Curing Time on the $T_2$ values

<table>
<thead>
<tr>
<th>Amount of Curing (s)</th>
<th>$T_2(2)$ (s)</th>
<th>$T_2(1)$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0745 ± 0.0006</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>0.091 ± 0.005</td>
<td>0.0018 ± 0.0001</td>
</tr>
<tr>
<td>20</td>
<td>0.071 ± 0.009</td>
<td>0.0015 ± 0.0001</td>
</tr>
<tr>
<td>30</td>
<td>0.031 ± 0.004</td>
<td>0.00111 ± 9E-05</td>
</tr>
<tr>
<td>40</td>
<td>0.013 ± 0.003</td>
<td>0.0008 ± 0.0001</td>
</tr>
<tr>
<td>50</td>
<td>0.014 ± 0.003</td>
<td>0.0009 ± 0.0001</td>
</tr>
<tr>
<td>60</td>
<td>0.016 ± 0.005</td>
<td>0.0010 ± 0.0001</td>
</tr>
<tr>
<td>70</td>
<td>0.014 ± 0.003</td>
<td>0.0009 ± 0.0001</td>
</tr>
</tbody>
</table>
DELM Data:

Table 4:

The Effect of Curing time on the LM Intensity Slope and Slope Ratio

<table>
<thead>
<tr>
<th>Amount of Curing (s)</th>
<th>Slope of initial LM intensity (arbitrary units)</th>
<th>Slope Ratio (arbitrary units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.126 ± 0.004</td>
<td>1.000</td>
</tr>
<tr>
<td>10</td>
<td>-0.9 ± 0.1</td>
<td>7 ± 1</td>
</tr>
<tr>
<td>20</td>
<td>-3.2 ± 0.4</td>
<td>24 ± 3</td>
</tr>
<tr>
<td>30</td>
<td>-3.6 ± 0.7</td>
<td>28 ± 6</td>
</tr>
<tr>
<td>40</td>
<td>-4.3 ± 0.6</td>
<td>33 ± 4</td>
</tr>
<tr>
<td>50</td>
<td>-4 ± 1</td>
<td>33 ± 8</td>
</tr>
<tr>
<td>60</td>
<td>-4.9 ± 0.7</td>
<td>38 ± 5</td>
</tr>
</tbody>
</table>
APPENDIX B:

Data Processing Script 1:

The $T_2$ Data Processing Script—Provided by Tyler Meldrum, edited by Frankie Morin

T2Fit_Kea.m

clear
clc
close all

%%

% Load Data and Parameters

parfilestem = 'C:\Users\fjmorin\Desktop\PEGDA50%EHA50\Slide1_test\1\acqu';

params.acqTime = readpar_Kea(strcat(parfilestem,'.par'),'acqTime');
params.bandwidth = readpar_Kea(strcat(parfilestem,'.par'),'bandwidth');
params.nrScans = readpar_Kea(strcat(parfilestem,'.par'),'nrScans');
params.rxPhase = readpar_Kea(strcat(parfilestem,'.par'),'rxPhase');
params.rxGain = readpar_Kea(strcat(parfilestem,'.par'),'rxGain');
params.nrPts = readpar_Kea(strcat(parfilestem,'.par'),'nrPnts');
params.repTime = readpar_Kea(strcat(parfilestem,'.par'),'repTime');
params.repTime = readpar_Kea(strcat(parfilestem,'.par'),'repTime');
params.blFreq = readpar_Kea(strcat(parfilestem,'.par'),'blFreq');
params.nrEchoes = readpar_Kea(strcat(parfilestem,'.par'),'nrEchoes');
params.echoTime = readpar_Kea(strcat(parfilestem,'.par'),'echoTime');

% New Data files
file = 'C:\Users\fjmorin\Desktop\PEGDA50%EHA50\Slide1_test\1\data2.csv';
FTdata = load(file);

FTdata = reshape(FTdata,(params.nrEchoes*2),params.nrPts);
dataRe = FTdata(1:params.nrEchoes,:);
dataIm = FTdata((params.nrEchoes+1):(params.nrEchoes*2),:);
dataCp = complex(dataRe,dataIm);
dataCp = abs(dataCp);

%% Nlinfit for non-transformed Data

%Sum Normalized Data
for i = 1:params.nrEchoes
    sumData(i,1) = sum(dataCp(i,:));
end
maxVal = max(sumData);
maxVal = max(maxVal);
sumData = sumData/maxVal;
%% Summed Data BiFit
echoVector = (1:params.nrEchoes)*60e-6;

guess = [.5;1e-3;.5;10e-3];
for i=1:10
  % Be sure to change the echotime
  [beta,Resids,J,covB] = nlinfit(echoVector',sumData,@t2bifit_simple,guess);
  % Confidence Interval and Margin of Error (+/-)
  CI=nlparci(beta,Resids,'jacobian',J);
  MOE_T2 = (CI(2,2) - CI(2,1))/2;
  guess = beta;
end

ypred = t2bifit_simple(beta,echoVector');

figure(1)
hold on
plot(echoVector,sumData);
plot(echoVector,ypred)
Data Processing Script 2:

DELM Data Processing Script – provided by Tyler Meldrum, edited by Frankie Morin

DELMDataRead.m

% DELM data proc
% 2 Sept 2015, TKM

clear
clc
close all

%% load data, parameters
.datadir = 'C:\Users\fjmorin\Desktop\PEGDA100%\PEGDA100\slide6_DELM_50s_9Feb\2';
datafile = 'dataRe.dat';
paramsfile = 'acqu.par';

params.acqTime = readpar_Kea(strcat(.datadir,paramsfile),'acqTime');
params.bandwidth = readpar_Kea(strcat(.datadir,paramsfile),'bandwidth');
params.nScans = readpar_Kea(strcat(.datadir,paramsfile),'nrScans');
params.rxPhase = readpar_Kea(strcat(.datadir,paramsfile),'rxPhase');
params.rxGain = readpar_Kea(strcat(.datadir,paramsfile),'rxGain');
params.nPts = readpar_Kea(strcat(.datadir,paramsfile),'nrPnts');
params.repTime = readpar_Kea(strcat(.datadir,paramsfile),'repTime');
params.blFreq = readpar_Kea(strcat(.datadir,paramsfile),'blFreq');
params.nEchoes = readpar_Kea(strcat(.datadir,paramsfile),'nrEchoes');
params.tE = readpar_Kea(strcat(.datadir,paramsfile),'echoTime');

.timefile = 'data.dat';

data = load(strcat(.datadir,datafile));
tauTimes = load(strcat(.datadir,timefile));
tauTimes = tauTimes(:,1);
tauTimes2 = tauTimes.^2;

.echoVector = (params.tE:params.tE:params.nEchoes*params.tE)*1e-6;

data2 = reshape(data,length(tauTimes),params.nPts,params.nEchoes); %data2 sums each complex point in an echo to produce one value for each echo
.data2 = sum(data2,2);
data2 = reshape(data2,length(tauTimes),params.nEchoes);

data3 = sum(data2,2); %data3 sums up all the echoes for one tau point
.data3 = data3./max(data3);

figure(1)
% line error calc
Sx = sum(tauTimes2(startind:endind));
Sy = sum(data3(startind:endind));
Sxx = sum(tauTimes2(startind:endind).^2);

%fit
[p,S] = polyfit(tauTimes2(startind:endind),data3(startind:endind),1);
[t2Line, delta] = polyval(p,tauTimes2,S);

%add to plot
figure(3)
hold on
plot(tauTimes2,data3,'-ok');
plot(tauTimes2,t2Line,'-r')
xlim([min(tauTimes2) max(tauTimes2)]);
ylim([0 1])
% title('DELM for 6 mins UV','fontsize',20)
xlabel('\tau^2 (ms^2)','fontsize',10)
ylabel('Normalized LM Intensity (arb)','fontsize',15)

del = delta - t2Line;
del = mean(del);
S = Sy - Sxx - del^2;

figure(1)

% title('DELM for 6 mins UV','fontsize',20)
xlabel('tau [ms]','fontsize',10)
ylabel('Normalized LM Intensity (arb)','fontsize',15)
set(gca,'fontsize',15,'fontweight','bold')

figure(2)

% title('DELM for 6 mins UV','fontsize',20)
xlabel('tau^2 [ms^2]','fontsize',10)
ylabel('Normalized LM Intensity (arb)','fontsize',15)
set(gca,'fontsize',15,'fontweight','bold')

figure(3)

% title('DELM for 6 mins UV','fontsize',20)
xlabel('tau^2 [ms^2]','fontsize',10)
ylabel('Normalized LM Intensity (arb)','fontsize',15)
set(gca,'fontsize',15,'fontweight','bold')

Sx = sum(tauTimes2(startind:endind));
Sy = sum(data3(startind:endind));
Sxx = sum(tauTimes2(startind:endind).^2);
Syy = sum(data3(startind:endind).^2);
Sxy = sum(tauTimes2(startind:endind).*data3(startind:endind));
N = endind - startind + 1;
D = N*Sxx-Sx^2;
slope = p(1)
int = p(2);
sig_int = ((Sxx*(Syy-p(1)*Sxy-p(2)*Sy))/((N-2)*D))^0.5;
sig_slope = (N/Sxx)^0.5*sig_int