ANALYSES OF DENSELY CROSSED LINKED PHENOLIC SYSTEMS USING LOW FIELD NMR

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ANALYSES OF DENSELY CROSSLINKED PHENOLIC SYSTEMS USING LOW FIELD NMR

A Dissertation Presented

By

JIGNESHKUMAR P. PATEL

Submitted to the Graduate School of the University of Massachusetts in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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Polymer Science and Engineering
ANALYSES OF DENSELY CROSSLINKED PHENOLIC SYSTEMS USING LOW FIELD NMR

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E. Bryan Coughlin, Department Head
Polymer Science and Engineering
To my grandfather

Ramjibhai M Patel
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With that I come to thanking the most important people in my life. Words cannot express how grateful I am to my grandmother, grandfather, mother, father, sister and brother in-law for all their sacrifice to help me. Their prayers and wishes have kept me going. I would also like to thank all my friends who pushed me towards my goal. Finally, I would like to express appreciation to my beloved wife Heena who was always my support in the moments that mattered most.
A uniform dispersion of reactants is necessary to achieve a complete reaction involving multi-components, especially for the crosslinking of rigid high-performance materials. In these reactions, miscibility is crucial for curing efficiency. This miscibility is typically enhanced by adding a third component, a plasticizer. For the reaction of the highly crystalline crosslinking agent hexamethylenetetramine (HMTA) with a strongly hydrogen-bonded phenol formaldehyde resin, furfural has been traditionally used as the plasticizer. However, the reason for its effectiveness is not clear. In this doctoral thesis work, miscibility and crosslinking efficiency of plasticizers in phenolic curing reactions are studied by thermal analysis and spectroscopic methods to elucidate the role of furfural.

By combining information from NMR, infrared spectroscopy and differential scanning calorimetry, we show that the presence of furfural increases segmental mobility, disrupts the hydrogen-bonded matrix and frees the hydroxyl units, which further increases HMTA solubility. The higher solubility and segmental mobility increases the extent of crosslinking in the phenolic system. Extent of crosslinking is determined from the spin lattice relaxation time $T_1$ measured by low field NMR (LFNMR). We demonstrate the effectiveness of this method for phenolic
systems, where other methods like infrared spectroscopy and differential scanning calorimetry are inappropriate. For validation, we have also correlated extent of crosslinking with $T_1$ using epoxy. The utilization of LFNMR in this work demonstrates its value for characterizing crosslinking of rigid thermosets.

Two alternative plasticizers to furfural are substituted in these phenolic curing reactions because of their environmental friendliness: the non-reactive methyl benzoate and the reactive methyl anthranilate. Their effect on the extent of crosslinking is evaluated and compared with the traditional reactive plasticizers furfuryl alcohol and furfural.
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CHAPTER 1

INTRODUCTION

1.1 Thesis overview

This thesis is divided into eight chapters. Chapter 1 introduces dispersion of rigid reactant for efficient crosslinking reaction of phenolic and characterization of the crosslinking in this system. Chapter 2 presents the detailed understanding of relationship of the spin lattice and spin-spin relaxation time to molecular mobility and explains why the spin lattice relaxation time is more appropriate for the characterization of the mobility in the rigid system. In chapter 3, the correlation between the amount of crosslinking and the low filed NMR (LFNMR) spin lattice relaxation time in the rigid thermoset system epoxy is developed. Due to simple chemistry of the epoxy system, it is used in this validation study. Chapter 4 has the characterization and physical properties of the two-main rigid phenolic curing reactants – crystalline crosslinker hexamethylenetetramine (HMTA) and the hydrogen bonded phenolic prepolymer. It focuses on the role of plasticizer in dispersing these two rigid reactants. chapter 5 includes the characterization of crosslinking in the phenolic system. After validating the LFNMR spin lattice relaxation time method in epoxy based thermoset system in chapter 3, the method is used for the phenolic system. This will give the crosslinking efficiency of the plasticizer. Traditionally, furfural is used as a plasticizer for this technology. However, it is toxic. Therefore, in chapter 6 and chapter 7 by understanding the role of furfural, new green plasticizer liquids are discovered. In chapter 6 characterization of the dispersion of the rigid reactants and the amount of crosslinking using non-reactive plasticizer is shown. Chapter 7 explain how the reactive
plasticizer will affect the dispersion and the curing reaction will be understood. Chapter 8 has the conclusion of the thesis.

1.2 Background on phenolic

Phenolic is the first synthetic polymeric material with more than 140 years of history. It was first synthesized by German Nobel laureate Adolf von Baeyer in 1872. However, the economic development of phenolic was possible after the 1907’s famous heat and pressure patent by Leo H Baekeland. He named the phenolic as Bakelite with the symbol \( B_\infty \) (resins for an infinite applications). Within the span of 3 years, he filled 400 patents on this resin for various applications such as molded parts, binder in the bonded abrasive kinds of composite, plywood, paper and refractory.

It is one of the most rigid crosslinked polymeric system which can usually accommodate more than 80% by mass of fillers and reinforcing agent. This is the main advantage of these polymer in comparison to thermoplastic system which has approximately 30% by mass maximum amount of fillers capacity. This property and its superior mechanical properties at higher temperature makes it main binder polymeric component in the bonded abrasive types of organic inorganic polymeric composite.

1.3 Phenolic resin

Phenolic resins comprise a large family of oligomers and polymers which are products of phenols and its derivative reacted with formaldehyde. Depending on the catalyst used and the molar ratio of formaldehyde to phenol, there are two kinds of phenolic resin such as novolac and the resole resin. The novolac is synthesized in the presence of acid catalyst and it is formaldehyde deficient resin. Resole is synthesized in the presence of base and it is phenol
deficient resin \(^1\text{-}^3\). The resole resin is known as the one step resin \(^1\text{-}^3\) due to its ability of self-polymerization at high temperatures. However, in the novolac resin addition of the crosslinker is required for the curing hence it is known as the two-step resin \(^1\text{-}^3\). In this study, novolac kind of resin is used, which is the main component of binder of high performance polymeric composite such as bonded abrasive.

1.3.1 Novolac phenolic resin

Phenol has three reactive sites – one para and two ortho. The reaction of formaldehyde with these three reactive sites of phenol can produce three different kinds of methylene linkages such as ortho-ortho, ortho-para, and para-para. For a novolac chain with ten phenol groups, more than 10,000 isomers can be statistically possible \(^4\). This will make the separation of pure phenolic compounds from phenolic resin nearly impossible. The complexity of the isomers leads to amorphous materials \(^4\).

Novolac is synthesized by the reaction of the phenol and formaldehyde in the acidic or the lower pH region. The reaction is carried out at the molar ratio of 1 mole phenol to 0.75-0.85 mole of formaldehyde \(^1\text{-}^3\). The most common acidic catalysts for this reaction are oxalic acid, hydrochloric acid, sulfuric acid, p-toluene sulfonic acid or phosphoric acid \(^1\text{-}^3,^5\). The schematic of the reaction is shown in the Figure 1.1 and 1.2. In the first Figure, formation of hydroxymethylene carbonium ion \(^1\text{-}^3\) from formaldehyde is shown.
The electrophilic addition of the hydroxyalkylating ion to phenol happens slowly and it is a rate determining step (Figure 1.1)\textsuperscript{1-3}. This reaction produces the methylol phenol substance. This methylol group is very unstable in the acidic medium and converts to Benzylic carbonium ions\textsuperscript{1-3} (Figure 1.2). It will react at the ortho or the para site of phenol and produce dihydroxy diphenylmethane\textsuperscript{1-3}. The polymerization reaction is shown in the Figure 1.2. The reaction rate is higher at lower pH. The slow step of the condensation follows the second order kinetics\textsuperscript{1}. This kind of reaction will produce the random or the statistical phenolic prepolymer.

The novolac prepolymer is also produced at the lower acidic condition (pH 4 to 6) by the use of specific bivalent metal salt\textsuperscript{1,2,6}. This kind of reaction will produce higher ortho linkages in the prepolymer. The resin produce is known as the high ortho phenolic resin.
1.4 Curing of phenolic using hexamethylenetetramine

Novolac phenolic resin is the formaldehyde deficient resin so it is generally cured by adding the crosslinking agent with the formaldehyde source such as hexamethylenetetramine (HMTA), para formaldehyde or trioxane. The most commonly used crosslinking agent is HMTA. The detailed physical properties of phenolic resin and crosslinker HMTA is described in the chapter 4. The mechanical, electrical and thermal properties of novolac cured part depends on the ratio of the two reactants. Usually novolac is cured by adding approximately 8 to 15 % w/w HMTA.

The complete reaction of one molecule of HMTA can give 6 methylene units and 4 ammonia gas. Therefore, the complete dissociation can give maximum 12 functionalities. However, due to rigid nature of HMTA and prepolymer the complete dissociation of HMTA is not possible. Many different kinds of linkages such as amine, imine, imide, amide and methylene linkages are observed in the final product. The literature suggests two different kinds of mechanism for the reaction of HMTA with phenolic resin. One is through hydrolysis of HMTA and the other is via hydrogen bonding between phenolic monomer and crosslinker HMTA.

1.4.1 Reaction through hydrolysis of HMTA

Due to hydrophilic nature of phenolic resin, it always has some small amount of (less than 2 % w/w) moisture. At higher temperature, this moisture leads to hydrolysis HMTA molecule. Schematic diagram of the hydrolysis of HMTA is shown in the Figure 1.3. The hydrolysis of HMTA produces formaldehyde and some amino methylated products. Formaldehyde can directly react with the reactive ortho or the para site of the resin and form the...
methylene linkages\textsuperscript{1,2,4,7}. The amino methyl compound reacts with the phenolic ortho or para site via the Manich reaction mechanism\textsuperscript{1,2,4}.

\begin{center}
\begin{tikzpicture}
\node (n1) at (0,0) {\HMTA};
\node (n2) at (1,0) {H_2O};
\node (n3) at (2,0) {\text{NH}};
\node (n4) at (3,0) {\text{NH}};
\node (n5) at (4,0) {\text{H}_2\text{O}^*};
\node (n6) at (5,0) {\text{H}_2\text{O}^*};
\node (n7) at (6,0) {\text{NH(\text{CH}_2\text{OH})}_2};
\node (n8) at (0,-1) {\text{H}_2\text{N} \text{C} \text{NH}_2};
\node (n9) at (1,-1) {2\text{H}_2\text{O}^*};
\node (n10) at (2,-1) {\text{CH}_2\text{NH} \text{NH}};
\node (n11) at (3,-1) {\text{CH}_2\text{NH} \text{NH}};
\node (n12) at (4,-1) {\text{NH(\text{CH}_2\text{OH})}_2};
\node (n13) at (5,-1) {2\text{H}_2\text{O}^*};\end{tikzpicture}
\end{center}

Figure 1.3 Hydrolysis of hexamethylenetetramine

1.4.2 Reaction through hydrogen bonding

It has been shown by Tsubomura that the hydrogen bonding between HMTA and phenol is one of the strongest hydrogen bonding\textsuperscript{15}. Using infrared spectroscopy, he observed that as strength of hydrogen bonding increases, its polarizability increases\textsuperscript{15}. Due to higher polarizability of the hydrogen bond of phenol and HMTA, the hydrogen of phenol can easily be transferred to HMTA. In the next step, the HMTA molecule will have a positive charge which will make it unstable\textsuperscript{7-9,16} molecule as shown in Figure 1.4. So, its C-N bond will break and methylene of HMTA will attack the electron rich sites of the phenolic ring which are at the ortho or the para positions\textsuperscript{7-9,16}. Further dissociation of HMTA molecule will occur by formation of hydrogen bonding of the nitrogen of dissociated HMTA and the hydroxyls of phenolic resin\textsuperscript{7-9,16}. The step by step dissociation of HMTA is shown in the following Figure 1.4. The reaction mechanism
shows that the dissociation or the total functionality of HMTA used during curing is dependent on availability of the free hydroxyls of the phenolic resin and its mobility.

Figure 1.4 Reaction through hydrogen bonding

In the initial stage of the reaction, compound A will further dissociate and produce linkages of benzyl amine and the benzoxazine intermediate which is shown in the Figure.
1.4. Some of these kinds of intermediate will further dissociate and produce methylene linkages, some will stay as amine based linkages or oxidize at higher temperature and give ether, amide or imide based linkages\textsuperscript{7,9}. Therefore, the final product may contain all of these linkages. Solomon shows that approximately 15 different kind of linkages\textsuperscript{4,7-14,16} are observed and some of these linkages are shown in Figure 1.5.

Due to rigid nature of phenolic which mostly comes from the intra and inter hydrogen bonding, there are few free hydroxyl groups available for the dissociation of HMTA molecule. So, the complete dissociation of HMTA molecule is not possible during the curing reaction. Therefore, we have observed not only methylene linkages but other linkages such as primary amine, secondary amine, tertiary amine, imine kinds of 15 different linkages\textsuperscript{4,7-14,16}. Addition of plasticizer increases the mobility of prepolymer and the free hydroxyls group. Both of these phenomena increases the dissociation of HMTA and reactive functionalities usage during the curing\textsuperscript{7-9,17-21}.
Figure 1.5  Some of the linkages produce from reaction of hexamethylenetetramine and phenolic resin

It has been shown that in the case of lower amount of HMTA more methylene linkages and less nitrogen based linkages are observed in the final product\(^7\). This is due to the presence of higher unreacted ortho and para sites available and also the higher mobility of the free
hydroxyl groups in the lower amount HMTA system. Therefore, in this case more dissociation of the benzyl amines and benzoxazines will occur\textsuperscript{7}. This will give more methylene linkages\textsuperscript{4,7-14,16}. However, in higher HMTA case, due to less number of unreacted sites and the lower mobility of free hydroxyls in the later stage of the curing, the dissociation of HMTA will be difficult. The final product will have higher amine based linkages. The elemental analysis of the cured phenolic shows that after curing at 205 °C for the 4 hrs gives 30 to 50 % w/w nitrogen containing linkages in the high HMTA sample\textsuperscript{7-9,21}. The loss of nitrogen will occur by the formation of ammonia gas.

1.5 Dispersion of reactants in crosslinking reaction

In many applications, in order to achieve exceptionally high mechanical performance, it is necessary to employ various chemical reactions involving drastically different components. Because of the different physical parameters of each component, such as molecular weight, inter-molecular interactions and crystallization behavior, the mixtures studied can exhibit significantly different phase behavior. However, a uniform mixture is necessary, especially when chemical reactions are involved. The kinetics or the resultant products of various chemical reactions associated with multi-components systems is impossible to predict when an immiscible mixture is used. In those cases, it is impossible to analyze the reaction when a true stoichiometry of the reactants cannot be assessed or controlled. Therefore, in this work, a fundamental understanding of the dispersion process of the individual components in reactive mixtures will be carried out in order to characterize the reaction that takes place.
1.5.1 Use of plasticizer in phenolic curing reaction

The specific example that we have studied is the crosslinking reaction between crystalline crosslinker HMTA and the rigid hydrogen bonded phenol formaldehyde polymer (Figure 1.6). Although this area has a long history of study \(^{22,23}\), a number of fundamental questions remain unresolved because the curing reaction is complicated and there are difficulties in the characterization of a crosslinked structure. Our current study reported here clarifies the role of plasticizer, to induce miscibility at molecular level of the two principal components, phenolic resin and HMTA. HMTA is highly crystalline (>99% crystallinity) and has a melting temperature of nearly 280 °C \(^{1,2,16}\). Because of the energy consideration most of the curing or crosslinking reaction is carried out at the temperature no higher than 200 °C. In order to induce
crosslinking reaction dissolution of HMTA is necessary at the curing reaction temperature. Previous studies have revealed that HMTA can be “solubilized” using the monomer of phenolic resin such as phenol, xylenol, and resole. These monomers of phenolic resin can form hydrogen bonds with the nitrogen of HMTA. However, the rigidity of the phenolic resin which is mostly coming from the extensive intra- or inter-molecular hydrogen bonds and the kinked structure of phenyl rings, prevents the interaction of HMTA and the phenolic monomers and reduces the solvation of HMTA molecule.

Although, temperature has the ability to disrupt the hydrogen bonds and introduce higher segmental mobility in phenolic resin, by adding plasticizer we can increase the efficiency of this process. This will increase the solvation of HMTA and the molecular level interaction of phenolic resin and HMTA molecule which will enhance the curing reaction kinetic and amount of crosslinking. One additional fact that also needs to be considered is that the resin usually incorporates water in its structure. Water is an excellent solvent for HMTA. Freeing this water because of higher segmental mobility in the presence of plasticizer may be another factor that needs to be considered in the dissolution and the subsequent reaction. Also, due to presence of hydrogen donating group in the case of some of the plasticizer they can directly solubilize HMTA.

Plasticizer is not only helpful in the dispersion of these rigid reactants but also enhances crosslinking in the diffusion controlled regime of the reaction. Due to rigidity of phenyl ring, the glass transition temperature can rise quickly during the crosslinking reaction creating a vitrified structure rapidly. When the vitrification point is approached, curing kinetics will be diffusion controlled and strongly dependent on the local viscosity. The plasticizer added will
decrease the local viscosity and increase the amount of crosslinking reaction during the diffusion controlled regime

Traditionally, furfural has been used as a plasticizer to enhance the crosslinking ability of the phenol formaldehyde resin. Although there is a long history associated with this system (> 80 years), due to complexity of curing reaction and difficulty in characterizing the crosslinking in this system, there is no systematic study to elucidate the role of furfural in the dispersion of HMTA and prepolymer. The only problem with furfural is that it is a toxic liquid with the toxicity to human is 4/4 (Sigma-Aldrich MSDS). Therefore, an understanding of the role of furfural liquid in the crosslinking reaction will provide the clue to search for new plasticizers that would be equally as effective as furfural without its toxicity issues.

In the case of furfural, due to absence of proton donating group it might not have the ability to dissolve HMTA directly. However, the aldehyde group and the positively delocalized five-member ring might have the ability to break the internal hydroxyls groups of phenolic resin. This breakage of internal hydroxyls will create free hydroxyl groups which will solubilize HMTA. Due to presence of proton accepting group aldehyde in furfural, it will be interesting to use other environmental friendly liquids which have proton accepting groups such as ester, aldehyde and ketone and which might follow the same solvation mechanism as furfural.

The other solvation method in which the plasticizer will have the hydrogen donating functional group and directly solubilize HMTA and plasticize prepolymer. This class of plasticizer generally has proton donating group such as alcohol, amine etc. They can then form hydrogen bond with HMTA and solubilize it. Although this class of plasticizer can block the
reactive functionality of HMTA molecule, they can also yield high crosslinking if they have more than one functionality.

We also considered the reaction of highly mobile plasticizer in this rigid mixture. Because of its high mobility compared to the other reactants, the reaction of plasticizer mostly would be chemically controlled. Depending on the nature of reactivity and functionality, the reaction of plasticizer would either act as terminating or crosslinking. For example, in the case of furfuryl alcohol due to presence of only one functionality, hydroxyl unit acts as a terminating agent. However, in the case of furfural it might provide more than one functionality for the reaction and might give extra crosslinked junction during curing. Moreover, it is interesting to try other more environmental friendly plasticizers which will have higher reactive multi-functional groups.

1.6 Characterization of highly crosslinked thermoset

The merits of densely crosslinked polymers (thermosets such as epoxy, imine and phenolics) include high mechanical performance and dimensional stability even at elevated temperatures. However, these attractive physical attributes are also the reasons they are extremely difficult to characterize. Although the molecular mobility of these crosslinks is extremely important in the consideration of macroscopic mechanical, thermal and electrical properties, most of the past analyses have employed Gaussian chains applicable to lightly crosslinked systems. Although macroscopic properties can be predicted empirically, the description of the segmental dynamics of the crosslinks of densely crosslinked polymers remains an important challenge. In this study, the characterization of crosslinking is done by measuring the chain dynamics.
The crosslinking reaction in phenolic is very complex due to the formation of 15 or more different kinds of linkages (Figure 1.5)\textsuperscript{7-9}. These linkages either exist as crosslinks or as dangling chains\textsuperscript{7-9}. Therefore, by only knowing the type of these linkages using infrared or solid state NMR spectroscopy, it is difficult to correlate them with the actual crosslinking reaction and the mechanical properties obtained. Addition of a third component plasticizer, further complicates the elucidation of the crosslinking. To overcome these problems, we have used Low Field NMR (LFNMR) spin-lattice relaxometry ($T_1$) to characterize the stiffness arising from the amount and type of crosslinks in the highly crosslinked phenolic system described in chapters 5, 6 and 7\textsuperscript{18,19}. This molecular stiffness governs the mechanical and thermal properties of the system.

This unconventional usage of LFNMR has shown to be extremely effective in establishing the correlation between the spin lattice relaxation time and the mechanical properties obtained for the various types of crosslinks employed. In addition, the reaction used to form crosslinks could be monitored using infrared spectroscopy and thermal analysis as mentioned in chapter 5, 6 and 7\textsuperscript{18,19}. However, this phenolic system can be affected by the presence of plasticizers, water, unreacted functional groups, chain termination reaction, strong interchain interactions including hydrogen bonding, and additives introduced, thus perturbing the LFNMR $T_1$ measurements or the relationship between the degree of crosslinking and $T_1$ relaxation time. Hence, by using a simpler system such as epoxy with known crosslink density, a more quantitative analysis of the crosslinking density to the $T_1$ relaxation time can be achieved as described in chapter 3.

In NMR relaxometry, broadening of the resonance line which comes from the phenomena known as the motional narrowing is mostly used for the measurement of the molecular motion. In the case of rigid system, the resonance line width does not change
significantly to a measurable extent in a wide range of temperature \(54-56\). However, due to spin diffusion event in the rigid system, it is possible to measure the small perturbation in the rigid system \(57-59\) using spin lattice relaxation time. In the case of rigid crosslinked system, these perturbations originate from the highly mobile region of the chains such as unreacted function group or the dangling end. These perturbations will decrease as crosslinking increases. Hence, it is possible to measure the amount of crosslinking in the rigid system using the \(T_1\) relaxometry. The detailed study of why \(T_1\) is used and not \(T_2\) relaxation time for this study is explained in chapter 2. Also, in chapter 2 and 3 the relationship of the \(T_1\) relaxation time and the molecular mobility is described.

1.7 References


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CHAPTER 2

BASICS OF LOW FIELD NMR RELAXOMETRY

2.1 Chapter overview

In this chapter, basic theory of NMR relaxometry is explained. After perturbing the equilibrium population of the spin immersed in the external uniform magnetic field by applying the radiofrequency pulse, they will again come to the equilibrium with the two-independent relaxation times, spin-lattice relaxation time ($T_1$) and the spin-spin relaxation time ($T_2$). Here, the fundamental understanding of what these two relaxations are and how they relate to the molecular motion needs to be described. BPP theory developed by N. Bloembergen, E. M. Purcell, and R. V. Pound correlates the $T_1$ and $T_2$ relaxation times to the molecular motion. This theory explained how the $T_1$ and $T_2$ relaxation times are related to the simple uncorrelated motion such as tumbling motions of the water. The modified BPP theory for the correlated motion which is usually the case in polymeric system is shown in the chapter 3. In this chapter, we also answered the question why $T_1$ is better for the characterization of the motion in a rigid crosslinked system than $T_2$ relaxation time.

2.2 Background on low field NMR (LFNMR)

In 1939, Rabi observed that a stream of hydrogen in a uniform magnetic field deflect after absorbing a particular radio frequency $^1$. This was the first observation of NMR and for that he received a Noble prize in physics in 1944. However, the NMR method for the bulk material was developed independently by Bloch at Stanford $^2$ and Purcell at Harvard in 1946 $^{3,4}$. The major use of NMR in analytical chemistry and in the medical science started after the development of
pulse NMR and the development of the Fourier transform technique to analyze the time domain
signal by R. Ernst 5.

The current trend in NMR is to increase the sensitivity and the spectral resolution by
enhancing the strength of magnetic field 6-8. Currently, super conducting magnet with the 1 GHz
proton larmor frequency NMR are available 6-8. These kinds of magnets are heavy, and
delicate in purchase and maintenance. Moreover, the operation of high-field spectrometers is
rather complex. Lighter in weight and inexpensive low-field proton NMR may provide valuable
insights in structure. Low-field spectrometers are easy to handle since they use permanent
magnets and comparably simple technology 6. Admittedly, due to the weak magnetic field and its
rather strong inhomogeneity, chemical resolution cannot be achieved here 6,7. Hence, low-field
devices are mainly used for standard T$_1$ and T$_2$ relaxometry study of the material.

2.3 Theory of NMR

In addition to charge and mass every proton has one more intrinsic property which comes
from the spinning of proton around its axis 8. This property called spin, also known as the
angular momentum of the proton was first discovered by Pauli 9. The spinning charge can
generate the magnetic moment. Therefore, in the presence of external magnetic field, the
resultant vector of proton spin will align either in parallel or the anti-parallel to the direction of
external magnetic field. Due to random orientation of the initial angular momentum, the spin axis
will not perfectly align with the external magnetic field but it will precess around it 8. The spin
precessing along the anti-parallel to the external magnetic field has higher energy than the
parallel one. The energy difference between two state will be 8

\[ E = \mu. \frac{H_0}{I} = 2\mu. H_0 = \gamma hH_0 \]
Where, $\mu$ is the magnetic moment, $H_0$ is the external magnetic and $\gamma$ is the magnetic gyrometric ratio and $\hbar$ is the $h/2\pi$. The $h$ is the Plank constant.

This energy fall into the radio frequency region. Therefore, by applying the radio frequency pulse, we can perturb the equilibrium spin population. The separation of nuclear magnetic energy level is small. For 14.1 T external field (600 MHz NMR) this difference is approximately 0.5 J$^{8,10}$. Therefore, this NMR resonance energy will not affect the thermal motion of the material to the measurable extent except for temperatures close to 0º K$^8$.

2.3.1 $T_1$ and $T_2$ relaxation times using NMR

The correlation of the molecular motion to the NMR phenomena are carried out mainly using spin lattice relation time $T_1$ and the spin-spin relaxation time $T_2$. In this chapter the basic of the spin lattice and the spin-spin relaxation time and how they are correlated with the molecular motion are explained.

2.3.1.1 Spin lattice relaxation ($T_1$):

In the presence of external magnetic field $H_0$, the lower energy spin population (parallel to external magnetic field) will be more populated. The relative ratio of the lower and the upper energy population is described using the Boltzmann relationship which is the following.

$$\frac{N_+}{N_-} = \exp \left( \frac{2\mu H_0}{k T_s} \right) \approx 1 + \frac{2\mu H_0}{k T_s}$$

Equation 2.2

Where $N_+$ and $N_-$ are the number of protons per unit volume in the upper and lower state and $T_s$ is the spin temperature. The surplus spin population ratio at room temperature and with magnetic
field of 600 MHz is approximately $10^{-6}$ \cite{8,10}. This small but important difference in the spin population is responsible for the NMR spectroscopy.

This small energy difference \((2\mu H_0)\) falls in the radiofrequency region. By applying this appropriate radiofrequency pulse for a specific time, the lower energy protons (parallel) will populate the upper energy level (anti parallel). Eventually the population in the upper and the lower spins will be identical and the system will be saturated. At this point, the spin system will have the highest spin temperature \((T_s)\) as shown in equation 2.2. After that the spins will cool down by attaining the equilibrium with the surround environmental temperature or lattice temperature \((T_L)\). The lattice usually is a term used for the array of crystal but here we are using it for any kind of solid, liquid or gas sample \cite{11}. The rate of nuclear energy transfer from spin system to lattice follows the first order of kinetics \cite{8}. The characteristic time constant of this process is known as the spin lattice relaxation time \(T_1\).

The \(T_1\) NMR relaxometry is completely different and does not strongly couple with the molecular motion \cite{11-14}. In NMR, when we remove the external magnetic field, the decay of the magnetization occurs slowly and in the time scale of seconds or minutes \cite{11-14}. The rotation or the translation time scale of the molecule is approximately $10^{-5}$ to $10^{-10}$ sec \cite{11-14}. However, in the case of dielectric spectroscopy, after the removal of the electric field, macroscopic electric dipole decays with rate comparable to the molecular reorientation \cite{11,13}. Also in the case of viscoelastic experiment, the strain decay is comparable to the rate of molecular translation or the orientation motion after the removal of stress \cite{11,13}. This kind of behavior of the magnetic field and the molecular motion makes the correlation more complex. However, the NMR relaxometry method has certain advantages over the other methods. In NMR, magnetic force field is uniform over the molecular scale which is difficult to achieve in the viscoelastic measurement due to the difficulty
to prepare uniform sample and the inhomogeneity coming from the material such as aggregation or the crystal in it \(^{15}\). For the dielectric spectroscopy method polarizability of the bond is necessary.

In the \(T_1\) relaxometry experiment, the temperature of the spin immersed in the external magnetic field increases by applying appropriate radio frequency pulse \(^{11-14}\). After that the spins cool to the surrounding temperature. The cooling down of the spin occurs efficiently if the frequency of molecular motion is close to nuclear magnetic resonance frequency \(^{12,16,17}\). One can vary the molecular motion by changing the temperature. The temperature at which molecular motion frequency is close to magnetic resonance frequency, characteristic time for the transfer of spin energy will be the lowest. Hence, \(T_1\) minima will be observed at that temperature. The molecular motion occurring at faster or slower rate than the magnetic resonance frequency is less effective and do not properly couple with the nuclear spin \(^{12,16,17}\). In this case, it will take more time for the transfer of spin energy to thermal energy. In the case of LF NMR, the resonance occurs at the lower frequency than the high field NMR. Hence, it will be more sensitive toward the long-range motion of the rigid crosslinked thermoset than the high field NMR experiment. Therefore, the LFNMR is used in this study.

2.3.1.2 Spin-spin relaxation time \((T_2)\)

In addition to spin lattice interaction, there is another relaxation in which the nuclei spins interact among themselves. In the sample, the proton not only experience the external magnetic field \(H_0\) but also the magnetic field from the neighboring spin \(^{17}\). This local magnetic field either adds or subtracts from external magnetic field depending on the orientation and the motion of the molecule. By considering this field, we can rewrite the equation 2.1 again,

\[
E = h\gamma = 2\mu (H_0 \pm H_{loc})
\]
The local magnetic field is

\[ H_{loc} = \left( \frac{3 \mu}{r^3} \right) (3 \cos^2 \theta - 1) \]

Equation 2.3

Where, \( r \) is the internuclear distance and the angle \( \theta \) is the angle between internuclear vector with the external magnetic field \( H_0 \).

The magnitude of the local magnetic field is much smaller than the external magnetic field. However, it significantly changes the amount of total magnetic field experienced by the nucleus. Due to this it will not only have two discrete nuclear populations (in proton case) but also have a continuous distribution of the energy levels at both the levels. Therefore for the radiofrequency signal, resonance occurs not only at one frequency but also at a continuous range of frequencies. This phenomenon known as the line broadening or the dipolar coupling.

When a nucleus put in an external magnetic field it precesses uniformly with the larmor frequency of \( \omega = \gamma H_0 \), where \( \omega \) is the angular frequency of precession and the \( \gamma \) is the gyrometric ratio of nuclei. Due to presence of dipolar coupling from the field \( H_{loc} \) the change in the nuclei precession frequency (broadening) will be \( \Delta \omega = \gamma H_{loc} \). The time required for the frequency broadening is known as the spin-spin relaxation time.

In the case of liquid or in some solids, the protons are always in motion. The thermal motion of the spin changes the local arrangement or the local configuration of the spin system. Owing to this, it will sometimes precess rapidly and in other cases slowly. Because of this the departure from its mean frequency or the phase angle will be decreased. This will narrow down the line width of processional frequency. Using equation 2.4, we can also understand
this phenomenon. If the nuclei take most of the value of $\theta_{ij}$ over the unit sphere in a short time, then the value of $(3\cos^2\theta_{ij} - 1)$ will go to zero. This shows that the faster motion reduces the $H_{local}$ and line width of the system. The phenomena which correlates the dipolar coupling and the motion of the nuclei are known as the motional narrowing\(^{16,18}\).

Slichter gave the most complete theoretical explanation on how the dipolar coupling is related to the motion of the nuclei\(^ {16}\). In that model, he developed the theory for the idealized case of a nucleus which has one neighbor at a time and the neighbor is changed with every $\tau$ time period\(^ {16}\). The field coming from this neighboring nucleus can change the precession frequency by $\delta\omega = \pm\gamma H_{loc}$; $\delta\omega$ is line width in the absence of the thermal motion of the nuclear spin\(^ {16}\). The $\pm$ comes from the local field which can add or oppose the external field and so, the precession frequency could increase or decrease. Suppose the neighboring nucleus stays for the time $\tau$, then in this time the extra phase angle can either gain or lose\(^ {16}\),

$$\delta\phi = \pm\delta\omega \tau$$

Equation 2.5

After $n$ such time intervals the mean square phase angle will be,

$$\Delta\phi^2 = n\delta\phi^2 = n(\delta\omega)^2\tau^2$$

Equation 2.6

If the total time is $T$ then $n$ will be,

$$n = T/\tau$$

Equation 2.7
The spin-spin relaxation time ($T_2$) is defined by the time when the initial phase is completely lost which is when $\Delta \phi^2 \approx 1^{16}$.

$$1 = \left(\frac{T_2}{\tau}\right)(\delta \omega)^2 \tau^2$$

Equation 2.8

The effective spread in the precession frequency (line width) is also defined by

$$\Delta \omega = 1/T_2$$

Equation 2.9

Therefore,

$$\Delta \omega = ((\delta \omega)^2 \tau) = (\tau \delta \omega) \delta \omega$$

Equation 2.10

The equation 2.10 shows that as the thermal motion of the nuclei increases (smaller $\tau$) then the precession frequency width ($\Delta \omega$) gets smaller. The above equation is only valid if the thermal motion of the spins ($\tau$) is faster than the sizable dephasing time ($1/\delta \omega$) $^{16}$. So, we can get line narrowing condition with the equation 2.11.

$$\tau < \frac{1}{\delta \omega} \Rightarrow \delta \omega \tau < 1$$

Equation 2.11

In the case of rigid system or the molecular relaxation with large $\tau$, $\Delta \omega \approx \delta \omega$.

Therefore, the equation 2.11 is only valid for $\delta \omega \tau \leq 1^{16}$. This shows that at lower temperature
nothing occurs to line width unless $\tau$ reduces to a level $\delta \omega \tau \leq 1$\textsuperscript{16}. Hence, the line narrowing is not a good method for the characterization of the rigid crosslinked system which has glass transition temperature very high. Therefore, in this study the characterization of the rigid crosslinking is done using spin lattice relaxation time.

### 2.4 BPP theory

The spin lattice relaxation time is the time related to the exchange of energy between the spins and their surroundings. Without the thermal motion of the spins, its value will be in the range of the $\sim 10^{15}$ seconds and does not correlate to the physical properties of any material\textsuperscript{12}. This value reduces to a small dimension when the nuclear spins are coupled via the thermal motion\textsuperscript{12}. Bloembergen, Purcell and Pound developed BPP theory\textsuperscript{12} which describes how the spin thermal motion will affect the spin-spin and the spin lattice relaxation times.

To understand this BPP theory first the relationship between the spin lattice relaxation time and the probability for a single transition per second is developed for the proton system with the spin energy level $+I/2$ and $-I/2$. For simplicity, the $+I/2$ level is denoted by + and the $-I/2$ level is denoted by the -. The energy difference between these two spin in the external magnetic field $H_o$ is $\gamma h H_o$ shown in equation 2.1

Let the probability for the + to – transition per sec is $U(\rightarrow -$) = $U$

Using Boltzmann distribution concept, we can estimate the probability of the – to +\textsuperscript{18},

$$U(-\rightarrow +) = U \exp \left( \frac{\gamma h H_o}{kT} \right)$$

Equation 2.12
In the nuclear transition the energy is very low than $kT$. So, from Taylor series approximation

$$U(-\rightarrow +) = U \left( 1 + \frac{\gamma \hbar H}{kT} \right)$$

Equation 2.13

The number of protons at the higher energy and at the lower energy state in the unite volume at time $t$ are denoted by $N(-)$ and $N(+)$ respectively.

The excess population in the lower state will be,

$$n = N(+) - N(-)$$

Equation 2.14

Therefore, the change in the excess population with time is

$$\frac{dn}{dt} = 2 \left[ N(-) \ U(-\rightarrow +) - N(+) \ U(\rightarrow -) \right]$$

Equation 2.15

The factor 2 is due to the transfer of single spins can change the value of $n$ by 2$^8$.

From equation 2.12 to equation 2.15,

$$\frac{dn}{dt} = 2U \left( N(-) \left[ 1 + \frac{\gamma \hbar H}{kT} \right] - N(+) \right)$$

Equation 2.16
In the above equation, term \( N(\cdots) \left[ \frac{\gamma h H}{kT} \right] \) describes the excess population in the lower state at the equilibrium and it is denoted by \( n_0 \). 

Using equation 2.14 and by inserting \( n_0 \) in the equation 2.16,

\[
\frac{dn}{dt} = 2U (n_0 - n)
\]

Equation 2.17

The above equation is similar to the first order chemical kinetics equation with the rate constant is \( 2U \). The corresponding time constant will be \( 1/2U \). The time constant related to the excess spin population \( (n) \) reaches to the equilibrium spin population \( (n_0) \) is known as the spin lattice time constant \( T_1 \). 

Therefore, the relationship between the spin lattice relation time \( T_1 \) and the spin energy absorbance probability per unit time is

\[
T_1 = \frac{1}{2U}
\]

Equation 2.18

2.4.1 Relationship between the motion of protons and \( T_1 \) and \( T_2 \)

One of the way to study the thermal motion of the molecule is by using the correlation function. The correlation function provides a concise method for expressing two dynamical properties correlated over a period. The autocorrelation function measures the similarity between two fluctuating process at \( A(\tau) \) and \( A(\tau + t) \) and how the correlation function varies with time. The random continuous fluctuations are highly correlated for the short time intervals.
However, for the large time interval they are not correlated $^{19,20}$. In the case of small liquid molecules, the random fluctuations arise from the rotatory Brownian motion $^{21-23}$. Its correlation function decays exponentially with single relaxation time which was first shown by Debye in the study of dielectric spectroscopy of small molecular liquid $^{23}$. Bloembergen, Purcell and Pound use the same autocorrelation function for explaining the tumbling motion of water at different temperature using spin -lattice relaxation time ($T_1$) $^{12,20}$. The following is equation they derive for the spin energy transfer rate ($1/T_1$)

$$
\frac{1}{T_1} = \frac{3}{10} \frac{\gamma^4 \hbar^2}{r^6} \left[ \frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega^2 \tau_c^2} \right]
$$

Equation 2.19

Here we are showing the method how they derived the equation 2.19 by considering relationship of the spin interaction with the motion of them. For the system with N total spins in the unit volume, the interactions of them we can define by $^{12}$

$$
V = \sum_{i=1}^{N} \sum_{j>i} V_{ij}
$$

Equation 2. 20

Here $V_{ij}$ is defined by the dipole-dipole coupling between the spins $i$ and $j$. The Bloembergen, Purcell and Pound define it by the equation 2.21 $^{12}$, using spherical coordinate system with respect to z axis is the axis of external magnetic field, the polar angle $\theta$, and the azimuthal angle $\varphi$ and the radial vector $r$.

$$
V_{ij} = \gamma^2 \hbar \frac{r_{ij}^{-3}}{(A + B + C + D + E + F)}
$$
The terms A, B, C, D, E and F are all the possible interaction of the spins $i$ and $j$. A and B denotes the interaction in which spin’s z component quantum number does not change. So, the $\Delta m = 0$.

Where,

$$A = I_{zi} I_{zj} \left(1 - 3 \cos^2 \theta_{ij}\right)$$

$$B = -\frac{1}{4} \left[ (I_{xi} - i I_{yi}) (I_{xj} + i I_{yj}) + (I_{xi} + i I_{yi}) (I_{xj} - i I_{yj}) \right] \times \left(1 - 3 \cos^2 \theta_{ij}\right)$$

Both the above terms (A, B) are time independent and in this kind of spin interactions spin energy does not change. A is corresponding to the changes in the $H_{loc}$ or precessional frequency of the spin $i$ due to presence of the magnetic field coming from the neighboring spin $j$\textsuperscript{12}. This field will be small in nature and it will slightly change the Larmor frequency of the spin system. The term B is related to the simultaneous flopping of the two spins. In which the $z$ component of the one spin will go to $\Delta m_i = +1$ and the other spin system will go to the $\Delta m_j = -1$ or vice versa in a pair of spins\textsuperscript{12}. Due to adiabatic nature of these kinds of transition they are related to the spin-spin relaxation time $T_2$. These kinds of transition are responsible for spin energy diffusion from one place to the other.

The terms C, D, E and F are related to the spin-spin interaction in which spin system’s total energy is not conserved or changed due to interaction\textsuperscript{12}.

$$C = -\frac{3}{2} \left[(I_{xi} + i I_{yi}) I_{zj} + (I_{xj} + i I_{yj}) I_{zi}\right] \times \sin \theta_{ij} \cos \theta_{ij} e^{-i\varphi_{ij}} e^{i\gamma H_0 t}$$
\[ D = -\frac{3}{2} \left( (I_{x_i} - i I_{y_i})I_{x_j} + (I_{x_j} - i I_{y_j})I_{z_i} \right) \times \sin \theta_{ij} \cos \theta_{ij} e^{i\varphi_{ij}} e^{-i\gamma H_0 t} \]

\[ E = -\frac{3}{4} (I_{x_i} + i I_{y_i}) (I_{x_j} + i I_{y_j}) \sin^2 \theta_{ij} \times e^{-2i\varphi_{ij}} e^{2\gamma H_0 t} \]

\[ F = -\frac{3}{4} (I_{x_i} - i I_{y_i}) (I_{x_j} - i I_{y_j}) \sin^2 \theta_{ij} \times e^{2i\varphi_{ij}} e^{-2\gamma H_0 t} \]

Equations 2.23

C and D are corresponding to \( \Delta m = 1 \) and \( \Delta m = -1 \) \(^{12}\) respectively and E and F are corresponding to \( \Delta m = 2 \) and \( \Delta m = -2 \) \(^{12}\) respectively in a pair of spin. They will change the total z direction magnetic dipole in a pair of spin. C, D, E, and F are non-adiabatic spins transitions and are related to the \( T_1 \) \(^{12}\).

The thermal motions of the spins which is mostly due to the Brownian motion of the molecule on which spins or the proton are laid on. Due to these thermal motions of the molecule or atom the coordinates \( r_{ij}, \theta_{ij} \) and \( \varphi_{ij} \) of the spin changes with the time. This will induce the interaction describes in \( V \) of the equation 2.21. The different position coordinates (equation 2.22 and 2.23) are converted into a Fourier integrals. The intensity of the Fourier spectra is defined by the three different position functions.

\[ \langle \sum_j \left| \left( 1 - 3 \cos^2 \theta_{ij}(t) \right) r_{ij}^{-3}(t) \right|^2 \rangle_{avg} = \int_{-\infty}^{\infty} J_0(v) dv \]

\[ \langle \sum_j \left| \sin \theta_{ij}(t) \cos \theta_{ij}(t) e^{i\varphi_{ij}(t)} r_{ij}^{-3}(t) \right|^2 \rangle_{avg} = \int_{-\infty}^{\infty} J_1(v) dv \]

\[ \langle \sum_j \left| \sin^2 \theta_{ij}(t) e^{2i\varphi_{ij}(t)} r_{ij}^{-3}(t) \right|^2 \rangle_{avg} = \int_{-\infty}^{\infty} J_2(v) dv \]

Equations 2.24
At the frequency $2\pi v_0 = \gamma H_0 \cdot J_1(v_0)$ and $J_1(-v_0)$ are different from zero and at this frequency the time dependent term cancel out and C and D become the secular perturbation or time independent terms. Similarly, E and F become secular perturbation at $v_0$. Therefore, the non-adiabatic spin transition in which the magnetic quantum number 1 and 2 are possible are the NMR resonance frequency dependent.

In the rigid system, the local field at $i$ due to the neighboring spin $j$ has two parts. One is the static part which is $I_{ij}$ and the rotating part $I_{ij} - iI_{ij}$. The motion of $j$ will fluctuate the $H_{loc}$ coming from $j$ spin to $i$ spin. If the spin $j$ has the thermal motion and its frequency is close to the precession frequency of $i$, then the nucleus $i$ will find itself exposed to radiofrequency field capable to induced the transition. These kinds of transitions are occurring in the C and D. Here, simple explanation for $m=1$ transition was given. One can also understand the $m=2$ transitions with the similar way which are observed in the case of E and F.

We can now compute from the above discussion the probability of the absorbance transition per sec in the proton system. This probability is:

$$U = \frac{3}{4} \gamma^4 h^2 I(I + 1) \left( J_1(-v_0) + \frac{1}{2} J_2(-2v_0) \right)$$

Equation 2.25

By inserting the above equation 2.25 in the equation 2.18, we get the spin lattice relaxation time,

$$\left( \frac{1}{T_1} \right) = \frac{3}{2} \gamma^4 h^2 I(I + 1) \left[ J_1(-v_0) + \frac{1}{2} J_2(-2v_0) \right]$$

Equation 2.26

Now we can apply this theory to the simple molecule such as water. For that it is necessary to develop the Fourier spectra of the functions of position coordinates. The following time domain equations are converted into the molecular frequency domain by Fourier spectra.
\[ F_{0j} = \left( 1 - 3\cos^2 \theta_{ij}(t) \right) r_{ij}^{-3}(t) \]

\[ F_{1j} = \sin \theta_{ij}(t) \cos \theta_{ij}(t) e^{i\varphi_{ij}(t)} r_{ij}^{-3}(t) \]

\[ F_{2j} = \sin^2 \theta_{ij}(t) e^{2i\varphi_{ij}(t)} r_{ij}^{-3}(t) \]

Equation 2.27

Due to presence of the Brownian motion in the liquid such as water, the position coordinates of it changes randomly. The motion will be isotropic on average and so the time average of each function of \( F \) will be zero \(^{12}\). However, for the short time interval the motion of the molecule will be correlated \(^{12}\). This time is the time required from the one molecular configuration to another configuration or time between two collisions \(^{12}\). This time is known as the characteristic time \( (\tau_c) \). Usually viscosity of the liquid is inversely related to this time interval. This phenomenon is understood by the autocorrelation function,

\[ K(\tau) = \langle F(t) F^*(t + \tau) \rangle_{avg} \]

Equation 2.28

Equation 2.28 is known as the autocorrelation of \( F(t) \). It is assumed that it is an even function of \( \tau \) and it is not dependent on the time for a long time interval. Function \( K(\tau) \) approaches to 0 for the long value of time. The Fourier spectrum of \( F \) enables us to write for the spectral density,

\[ j(v) = \int_{-\infty}^{+\infty} K(\tau) e^{2\pi iv\tau} d\tau \]

Equation 2.29
For simplification, we assumed our decay function of the autocorrelation is exponential. It was first used by Debye for understanding of the dielectric spectroscopy of small molecule\textsuperscript{12}. Therefore, the equation 2.30 is known as Debye autocorrelation function.

\[ K(\tau) = \langle F(t)F^*(t) \rangle_{avg} e^{-\frac{t}{\tau_c}} \]

\text{Equation 2.30}

By integrating equation 2.30 we can get,

\[ J(v) = \langle F(t)F^*(t) \rangle_{avg} 2\tau_c(1 + 4\pi^2 v^2 \tau_c^2)^{-1} \]

\text{Equation 2.31}

For the simple liquid, such as H\textsubscript{2}O, we can correlate the motion of water molecule to T\textsubscript{1} and T\textsubscript{2} relaxation time. By only taking the tumbling motion of two protons of a H\textsubscript{2}O molecule into the consideration, we can say that the vector connecting the two protons varies randomly\textsuperscript{12}. The distance between two protons in the same molecule is \( b \). So, we can write the positional coordinate in terms of \( r_{ij} = b \) (which is constant) and \( \theta_{ij} = \theta \) (which is vary with the time)\textsuperscript{12}.

\[ F_{0j} = \left(1 - 3\cos^2\theta_{ij}\right)/b^3 \]

\[ F_{1j} = \sin\theta_{ij}(t) \cos\theta_{ij}(t) e^{i\phi_{ij}(t)}/b^3 \]

\[ F_{2j} = \sin^2\theta_{ij}(t) e^{2i\phi_{ij}(t)}/b^3 \]

\text{Equation 2.32}

The statistical average over the spatial coordinate are following for the water\textsuperscript{12},
\[
\langle F_0(t)F_0^*(t) \rangle_{avg} = \frac{4}{5} b^6
\]

\[
\langle F_1(t)F_1^*(t) \rangle_{avg} = \frac{2}{15} b^6
\]

\[
\langle F_2(t)F_2^*(t) \rangle_{avg} = \frac{8}{15} b^6
\]

Equation 2.33

By substituting equation 2.33 in T_1 equation 2.26, we can derive the BPP equation for the water tumbling motion and the spin lattice relaxation time. Which is the equation 2.19.

\[
\frac{1}{T_1} = \frac{3}{10} \frac{\gamma^4 h^2 \tau_c}{r^6} \left[ \frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{2\tau_c}{1 + 4 \omega^2 \tau_c^2} \right]
\]

The contribution from the translation motion is not included in the above equation. If we considered the translation motion than the above equation is written as,

\[
\frac{1}{T_1} = C_1 \frac{\tau_c}{1 + \omega^2 \tau_c^2} + C_2 \frac{2\tau_c}{1 + 4 \omega^2 \tau_c^2}
\]

Equation 2.34

\(C_1\) and \(C_2\) dependent on the static parameter

The spin-spin relaxation time is adiabatic and related to the transition in which energy does required, \(J_o(v)\) which are related to the terms A and B. Its relationship with \(T_2\) will be \(^{12}\)

\[
\frac{1}{T_2^2} = \frac{3}{2} \gamma^4 h^2 I(I + 1) \int_0^{\alpha/T_2} J_0(v) \, dv
\]

Which integrates to
\[
\left( \frac{1}{T_2} \right)^2 = \left( \frac{1}{T_0^2} \right)_{rigid} \left( \frac{2}{\pi} \right) \tan^{-1} \left( \frac{2 \pi \alpha \tau_c}{T_2} \right) 
\]

Equation 2.35

Due to single relaxation in the equations 2.34 and 2.35, they are not applicable to describe the relationship between the molecular motion and \( T_1 \) (or \( T_2 \)) in the complex structure such as polymer. Polymer material has various type of molecular motions with widely different rates. Some of the motions are tumbling of the chain, translation motion of the large portion of the chain and the localized segmental motion such as gauche-trans isomerization, ring flipping and methyl group rotation \(^{14,15,24}\). Therefore, multiple correlation time is required to describe the whole range of motion \(^{15,19,21,25-29}\). The distribution of correlation time function such as Gaussian, Fuss Kirkwood, Cole-Cole are used in the dielectric spectroscopy for explaining motion in polymeric material \(^{15,21,25,30}\). The detailed theory of the relationship between \( T_1 \) and in the cooperative motion system such as polymer is described in chapter 3.

2.5 Why using \( T_1 \) for crosslinking measurement
Figure 2.1  \( T_1 \) and \( T_2 \) relaxation time with molecular relaxation time

\( T_1 \) is the time required for the nuclear spin system to transfer energy into the thermal motions of the molecules\(^{12,31}\). \( T_2 \) is the characteristic time for the nuclear spin to transfer its nuclear energy to other nuclear\(^{31}\). In Figure 2.1, the theoretical prediction of the \( T_1 \) and \( T_2 \) with the relaxation time of the molecule is illustrated. These theoretical predictions are done using equation 2.34 and 2.35. In the case of \( T_1 \), we can see the minima with the correlation frequency close to the nuclear resonance frequency. In the case of our LFNMR the value of correlation resonance frequency is 31.5 MHz (\( \omega \tau_c @ T_1 \text{minima} = 0.616 \) & \( \nu_c = \frac{1}{2\pi \tau_c @ T_1 \text{minima}} \)) and NMR resonance frequency is 20 MHz. The molecule relaxing faster or slower than the correlation resonance frequency takes longer time for the transfer of the spin energy to the lattice in the form of heat\(^ {31}\). In the case of \( T_2 \), it decreases by cooling down the system and at lower temperature it attains a constant value. Therefore, for characterization of the rigid system such as highly
crosslinked thermoset which has the glass transition temperature way more than the room temperature are better characterized by the spin lattice relaxation then the spin-spin relaxation time.

In the rigid lattice (T_2 \ll T_1) there is negligible motion of the spin system, so the spin energy will stay in the system for a long time^{12,31}. In this system, the spin will interact with the other spins by terms A and B of the equation 2.21. The term B is related to the spin flip-flop with the neighboring spin. Although, this is an adiabatic transition but it will transfer the spin energy from one region to other. By doing this it will go to the system with the paramagnetic impurity or at the lattice imperfections or the segment with higher mobility. All of these regions will have short T_1 value. At this region, spin energy will be converted to the thermal energy due to the motion of the spin close to resonance correlation frequency. Therefore, paramagnetic impurity or the highly mobile region of the sample act as a thermal sink and phenomenon is known as the spin diffusion^{12,31}.

Because of the spin diffusion phenomena using T_1 relaxation it is possible to measure the small tumbling motion in the rigid system. In the case of crosslinked thermoset system which is very rigid material, some perturbations even come from the chain ends or the dangling end. These perturbations will decrease as we increase the crosslinking. So, it is possible to correlate the amount of crosslinking and the T_1 relaxation for the rigid thermoset system.

Also explained in the section 2.2 of this chapter is that in the case of rigid system, \( \Delta \omega \approx \delta \omega^{16} \). Therefore, equation 2.10 is only valid for \( \delta \omega \tau \leq 1^{16} \). This shows that at the lower temperature nothing occurs to line width unless \( \tau \) reduces to \( \delta \omega \tau \leq 1^{16} \). Hence, we can see the constant value of T_2 in the rigid system in Figure 2.1. Therefore, the line narrowing is not a good
method for the characterization of the rigid crosslinked system which has very high glass transition temperature. In this study, the characterization of the rigid crosslinking is done using spin lattice relaxation time.

The $T_2$ measurement in rigid sample done by using line width (free induction decay) and magic angle echo $^{32,33}$. The method such as Hanh spin echo and CPMG are not good for a very rigid system such as epoxy or the phenolic $^{34}$. The line width always has the contribution from the transversal relaxation time $T_2$ and the magnetic inhomogeneity coming from the external magnet. Due to the weak magnetic field and its strong inhomogeneity in LFNMR, it is not an accurate method for measuring $T_2$ relaxation time using simple free induction decay method (FID) in the rigid sample $^{8,10}$. Also, the receiver dead time of the instrument is close to 10 μs which is close to the $T_2$ of rigid systems, therefore the measurement of $T_2$ close to this dead time is not possible using simple FID method. Consequently, some researchers use more sophisticated pulse programming method for the measurement of $T_2$ but due to lack of resources, this research will focus on $T_1$ measurement.

In the case of LF NMR, the resonance occurs at the lower frequency than the high field NMR. So, it will be more sensitive toward the long-range motion of the rigid crosslinked thermoset than the high field NMR experiment. The measurement of $T_1$ done using the inverse recovery method and the receiver dead time does not have effect on the measurement. Also, the $T_2$ measurement does not depend on the frequency of the NMR. Hence, there is no advantage with the lower Larmor frequency. Therefore, the LFNMR and $T_1$ is better for the characterization in this study. First, the validation study is done on the simple epoxy system using $T_1$ and amount of crosslinking. Further, this knowledge was used for the measurement of the crosslinking in the phenolic system. The validation study and the detailed understanding of how $T_1$ and $T_2$ related to
molecular mobility in the crosslinked system is describe in the chapter 3. The crosslinking characterization of the phenolic using LFNMR is done in chapter 5.

2.6 References

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CHAPTER 3

CROSSLINKING VALIDATION STUDY

3.1 Chapter overview

This low field NMR study established the correlation between the degree of crosslinking in the rigid epoxy model system to the proton spin lattice relaxation time (T₁) measured. Our data have shown that as the number of crosslinks increases the T₁ minima shift toward higher temperatures. In addition, the magnitude of the T₁ minimum is also observed to shift to higher values or slower decay. These trends are consistent with the predictions of the Bloembergen, Purcell and Pound analysis. In these highly crosslinked systems, it was necessary to incorporate the Fuoss Kirkwood distribution function for describing the coupled dynamics of the individual monomer units of each crosslink. By fitting the spin lattice relaxation data at different temperatures to the Fuoss Kirkwood modified BPP theory, the average activation energy for the molecular motion and the breadth of the relaxation spectrum were obtained. For these model crosslinked epoxy systems, the increase in the activation energy to achieve mobility and the broadening of relaxation distribution has been determined quantitatively. The results of this study provide the foundation for using T₁ to analyze the crosslinking process of various polymeric systems.

3.2 Epoxy system for validation

In chapters 5, 6 and 7, we have used LFNMR spin-lattice relaxometry (T₁) to characterize the amount and type of crosslinks in a highly crosslinked phenolic resin ¹,². However, due to complex curing reaction, it is difficult to use phenolic system for the crosslinking validating
method. Therefore, using simpler thermoset system such as epoxy, the more quantititate study of the crosslinking and the $T_1$ relaxation time is illustrated.

One of the principal advantages of using this rigid model epoxy system is the ability to “tune” the network architecture by varying the crosslinked density or by changing the stiffness of the chemical bonds. In order to analyze the segmental dynamics, crosslinks of polypropylene glycol diamine of different lengths were used in the model epoxy system. The average length between crosslinked junctions of varies from 2.4 to 33 monomer units for the three samples studied. This type of epoxy can be fully cured and are stable even at elevated temperatures when our experiments are conducted.

As the crosslinking proceeds the concentration of the free ends of the epoxy resin and the Jeff amine harder decreases. This will reduce the conformational entropy of the crosslinked system and enhances stiffness of the crosslinked system. The segmental motion in the stiff polymeric system is coupled and the size of the coupled domain increasing with the stiffness or in our system the amount of crosslinking. By characterizing the magnetic energy loss spectrum using the modified BPP theory, the activation energy and the Fuoss Kirkwood width parameter are estimated. Using these parameters, qualitative understanding of the amount of coupled motion with crosslinking is carried out. This gives idea about the kinds of motion, LFNMR and $T_1$ relaxation time measured in the rigid crosslinked epoxy system.

### 3.3 BPP theory for polymeric system

In BPP theory, the different possible interactions among the pair of spins are calculated. In the case of spin lattice relaxation, spin interactions which produce the single or double transitions in a pair of spin are taken. For spin-spin relaxation, spin interactions are coming from the non-adiabatic transitions are taken. In the case of proton, the interaction is highly
depending on the distance and angle between the protons. This distances and the angle change by
the thermal motion of the molecules. The BPP theory correlate the thermal motion (Debye kinds
of relaxation) of the molecule with the spin interactions. The detailed theoretical description
of the BPP theory is shown in the chapter 2. The following is equation they derive for the spin
energy transfer rate \(1/T_1\)

\[
\frac{1}{T_1} = \frac{3}{10} \frac{\gamma^4 h^2}{r^6} \left[ \frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{4\tau_c}{1 + 4 \omega^2 \tau_c^2} \right]
\]

Equation 3.1

Due to complex motion of the polymeric system, it is difficult to predict how the proton-
proton distance vector and its angle to the external magnetic field changes with the temperature.
Also, in the polymeric system the different protons are connected with each other to a covalent
bond. The motion of the protons is not independent but corelated with each other.

This kind of coupled motion in the macromolecule we cannot describe with a single
relaxation time. Also, the correlation function is not the exponential decay like Debye function
but it will be non-exponential and the decay is slower than the small molecule correlation time.
Therefore, in the case of polymer it is often describe in terms of a distribution function with the
width parameter which is describe by brooding of the decay \(^{8-15}\). In this study, Fouss Kirkwood
symmetric distribution function which has been used in understanding of polymeric motion using
dielectric spectroscopy is used \(^{10,16}\).The Fouss Kirkwood distribution function is

\[
F(s) = \frac{\beta}{\pi} \frac{\cos \left( \frac{\beta \pi}{2} \right) \cosh(\beta s)}{\cos^2 \left( \frac{\beta \pi}{2} \right) + \sinh^2(\beta s)}
\]

Equation 3.2
In the above equation, \( s = \ln \left( \frac{t}{\tau_c} \right) \), \( \beta \) describes the width parameter and the \( \tau_c \) characteristic relaxation time or the dominant relaxation time of the distribution spectrum. BPP modified equation for the polymeric system was taken from the paper by Miyaka. He derives this equation 3.3 for the system with the proton or the spins located uniformly in the polymeric system.

\[
\frac{1}{T_1} = \text{constant} \left\{ \int_0^\infty \frac{\omega t F(t)dt}{1 + (\omega t)^2} + \int_0^\infty \frac{4\omega t F(t)dt}{1 + 4(\omega t)^2} \right\}
\]

Equation 3.3

By inserting the couple motion distribution function (equation 3.2) in to equation 3.3, we can get the modified BPP equation for the polymeric system. The \( T_1 \) relaxation time for the couple motion is,

\[
\frac{1}{T_1} = A \left( \frac{\beta}{\omega} \right) \left[ \frac{(\omega \tau_c)^\beta}{1 + (\omega \tau_c)^{2\beta}} + \frac{(2\omega \tau_c)^\beta}{1 + (2\omega \tau_c)^{2\beta}} \right]
\]

Equation 3.4

By assuming the Arrhenius behavior of the relaxation time,

\[
\tau_c = \tau_0 \exp \left( \frac{E}{RT} \right)
\]

Equation 3.5

In the equation 3.5, \( \tau_0 \) is the relaxation time at infinite temperature, \( E \) is the activation energy for the molecular relaxation, \( R \) is the universal gas constant and the \( T \) is the temperature.
By inserting equation 3.6 into the equation 3.5 we can get the following equation which we have used for the fitting of $T_1$ and $T$.

$$
\frac{1}{T_1} = A \left( \frac{\beta}{\omega} \right) \left[ \frac{\left( \omega \tau_0 \exp\left( \frac{E}{RT} \right) \right)^\beta}{1 + \left( \omega \tau_0 \exp\left( \frac{E}{RT} \right) \right)^{2\beta} + \left( 2\omega \tau_0 \exp\left( \frac{E}{RT} \right) \right)^{2\beta}} \right]
$$

Equation 3.6

3.4 Experimentation

3.4.1 Materials

Aromatic epoxy resin Bisphenol A diglycidyl ether (DGBA) with equivalent weight of epoxy approximately 178 geq-1 was purchased from the Dow Chemical. The different length polyether amine hardeners, Jeffamine D-230 ($M_w = 230$, amine equivalent = 59 g eq$^{-1}$), Jeffamine D-400 ($M_w = 400$, amine equivalent = 107 g eq$^{-1}$), and Jeffamine D-2000 ($M_w = 2056$, amine equivalent = 514 g eq$^{-1}$), were purchased from Huntsman. The structure of amine and epoxy are shown in the Figure 3.1. The equivalent weight and the appropriate length of hardener is taken from the Huntsman catalog$^4$.

![Epoxy resin DGEBA](image1)

![Jeffamine D-230](image2)

<table>
<thead>
<tr>
<th>Hardener</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jeffamine D-230</td>
<td>$n \sim 2.4$</td>
</tr>
<tr>
<td>Jeffamine D-400</td>
<td>$n \sim 6$</td>
</tr>
<tr>
<td>Jeffamine D-2000</td>
<td>$n \sim 33$</td>
</tr>
</tbody>
</table>
3.4.2 Sample preparation

0.5 gm of epoxy resin transfer in a 20 mL vial then mixed with an equivalent amount of Jeffamine hardener. The mixture was mixed for 10 minute at ~ 40 °C then transferred into the 1 cm diameter NMR tube which was then put in to the oven at 160 °C for 90 min. This sample was used for the NMR and DSC measurements.

3.4.3 Differential scanning calorimetry

Approximately 5 mg of cured sample was sealed in aluminum hermetic pans for DSC measurements. A TA instrument Q100 was used. The DSC was calibrated using sapphire and indium. For measuring the glass transition temperature, the sample was first heated to 220 °C then cooled down to − 50 °C and again heated to 220 °C. The heating rate was maintained at 5°C/min. T_g was measured in the second heating.

The thermograms are shown in Fig. 2. The glass temperatures of the 3 samples increase as the molecular weight between two crosslinked junctions decreases. The highest T_g was found in D230; the lowest T_g found in D2000. These T_g values agree with the ones found for 100% crosslinked samples. \(^3,^4\)
3.4.4 Low field NMR

Bruker MQ20 low field NMR was used for measuring the $T_1$, spin lattice relaxation time. Approximately, 300-400 mg of sample is taken in NMR tube with the diameter 1 cm and the length 20 cm. The $T_1$ relaxation time was measured using the traditional inverse pulse sequence method (180-$t_1$-90) with more than 20 data points and 4 scans for each set of data points. The recycle time was $> 5$ to $6$ times $T_1$ value of the sample. The instrument was calibrated daily. The collected data points were fitted with one exponential $T_1$ relaxation curve (equation 3.7) using the software provided by Bruker. For different temperature measurements, the sample was equilibrated for at least 5 minutes before the $T_1$ measurement and repeated twice.

$$M_z = M_0(1 - 2e^{-\frac{t_1}{T_1}})$$

Equation 3.7
3.5 Crosslinking and $T_1$ of epoxy system

The $T_1$ measured for the three crosslinked samples are shown in Figure 3.3. Each plot as function of temperature exhibits a minimum. The decrease in $T_1$ at low temperatures for D230 and D400 samples suggest there are other localized transitions taking place. The lower temperature transitions may be assigned to the rotation of methyl groups $^{13}$ of the epoxy resin and the polypropylene of the hardener. This type of parabola shaped plot is expected since at low temperatures (low segmental mobility) the relaxation is inefficient. $^{18}$ This is also true at elevated temperatures (high segmental mobility), the relaxation also cannot take place efficiently because fewer segments are moving at the RF field frequency (~20 MHz). Clearly the shape at the minimum and the magnitude of $T_1$ are dependent on the crosslinking density. The highly crosslinked epoxy such as D230 has the $T_1$ minimum at ~160 $^\circ$C. The lower crosslinked sample such as D2000 occurs at 50 $^\circ$C. The magnitude of the $T_1$ minimum decreases from 65 to 37 ms as

Figure 3.3 Spin lattice relaxation time for different crosslinked epoxy

The $T_1$ measured for the three crosslinked samples are shown in Figure 3.3. Each plot as function of temperature exhibits a minimum. The decrease in $T_1$ at low temperatures for D230 and D400 samples suggest there are other localized transitions taking place. The lower temperature transitions may be assigned to the rotation of methyl groups $^{13}$ of the epoxy resin and the polypropylene of the hardener. This type of parabola shaped plot is expected since at low temperatures (low segmental mobility) the relaxation is inefficient. $^{18}$ This is also true at elevated temperatures (high segmental mobility), the relaxation also cannot take place efficiently because fewer segments are moving at the RF field frequency (~20 MHz). Clearly the shape at the minimum and the magnitude of $T_1$ are dependent on the crosslinking density. The highly crosslinked epoxy such as D230 has the $T_1$ minimum at ~160 $^\circ$C. The lower crosslinked sample such as D2000 occurs at 50 $^\circ$C. The magnitude of the $T_1$ minimum decreases from 65 to 37 ms as

52
the propylene oxide crosslink increase from the 2.4 to 33. The lesser crosslinked chains are able to transfer energy to the surrounding more efficiently than the rigid ones.

The spin lattice relaxation time measured at different temperature is fitted in equation 3.6 using MatLab fitting tool software. In all the three-different epoxy systems the fitting is achieved with R² value more than 0.95. The fitting was done only in the high temperature T₁ minima transition. The fitted curve with the experimental data points are shown in the Figure 3.4. From the fitting the unknown parameters such as average activation energy E, Fuoss Kirkwood width parameter β, activation energy ΔE, τ₀ and A is calculated. The value of τ₀ was in the range of 10⁻¹⁷ s.

![Graph](image_url)

Figure 3.4 Spin lattice relaxation and the temperature fitted curves of crosslinked epoxy systems
Table 3.1  Activation energy and Fuoss-Kirkwood width parameters

<table>
<thead>
<tr>
<th>Crosslinker</th>
<th>Activation energy (E_a) (kcal/mole)</th>
<th>Fuoss-Kirkwood width parameter (β )</th>
</tr>
</thead>
<tbody>
<tr>
<td>D230</td>
<td>17.0</td>
<td>0.32</td>
</tr>
<tr>
<td>D400</td>
<td>14.1</td>
<td>0.53</td>
</tr>
<tr>
<td>D2000</td>
<td>11.5</td>
<td>0.80</td>
</tr>
</tbody>
</table>

These data agree with our expectations. In samples with a low degree of coupling with all monomers relax independently, the width parameter, β, approaches 1. As one can see, the least crosslinked sample, D2000 exhibits the largest β value. If the coupling is perfect, i.e. only one conformation exists, β should be 0 \(^{19}\). The rigid D230 has the lowest value. This will occur at temperatures well above the glass transition temperature of the polymeric system \(^{6,19}\).

It should also be noted that at any temperature there are segments of different sizes that may be correlated. The β parameter measured is then related to the most probable “domain” size of the monomeric segments. This domain size is also known as the “characteristic size “\(z_c\)\(^{19}\). In our study, we considered a β value that does not change with the temperature. Therefore, the value of β we report is only an average value. Our primary focus is to show how \(T_1\) measured in LFNMR can disclose changes in segmental dynamics as a function of crosslinking.

3.5.1 Molecular motion relaxation spectrum in crosslinked epoxy using \(T_1\)

In all the three crosslinked samples, the \(T_1\) minimum occurs at ~70 to 80 °C above the glass transition temperature measured in DSC. It is interesting to speculate whether the spin lattice relaxation in crosslinked systems can also attributed to the fundamental molecular motions...
which are responsible for the mechanical and the dielectric spectroscopy. Previous studies have indeed attributed the T$_1$ minimum to be correlated to the glass transition. Due to the high probe frequency of the LFNMR and completely different physical mechanism for relaxation, it is impossible to correlate our measurements to alpha, beta and gamma transitions measured using other techniques of polymeric motions.

The activation energies measured (Table 1) for these epoxy systems are lower than the energy measured near the glass transition temperatures. In those studies the activation energy falls in the range 50 to 100 Kcal/mole. The differences are not unexpected since glass transition may involve far more restricted motions than our model systems. Our crosslinked epoxy consist of diphenylpropane units, hydroxy ether groups and the different lengths of Jeffamine based polypropylene glycol. Therefore, rotation about the pheynyl ring, rotation of methyl groups, trans - gauche transformation of the hydroxy ether unit connected to phenyl ring and propylene glycol units of the Jeffamine hardener can all take place. Out of all of these motions, rotation of methyl groups requires only an activation energy of ~2 kcal/mol or lower. The low activation energy and extremely rapid nature of this motion makes it an unlikely candidate for extensive correlation. Therefore, it does not contribute in the measured motion of the T$_1$ minima (high temperature one) described in this study.

The other motions such as the trans-gauche isomerization in the propylene glycol units of Jeffamine and the hydroxy ether connected to ring motion and the motion of the ring requires the activation energy to be in the range of 9-14 kcal/mol. The trans-gauche isomerization which is responsible for the rotation of the segment of the polypropylene glycol has a lower activation energy than the other two motions described above. The crosslinking causes all these motions to be coupled. This is shown in terms of the reduction of $\beta$ in Table 1. Our LFNMR data have
shown that spin lattice relaxation can be highly coupled as the crosslinking increasing. Therefore, it is possible to conclude that the spin lattice relaxation time is related to the amount of crosslinking. This study validates the use of LFNMR $T_1$ for measuring crosslinking in polymeric systems.

3.6 Conclusions

In this study, the degree of crosslinking in rigid epoxy systems has been demonstrated to be strongly correlated to the LFNMR spin lattice relaxation time $T_1$. As crosslinking increases, the $T_1$ minimum occurs at a higher temperature and the length of $T_1$ also increases. Due to complexity of coupled motions in polymeric systems, the segmental dynamics responsible for $T_1$ can only be explained in terms of the Fuoss Kirkwood distribution function. By fitting the spin lattice relaxation data at different temperatures using the modified Bloembergen, Purcell, and Pound theory, activation energy and width parameter have been calculated. As the crosslinking increases the activated energy increases. At the same time, as expected, the Fuoss Kirkwood width parameter decreases. The activation energy values obtained are associated with segmental dynamics. The lower values obtained are associated with looser chains. But the exact nature of these motions are unclear at this time. The width parameter obtained can also be correlated to the coupling of the spins along the chain. Even with these uncertainties, it is clear that $T_1$ relaxation can be used to monitor the crosslinking process that we observed empirically in other rigid crosslinked systems.

3.7 References


CHAPTER 4

DISPERSION OF REACTANTS USING PLASTICIZER


4.1 Chapter overview

A uniform dispersion of reactants is necessary to achieve a complete reaction involving multi-components. In this study, we have examined reaction of two rigid reactants: a highly crystalline crosslinking agent hexamethylenetetramine (HMTA) ($T_m \approx 280 \, ^\circ C$) and a strongly hydrogen bonded phenol formaldehyde resin. The efficiency of the curing reaction and the crosslinked structures is strongly dependent on the miscibility of these two reactants achieved by adding third component we called as plasticizer. Therefore, in this chapter, using NMR and infrared spectroscopy, the investigation of the role of specific intermolecular interactions necessary for the plasticizer to dissolve the highly crystalline HMTA and to plasticize the phenol formaldehyde resin are explained. The presence of the plasticizer increased the segmental mobility, disrupted the hydrogen bonded matrix, and freed the hydroxyl units, which further increased the solubility of the HMTA. The higher solubility of HMTA in the presence of plasticizer increases the amount of crosslinking. The detailed characterization of crosslinking reaction is in the presence of plasticizer is described in the chapter 5.
4.2 Crosslinker hexamethylenetetramine

HMTA has been known for over 140 years and it was the first organic compound studied by X-ray crystallography \(^1\). It is widely used in chemical industry\(^2\), medicine\(^3\), explosive industry\(^5\) and astrochemistry\(^6\),\(^7\). Its great interest in various fields is due to the rigid cage like structure of its molecule, which belongs to the point group of symmetry T\(_d\) in the solid as well as in gas phase \(^7\),\(^8\). The high symmetry of the highly crystalline structure has a melting point temperature around 280 °C and resultant zero dipole. The symmetric structure of HMTA molecule is shown in the following Figure 4.1.

![Symmetric structure of hexamethylenetetramine](image)

In the T\(_d\) symmetric condition, there are 60 intramolecular normal vibrations which are represented as 4A\(_{1}\)+ A\(_{2}\)+5E+6F\(_{1}\)+9F\(_{2}\)\(^8\). In the gas phase and in the solid under zero wave vector approximation 4A\(_{1}\)+5E+9F\(_{2}\) modes are Raman active and the 9 F\(_{2}\) modes are infrared active\(^8\)-\(^10\). In Figure 4.2, the infrared spectra and in the table 4.1 its corresponding vibrational signatures of HMTA are shown.
Figure 4.2  Infrared spectrum of hexamethylenetetramine crystal

Table 4.1  Selected infrared peaks of hexamethylenetetramine and their assignment

<table>
<thead>
<tr>
<th>Observed infrared peak</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2950</td>
<td>Asym CH$_2$ stretch</td>
</tr>
<tr>
<td>2873</td>
<td>Sym CH$_2$ stretch</td>
</tr>
<tr>
<td>1458</td>
<td>CH$_2$ deformation</td>
</tr>
<tr>
<td>1370</td>
<td>CH$_2$ wagging</td>
</tr>
<tr>
<td>1235</td>
<td>CN stretch</td>
</tr>
<tr>
<td>1005</td>
<td>CN stretch</td>
</tr>
<tr>
<td>812</td>
<td>CH$_2$ rocking</td>
</tr>
<tr>
<td>671</td>
<td>CNC deformation</td>
</tr>
</tbody>
</table>

4.3  Characterization of phenolic prepolymer

In this study, phenolic prepolymer is used which is usually synthesized in acidic condition with the lower formaldehyde compared to phenol monomer.
4.3.1 Molecular weight of prepolymer

The molecular weight of the phenolic prepolymer is measured using GPC and HNMR method. The NMR spectra were acquired using Bruker 400 MHz NMR with acetone-d6 as a solvent. The HNMR spectrum is shown in the following Figure 4.3.

![HNMR spectrum](image)

Figure 4.3  HNMR of phenolic prepolymer in acetone-d6

The aliphatic hydrogen comes from the methylene linkages which are around 3.8 ppm. The aromatic hydrogen HNMR signature mostly originates from the phenolic ring hydrogens. They are at approximately 7.0 ppm. From the equation 4.1 mention by Dargaville\textsuperscript{11}, we can estimate the molecular weight of the phenolic system. The calculation suggests that phenolic prepolymer has approximately 8 monomeric units per chain.

\[
\frac{[CH_2]}{[Ar-H]} = \frac{2n-2}{3n+2}
\]

Equation 4.1
We have also measured the molecular weight of phenolic prepolymer using GPC with the polystyrene as standard and THF as solvent. The GPC molecular weight $M_n$ is 1117 gm/mol and PDI is 2.5. The GPC is shown in Figure 4.4. Due to complexity of structure coming from the many isomeric forms, it is difficult to give definitive answer about the molecular weight using GPC.

![Figure 4.4  GPC of phenolic prepolymer](image)

4.3.2 Configuration of prepolymer

The C-NMR of phenolic prepolymer is done in 1:1 volume ratio of CD$_3$OD: to CD$_2$Cl$_2$ solvent. For C-NMR, 400 MHz was used and 1024 scans were taken. The spectra are shown in the Figure 4.5 and Figure 4.6. Figure 4.5 suggests that prepolymer has o-o:o-p:p-p linkages ratio is 1:2:1. This shows that phenolic prepolymer is random in nature. Figure 4.6 shows that our prepolymer unreacted o to unreacted p sites ratio is 6:1. The predicted structure of this kind of random prepolymer is shown in the Figure 4.7. The % unreacted sites of ortho and para site per prepolymer is approximately 53%. The CNMR signature for the phenolic resin is taken from the literature $^{12, 13}$. 

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Figure 4.5  C-NMR of methylene carbon of phenolic prepolymer

Figure 4.6  C-NMR of unreacted ortho (o) and para (p) sites of phenolic prepolymer
4.3.3 Molecular forces in prepolymer

The flow activation energy of the phenolic prepolymer is high even at high temperature $^{14}$. This suggests high friction coefficient for the chain sliding motion. This high sliding resistance is due to the three main kinds of the molecular forces: 1. internal hydrogen bonding between hydroxyls, 2. hydrogen bonding between hydroxyls and phenolic ring, and 3. phenolic delocalized ring-ring interactions $^{14-16}$. Out of these three, hydrogen bonding interaction will be the dominant one. Therefore, the glass transition temperature of prepolymer with approximately 8 monomeric units is approximately 67 °C which is shown in chapter 5. Megson bond angle and molecular dimension calculation show that due to steric hindrance two phenolic rings cannot lie in one plane $^{17}$. This will make the structure of phenolic highly asymmetric with lots of kinks. At higher temperature, the phenolic backbone strain energy will be reduced and the two-reactive sites can easily come close to each other $^{17}$. These discussions prove that phenolic resin is a rigid system.
The infrared spectrum of phenolic prepolymer is shown in the Figure 4.8. This shows the broad hydrogen bonding peak at 3280 cm\(^{-1}\). In table 4.2 the assignment of the selected infrared signature\(^\text{18,19}\) is tabulated.

![Infrared spectrum of phenolic prepolymer](image)

**Figure 4.8** Infrared spectrum of phenolic prepolymer

**Table 4.2** Selected infrared peaks of phenolic prepolymer and their assignments

<table>
<thead>
<tr>
<th>Observed infrared peak (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3280</td>
<td>-O-H stretching</td>
</tr>
<tr>
<td>3115</td>
<td>Aromatic C-H stretching</td>
</tr>
<tr>
<td>2905</td>
<td>Aliphatic asymmetric CH(_2) stretching</td>
</tr>
<tr>
<td>2835</td>
<td>Aliphatic symmetric CH(_2) stretching</td>
</tr>
<tr>
<td>1609</td>
<td>Quadrant ring stretch</td>
</tr>
<tr>
<td>1594</td>
<td>Quadrant ring stretch</td>
</tr>
<tr>
<td>1510</td>
<td>Semicircle ring stretch</td>
</tr>
<tr>
<td>1478</td>
<td>Semicircle ring stretch</td>
</tr>
<tr>
<td>1434</td>
<td>Aliphatic CH, scissor bending</td>
</tr>
<tr>
<td>1360</td>
<td>Phenolic OH in-plane deformation</td>
</tr>
<tr>
<td>1209</td>
<td>Alkyl-phenol C-O stretch</td>
</tr>
<tr>
<td>1170</td>
<td>Alkyl-phenol C-O stretch</td>
</tr>
<tr>
<td>1098</td>
<td>Aromatic CH in-plane deformation (1,2,4)</td>
</tr>
<tr>
<td>814</td>
<td>Out-of-plane ring deformation (1,2,4)</td>
</tr>
<tr>
<td>754</td>
<td>Out-of-plane ring deformation (1,2,6)</td>
</tr>
<tr>
<td>692</td>
<td>Free phenol</td>
</tr>
</tbody>
</table>
4.4 Experimental

4.4.1 Materials

Phenolic prepolymer, furfural and HMTA have been supplied by Durex Corporation. The amount of water is 1.83 %w/w by weight determined using H-NMR. Duroquinone and 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) were purchased from Sigma Aldrich. They were used as internal standards in NMR measurements\textsuperscript{20,21}.

4.4.2 Infrared spectroscopy

A Perkin Elmer Spectrum 100 with an ATR assembly was also used. Solid or liquid samples can be measured using the ATR technique. In each case, 32 scans were signal-averaged for analysis.

4.4.3 NMR spectroscopy

A Bruker 400MHz instrument has been used for all NMR measurements. The solubility of the crosslinking agent HMTA in plasticizer and the mixture of plasticizer and prepolymer are measured by using duroquinone as the internal standard. There are two main reasons for choosing duroquinone as the internal standard. First, duroquinone is highly soluble in the most of the plasticizers used in this study. Second, resonances assigned to duroquinone do not overlap with most of the plasticizer, HMTA or the prepolymer. DSS (4,4-dimethyl-4-silapentane-1-sulfonic acid) is a chemical compound used in proton- and carbon-related NMR spectroscopy as a calibration standard, like tetramethylsilane (TMS), but with much higher water solubility.

In a 20 mL glass vial containing 4.8 mL of plasticizer or D\textsubscript{2}O, 0.2 mL of concentrated (20 mg/mL) internal standard (duroquinone or DSS) solution will be added. In this 5 mL of sample, a
different amount of powder foam of HMTA or prepolymer or both will be added and then the mixture will be stirred using a magnetic stir bar for 12 hrs at room temperature. Each sample will be filtered with 0.45 um Teflon filter and then studied by NMR.

To validate this NMR technique, we have measured the solubility of HMTA in water. The H-NMR spectra obtained for different concentrations of hexa in the 99.8% pure D₂O with the DSS (4,4-dimethyl-4-silapentane-1-sulfonic acid) as the internal standard. The obtained solubility from HNMR is 5.58 moles/liter, which is nearly identical to the 5.57 moles/liter reported previously using a scattering technique. The HNMR spectra of HMTA in D₂O is shown in Figure 4.9 and the resultant solubility from the calculation of HMTA peak is shown in Figure 4.10.

Figure 4.9  H-NMR of hexamethylenetetramine (HMTA) in D₂O
4.5 Solubility of reactants in plasticizer

4.5.1 Solubility of hexamethylenetetramine

During the curing reaction, the prepolymer can only react with molecular HMTA. The fact that the thermal transitions observed for the same molar ratio of HMTA to the phenolic resin were dependent on the plasticizer furfural content suggests the dispersion is incomplete which is shown in chapter 5. It is then crucial to determine the state of each reacting component with or without furfural. HMTA is a very crystalline material (>99% crystalline) and its melting point is 280 °C. Therefore, it is reasonable to assume that during the curing reaction of the prepolymer the first step is the dissolution of the HMTA $^{21-27}$. The curing reaction rate and the percentage of curing will be related to the available molecular HMTA in the reaction mixture. There are several techniques that can be used to measure the solubility of HMTA in various solubilizing liquids.
We have used the NMR method to assess the solubility of HMTA in furfural plasticizer. The advantage of using duroquinone as the internal standard is its high solubility in furfural because all its hydrogens are equivalent to one prominent resonance at 2 ppm. The H-NMR data with duroquinone as the internal standard are shown in Figure 4.11. Typically, two resonances are observed with a strong peak at \( \sim 5.0 \) ppm (4.9–5.1 ppm) and a weak peak at \( \sim 5.6 \) ppm (5.2–5.8 ppm). The HMTA is a symmetric molecule and all its methylene units are equivalent. As the HMTA concentration increases, the strong peak shifts up field with the weak shifting downward. Since the weak resonance is dependent on the plasticizer used, we have attributed it to furfural impurity that is capable of interacting with HMTA. As shown in Figure 4.12, the solubility of HMTA in furfural is quite limited as compared to water with a limiting value in furfural of only 0.14 mol/L. This surprising result suggests that furfural or other solubilizing liquids may not directly solubilize HMTA in the reactive mixture. Instead, a different physical basis involving furfural and the phenolic resin needs to be investigated.
Figure 4.11  H-NMR spectra of different concentration of hexamethylenetetramine (HMTA) in furfural (a) 0.07 mmol/L HMTA in furfural (b) 0.14 mmol/L HMTA in furfural (c) 0.25 mmol/L HMTA in furfural
Figure 4.12  Solubilized hexamethylenetetramine (HMTA) in furfural is plotted with the total HMTA content in furfural

4.5.2 Solubility of phenolic resin

Two resonances are associated with the methylene hydrogens in the phenolic resin (Figure 4.13) with the 4.1 ppm one being the weak one and another strong component at 3.9 ppm. These components have been assigned to the different configurations of the resin. Previous studies have assigned the lower resonance to be associated with p-p configuration and the higher one to the o-o or the o-p configuration\textsuperscript{28}. The width of these resonances, as expected, is dependent on the sample concentration or the relaxation times of the sample. Based on these NMR data, we have calculated the relative molar concentration of each configuration. It was revealed that the o to p ratio is statistical in distribution at 1:2:1 or random in distribution. The different configurations have different accessibility to the hydroxyl units causing different reactivity between the phenolic resin to the crosslinker, HMTA\textsuperscript{29}. 
Our GPC data was used to calculate the molecular weight ($M_n = 1117$; PDI = 2.5) of the phenolic resin. Therefore, the molar solubility calculated cannot be precise. Instead, we used the integrated intensities of the methylene peaks to the internal standard, duroquinone. This is shown in Figure 4.14. The solubility of prepolymer is surprisingly high in furfural. It is measured at higher than 60 % w/w. The peak at ~ 4.8 ppm is assigned to water. Using this peak, the amount of water in the prepolymer and furfural mixture can also be calculated to be 1.8 % w/w in the mixture. Undoubtedly, the introduction of the furfural increases the mobility of the phenolic chain segments, but the effects of water should also be considered. Previous studies have shown that the water content in the reactive mixture of phenolic prepolymer and HMTA increases the rate of curing reaction\textsuperscript{30,31}. Therefore, the determination of the water content is important to assess whether the dissolution of HMTA by water is one factor for the increase in the rate of curing reaction when the plasticizing liquid is introduced. As shown in Figure 4.9 the solubility of HMTA in water is 40 times of HMTA in furfural.
Figure 4.13  H-NMR spectra of different concentrated prepolymer in furfural (a) 50 mg/mL prepolymer in furfural (b) 200 mg/mL prepolymer in furfural (c) 400 mg/mL of prepolymer in furfural (d) 600 mg/mL of prepolymer in furfural
4.5.3 Solubility of HMTA in furfural and prepolymer mixture

Based on NMR data, the overall solubility of HMTA in the phenolic resin and furfural is shown in Figure 4.15. In this case, only one strong peak of HMTA at 4.91 ppm was observed. Because of the overlap between water resonance (4.78 ppm) and HMTA (4.81 ppm), the water contribution cannot be determined exactly. Therefore, the calculation of HMTA solubility is carried out by subtracting the expected water contribution (1.8 % w/w) as mentioned above. In this analysis, it was assumed that the amount of water in the highly crystalline HMTA is negligible, if any at all. After subtracting the water contribution, the solubility of HMTA is shown in Figure 4.16. In this case, the dissolved HMTA is plotted against the amount of prepolymer added into the mixture. The plot suggests that the prepolymer increases the solubility of HMTA considerably as compared to the furfural alone. By adding just 200 mg/mL.
prepolymer in the mixture almost all of the HMTA went into the solution. These observations provide a very interesting scenario for dissolving HMTA. The plasticizer does not need to dissolve the HMTA directly. Instead, by providing more mobility to the resin “releasing” the hydroxyl units, HMTA became extremely soluble thus achieving the dispersion at the molecular level needed for an efficient crosslinking reaction.

![H-NMR spectra of hexamethylenetetramine (HMTA) in the mixture of prepolymer and furfural](image)

Figure 4.15  H-NMR spectra of hexamethylenetetramine (HMTA) in the mixture of prepolymer and furfural (a) 50 mg/mL prepolymer in 0.5 mmol/L HMTA in furfural (b) 100 mg/mL prepolymer in 0.5 mmol/L HMTA in furfural (c) 200 mg/mL prepolymer in 0.5 mmol/L HMTA in furfural
Figure 4.16 Solubility of hexamethylenetetramine (HMTA) in the mixture of pre-polymer and furfural

4.6 Analysis of the molecular interaction between HMTA and the prepolymer

Obviously, based on the data presented above, the solubility of HMTA in either the furfural or in the mobilized prepolymer depends on the molecular environment. An analysis of the hydrogen bonded environment around HMTA is crucial in identifying the differences in the solubilization of HMTA and the eventual reactivity. The most likely intermolecular interaction has been attributed to the possibility of hydrogen bonding that can form between the 4 equivalent nitrogens of HMTA and electron accepting functional groups. For example, previous diffraction studies have shown the possibility of one HMTA can crystallize with phenols$^{32,33}$. The
corresponding $^{14}$N quadrupole resonance spectroscopy has generally been used to characterize the intermolecular interactions, including hydrogen bonds\textsuperscript{32}.

Since we are dealing with various solutions and the need to follow the crosslinking reaction, instead of using NMR, we have used infrared spectroscopy to characterize intermolecular interactions in the prepolymer and furfural. In order to follow the reaction, it is also easier to use infrared spectroscopy which has a high temporal and spatial resolution. However, because of the non-polar nature of HMTA, the change in dipole moment is small. Therefore, the intensity of infrared active bands is weak and difficult to assign. The HMTA in the mixture of prepolymer and furfural shows two different C-N stretching vibrations (Figure 4.17). The lower frequency vibration is at 1233 cm$^{-1}$ with a higher frequency component at 1239 cm$^{-1}$. The literature provides guidance for their assignments\textsuperscript{34}. As shown in Figure 4.17, the totally degenerate C-N stretching vibration for crystalline HMTA is observed at 1235 cm$^{-1}$. In this case, the C-N stretching vibration undoubtedly is also perturbed by various secondary forces. The isolated C-N stretching vibration can only be found for HMTA in the upper atmosphere and is located above 1240 cm$^{-1}$\textsuperscript{34}. Therefore, when hydrogen bonds form, it is expected that C-N stretching should shift downwards. Based on these previous assignments, we have assigned the 1239 cm$^{-1}$ component to be associated with isolated HMTA and the peak at 1233 cm$^{-1}$ to the hydrogen bonded C-N of the HMTA molecule. The shift downwards of C-N stretching should depend on both the strength and number of nitrogens participating in the hydrogen bonding scheme. By measuring the relative intensity of the two bands provides us with a methodology to characterize quantitatively the molar percentage of the hydrogen bonded HMTA in the solution of prepolymer and plasticizer. This is shown in Figure 4.18. Moreover, a limiting solubility value can also be characterized when a saturated state is reached. Other vibrations can also be used to
characterize the solubilized HMTA molecules. For example, we have observed similar
downward shifts for the 670 cm\(^{-1}\) band, which is a combination of the deformation of CNC angle
bending and the stretching of C-N stretching\(^8\). The soluble HMTA has this peak at 667 cm\(^{-1}\)
while the crystalline HMTA has this peak is at 671 cm\(^{-1}\).

Figure 4.17 Mid-IR spectra of –CN stretching peak of hexamethylenetetramine (HMTA) (a)
400 mg/mL of prepolymer in furfural (b) 0.5 mmol/L HMTA in the mixture of
400 mg/mL prepolymer in furfural (c) 1.25 mmol/L HMTA in the mixture of 400
mg/mL prepolymer in furfural (d) crystalline HMTA
Analysis of the solubility limit of HMTA in plasticized prepolymer

During the curing reaction of phenolic, the solubilization of HMTA occurs through the formation of the hydrogen bonding between the nitrogen atoms of HMTA and the hydroxyl units of the phenolic prepolymer. HMTA is a highly symmetric molecule with 4 equivalent nitrogen atoms and 6 equivalent methylene groups. Due to its symmetry, these 4 nitrogen atoms have the same capability to form hydrogen bonds with the hydroxyl units of prepolymer. However, due to steric hindrance not all of the possible hydrogen bonds can be formed at any particular time. In our case furfural indirectly increases the solubility of HMTA by increasing the number of free...
hydroxyl units of the phenolic prepolymer, which are responsible for the hydrogen bonding between the prepolymer and HMTA. Therefore, it is important to seek information regarding the coordination number (hydrogen bonds formed per HMTA molecules) in order to obtain a better understanding of the solvation process. In the curing reaction, the hydrogen bond formed between HMTA and the hydroxyl units of prepolymer weakens of the C-N bond of HMTA and its reaction with the phenolic prepolymer. It is our hypothesis that a highly coordinated HMTA with weakened C-N bonds will react at a lower temperature than less coordinated HMTA molecules. Therefore, in a perfectly dispersed mixture, HMTA molecules will exist in the form of high coordinated number, with the maximum being 4. This information will be useful in determining the quality of furfural or other plasticizers for an effective curing reaction. In Figure 4.19 the solubility of HMTA is plotted against the moles of hydroxyls of prepolymer available. In addition, the experimental solubility of HMTA is compared with the perfectly ideal (coordination number 4) plasticizing liquid. The solubility of HMTA in the perfectly ideal condition was calculated from the following equation. This is shown in Figure 4.19 as theoretical HMTA solubility.

\[
\text{Soluble HMTA} = \left( \frac{\text{moles of hydroxyls from phenolic prepolymer}}{4} \right) + \\
(\text{soluble moles of HMTA from plasticizing liquid}) + \\
(\text{soluble moles of HMTA from water})
\]

Equation 4.2

This expression takes into account that each HMTA has four equivalent sites to interact with the hydroxyl units of the prepolymer. It also incorporates contributions from furfural and water contained in the prepolymer of ~0.14 and 5.58 moles/liter, respectively. As shown in Figure 4.19, the experimental values clearly are lower than the calculated ones. This implies not
all the hydroxyl units are interacting with HMTA or solvating the crosslinker. This plot also
suggests that the solubility limit of HMTA in plasticized prepolymer is considerable.

Figure 4.19  Theoretical and experimental solubility of hexamethylenetetramine (HMTA) is
plotted against the number of hydroxyls units of prepolymer (a) theoretical
solubility limit of HMTA (b) experimental solubility limit of HMTA

The changing environment of the hydroxyl units in the presence of the plasticizer can
clearly be seen in the infrared spectra obtained. The –OH stretching vibrations of prepolymer has
3270 cm\(^{-1}\) and the prepolymer in furfural has 3346 cm\(^{-1}\) and these were shown in Figure 4.20.
The data obtained clearly show that prepolymer surrounded by the plasticizing liquid furfural has
a higher –OH stretching frequency or weaker hydrogen bonds as compared to the prepolymer
without any plasticizer. Generally speaking, the shift downward in this vibration has always been
assigned to the hydrogen bond formation. The higher –OH stretching frequency of prepolymer surrounded by the plasticizing liquid has more free hydroxyl units than the rigid neat prepolymer. The free hydroxyl groups can then dissolve HMTA as seen above.

Figure 4.20 -OH stretching peak of prepolymer and prepolymer in plasticizing liquid furfural (a) of rigid prepolymer (b) of prepolymer in furfural with prepolymer concentration of 200 mg/mL (c) of prepolymer in furfural with prepolymer concentration of 600 mg/mL

4.8 Conclusions

The crosslinking reaction between phenolic formaldehyde resin and HMTA has been studied previously. However, to our knowledge, the role of a plasticizer such as furfural in such reaction has never been characterized. Using an array of characterization techniques, we were
able to demonstrate the effectiveness of furfural. Surprisingly, the role of furfural in dissolving the highly crystalline HMTA does not seem to be necessary. The integrated intensity of NMR normalized to a new internal standard, duroquinone, we were able to deduce quantitatively the solubility of HMTA in furfural. The limiting value was found to be only 0.14 mole/liter, a small fraction of the amount of HMTA dissolved in water, which is 5.58 mole/liter. However, the role of furfural in the plasticization of the prepolymer is significant. Based on both infrared and NMR data, it was clear that HMTA is highly soluble in the plasticized prepolymer. By calibrating the infrared active C-N stretching vibration against an isolated HMTA molecule found in the upper atmosphere it was able to establish that hydrogen bonding may have formed between the HMTA and either furfural or free hydroxyl units due to the presence of furfural. In this study, we have deduced the molecular origin of the intermolecular interaction between HMTA, furfural and the prepolymer, thus able to explain the crosslinking reaction better. This also suggests a methodology to seek new plasticizers.

4.9 References


34. Pirali, O.; Boudon, V.; Carrasco, N.; Dartois, E. Astronomy & Astrophysics 2014, 561.
CHAPTER 5

CHARACTERIZATION OF CROSSLINKING IN PHENOLIC

5.1 Chapter overview

In chapter 4, we have understood how the plasticizer liquid dispersed the two rigid reactants - internally hydrogen bonded phenolic resin and the crystalline crosslinker HMTA. In this chapter, the quantitative understanding of the plasticization process from the interaction of the aldehyde group and the positively delocalized ring of furfural plasticizer with the phenolic resin is carried out. This interaction will increase the free hydroxyls groups responsible for the solvation of HMTA. It will increase the amount of crosslinking. The aim of this chapter is to characterize the crosslinking in phenolic and figure out the efficiency of the plasticizer furfural in terms of crosslinking. The characterization of crosslinking is done using thermal analysis, infrared spectroscopy and with LF NMR. Mid infrared spectroscopy clarifies the dissolution process of the crystalline crosslinker and its temperature dependent reaction, the thermal analysis enabled us to follow the curing reaction as a function of temperature. By measuring the physical interaction at elevated temperature using near infrared spectroscopy, it was shown that in the crosslinked phenolic, segmental mobility mainly influences by the chemical crosslinking. LFNMR spin lattice relaxation time $T_1$ is used for the measurement of this segmental mobility in crosslinked phenolic. In chapters 2 and 3, we have described the detailed investigation of the segmental mobility and $T_1$ relaxation time. Due to complexity of phenolic curing reaction, the method other than LFNMR does not give definitive answer to the amount of crosslinking. However, thermal analysis and infrared spectroscopy will provide the way to corroborate the
LFNMR method. The LFNMR results suggest that addition of approximately 10 % w/w furfural plasticizer increases around 50 % crosslinking in the phenolic system.

5.2 Experimental
5.2.1 Sample preparation

In the multi component system proper mixing method can affect the phase separation behavior. In this system, uniform mixture of solid prepolymer, solid crosslinker and the liquid plasticizer furfural will be achieved by mixing them at the liquid nitrogen temperature in homemade dry box. First HMTA was ground in a dry box to reduce the particle size and then mixed with an appropriate amount of the pre-polymer. If plasticizer was required, it was added dropwise into the prepolymer/HMTA mixture in a 20 mL vial. Then the mixture was transferred into a mortar. In this mixture, the liquid nitrogen was added so everything will become solid. The mortar with the mixture was kept and ground in a home-made dry box with a relative humidity <10 %. The low relative humidity inside the dry box was achieved by flushing nitrogen gas. The resin, HMTA and plasticizer mixture was ground for 1 to 2 min to achieve uniformity. This uniform mixture was cured using the home-made reactor with the heating rate 5 °C/min using three Omega 200 W heating electrodes and the Watlow SD6C-HCAA-AARG temperature controller. The homemade aluminum reactor and the PID heating controller is shown in the following Figure 5.1.
5.2.2 Thermal analysis

A Q100 TA DSC instrument with an RCS cooling system was used for the measurement of the curing energy. The instrument is calibrated with indium with the onset melting temperature 156.6 °C and an enthalpy of fusion 28.6 J/gm. For the curing experiments, each sample is heated at a 5 °C/min rate from -20 °C to 280 °C. Each experiment is repeated three times and the average value of three is used for our analysis. In the glass transition measurement experiment, phenolic prepolymer or the mixture of prepolymer and plasticizer was first heated to 110 °C and then cooled to the -50 °C. Finally, again heated to the 150 °C. For this experiment the heating rate was maintained to 10 °C/min. In both the experiments approximately 3 mg of sample was taken in aluminum hermetic pan.

5.2.3 Infrared analysis

A Perkin Elmer Spectrum 100 is used for mid-infrared analysis. In addition, a Perkin Elmer Frontier near infrared spectrometer was used for near-infrared analysis. In all cases, the
samples measured have the same thermal profile as the ones used for thermal analysis. Using a home built heater (figure 5.1) the sample is cured at different temperature from Room temperature to 180 °C and then the mid infrared spectrum is taken at room temperature using Perkin Elmer Spectrum with an ATR accessory. The near-infrared data were obtained using integrated sphere diffuse reflectance cell. The mixtures of prepolymer and furfural were heated using a heater built in our laboratory for use with this cell. The same set up was used for the characterization of amount of hydrogen bonding in cured sample. In that experiment, the sample was heated from room temperature to130 °C. In figure 5.2, the image of the home built heater with the diffuse reflectance accessory is shown. For mid infrared measurements, 256 scans of 1 cm\(^{-1}\) resolution were signal averaged. For near infrared measurements 32 scans of 1 cm\(^{-1}\) resolution were signal averaged. Each experiment is repeated 4 times. For the diffuse reflectance measurements, all spectra were converted into KM (Kubelka-Munk) units using the Perkin Elmer software provided.

![Home-made reactor and diffuse reflectance set up for near infrared](image)

**Figure 5.2** Home-made reactor and diffuse reflectance set up for near infrared
5.3 Plasticization in prepolymer

The thermograms of different mixtures of the phenolic prepolymer with plasticizer are shown in Figure 5.3. The glass transition temperature $T_g$, of the prepolymer decreases as a function of plasticizer concentration as summarized in Figure 5.4. These data are consistent with the fact that many solvents when added to the polymer increase the free volume and thus segmental mobility. Our GPC measurement shows that the molecular weight of our prepolymer is 1,117 gm/mol (~11 monomer units). Usually such a low molecular weight polymer does not have significant chain relaxation and their $T_g$ is usually lower than room temperature \(^1,2\). The unusually high $T_g$ observed for the phenolic prepolymer is due to the extensive intramolecular hydrogen bonds present. The presence of aromatic units also adds considerable chain rigidity.

![Graph showing DSC calorimetric data and observation of $T_g$ depression](image)

**Figure 5.3** DSC calorimetric data and observation of $T_g$ depression obtained for the phenolic prepolymer with different amounts of furfural (i) No furfural (ii) 5% w/w furfural (iii) 11% w/w
In this study, we clarified the details of the curing reaction involving the three components, HMTA, phenolic prepolymer and furfural. The near-IR data assignable to overtones or combinations at various temperatures (Figure 5.5) are especially revealing. In order to carry out quantitative analysis, we have normalized all the intensities to the aliphatic CH$_2$ peak at 5,666 cm$^{-1}$. The first overtone region of hydroxyl units of prepolymer shows two different peaks. The lower frequency broad peak is the hydrogen bonded 1$^{st}$ overtone of –OH stretching peak while the higher frequency sharp peak is assigned to the free hydroxyls group. The width of the hydrogen bonded component reflects the broad distribution of the hydrogen bond strength. It is clear that at elevated temperatures, disruption of hydrogen bonds occurred, causing the relative band intensity to change for the two components.

In Figure 5.6, the amount of free hydroxyls as a function of furfural is measured based on normalized band intensity. The amount of free hydroxyls increases with plasticizer concentration. The fact that the signature feature of free hydroxyls is present suggests that
furfural can disrupt the prepolymer structure but does not form explicit bonds with the hydroxyl units. In this system, furfural can be characterized as a plasticizer/lubricant, reducing the amount of hydrogen bonding interaction and thus increasing segmental motion.

Figure 5.5 1\textsuperscript{st} overtone region of $-\text{OH}$ stretching of prepolymer at different temperature in the order of lower temperature to higher temperature from 22, 70, 90, 120, 140, 160 to 180 $^\circ$C
Figure 5.6 The normalized peak height of free hydroxyl (i) prepolymer (ii) prepolymer with 5 % w/w furfural (iii) prepolymer with 10 %w/w furfural

5.4 Thermal and spectroscopic analysis of curing

In order to understand and follow the crosslinking reaction, it is crucial to determine the structural changes in solubilized HMTA during curing. As described in chapter 4, we have assigned a number of vibrations in the mid-infrared region that are characteristic of the dissolution process. The band most characteristic of changes in the intermolecular interaction is the C-N stretching vibration in the ~1,240 cm\(^{-1}\) region. When intermolecular interaction is present, this band shifts downward as compared to an isolated molecule. Based on our studies in chapter 4, it was deduced that the solubilization of HMTA occurs through the formation of hydrogen bonds between the hydroxyls of prepolymer and the nitrogen of HMTA. It is then possible to monitor the solubilization process of HMTA by measuring the relative intensity of
the 1240 cm\(^{-1}\) peak and its shifts. Several other vibrations (1,014 or the 690 cm\(^{-1}\)) characteristic of the HMTA molecule also exhibit similar changes when HMTA is solubilized \(^3\,^5\).

HMTA is an extremely symmetric molecule with a \(T_d\) symmetry. In the solubilized state this symmetry decreases because not all the Nitrogen atoms may form specific interactions with surrounding molecules \(^6\). Although this C-N stretching is typically used to analyze hydrogen bonding to the Nitrogen atom, the difference in optical activity may influence the relative band intensity of the HMTA that is in the presence of the hydroxyl units of the prepolymer or furfural. Therefore, we have also used the CNC bending vibration at 690 cm\(^{-1}\) for analysis \(^5\,^7\). This band is totally absent for a crystalline HMTA. In Figure 5.7, the peak intensity of this 690 cm\(^{-1}\) peak is shown for the mixture of HMTA and prepolymer at different temperatures. All the spectra were normalized to the isolated ring vibration at 1,591 cm\(^{-1}\). The intensity of this 690 cm\(^{-1}\) peak increases as a function of temperature up to 130 °C, then begins to decrease. The increase in intensity is because HMTA is being dissolved. The subsequent decrease is attributed to the curing reaction. This is consistent with our NMR analysis reported previously in chapter 4 \(^3\).
Figure 5.7  Change of hexamethylenetetramine (HMTA) dissolution peak during curing reaction of 1 to 8 mole ratios of HMTA and the prepolymer monomer (a) at room temperature (b) at 120 °C (c) at 130 °C (d) 180 °C.

In Figure 5.8, the change of the 690 cm\(^{-1}\) normalized intensity with temperature and the amount of plasticizer is shown. The DSC thermograms of the samples containing different amount of are shown in Figure 5.9. These two sets of experiments are carried out with an identical thermal profile. These two different sets of experimental data clearly are correlated. The infrared intensity data yields the amount of solubilized HMTA present and reacted at various temperatures. The DSC data yields the amount of curing that has occurred by measuring the energy under the exotherms found. As mentioned above, we do not have the inherent absorptivity of this 690 cm\(^{-1}\) band for different molecular geometry to analyze the amount of dissolution quantitatively. However, there is no question that the infrared and thermal analyses
yield an interesting correlation to interpret the changing molecular structure during the curing reaction.

Figure 5.8 Solubilization and the reaction of hexamethylenetetramine (HMTA) in curing reaction energy (a) 8:1 mole ratio of prepolymer to HMTA (b) 8:1:0.6 mole ratio of prepolymer to HMTA to furfural (c) 8:1:1.2 mole ratio of prepolymer to HMTA to furfural

The principal role of furfural is to plasticize the phenolic prepolymer and to dissolve HMTA for the crosslinking reaction. Therefore, it is important to assess the number of available sites, \( f \), that are actually utilized as a function of the amount of plasticizer present and at different reaction temperatures as shown in equation 1. However, by considering the total exotherm in
DSC to be associated with HMTA reaction alone, this calculation only provides an upper estimate of the functionality associated with HMTA that have reacted.

\[ f = \frac{12(\Delta H \text{ of exotherm measured})}{\text{Total reaction energy expected (}\Delta H_{\text{total}}\text{)}} \]

Equation 5.1

The total reaction energy expected, \( \Delta H_{\text{total}} \), is calculated using the group contribution method as shown in Table 5.1. Both the solvation/dissociation of HMTA and the subsequent reaction need to be incorporated in the calculation. We obtained a value of 294 kJ/mol for \( \Delta H_{\text{total}} \).
Figure 5.9  Effect of plasticizer on the curing energy (a) 8:1 mole ratio of prepolymer monomer to hexamethylenetetramine (HMTA) (b) 8:1:0.6 mole ratio of prepolymer monomer to HMTA to furfural (c) 8:1:1.2 mole ratio of prepolymer monomer to HMTA to furfural
Table 5.1  Calculation of the $\Delta H_{\text{total}}$ for the complete reaction of hexamethylenetetramine

<table>
<thead>
<tr>
<th>Solvation of HMTA</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Terms</td>
<td>Enthalpic energy (kJ/mole)</td>
</tr>
<tr>
<td>Formation of crystalline HMTA</td>
<td>180.5</td>
</tr>
<tr>
<td>Solvation of HMTA using phenol</td>
<td>-79.7</td>
</tr>
<tr>
<td>Formation of soluble HMTA</td>
<td>100.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction of 1 mole of HMTA b</th>
<th>Group Additive values c (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terms</td>
<td></td>
</tr>
<tr>
<td>4 x NH$_3$</td>
<td>-184.0</td>
</tr>
<tr>
<td>12 x C$_{ar}$-(H)</td>
<td>165.6</td>
</tr>
<tr>
<td>12 x C$_{ar}$-(C)</td>
<td>276.0</td>
</tr>
<tr>
<td>6 xC-(C$_{ar}$)$_2$ (H)$_2$</td>
<td>-120.0</td>
</tr>
</tbody>
</table>

a. Heat of formation values are taken from reference 8.
b. It is assumed that a complete reaction of 1 mole of HMTA produces 4 moles of ammonia gas and 6 methylene (-CH$_2$-) units. The 6-methylene units can then react with 12 o or p reactive sites of prepolymer yielding a maximum 12 functionalities. C$_{ar}$ is an o or p aromatic carbon.
c. Heat of formation values are taken from reference 9,10.

Using the calculated $\Delta H_{\text{total}}$ value, Figure 5.10 clearly shows that the average reacted functionalities $f$ of HMTA increases with the curing reaction temperature and with the amount of furfural used. It has been shown that during the curing reaction, HMTA molecule will dissociate in a systematic fashion with the temperature$^{11-19}$. The primary linkages such as benzyl amine, dibenzylamine, benzoxazine will form and these linkages then further react with the unreacted ortho or para sites to further dissociate HMTA. These two dissociation/solubilization processes of HMTA are responsible for the increase of the reacted functionalities $f$ with the temperature.
Figure 5.10  The comparison of functionalities used at different temperatures and at different contents of furfural (a) 8:1 mole ratio of prepolymer to hexamethylenetetramine (HMTA) (b) 8:1:0.6 mole ratio of prepolymer to HMTA to furfural (c) 8:1:1.2 mole ratio of prepolymer to HMTA to furfural

A complete dissociation of a HMTA molecule should yields a maximum 12 functionalities. However, our estimate plotted in Figure 5.10 shows that only a small fraction of all possible reaction sites of HMTA molecule has reacted. This small amount of crosslinking achieved is due to the lack of mobility even when few crosslinks are formed. This is true even when a large amount (14% w/w) of HMTA is used. The exceedingly high $T_g$ as compared to the reaction temperature is also a factor in limiting the reactions possible. There is no question that furfural enhances segmental mobility and dissolution of HMTA.

Our DSC and infrared data provided a consistent trend showing the dissolution of HMTA and the subsequent reaction with the phenolic prepolymer. HMTA dissolve readily at elevated
temperatures until reaction initiates at ~135 °C. This is especially true for systems containing furfural. For the latter cases, the reaction always starts at lower temperatures as shown in Figure 5.8 and Figure 5.9. When furfural is used the higher number of hydrogen bonds formed will cause the weakening of the C-N bonds and greater number of crosslinking reactions. Therefore, the quantity of the reacted HMTA increases with the amount of furfural as shown in Figure 5.8.

5.5 Monitoring crosslinking reaction using LFNMR

Even with a detailed analysis of the thermal and infrared data, it is difficult to prove directly that plasticization raises the degree of crosslinking. As mentioned above, the prepolymer and HMTA curing reaction is complex since 15 or more different types of linkages can form and some of the linkages are shown in the chapter 1. Many of these linkages are formed only as dangling chains and do not yield the crosslinks needed for effective mechanical properties. It is difficult to differentiate the various linkages using infrared spectroscopy. The most direct method to seek information on the crosslinking process and the degree of crosslinking achieved is to use low field NMR. The detailed information about how the low field NMR is related to the degree of crosslinking is shown in the chapter 3. This technique directly measures the segmental dynamics that are correlated to the \( T_1 \) spin-lattice or \( T_2 \) spin-spin relaxations. For rigid materials such as crosslinked phenolic resin, the \( T_2 \) spin–spin relaxation time usually remains constant. However, the \( T_1 \) spin-lattice measurements should change significantly with curing at different experimental conditions. The reasons behind why \( T_1 \) is better for the measurement of segmental dynamics in the rigid crosslinked sample is provided in chapter 2.

LFNMR measurements can yield information regarding the degree of crosslinking, supporting the analyses based on DSC and infrared data. As the crosslinking proceeds, tri and tetra substituted phenolic rings will be formed. Most of tetra substituted rings will act as a
crosslinked junction. The formation of these kinds of covalent crosslinked junction will change the segmental mobility of the system. Segmental mobility in crosslinked polymer is mostly affected by molecular forces such as the hydrogen bonding in the phenolic system, entanglements and chemical crosslinking. It has been shown by simulation that entanglement and the hydrogen bonding do not have significant contribution on the overall segmental mobility in the crosslinked phenolic system. We have also measured the amount of hydrogen bonding in the crosslinked phenolic using near infrared spectroscopy at different temperature. The results are shown in the Figures 5.11 and 5.12. They suggest that intensity and the frequency of the free hydroxyls peak does not significantly change with temperature such as changes observed in the phenolic resin which is shown in Figure 5.5. The intensity of free hydroxyl peak at the lower temperature is higher in the crosslinked sample. Figure 5.13 shows that the frequency of free hydroxyls at the room temperature is around 6950 cm\(^{-1}\) and the uncured hydrogen bonded prepolymer at 6914 cm\(^{-1}\). These prove that the crosslinked phenolic system does not have significant hydrogen bonding. We can say that chemical crosslinking affects the most in the crosslinked phenolic the segmental mobility. By measuring the segmental dynamics using spin lattice relaxation time \(T_1\) we can correlate it to the amount of crosslinking.
Figure 5.11  1st overtone region of –OH stretching of 180 °C crosslinked phenolic (1:8 mol ratio of hexamethylenetetramine (HMTA) to phenolic monomer) at different temperature in the order of lower temperature to higher temperature from 22, 50, 90, 130 °C
Figure 5.12 1\textsuperscript{st} overtone region of –OH stretching of 180 °C crosslinked phenolic (1:8:1.2 mol ratio of hexamethylenetetramine to phenolic monomer to furfural) at different temperature in the order of lower temperature to higher temperature from 22, 50, 90, 130 °C
Figure 5.13 -OH stretching 1\textsuperscript{st} overtone free hydroxyls peak’s frequency at different temperature (a) Pure prepolymer (b) 8:1 mole ratio of prepolymer to hexamethylenetetramine (HMTA) cured at 180 °C (c) 8:1:1.2 mole ratio of prepolymer to HMTA to furfural cured at 180 °C

The spin-lattice relaxations for various samples are shown in Figures 5.14 to 5.19. All the data were fitted with a one-exponential relaxation equation 3.7 shown in the chapter 3. The T\textsubscript{1} relaxation times measured for the prepolymer and HMTA with and without plasticizer at different temperatures are consistent with our expectations for such a rigid polymer. In the case of the uncured prepolymer, hydrogen bonding dominates at low temperatures and a very high T\textsubscript{1} value was observed. The plasticizer breaks this hydrogen bonding and increases segmental mobility resulting in the higher overall mobility of the mixture reflected in the decrease of T\textsubscript{1}. This is especially true when the plasticizer is added. The low field NMR data are consistent with the DSC and infrared data presented in Figures 5.3 to 5.6. Those thermal data also illustrated the
changing segmental mobility in terms of a lowering of $T_g$ because of increasing segmental mobility.

Figure 5.14  $T_1$ spin relaxation data of different temperature crosslinked sample of 8:1:1.2 mole ratio of prepolymer monomer to hexamethylenetetramine to furfural sample showing the fitting curves of crosslinking.
Figure 5.15  $T_1$ spin relaxation data of different temperature crosslinked sample of 8:1 mole ratio of prepolymer monomer to hexamethylenetetramine (HMTA) showing the fitting curves for the solubilization of HMTA.
Figure 5.16  $T_1$ spin relaxation data of different temperature crosslinked sample of 8:1 mole ratio of prepolymer monomer to hexamethylenetetramine (HMTA) showing the fitting curves of crosslinking.
Figure 5.17  $T_1$ spin relaxation data of different temperature crosslinked sample of 8:1:0.6 mole ratio of prepolymer monomer to hexamethylenetetramine (HMTA) to furfural sample showing the fitting curves of crosslinking.

All these LFNMR observations are summarized in Figure 5.18. The uncured phenolic prepolymer exhibits a high $T_1$. In contrast, plasticized samples have a low $T_1$ relaxation value. As the curing temperature increases, the segmental mobility (measured using $T_1$ at 50 °C) increases for the neat unplasticized prepolymer with HMTA until crosslinking reaction starts in the proximity of 140 °C. This is due to solvation of HMTA (shown by infrared data) which acts as a plasticizer and break the internal hydrogen bonding of resin. After the curing onset temperature, the segmental mobility decreases due to the formation of chemical crosslinking. Therefore, the $T_1$ increases after onset temperature. Sample with plasticizer concentration shown in figure 19b and figure 19c. The slight increase of $T_1$, (~25 msec) was found for curing temperatures close to
120 °C and 100 °C for the two different concentration respectively. At higher than these corresponding curing temperatures in both these samples, increase in $T_1$ occurs at a faster rate due to the chemical crosslinking reaction. The change in structure starts at a lower temperature and occurs much more extensively when furfural is used. An identical trend is seen in the infrared data. In that case, only the solubilized HMTA characterized by the presence of the 691 cm$^{-1}$ is present. Its intensity only diminishes when the curing starts. The higher $T_1$ value of the crosslinked sample suggests that the furfural increasing the amount of crosslinking.

![Graph](image)

Figure 5.18  $T_1$ spin lattice relaxation time at different temperature crosslinked system (a) 8:1 mole ratio of prepolymer monomer to hexamethylenetetramine (HMTA) (b) 8:1:0.6 mole ratio of prepolymer monomer to HMTA to furfural (c) 8:1:1.2 mole ratio of prepolymer monomer to HMTA to furfural
Figure 5.19  High temperature $T_1$ of different phenolic system (a) phenolic prepolymer (b) 1:8 hexamethylenetetramine (HMTA) to phenolic monomer crosslinked at 180 °C (c) 1:8:1.2 HMTA to phenolic monomer to furfural crosslinked at 180 °C

In all of the above experiment, segmental mobility of the crosslinked phenolic was measured at the 50 ºC. We have also measured the $T_1$ at higher temperature after the crosslinking at 180 ºC which is shown in the figure 5.19. The result shows that the $T_1$ value decreases as the temperature increases in phenolic system. The changes in $T_1$ is not much significant in the crosslinked system compared to prepolymer. One of the reasons is that crosslinked phenolic does not have significant hydrogen bonding like prepolymer. Due to presence of strong hydrogen bonding in prepolymer its $T_1$ changes a lot compared to crosslinked sample. Also, the higher temperature measurement we can reduces the hydrogen bonding contribution coming from segmental mobility of the phenolic system. The data shows that the plasticized sample has higher $T_1$ at higher temperature also. All of these discussion shows that
T$_1$ is correlated with the amount of crosslinking and the higher T$_1$ means higher crosslinking. Furfural plasticizer increases the amount of crosslinking.

5.6 Conclusions

Using DSC and near infrared spectroscopy, it was shown that the plasticizer, furfural, increases the segmental mobility and the number of free hydroxyl units in the phenolic prepolymer. This increase in the free hydroxyl units are responsible for the higher solvation of HMTA to participate in the crosslinking reaction. Due to the well-dispersed reactants and increase in segmental mobility in the plasticized sample, more reactions that are efficient were produced. Infrared spectroscopy was used effectively to monitor the various states of HMTA. Using DSC curing energy data, a step-by-step dissociation of HMTA molecule was observed. Even with the complexity in the curing reaction, the low field NMR technique proved to be effective for measuring the extent of crosslinking achieved during curing. In addition, sample preparation for LFNMR is easy. The instrumentation is also relatively easy to operate. The various T$_1$ spin-lattice values obtained can be directly correlated to the segmental mobility, and thus to the extent of crosslinking. In every case, the result from LFNMR is supported by thermal and spectroscopic analyses. The combination of these three techniques have provided a clear explanation of the plasticization process and the subsequent crosslinking reaction at elevated temperatures. It is abundantly clear that the use of a plasticizer, furfural, increases the extent of crosslinking by increasing the overall mobility and dispersion of the reactants.

5.7 References


CHAPTER 6

CROSSLINKING WITH NON-REACTIVE PLASTICIZER


6.1 Chapter overview

Traditionally, furfural has been used as a plasticizer to enhance the crosslinking ability of the phenol formaldehyde resin. In chapter 4 and 5, the role of furfural in the crosslinking of phenolic is understood in detail. However, the main problem with furfural is its toxicity. Therefore, in this chapter we have used the knowledge of furfural for finding of the environmental friendly plasticizer. We have initiated this study by choosing green plasticizer methyl benzoate. Its positively charged delocalized aromatic structure and polar ester group can disrupt three types of inter-molecular interactions in the phenolic resin namely –OH----OH hydrogen bonding, OH--- π hydrogen bonding and π-π ring-ring interaction. This will reduce the rigidity in phenolic prepolymer and increases the free hydroxyls. These free hydroxyls are responsible for the solvation and the dissociation of HMTA molecule. Due to higher solvation and dissociation of HMTA in the sample with methyl benzoate, it will increase the crosslinking. The crosslinking is characterized by DSC, infrared spectroscopy and by measuring the segmental mobility using LFNMR. The infrared spectroscopy measurement does not show reaction of methyl benzoate plasticizer during the curing. This study demonstrates that this kind of
nonreactive plasticizer can induce highly crosslinked structures without any of the environmental impact of the current technology.

6.2 Dispersion of reactants using methyl benzoate:

As we have discussed in chapter 4 and 5 that phenolic resin is extremely rigid due to the extensive hydrogen bond network and its kinked structure \(^1\)\(^-\)\(^3\). Although much of the details of the reaction mechanism and the reaction products remain to be characterized, there is no question that segmental mobility is a necessary condition for any reaction to take place. The detailed procedure for the characterization of the segmental mobility using DSC was shown in the chapter 5.

It is possible to disrupt the hydrogen bonds by elevating the sample temperature to facilitate the reaction between the phenolic resin and crosslinkers \(^3\). The crosslinking reaction is much more efficient when plasticizers are used. Therefore one of the key element of an effective plasticizer is to disrupt the hydrogen bonded matrix, thereby dissolve the crystalline crosslinker such as HMTA without suppressing the reactive sites\(^4\).

The phenolic resin has been characterized in chapter 4. It has a low molecular weight of only \(~\)10 monomers units long. Yet it has a well-defined glass transition temperature \((T_g)\) at 66-67 °C due to the hydrogen bonds present. By adding a small amount of methyl benzoate, the glass transition temperature of the resin drops significantly as shown in Figure 6.1. The thermograms clearly demonstrate the reduction in \(T_g\) with data summarized in Figure 6.2. This reduction in \(T_g\) is comparable to other effective plasticizers studied shown in chapter 4 and 5. It should be emphasized and as shown below that the depression of \(T_g\) or increase in the segmental mobility is not the sole criterion in the determination of crosslinking reaction.
Figure 6.1  DSC calorimetric data and observation of $T_g$ depression obtained for the phenolic prepolymer with different amounts of methyl benzoate (MB) (a) pure prepolymer (b) 0.04 mole fraction MB in prepolymer (c) 0.08 mole fraction MB in prepolymer (d) 0.12 mole fraction MB in prepolymer
Figure 6.2  The depression of $T_g$ of the phenolic resin as a mole fraction of methyl benzoate concentration.

The reduction of $T_g$ suggests that methyl benzoate has the ability to weaken the intermolecular hydrogen bonding in phenol formaldehyde prepolymer. As stated above methyl benzoate is selected because of its ability to dissociate the phenolic resin yet having weak specific interactions with HMTA. The second point is easy to demonstrate since HMTA is insoluble in methyl benzoate. In addition, no discernable NMR signals were measured that would suggest any soluble HMTA exists in methyl benzoate. The solubility of HMTA in methyl benzoate is measured using the method describe in chapter 4. However, there are abundant amount of evidence showing the disruption of the hydrogen bonded matrix when methyl benzoate is introduced.

There are three types of intermolecular interactions in the phenolic resin, $\pi-\pi$ interaction, $\pi$-OH interaction and most prevalent, hydrogen bonded hydroxyl groups that stabilizes its structure$^{5,6}$. Methyl benzoate has the physical features that can potentially disrupt all three types of intermolecular interactions. The specific infrared active features that can be used to
characterize the changes are typically the O-H stretching, ring stretching or the ring bending vibrations of the phenolic resin. The C=O stretching vibration of the ester groups in methyl benzoate also is extremely sensitive to changes in the intermolecular interactions.

In conjunction with ATR mid-infrared spectroscopy, we have used near infrared spectroscopy to characterize the changes in the intermolecular interactions. The detailed description for the sample preparation for ATR mid infrared and near infrared are shown in the chapter 4 and 5. As can be seen in Figure 6.3, the hydrogen bonded component is cleanly separated from the O-H stretching free of hydrogen bonding. The width of the hydrogen bonded component reflects the diverse hydrogen bonds formed in the resin. As we have discussed previously, this resin is random in configuration and capable of forming ortho- or para-linkages that would also influence the different formation of hydrogen bonds. At elevated temperatures, the free O-H stretching vibration is clearly present and can be used to monitor the structural changes. The influence of methyl benzoate is clearly seen in Figure 6.4. The plasticization effect of methyl benzoate in freeing the OH groups is dramatic.
Figure 6.3  The O-H stretching vibration (overtone) observed for the phenolic resin with 0.12 mole fraction of methyl benzoate at 30 °C, 70 °C, 100 °C, 120 °C, 130 °C, 140 °C, 150 °C, 160 °C and 180 °C
Figure 6.4  Comparison of the fraction of free O-H vibrations (a) in the pure phenolic resin and (b) in 0.12 mole fraction of methyl benzoate in pure phenolic resin as a function of temperature.

It is easy to monitor the changes in the C=O vibration of methyl benzoate. This vibration is extremely intense and shifts by nearly 20 cm$^{-1}$ (Figure 6.5) when interacting with the hydroxyl units of the resin. The upward shift of the O-H stretching with the corresponding downward shift of the C=O stretching is characteristic of the interactions associated with the interaction between methyl benzoate and the resin. We do not have the capability to obtain ATR data at elevated temperatures. But it is clear that the interaction exists between the two components as expected.
Figure 6.5  Infrared data obtained for the methyl benzoate when added to the phenolic resin.

(a) pure methyl benzoate (b) 600 mg/mL prepolymer in methyl benzoate (c) 200 mg/mL prepolymer in methyl benzoate (d) pure prepolymer

As mentioned above, there are other two types of intermolecular or intra-molecular interactions involving the aromatic rings in the resin and between the resin and methyl benzoate. Because of the various overlapping features the only band that can employ to characterize the interactions is the C-H bending in the 700 cm$^{-1}$ region (Figure 6.6). Although small, there is no question that this ring vibration of methyl benzoate changes in the presence of the phenolic resin. The relative strength of the three types of inter-molecular interactions are well established with the hydrogen bonded interaction being the dominant one.
Figure 6.6  C-H ring bending vibration of the methyl benzoate in the presence of phenolic resin. (a) pure methyl benzoate (b) 600 mg/mL prepolymer in methyl benzoate (c) 200 mg/mL prepolymer in methyl benzoate (d) pure prepolymer

6.3 Crosslinking using methyl benzoate plasticizer

The highly mobile and the loosely interacting polymer chains of plasticized prepolymer can easily allow the crosslinking agent, HMTA, to enter between them. This phenol formaldehyde system will have higher free hydroxyl groups. It has been shown in our previous study that these free hydroxyls are responsible for the solvation of HMTA $^4$. In the Figures 6.7 and 6.8, the solubilization process is monitored during the curing reaction by measuring the frequency shifting in C-N stretching band of HMTA for the unplasticized and plasticized resin. In hydrogen bonded or solvated HMTA, the C-N stretching frequency shifts from 1235 downward to 1230 cm$^{-1}$.$^4$ In the sample with 0.06 mole fraction methyl benzoate almost all the HMTA is solubilized at approximately 120 °C. While in the sample without plasticizer solvation
of HMTA occurs at approximately 140 °C. There is no question that using methyl benzoate as a plasticizer reduces the solvation activation energy of HMTA. As stated above, it is the freeing of the hydroxyl units that solubilizes HMTA.

![Infrared spectra of CNC stretching peak of hexamethylenetetramine (HMTA) in sample of 1:8 mole ratio of HMTA: phenolic prepolymer monomer at different temperatures](image)

Figure 6.7 Infrared spectra of CNC stretching peak of hexamethylenetetramine (HMTA) in sample of 1:8 mole ration of HMTA: phenolic prepolymer monomer at different temperatures.
Figure 6.8    Infrared spectra of CNC stretching peak of hexamethylenetetramine (HMTA) in sample 1:8:0.6 mole ratio of HMTA: phenolic prepolymer monomer: methyl benzoate at different temperatures

HMTA is virtually insoluble in methyl benzoate. Using duraquinone as an internal standard our proton NMR spectra revealed a solubility of no more than 5 mg/mL. The high solubility of HMTA results directly from the plasticized phenolic resin. As we have postulated the two step process is a necessary one. Methyl benzoate does not directly interact with HMTA but it plasticizes the prepolymer and the plasticized prepolymer then interacts with HMTA. In this scheme methyl benzoate indirectly increases the interaction between the two reactants, the crosslinker HMTA and the phenolic prepolymer.

The curing process is demonstrated in Figure 6.9. The endotherm seen at ~60 °C is associated with the dissociation of the prepolymer. The exotherms are associated with the crosslinking process. It is clear that with the addition of methyl benzoate there is a lowering of
curing temperature with the use of methyl benzoate. In addition, it is also clear that the curing energy or the degree of crosslinking increases with the use of methyl benzoate. This is shown in Figure 6.9.

Figure 6.9  Effect of plasticizer on the curing energy (a) 8:1 mole ratio of prepolymer monomer to hexamethylenetetramine (HMTA) (b) 8:1:0.6 mole ratio of prepolymer monomer to HMTA to methyl benzoate (c) 8:1:1.2 mole ratio of prepolymer monomer to HMTA to methyl benzoate
The curing energy measured for the phenolic resin with hexamethylenetetramine (HMTA) as a function of methyl benzoate employed

The principal role of methyl benzoate is to plasticize the phenolic prepolymer which then dissolves HMTA for the crosslinking reaction. Therefore, it is important to assess the number of available sites, $f$, that are actually utilized as a function of the amount of plasticizer present as shown in equation 5.1. HMTA has 4 different nitrogen atoms and 6 methylene units. In the ideal case, these 6 methylene units can form 12 different chemical bonds with the unreacted ortho or para reactive sites of the phenolic prepolymer. Thus, the maximum functionalities of HMTA molecule is 12. Using DSC curing energy and equation 5.1, the functionalities of HMTA reacted with different concentrations of plasticizer are calculated. The total reaction energy expected, $\Delta H_{total}$, is calculated using the group contribution as before. Both the solvation/dissociation of HMTA and the subsequent reaction need to be incorporated in the calculation. We obtained a
value of 294 kJ/mol for $\Delta H_{\text{total}}$. The detailed explanation of the calculation has been provided previously in equation 5.1.

Since we have demonstrated that HMTA is virtually insoluble in methyl benzoate, we have considered the total exotherm in DSC (Figure 6.9) to be associated with HMTA reaction alone, this calculation of functionality (Figure 6.11) is an upper estimate of the functionality associated with HMTA that can react.

![Graph showing the relationship between mole fraction of methyl benzoate and functionality of HMTA reacted at 180°C.](image)

**Figure 6.11** Functionality calculated for hexamethylenetramine (HMTA) with different mole fraction of methyl benzoate.

### 6.3.1 Monitoring crosslinking reaction with LFNMR

Even with a detailed analysis of the thermal and infrared data, it is difficult to prove directly that plasticization raises the degree of crosslinking. As mentioned previously, the
The prepolymer and HMTA curing reaction is complex since 15 or more different types of linkages can occur. Many of these linkages act only as a dangling chain and do not yield the crosslinks needed for effective mechanical properties. It is difficult to differentiate the various linkages using infrared spectroscopy. The most direct method to seek information on the crosslinking process and the degree of crosslinking achieved is to use LFNMR. This technique directly measures the segmental dynamics that are correlated to the $T_1$ spin-lattice or the $T_2$ spin-spin relaxations. For such rigid materials, such as crosslinked phenolic resin, we have elected to use the $T_1$ spin-lattice measurements to obtain information regarding the degree of crosslinking, supporting the analyses based on DSC and infrared data.

The spin-lattice relaxations for phenolic resins during curing with and without benzoate are shown in Figure 6.12. All the data were fitted with one exponential fitting equation which is described in chapter 3 of equation 3.7.
Figure 6.12  

T\textsubscript{1} spin relaxation of 180 °C cured sample (a) 8:1 mole ratio of prepolymer monomer to hexamethylenetetramine (HMTA) (b) 8:1:0.4 mole ratio of prepolymer monomer to HMTA to methyl benzoate (c) 8:1:0.8 mole ratio of prepolymer monomer to HMTA to methyl benzoate (d) 8:1:1. 2 mole ratio of prepolymer monomer to HMTA to methyl benzoate

The T\textsubscript{1} relaxation times measured for the prepolymer and HMTA with different concentration of methyl benzoate and without are shown in Figure 6.13. The increase in T\textsubscript{1} as a function of methyl benzoate used agree well with the DSC and infrared data consistent with our expectations for such a rigid crosslinked system. The drop off in relaxation at extremely high concentration of methyl benzoate is interesting. This suggests there is a maximum of efficiency as a function of plasticizer concentration.
Figure 6.13   The $T_1$ measured for the crosslinked resin as a function of methyl benzoate used

As seen in Figure 6.11, the actual number of crosslinks formed is only a small fraction of the sites available, no more than 33%. Although only one bond is needed between every two chains to form a gel state, the modulus of a crosslinked system depends on the crosslink density. The objective for a high performance system is to raise the crosslink density to be as high as possible. The addition of methyl benzoate certainly enables that process to occur. However, methyl benzoate also disrupts the phenolic resin, add free volume, thus increasing segmental mobility. Therefore, it is our hypothesis that the addition of too much plasticizer actually increase segmental mobility to reduce the merits of the crosslinking reaction as shown in Figure 6.13.
The usual crosslinks that is formed is the inter-methylene bridges$^{8-12,14}$. During the course of this study, we have identified a number of plasticizers that react in the presence of HMTA and phenolic resin and were incorporated into as part of the crosslink structure. For those plasticizers, we can only account for the exotherms measured by considering that plasticizers also react contributing to the unexpected large exotherms measured.

Another interesting feature of methyl benzoate is that we have not found any evidence that it reacted during the curing reaction as shown in Figure 6.14. The carbonyl stretching vibration did not change with temperature as the curing reaction proceeded. Due to ring positive charge nature in this case it is very difficult to carry out any electrophilic substitution reaction. This plasticizer neither reacts during the curing nor interact with HMTA. Therefore, it does not block any functionality of HMTA making it a very efficient plasticizer.
6.4 Conclusions

Using DSC, it was shown that the plasticizer, methyl benzoate increases the segmental mobility and the number of free hydroxyl units in the phenolic prepolymer. These increases are responsible for the higher solvation of HMTA during its reaction. Due to higher dissociation and segmental mobility in the plasticized sample higher amount of the functionalities of HMTA reacted. The functionality of HMTA reacted is monitored using DSC curing energy. By
measuring the segmental mobility of the crosslinked product using low field NMR it is proved that up to certain level of concentration of plasticizer the crosslinked density increases.

6.5 References


CHAPTER 7

CROSSLINKING WITH REACTIVE PLASTICIZER

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7.1 Chapter overview

Using a combination of infrared spectroscopy, thermal analysis and low field NMR, we have elucidated the role of three types of reactive plasticizers on the crosslinking reaction between hexamethylenetetramine and phenol formaldehyde resin. These two rigid reactants are responsible for the exceptionally high mechanical strength in a number of organic-inorganic composites. The efficiencies of the curing reaction and the crosslinked structures achieved are strongly dependent on the type of plasticizer employed. Infrared active vibrations are used to characterize the changing molecular structures of the individual plasticizer as a function of temperature. The $T_1$ spin-lattice relaxation time measured using low field NMR is used for the characterization of segmental dynamics of the chains in the formation of the crosslinked product. This study shows that the amount of crosslinking and the crosslink structure can be very different for the three types of reactive plasticizers and different in comparison to non-reactive plasticizer methyl benzoate which is explained in chapter 6. We are also able to correlate the reactivity and the functionality of the plasticizer to the crosslink density in the reacted product.
7.2 Classification of plasticizers

We have focused on two categories of plasticizers, reactive and non-reactive, for use in the crosslinking reactions. The non-reactive plasticizers serve only as facilitators for plasticization and dissolution of the crosslinker. In the second category, we sought other plasticizers that may react with the products of the primary reaction between the phenolic resin and HMTA, namely primary, secondary, tertiary amines and benzoxazines \(^1\)\(^-\)\(^4\). These reactions can produce high mechanical properties by creating crosslinked structures that exhibit even higher modulus than the ones usually associated with the inter-methylene bridges formed between HMTA and the phenolic resins \(^5\)\(^,\)\(^6\). Methyl benzoate (MB) is an example of the first category, where other candidates such as furfural (F), furfuryl alcohol (FA) and methyl anthranilate (MA) are examples of the second category. The structure of these plasticizers is shown in the Figure 7.1.

![Figure 7.1](image)

In order for both types of plasticizers to function, achieving uniform dispersion of the reactants, we have deduced the structural features that are necessary for their effectiveness.
Because of the π-OH, π-π and hydrogen bonds present in the phenolic resin, having an aromatic ring is important. We speculate that the delocalized cyclic structure interacts favorably with the negatively delocalized phenyl ring of phenol in phenol formaldehyde prepolymer. All plasticizers should also have a strong polar group that can disrupt the hydrogen bonds in the resin.

In this current study, we have explored plasticization candidates that can also participate in the crosslinking reaction between phenolic resin and HMTA in order to raise the mechanical performance. The structural characteristics that we have established in previous studies provided us with the clues to search for new plasticizers that would be equally as effective as F and at the same time to minimize the toxicity issues. For each of the plasticization candidates considered, we assume that it can react directly with the prepolymer and HMTA used or with their various intermediates to form the crosslinks. Because of the complexities associated with the reaction, we have used the most simplistic definition of functionality, i.e. the highest number of bonds that can be formed in the final crosslinked product as shown below in various reaction schemes. FA or benzyl alcohol are mono-functional; cinnamaldehyde, ortho and para cresol, F are di-functional and MA, glycerol, anisole, resole, aniline and m-cresol are multi-functional. For some candidates, although significant exotherms were observed in DSC, neither infrared spectroscopy nor LFNMR showed any features that would be consistent with extensive crosslinking reaction. For others, such as MA, the crosslinking density seems to increase significantly as a function of concentration. Although infrared spectra of non-reactive plasticizer such as MB, remain unchanged, the infrared spectroscopic features of some plasticizers can change in both intensity and frequency as crosslinking proceeds. This observation when combined with the lack of
correlation between expected and measured exotherms suggests that plasticizers themselves also participate in the crosslinking reaction.

Based on these observations, we initiated three parallel but independent lines of investigation to search for reactive plasticizers that can potentially improve the mechanical performance of crosslinked structures at elevated temperatures. We sought candidates that can react with HMTA and/or phenolic resin or their reaction products. The reaction between HMTA and phenolic resin is extremely complex, potentially forming a large array of products. The reaction products always form both primary and secondary amines. The candidates that we sought are in the family of aldehyde, ethers, alcohol, amine and ester. Each can react differently. For example, FA should terminate the crosslinking reaction leading to ineffective physical properties. In contrast, F, generally used in commercial applications, can react with both primary and secondary amines. But its molecular structure allows a fairly narrow number of chain configurations. Although its reaction schemes have yet to be clarified, there is no doubt it is an exceptional plasticizer for commercial applications. Lastly, we designed another class of reactive plasticizers, such as MA, that has the potential to have multi-functionality to form crosslinks even more efficiently.

By combining information from low field NMR, infrared spectroscopy and differential scanning calorimetry, we were also able to clarify the efficiency of each type of plasticizer. The relative effectiveness of the three categories is as we postulated. Their efficiency and possible structures formed are reported here.

7.3 Plasticization efficiency of F, FA and MA

As discussed in the previous chapters, phenolic resin is extremely rigid due to the extensive hydrogen bond network. Although many of the details of the reaction mechanism and the
reaction products remain to be characterized, there is no question that segmental mobility is a necessary condition for any reaction to take place. Phenol formaldehyde prepolymer used in this study has a glass transition temperature at approximately 67 °C. This high \( T_g \) is due to the presence of three types of intermolecular interactions: the internal hydrogen bonds formed between hydroxyl groups (–OH--OH) and -OH-π and also π-π interactions \(^7,^8\). By adding plasticizer such as F, MA or FA to this prepolymer it is possible to depress the glass transition temperature significantly as shown in Figure 7.2. Therefore it is clear that these plasticizers are effective in disrupting inter-molecular interactions which increases the free volume or segmental mobility in the phenol formaldehyde resin. The figure shows that the FA has a higher ability to plasticize than the other two.

![Graph showing the effect of plasticizer on the glass transition temperature (\( T_g \)) of prepolymer](image)

Figure 7.2  Effect of plasticizer on the glass transition temperature (\( T_g \)) of prepolymer (a) Furfural, (b) Methyl anthranilate (c) Furfuryl alcohol

### 7.4 Curing with F, FA and MA plasticizers

The thermograms for the different amounts of plasticizers are shown in Figure 7.3. It is clear for each sample that the onset of curing is lower for the plasticized samples than the binary
mixture of HMTA and phenolic resin. The endotherms at ~60 °C is attributed to the disruption of intra-molecular hydrogen bonds of the resin. The exotherms centered in the 135-150 °C range are attributed to the crosslinking reaction \(^{15}\). For FA there is another reaction with the exotherm centered at approximately 175 °C. As shown in Figures 7.3 and 7.4, the curing energy of the plasticized sample differs significantly when each plasticizer is added to the HMTA and resin mixture.

In order for the crosslinking to proceed between the crystalline HMTA and the hydrogen bonded resin, the segmental mobility needs to be increased and the HMTA needs to be dissolved. It has been our hypothesis that the plasticizer introduced into the formulation needs to accomplish both objectives. It was clear that a plasticizer such as MB disrupted the intermolecular interactions in the phenolic resin, freeing the hydroxyl units, then dissolving the HMTA which facilitates the crosslinking reaction \(^{15}\). There is no evidence that MB can react with either HMTA or the phenolic resin. Therefore, using the group contribution approximation, the total reaction energy of each HMTA can be calculated to the 294 J/g \(^{16-18}\). The detailed description of calculation is shown in chapter 5. Based on the infrared features and the DSC data obtained, it is then possible to ascertain the effective functionality of HMTA in the reaction mixture and its changes as the crosslinking reaction proceeds.

The curing energies of the three plasticizers used in this study increased with the amount of plasticizer introduced (Figures 7.3 and 7.4). The highest curing reaction occurs when F is used and the lowest is associated with FA. However, the magnitude of the curing energies measured clearly suggests a different mechanism as compared to the MB case. All three plasticizers have the ability to break internal hydrogen bonding in the prepolymer and free up the hydroxyl groups. As seen in Figure 7.2, FA clearly is most effective in depressing \(T_g\) as compared to the
other two candidates. This would suggest a higher segmental mobility to facilitate the
crosslinking reaction between FA with HMTA and the phenolic resin, which is not the case. In
fact FA is the least effective of the three, with the lowest curing energy, on the molar basis.

We then measured the solubility of HMTA in each plasticizer. The data are summarized
in Table 7.1. FA and MA exhibit virtually identical solubility with more than 10 times that of the
HMTA being dissolved in F. Therefore, for these three plasticizers, it is clear that the curing
energies measured are not correlated to the conditions needed for reaction, i.e. the mobility of
the resin and access when HMTA is dissolved. In the subsequent sections, it will be shown that
plasticization of the resin and solvation of HMTA are not the primary factors deciding the
crosslinking for these three types of plasticizers. These plasticizers can react with either HMTA,
the resin or their reaction products in forming the final crosslinked structures. In fact, it is our
conclusion that these three plasticizers fall in the reactive category and how the reaction takes
place in each case will determine the final crosslinked structure.
Figure 7.3 Effect of plasticizer on the curing energy (a) 8:1 mole ratio of prepolymer monomer to hexamethylenetetramine (HMTA) (b) 8:1:0.6 mole ratio of prepolymer monomer to HMTA to furfuryl alcohol (c) 8:1:1.2 mole ratio of prepolymer monomer monomer to HMTA to furfuryl alcohol (d) 8:1:0.6 mole ratio of prepolymer monomer to HMTA to methyl anthranilate (e) 8:1:1.2 mole ratio of prepolymer monomer to HMTA to methyl anthranilate (f) 8:1:0.6 mole ratio of prepolymer monomer to HMTA to furfural (g) 8:1:1.2 mole ratio of prepolymer monomer to HMTA to furfural
Figure 7.4 The curing energies measured for the three classes of plasticizers as a function of their concentrations. (a) Furfural, (b) Methyl anthranilate and (c) Furfuryl alcohol

Table 7.1 Solubility of hexamethylenetetramine in different plasticizer

<table>
<thead>
<tr>
<th>Plasticizer</th>
<th>Solubility of hexamethylenetetramine (mg/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furfural</td>
<td>20</td>
</tr>
<tr>
<td>Methyl anthranilate</td>
<td>More than 300</td>
</tr>
<tr>
<td>Furfuryl alcohol</td>
<td>280</td>
</tr>
</tbody>
</table>

7.4.1 Reaction of plasticizers during curing

The most direct evidence showing that the three plasticizers are reacting is shown by using infrared spectroscopy (either mid- or near-). Because of the complexity of the resin and the plasticizers, it is difficult to observe clean distinguishable spectroscopic features for structural analysis. However, there are several localized vibrations that are characteristic of the functional groups present. In the case of F, we observed that the infrared active carbonyl stretching (1660 cm\(^{-1}\)) decreases as a function of time and temperature and completely disappears at a temperature
approaching 150 °C. However, the ring bending vibration assigned previously in the 600 cm\(^{-1}\) region remains unperturbed \(^9\). The infrared data are shown in Figure 7.5. These observations are consistent with the fact that F is reacting during the crosslinking reaction but some its structural features (aromatic rings) remain. Moreover, we have established that F does not react directly with either the prepolymer or HMTA since the F features in binary mixtures with either HMTA or with the prepolymer remain unperturbed. F only reacts in the ternary mixtures with both HMTA and the phenolic resin. In the presence of both, the infrared features assignable to F rapidly change before reaching a temperature of 160 °C. Hence it is possible to conclude that
furfural is changing its structure and in fact reacting with the intermediate products of HMTA and the phenolic resin.

![Graph showing infrared features of furfural](image)

**Figure 7.5** The reaction of furfural during curing of 8:1:1.2 mole ratio of prepolymer monomer to hexamethylenetetramine to furfural sample (a) at 160 °C (b) at 140 °C (c) at 20 °C

Similarly, we have obtained infrared features (Figure 7.6 to Figure 7.8) showing that FA and also MA react with mixtures of HMTA and phenolic resin. Figure 7.6 shows that at approximately 160 °C, the 1st overtone of CH aromatic peak starts shifting towards the lower frequency side. The lower frequency shift of this peak is due to a decrease in the electronegativity of the ring substituted functional group in FA. The infrared data obtained suggest that MA is even more reactive since it can directly react with HMTA and the binary
mixture of the prepolymer /HMTA as shown in Figures 7.7 and 7.8. The reaction of HMTA and MA produces a new peak at approximately 1510 cm\(^{-1}\) which is assigned to the substitution reaction at ortho and para sites \(^{21}\). Due to the overlapping of this peak with the highly substituted phenol in prepolymer we could not observe it in the ternary mixture of prepolymer, HMTA and MA. However, it is possible to observe the reduction in the ring vibration at 1560 cm\(^{-1}\) consistent with the reaction of MA \(^{21}\).

![Graph showing infrared data](image)

**Figure 7.6** Infrared data showing reacting furfuryl alcohol with hexamethylenetetramine and phenolic resin
Figure 7.7 Reaction of hexamethylenetetramine and methyl anthranilate (a). 70 % w/w hexamethylenetetramine and 30 % w/w methyl anthranilate at 20 °C (b). 70 % w/w hexamethylenetetramine and 30 % w/w methyl anthranilate at 150 °C
Figure 7.8  Reaction of methyl anthranilate, prepolymer and hexamethylenetetramine (a) pure methyl anthranilate (b) 8:1:1.2 mole ratio of prepolymer monomer to hexamethylenetetramine to methyl anthranilate sample without curing (c) 8:1:1.2 mole ratio of prepolymer methyl anthranilate sample after 180 °C

Due to the reactive nature of all three of these plasticizers, as stated above the curing energies measured reflect not only the reaction between HMTA and the resin but also the contribution from the reaction of plasticizer as well. In addition, due to the different functionality in each plasticizer, different types of linkages are produced and each linkage has its own curing energy. Therefore, the crosslinking behavior involving these plasticizers are complex and cannot be predicted easily. Since the principal goal of using plasticizer is to increase the crosslink density, the associated mechanical performance and stability at elevated temperatures, we have
constructed some possible structures that can be used to interpret the efficiency in forming crosslinks that we have obtained.

FA exhibits the least effectiveness in mechanical performance. The DSC obtained for FA has two exothermic peaks (Figure 7.3). As the concentration of FA is increased, the area of the higher temperature exotherm increases. We have concluded that the first peak is assignable to the reaction of prepolymer and HMTA and the second peak is associated with the reaction of FA. In addition, a previous study suggests that FA reacts in the latter stages of the curing reaction. In this case the reaction of FA in the curing of prepolymer and HMTA produces the dangling ends with furan ring, which is shown schematically in Figure 7.9. Although the total curing energy when FA is used is significant, the reaction results mainly in the chain terminating structure. Therefore, this structure using FA as a plasticizer will be unattractive in raising sample modulus since the only crosslinks formed will be limited to the few that will inevitably form even in the absence of any plasticizer.

![Figure 7.9](image)

**Figure 7.9** Linkage produces during curing reaction with furfuryl alcohol plasticizer

Probably the most studied of the three plasticizers is furfural. The crosslinking reaction of HMTA and phenol formaldehyde prepolymer may produce as many as 16 different types of linkages of benzoxazine, benzylamine, diamine, tibenzyamine, imine, imide, amide, methylene and others. Furfural can react with either primary or secondary amines formed as
the primary products between HMTA and the phenolic resin. The reaction between furfural and the two types of primary amine produces Schiff base or imine bonds. Similarly, to furfuryl alcohol, two different types of structures can result depending on the reaction with either primary or secondary amines. The formation of the dangling end is shown in Figure 7.10.

![Schiff base (imine) formation reaction of furfural](image)

We have indeed observed that as we increase the concentration of F in the curing mixture, more imine is produced. The characteristic infrared active imine vibrations increase with the concentration of F, time and temperature. It is then possible to conclude that the higher imine formation (-C=N-) is due to the reaction of F and the primary amine. If the structure is as shown in Figure 7.10, in this case, the presence of F does not provide any benefits to the crosslink density needed for mechanical performance.
Figure 7.11  Imine formation of the different sample after curing at 180 °C (a) 8:1 mole ratio of prepolymer to hexamethylenetetramine (b) 8:1:0.6 mole ratio of prepolymer to hexamethylenetetramine to furfural (c) 8:1:1.2 mole ratio of prepolymer to hexamethylenetetramine to furfural

Furfural can also react with the secondary amine forming an extremely attractive crosslinking node (Mannich reaction) \(^{11}\). This reaction as shown in Figure 7.12 is responsible for the increasing the amount of crosslinking density or structural rigidity during the curing reaction, which will be proved below.
Therefore, the reaction of F can produce both dangling ends (Schiff base) or be incorporated into the crosslink structures. Due to difficulty in monitoring the infrared active amine bands, it is impossible to predict the relative amount of the two types of curing products. However, there is no doubt that the development of crosslinks prevails since the mechanical properties achieved using F as a plasticizer are shown to be extremely attractive.

Due to the electron rich ring in MA, ortho and para reaction sites, shown as stars in Figure 7.13, can easily react with the HMTA molecule. In the following figure, the reaction between MA, prepolymer and HMTA molecule is shown. This figure is consistent with the emergence of a new peak at approximately 1500 cm$^{-1}$ which is assignable to highly substituted rings. This observation demonstrates that MA has the ability to dissolve HMTA crystals and reacts with it. We predict that it interacts via the hydroxyl units similar to the interaction between HMTA and plasticized phenolic resin. When all three components are mixed, the prepolymer vibration at 1500 cm$^{-1}$ overlaps with the HMTA and the reacting MA. Therefore, this peak cannot be used for structural analysis. However, the other ring vibration of MA is clearly decreasing in intensity with the curing temperature. That observation is consistent with the fact that MA is reacting with HMTA and phenolic resin.
This scheme shows that MA has the highest reactive functionality followed by furfural and FA. Furfural produces both crosslinked junctions and dangling ends while FA only produces dangling ends. Therefore, it is possible to conclude that MA will show a higher amount of crosslinking as compared to either furfural or FA.

7.4.2 Monitoring crosslinking using LFNMR

Due to the complexity of the curing reaction and the formation of dangling ends in phenol formaldehyde resin$^{1-4}$, it is difficult to measure the amount of crosslinks formed. As shown above, measurements of curing energy do not always relate to the amount of crosslinking achieved. In this study, the amount of crosslinking is measured by measuring the $T_1$ relaxation time using low field NMR (LFNMR). The $T_1$ relaxation time is related to the segmental dynamics of the crosslinked chains. These measurements are carried out at 50 ºC, significantly below the actual glass transition temperature of the crosslinked structure. Therefore, the $T_1$ relaxation time does not originate from the long range cooperative motion of the chain but from the short range ones. As the crosslinking proceeds, this motion will be increasingly restricted, raising the $T_1$ relaxation value. Although all the plasticizers have the ability to plasticize the resin
and to dissolve crystalline HMTA, the crosslinked structures achieved can be quite different depending on the plasticizer used.

Typical data measured for any of the samples are shown in Figure 7.14. It can be seen that the T₁ increases rapidly as a function of time and reaction. The T₁ relaxation times obtained for the crosslinked polymer with different plasticizers as a function of concentration are shown in Figure 7.15. It is clear that MA is the most effective of the three studied. This is consistent with the functionality of each plasticizer as discussed above. The data suggests that MA will have higher functionalities than F. For lower concentrations, the value of T₁ is always greater than the value of T₁ of F. Secondly, it requires less concentration of MA to achieve maximum crosslinking compared to F. This can only be possible if the functionality of MA is higher than F. In the case of FA, the decrease in crosslink density occurs at much lower concentrations. Therefore, it proves that the reaction of FA is not as effective in the generation of the crosslinking but instead increases the number of dangling ends.

Figure 7.14 Magnetization of different plasticized crosslinked product (a) 8:1 mole ratio of prepolymer to hexamethylenetetramine (b) 8:1:0.6 mole ratio of prepolymer to
hexamethylenetetramine to furfural (c) 8:1:0.6 mole ratio of prepolymer to hexamethylenetetramine to furfuryl alcohol (d) 8:1:0.4 mole ratio of prepolymer to hexamethylenetetramine to methyl anthranilate

Figure 7.15  Spin-lattice relaxation $T_1$ vs. mole fraction of different plasticizers (a) furfural (b) methyl anthranilate (c) furfuryl alcohol

It is also important to see that each plasticizer behaves quite differently as a function of concentration. In the case of MA and F, $T_1$ increases up to 0.16 and 0.24 mole fraction respectively, whereas FA is the least effective. For FA, its ineffectiveness can be attributed to the total lack of any enhancement in the crosslink density. The relative difference between MA and F can also be attributed to its extremely high effectiveness in generating crosslinks in MA as
compared to the two types of crosslinks that can exist for F. Based on the data obtained, it is not possible to conclude the origin of this concentration dependence. The function of plasticizer is to plasticize the resin and to dissolve and then disperse HMTA. Since so few of the possible reaction sites actually participate in the crosslinking reaction before segmental mobility effectively ceases, it is impossible to separate the plasticization effect, lowering $T_1$ from the crosslinking reaction, raising $T_1$. The relative amount of dangling ends versus crosslinking in the F reaction is also not known; however, it is clear that these plasticizers react and contribute to the physical properties very differently.

7.5 Conclusions

Furfuryl alcohol, furfural and methyl anthranilate, representing types of reactive plasticizers, have been studied. Their use in dispersing hexamethylenetetramine (HMTA) and phenolic resins to enhance the formation of mechanically robust crosslinked structures has been characterized. The extensive hydrogen bonded network of the resin was disrupted by all three plasticizers. The effectiveness of plasticization was quite different. Since HMTA is highly crystalline, its dissolution in the reaction formulation is also extremely important. In this study, we found the three plasticizers can react with HMTA, resin or its primary reaction products. The crosslinked structures that were formed reflect those differences. Furfuryl alcohol can form mainly chain terminated structures. Therefore its maximum crosslink density as verified by LFNMR is the lowest in this study. Furfural, the most studied of the three, which is used in many organic and inorganic composites, has the potential to form both dangling chains (terminated) or incorporated into the crosslinks. Lastly, methyl anthranilate exhibits the highest potential to form extensive crosslinked structures. This is due to the higher reactive functionalities of methyl anthranilate. Hence, methyl anthranilate is the best candidate suitable for superior mechanical
properties. The hypothesized structures are verified by our various experiments. Although some of the details of the crosslinking reaction and the final structures remain unresolved, our studies have raised our understanding regarding the role of plasticizers in the reaction of dissimilar components.

7.6 References


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CHAPTER 8

CONCLUSIONS AND FUTURE WORK

8.1 Conclusions

In this thesis, the role of dispersing agent plasticizer for the molecular dispersion of two rigid reactants- a crystalline crosslinker hexamethylenetetramine (HMTA) and hydrogen bonded phenolic resin was studied. The plasticizer with polar functional group and delocalized ring can break the –OH----OH hydrogen bonding, OH--- π hydrogen bonding and π-π ring-ring interaction. This increases the segmental mobility and the free hydroxyls. Using infrared spectroscopy, DSC and NMR enhancement of the segmental mobility was characterized with the traditional plasticizer furfural. This was described in chapter 4 and 5.

Additionally, for furfural the mechanism for the dissolution of crystalline crosslinker HMTA was understood using the newly developed internal standard NMR method with duroquinone as an internal standard. The solubility of HMTA in furfural was found to be only 0.14 mole/liter, however, the role of furfural in the plasticization of the prepolymer was significant. By calibrating the infrared active C-N stretching vibration against an isolated HMTA molecule found in the upper atmosphere we were able to establish that hydrogen bonding may have formed between the HMTA and free hydroxyl units prepolymer. Based on both infrared and NMR data, it was clear that HMTA is highly soluble in the plasticized prepolymer. In this study, we have deduced the molecular origin of the intermolecular interaction between HMTA, furfural and the prepolymer, thus able to explain the crosslinking reaction better.
The efficiency of furfural in terms of the crosslinking was measured using infrared spectroscopy, DSC and LFNMR. Infrared spectroscopy was used effectively to monitor the various states of HMTA. Using DSC curing energy data, a step-by-step dissociation of HMTA molecule was observed. Even with the complexity in the curing reaction, the low field NMR spin lattice relaxation time $T_1$ technique proved to be effective for measuring the extent of crosslinking achieved during curing. In addition, sample preparation for LFNMR is easy. The instrumentation is also relatively easy to operate. The various $T_1$ spin-lattice values obtained can be directly correlated to the segmental mobility, and thus to the extent of crosslinking. In every case, the result from LFNMR was supported by thermal and spectroscopic analyses. The combination of these three techniques have provided a clear explanation of the plasticization process and the subsequent crosslinking reaction at elevated temperatures. It is abundantly clear that the use of a plasticizer, furfural, increases the extent of crosslinking by increasing the overall mobility and dispersion of the reactants.

We have shown that for the measurement of the crosslinking LFNMR $T_1$ is the most appropriate method in phenolic system in chapter 5. For this we also needed to validate the relationship between the segmental mobility measured from LFNMR spin lattice relaxation time and the amount of crosslinking. In chapter 3, we have correlated the amount of crosslinking in rigid epoxy system with the LFNMR spin lattice relaxation time. As the crosslinking increasing the $T_1$ minima occurs at the higher temperature and the magnitude of $T_1$ minima also increases. Due to high frequency probe in the LFNMR than the dynamic and the dielectric relaxometry, the measured molecular motion at the $T_1$ minima is coming from the short range motion. Due to complexity in the motions in polymeric system, this short-range motion was explained in terms of the Fuoss -Kirkwood distribution function. By fitting the spin lattice relaxation data at
different temperatures in the modified BPP theory, activation energy and width parameter were calculated. As the crosslinking increases the activation energy and the width of the relaxation spectrum increases. This is because of the higher coupled motion in the more crosslinked epoxy system.

After understanding the role of traditional toxic plasticizer furfural and developing the method for characterizing the amount of crosslinking using LFNMR, we have discovered the different class of green plasticizers for the phenolic crosslinking. We have characterized the plasticizers in two categories. One which react and the other which does not react. In the first category, we have used the methyl benzoate as a green plasticizer liquid. The infrared data of cured product shows its non-reactivity during the curing. Using DSC, it was shown that the plasticizer, methyl benzoate increases the segmental mobility and the number of free hydroxyl units in the phenolic prepolymer. These increases are responsible for the higher solvation of HMTA during its reaction. Due to higher solvation and segmental mobility in the plasticized sample higher amount of the functionalities of HMTA reacted. The functionality of HMTA reacted is monitored using DSC curing energy. By measuring the segmental mobility of the crosslinked product using low field NMR it was proved that up to certain level of concentration of methyl benzoate the crosslinked density increases.

Furfuryl alcohol, furfural and methyl anthranilate, representing types of reactive plasticizers, have been studied. Their use in dispersing hexamethylenetetramine (HMTA) and phenolic resins to enhance the formation of mechanically robust crosslinked structures has been characterized. The extensive hydrogen bonded network of the resin was disrupted by all three plasticizers. The effectiveness of plasticization was quite different. Since HMTA is highly crystalline, its dissolution in the reaction formulation is also extremely important. In this study,
we found the three plasticizers can react with HMTA, resin or its primary reaction products. The crosslinked structures that were formed reflect those differences. Furfuryl alcohol can form mainly chain terminated structures. Therefore, its maximum crosslink density as verified by LFNMR is the lowest in this study. Furfural, the most studied of the three, which is used in many organic and inorganic composites, has the potential to form both dangling chains (terminated) or incorporated into the crosslinks. Lastly, methyl anthranilate exhibits the highest potential to form extensive crosslinked structures. This is due to the higher reactive functionalities of methyl anthranilate. Hence, methyl anthranilate is the best candidate suitable for superior mechanical properties. The hypothesized structures are verified by our various experiments. Although some of the details of the crosslinking reaction and the final structures remain unresolved, our studies have raised our understanding regarding the role of plasticizers in the reaction of dissimilar components.

8.2 Future work

The main objective of this thesis is to understand the role of plasticizer in phenolic curing reaction and the establishment of the method for characterization of crosslinking in rigid phenolic system using low field NMR. We have not focused on the effect of the plasticizer on the mechanical properties. Therefore, it will be interesting to study the relationship between the elastic modulus, toughness, yield strength and stiffness to the amount of crosslinking. Due to rigid nature of phenolic system, the room temperature elastic modulus does not depend on the amount of crosslinking. Hence, the measurement of the mechanical properties at elevated temperatures will be more beneficial. This study can be done both in tension and compression modes using an Intron with environmental chamber. Dynamic mechanical analysis studies and ultrasonic sound wave propagation can give vital information about the mechanical properties as
well. Owing to the non-Gaussian behavior of the chain between two crosslinked junctions, the relationship of the modulus and crosslinking will not follow the rubber elasticity model. Therefore, it will be interesting to see how much the rubber elasticity model differs in this kind of highly crosslinked rigid sample. This will be important for the application and for the development of new physics regarding the micro and macro properties correlation.

I strongly believe that the dissociation of HMTA and the functionalities use of HMTA molecule highly depends on its hydrogen bonding coordination number. A theoretical determination of the coordination number can be done using group contribution methods. Experiments can also be done to see if there’s any deviation from theoretical predictions. One can experimentally measure the hydrogen bonding co-ordination number changes at high temperature by monitoring the changes of the C-N stretching and the C-N-C bending infrared assignments. This experiment was not done in my study due to lack of high temperature diffuse reflectance accessory for the mid infrared spectroscopy. Moreover, by comparing the infrared spectrum for different hydrogen bonded coordinated HMTA with measurements done at high temperatures, we can experimentally evaluate the changes in the co-ordination number and its effect on the amount crosslinking. This will give a more molecular insight about the role of different plasticizer.

In this study, we have not done a detailed quantitative study of the characterization of the different types of chemical linkages produced with different plasticizers due to complexity associated with the linkages. Quantitative studies can be done using solid state NMR with the 13C labelled HMTA molecule and the plasticizer molecules. By synthesizing the crosslinker HMTA and the plasticizer molecule using 13C labelled we can increases the signal to noise ratio in solid state NMR and can measure small amounts of linkage in it. Moreover, by measuring the
T1C relaxation time of the different linkages we can also characterize the stiffness of different linkages produced due to the reaction of plasticizer. This will be very important study for the selection of new plasticizer which provide high stiff linkages.

In this study, we have developed a new characterization method using the spin lattice relaxation time $T_1$ of LFNMR for the crosslinking measurement in rigid crosslinked thermoset. We do not have a proper comparison of the relationships between the $T_1$ derived from LFNMR and the mobility measured by other methods such as dynamical mechanical analysis, dielectric spectroscopy, ultra sound spectroscopy and so on. By doing a frequency temperature correlation, by changing the frequency from 0.1 Hz region to MHz region with different spectroscopy. We can qualitatively correlate the motion measured by $T_1$ with other spectroscopy methods. Moreover, the molecular mobility is important for the detailed understanding of the physics of polymer crystallization, polymer aging, phase separation kinetic in polymeric systems, absorption and desorption of small molecules in polymeric system.
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