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Molecular Interpretation of a Trigger for Controlling an Amine Isocyanate Polyurethane Reaction

Katherine V. Carrasquillo
University of Massachusetts Amherst

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MOLECULAR INTERPRETATION OF A TRIGGER FOR CONTROLLING AN
AMINE ISOCYANATE POLYURETHANE REACTION

A Thesis Presented

by

KATHERINE V. CARRASQUILLO

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

Master of Science

September 2015

Polymer Science and Engineering

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Approved as to the style and content by:

Shaw Ling Hsu, Chair

Jessica Schiffman, Member

David Hoagland, Department Head
Polymer Science and Engineering

DEDICATION

I would like to dedicate this to all of those that have invested in the person I am today. I could have not reached my goals in life if they had not taken the time to poured their knowledge and wisdom into my life.

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I want to express my deepest gratitude to the members of my thesis committee for all their support, input, and guidance. Dr. Shawn Ling Hsu, my committee chair, I truly appreciate the opportunity of working with him and learning from him during this journey. Dr. Jessica Schiffman, my committee member, I am grateful for her input and her willingness to help during the course of my thesis work.

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Finally, and above all, I want to thank God for sustaining me throughout this entire process.

ABSTRACT

MOLECULAR INTERPRETATION OF A TRIGGER FOR CONTROLLING AN AMINE ISOCYANATE POLYURETHANE REACTION

SEPTEMBER 2015

KATHERINE V. CARRASQUILLO, B.A., UNIVERSITY OF PUERTO RICO AT
HUMACAO

M.A. UNIVERSITY OF MASSACHUSETTS AMHERST

Directed by: Professor Shawn Ling Hsu

The temperature profile needed to complete the reaction between the sodium-diamine complex and the isocyanate terminated prepolymer has been established. The sodium diamine complex has the advantage of blocking the nearly instantaneous reaction between the diamine and isocyanate from taking place until it is released at elevated temperatures. Because of its low melting temperature (~40 °C) and its low molecular weight (low viscosity), this chain extension reaction is not dependent on the participation of the prepolymer. Instead, the rate of reaction is dependent on the dissolution of the 4,4'-methylenedianiline (MDA) complex into the system. The dissolution of the MDA complex has been demonstrated to be strongly dependent on particle size. Both the plasticizer Bis(2-ethylhexyl) adipate and the quaternary ammonium compound found in soy lecithin play crucial roles for this reaction. The quaternary ammonium compound is crucial in the dissolution of the complexes. Although the plasticizer has been shown to dissolve the complex to a small extent, the principal role of the plasticizer is to disperse the complexes and to prevent their agglomeration. Other additives such as Dimethyl Sulfoxide (DMSO) have demonstrated to be highly efficient in dissolving the complex. However its effectiveness limits the mixing window needed before reaction take place, resulting in a disadvantage.

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CHAPTER 1

CONTROLLED POLYUREA REACTION

1.1 Introduction

Polyurethane chemistry comprises of more than 50 years of history and development with more than 1,000 research papers in publication. Polyurethanes have widespread use in industrial, medical and automotive application due to their versatile application as adhesive, flexible foams, elastomers, coating and others.¹ The well established chemical reaction consists of a diol or an amine reacting with a diisocyanate group in order to form urethane linkages or urea linkages respectively.² The main objective of this research is to control the rate of a polyurea reaction at a time scale suitable to form large scale objects.

It was brought to our attention that a commercially available system involving an isocyanate terminated prepolymer and sodium-diamine complex can be used for creating large elastomeric polyurethane.^{3, 4} The curative (sodium-diamine complex) in this system has the advantage that it blocks the nearly instantaneous reaction between isocyanate and the diamine units, inhibiting the reaction to take place until the amine is release at elevated temperatures. This allows a significant improvement in the mixing time needed to create large objects. However, the ability to extract the Na^+ atoms from the diamine complex is virtually unstudied. In this study we have explored the various aspects to control the ability to extract Na^+ atoms as a function of temperature, size, plasticizing liquid and other additives.

The structure of the complex was first reported by Jarvis and Owston in 1971 to be an octahedral structure formation where all six amino group are coordinated to sodium

chloride⁵ (Figure 1). The complex demonstrated to have a structure where all six nitrogen of the amine formed a bond with the sodium (N-Na) and only one of the hydrogen of each amine formed a bond with the chloride (H-Cl). The second hydrogen of each diamine does not have explicit interaction with Cl⁻. It is this interaction between the nitrogen and sodium that cause the structure of the MDA to form a paracyclophane⁶ structure barricading it from reacting with NCO. At elevated temperatures (~170 °C) the sodium can be extracted and the reaction is able to take place.⁷

The need of elevated temperature for the removal of the Na⁺ ion presents high energy cost inefficiency, therefore in order to improve the mechanics of the reaction and its efficiency the temperature needed to release the NH₂ must be lowered. The rate of reaction is fully dependent on the ability to dissociate the MDA complex.

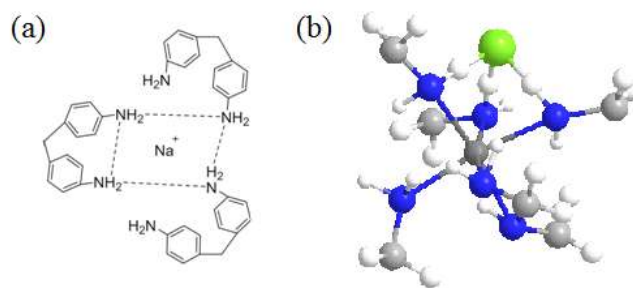


Figure 1 Synthesized MDA complex structure (a) upper 1D view (b) 3D view, where green is Cl⁻, dark center gray is Na⁺, blue is N, white is H and light gray is C.

Processing large scale products of the curative system requires an external heating source where the complex has to be able to reach a threshold dissociation temperature for curing to take place. Elastomeric polyurethanes have been known to be poor thermal conductors⁸, leaving a significant temperature gradient between the inner and outer section of the products. Concerning a cylindrical polyurethane system curing (Figure 2) with an

external heating source of 90 °C, and a thermal conductivity of $k_{pu}=0.02\text{W/mK}$ at heating rate of $q=1$, the calculated temperature gradient can be as high as 36 °C. Therefore inhomogeneity exists in such a system with only partial curing on the inside of the cylinder.

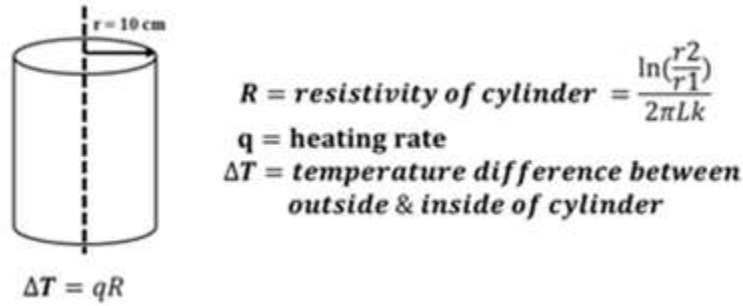


Figure 2 Thermal conductivity calculations.

The dissociation temperature of the MDA complex have been studied to be size dependent, where smaller particles have a lower dissociation temperature than larger ones, therefore dissolving easier into the system.⁹ The dependence of size in particle solubilization is shown in the equation illustrated in Figure 3, where the MDA complex is assumed to be spherical for simplicity. Evaluating a particle with a size of $5\mu\text{m}$ that contains a layer thickness of 1nm would results in less than 1% of the surface being solubilized. Nevertheless controlling particle size still presents a difficult task in this research. Consequently for the purpose of this study the same batch of particle will be used for every comparative analysis with the assumption that their size distribution is relatively the same.

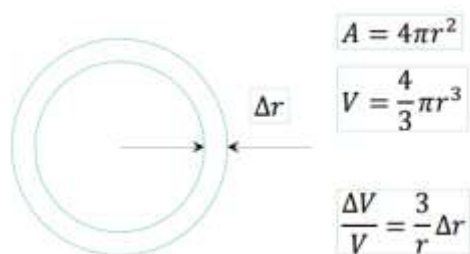


Figure 3 Kinetics of dissolution.

In order for a uniform chemical reaction to occur, it is necessary to disperse these complexes at the molecular level. As mentioned previously small particles results in lower dissociation temperatures, however they also show a tendency towards agglomeration. Therefore a plasticizer will be studied for the purpose of promoting dispersion and suspension of the complex. The effect of this plasticizer on the dissociation of the complex will also be address.

The dissociation of the complex has been address by physical mean (grinding); however the effects of chemical additives will also be taken into consideration. The effect of charge additive on dissociating the complex is studied by implementing the principle of charge neutrality where the removal of one of the ion induces its counter ion to follow.¹⁰ The charge additive used for this study is soy lecithin, a naturally occurring organic compound containing two quaternary ammonium compounds. The quaternary ammonium compound is thought to be responsible for the extraction of the salt ion, which occurs at elevated temperature due to soy lecithin high viscosity slowing down the ion extraction process.

Beside the effects that the charge in additives has on the dissociation of the complex, polar additives will also need to be considered, to dissolve the complex

efficiently. Dimethyl sulfoxide (DMSO) being a highly polar molecule with a relatively large dipole will be studied for its ability to dissolve the MDA complex. The dissociation of the complex can occur by two means, solubilizing one of its components which would cause the other to precipitate or solubilizing the entire complex.¹¹

The effectiveness of these additives will be studied in terms of complex dissociation temperature, curing temperature and urea formation. These chemical additives must be compatible with the complex, prepolymer, and plasticizer since inadequate miscibility will lead to a phase separation in the system, hindering curing. Finding one single component that can address these considerations will be the ideal scenario. However, the possibility of adding a multi-component system to enhance the dissociation of the complex will also be considered.

Therefore controlling the rate of reaction requires controlling the dissociation of the complex at a low temperature that also allows for adequate mixing. The dissociation of the complex will be studied under the effects of physical grinding and chemical compounds (plasticizer and additives). The effects of these properties on the complex will be addressed in order to lower the dissociation temperature and enhance the solubilization of the complex in the cured system while maintaining a controlled reaction.

1.2 Experimental section

1.2.1 Materials and preparation

1.2.1.1 MDA complex

The commercially available product known as Duracure C3LF is already dispersed in a DOA plasticizer and may contain additional additive making it inconvenient to characterize. Therefore the neat form of MDA complex was synthesized in order to study its dissociation kinetics. This MDA sodium complex was obtained by solution precipitation of a sodium chloride salt with 4,4'-methylenedianiline (MDA).¹² The synthesized compound consisted in first dissolving 4,4'-methylenedianiline in methanol in a respective weight ration of 1:4. The salt was then dissolved in water in a weight ratio of 0.2:1, respectively. Both were then mixed and heated to 50 °C for 3 hours.³ After the precipitate of the complex is formed, it is then filtered. The re-crystallization of the complex is also conducted in an aqueous solution of 4:1 methanol-water which give a yield of 65-75% isolated tris(4,4'-diaminodiphenylmethane) sodium chloride referred here as MDA sodium complex.¹³ After the sample has been air dried it was characterized using attenuated total reflectance (ATR).

1.2.1.2 Prepolymer C900

One pint of the isocyanate terminated polycaprolactone polyester prepolymer commercially known as C900 was obtained from Chemtura Corporation. In order to extract the prepolymer the pint was heated at 70 °C for 16-24 hours, since at room temperature the prepolymer is semicrystalline. The C900 is then place in a nitrogen filled glove bag were several sample can be extracted using a syringe containing a large tip. The samples were then place inside a small plastic container, where they are later place in a

sealed container with desiccants which was stored inside a nitrogen filled glove box, in order to avoid any reaction with moisture.

1.2.1.3 Plasticizer

Although many plasticizers are commercially available, for the purpose of this research the role of the plasticizer used in the Duracure system known as Bis(2-ethylhexyl) adipate (BEHA) was studied.¹⁴ A total of 100 g of this plasticizer was purchased from Alfa Aesar and stored at room temperature.

1.2.1.4 Additives

Two main additives were studied in this research based on polarity and charge (referred to chapter on additives)

- Dimethyl sulfoxide (DMSO)

This chemical was purchased from Fisher Science at a volume of 100 ml and was considered in term of polarity and ability to dissolve the complex.

- Soy lecithin

This compound was obtained from Chemtura Corporation Lot # T18000 2842-98 and was considered based of charge molecules.

1.2.2 Component mixing

1.2.2.1 Mixing C900 and MDA complex

A Denver Instrument A-250 balance was used to determine the amount of complex and prepolymer needed. A sealed glass vial was first weighed and placed in the glove box. This vial was then purge with nitrogen before inserting a small amount of the C900. In order to avoid excess thermal history the sample of C900 was taken at room temperature by breaking off a piece using a spatula.¹⁵ Once placed in the vial, it was sealed and the

amount of gram of C900 was measured. A 1:1 equivalent mole ratio of NCO to NH₂ was calculated base on the chemical structure. Knowing that there are two NCO groups in one prepolymer chain and six NH₂ group for one complex the following equations were established:

$$1 \text{ mol C900} = 2 \text{ mol of NCO} \quad (1)$$

$$1 \text{ mol of complex} = 6 \text{ mol of NH}_2 \quad (2)$$

Hence from this we note that

$$\frac{1}{2} \text{ mole of C900} = 1 \text{ mol of NCO} \quad (3)$$

$$\frac{1}{6} \text{ mole of complex} = 1 \text{ mol of NH}_2 \quad (4)$$

Therefore having determined the molecular weight of the complex to be 653.25 g/mol and the molecular weight of the prepolymer to be 2212.6 g/mol we divided them by the mol of NCO and NH₂ respectively.

$$\frac{653.25 \text{ g/mol}}{6} = 108.9 \text{ g} \quad (5)$$

$$\frac{2212.6 \text{ g/mol}}{2} = 1106.3 \text{ g} \quad (6)$$

Finally the ratio of complex to prepolymer was obtained

$$\frac{108.9}{1106.3} = \frac{\text{Complex}}{\text{C900}} \quad (7)$$

From this ratio the amount of complex needed can be calculated. Once this amount was measured in a separate vial, the prepolymer was heated alone at 50 °C until it reaches

the molten state, this can take a few minutes depending on the amount of C900 inside the sealed vial. Then both vials (complex and C900 vials) are placed in the glove box and mixed together using a spatula.

1.2.2.2 Mixing MDA complex with plasticizer

A constant amount between plasticizer and complex that was established for the commercial product Duracure C3LF was used with the purpose of understanding the role that plasticizer has in the dissociation and curing of the system.¹⁶ The weight percent used in this mixture is 44% of MDA complex in 56% of BEHA.¹⁴ This mixture is referred here as a 44complex. This mixture can be prepared in two ways.

- An amount of MDA complex is weighted and mixed with 56% by weight of plasticizer for 30 minutes until the mixture is milky white due to partial solubilization. Once this solution is obtained the complex is hand grinded for 2 minutes to eliminate chunks.
- Before mixing the MDA complex and plasticizer the complex is grinded in a ball mill (ICL C32003A grinder) for 10 minutes. Afterwards the MDA complex is mixed with 56% by weight of plasticizer for approximately 30 minutes until its appearance is milky white.

1.2.2.3 Mixing C900 with the 44complex

The amount of prepolymer was obtained following the same procedure as described above. The mixture of C900 and 44complex was done in a 1:1 equivalent mol ratio of NCO to NH_2 . To determine the amount of complex needed the same equations used for the C900 and the complex were used here with the exception that the amount of plasticizer

must now be taken into account. This was done considering the weight ratio of plasticizer to complex in the following matter:

$$\frac{56 \text{ wt } \%}{44 \text{ wt } \%} = \frac{\text{plasticizer}}{108.9g} \quad (8)$$

$$138.6g = \text{plasticizer} \quad (9)$$

This amount of plasticizer was then added to the amount of complex of 108.9 g to give a total of (247.5 g). Hence the ratio of 44complex to prepolymer becomes:

$$\frac{247.5 \text{ g}}{1106.3 \text{ g}} = \frac{44\text{Complex}}{C900} \quad (10)$$

From this we can calculate the amount of the 44complex needed. The prepolymer was then melted at 50 °C and then mixed with the 44complex inside the glove box to avoid any reaction with moisture.

1.2.2.4 Mixing additives

Additives were added into the system by first mixing them with the plasticizer in a weight ratio of 5% additive into 95% plasticizer. Afterward the solution of 44complex was made by combining the 56% by weight of this solution with 44% by weight of complex. This solution was then stirred until the mixture is milky white.

CHAPTER 2

CHARACTERIZATION TECHNIQUES USED

2.1 Differential scanning calorimetry (DSC)

A TA Q100 differential scanning calorimetry (DSC) instrument with RCS cooling system was used for the determination of curing profile and dissociation kinetics of both prepolymer and complex. The instrument temperature was calibrated using the onset melting temperature of indium oxide of 156.6 °C. The heat of flow was calibrated using the heat of fusion of Indium oxide (28.6 J/g). An aluminum hermetic pan were used to sealed the samples (3-10 mg) and run at a heating/cooling rate of 5 °C/min in nitrogen flow environment of 50 ml/min. All samples were prepared inside a nitrogen filled glove box in-order to avoid exposure to the moisture in the environment. A TA instrument Universal Analysis software was used for sample analysis. The melting, dissociation and curing temperature were taken over the midpoint between the onset and inflection of the tangent of these peaks and the energy associated with these profiles were taken to be the area of the endothermic or exothermic peaks.

2.2 Thermogravimetric analysis (TGA)

For the degradation of the components Q50 TA instrument was used under nitrogen flow. No more than 10 mg of samples were placed in a platinum TGA pan and then heated from an equilibration of 0 to 900 °C. A TA instrument Universal Analysis software was used in sample analysis.

2.3 Nuclear magnetic resonance (NMR)

To determine molecular weight of the prepolymer and composition, proton NMR was carried out using a 400 MHz Bruker NMR at room temperature. The prepolymer was

dissolved using d₆ DMSO obtained by Cambridge Isotope Laboratories and placed in a Chemglass Life science 7" long 400 MHz glass NMR capped tube. Analyses of the samples were done using MestReNova software and the deuterated solvent peak was used as the internal calibration standard.

2.4 Infrared Spectroscopy

Both Perking Elmer FTIR Spectrum 100 and Spectrum 400 were used to conduct high temperature transmission infrared spectroscopy. Using two unpolished KBr windows (25mm X 5mm) obtained from International Crystals Labs and polishing them using a polishing kit, a thin amount of the sample was placed between the two windows. This was done inside the glove box in order to avoid moisture exposure to the sample. The sample assembly was then placed in a heating stage and heated at a rate of 5 °C/min using a Watlow SD6C-HCAA-AARG temperature controller. The infrared scans were obtained every 10 minutes to assure that uniform temperature was achieved.

Since the complex and the prepolymer are solid at room temperature, ATR was conducted on the prepolymer and MDA complex using a Perking Elmer FTIR Spectrum 100 together with a universal ATR sampling accessory. A diamond crystal was used as the reflectance unit and pressure was applied on the samples using a pressure arm. The sample was scanned at room temperature and the background for each sample was scanned using the finished side of a piece of aluminum foils.

CHAPTER 3

MATERIAL CHARACTERIZATION

3.1 Complex synthesized

3.1.1 Structural analysis

ATR was conducted on the synthesized MDA complex to confirm its formation. The absorption spectra of the MDA complex (Figure 4) shows two characteristics absorption bands¹³ at 3377 and 3276 cm^{-1} (Figure 4 inset (a)). These two absorption bands were attributed to the complex asymmetric and symmetric NH stretchings.^{13, 17} The complex structural configuration causes the aromatic ring of the complex to forms a paracyclophanes structure with a characteristic band at 856 cm^{-1} , demonstrated in inset (b) of Figure 4. This band plays a role in determining complex dissociation since the dissociation of the structure will cause this band to diminish and shift. The presence of these reported bands confirms the synthesis of the MDA complex.

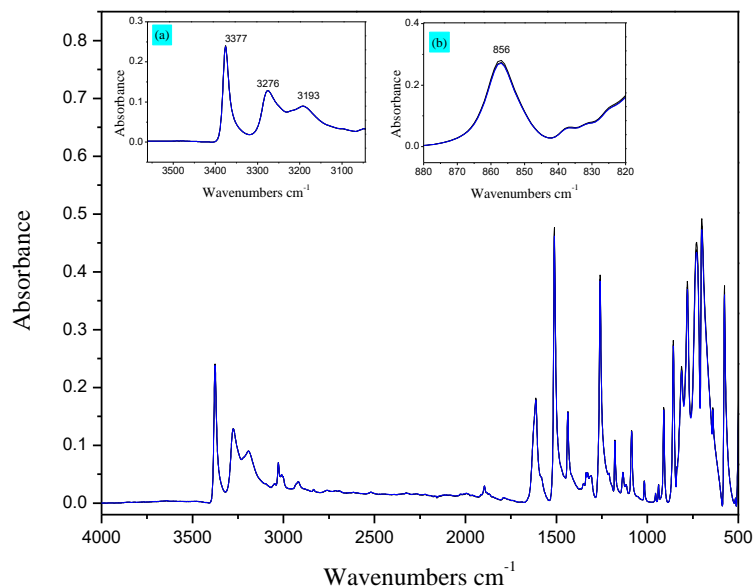


Figure 4 ATR data of MDA complex. Inset: (a) MDA complex NH region (b) The MDA complex paracyclophane peak at 856 cm^{-1} .

3.1.2 Temperature degradation analysis

Since the dissociation of the complex is triggered by temperature it is important to understand when degradation occurs. Thermogravimetric analysis (TGA) was conducted on the MDA complex and the pure MDA for comparative purposes (Figure 5). Both the MDA and the complex show similar degradation profile, as would be expected. The MDA complex shows a further weight loss of 8.72% that was attributed to the salt degradation. For means of analysis three temperatures were selected 200 °C, 175 °C and 150 °C. The TGA data of these temperatures shows that at the highest temperature of 200 °C there was a lost in weigh of ~10%, at 175.4°C there was a weight loss of 2% and at 150 °C there was no measurable weight loss. The complex as mentioned earlier presents dissociation around 170 °C with a relatively small degradation of ~2%. At 200 °C and above the degradation of the MDA become more significant.

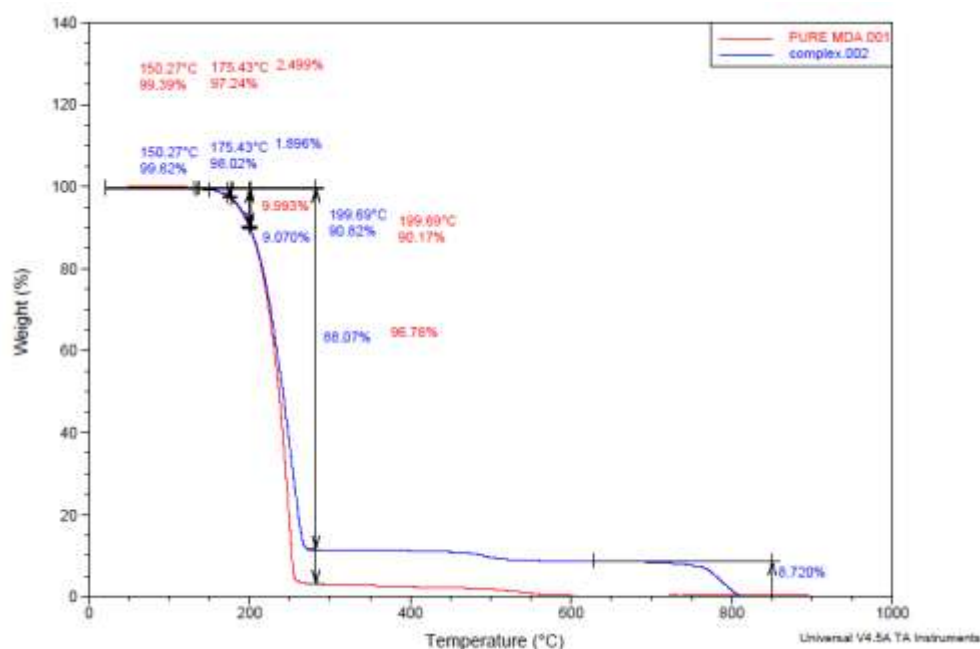


Figure 5 Thermogravimetric analysis of both the MDA complex and the pure MDA.

3.2 Prepolymer (C900)

3.2.1 Molecular weight analysis

The molecular weight and composition of the C900 was determined using ^1H NMR. The NMR data (Figure 6) shows a multitude of peaks in the aromatic region at 7 ppm due to the presence of MDI. Table 1 shows the NMR peaks related to the C900 prepolymer.¹⁸ The molecular weight of C900 was determine to be 2212.6 mg/mol by using the peak related to NH at 9.5 ppm (inset in Figure 6) as a known moiety¹⁹ and applying equation 11 to calculate the prepolymer repeat unit.

$$n_x = \frac{a_x m_y n_y}{a_y m_x} \quad (11)$$

Where a_y is the peak area of the known moiety which in this case is NH m_y and n_y is the number of proton and the repeat unit respectively of NH. The a_x is the total area of all the peaks related to the prepolymer; m_x is the number of protons present in the prepolymer while n_x will be the obtained repeat unit²⁰. Once the repeat unit is obtained the molecular weight can be calculated by multiplying the molecular weight of the prepolymer with the repeat unit and adding the total molecular weight of the end groups as shown in equation 12.

$$M_w = M_{eg} + n_x M_{pp} \quad (12)$$

Where M_{eg} is the molecular weight of the end groups and M_{pp} is the molecular weight of the prepolymer.

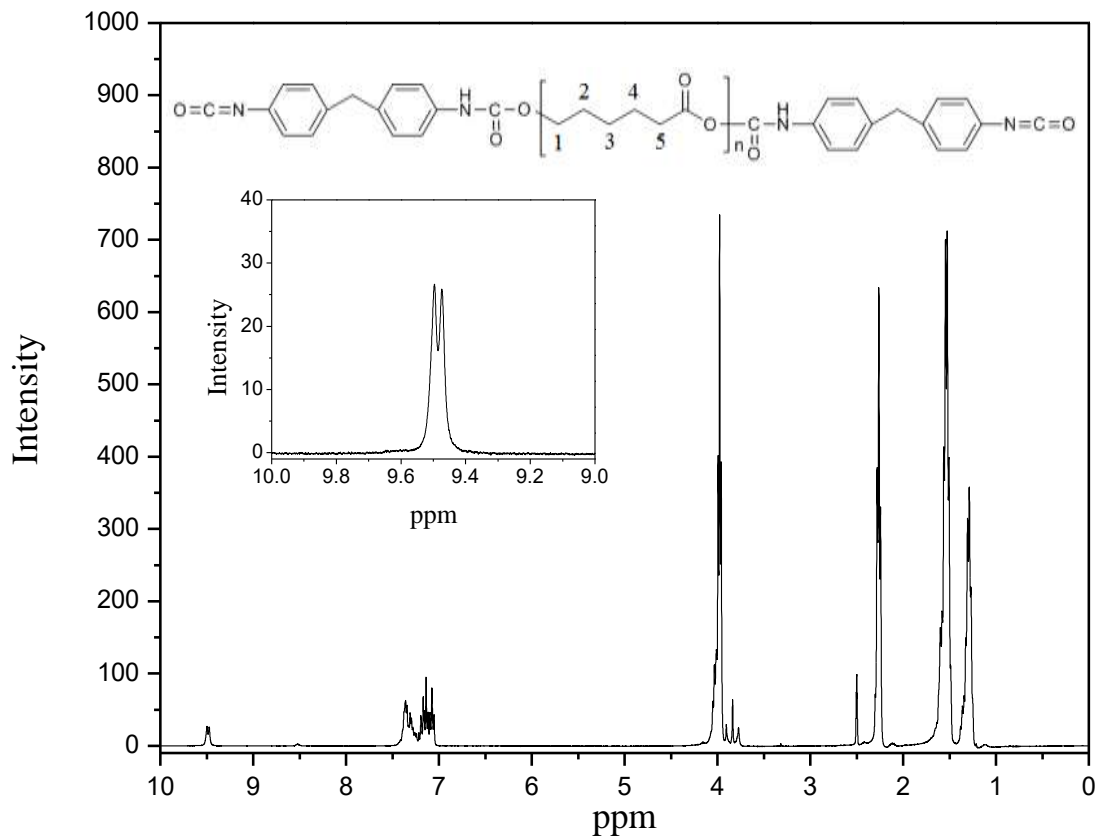


Figure 6 ^1H NMR of C900.

Table 1 ^1H NMR data of the C900 prepolymer

δ (PPM)	Assignments
4.01	H_1 (t)
2.25	H_5 (t)
1.52	$\text{H}_2 + \text{H}_4$ (m)
1.29	H_3 (m)

3.2.2 Structure

The ATR spectrum of the prepolymer was conducted in order to identify changes in the spectrum after curing. Figure 7 present an absorption band at 2260 cm^{-1} attributed to the presence of NCO. The NH of the aromatic MDI is shown at 3350 and 1520 cm^{-1} along with the aromatic rings at 1600 cm^{-1} marked by the arrow in Figure 7 while the sharp band at 1710 cm^{-1} is the internal ester.²¹

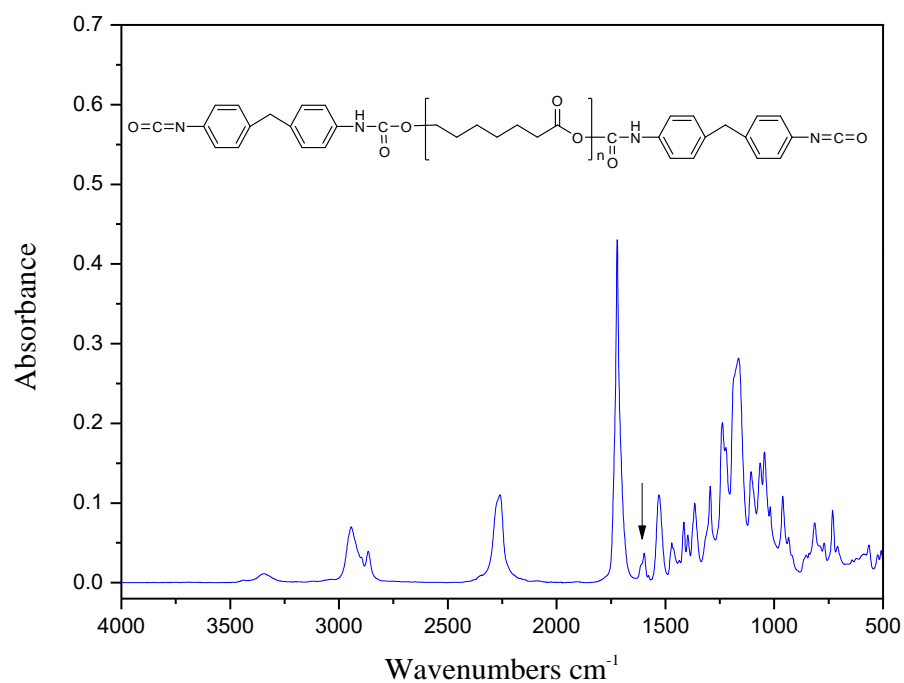


Figure 7 ATR spectroscopy of C900.

3.3 Plasticizers

3.3.1 Bis(2-ethylhexyl) adipate structure

The structure of BEHA is shown in Figure 8 along with its IR spectrum where the C=O (carbonyl) shows a strong absorption band at 1734 cm^{-1} and the CH stretching is shown as several peaks in the region of $2800\text{-}3000\text{ cm}^{-1}$.

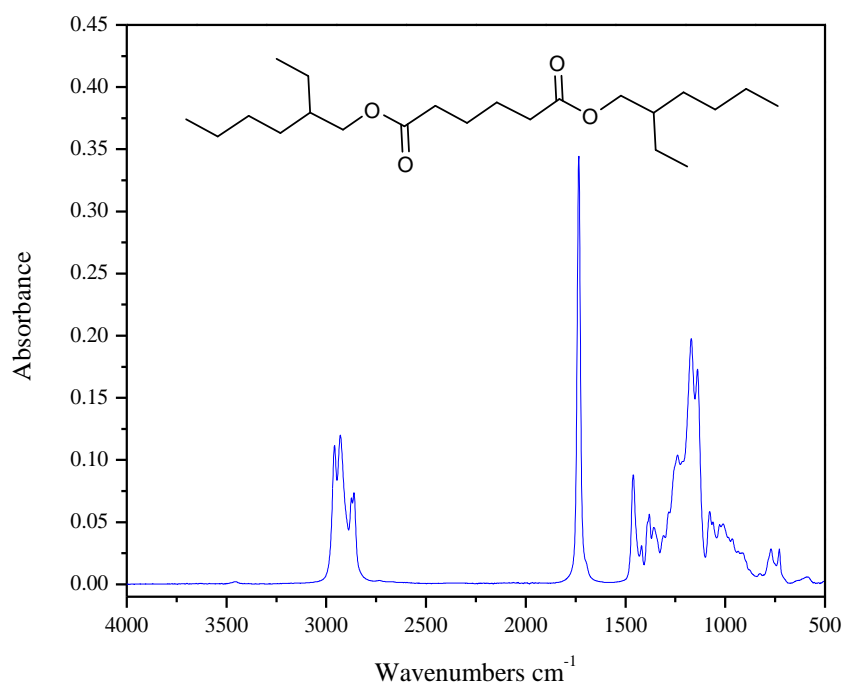


Figure 8 FTIR of Bis(2-ethylhexyl) adipate.

3.4 Soy lecithin

3.4.1 Structure

The molecular structure of soy lecithin contains two charged molecules of interest as shown in Figure 9 (a). From the IR spectrum in Figure 9 (b) several bands can be identify such as the bonded OH at 3305 cm^{-1} , a strong CH stretching band at $3113\text{-}2855\text{ cm}^{-1}$ and a sharp C=O at 1749 cm^{-1} .

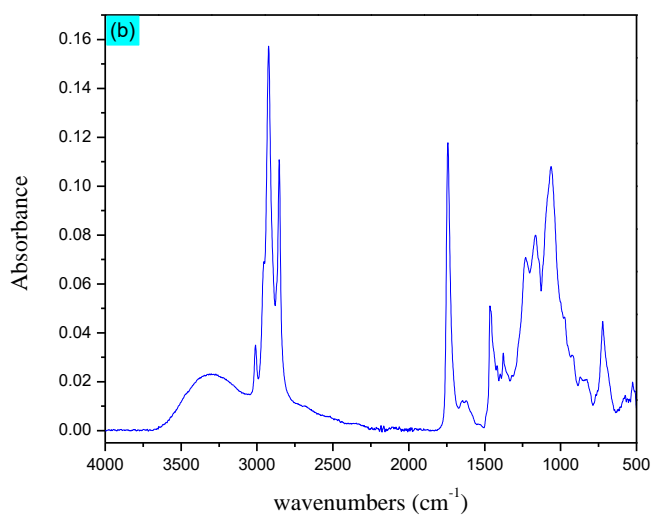
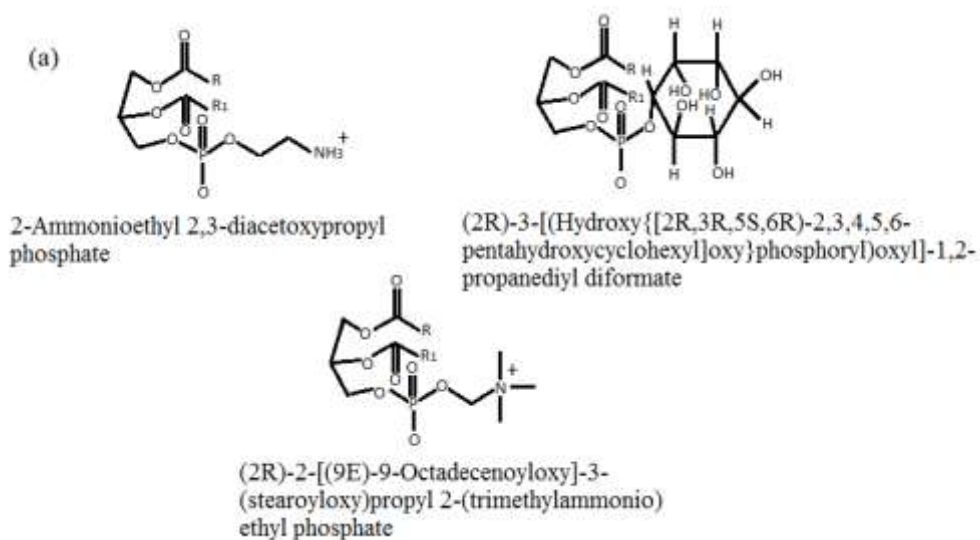


Figure 9 Soy lecithin: (a) Chemical structure (b) Infrared spectrum.

CHAPTER 4

CURING CHARACTERIZATION

4.1 MDA complex dissociation analysis

The dissociation of the pure complex was studied in order to understand the effect that plasticizer and additives have on the polyurea reaction kinetics. Using high temperature IR the molecular changes during the dissociation of the complex can be studied by monitoring the paracyclophane absorption band at 856 cm^{-1} . This band is associated to the structural formation of the complex and is shown in Figure 10 inset b. For clarity this figure only demonstrates the temperatures that showed the most significant changes in this band. As the complex dissociates this band is seen to decrease and shifts to lower wavenumbers. This shift from 856 to 851 cm^{-1} is associated to the complex dissociation which occurs at the temperature of $150\text{ }^{\circ}\text{C}$. The change in intensity observed for this band can be related to structural alteration of the complex at the molecular level; due to its dissociation as a function of temperature.

Along with the changes seen in the paracyclophane band there are also expected changes in the NH_2 region that occur with the release of the MDA from its complex form. The broad NH_2 absorption band in inset a of Figure 10 is shown to disappear as temperature increases and two new bands appear at 3211 and at 3445 cm^{-1} . These new peaks occur at $150\text{ }^{\circ}\text{C}$ which correlate with the dissociation of the complex and the release of MDA.

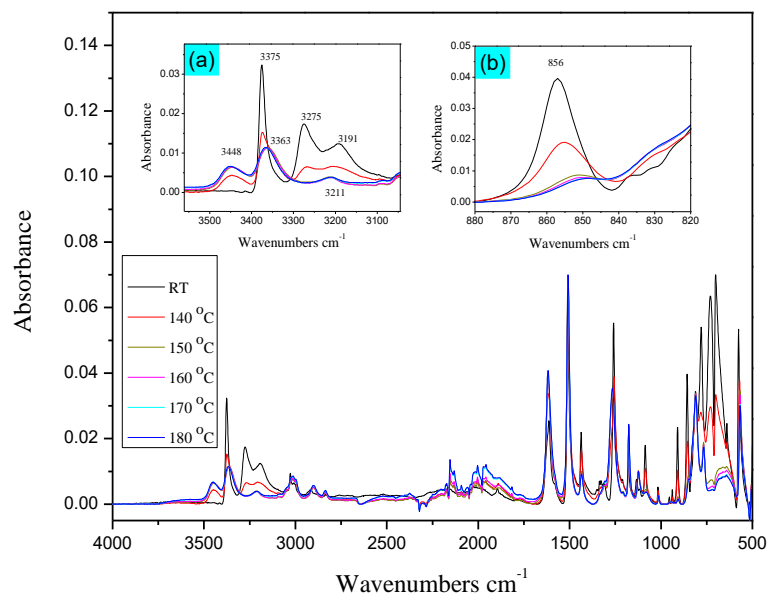


Figure 10 High temperature FTIR spectrum of the dissociation of the MDA complex. Inset: (a) The changes in the NH₂ region as a function of temperature (b) The changes in the paracyclophane absorption band (856 cm⁻¹) as a function of temperature.

Along with the high temperature infrared analysis of the complex dissociation process, DSC analysis of the MDA complex was also carried out. Unlike FTIR, DSC presents a closed system that can provide a better overall temperature control. This along with the automation of the DSC instrument can lead to more accurate reproducible data and less human error; since for IR each scan was carried out individually and the amount of sample was not taken into consideration. The complex DSC dissociation profile (Figure 11 and Table 2) presents an endothermic peak at 170 °C. This is associated with the dissociation of the complex. The dissociation endothermic peak starts at 150 °C which correlate with the IR analysis on the dissociation of the complex. As we cool and heat for a second time another endothermic peak appears at 92.9 °C which correlate to the melting

of pure MDA. The appearance of this MDA melting peak reinforces the notion that the complex has dissociated.

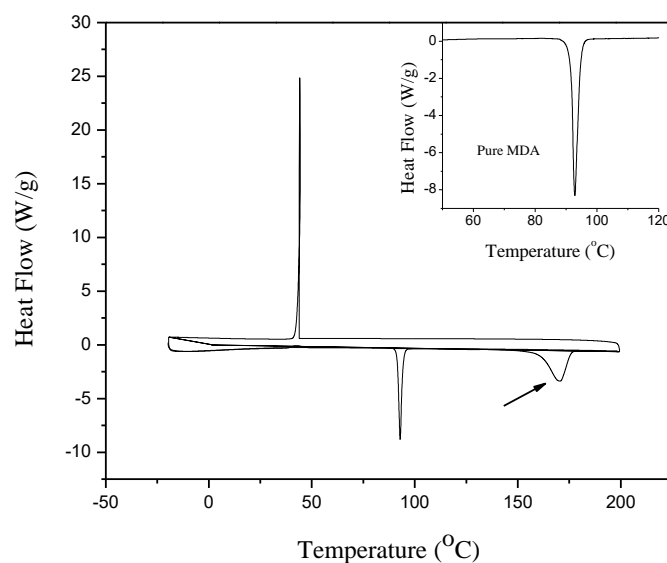


Figure 11 DSC profile of MDA complex dissociation. Inset shows the melting of pure MDA.

Table 2 DSC data for the complex dissociation.

Sample	T_d (°C)	T_{on} (°C)	E (kJ/mol)
Complex	171	161	102

4.2 Size dependence of MDA complex

The size of the particle has demonstrated to have an effect on the dissociation of the complex. In order to address its effects, the MDA complex was grinded in a ball mill for 10 minutes and the thermal profile was compared to that of an ungrounded sample (Figure 12). These results demonstrated that the ball mill grinded complex has a decrease in the dissociation temperature of 17 degrees, with an increase in the dissociation energy that can be attributed to the increased of the exposed surface area (Table 3). The grinded

complex also presents a narrower peak in comparison to the ungrounded sample. In the tabulated DSC data of Table 3 ΔT represents the width of the peak. The width of the grinded sample results in ~ 2.2 factor smaller than the ungrounded sample. This indicates that the grinded sample has a smaller size distribution than the ungrounded sample.

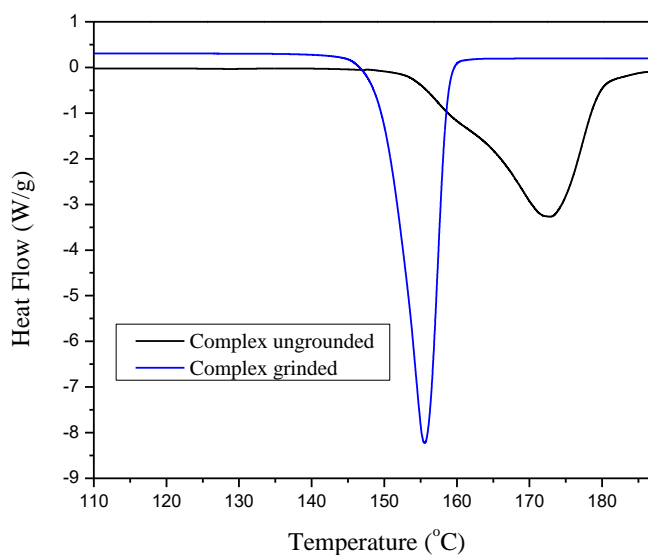


Figure 12 DSC temperature profile of MDA complex relative to size.

Table 3 DSC data for ungrounded and grinded MDA complex.

Sample	T_d (°C)	T_{on} (°C)	E (kJ/mol)	ΔT (°C)
Ungrounded	173	159	115	47
Ball mill Grinded	156	150	121	21

CHAPTER 5

ROLE OF PLASTICIZER

5.1 Bis(2-ethylhexyl) adipate

5.1.1 MDA complex dissociation

To avoid particle agglomeration and to propagate the dispersion of the complex an ester plasticizer known as Bis(2-ethylhexyl) adipate (BEHA) was added to the system.

Table 4 shows some of the physical properties related to the plasticizer along with that of the C900 pre-polymer. Of all these qualities the most attractive being the similarity with the solubility parameter of pre-polymer.²² The viscosity in BEHA is an important property for the suspension and dispersion of the complex. Nonetheless particles have a tendency to precipitate after a few minutes and a visible phase separation between the complex and plasticizer was seen as indicate by the arrow in Figure 13.

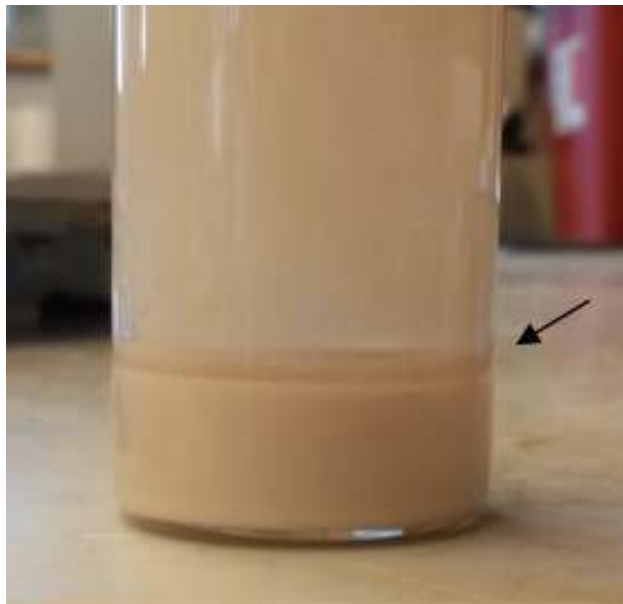


Figure 13 Shows the complex hand grinded in the BEHA. The arrow indicates the phase separation between the complex and BEHA.

Table 4 Physical properties of BEHA and C900.

Product	M _w (g/mol)	Density (g/cm ³)	Viscosity (cP)	Boiling (°C)	Solubility parameter ^δ (MPa ^{0.5})
BEHA	370.6	0.99	13 at 25 °C	417	17.6
C900	2212.6	-	5500 at 50 °C	-	17

The effects that BEHA has on the dissociation temperature of the complex have been studied by taking into consideration the effects of particle sizes. For this study a ball mill grinded sample and an ungrounded sample were mixed with plasticizer and compared with the previous data of the neat complex (Figure 14). The grinded sample with plasticizer shows an increase in peak width, indicating that plasticizer increases the particle size distribution of the complex. Similar results are observed when comparing the ungrounded samples with and without plasticizer.

The tabulated DSC data in Table 5 shows that plasticizer clearly decreases the dissociation temperature between the samples by an average of 12 degrees. This reduction in temperature is a clear indication that BEHA has an effect in the dissociation temperature of the complex that seems to increase especially for smaller particles. The energy associated with the amount of the complex also demonstrates a significant decrease which can be an indication of the plasticizer decreasing intermolecular forces and dissolving some of the particles.

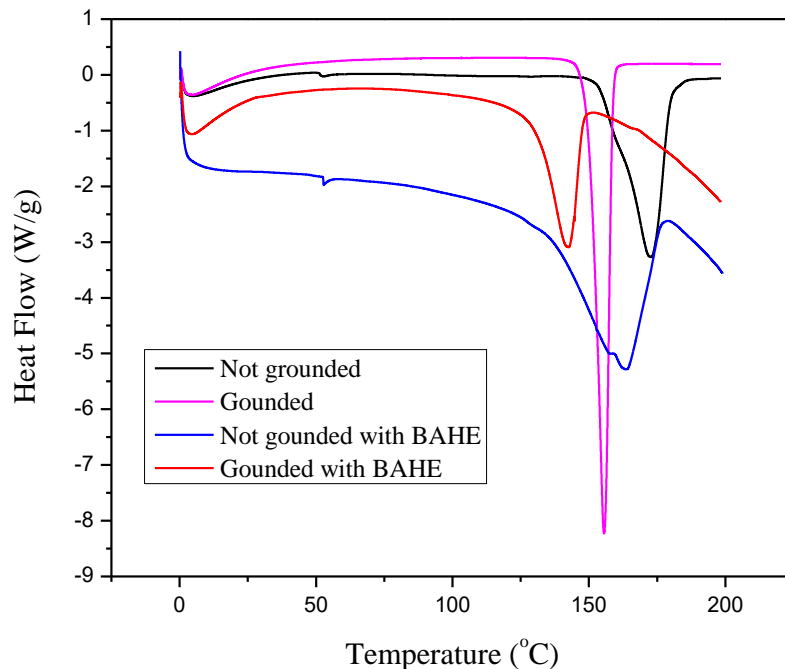


Figure 14 DSC temperature profile of grinded and ungrounded complex in Bis(2-ethylhexyl) adipate.

Table 5 DSC data related to the effect of Bis(2-ethylhexyl) adipate on the grinded and ungrounded MDA complex.

Sample	T_d (°C)	T_{on} (°C)	E (kJ/mol complex)	ΔT (°C)
Ungrounded	173	159	115	47
Ball mill Grinded	156	150	121	21
Ungrounded with BAHE	163	136	80	54
Ball mill Grinded with BAHE	143	131	65	44

The effect that the amount of plasticizer has on the dissociation of the particle was considered by varying the concentration of the 44complex i.e., adding plasticizer or complex and measuring the temperature profile (Figure 15). The relationship between the percentage of plasticizer and the dissociation temperature of the complex shows a linear trend where the increase of plasticizer lowers the complex dissociation temperature. The

reduction in the dissociation temperature between the two extremes is relatively small, only 4 degrees. Hence, the ability of plasticizer to dissolve the complex is relatively low independent of the particle size. The reason that a higher amount of plasticizer shows a decrease in the dissociation temperature can be due to the increases in volume allowing for higher dispersion of complex, minimizing the intermolecular interaction. Although more plasticizer leads to a slight decrease in the dissociation temperature, this may not be favorable when it comes to curing since there is less MDA available to react and chain extend.

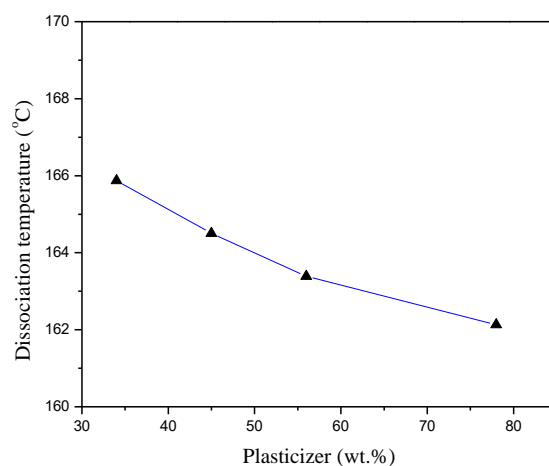


Figure 15 The relationship between the dissociation temperature of the MDA complex in relation to the amount of plasticizer.

Therefore, the main role of plasticizer is to promote the dispersion of the complex and avoid agglomeration. This in turn lowers the dissociation temperature of the complex, by limiting intermolecular interaction. The smaller the particles the higher is the effectiveness of the plasticizer in dispersing them. Along with dispersion, the plasticizer can also dissolve the particle to a very small extent. This dissolution of the complex is

thought to occur relatively slow as a consequence of the plasticizer inability to enter and disrupt the complex due to its high viscosity. Figure 16 illustrates these concepts schematically. As plasticizer interacts with the complex it decreases its intermolecular forces, which will minimize the amount of neighboring H around Cl^- . This consequently lowers the energy needed for its extraction, which as a result lowers the complex dissociation temperature.

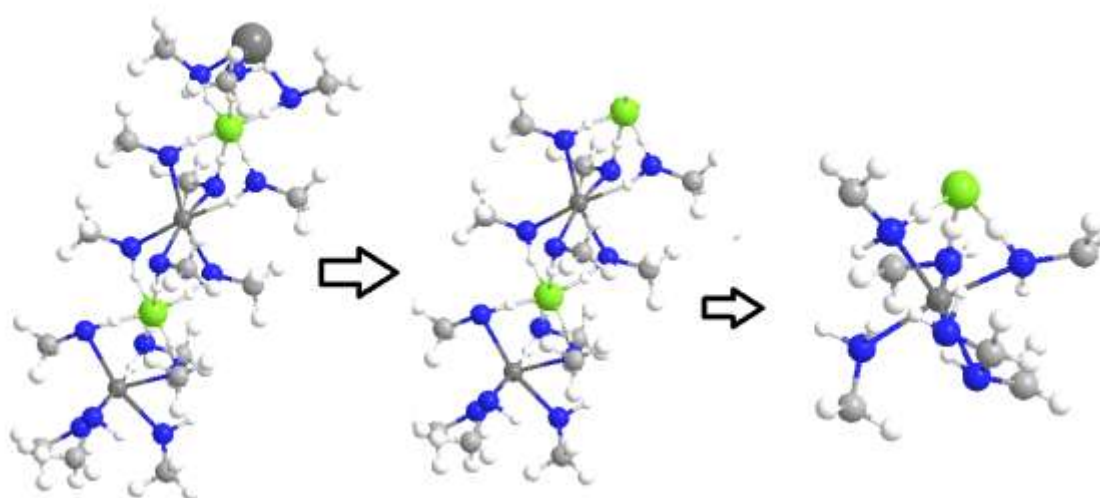


Figure 16 Shows a schematic representation of the complex dispersing due to the presence of BEHA. The green sphere represents the Cl^- atom that loses three neighboring hydrogen as dispersion occurs.

5.1.2 Curing

To understand the effects that the plasticizer has on the curing, a temperature profile of the curing was performed with and without plasticizer (Figure 17). The ratio used for both cases was a 3 to 1 mol ratio of C900 to complex. The exothermic peak shown in the DSC curve is associated with the curing of the prepolymer. The sample that has no plasticizer shows a broader peak with a small shoulder shifting upward indicated

by the arrow, which can be an indication of poor dispersion and some particle agglomeration unlike C900 in 44complex. The curing window for the system with plasticizer also demonstrated a slightly increase of ~5 degrees in comparison to the system without plasticizer. The quantitative DSC data tabulated in Table 6 demonstrates an insignificant reduction in curing temperature and energy for the system containing plasticizer. This indicates that plasticizer although useful in promoting mixing and dispersion has little to no effects on the curing.

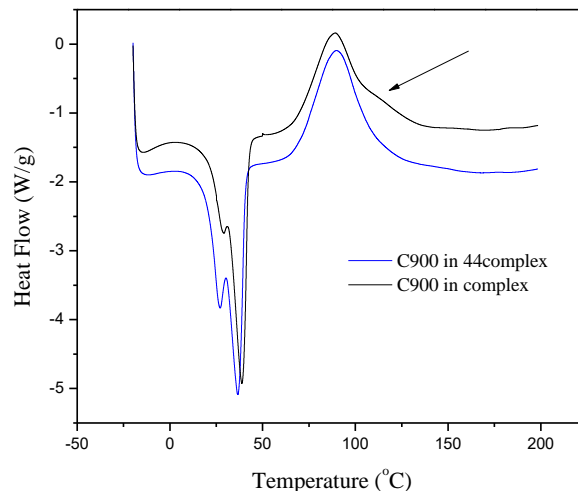


Figure 17 DSC curing of C900 in 44complex and C900 in complex without plasticizer.

Table 6 DSC data of the curing system with and without plasticizer.

Sample	Curing temperature (°C)	Onset of curing (°C)	Curing energy (kJ/mol complex)
C900 with complex	90.6	65.6	396.5
C900 with 44complex	92.7	71.1	398.7

CHAPTER 6

ROLE OF ADDITIVES

6.1 Function of Dimethyl sulfoxide (DMSO)

6.1.1 MDA complex dissociation

Dimethyl sulfoxide being a highly organic polar molecule was studied for its ability to dissociate the complex. When DMSO was mixed with the MDA complex complete dissolution was seen to occur at room temperature. To determine the state of the complex when solubilization occurs ^1H NMR was conducted on the MDA complex by dissolving it in dimethyl sulfoxide- d_6 . The NMR spectrum in Figure 18 shows all the expected peaks related to pure MDA²³ indicating that DMSO has dissociate the MDA complex. The dissociation of the complex at room temperature is an indication of the high efficiency of DMSO as a solubilizing additive.

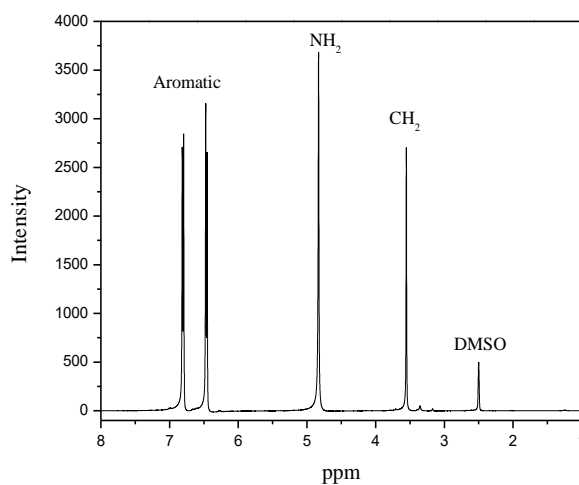


Figure 18 ^1H NMR of the complex dissolved in d_6 DMSO.

Considering that DMSO can dissociate the complex at room temperature only 5% of DMSO by weight of plasticizer was mixed with the complex. As DMSO was mixed in the plasticizer immiscibility between the two was clearly seen. The dissociation profile of the complex shows a broadening of the dissociation peak with the addition of DMSO (Figure 19) that is due to the accessibility of the DMSO to solubilize some of the complex. The effectiveness of DMSO to dissolve the complex is seen in both the reduction of the dissociation temperature and energy (Table 7). The dissociation temperature of the complex as demonstrated to reduce by ~13 degrees in comparison with the 44complex. Nevertheless too much DMSO would result unfavorable in limiting or even eliminating the control in the reaction kinetics.

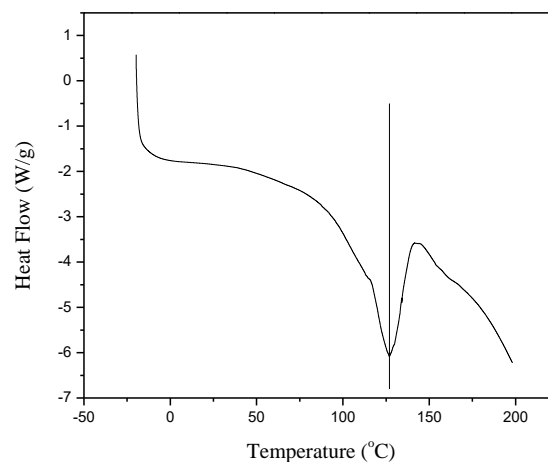


Figure 19 Average DSC profile of the dissociation of the complex with 5% DMSO.

Table 7 DSC data of the dissociation of the MDA complex with 5% DMSO.

Dissociation temperature (°C)	Onset of Dissociation (°C)	Dissociation energy (kJ/mol complex)
129.7	118.1	46

6.1.2 Curing

Due to the effectiveness of DMSO to dissociate the complex, the stability of the system during the mixing process must also be taken into account. The DSC curing profile (Figure 20 and Table 8) shows that the addition of DMSO into the system reduces the curing temperature significantly. This has the disadvantage in reducing the system mixing window. When repeating the DSC experiment of the mixed batch (inset in Figure 20) the curing peak can no longer be clearly seen. This indicates that the reaction has occurred at room temperature. The small curing energy obtained in the first sample (Table 8) can be attributed to prior system curing. Therefore the energy of curing cannot be measured accurately since the system cures at room temperature.

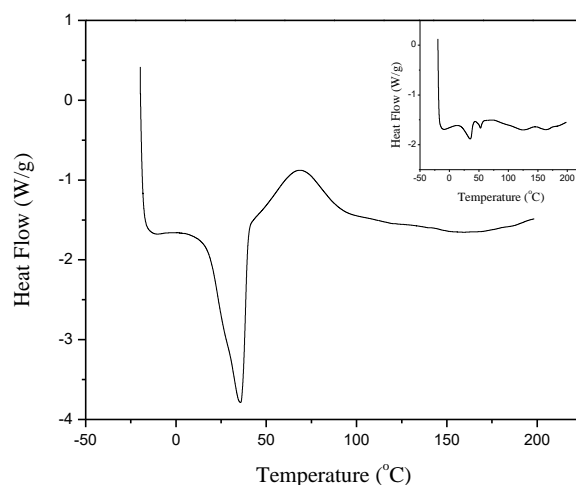


Figure 20 DSC profile of the system curing with 5% DMSO.

Table 8 DSC data of the system curing with 5% DMSO.

Curing temperature (°C)	Onset of curing (°C)	Curing energy (kJ/mol complex)
68.43	45.35	169.0

The aggressiveness of DMSO to promote the reaction is also shown in the high temperature IR studies (Figure 21). In the IR spectrum the urea band located at 1647 cm^{-1} appears at room temperature.^{24, 25} The band intensity does not demonstrate any further change indicating that urea formation has already taken place at room temperature. The residual presences of the NCO absorption band in the system may be due to the presence of excess prepolymer and MDI.

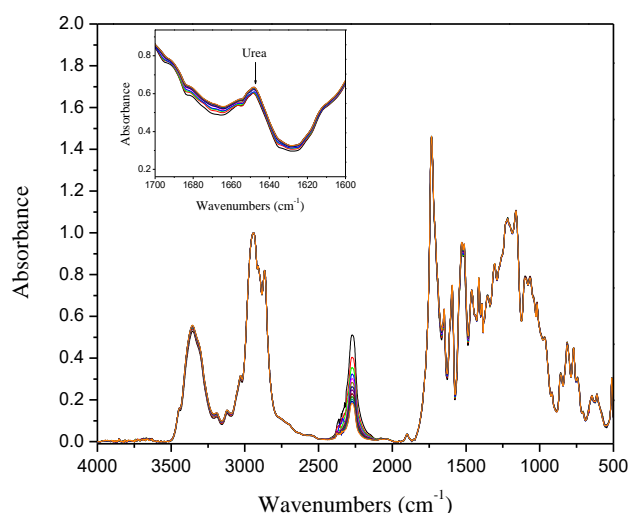


Figure 21 High temperature infrared profile of the curing with 5% DMSO.

6.2 Function of soy lecithin

6.2.1 MDA complex dissociation

Soy lecithin is a viscous organic molecule containing a charged quaternary ammonium compound. It is studied for its ability to dissociate the complex by the removal of the Cl^- ion. At room temperature the efficiency of soy lecithin to remove this ion is low due to its high viscosity preventing it from entering the MDA complex. However as temperature is increased its ability to remove the ion in the complex improves. A sample

with 5% by weight of soy lecithin has shown to dissociate the complex at 136 °C (Figure 22 and Table 9) which is 7 degrees lower than the ball mill grinded complex (small in size) in the plasticizer.

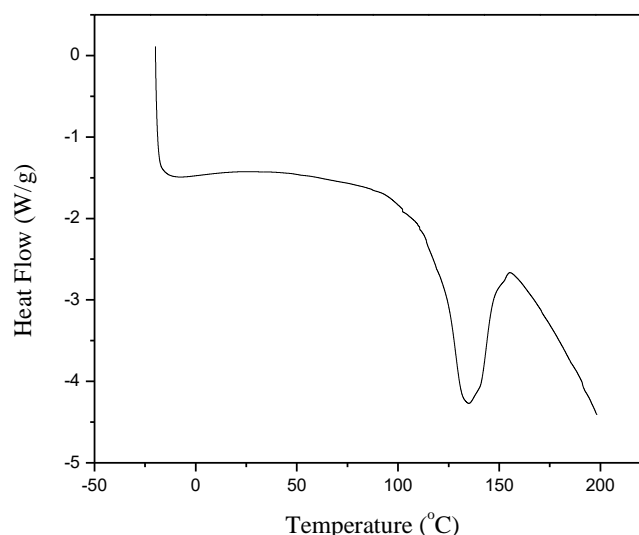


Figure 22 Average DSC profile of the dissociation of the complex with 5% soy lecithin.

Table 9 DSC data of the dissociation of the MDA complex with 5% soy lecithin.

Dissociation temperature (°C)	Onset of Dissociation (°C)	Dissociation energy (kJ/mol complex)
136.2	121.0	104

6.2.2 Curing

The DSC curing profile of 5% soy lecithin (Figure 23) demonstrated that soy lecithin is less aggressive than DMSO in promoting dissociation. The curing system is stable even at elevated temperatures which is not the case for DMSO mixtures. The curing temperature and curing window of 5% soy lecithin is very similar to the system containing C900 and 44complex, with the exception of the curing curve being a bit more symmetric.

The lower curing energy in comparison with the C900 in 44complex system can be due to of the prepolymer reacting with some of the OH present in soy lecithin before dissociation of the complex can be taken into full effects.²⁶

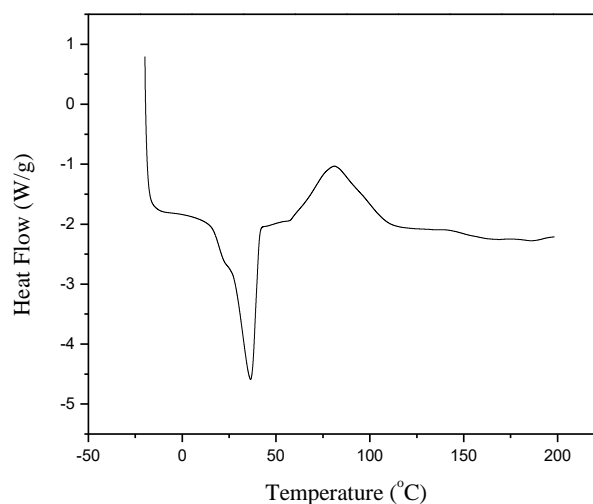


Figure 23 DSC profile of the system curing with 5% soy lecithin.

Table 10 DSC data of the system curing with 5% soy lecithin.

Curing temperature (°C)	Onset of curing (°C)	Curing energy (kJ/mol complex)
90.7	70.2	326

The high temperature infrared spectrum further confirms the relative reaction kinetics found for soy lecithin in comparison to DMSO. By monitoring the 1647 cm^{-1} urea band intensity^{27, 28} (Figure 24), we see that unlike DMSO the urea peak does not appear at room temperature instead it starts to appear at 90 °C which correlates with the curing peak shown in DSC. The increase of the urea peak area as a function of temperature is plotted in Figure 25. The data shows that the highest amount of urea occurs at 140 °C. Holding at 140 °C as a function of time the urea formation shows no further changes (Figure 26).

Therefore at 140 °C the reaction has culminated; nevertheless the presence of the NCO band once the reaction has occur can be an indication of the low content of available MDA in the system which can be due to a hindrance in mobility due to the viscosity of the overall system.

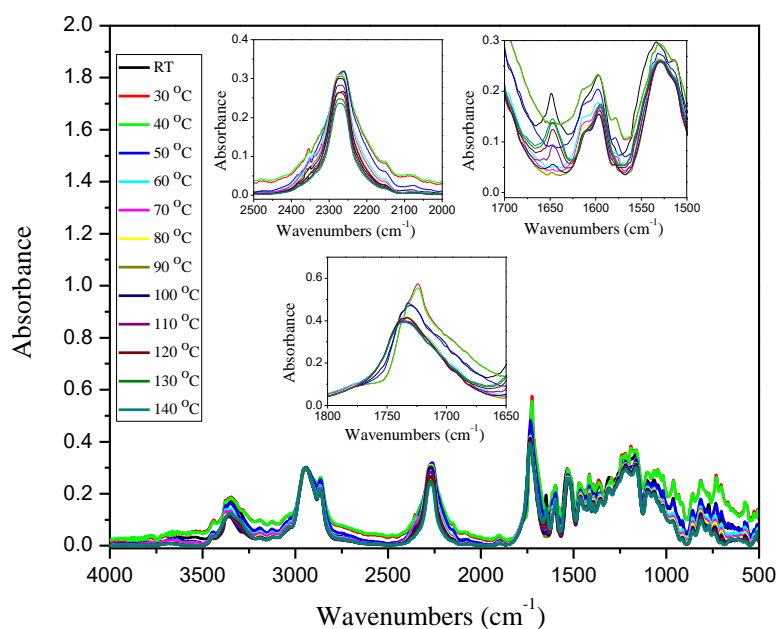


Figure 24 High temperature IR spectrum of C900 with 44complex with 5% soy lecithin. The inset demonstrate the NCO band 2270 cm⁻¹, the Urea band 1647 cm⁻¹ and the 856 cm⁻¹ complex dissociation band.

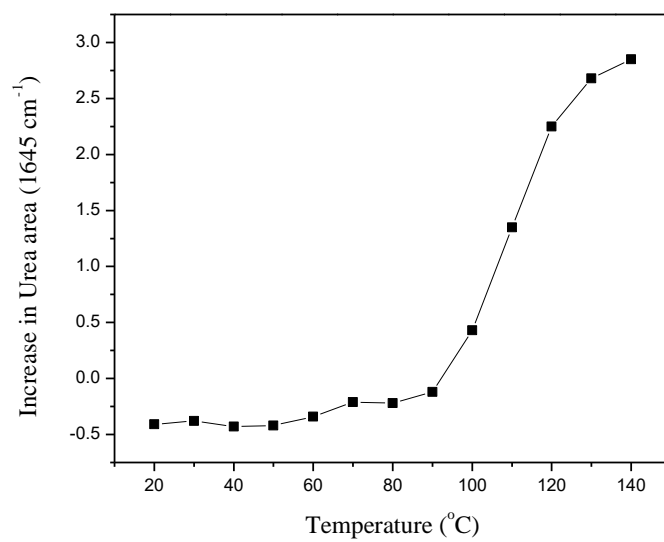


Figure 25 Urea area increment as a function of temperature.

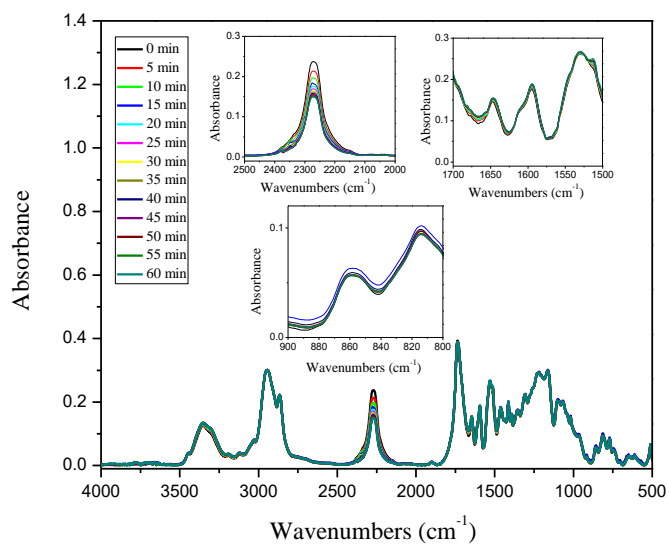


Figure 26 High temperature IR spectrum of C900 with 44complex and 5% soy lecithin held at 140 °C. The inset demonstrate the NCO band 2270 cm⁻¹, the Urea band 1647 cm⁻¹ and the 856 cm⁻¹ complex dissociation band.

CHAPTER 7

CONCLUSION

An available system consisting of a reaction between an isocyanate terminated prepolymer and amine complex was studied with the objective of controlling the rate of the polyurea reaction. The advantage of this system is in the barrier created between the diamine and the isocyanate, which prevents the nearly instantaneous reaction from taking place. This allows for the higher mixing time in the formation of large scale objects. The rate of reaction has been established to be dependent on the ability of the MDA complex to dissociate. In this study, we have addressed the various possibilities in extracting the Na^+ as a function of temperature, size, plasticizer and other additives. The prepolymer due to its low melting temperature, high reactivity and low molecular weight presents no issue in the reaction.

This study is directed towards understanding the dissociation mechanism of the complex and the various components that affects it. It has been shown that at elevated temperatures ($\sim 170^\circ\text{C}$) the complex can dissociate. The need of this extremely high temperature is inconvenient and energy inefficient. In addition, because polyurethanes are normally poor thermal conductor, a significant temperature gradient exists between surface and interior leading to incomplete curing for large scale samples. Therefore various possibilities to reduce the dissociation temperature of the complex by physical or chemical means have been investigated.

It has been demonstrated that when it come to the dissociation of the complex size matter. Smaller particles have a lower dissociation temperature in comparison to large ones, “dissolving” more easily into the system. A simulation of a $5\mu\text{m}$ particle size

demonstrate that the surface solubilization is less than <1%. Therefore particle size presents a crucial component in complex solubility. Nevertheless, small particles present a tendency toward agglomeration due to their exposed surface area. The effects of particle agglomeration can be seen in both the increase in dissociation energy due to intermolecular forces and a broader band in the exothermic curing peak in DSC.

For a uniform chemical reaction to take place it is necessary to disperse the complex at a molecular level. In this study, we have found that the role of a plasticizer known as Bis (2-ethylhexyl) adipate is to promote dispersion and prevent particle agglomeration. In the presence of plasticizer the dissociation temperature of the complex lowers due to the dispersion of the complex, minimizing intermolecular forces. There are no significant energy changes observed in the comparison of the curing system with and without plasticizer. This indicates that plasticizer has not directly contributed to the curing reaction. Plasticizer has a small role in dissolving the complex. However its efficiency is poor and slow due to lack of mobility, i.e., its high viscosity.

Therefore other additives based on polarity and charge were explored. Their ability of dissolving the complex and lower the dissociation temperature has been evaluated. Dimethyl sulfoxide (DMSO) is a highly polar organic solvent that was studied for its potential of dissolving the complex. It has been found that DMSO is extremely efficient in dissolving the complex, so much so, that it induced the reaction to occur at room temperature. This aggressiveness of DMSO in as little as 5% by weight, eliminates the mixing window needed before curing takes place, which is very unfavorable for controlling the reaction.

Based on the principle of charge neutrality the extraction of the ion or counter ion is treated as the same. We have examined the effect of a quaternary ammonium compound found in soy lecithin. This compound has been found to be a crucial component in extracting the counter ion in the MDA complex freeing the amine for reaction. Soy lecithin has been found to decrease the dissociation of the complex. Its high viscosity inhibits the reaction from taking place at room temperature, presenting a larger mixing window in comparison to DMSO. However, one of the disadvantages that soy lecithin has is that it contains OH that can also participate as part of the reaction.

In this investigation several factors affecting the dissociation of the MDA complex for the controlled polyurea reaction have been studied. Size has been found to be a crucial component in the solubilization of the complex. The role of the plasticizer as a dispersing agent to avoid particle agglomeration has been established. Other additives have been explored in order to promote complex dissociation based on polarity and charge. Among these the quaternary ammonium compound found in soy lecithin has demonstrated to have the most promising results.

CHAPTER 8

FUTURE STUDIES

The results presented here have demonstrated several properties that affect the dissociation of the MDA complex with the purpose of controlling the rate of polyurea formation. However this system can be further developed in a number of ways:

The effects of other diamine compounds including aliphatic candidates

The formation of other complexes of different diamine including aliphatic candidates possessing lower conjugation and therefore higher reactivity will be studied. The structure of these new complexes should be established using IR and X-ray scattering and compared with the known MDA complex structure. These new candidates will be studied in term of dissociation temperature and curing characteristics. The selection of these diamines will be done by correlating the melting point, reactivity, and electrostatic interaction with the ionic salt.

Different salt complexes

The effects in changing the ionic barrier in the MDA complex using different salts will be investigated. These new salt complexes will be synthesized by taking into consideration ion size and electrostatic binding force. The changes in the binding energy will be studied by varying the ion or counter ion while leaving the diamine molecule unchanged. Utilizing IR and DSC a comprehensive quantitative analysis on the dissociation of the complex will be conducted, along with curing kinetics.

Effect of ionic liquids

Considering the effectiveness of the quaternary ammonium ion in the dissociation of the MDA complex, the effectiveness of various ionic liquids on complex dissociation will be investigated. The selection of ionic liquid will be based on the ionic strength, viscosity, availability and compatibility with prepolymer, complex and plasticizer. In regard to availability the most common ionic liquids known as imidazolium, ammonium and phosphonium will be studied. The stability of the complex and the amount of dissociation in the presence of the ionic liquid will be investigated, along with its effects on the curing reaction.

Different polyols

Once a firm understanding on the parameters relating to the dissociation of the complexes is established, the curing kinetics of different polyols will be investigated. The polyol will be selected based on molecular weight, reactivity and functionality. Each sample will be classified in terms of curing temperature, curing energy and amount of chain extension. Mechanical testing will also be conducted in order to determine mechanical strength and which polyol presents the best properties.

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