Structural characterization of polyurethane foam and implications of aging

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University of Nevada, Las Vegas

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STRUCTURAL CHARACTERIZATION OF POLYURETHANE FOAM AND
IMPLICATIONS OF AGING

by

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University of Colombo, Sri Lanka
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ABSTRACT

Structural Characterization of Polyurethane Foam and Implications of Aging

by

Gayani Chandima Kodippili

Dr. Linda S Sapochak, Dr. David Hatchett, Examination Committee Co-Chair
Assistant Professor of Chemistry
University of Nevada, Las Vegas.

Polyurethane (PU) foam is used as a shock mitigation material in the national stockpile, which degrades over time. A replacement foam, ReCrete was shown to exhibit acceptable mechanical properties after aging, but fractured with impact testing. Previously, processing ReCrete foam at elevated temperature resulted in a decrease of the modulus (stiffness), which was believed to be related to chemical changes during processing. In this thesis, chemical and structural analysis of ReCrete processed at 25°C and 85°C were performed using photoacoustic infrared spectroscopy, IR imaging, and thermal analysis. The change in modulus was related to thermal decomposition of uretoneimine linkages in the diisocyanate starting material by monitoring the change in intensities of diisocyanate, carbodiimide, and uretoneimine bands in the IR spectra. Thermal analysis (DSC and TMA) were consistent with IR finding, where endothermic and exothermic events could be associated with chemical changes in the foam.
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CHAPTER 1

POLYURETHANE FOAM

1.1 Introduction

Rigid polyurethane (PU) foams are used as encapsulants for electronic components to mitigate harsh thermal and mechanical shock and to provide electrical isolation.\textsuperscript{1,2} There are many applications of these foams in our everyday life such as use in industry as low-density insulating material in applications such as construction panel sandwich structures and domestic refrigerators.\textsuperscript{3,4} PU foams are also used as encapsulates in our national stockpile of nuclear weapons. The deterioration of shock mitigation properties are a major concern as the foam undergoes thermal and radiative exposure degradation over time. These factors are a general concern when considering the safety of the national stockpile of nuclear warheads.\textsuperscript{1,2}

The general reaction of isocyanate with polyol in Figure 1.1 shows the basic structural backbone of the polyurethane polymer. Typical R' groups of the polyol include polyether and polyester units. Industrially important diisocyanates include 2, 4- and 2, 6-toluene diisocyanate (TDI), 4, 4'-methylene diphenyl diisocyanate (MDI), and 1, 6-hexamethylene diisocyanate (HDI). The R groups can be either aromatic rings (increase rigidity) or alkyl chains (increase flexibility). More flexible R and R' groups and low functionality of the isocyanate and polyol favors more flexible foams, whereas rigid R
and R groups and high functionality favors more rigid foams. However, depending on how the PU is formed and processed the reaction can lead to a complicated microstructure that influence the structure and rigidity of the material.\textsuperscript{5,6,7}

\[
\begin{align*}
\text{Diisocyanate} & \quad + \quad \text{Polyol} \\
\rightarrow & \quad \text{Polyurethane}
\end{align*}
\]

Figure 1.1. General reaction of diisocyanate and polyol to form polyurethane. R represents functional groups that influence the basic structural backbone.

1.2 History and Development of Polyurethanes

The German chemist, Fredrich Bayer in 1937, reacted toluene diisocyanate with dihydric alcohols to produce the first PU prototypes. This lead to the development of one of the first crystalline PU fibers called Perlon U. The first elastic PU was developed during World War II while attempting to find a replacement and additive material for natural rubber. After finding that the PU could be made in to fine threads the commercial production of flexible PU foams began in the United State. These studies lead to the development of Rigid PU foams.\textsuperscript{8,9} In addition to foams, adhesives, elastomers, binders, coatings and paints can also be produced using PU chemistry. Due to their unique properties polyurethane derivatives have found a wide variety of applications in the industry as seating exterior panels, structural foams, furniture, housing for electric equipment, shoe and boot soles and refrigerator insulation materials.\textsuperscript{3,4,10}
1.3 Rigid Polyurethane Foams

PU or polycarbamates belongs to the family of condensation polymers where the diisocyanate and diol react with each other with loss of a water molecule. PU foam can be either rigid or flexible depending on the cell structure. An open cell structure, which is a permeable structure with the cell walls have been broken, results in flexible PU foam. If the foam has closed cell microstructure, each individual bubble is completely sealed from its neighbors by the cell walls, it is considered rigid.

Rigid foams have the highest insulating value of any conventional insulation commercially available today. They have very low thermal conductivity; gases trapped in the closed cell structure reduce heat transfer by conduction. The isolated cells thereby further increasing the thermal efficiency of the foams. In fact, the small cell size practically eliminates convection. Every cell wall acts as a barrier to energy transmission by radiative heat transfer.\textsuperscript{11,12}

1.4 Isocyanate Chemistry

1.4.1 Primary Reactions

The chemistry involved in the synthesis of PU foam is based on isocyanate reactivity. The positive charge density of, the carbon atom in the cumulative double bond sequence consisting of nitrogen, carbon, and the oxygen, yields the high reactivity towards the nucleophilic reagents such as polyols and water. If the system has aromatic character the reactivity of the system even more enhanced. This electronic structure of the isocyanate group can be represented with several resonance structures, which are illustrated in Figure (1.2).\textsuperscript{5,6,13}
As it illustrated on resonance structures of isocyanate, the positive charge stays at the carbon atom and negative charge is delocalized on to the oxygen atom, nitrogen atom or aromatic group. The high resonance stability of aromatic isocyanate ensures distinctly higher reactivity over aliphatic isocyanate. Also the substitutions on the aromatic ring can influence the positive character of nitrogen, carbon and oxygen in the NCO group.

Polyurethane's are typically prepared by the reaction of the isocyanate group and hydroxyl group to yield the urethane linkages as shown below (Figure1.3). The urethane linkages are the basic backbone of the polyurethane foam. However the Chemistry of polyurethane is much more complicated than this, in fact the 'urethane' bond is the minority component in the resulting polymer.\textsuperscript{5,7,13-15}

PU foams are prepared by the simultaneous reaction of multifunctional isocyanate and polyols (gel reaction) with a gas liberation reaction (foaming reaction). It can be either water blown PU foam (water acts as a key chemical reactant which provides the
CO₂ gas) or solvent blown PU foam (solvent such as HCFC, which provides gas (CFC-Chloro Floro Carbon). Here the foaming occurs by the reaction of diisocyanate (1) with water resulting in the formation of an unstable carbamic acid (2), which decomposes to form a primary amine (3) and carbon dioxide. The evolution of CO₂ gas results in the expansion of the polymer into the encapsulation cavity. The diisocyanate further reacts with the primary amine to form urea linkages (4), another component of the microstructure of PU foams. This is illustrated in Figure 1.4⁵,⁷,¹³-¹⁵

\[
\text{O}=\text{C}=\text{N} - \text{R} - \text{N} = \text{C} = \text{O} + \text{H}_2\text{O} \rightarrow \text{O}=\text{C}=\text{N} - \text{R} - \text{NH} - \text{C}=\text{O} \rightarrow \text{O}=\text{C}=\text{N} - \text{R} - \text{NH}_3 + \text{CO}_2
\]

Figure 1.4. Urea formation

1.4.2 Secondary Reactions

The urethane and urea formed from the previous reaction and still contain active hydrogen. Even though the reactivity of these compounds is lower than the starting reactants, alcohol and amine, they still capable of a nucleophilic attack with isocyanate. The extent reaction of urethane with isocyanate results in the formation of allophanates (5), whereas reaction of urea with isocyanate results in the formation of
biuret(6). These reactions cause further crosslinking in the main polymer chain. These reactions are shown in Figure 1.5 and 1.6.\textsuperscript{5,14-16}

\begin{align*}
\text{O}=\text{C} & \equiv \text{N} \text{--R--N} \equiv \text{C} = \text{O} + \text{O}=\text{C} & \equiv \text{N} \text{--R} \equiv \text{N} = \text{C} = \text{O} \rightarrow \\
\text{Urethane linkages} & \\
(1) & \\
\text{O}=\text{C} & \equiv \text{N} \text{--R--N} \equiv \text{C} = \text{O} + \text{O}=\text{C} & \equiv \text{N} \text{--R} \equiv \text{N} = \text{C} = \text{O} \rightarrow \\
\text{O}=\text{C} & \equiv \text{N} \text{--R--N} \equiv \text{C} = \text{O} + \text{O}=\text{C} & \equiv \text{N} \text{--R} \equiv \text{N} = \text{C} = \text{O} \rightarrow \\
\text{Allophanate} & \\
(5) & \\
\end{align*}

Figure 1.5. Formation of Allophanate

\begin{align*}
\text{O}=\text{C} & \equiv \text{N} \text{--R--N} \equiv \text{C} = \text{O} + \text{O}=\text{C} & \equiv \text{N} \text{--R} \equiv \text{N} = \text{C} = \text{O} \rightarrow \\
\text{Biuret} & \\
(6) & \\
\end{align*}

Figure 1.6. Formation of Biuret

Allophanate are usually formed between 120°C and 150°C and biurets are formed between 100°C and 150°C as a result of their low thermal stability, allophanates and biurets will dissociate into starting components above the temperature concern during the formulation (150°C-200°C). This results in a small amount of excess isocyanate functionality which remains unreacted after the processing. The unreacted isocyanate can be used to promote crosslinking within the polymer after processing.\textsuperscript{13}

In addition to these secondary reactions isocyanate can also dimerize (uretidinedione) and trimarize (isocyanurate) as illustrated in figure 1.7 and 1.8. Dimerization is limited to aromatic isocyanate and it is inhibited by the ortho substituents. While MDI dimerizes slowly at room temperature, 2, 4 and 2, 6- TDI do not dimerize. In addition dimerization
is readily reversible reaction above 150°C. Isocyanurate can be formed from both aromatic and aliphatic isocyanate, it is thermally stable and the reaction cannot be easily reversed. Thermodynamically stable species also contribute to the stability of polymer via crosslinking.13,17,18

![Figure 1.7. Dimerization of isocyanate](image)

Another important reaction of an isocyanate is the formation of carbodiimide by reacting with two isocyanate functionality as illustrated in Figure 1.9.19,13,19-24

![Figure 1.8. Trimerization of isocyanurate](image)

![Figure 1.9. Formation of Carbodiimide](image)
Carbodiimide is also considered an aging inhibitor against heat and moisture in polyester or isocyanate. This property is based on the NCN group's ability to react with carboxyl group to form acylate ureas as illustrated in Figure 1.10. Although the carboxyl groups can auto catalyzed the degradation by giving rise CO$_2$ in polymer that carboxyl groups rendered ineffective by the reaction with carbodiimide.$^{19}$

\[ R - N = C = N - R + R' - COOH \]

\[ \begin{array}{c}
R - NH - C = N - R \\
\text{O} \\
\text{C} = \text{O} \\
\text{R'}
\end{array} \]

\[ \rightarrow R - NH - C = N - R \\
\text{O} \\
\text{C} = \text{O} \\
\text{R'}
\]

Figure 1.10. Formation of acylated ureas

Isocyanate can also react with carbodiimide to give thermally stable adducts called uretidinedione imines or uretoneimines. The dimerization products of aromatic isocyanate are illustrated in Figure 1.11.$^{17-20}$ Uretoneimine are important structures in PU foams because they are strongly influent by heat. Degradation of these groups in the PU foam is thermally activated and one of the focus of the current studies.
1.5 Carbodiimide Modified Methylene Diisocyanate (MDI) or (Liquid MDI)

Isocyanates are the raw materials from which all polyurethane products are made. The most widely used isocyanates are shown in Table 1.1. The most common isocyanate used in polyurethane is the liquid MDI. MDI was developed as a replacement material for TDI based on the hazardous properties of the material. One of the commercial names given for liquid isocyanate is the rubinate. In addition to that Centari, Niax, Nacconate, and Imron are some of the other available commercial isocyanates. Liquid MDI primarily consists of carbodiimide, groups which are prepared by reacting MDI. Pure MDI is a solid at room temperature and melts at 38°C. Most of the MDI based isocyanates are sold as crude products such as polymeric MDI (PMDI) and liquid MDI (modified MDI). The main constituents of polymeric MDI are the 40-60% 4, 4'-MDI, of MDI (2, 4'- and 2, 2') trimeric species and higher molecular weight oligomers.
### Table 1.1 Diisocyanate for Polyurethane

<table>
<thead>
<tr>
<th>Diisocyanates</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4'-methylenediphenyl diisocyanate (MDI)</td>
<td><img src="image" alt="Structure 1" /></td>
</tr>
<tr>
<td>2,4'-methylenediphenyl diisocyanate (MDI)</td>
<td><img src="image" alt="Structure 2" /></td>
</tr>
<tr>
<td>2,4'-toluene diisocyanate (TDI)</td>
<td><img src="image" alt="Structure 3" /></td>
</tr>
<tr>
<td>2,6-toluene diisocyanate (TDI)</td>
<td><img src="image" alt="Structure 4" /></td>
</tr>
<tr>
<td>1,5-Naphthalene diisocyanate (NDI)</td>
<td><img src="image" alt="Structure 5" /></td>
</tr>
<tr>
<td>1,6-hexamethylene diisocyanate (HDI)</td>
<td><img src="image" alt="Structure 6" /></td>
</tr>
</tbody>
</table>

#### 1.6 Chemistry of Carbodiimide modified MDI

Synthesis of modified MDI and derivatives is carried out by the reaction of polyamine with phosgene as illustrated in Figure 1.12. The first step is the acid catalyzed condensation of aniline with formaldehyde. This yields a mixture of isomeric forms of diphenylmethane dianilines (MDA’s), which contains two or more aromatic rings. Phosgenation of MDA leads to formation of crude MDI. The non distilled or crude MDI
mixture, or polymeric MDI, consists mainly of 4,4′-MDI, 2,4′- and 2,2′- isomers, and condensation products with more than two aromatic rings. This can be separated to obtain pure MDI.\textsuperscript{18,25-27} Pure or monomeric MDI (4,4′ isomer) is a white or yellowish solid, which forms dimers when stored above 40°C. However, modified MDI’s are liquid at room temperature and show little tendency towards dimerization. These have high degree of ortho and para isomers and are highly stable.

One way to obtain the modified pure MDI is the convert part of the isocyanate into carbodiimide, which then reacts with the excess isocyanate yielding uretonemine, with three unreacted isocyanate groups. This is illustrated in Figure 1.13. This compound mixed with pure MDI results in a liquid carbodiimide modified MDI, which is stable and slightly viscous, with a melting point below 20°C.
1.7 Thermal Aging Studies of Rigid PU Foams

The rigid PU foam, BKC44402 is water blown, toluene diisocyanate (TDI) based foam, which is prevalent in the national stockpile. Studies of the thermal aging effects in air of BKC44402 were reported by Sandia National Laboratory (SNL) researchers, Whinnery and Goods. Aging information is important for theoretical modeling of potential accident scenarios of weapons that contain PU foams as encapsulants and how changes in the chemical and mechanical properties of foams might affect their reliability for ensuring the safety of the national stockpile.

Whinnery and Goods prepared foam samples with a target density of 0.1g/cm$^3$ and cut the PU foam into 6.4 cm$^3$ cubes with the outer skin removed and thermally aged the
samples in air for, 3 months, 7 months, 1 year, and 2 years. They reported a ~20% change in the energy absorption (or toughness) and crush strength of TDI foam after 1 year of aging at elevated temperatures (60°C and 80°C). They also developed a new rigid PU foam, ReCrete, and found similar aging characteristics. The ReCrete was more brittle in comparison to the TDI foam after aging. However the decrease in energy absorption was still ~20%.

The general mechanism proposed for the decomposition of urethane/isocyanate foam based on MDI is outlined in Figure 1. As shown there urethane fission occurs above 150°C to generate isocyanates which react further to generate the corresponding carbodiimide. The same phenomena can be happened during foam formulation too. This polycarbodiimide decomposed above 500°C to give a complex mixture of volatile products, leaving behind a porous carbonaceous mass. This is important to understand the thermal behaviors exhibits in differential scanning coulorimetry, when the foam sample is heated as a function of temperature.
Figure 1.14. Proposed mechanism for thermal decomposition of urethane/isocyanate

Previous studies of PU foams by Brachos and Douglas showed that the foam core and core/skin properties had a significant effect on energy absorption properties of foam-cored composites. This is significant, because the aging studies conducted by Whinnery and Goods were tested on samples without skin and taken from the main foam block so that density was constant. The presence of a density gradient and presence of skin may affect the aging characteristics of PU foams and resulting mechanical properties. To address this, the O'Toole group prepared ReCrete foam at different
processing temperatures in small cylinders, similar in size to the test samples used by Whinnery and Goods. This allowed samples to be tested that have the outer skin intact. In addition, the samples had different density gradients depending on the processing conditions.\textsuperscript{28}

O'Toole, et al prepared ReCrete foam processed at 0°C (ice bath), 25°C (ambient), 25°C, 40°C, and 90°C in a water bath according to the specification of Whinnery and Goods formulation, with a target density of 0.1 g/cm\textsuperscript{3}. Average density and density gradients were measured, and found to decrease with increasing processing temperature in agreement with Harbon's studies. The collapse stress and modulus were then measured and it was shown that both properties decreased with increasing processing temperature and decreasing density. Both modulus (the slope of stress strain curve) and collapse stress were obtained from the stress, strain curve. However, after normalization of the data to the target density, it was found that although the collapse stress showed the same trend, the modulus appeared to be higher for sample with smaller density gradients. However, processing conditions can also alter the nature of the complex chemical reactions during the formation of the PU foam. Therefore, changes in modulus could be directly related to changes in the density gradient or to the chemical differences in the foam structure due to the processing conditions.

1.8 Purpose of Thesis

The purpose of this thesis was to conduct a detailed analysis of the chemical structures of ReCrete PU foam prepared at different processing conditions and to determine whether the changes in mechanical properties such as decrease in modulus
with increase processing temperature reported by O'Toole could be related to the chemistry differences in the foamed samples. The ReCrete foam samples were prepared in collaboration with Professor O'Toole’s group in the Mechanical Engineering Department at UNLV. Systematic structural analysis by infrared spectroscopy and thermal analysis was conducted for samples prepared at different processing conditions. Infrared analysis was initially studied on samples pressed into KBr pellets and later studied by non-destructive techniques including photoacoustic IR and IR imaging. Correlation of the density gradients induced by different processing conditions was established by examining foam samples at different positions of the foam cylinder by scanning electron microscopy (SEM), and optical microscopy. Furthermore, changes in the chemical structure of ReCrete foam aged at room temperature in air was monitored over a 3 month period.

This thesis is organized in the following manner: Chapter 2 outlines the experimental procedures for the synthesis and characterization techniques utilized in this work; Chapter 3 reports the results of the morphological studies of ReCrete foam; Chapter 4 contains the infrared spectroscopic results; Chapter 5 reports the thermal analysis results; and Chapter 6 presents the conclusions of the chemical stability upon aging as related to processing temperature of the RECRETE PU foam and a discussion of the utility of Recrete as a replacement encapsulant foam for TDI based foams in the national stockpile.

1.9. References


17. http://www.eat.lth.se/staff/marten/publications/lic/lic.html


25. 


26. Eurocoat 2002, Barcelona, Spain, June **2002**


CHAPTER 2

EXPERIMENTAL METHODS

2.1 Introduction

Traditional foam encapsulants have utilized toluene diisocyanate (TDI) as a chemical reactant. TDI is a known carcinogen and is difficult to use safely due to its high volatility. Therefore foams using alternative chemical components have been developed. However, prior to their use as a replacement foam, the chemical, physical, and mechanical properties must be examined and compared to the existing TDI based foam to ensure that complementary or superior properties exist. ReCreate polyurethane foam is being utilized as a replacement material for TDI.

Infrared spectroscopy, IR-imaging, DSC (differential scanning colorimetry), TMA (Thermal mechanical analysis) and mechanical analysis are used to evaluate the chemical, physical and mechanical properties of the foam samples. TMA provides information about coefficient of thermal expansion, shrinkage, and the softening points of foam samples. DSC provides the information about the degree of polymerization, gelation and curing. DSC and TMA together provide information concerning the physical and chemical state of the foam, as a function of temperature. In contrast, IR provides information about the chemical and molecular structure of the foam. These techniques can be used for both qualitative (to identify the presence of functional groups in the final
structure) and quantitative (concentration, aging) purposes. In addition, IR microscopy can be used to map surfaces and ascertain the distribution of functional groups within a structure. For example, the identification and the distribution of certain compounds like isocyanate in cells and struts is possible. Optical microscopy and SEM were used to examine morphology from the center to side of samples to see how the processing affects the structure or morphology a sample. The correlation of chemical and physical properties is essential to determine whether ReCreate is a suitable PU foam replacement for TDI based foam.¹²³⁴

2.2 Fabrication and Processing of ReCrete Polyurethane Foam

ReCrete foam was fabricated using the following five chemicals, Voranol 490, DC 193 Surfactant, Polycat 17 amine catalyst, distilled water, and rubinate 1680. The mass of each component is selected to produce a target foam density of 0.1 g/cc.⁵

The chemicals were weighed in a 1-liter plastic container with a height of 127.0 mm, making the inner diameter 75.9 mm at the base and 95.0 mm at the rim. The Voranol (84.24g) was added first to the plastic container in a chemical hood using a digital scale. Following the Voranol, the DC surfactant (2.13g), Polycat 17 amine catalyst (0.49g), and the distilled water (0.98g), were added using an eye dropper at different places in the plastic container to limit early reactions. The chemicals were then mixed for two minutes by hand in a circular motion with a spatula to minimize the formation of air bubbles. Before adding the Rubinate (128.51g), the spatula was scraped clean in to the plastic container using a wooden applicator stick to avoid wasting any of the chemicals.
The completed formulation was mixed with an overhead mixer for 90 seconds, and poured into six 28.7 mm inner diameter cylindrical aluminum molds. All six of the cylindrical molds were 143 mm tall. The molds were open on the top so the foam could rise freely. A sufficient amount of the formulation was poured into each mold to produce a small mushroom on the top of each cylinder. All six cylinders bottoms were threaded with screw-on caps, fitted with o-rings and Teflon tape to prevent both foam from seeping out and water from seeping in when processed in a water bath. Mold release (PTM and W Industries # PA 0801) was applied to the inside of each cylindrical mold to help in extracting the foam once it was cured.

The molded foam samples were allowed to rise freely in the cylindrical molds for thirty minutes under five different thermal conditions. Three sets of samples were processed at 85°C, 40°C, and 25°C in a controlled water bath. All six cylindrical molds were extended approximately 12.5 mm out of the water. For these samples, the rising foam completely filled the cylindrical mold and a mushroom shape was formed at the top (Figure 2.1). Two additional processing conditions were performed in packed ice (0°C) and at ambient conditions (~25°C) with no attempt to control the temperature (Figure 2.1). For 0°C processing, the foam only rose about 50% during the 30 minutes in the ice bath and completed rising during the post-curing process. Post-curing of all foam samples was conducted in recirculating air oven at 150°C for four hours, after which samples were extracted from the molds by unscrewing the tube cap and pushing lightly on the bottom end of the foam.

Using a band saw, the mushroom top was removed from each molded foam samples and then the remainder of each molded foam sample was cut into three or four sections.
The foam samples cut into four sections are shown in Figure 2.2. To assure sample consistency, the top and bottoms of each section were sanded to achieve a 25.4 mm height. Samples were analyzed from the center and side of each section. The aging study of the samples was carried out by cutting the large cylinders into three sections.\textsuperscript{6}

![Figure 2.1: PU foam samples prepared at different processing temperatures](image)

Figure 2.1. PU foam samples prepared at different processing temperatures

![Figure 2.2: Sectioning of the PU foam samples for analysis](image)

Figure 2.2. Sectioning of the PU foam samples for analysis

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2.3 Characterization

Polyurethane foam samples were characterized by elemental analysis, density gradient measurements, Optical microscopy, Scanning electron microscopy, Infrared spectroscopy, Photoacoustic IR, and Thermal analysis (DSC and TMA).

2.3.1 Elemental Analysis

Elemental analysis of the %C, %H, and %N composition was determined by NuMega Resonance Labs, Inc. San Diego, CA. The data used to examine the differences in those elements with time and with processing conditions. The data shows no significant difference of percentage in percentage of C, N, and H with time and with processing conditions.

2.3.2 Density Gradient

Radial density gradient analyses for all samples were performed by cutting out cylindrical samples with a cork borer in a spiral pattern as illustrated in Figure 2.3. Radial density gradient analysis was performed by measuring the density of 3 mm diameter cylindrical sections, removed from the 25.4 mm high sectioned samples at predetermined radial positions. Density was measured as a function of vertical and radial position. The density and the density gradient data were used to correlate the cellular distribution between center and side samples prepared at different processing temperature.
2.3.3 Optical Microscope

Optical images were collected by Olympus DP11 2.5 million resolution microscope and were saved on Smart media card. Images were used to examine morphology changes due to different processing conditions at the center and side of each sample.

2.3.4 Scanning Electron Microscope

The foam samples were examined by JSM 500 Scanning Electron Microscope. These foam samples are insulating. To make the foam samples to be conductive a thin layer of gold was coated using a metal sputter coater. To gather the topological images the secondary electron detector was used. Also SEM allows focusing much greater depth than the optical microscope. Therefore, SEM can produce an image which is a good representation of the detailed three dimensional image of the sample at higher magnification. The SEM images were used to examine the morphological differences between the center and side samples processed at different temperature.
2.3.5 Photoacoustic IR

Photoacoustic data were obtained on DIGILAB FTS 7000 spectroscopy. A flow rate of 20 mL/min of helium was utilized to purge the cell and sample prior to measurement. In addition, the trapped helium gas in the cell acts as the signal transducer in PAS. Background scans was collected with a MTEC glassy carbon reference. Samples were prepared by cutting a 3.25 mm diameter, using a cork borer. At least 64 scans were collected and averaged at 4 cm$^{-1}$ resolution for each individual spectrum. All the photoacoustic spectra were normalized to the out of plane C-H band for the aromatic ring at 817 cm$^{-1}$. This band shows little change during curing or aging. This technique provides the absorption spectra of the foam sample, allowing chemical identification and quantification. This is easy to use technique with the expanded capabilities of depth profiling, without sample modification.

2.3.6 Infrared Imaging from Single Point detector (SPD)

Infrared imaging was performed using a DIGILAB UMA 600 infrared Microscope operated in the reflection view mode. A gold plated slide was used to collect the reference and background spectrum. The samples were prepared by slicing the 3.25mm diameter sections into sections less than 0.8mm thick. A minimum of 64 scans were collected and averaged at 8 cm$^{-1}$ resolution for each spectrum presented. The standard objective lens is 15X. A liquid nitrogen cooled and MCT detector was used to obtain the data over a wide area and averaged into a single spectrum. The IR microscope can be used to measures small samples and spatial, small components of larger samples. Therefore, this technique can be used to distinguish the differences in chemistry between cells and struts of the PU foam.

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2.3.7 IR Imaging from multi point detector (MPD)

The IR images were obtained using a UMA 600 IR microscope. The imaging technique was used to generate an IR spectroscopic chemical image. This allows one to perform chemical analysis of a sample with the power of spatial resolution. The result is a chemical image and analysis system suited to non-invasive chemical characterization of foam samples that are morphologically complex.\textsuperscript{10}

2.3.8 Thermal Analysis

2.3.8.a Simultaneous Thermal Analysis (STA)

Simultaneous thermal analysis was conducted using a Netzsch STA 449 C instrument. Simultaneous differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed on all foam samples under N\textsubscript{2} purge gas at a heating rate of 10°C/min up to 540°C. Samples were placed in aluminum pans that were capped with a lid and crimped. Thermal gravimetric analysis (TGA) traces any weight loss the materials undergo upon heating including decomposition temperatures. Differential scanning calorimetry (DSC) is sensitive to any phase changes or chemical reactions the sample may undergo during thermal cycling. The graphs were plotted by Origin 7 program.\textsuperscript{11,12}

2.3.8.b Thermal Mechanical Analysis (TMA)

Thermal mechanical analysis (TMA) was conducted using Netzsch TMA 202 instrument. Thermal mechanical analysis experiments were run at 10k/min, from 25°C to 250°C under N\textsubscript{2} gas (50ml/min) with a constant force of 5cN applied to the sample. This measures the sample expansion and collapse steps under constant force with respect to temperature.\textsuperscript{13}
2.4 References

7. http://mse.iastate.edu
11. http://www.psrc.usm.edu/macrog/dsc.htm

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CHAPTER 3

PU FORM MORPHOLOGY AND IMAGING

3.1 Introduction

SEM and Optical microscopy are utilized to conduct extensive morphological studies of the polyurethane foam. The data collected using these techniques provides important information with respect to cell distribution, cell size and skin thickness. This data also provides information about cell and skin morphology. PU foam formation is an exothermic reaction, with higher temperature in the center, decreasing radially to the side. The temperature gradient is the direct result of conduction. The temperature gradient that occurs between the center and the side, results in the difference in morphology in foam. The temperature gradient is primarily responsible for the difference in chemistry (IR, DSC, and TMA) between the center and the side, as well as the mechanical properties.

3.2 Comparison of PU Foam Processed at Different Processing Temperature

The optical images are obtained from the center of 25°C water bath (WB), 40°C WB, and 85°C WB, and are shown in Figure 3.1. All the images were obtained at the same magnification. The 25°C WB sample exhibits many different cell sizes. In contrast, the 85°C WB sample exhibits a higher uniformity in cell size. The 40°C WB foam sample features an intermediate cell size, somewhere in between the 25°C WB and the
85°C WB. Measuring the distribution of cells is qualitative and limited by the geometric area analyzed. However, the pictures are useful in identifying the trends in morphology as a function of processing temperature. In conclusion, the foam processed at higher temperature exhibits a higher degree of uniformity in cell and strut distribution when compared to the lower temperatures. This is consistent with the average density data obtained for 25°C to 85°C. As it is shown in Figure 3.2, the average density decreases with increasing temperature. The chemical differences between the cells and struts are discussed in Chapter 4.

![Figure 3.1. Optical images of 25°C WB (A), 40°C WB (B) and 85°C WB (C) center samples](image-url)
3.3 Comparison of PU Foam Center and Side

Morphological differences are observed and identified at specific location within a single sample. These locations are designated as the center and side, respectively as illustrated in Figure 3.3.

![Sampling locations of PU foam](image)

The overall cell size appears to be larger and less uniform in distribution, for a 25°C WB center when compared to the 25°C WB side sample (Figure 3.4). The side and center samples of the 85°C WB are very similar. Both samples cells appear more uniform with respect to cell size and distribution. Also with the increase temperature cells become

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larger that results larger window space and less struts material allowing foam to be less compact and more uniform in cellular distribution. Therefore 25°C WB sample exhibits the higher radial density gradient compared to the 85°C WB. The density was measured as a function of radial position as describe in the experimental chapter. The radial density increased from center to side as illustrated in Figure 3.5. An increase in temperature decreases the density gradient.

![Figure 3.4. SEM images of 25°C (A) and 85°C WB (B) center (left) and side (right)](image)

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Figure 3.5. Density variation of different processing conditions as a function of radial position

3.4 Skin Morphology at Different Processing Temperatures

The SEM images of skin of ReCrete PU foam samples processed at different temperature are shown in Figure 3.6. As opposed to the skin sample processed at lower temperature, skin samples processed at higher temperature exhibits larger, more elongated cells resulting decrease in uniformity with thinner skin. Thinner the skin results the lower skin density. Therefore at higher temperature exhibits lower skin density. Figure 3.6, D is an example of skin processed at higher temperature. However no extensive or complete analysis of skin was conducted during the morphological exploration.
Figure 3.6. SEM images of 25°C WB (A), 40°C WB (B), 66°C WB (C) and 85°C WB (D) skin samples

3.5 Conclusion

An SEM and optical microscopy study of the cells strut and skin morphology of the effect of sampling position, processing temperature and the effect of density gradient were presented in this chapter. The data shows that the increase of processing temperature results in larger cells with greater uniformity. An increase in processing temperature results in thinner skin and more elongate cells. Also noted is that average densities both decrease and were less variable as processing temperature increased. Therefore it is likely that morphology will effect the chemical, physical and mechanical properties of the foam.
CHAPTER 4

INFRARED SPECTROSCOPY

4.1 Background

FTIR spectroscopy is a tool used to identify chemical species and functional groups in a variety of complex samples. The chemistry of PU foams can be probed using FTIR/PAS (Photoacoustic) spectroscopy and FTIR microscopy (single point/3-D imaging), which can provide valuable chemical and spatial information. The main goal of the IR study is to identify the fundamental groups in the PU foam and determine the effect of curing temperature and aging on the chemistry of the system. Many functional groups give characteristic IR absorption at specific and narrow frequency ranges. IR spectroscopy/microscopy is essential for the detection, examination and identification of changes in composition and chemical functional groups in the compound.¹ ²

Photoacoustic spectroscopy (PAS) is a useful tool in the analysis of highly absorbing samples. Samples that are difficult to analyze by conventional IR methods are easily examined using PAS. In addition PAS spectra is obtained with minimal sample preparation and without physical alteration of the samples (i.e. no grinding, mixing with KBr). The size, shape and crystalinity of a sample is not detrimental in using this technique. Furthermore, PAS is capable of profiling a sample at various depths from 1-20 µm without slicing the sample. This is accomplished through deconvolution of the time dependent signal which is related to the penetration depth of the thermal wave in the
sample. FTIR-PAS can provide both quantitative and quantitative data about samples due to the reliability, reproducibility, and strong data processing capabilities of the instrument.

Infrared microscopy study is conducted by using either single point detector (SP) or multi point detector (MP). IR microscope measures the spectra of small samples or small part of large sample such as a cell and strut contained within a given sample. SP provides the image as well as an average spectrum of the selected area. The MP provides a 3-D image and individual IR spectra in the selected area. Therefore MP provides the information containing the spatial distribution of functional groups within a sample.¹

4.2 FTIR Photoacoustic Spectrum of Rubinate

Rubinate, Voranol, Silicone surfactant and amine catalyst are utilized as starting materials in the synthesis of PU foam. Although the foam is a complex mixture of these components the Rubinate is the key constituent in the reactivity and the functionality of the PU foam. The FTIR/PAS spectrum of Rubinate is shown in Figures 4.1. The spectrum is helpful in identifying the specific IR bands corresponding to key functional groups present in the unreacted Rubinate and the reacted PU foam. We will use this data as a guide in the identification of bands in the IR spectrum of the PU foam. Rubinate is a mixture of partially reacted and unreacted MDI. The reacted MDI is identified by the uretioneimine ring structure shown in Figure 4.1. In contrast, unreacted MDI is indicated by the appearance of the broad diisocyanate (NCN) band in the spectrum.

At higher processing temperature, the thermally unstable uretioneimine degrades giving equal molar quantities of isocyanate and carbodiimide (spectrum a). Uretioneimine carbonyl stretch appears in the IR spectrum at 1730 cm⁻¹ and the C-N stretch of the ring
structure appears at around 1379 cm\(^{-1}\).\(^{3,4}\) Uretoneimine exists as a thermally unstable four membered ring structure, where heat energy initiates the structure degradation. Thus, at higher temperatures, decreases in the uretoneimine carbonyl peak at 1721 cm\(^{-1}\), and C-N stretch peak at 1384 cm\(^{-1}\), are observed. This trend is shown in the IR spectra in Figure (4.2 A, B, C). These spectra are normalized versus the C-H out of plane bending band at 817 cm\(^{-1}\). This normalization is helpful in identifying changes that occurred in the PU foam at higher processing temperature, such as the decreases in intensity of the C-N stretch at 1384 cm\(^{-1}\). Compared to isocyanate, carbodiimide is a stable functional group that does not react appreciably at higher processing temperature. The result is a high intense peak at higher processing temperatures that doesn't diminish over time in comparison to NCO which continuous to react. By heating rubinate it can be confirmed that the carbodiimide peaks present in the IR spectrum of PU foam at 2100 cm\(^{-1}\) and 2136 cm\(^{-1}\) is the direct result of the dissociation of uretoneimine ring structure as well as the self reaction of unreacted isocyanate which is present.
4.3 FTIR Photoacoustic Spectrum of PU Foam.

With the structural identification of Rubinate, the identification of functional groups within the PU foam is also possible. A typical FTIR spectrum of polyurethane foam is shown in Figure 4.3 with important functional groups labeled for clarity. Key absorption bands in the PU foam are shown in the figure. For example IR bands at 3340 cm\(^{-1}\) (Urethane N-H), 1726 cm\(^{-1}\) (C=O stretch of urethane), and 1082 cm\(^{-1}\) (C-O-C stretch) are indicative of the urethane linkages in the foam. The O=C=N stretch band at the 2269 cm\(^{-1}\) can be attributed to unreacted isocyanate. The uretoneimine ring structure can be identified using bands at 1726 cm\(^{-1}\) (C=O stretch of the ring) and 1379 cm\(^{-1}\) (C-N and C=N stretch of the ring). The trimerized form of reacted isocyanate is also clearly visible at 1413 cm\(^{-1}\) using the C-N of isocyanurate. The two absorption bands at 2136 cm\(^{-1}\) and
Figure 4.2. FTIR Photoacoustic spectrum of Rubinate at room temperature and at elevated temperature; expand region of 4000-1800 cm\(^{-1}\) (A), and finger print region (B)

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2100 cm\(^{-1}\) are indicative of the formation of carbodiimide a byproduct of uretoneimine decomposition. Finally the doublet at 2360 cm\(^{-1}\) (O=C=O) and sharp spike at 667 cm\(^{-1}\) show that trapped CO\(_2\) is present in polyurethane foam.\(^3\)\(^,\)\(^4\) The FTIR assignments are given in Table 4.1.

4.3. FTIR spectrum of polyurethane foam

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Table 4.1 Assignment of FTIR spectrum of PU Foam²,³

<table>
<thead>
<tr>
<th>Wave number (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3340</td>
<td>ν(N-H ) Urethane</td>
</tr>
<tr>
<td>3325</td>
<td>ν (N-H H- bonded ) Urea</td>
</tr>
<tr>
<td>3321</td>
<td>ν (O-H ) in Polyol</td>
</tr>
<tr>
<td>2940</td>
<td>ν (C-H ) in CH₂</td>
</tr>
<tr>
<td>2855</td>
<td>vs(C-H ) in CH₂</td>
</tr>
<tr>
<td>2360</td>
<td>va(O=C=O )</td>
</tr>
<tr>
<td>2269</td>
<td>ν(N=C=O) in isocyanate</td>
</tr>
<tr>
<td>2136,2100</td>
<td>ν(N=C=N) in carbodiimide</td>
</tr>
<tr>
<td>1726</td>
<td>ν(CO) in ester, Urethane H bonded, Uretoneimine carbonylic acid</td>
</tr>
<tr>
<td>1600</td>
<td>ν(C=C) aromatic</td>
</tr>
<tr>
<td>1529</td>
<td>p(CH₂)</td>
</tr>
<tr>
<td>1527</td>
<td>ν(C-N) + δ(N-H) Amide II</td>
</tr>
<tr>
<td>1414</td>
<td>ν(C=C) isocyanurate ring</td>
</tr>
<tr>
<td>1379</td>
<td>ν(C-N) Uretoneimine</td>
</tr>
<tr>
<td>1314</td>
<td>ν(N-C=N-N) Uretoneimine</td>
</tr>
<tr>
<td>1226</td>
<td>ν(C-N) + ν(N-H) Amide II (weaker)</td>
</tr>
<tr>
<td>1102</td>
<td>va (C-O-C) aliphatic ether</td>
</tr>
<tr>
<td>1100</td>
<td>ν(Si-O-Si)</td>
</tr>
<tr>
<td>1082</td>
<td>ν(C-O-C) in Urethane O=C-O-C</td>
</tr>
<tr>
<td>1030</td>
<td>ν(Si-O)</td>
</tr>
<tr>
<td>817</td>
<td>p(C-H ) in aromatic</td>
</tr>
<tr>
<td>667</td>
<td>Sharp spike due to CO₂</td>
</tr>
<tr>
<td>560</td>
<td>Ring bending band</td>
</tr>
</tbody>
</table>

ν - Stretching mode  
p - out of plane bending  
va- Asymmetric stretching  
vs- Symmetric stretching  
δ - in plane bending or scissoring

4.4 FTIR/PAS Comparison of Center and Sides of PU Foams (25°C and 85°C)

The center and side PU samples of each temperature were compared to determine the chemistry difference between the two regions. The foam formulation is an exothermic
reaction, which begins in the middle of the cylinder, and proceeds to diffuse outwards to the side of the cylinder. The side of a foam tube will be at lower temperature than center based on conduction. This temperature gradient results in a difference in morphology and cell distribution. In addition, there is a high probability of thermal dissociation of the uretoneimine ring in the center of the cylinder in comparison to the side. The temperature difference between the center and side of PU foams processed at different temperature should have a direct influence on the degree of uretoneimine decomposition, carbodiimide formation, and the concentration of isocyanate and continued reactivity of PU foam.

The IR spectra of PU foam processed at 25°C for the center and side are shown in Figure 4.4. The spectra for the center and side are very similar with minor changes observed for the isocyanate band located at 2269 cm\(^{-1}\). The elevated temperature facilitates the continued reaction of isocyanate at the centre causing the decrease in intensity of the band. The uretoneimine structures are thermally stable at 25°C and the ability to convert to isocyanate and carbodiimide is kinetically limited. We see only a small amount of carbodiimide in the spectra both the side and center. From the spectrum for 25°C we see only a minor decrease in the isocyanate intensity with corresponding increases in the bands associated with urethane linkages.

The PU foam processed at 85°C is significantly different. The processing temperature is sufficiently high to cause the thermal degradation of the uretoneimine ring in the center and the side of the polymer. In addition, since the core temperature of the foam is higher we would expect foams processed at 85°C to have a higher degree of dissociated uretoneimine at the center. The thermal activation of uretoneimine decomposition results
in increase in the concentration of isocyanate and carbodiimide groups in the PU foam. However the carbodiimide is less reactive than isocyanate. Therefore at higher temperature the carbodiimide peak emerges and remains constant while isocyanate continues to react.

The center and side FTIR/PAS analysis of 85°C PU foam is presented in Figure 4.5. Clearly the carbodiimide intensities at the center and side have increased in comparison to the 25°C PU foam center and side. This is a direct consequence of the higher degree of bond dissociation of uretoneimine at 85°C. In fact there are slight differences in the degree of dissociation between the center and the side of the 85°C PU foam. These changes are so small that we see no appreciable change in the carbodiimide band. In addition, the concentration of unreacted isocyanate is again higher for the side in comparison to the center of the foam. This indicates that a difference in the core temperature increases the reactivity of the unreacted isocyanate in the center of the polymer in comparison to the side for the 85°C PU foam. These results indicate that the processing the PU polymer at 85°C results in a heterogeneous PU foam. Density gradients with changing morphology are the direct result of the chemistry change. The results suggest that the complex chemistry changes will influence the modules of the foam based on rigid functional groups (uretoneimine) as processing temperature increases.
Figure 4.4. FTIR Photoacoustic normalized spectra of 25°C WB center and side; expand region of 4000-1800 cm$^{-1}$ (A), and fingerprint region (B)
Figure 4.5. FTIR Photoacoustic normalized spectra of 85°C WB center and side; whole spectrum (A), expand region of isocyanate (B), and finger print region (C)

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4.5 Comparison of PU Foam Processed at Different Temperatures.

The processing temperature has been shown to change the chemical and mechanical properties of the foam previously. The thermal activation of uretoneimine decomposition with increasing temperature results in increase in the concentration of isocyanate and carbodiimide groups in the Rubinate (Figure 4.2). Similar behavior should be observed in PU foams containing uretoneimine structures. However, a key difference is the ability of isocyanate to continue to react with functional groups in the PU foam. Furthermore, the dissociation of the ring and continued reaction of isocyanate can result in the formation of new functional groups such as carbodiimide and isocyanurate discussed previously with respect to Rubinate.5,6,7

The thermal activation of uretoneimine decomposition and the continued reaction of isocyanate should result in a decrease in intensity of the bands at 1726 cm\(^{-1}\) (\(\nu\) CO of isocyanate) and 2269 cm\(^{-1}\) (\(\nu\) N=C=O of isocyanate) at higher processing temperature for the PU foams. Also the dissociation of uretoneimine into isocyanate and carbodiimide should be signaled by the emergence or increase in intensity of the N=C=N band located at 2136 cm\(^{-1}\). The FTIR spectra of PU foams processed at 25°C and 85°C are presented in Figure 4.6. All samples were analyzed within three days of preparation to maximize the chemical changes that occur as the PU foam ages. The only difference between the two samples is the processing temperature.
Figure 4.6. FTIR Photoacoustic spectrum of 25°C and 85°C PU Foam: expand region of 4000-1800 cm⁻¹ (A), finger print region (B)
It is clear from the data that the PU foam processed at 25°C is different than that processed at 85°C. The 25°C PU foam has a larger degree of unreacted isocyanate in the polymer matrix indicating that the continued reaction of the species is minimized at lower processing temperature. In contrast, the 85°C sample shows a large decrease in the isocyanate peak intensity consistent with the continued reaction of this species during processing of the PU foam. The reduction of uretoneimine in the 85°C sample is signaled by a decrease in the IR bands associated with ring structure located at 1379 cm⁻¹, and 1731 cm⁻¹. Increases in the isocyanurate peak intensity are the result of the formation of the isocyanate trimer species located at 1413 cm⁻¹. Finally the conversion of the uretonimine structure in the 85°C PU foam results in a significant increase in the thermally stable carbodiimide structure at 2136 cm⁻¹ and 2100 cm⁻¹. This structure is minimized in the PU foam processed at 25°C.

The complex chemistry changes associated with the chemistry are consistent with the morphological differences observed with SEM and optical microscopy (chapter 3). However, a direct correlation does not exist at this point because the morphological studies are purely qualitative. However, it is clear that significant changes in the chemistry occur as a function of increased processing temperature. The degradation of single linkages with high rigidity (uretoneimine) into multiple less rigid linkages (carbodiimide, isocyanate) should have a direct impact the thermal and mechanical properties of the PU foam. The modulus is a largely a measurement of the stiffness or rigidity of the polymer. As processing temperature increases, the rigidity of the polymer decreases decreasing the modulus of the foam.
4.6 Aging of PU Foams Processed at Different Temperatures.

The aging study of 25°C and 85°C water bath PU foams were carried out using FTIR/PAS. There are really two issues that must be examined in the aging of PU foams processed at different temperatures. First, the initial concentration of uretoneimine is going to be significantly larger in the 25°C PU foam in comparison to the 85°C PU foam. This trend was shown above in Figure 4.6. However we also stated that the isocyanate concentration changes as side reactions occur in the PU foam. In addition, the center and side sample of the 25°C and 85°C PU foam have significantly different concentrations of uretoneimine, carbodiimide, and isocyanate. The concentrations of functional groups in the foam are strictly related to the processing temperature and core reaction temperature. However, we expect that the chemistry of the foams will change as a function of unreacted isocyanate in the PU foam over time. Therefore, the isocyanate peak intensity should decrease as a function of time for both samples giving rise to changes in the FTIR/PAS over time. In contrast we believe that the uretoneimine structures remaining in the PU foam after processing will remain relatively constant over time.

The time dependence study of the 25°C and 85°C PU foam are presented in Figure 4.7 and 4.8, respectively. The short aging study was conducted for two month for both the 25°C and 85°C water bath center samples. In Figure 4.7 there is a clear loss in intensity of the isocyanate (2269 cm\(^{-1}\)) band in the FTIR/PAS spectra as a function of time. The trend indicates that the isocyanate continues to react over time reducing the concentration of this species in the PU foam. As the isocyanate band decreases the overlap with the carbodiimide band decreases allowing the resolution of this species. It is clear in the PAS spectra that the concentration of carbodiimide does not change over
Figure 4.7. FTIR Photoacoustic spectrum of 25°C water bath PU Foam; expand region of 4000-1800 cm$^{-1}$ (A), fingerprint region (B)

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time. This band will change if uretoneimine ring structures dissociate to produce carbodiimide and isocyanate. However, we see little change in the band intensity for uretoneimine (1377 cm\(^{-1}\)) in Figure 4.7C. The changes we observe are consistent with the formation of urethane linkages only. For example, increases in the urethane linkages can be observed as increases in band intensities at 1727 cm\(^{-1}\) and 1082 cm\(^{-1}\) in Figure 4.7C.

The trends observed in the 25°C PU foam are similar to the changes observed in the 85°C PU foam. In figure 4.8 it is clear that a significant amount of carbodiimide is present in the foam as a result of the uretoneimine degradation with processing temperature. In addition, there is clearly a decrease in intensity of the isocyanate band located at 2269 cm\(^{-1}\). The carbodiimide bands located at 2136 cm\(^{-1}\) and 2100 cm\(^{-1}\) show a slight variation in peak intensity as a function of aging. However, the change is negligible in comparison to the change in isocyanate intensity. Although the amount of unreacted isocyanate is significantly less in the 85°C PU foam in comparison to the 25°C PU foam, the changes in chemistry are strongly related to the continued reaction of this species. For example, the bands attributed to the urethane linkage (1727 cm\(^{-1}\) and 1082 cm\(^{-1}\)) increase in intensities, (Figure 4.8) in the same manner as 25°C PU foams.

As shown in Figures 4.7 and 4.8, there is a decrease in the intensity of isocyanate, which is likely due to the reaction of other chemical species present in the polyurethane network for both the 25°C and 85°C as a function of time. The remaining isocyanate can in turn react to form additional urethane linkages and new species including isocyanurate. Normalized data indicates the presence of isocyanurate (1413 cm\(^{-1}\)) in the PU foams processed at 25°C and 85°C. The aging studies for both foams are fairly consistent after processing. The rigidity of the PU foam is a function of the concentration of rigid
structures in the polymer matrix. As stated previously uretoneimine is the primary species that imparts rigidity to the foam structure. Breaking of the uretoneimine ring is result in the conversion of one rigid linkage into two more flexible linkages (carbodiimide, isocyanate). The conversion of rigid structures to more flexible structures will have a direct impact on the mechanical properties of the foam. Therefore, the chemistry changes will directly effect the modulus of the foam. However, more flexible PU foam may eliminate the fracturing observed by Winnery and Goods during impact testing.
Figure 4.8. FTIR Photoacoustic spectrum of 85°C water bath PU Foam; expand region of 4000-1800 cm\(^{-1}\) (A), fingerprint region (B)

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4.7 Comparison of Struts and Cells in PU Foams Using SP IR Microscopy

IR imaging is a surface analytical technique, which provides spatial chemical characteristics of the PU foam structure. As illustrated in Figure 4.9 the IR spectrum of a single cell in the foam is distinguished from the struts surrounding it. The isolation of chemical structures is crucial in the comparison of the cell properties of the PU foams in comparison to the thicker struts surrounding a cell. The ability to probe the chemistry changes at structurally different components of a heterogenous mixture (foam) allows very distinct chemistry changes to be differentiated. In fact, the data shows a higher degree of intermolecular interactions exists at the strut in comparison to the thin cell due to the packed chemical structure. The packing causes a broadening in the N-H and C=O stretch for the chemical signature of the struts. A decrease in the overall resolution of bands in the struts is a direct result of the band broadening.

The IR spectra of the 25°C and 85°C WB with the optical image a collection area are presented in Figure 4.9A-D. The same trends observed previously for processing temperature are observed in these figures. First, the PU struts and cells change dramatically as the processing temperature increases. The carbodiimide bands are clearly larger for PU foams processed at high temperature. These results are consistent with the studies conducted previously with respect to center versus side and processing temperature. However, the fact that struts show the same chemical change is important. The closed structure of rigid PU foams is based on each cell having a closed structure (struts surrounding an individual cell). The fact that this chemistry changes as a function of processing temperature supports the premise that the rigid structure and the modulus of the PU foam are the direct results of the chemistry.
Figure 4.9. FTIR spectrum of 25°C WB center cells (A), strut (B), 85°C WB center cells (C) and strut (D)

4.8 IR Imaging Multi Point Detector (MPD)

IR imaging from the multi point detector is a complimentary technique that provides the spatial distribution of the chemical characteristic for the sample analyzed over a two dimensional array. The spatial distribution of carbodiimide (2110 cm⁻¹) and uretoneimine (1373 cm⁻¹) are extremely important and can be easily identified in two dimensions for the foam samples processed at different temperatures. The distribution of chemical species and their intensity in the images is indicated with the colors red and yellow to indicate high concentration. Low intensity or concentration is indicated by light and dark blue colors.

The distribution of carbodiimide (2110 cm⁻¹) and uretoneimine (1373 cm⁻¹) for the 25°C WB foam are presented in Figure 4.10 and 4.11. It is clear from the images shown in 4.10 that the concentration of carbodiimide is relatively low in concentration with very little high intensity red or yellow in the image. However, in contrast the image
corresponding to uretoneimine shows high intensity yellow and orange in the strut of the foam as shown in the image. This agrees with the data presented previously showing that the uretoneimine structure remains largely intact with low processing temperature.

The distribution of carbodiimide and uretoneimine for the 85°C WB foam are presented in Figure 4.12 and 4.13. The effect of processing temperature on carbodiimide and uretoneimine is obvious. In the case of carbodiimide we see high intensity of the species in the struts of the foam. In addition, very little of the carbodiimide is observed in the cells of the foam. In contrast, the concentration of uretoneimine decreases relatively to the concentration of the carbodiimide for the foam processed at 85°C. very little uretoneimine is observed in the struts in comparison to carbodiimide. Clearly, the uretoneimine decomposition has resulted in the increase of the carbodiimide in the PU foam. Interestingly we find the opposite trend in the cell structure. In the cell the uretoneimine concentration is significantly higher in the cells at 85°C in comparison to carbodiimide. We are not quite sure why the uretoneimine concentration within a cell would be less. However, we will continue to examine the differences using the imaging technique to determine if this trend is common to PU foams processed at high temperature.

The result confirm single point measurements indicating the rigid uretoneimine structure decreases a function of processing temperature in the struts of the foam. Since the struts are the key to the rigidity of the foam, it is not surprising that the modulus would be affected by the changes in the chemistry of the structure. As uretoneimine structure degrade in the struts the rigidity of the structure decreases and the foam becomes more flexible.
Figure 4.10. IR images of the spatial distribution of carbodiimide at 25°C WB PU foam; A-digital image of the surface, B-Flat view obtained at 2110 cm\(^{-1}\), and C-IR spectrum of the marked point on the flat view.
Figure 4.11. IR images of the spatial distribution of uretoneimine at 25°C WB PU foam; A- digital image of the surface, B-Flat view obtained at 1373 cm$^{-1}$, and C-IR spectrum of the marked point on the flat view.
Figure 4.12. IR images of the spatial distribution of carbodiimide at 85°C WB PU foam; A-digital image of the surface, B-Flat view obtained at 2110 cm$^{-1}$, and C-IR spectrum of the marked point on the flat view.
Figure 4.13. IR images of the spatial distribution of uretoneimine at 85°C WB PU foam; A- digital image of the surface, B-Flat view obtained at 1373 cm\(^{-1}\), and C-IR spectrum of the marked point on the flat view.
4.9 Conclusions

The IR spectroscopy and microscopy study of PU foams (center and side) processed at different temperatures consistently shows that the degradation of uretoneimine structures is a critical component of the foam chemistry. In addition, the continued reaction of isocyanate changes the chemistry of the system over time. The data shows that the processing temperature has a significant effect on the aging and the stability, of the foam. The decomposition of rigid structures will likely have a direct effect on the mechanical properties and stability of the PU foams.

Increase processing temperature showed in increasing carbodiimide peak intensity with a decrease in isocyanate intensity due to the dissociation of thermally unstable uretoneimine ring. The center samples showed higher carbodiimide intensity compare to the side results of the exothermic foam formulation leading to dissociation more ring structures in center than side. The formation of more carbodiimide with time due to reaction of unreacted isocyanate groups also occurs with aging. The microscopy provided evidence that chemical differences between cells and struts exist in the same sample. The examination of the foam skin, tensile strength, and adhesion will aid in further correlation between chemical, physical and mechanical properties of the PU foam systems using IR analysis. Determination of the foam skin, tensile strength, adhesion will aid in further correlation between chemical, physical and mechanical properties of PU foam systems.

4.10 Reference


CHAPTER 5

THERMAL ANALYSIS STUDIES

5.1 Introduction

Thermal analysis data of PU foam was obtained from simultaneous thermal analysis (STA-DSC/TGA) and Thermal mechanical analysis (TMA). These techniques are used to monitor the difference in magnitude and the number of endothermic (heat absorbed) and exothermic (heat released) transition steps in DSC and the number of expansion and compression transition in TMA during thermal cycling. The magnitude and the temperature of the transitions (endothermic/exothermic) were dependent on both processing conditions and the sampling position. Therefore, the data is used to probe the chemical changes such as exchange reactions and cleavage of uretaneimine to form isocyanate and carbodiimide. Evaporation of trapped water molecules is also possible in foam samples. The ReCrete PU foam was examined with respect to position (center and side) and with aging. However the magnitude and temperature of transitions were dependent on both processing conditions and sampling position.$^{1,2}$
5.2 Results

5.2.1 Effect of Processing Temperature

5.2.1a Analysis of Samples From Center Position

A comparison of the DSC and TMA plots are shown for foams processed at 25°C and 85°C and analyzed within day of preparation in Figure 5.1. There were many more distinct transitions observed for the foam processed at 25°C with a strong endothermic transition at ~100°C followed by a broad exotherm (120°C) that corresponded with a steep contraction step in the TMA curve (depicted with vertical dotted line). Initially the transition ~100°C is believed to be due to water. But simultaneous analysis of TG with DSC doesn't show any weight loss as in Figure 5.2. Therefore this may be the result of thermal activated ring cleavage of the uretoneimine functionality consistent with the temperature range of 80-150°C reported in the literature. The fact that these transitions were not observed in the foam sample processed at 85°C is consistent with fewer of these functionalities present as shown by IR analysis. At higher temperature both foam samples exhibited a broad endotherm (~140-150°C) followed by an exotherm at ~185-188°C accompanied by expansion in the TMA curves. This is believed to be the result of further reaction of unreacted isocyanate groups, where the exotherm is broader and weaker for the foam processed at 85°C consistent with fewer unreacted isocyanate functionalities identified by IR. The fact that the DSC transitions were much weaker and the contraction steps for the 85°C processed foam were less steep and occurred at higher temperatures are all consistent with a foam sample that is more fully reacted compared to the sample processed at 25°C.
Figure 5.1. Comparison of DSC (top) and TMA (bottom) plots of foams processed at (a) 25°C and (b) 85°C and analyzed one day after preparation. Samples were taken from the center of the cylinder. The vertical dotted lines in the TMA plots show the contraction and expansion steps that correspond to the major transitions in the DSC.
5.2.1b Analysis of Samples from Side Position

Foam samples taken from the side position were also examined. An analysis of the DSC and TMA plots of side samples are shown for foams processed at 25°C and 85°C in Figure 5.3. The DSC transitions observed for side samples were similar to the center samples, but much more distinct for the foam processed at 25°C as a result of more unreacted functionalities. The first derivative of the DSC (DDSC) is shown in Figure 5.2 for the foam processed at 25°C, which helped to identify the transitions. The exotherm following the endothermic transition at ~100°C occurred at lower temperature corresponding to a steeper contraction step in the TMA compared to the center sample. As a result of this steep contraction, the expansion step is weaker, but is still observed at ~185°C corresponding to an exotherm in DSC. In the case of the foam sample processed at 85°C, both the endotherm and exotherm observed for the center sample was also observed for the side sample, but both occur at lower temperature. The corresponding
TMA curve shows a steeper contraction step for the side sample, but not as steep and at a higher temperature compared to the side sample taken from the foam processed at 25°C. Expansion was also observed corresponding to the exotherm at 180°C for the foam processed at higher temperature.

![Figure 5.3](image)

Figure 5.3. Comparison of DSC and DDSC (top), and TMA (bottom) plots for side sample of foam processed at (a) 25°C and (b) 85°C, both analyzed one day after preparation. Vertical lines in TMA plot show contraction and expansion steps that correspond to major transitions in DSC.

The reason for the differences observed for samples taken from the center position versus the side position and at different processing temperatures can be explained in the
following manner. The reactions leading to foam formation are highly exothermic and as the foam expands the center of the cylinder is insulated resulting in a temperature gradient. Therefore, the side position, which is closest to the aluminum mold, will be cooler. In the case of the foam processed at 25°C, some of the heat can be dissipated to the water bath. However, in the case of the foam processed at 85°C, the water bath is hotter and there is subsequently less dissipation of the heat evolved during the exothermic reactions forming the foam. The differences observed in the DSC and TMA for different processing temperatures and sampling positions are consistent with more unreacted isocyanate functionalities and a greater number of labile uretonimine ring structures for foams processed at 25°C and at the side positions. Even though IR analysis showed that the foam processed at 85°C also contains uretoneimine rings, the fact that no endothermic/exothermic transitions were observed near 100-130°C, as observed for the 25°C processed foam may be a consequence of small sample size of the DSC experiment, or that the uretoneimine rings are more “locked” into the structure and are not as easily cleaved.

5.2.2 Room Temperature Aging Studies

The same foam cylinders were analyzed 1 week and 2 months after processing to access any changes in thermal properties after storage in plastic bags at room temperature. The DSC and TMA results for foam processed at 25°C and analyzed 1 week after preparation are shown in Figure 5.4. The DSC transitions as described in preceding sections were still visible, but weaker, which was more obvious for the sample taken from the side of the cylinder. Little change was observed in the TMA plot of the center sample, with only a weaker expansion step at ~185°C. However, the 1 week aged side
sample showed a less steep contraction step that occurred at ~4°C higher temperature compared to the same sample analyzed within 1 day of preparation. The thermal analysis results for the same foam analyzed 2 months after preparation are shown in Figure 5.5. The DSC transitions so prominent on earlier analysis at ~100-130°C were hardly discernable in both the center and side samples. The exotherm believed to correspond to further reaction of isocyanate was still observable and larger for the side sample, but at a slightly lower temperature for both sampling positions. The effect of aging on TMA plots showed a progressive increase and decrease of the steepness of the major contraction step for both side and center samples, where the side sample contraction was still greater.
Figure 5.4. Comparison of DSC (top) and TMA (bottom) plots of foam processed at 25°C and analyzed 1 week after preparation. Analysis of samples from the (a) center and (b) side positions of the cylinder are shown. Vertical lines in the TMA plots show the contraction and expansion steps that correspond to major transitions in the DSC.
Figure 5.5. Comparison of the DSC (top) and TMA plots for foam processed at 25°C and analyzed 2 months after preparation. Analysis of samples from the (a) center and (b) side positions of the cylinder are shown. Vertical lines in the TMA plots show the contraction and expansion steps that correspond to major transitions in the DSC.

The DSC and TMA plots of foam processed at 85°C and analyzed 1 week and 2 months after preparation are shown in Figures 5.6 and 5.7, respectively. Compared to the thermal analysis of the same sample analyzed 1 day after preparation, the most dramatic changes observed in the DSC were that the temperature of the endotherm and exotherms were increased. The corresponding TMA plots also showed a progressive increase in temperature and broadening out of the contraction of the foam, which was more pronounced for the side samples.
Figure 5.6 Comparison of DSC (top) and TMA (bottom) plots of foam processed at 85°C and analyzed 1 week after preparation. Analysis of samples from the (a) center and (b) side positions of the cylinder are shown. Vertical lines in the TMA plots show the contraction and expansion steps that correspond to major transitions in the DSC, and are found at higher temperature compared to foam processed at 25°C.
Figure 5.7 Comparison of the DSC (top) and TMA plots for foam processed at 85°C and analyzed 2 months after preparation. Analysis of samples from the (a) center and (b) side positions of the cylinder are shown. Vertical lines in the TMA plots show the contraction and expansion steps that correspond to major transitions in the DSC.

5.3 Summary of Thermal Analysis Results

A summary of the temperatures of the first major contraction step in the TMA and final expansion step is listed in Table 5.1. In general for both foam samples processed at different temperatures, the first contraction step became less steep and occurred at higher temperature as the foam sample cured over time at room temperature. The trends were the same for samples taken from the center of the foam cylinder and the side, but the contraction step believed to be associated with uretoneimine ring opening occurred at a
lower temperature for all side samples. This is consistent with a larger concentration of these ring structures at the side positions, as determined by IR analysis. There was less variation over time in the temperature of the final expansion step, which corresponded to an exotherm in the DSC at ~180-190°C for all samples. The appearance of this expansion step was dependent on how much the foam contracted initially. Finally, the temperatures of the first contraction and final expansion of the foam processed at 25°C after 2 months was similar to the foam processed at 85°C after 1 day of cure, supporting the fact that the latter sample is more fully reacted after initial processing.

Table 5.1  Temperatures of First Major Contraction and Final Expansion Steps in TMA as a Function of Sampling Time and Correlated with Major Transitions in DSC

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time of Analysis</th>
<th>Contraction Center (°C)</th>
<th>Contraction Side (°C)</th>
<th>Expansion Center (°C)</th>
<th>Expansion Side (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C proc.</td>
<td>1 day</td>
<td>120</td>
<td>110</td>
<td>185</td>
<td>185</td>
</tr>
<tr>
<td>25°C proc.</td>
<td>1 week</td>
<td>120</td>
<td>114</td>
<td>184</td>
<td>185</td>
</tr>
<tr>
<td>25°C proc.</td>
<td>2 months</td>
<td>150</td>
<td>135</td>
<td>182</td>
<td>182</td>
</tr>
<tr>
<td>85°C proc.</td>
<td>1 day</td>
<td>150</td>
<td>135</td>
<td>188</td>
<td>188</td>
</tr>
<tr>
<td>85°C proc.</td>
<td>1 week</td>
<td>163</td>
<td>143</td>
<td>188</td>
<td>---</td>
</tr>
<tr>
<td>85°C proc.</td>
<td>2 months</td>
<td>174</td>
<td>146</td>
<td>189</td>
<td>191</td>
</tr>
</tbody>
</table>

5.4 References


CHAPTER 6

CONCLUSIONS

This thesis investigated the effects of processing temperature on the chemical structure, and morphology of ReCrete PU foam. In particular, the effect of time and temperature was correlated to the chemistry of Rubinate, which contains unstable uretoneimine linkages and unreacted diisocyanate. The stability, was shown to be affected by the processing temperature and aging of foam made from Rubinate. These investigations were accomplished through careful analysis of the chemical structure of the foam using a variety of techniques, including IR, PAS, and thermal analysis (DSC, TMA).

Previous aging studies of ReCrete indicated that samples exposed to air, for a year at elevated temperature (60-80°C) resulted in a ~20% decrease in energy absorption and impact strength. Although similar detrimental changes in mechanical properties were observed for TDI based PU foam, the ReCrete foam fractured into pieces during impact testing, most likely a result of a more brittle structures formed after thermal aging. The aging characteristics may be a direct result of the decomposition of the uretoneimine linkage prevalent as a major functionality in the diisocyanate starting material in the ReCrete foam (absent in TDI-based foam). Although density gradients were induced in PU foam samples processed at different temperatures, the change in modulus with processing temperature was more likely a result of the breaking of the uretoneimine ring.
during high temperature (85-90°C) processing. The result is foam with a higher degree of crosslinking with less rigidity. A concise summary of the major results of this thesis that justify these two suppositions are presented below.

Infrared analysis confirmed that foam processed at high temperature exhibited a higher intensity and consequently larger amount of carbodiimide and urethane functionalities relative to unreacted isocyanate groups. In comparison the foam processed at low temperature showed a larger contribution of uretoneimine C=N vibrations. Infrared analysis of the diisocyanate functional groups in urea was used to examine and identify changes in uretoneimine functionality of rubinate as the materials were heated. The same phenomena occurred during high temperature processing of ReCrete foam. The same trend was examined for PU foams. The data indicates that processing temperature directly influences the concentration of the rigid uretoneimine structures in the foam.

Thermal degradation of the units in PU foams results in the generation of equal molar quantities isocyanate and carbodiimide in the foam. The continued reactivity of isocyanate is observed over a period of three months indicating the chemistry of the PU is changing over time.

Thermal analysis of foams processed at room temperature showed a predominant endothermic transition at ~100°C consistent with the temperature range reported for the exchange reaction of the uretoneimine functionality to form isocyanate and carbodiimide. As the time progressed, the 25°C WB sample exhibited more variation in DSC, TMA and IR than 85°C, due to the initial low curing compared to 85°C. Closer inspection of these species is imperative, because it plays significant role in stability of foam samples.

An idealized schematic of how ReCrete processed at higher temperatures could have both a lower modulus but also have a higher number of crosslink points is shown in

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Figure 6.1. Foam processed at room temperature have many more uretoneimine rings intact (Fig. 6.1a), consistent with IR analysis. During high temperature foam processing, cleavage of the uretoneimine ring leads to new isocyanate functionalities (Figure 6b), which further react to form additional crosslink points. However, comparing structures 6a and 6c, note that the presence of the uretoneimine linkage results in a more rigid structure, whereas the material with more crosslink points (higher temperature processing) would be less rigid, and result in a lowered modulus.
Low temp. processing: Rigid structure (higher modulus) w/3 crosslink points.

High temp. processing: Less rigid structure (lower modulus), but w/4 crosslink points.

Figure 6.1. Idealized schematic showing how processing ReCrete foam at elevated temperatures could result in a structure with higher crosslink density but slightly lower modulus. As foam reaction occurs the Rubinate diisocyanate mixture reacts with Polyol (squiggly line) to form urethane linkages, then: (a) uretoneimine ring structure is in tact and remains in tact during room temperature processing; but (b) at elevated temperature the uretoneimine ring can cleave to give a carbodiimide linkage and new isocyanate functionality, which (c) can further react to form a new urethane linkage.
Processing temperature, affects the mechanical and chemical properties of the ReCreate PU foam. It likely will also affect the shock properties due to the loss of chemical structures within the polymer matrix. Perhaps future investigation should explore intermediate processing temperatures between 25°C and 85°C, which may give rise to foams with better mechanical and chemical properties. Finally, and importantly alternative products other than Rubinate should be considered, and exploration of MDI in pure form can continue in search of specific desired properties of PU foam.

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