Continuous Polymer Reactor Design

David Sujay Kingsley
University of Southern Mississippi

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CONTINUOUS POLYMER REACTOR DESIGN

by

David Sujay Kingsley

Abstract of a Dissertation
Submitted to the Graduate School
of The University of Southern Mississippi
in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy

December 2014
Twin screw extruders can be used as continuous polymer reactors to process polymers, which are conventionally made through batch reactors. Batch processes have certain undesirable qualities such as improper mixing and the inability to precisely control the reaction, which leads to variation between batches and potential exotherms. The work presented in this dissertation investigates the use of continuous polymer reactor designs to efficiently process renewable sourced thermoplastic polyurethanes (TPU), and prepreg epoxy matrix prepolymer.

The overall goal of this research is to highlight the modularity of twin screw extruders as continuous polymer reactors to synthesize the relevant polymers. Chapter I defines the specific goals that pertain to this research. Chapter II provides a brief overview of extruders and reaction extrusion. Different types of extruders are briefly reviewed, but the focus is on intermeshing co-rotating twin screw extruders, which are ideal for use as continuous polymer reactors. The chapter also discusses reaction extrusion and the advantages it offers over batch reaction.

The next two chapters delve into the core of the research. Chapter III presents a continuous polymer reactor design for renewable sourced Cerenol based TPUs. TPUs comprised of polyol soft-blocks of renewable sourced...
polytrimethylene ether glycol, Cerenol, were compared with TPUs comprised of polyol soft-blocks of polytetramethylene ether glycol (PTMEG). Cerenol and PTMEG based TPUs were successfully processed via reaction extrusion utilizing nearly identical process conditions. Chapter IV presents lab-scale and industrial-scaled up continuous polymer reactor designs for synthesizing and partially curing two commercially used prepolymerms, 8281 and 5208. Both of these prepolymerms are widely used in the aerospace industry.

The final chapter, Chapter V, provides recommendations for future work. Overall, three continuous polymer reactor designs were successfully invented to formulate three different polymers. The modularity and modification of a single twin screw extruder can be used to synthesize different polymers in a continuous process.
The University of Southern Mississippi

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A Dissertation
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December 2014
DEDICATION

I would like to dedicate my work to my beloved wife, Nishy Kingsley, and my loving parents, Drs. Nalini and Kingsley Sathiakumar, who have provided me with the encouragement and support I needed to complete this lifelong goal. Thank you to my family and friends, especially my Mom, who has always supported me with the choices I have made. I cannot thank them enough for their love and support through the years. Their encouragement has pushed me to strive in every aspect of my life. Finally, thank you to my wife, who has been such a source of joy and brought such meaning to my life. I look forward to our life together.
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I would like to express my sincere appreciation and gratitude to my advisor, Dr. Jeffrey Wiggins, for his unconditional support and friendship through the years. Dr. Wiggins provided me with many opportunities during my graduate career, which allowed me to succeed professionally. Those opportunities have directly led me to where I am today, a Lead Engineer at GE Aviation. He has also given me the guidance to develop into a better person and I am so grateful for our friendship.

I would also like to thank my doctoral committee, Dr. Gary Krebs, Dr. Sarah Morgan, Dr. Derek Patton, and Dr. Robson Storey for their time and their consideration. Similarly, I would like to thank the current and past members of the Wiggins Research Group for their support and friendship. Specifically, the work of Dr. Jinhai Yang, Xiaole Cheng, Lawrence LaBeaud and Tim Kelly has made a significant contribution to my research.

I have also had the opportunity to work with and receive funding from several companies and entities – these include Boeing, Cytec, DuPont, GE Aviation, Mississippi Development Authority, and the United States Air Force. I thank Eastman Chemical Company for granting me an Eastman Chemical Graduate Fellowship that allowed me to participate with the University of Alabama at Birmingham in an Engineers Without Borders project in Zambia, Africa. A special thanks to GE Aviation for not only providing me with a graduate student internship, but also a professional career that impacts people’s lives.
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<tr>
<td><strong>BD</strong></td>
<td>1,4-butaneol</td>
</tr>
<tr>
<td><strong>CR</strong></td>
<td>Compression ratio</td>
</tr>
<tr>
<td><strong>DBTDL</strong></td>
<td>Dibutyltin dilaurate</td>
</tr>
<tr>
<td><strong>44DDS</strong></td>
<td>4,4'-diaminodiphenylsulfone</td>
</tr>
<tr>
<td><strong>DGEBA</strong></td>
<td>Diglycidyl ether of bisphenol A</td>
</tr>
<tr>
<td><strong>DMA</strong></td>
<td>Dynamic mechanical analysis</td>
</tr>
<tr>
<td><strong>DOE</strong></td>
<td>Design of experiments</td>
</tr>
<tr>
<td><strong>DSC</strong></td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td><strong>L/D</strong></td>
<td>Length/Diameter</td>
</tr>
<tr>
<td><strong>MDI</strong></td>
<td>Methylene diphenyl 4,4'-diisocyanate</td>
</tr>
<tr>
<td><strong>MW</strong></td>
<td>Molecular weight</td>
</tr>
<tr>
<td><strong>NCO/OH</strong></td>
<td>Isocyanate-hydroxyl ratio</td>
</tr>
<tr>
<td><strong>NIR</strong></td>
<td>Near-infrared reflectance spectroscopy</td>
</tr>
<tr>
<td><strong>PEG</strong></td>
<td>Polyethylene glycol</td>
</tr>
<tr>
<td><strong>PPG</strong></td>
<td>Polypropylene glycol</td>
</tr>
<tr>
<td><strong>PTFE</strong></td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td><strong>PTMEG</strong></td>
<td>Polytetramethylene ether glycol</td>
</tr>
<tr>
<td><strong>RPM</strong></td>
<td>Revolutions per minute</td>
</tr>
<tr>
<td><strong>SU-8</strong></td>
<td>4-[2-(4-hydroxyphenyl) propan-2-yl] phenol</td>
</tr>
<tr>
<td><strong>T_g</strong></td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td><strong>T_m</strong></td>
<td>Melting point temperature</td>
</tr>
<tr>
<td><strong>TGA</strong></td>
<td>Thermogravimetric analysis</td>
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**TGDDM**  N, N, N', N'-tetraglycidyl-4,4'-diaminodiphenylmethane

**TPE**  Thermoplastic elastomers

**TPU**  Thermoplastic polyurethanes
CHAPTER I

OBJECTIVES OF RESEARCH

Twin screw extruders can be used as continuous polymer reactors to process polymers, which are conventionally made through batch reactors. The overall goal of this research was to highlight the modularity of twin screw extruders as continuous polymer reactors to synthesize relevant polymers. The work presented in this dissertation investigated the use of continuous polymer reactor designs to efficiently process renewable sourced thermoplastic polyurethanes (TPU), and prepreg epoxy matrix prepolymer. The challenge depended on understanding the requirements for the different polymers and designing continuous polymer reactor systems that fit the need of the specific polymers.

Reaction Extrusion of Renewable Sourced Thermoplastic Polyurethanes

Commercial TPUs are traditionally synthesized from petroleum-based reactants. The push for greener technologies and reactants led DuPont to produce Cerenol, a completely sustainable poly(1,3-propane diol) polyl derived from renewable resources and environmentally friendly chemical processes. Using Cerenol as the TPU soft-block, specialized TPUs were synthesized, which had significant weight fractions of renewable material content and optimized thermo-mechanical properties to potentially replace petroleum-derived polymer products.
The specific goals of this research were to:

(1) Evaluate the kinetics of renewable sourced Cerenol polyols versus conventional petrochemical sourced polytetramethylene ether glycol (PTMEG) polyols;

(2) Define optimal formulations for 70A, 85A, and 50D hardness Cerenol based TPU s and PTMEG based TPU s;

(3) Design a continuous polymer reactor system that can complete TPU polymerization from base reactants using the “one shot” method;

(4) Optimize screw design to complete reaction, maximize throughput, and minimize thermal degradation;

(5) Analyze thermo-mechanical properties of resultant TPU s using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and other testing methods;

(6) Compare Cerenol based TPU s and PTMEG based TPU s; and

(7) Determine if Cerenol can be used as a drop in replacement for existing polyols in TPU processes.

**Prepreg Epoxy Matric Prepolymers From Continuous Polymer Reactor Design**

Prepreg epoxy matrix prepolymer s are customarily made in batch reactors, which can lead to undesirable prepolymer properties. Thus, continuous polymer reactor designs were used to synthesize and partially cure two commercially used prepolymer s: 8281 and 5208. 8281 and 5208 are epoxy systems widely used in the aerospace industry.
The specific goals of this research were to:

1. Design continuous polymer reactor systems that can B-stage 8281 and 5208 prepolymers;
2. Optimize screw design to advance reaction, maximize throughput, minimize thermal degradation, and prevent exotherm and gel;
3. Evaluate B-staging, advancement of the reaction, using batch reactor techniques;
4. Obtain target glass transition temperatures and viscosities for the prepolymers so that prepolymer can be successfully processed into prepreg;
5. Perform design of experiments to investigate the effect of extruder variables on B-staging prepolymer; and
6. Compare cured batch reactor produced prepolymers to cured continuous polymer reactor produced prepolymers using DSC, near-infrared reflectance spectroscopy (NIR), dynamic mechanical analysis (DMA), MTS, viscometer, etc.

Completion of the above goals will provide a better understanding of the use of continuous polymer reactor designs to make applicable polymers. The work on Cerenol based TPUs can be used to produce greener, high renewable content TPUs. Further, the results could provide insight for the implementation of Cerenol into existing TPU manufacturing processes. The work on prepolymers is novel in that thermoset polymers are B-staged in a continuous process, which deviates from the industry norm of prepolymer synthesis from batch reactors.
8281 and 5208 are prepolymer currently used in the aerospace industry; thus, the work on these prepolymer could provide useful to prepreg manufacturers. Synthesizing prepolymer with constant B-staging level can lead to the production of consistent prepreg that can translate to better composite parts.
Chapter II provides a brief overview of extruders and reaction extrusion. There are many types of extruders, but the focus will be on intermeshing co-rotating twin screw extruders, which are ideal to use as continuous polymer reactors. The background will also focus on reaction extrusion and the advantages it offers over batch reaction. The scope of this thesis is to highlight the modularity of twin screw extruders as continuous polymer reactors to make relevant polymers: high renewable content thermoplastic polyurethanes, and prepreg epoxy matrix prepolymers. The use of three different continuous polymer reactor designs was necessary for the different polymers synthesized in this research.

2.1 Extruders

Extrusion is the process of forcing a ductile material, such as a polymer, through a die of a desired cross-section.\(^1\) Besides polymers, other commonly extruded materials include metals, ceramics, concrete, and even food and drugs. Extruders are used to melt, homogenize, pump, and shape polymers into finished plastic commodities. Single and twin screw extruders are used for polymer processing with twin screw extruders having a wider application than single screw extruders.\(^2,3\)

There are several advantages to using extruders over other polymer manufacturing processes, such as batch reactors. Extruders are modular in that a single extruder can be altered to carry out a wide range of reactions. Further,
polymers are reacted in a continuous manner in finite quantities; hence, there is potential for generating high quality products due to brief exposure to heat that minimizes degradation. Extrusion processes are more energy efficient and have a lower processing cost when compared to batch reactor processes.

2.1.1 Historical Background

The origins of polymer processing techniques and machines date back to the 19th century and involved the processing of natural rubber. In 1820, Thomas Hancock invented a rubber “masticator,” a machine that had a toothed rotor inside a toothed cylindrical cavity, which was designed to shear rubber. Hancock found that when natural rubber was sheared or masticated, its viscosity decreased so it could flow and hence, be processed more efficiently.

The history of extruders, specifically for thermoplastic materials, dates back to 1935 when Paul Troester developed the first single screw extruder. Soon after in 1937, the first commercial non-intermeshing co-rotating twin screw extruder was designed by Roberto Colombo for I.G. Farbenindustrie (now BASF). Werner and Pfleiderer then developed an intermeshing, self-wiping, co-rotating twin screw extruder for Bayer in 1953. This machine came to be known as Zwei Schencken Knetter (ZSK). The ZSK has been the standard for twin screw extruders and especially for continuous polymer reaction extrusion. Since then, many companies have developed their own technology for twin screw extruders. The similarities, differences, and specific attributes of these different extruders will be discussed in this chapter.
2.1.2 Overview of Extruder Operations

The high-level, basic principle of an extruder is quite simple. A screw rotates in a barrel, while material is processed as it is transported downstream and extruded through a fixed cross-section to obtain a desired product.

Extruder operations begin with material entering the feed throat of an extruder. Material is usually gravity and starve fed, but can also be volumetrically fed via positive pressure into the feed throat. The material occupies the annular space between the extruder screw and the barrel. The screw vigorously rotates while the barrel is stationery. Material is then subjected to heat, pressure, and shear, which processes the material into a molten state that flows and can be molded. The screw executes functions of pumping, heating, mixing, and pressurizing. The melt experiences friction forces from the screw and the barrel, which propel the material down the barrel. As the material leaves the die, it takes on the shape of the die cross-section. The die exerts resistance to flow, generating positive pressure that is essential to force the material through the die.

2.1.3 Types of Screw Extruders

Contingent on the screw configuration, extruders are classified as either single screw or twin screw extruders. As inferred by their terminologies, a single screw extruder has one screw, while a twin screw extruder has two screws. Extruders may also be comprised of more than two screws, although such types of extruders are uncommon. The foremost distinction between single versus twin screw extruders is the manner in which melt flows through the
extruder. When compared to single screw extruders, the flow profile is much more complex in a twin screw extruder, details of which will be discussed later in the chapter. Twin screw extruders are modular in that they can be configured from the feeding zone to the die with relative ease. Depending on the particular configuration, twin screw extruders are able to transport, pump, heat, cool, mix, cook, compress, shear, and shape with a high degree of flexibility.\(^7\)

With the exception of higher cost, twin screw extruders offer the following benefits over single screw extruders:\(^7,10\)

1. A wide range of products can be produced with intra-batch and batch-to-batch reproducibility;
2. Material feeding is not as dependent upon material frictional properties, but rather on the feeding method and the screw elements used;
3. Materials have a narrower residence/reaction time distribution – as a result, there is less chance of material degradation;
4. Superior mixing ability with better kneading performance can subject materials to the same shear, pressure, and heat history;
5. More positive conveying capability – (i) in contrast to single screw extruders, the conveying mechanism is largely dependent on the screw configuration and input with less dependence on friction, (ii) it is less sensitive to die variations and pressure drops, so throughput will remain constant as a function of input;
6. Processing parameters (temperature, pressure, throughput, etc.) can be varied independently and are better controlled;
(7) Larger heat transfer due to increased surface area with fewer tendencies to over-heat;
(8) High input of mechanical energy due to the modularity of screw configurations; and
(9) Start-up and shutdown can be handled quickly.

Because of the above features, twin screw extruders are used more extensively than single screw extruders. They are used to handle complex processes such as homogenizing, dispersive and distributive mixing, alloying, reactive compounding, reactive extrusion, concentrating, devolatilizing, polymerizing, etc. On the other hand, single screw extruders are utilized for simpler processes such as melting, and distributive mixing.

2.1.4 Twin Screw Extruders

The screws in twin screw extruders may be co-rotating or counter-rotating, intermeshing or non-intermeshing, and conjugated or non-conjugated. In addition, the design of the screws can be modified by using forward conveying elements, reverse conveying elements, neutral elements, kneading blocks, mixing gears, or more complex elements in order to achieve a required effect. Regardless of the type, all twin screw extruders perform similar processes such as feeding, melting, mixing, venting, and developing die/localized pressure. Each of the subtypes of twin screw extruders is described next.
Co-rotating and Counter-rotating Screws

Twin screw extruders are categorized as co-rotating, rotating in the same direction, or counter-rotating, rotating in the opposite direction. Figure 1 illustrates the screw profiles of co-rotating and counter-rotating twin screws.

Figure 1. Co-rotating and counter-rotating screw profiles.

A co-rotating extruder has a radial shearing and plasticizing effect, while a counter-rotating extruder has an axial shearing and plasticizing effect. Industrially, co-rotating extruders are more essential as they can operate at higher screw speeds and throughputs to attain high outputs, while maintaining good mixing and conveying characteristics. Moreover, co-rotating extruders experience lower screw and barrel wear. Since the screws do not have a counter-rotating motion, there is no outward “pushing” effect. Counter-rotating extruders are used in applications that require high shear. The material is
pressed through the cavity between two screws when they come together, which subjects the material to elevated shear forces.\textsuperscript{11}

\textit{Intermeshing and Non-intermeshing Screws}

Co-rotating and counter-rotating screws may be fully, partially, or non-intermeshing. Figure 2 illustrates the cross-sections of these patterns. Non-intermeshing twin screw systems function comparably to single screw extruders in that each of the two screws acts independently of the other. On the other hand, intermeshing twin screws function in relation to each other. Material from one screw channel is transferred into the channel of the other screw, as the flights of one screw penetrate the channels of the other screw. The screws wipe each other, continuously transferring melt down the screw. Additionally, these screws provide supplementary energy input into the conveyed melt through shear heating. A high degree of intermeshing is compulsory for reaction extrusion as the residence time is more even for this type of screw design. Figure 3 displays a cross-section of intermeshing twin screws having complete intermeshing.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{screw_types.png}
\caption{Types of intermeshing screws.}
\end{figure}

Non-intermeshing \hspace{2cm} Partially intermeshing \hspace{2cm} Fully intermeshing
Figure 3. Cross-section of a fully intermeshing twin screw.

The degree/depth of intermeshing, $h^*$, is defined as:\cite{12}

$$h^* = D - l \quad (1)$$

where $D$ is the screw diameter, and $l$ is the interaxis distance. The depth of intermeshing can further be described as:

$$h^* = (D - D_R)/2 \quad (2)$$

where $D_R$ is the root diameter.

**Intermeshing and Conjugation**

Twin screw processes are contingent on the geometry between the base of the screws and the walls formed by intermeshing flights. This geometry is characterized by two parameters: the degree of intermeshing, and the extent of conjugation. The extent of conjugation is the closeness to which the profile of one screw fits into the channel profile of the other screw. Figure 4 shows a profile of a fully intermeshing, conjugated, co-rotating twin screw.
Figure 4. Intermeshing and conjugated screw profile.

Fully conjugated screws have restricted passage between screws since the flights of each screw virtually fill the channel of the other screw. These types of screws have high pumping efficiency but lose mixing efficiency. The melt can also experience high shear stresses when conjugation is high. Screw and barrel wear are also high. Consequently, screw revolutions per minute (RPM) is lower for these extruders.

Less conjugated systems have a larger passage between the screws, and facilitate mixing and compounding at the cost of lower pumping efficiency. Material transfer from one screw channel to the other is less constrained. Twin screw systems are designed to have some degree of conjugation. Intermeshing co-rotating twin screw extruders were used as the continuous polymer reactors in the research presented in this dissertation.

2.1.5 Intermeshing Co-rotating Twin Screw Extruders

The intermeshing co-rotating type of screw design is the most preferred type of twin screw extruder. The modular design and assembly arrangement of the screw and barrel sections, along with the use of special feeding and venting
ports, provide adequate flexibility for precise reactive extrusion tasks. They are universally used for compounding and as continuous chemical reactors.

Typically, fully intermeshing co-rotating twin screw extruders operate at high speeds, greater than 50 rpm. At the intermeshing part of the screws, the polymer material is forced to leave from one screw channel and move into the adjacent channel of the other screw. The transfer of materials from one screw to the other creates material movement around both screws in a figure eight pattern (Figure 5) as the material advances forward.

![Figure 5. Material flow in a figure eight pattern.](image)

The more conjugated the screws, the slower this cross movement and the greater propulsion across the extruder. The material does not accumulate at any point around the screws, and there is no buildup of any unbalanced pressure. Accordingly, there are no pressure forces to push the screws apart. The screws cleanse each other, and there is no material hang-up. All of the material advances at the same speed, equalizing residence time for all melt. The diverse paths the material takes and the stream splitting at the intermeshing areas yields uniform mixing. Figure 6 displays the material path around two intermeshing co-rotating screws.
Mixing

The primary benefit of intermeshing co-rotating twin screw extruders is their excellent mixing ability, which translates to consistent, high quality extruded products. There are two types of mixing that can be accomplished in an extruder: dispersive mixing and distributive mixing (Figure 7). The type of mixing function is accomplished by the utilization of specific screw elements. Dispersive mixing results in polymer melt subjected to extensional and planar shear that breaks down particles into smaller units. Distributive mixing results in the even dispersion of particles, which does not break down particles. In either type of mixing, the polymer melt is in a homogenous state at the end of an extruder.
Another benefit of intermeshing co-rotating twin screw extruders is that they are self-wiping. The self-wiping action is achieved by the crest edge of one screw wiping the flank of the other screw. Thus, material is transferred between screws with transport being achieved without creating high forces towards the barrel wall. This means that the extruder can operate at higher screw speeds without the risk of wear. By contrast, in counter-rotating screws, the material is squeezed in the gaps between the screws creating high forces towards the barrel wall causing wear.

2.1.6 The Extruder Screw

The extruder screw is the “heart of the extruder” making its design imperative to the success of any extrusion system. The screw is a long cylinder...

Figure 7. Distributive vs. dispersive mixing particle size distribution.

Self-Wiping
with a helical flight wrapped around it.\textsuperscript{5} It generally has three functional zones: feeding, compression, and metering zones. Numerous parameters influence the optimal functioning of the screw.\textsuperscript{15}

*Functional Zones of an Extruder Screw*\textsuperscript{16}

**Feeding Zone.** The feeding zone is where material is fed into the extruder and transported to the compression zone.\textsuperscript{17} The feeding zone generally has screws with a large pitch with deep channels that have maximum free volume to convey material away from the feed throat toward the compression zone. The feeding zone is also responsible for initial heating of the material, and building pressure. This is achieved by decreasing the pitch as it reaches the compression zone. To achieve maximum feeding efficiency, the feeding zone screw section must have a deep channel, a large pitch, and an ideal helix angle of \(45^\circ\), along with a theoretical coefficient of friction of zero between the screw and the material. The material must demonstrate a high level of slippage (low friction) on the screw channel surface and a low level of slippage (high friction) on the barrel. It is also imperative to ensure that feeding of material does not flood the metering zone by computation of the compression ratio (defined below).

**Compression Zone.** The compression zone is where material is heated, melted, and mixed into a homogenous melt. The diameter of the screw thread is enlarged and often integrates kneading blocks and mixing gears that apply a high degree of shear and energy to the material.\textsuperscript{18,19} The compression zone is also accountable for building pressure in the extruder, which is necessary to extrude
material through the die. Pressure is produced by restricting material flow into the metering zone, and by increasing melt viscosity.

*Metering Zone.* The metering zone is the final part of the screw. Its role is to act as a metering pump from which the melt is supplied to the die at constant volume and pressure.\(^{20,21}\) The ideal screw channel depth is closely related to the viscosity of the melt passing through this zone. The channel depth of the metering zone may need to be enlarged to avoid over-heating of the material if there is material build-up at the die. As in the compression zone, pressure must be developed prior to the melt reaching the die. Pressure drop at the die may also be overcome by increasing the length of the metering zone.

The movement of the melt in the screw channel is dependent on screw rotation, material type, temperature, and pressure. However, the most crucial factors are the geometrical characteristics of the screw.\(^7,16\)

*Screw Geometrics*

Screws consist of different elements purposed for a particular task: feeding, compression, metering, etc. A representation of a screw in the barrel is depicted in Figure 8, along with several geometrical characteristics of the screw. It is important to note that different screw elements have different geometrical characteristics.
Figure 8. Geometrical characteristics of a screw.

Channel Depth. Channel depth is a measure of the distance between the screw’s inner diameter and the barrel wall. Channel depth is largest in the feeding zone and smallest in the metering zone. It gradually decreases along the compression zone, which allows for more pressure to be applied to the material. The feeding and metering zones have uniform root diameters along their lengths, making the channel depths constant in these zones.

Pitch of the Screw. The pitch of the screw is termed as the distance between two consecutive flights (threads). The idyllic pitch, or alternatively the prime helix angle, can be estimated using the viscosity of the materials being processed. The feed zone is comprised of screw elements with large pitch. Screw pitch is then decreased to intensify pressure build-up.
**Flight width.** The flight width is a measure of the thickness of the flight for a screw element. A large flight width pulverizes and shears material, while a small flight width is less harsh on material.

**Helix Angle.** Helix angle, $\phi$, is the angle between the screw flight and the plane perpendicular to the screw axis. The pitch of the screw is proportional to the helix angle. Mathematically, this relationship can be expressed as:

$$\phi = \arctangent \left( \frac{\text{lead}}{\pi \times D} \right)$$

where $D$ is the screw diameter, and:

$$\text{Lead} = \text{Pitch} \times \text{Screw starts}$$

where *pitch* is the distance between two consecutive flights, and *screw starts* is the number of independent threads on the screw shaft. A specified helix angle must be selected for specific tasks. A sharp helix angle resists back pressure and polymer flow, while a shallow helix angle reduces shear on the melt.\(^\text{22}\)

**Flight Clearance.** Flight clearance is a measure of the distance between the screw’s outer diameter and the barrel wall. An ideal flight clearance is generally 0.1% of the screw diameter.\(^\text{7}\) Improper flight clearance will have an undesirable effect on screw performance. For example, having a small clearance can trigger excessive wear on the screws, whereas a large clearance can reduce melting efficiency along with the ability of the screw to move material downstream.

**Compression Ratio (CR).** The compression ratio is an essential parameter to examine in any screw design. It is defined by the ratio of the channel depth in the feeding zone to the channel depth in the metering zone.\(^\text{7}\) Channel depth is
recognized as depth CR and the channel volume is termed as volumetric CR. CR is defined as:

\[ CR = \frac{\text{Channel depth in feeding zone}}{\text{Channel depth in metering zone}} \] (5)

A CR is selected to suit the material that is being processed. It is also used to guarantee that the feeding of material does not flood the metering zone. The CR may vary from 1.5:1 to 4:1 depending on the material.23

*Length/diameter (L/D) Ratio.* The L/D ratio is another essential characteristic in screw design. It is also used to generally describe an extruder.24 The L/D ratio is outlined below:

\[ \frac{L}{D} = \frac{\text{Screw flighted length}}{\text{Screw outside diameter}} \] (6)

The L/D ratio describes the capacity of an extruder to transport melt regardless of screw design and on the rate at which heat is transferred from the barrel walls to the material. The extruder should have an adequate L/D ratio to accommodate the extrusion process such that the melt is in an optimal state when it enters the die. Industrial extruder L/D ratios range from 20:1 to 34:1.24 Lab-scale extruders are considerably smaller. The L/D ratio is contingent on the number of sections being considered in screw design, which in turn is governed by the application and the material being processed. For conventional screws with three functional zones (i.e. feeding, compression, and metering zones), the standard L/D ratio is 24:1.25

*Revolutions Per Minute (RPM).* The rotational speed of the screw influences the performance of an extruder. However, the throughput of a twin screw extruder does not increase in relation to an increase in screw speed. In
twin screw extruders, the output is determined by the input. Therefore, an economical speed, which gives the maximum output per unit of power is selected as the operating speed.

_Screw Elements_

As stated earlier, twin screw extruders are modular in that they can be configured from the feeding zone to the die with relative ease.\textsuperscript{12} Both the barrel and the screws can be modified for a specific task. Screws are designed with elements that perform one of three functions: conveying, kneading, or mixing. Conveying elements transport material through the extruder without much of a mixing effect. They are generally used in feeding and metering zones of the extruder. Kneading blocks and mixing gears are elements used in the compression zone of the extruder. Kneading blocks apply high shear and energy to the polymer melt to break down larger particles into smaller particles, and dispersively homogenize the melt. Mixing elements do not have the same shearing effect as kneading elements, but rather have a distributive mixing effect and homogenize two melt streams without breaking down particle size.\textsuperscript{13}

Screw elements may further be classified as single, double, or triple-flighted (Figure 9). Single flighted elements are used for conveying while double and triple flighted elements are used for kneading and mixing.
Figure 9. Flight profiles.

Table 1 below summarizes sections in the extruder and the corresponding screw elements that they may utilize.\textsuperscript{16}

**Table 1**

*Geometry and function of co-rotating screws by section of the screw*

<table>
<thead>
<tr>
<th>Section</th>
<th>Geometry</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feeding</td>
<td>Large diameter, small flight, optimal helix angle $\approx 75^\circ$, single flight, large channel depth</td>
<td>Transporting material</td>
</tr>
<tr>
<td>Pumping/melting</td>
<td>Small diameter, large flight, optimal helix angle $\approx 8^\circ$, multiple flights, average channel depth</td>
<td>Compression of material, melting, and shearing</td>
</tr>
<tr>
<td>Mixing</td>
<td>Smaller diameter, average flight, small helix angle, multiple flights, small channel depth</td>
<td>Division of polymer melt</td>
</tr>
<tr>
<td>Venting</td>
<td>Large diameter, small flight, large helix angle, single flight, average channel depth</td>
<td>Removing gas from material</td>
</tr>
<tr>
<td>Pumping</td>
<td>Small diameter, large flight, large helix angle, single flight, small channel depth</td>
<td>Developing melt pressure prior to die</td>
</tr>
</tbody>
</table>
2.1.7 Key Processing Characteristics for Extruders

Throughput and Pressure Profile

The primary determinant of the throughput is the device feeding the extruder. For most operations, the twin screw extruder is starve-fed, meaning that the majority of screw channels are only partially filled with material. However, the screw channels preceding the die are generally fully filled with material. This is compulsory to build pressure leading up to the die. Pressure in the extruder can only be generated when screw channels are completely filled. Placing a restrictive element such as a kneading element or a reverse flighted screw can also forcefully produce pressure. This design is used in reaction extrusion processes for dispersive mixing. Figure 10 shows the pressure profile during an extrusion process that has kneading elements and a reverse pitch screw to build pressure. It is important to manage the pressure in an extruder as too much pressure build-up can limit throughput. Material can also flow backward or stagnate.
Pump Equation. The pump equation expresses the flow of material, $Q$, through a starve-fed co-rotating twin screw extruder:

$$Q = Q_f + Q_p$$  \hspace{1cm} (7)

where $Q_f$ is the volumetric forward flow, and $Q_p$ is the backward volumetric pressure flow. In the above equation, leakage flow of material between flights and barrel is neglected which is:

$$Q = Q_f - Q_p$$  \hspace{1cm} (8)

The volumetric forward flow, $Q_f$, can be expressed as:

$$Q_f = \frac{1}{2} \pi^2 D^2 N h^* \tan \phi$$  \hspace{1cm} (9)

where $D$ is the screw diameter, $N$ is the screw RPM, $h^*$ is the intermeshing depth, and $\phi$ is the helix angle. The backward volumetric pressure flow, $Q_p$, depends on the pressure developed and the number of filled channels and is expressed as:

\[ \text{Figure 10. Pressure profile during extrusion.} \]

\[ \text{Note. RPS=Reverse pitch screw} \]
\[ Q_p = \frac{k_s(\Delta P)}{\mu u} \]  

(10)

where \( k_s \) is the screw passage conductance, \( \Delta P \) is the pressure, \( \mu \) is the viscosity, and \( u \) is the number of filled channels. The screw passage conductance is determined by screw geometry. For trapezoidal flight geometry, which can be used as a foundation for most conventional designs, screw passage conductance, \( k_s \), is the sum of two material passages: a passage between screws, and a passage between the flights and the barrel.  

\[
k_s = \left[ \frac{1}{2} \sqrt{D^2 - I^2} \right] \left[ \frac{1}{2} (t - 2E) \right]^3 / (6h^*) + \left( 2\pi D - \sqrt{2Dh^*} \right) \delta^3 / (12E)
\]  

(11)

where \( D \) is the screw diameter, \( I \) is the interaxis distance, \( t \) is the pitch length, \( E \) is the flight tip width, \( h^* \) is the intermeshing depth, and \( \delta \) is the clearance between the screw and the barrel.

**Residence Time**

Residence time is the interval of time material dwells in an extruder. It is a significant parameter in continuous polymer reactor design because it determines the time allowed for chemical reaction to occur. Residence time also has a direct effect on throughput. The residence time is proportional to screw length and inversely proportional to throughput. A longer screw with decreased input increases residence time, while a shorter screw and increased input decreases residence time. Residence time is also influenced by the screw elements that are employed. Residence time can vary from a few seconds to hours.

As mentioned earlier, co-rotating extruders are usually starve fed; therefore, segments of the extruder are not completely filled. To estimate the residence time, the degree of fill of the partially filled segments, and the length of
the entirely filled segments must be ascertained. The average residence time of material within the screw, $\theta$, is defined as:

$$\theta = \frac{V}{Q}$$ \hspace{1cm} (12)

where $V$ is the material volume, and $Q$ is the flow of material. The material volume within the pumping section is given by the equation:

$$V = \pi u D h^* \sin \phi (\pi D - 2\sqrt{D h^*})$$ \hspace{1cm} (13)

where $u$ is the number of filled channels of length $t$, $D$ is the screw diameter, $h^*$ is the intermeshing depth, and $\phi$ is the helix angle.

**Shear Rate**

The shear rate can be used to determine the amount of shear a material experiences in an extruder. Average shear rate, $\dot{\gamma}$, is a function of channel depth and screw rotation. The number of kneading elements also strongly influences the shear rate. High shear can lead to polymer degradation, while low shear can limit the extent of reaction or mixing capacity. The average shear rate is given by:

$$\dot{\gamma} = \frac{\pi D_e N}{h}$$ \hspace{1cm} (14)

where $D_e$ is channel diameter, $N$ is the screw RPM, and $h$ is the channel depth.

The channel diameter is given by:

$$D_e = \frac{2}{\pi} (\pi D - 2\sqrt{D h^*})$$ \hspace{1cm} (15)

where $D$ is the screw diameter, and $h^*$ is the intermeshing depth.

**Processing Characteristics**

The processing characteristics of intermeshing co-rotating twin screw extruders are summarized below:
(1). Throughput is determined by the feed into the extruder and not the screw speed. Thus, low RPM can be used to apply low shear rates and conversely high RPM can be used to apply high shear rates;

(2). Active forward conveying reduces material drag in the feed section;

(3). Self-wiping attribute generates an even residence time while reducing screw and barrel wear;

(4). Mixing can be performed efficiently and homogeneously without overheating of material;

(5). Pumping and mixing can be controlled by changing the depth of intermeshing and flight tip width; and

(6). Screws can be designed specifically for a material or process.

2.2 Reaction Extrusion

2.2.1 Overview

Reaction extrusion, or reactive extrusion, is the process by which chemical reactions are achieved in an extruder. Reaction extrusion can be used to perform two established polymer engineering processes: the manufacturing of polymers from base reactants, and the modification of existing polymers. Most reaction extrusion processes utilize intermeshing co-rotating twin screw extruders. These extruders are exceptionally appropriate for reaction extrusion because of their mixing capability at the molecular level. Further, twin screw extruders can handle high viscosity melts, which is essential when synthesizing high molecular weight (MW) polymers.
The reaction extrusion process starts with the feeding of base reactants into the feed throat or hopper. Reactants can be of many physical forms, such as liquids, solids, fibers, powders, etc. Reactants can also be introduced into the melt in any barrel section of an extruder. The reactive melt is transported through the extruder with a residence time sufficient for the reaction to be completed. During this time, the reactive melt is heated, mixed, compressed, pressurized, metered, and eventually homogenized and reacted to form a polymer. The polymer is then extruded through the die. The key concept is that a polymer can be synthesized from base reactants to a fully cured polymer in one continuous process.\textsuperscript{3}

Multiple chemical reactions can also be performed in the extruder. Barrel sections can be insulated from other barrel sections by incorporating melt seals, which stagnate and restrict melt for a period of time giving sufficient time for initial reaction to occur. The melt then enters the next section where further reaction can occur. The foremost limitation of an extruder as a chemical reactor is the residence time. For some polymers, the residence time may be too short for the reaction to occur.\textsuperscript{28} However, for polymers where the residence time is appropriate, reaction extrusion is a cost-effective, energy efficient method of synthesizing polymer.

2.2.2 Reaction Extrusion vs. Batch Reactor Processing

The reaction extrusion process is often considered as an alternative to batch reactor processing. In the polymer industry, reaction extrusion is most often preferred over batch reactor processing, and has become the norm. It
offers many advantages over batch reaction, some of which are discussed below. In general, reaction extrusion is much more efficient than batch reactor processing.

To begin with, reaction kinetics occur much faster in an extruder. Because polymer melt is constantly transferred from element to element, reactions occur in small quantities facilitating greater molecular interaction. Heat transfer is also very effective in an extruder, so reaction activation energy is easily achieved and reactions occur more rapidly.

As polymer is reacted and MW increases, melt viscosity also increases significantly. Extruders are very adept at handling high viscosity flow. The self-wiping effect, heat, and torque of an extruder can proficiently handle high viscosity melt without the use of solvents. Extruders can also resolve mass and heat transfer issues more efficiently than batch reactors. Batch reactors are limited in how much they can react a polymer as viscosity can become unmanageable and seize up the reactor. Thus, solvents are a necessity to run most reactions, and must be driven off to obtain the desired product.

The residence time in an extruder is also much shorter than that of batch reactors. Residence time, as explained earlier, is the time the polymer melt spends and reacts in an extruder. Since kinetics in batch reactors are much longer, the polymer is subjected to higher temperatures for longer periods of time to advance the reaction, which could cause polymer degradation.

Reaction extrusion is generally more cost efficient than batch reactors. Although initial start-up cost may be higher than batch reactors, the long-term
savings of extruders are greater. The ability of an extruder to handle materials of high viscosities without any solvents results in considerable budget savings in raw materials and in solvent recovery equipment. Extruders are also quite compact and require a smaller working area. Extruders are also much more energy efficient than batch reactors, thus providing additional cost savings.

2.2.3 Types of Reactive Extrusion Processing

Intermeshing co-rotating twin screw extruders are acknowledged as efficient distributive and dispersive mixers for performing continuous reactions and polymerizations. Previous research on reaction extrusion technology has found that several chemical reactions can be carried out in an extruder. In industry, extruders are utilized for synthesizing and processing high viscosity materials. Table 2 provides some examples of reactive extrusion applications.31-37

Table 2

Examples of reactive extrusion applications by reaction type, reactants and products

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Reactants</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyaddition</td>
<td>Polyol + diisocyanate + diol</td>
<td>Polyurethane</td>
</tr>
<tr>
<td>Polycondensation</td>
<td>Bis(hydroxybutyl) terephthalate</td>
<td>Poly(ethylene terephthalate)</td>
</tr>
<tr>
<td>Polycondensation</td>
<td>Precondensate</td>
<td>Polyamide</td>
</tr>
<tr>
<td>Free radical</td>
<td>Styrene + acrylonitrile prepolymer</td>
<td>SAN</td>
</tr>
<tr>
<td>copolymerization</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2 (continued).

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Reactants</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grafting</td>
<td>Polystyrene + maleic anhydride</td>
<td>Polystyrene maleic anhydride adduct</td>
</tr>
<tr>
<td>Ionic polymerization</td>
<td>Caprolactam</td>
<td>Nylon 6</td>
</tr>
<tr>
<td>Anionic copolymerization</td>
<td>1,3-diene + aromatic vinyl compound</td>
<td>Block copolymers of 1,3-diene and aromatic vinyl compounds</td>
</tr>
<tr>
<td>Hydrolysis</td>
<td>Polyurethane scrap</td>
<td>Polyol, amines</td>
</tr>
</tbody>
</table>

2.3 Summary

The intermeshing co-rotating twin screw extruder is the most widely used extruder for polymer processing. Many chemical reactions and reaction extrusions have been effectively carried out in these systems. The critical challenge is in designing the extruders to perform their intended task. For reaction extrusion, the balance is in completing the reaction in the shortest residence time possible. Short residence time is necessary for increased throughput and reducing the chance of material degradation, while longer residence time is necessary to complete the reaction and homogenizing the material. Therefore, the optimal features of each functional zone of the screw have to be carefully considered, along with screw parameters based on the rheological and thermal properties of specific polymers that are to be processed.
The next two chapters (Chapters III and IV) evaluate the use of continuous polymer reactors to make high renewable content thermoplastic polyurethanes, and prepreg epoxy matrix prepolymer. Polyurethanes are typically made through reaction extrusion. However, the incorporation of a new polyol reactant into an existing process can change the existing reactor design and must be evaluated. Research on using reaction extrusion for synthesizing prepreg epoxy matrix prepolymer is limited; thus, further assessment is essential in determining the feasibility of this approach. The use of three different continuous polymer reactor designs was used to synthesize polyurethanes and two prepolymer, with each design specially modified to meet the polymers' requirements.
REFERENCES


CHAPTER III
REACTION EXTRUSION OF RENEWABLE SOURCED
THERMOPLASTIC POLYURETHANES

3.1 Abstract

Thermoplastic polyurethanes (TPUs) using polyol soft-blocks of renewable sourced polytrimethylene ether glycol Cerenol polyols and polytetramethylene ether glycol (PTMEG) polyols were successfully processed by reaction extrusion utilizing an intermeshing co-rotating twin screw extruder as a continuous polymer reactor with nearly identical process conditions. The two polyols showed comparable reaction kinetics with methylene diphenyl 4,4'-diisocyanate and 1,4-butanediol. The reactants of the TPUs were varied to target Shore D hardresses of 70A, 85A and 50D. Cerenol TPUs needed slightly higher hard-block content to obtain the same hardness, and exhibited lower glass transition temperatures and higher thermal degradation temperatures than PTMEG TPUs. Further, Cerenol TPUs exhibited slightly lower tensile stresses and comparable tear strengths to PTMEG TPUs of the same hardness.

3.2 Introduction

Evolving environmental regulations in the last decade and the increasing understanding of the global environment have prompted the use of “green” technologies and chemistries to become an important area of research in the world today. Concurrent with this trend, the plastics industry has been triggered to develop new environmentally friendly products and processes. A worldwide increase in price and demand of crude oil, and a desire to decrease the
environmental impacts of fossil fuels are driving research to replace crude oil as a raw material in materials science. Raw materials derived from renewable resources such as the production of commercial polymers from sustainable feedstocks are economically, socially, and environmentally significant.\textsuperscript{1,2} Further, high-energy consumption processes are being phased out in favor of greener, more energy efficient technologies. As a result, governments and organizations, global and regional materials science-based corporations, and national and international consumer action groups have displayed an increased commitment to adopt, develop, and implement green technologies, and are often willing to pay a premium for sustainable alternative technologies.

This research was focused on developing high modulus, renewable sourced TPUs by reaction extrusion using an intermeshing co-rotating twin screw extruder continuous polymer reactor. Commercial TPUs are traditionally synthesized from petroleum based polyether and polyester polyols of varying compositions and molecular weights (MW). DuPont has developed Cerenol, which is a completely sustainable poly(1,3-propane diol) polyol derived from renewable resources and environmentally friendly chemical processes. Using Cerenol as the soft-block, specialized TPUs were synthesized, which had significant weight fractions of renewable material content and optimized thermo-mechanical properties to potentially replace petroleum-derived polymer products.
3.3 Background

3.3.1 Thermoplastic Elastomers

The family of thermoplastic elastomers (TPEs) including styrenic block-copolymers (Kraton types), co-polyesters (Hytrel types), co-polyamides (Pebax types), and TPU (Texin types) plays a significant role in the TPE industry and are often considered the “toughest” of thermoplastic materials. Other TPEs include polyolefin blends and alloys. TPEs are categorized by their morphological similarities, and chemically defined as immiscible segmented linear block-copolymers having defined hard-block and soft-block morphological domains. These unique morphologies provide melt-processable TPEs that are particularly tough across a broad range of temperatures, have very high abrasion, scratch and chemical resistance, and which are readily tailored for a broad range of physical properties. TPU is one of six generic classes of commercial TPEs.

3.3.2 Thermoplastic Polyurethanes

TPUs are an important class of materials within the family of TPEs and possess a broad range of chemical compositions and physical properties. Because of their chemical diversity, TPU are used in applications ranging from coatings, adhesives, films, sheets, high- and low-modulus elastomers, and flexible and rigid foams. TPU have pleasant tactile properties (soft-touch), are flexible over a broad range of temperatures, excellent in outdoor and weathering applications, and processed through a broad range of melt-processing technologies. In addition, TPU have superior adhesive and surface properties,
so they have printable surfaces and are often selected for durable decorative applications. These unique combinations of properties make TPUs attractive for numerous applications. TPUs are the sixth most popular polymer in the world following high-density polyethylene, low-density polyethylene, polypropylene, polyvinyl chloride, and linear low-density polyethylene.\(^4\) Global production of TPUs exceeds 250 million pounds a year.\(^5\)

TPUs are melt-processable and generally defined by their unique segmented and phase-separated block-copolymer morphologies. Their phase-separated morphologies are developed as a result of the specific chemistry selected from a broad combination of diisocyanates, short-chain diol “chain extenders” (diols), and polyether or polyester “polyol” diols (polyols). TPUs are produced via step-growth polymerization. The TPU reaction begins with the formation of the hard-block. Diols react with excess diisocyanates to form telechelic, isocyanate terminated hard-block domains that contain a high concentration of urethane linkages [-NH-CO-O]. Figure 11 illustrates the reaction between excess diisocyanates and diols to form a generic hard-block. The polyol, the soft-block, then reacts with the hard-block to form high MW TPU. The reaction between the polyol soft-block and the hard-block is shown in Figure 12. The soft-block reaction with the hard-block is kinetically slower than the diisocyanate-diol reaction.
Figure 11. Formation of isocyanate terminated hard-block from the reaction of excess diisocyanates and diols.

Figure 12. Addition of polyol soft-block to hard-block to form TPU.

The hard-block phase comprised of high concentrations of urethane moieties is relatively rigid and immobile due to high degrees of hydrogen bonding. It is crystalline, polar, melts at relatively high temperatures, and controls high-temperature and high-modulus thermo-mechanical properties. The soft-block phase comprised of polyols is flexible, mobile, amorphous, and controls low-temperature and low-modulus thermo-mechanical properties. Figure 13 depicts a schematic representation of the phase-separated hard-block soft-block morphology of a TPU. The relative concentrations of these two immiscible
regions phase separate and provide a broad range of thermo-mechanical properties for a given combination of monomers.\textsuperscript{5-8} It is this unique aspect of TPU chemistry that allows the use of the same exact chemistry to derive a variety of thermoplastic materials with a broad range of moduli.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure13.png}
\caption{Phase-separated hard-block soft-block TPU morphology.}
\end{figure}

TPU hard-blocks act as intermolecular physical crosslinks that bind the soft-blocks in a network structure. As opposed to chemical crosslinks, physical crosslinks are melt “reversible” and provide an advantage for the melt-processing of TPUs.\textsuperscript{5} In addition, hard-block physical crosslinks inhibit plastic flow of the polymer chains promoting elastomeric resiliency.\textsuperscript{6,7} Soft-blocks are amorphous in their relaxed state and exhibit distortional behavior under deformation. Under strain, soft-blocks align in the direction of the applied load and relax upon release, which contributes to desirable elastomeric properties. This unique combination of molecular mobilities and inter-molecular interactions contributes to the high tensile strength, toughness, durability, and wear and tear resistance associated with TPUs.
TPUs were first manufactured using batch reactors. Eventually, continuous polymer reaction extrusion became the most commonly used processing technique for production of TPUs. The reaction extrusion of TPUs can be traced back to the early 1960s. The two most common methods of TPU extrusion are the “one shot” method and the “prepolymer” method. In the “one shot” method, all reactants are fed into the extruder at the same time to form a TPU. In the “prepolymer” method, polyols are first reacted with extra diisocyanates to obtain soft-block “prepolymers,” which are then fed into the extruder with diols and additional diisocyanates to form a TPU. Regardless of the method used, reaction extrusion is the preferred choice for TPU production.

3.3.2.1 Critical TPU Ratios

There are two critical ratios that are of importance in the processing of TPUs. These ratios can be varied to obtain TPUs with different hardnesses. They can also be used to maximize MW and thermo-mechanical properties to influence ultimate TPU properties. The isocyanate-hydroxyl (NCO/OH) ratio is the ratio of the concentration of isocyanates to alcohols in the reaction.

\[
\text{Isocyanate} - \text{hydroxyl ratio} = \frac{[\text{NCO}]}{[\text{OH}]} \quad (16)
\]

where \([\text{NCO}]\) is the moles of isocyanate, and \([\text{OH}]\) is the moles of hydroxyls given by:

\[
[\text{OH}] = \text{moles of diol } [\text{OH}]_{\text{diol}} + \text{moles of polyol } [\text{OH}]_{\text{polyol}} \quad (17)
\]

The NCO/OH ratio is typically maintained between 1.01-1.05 to form high-quality TPUs. Previous research and experience have shown that excess diisocyanate is necessary to optimize properties. As explained earlier, excess
diisocyanate is required to advance the reaction by forming the TPU hard-block with isocyanate moieties so that it can react with the polyol soft-block. Further, additional need for excess diisocyanate is attributed to competing isocyanate side reactions such as isocyanate hydrolysis, and the formation of dimers, trimers, and allophanates, which consume isocyanates under normal TPU reaction conditions.

The ratio of hard-blocks to soft-blocks (hard-block content) is also an important factor in maximizing MW and thermo-mechanical properties. Hard-block content can be quantified using several methods, but for the purpose of this research, hard-block content was defined as the weight ratio of hard-block diol to the weight ratio of soft-block polyol.

\[
\text{Hard - block content} = \frac{\% \text{wt. diol}}{\% \text{wt. polyol}}
\] (18)

For this research, the hard-block content ranged from 5% up to 26%. The higher the hard-block content, the higher the weight ratio of diol to polyol. A TPU with low hard-block content has lower hardness, lower mechanical properties, but higher elasticity. Conversely, a TPU with high hard-block content has higher hardness, higher mechanical properties, but lower elasticity.

### 3.3.2.2 TPU Diisocyanates

The diisocyanates used to form TPU hard-blocks can be aromatic or aliphatic. Approximately 90% of TPUs use aromatic isocyanates because of the superior properties it offers compared to aliphatic isocyanates. The two most common aromatic isocyanates are toluene diisocyanate and methylene diisocyanate (MDI) with MDI accounting for approximately two-thirds of aromatic
isocyanate usage.\textsuperscript{14} Thus, for this research, MDI was selected as the diisocyanate to synthesize TPUs with high-quality thermo-mechanical properties.

### 3.3.2.3 TPU Polyols

There are two main types of polyols used for TPUs: polyester and polyether polyols. Polyester polyol TPUs usually demonstrate higher strength than polyether polyol TPUs of the same hard-block composition. This is because of the high molar cohesion energy of ester groups, 2.9 kcal compared to 1.0 kcal for the ether groups.\textsuperscript{15} The polar polyester flexible segments of the soft-block have greater compatibility with the polar rigid segments of the hard-block.\textsuperscript{16} However, polyester polyol TPUs exhibit lower hydrolytic stability than polyether polyol TPUs.\textsuperscript{17} Having ether bonds, decreasing the number of carbon atoms, or adding pendant groups on polyols decreases the strength and thermal stability of a TPU.\textsuperscript{10,18}

The TPU industry first began using polyester polyols because of their availability. Then in 1956, DuPont introduced the first commercially available polyether polyol, polytetramethylene ether glycol (PTMEG), by polymerizing tetrahydrofuran. Soon after, both polyethylene glycol (PEG) and polypropylene glycol (PPG) became commercially available. Polyether polyols supplanted polyester polyols in the TPU industry because they are of lower cost and have better hydrolytic stability. The ether group also bestows increased elasticity of polyether polyol TPUs.

The most popular polyether polyol is PTMEG, which contains four carbons on the polymer backbone repeat unit. PTMEG and most conventional polyols are
derived from petrochemical sources. However, recent advances in technology have allowed for the production of polyols from soybean oil, castor oil, sunflower oil, rapeseed oil, and corn starch.\(^4\) DuPont recently created a new renewable sourced polytrimethylene ether glycol polyol.

### 3.3.3 Cerenol Polyether Polyol

The push towards greener technology motivated DuPont to create a family of high performance “bio-based” diols and polyols. To begin, 1,3-propanediol is produced from corn starch stock via a bacterial-metabolic fermentation process.\(^{19,20}\) The bacteria used in the fermentation process are a metabolically engineered version of *Escherichia coli*.\(^{21}\) The renewable sourced diol, named Susterra, is the chemical raw material for Cerenol.

Cerenol, polytrimethylene ether glycol, is produced through acid catalyzed polycondensation of Susterra.\(^{22-27}\) Figure 14 depicts the chemical structure of Susterra and Cerenol. Unlike PTMEG, which contain four carbons in the polymer backbone repeat unit, Cerenol contains three carbons in the polymer backbone repeat unit. Polyols with three carbons in the backbone have been made in the past using propylene or a hydroformylation process from ethylene oxide. However, these processes were expensive, energy intensive, and of low yield; hence, they were abandoned.\(^{21}\)


Figure 14. Cerenol obtained from corn starch.

An opportunity exists to use Cerenol as a “drop-in” polyol for existing polyether polyols and into existing TPU manufacturing processes. Polyether polyols account for 75% of the polyol market. Since TPU formulations are typically greater than 60% by weight polyol, Cerenol offers a significant opportunity for developing a broad range of polymers with high renewable resource content that can have a significant impact on the TPU market.

Cerenol polyols have already been successfully implemented into various TPU products such as cast elastomers, foams, and coatings. Cast Cerenol TPU s demonstrated comparable properties with PTMEG TPU s. Cerenol has also been used to synthesize polyethylene glycol dimethylether solvent. The goal of this research is to produce Cerenol based TPU s utilizing a continuous polymer reactor design via an intermeshing co-rotating twin screw extruder.

Cerenol is 100% bio-based and biodegradable. It has a lower environmental footprint than PTMEG, which as stated earlier is the standard petroleum-based soft-block for high-performance TPU s. When compared to PTMEG, the production of Cerenol consumes 40% less energy, produces 42% less greenhouse gas, and has little to no toxicity. Further, Cerenol has high thermo-oxidative stability, is hydrolysis resistant, has a higher reactive hydroxyl
number, has low volatility, has a high flash point (>230°C), and has a lower viscosity than PTMEG at any temperature, and is thus easier to handle and process. Other critical polyol properties cited by DuPont include MWs of 500-4000 g/mol, melting point temperatures ($T_m$) from 10°C to 22°C, glass transition temperatures ($T_g$) from -75°C to -80°C, densities of 1.02 g/mL to 1.03 g/mL, and viscosities of 100 cP to 500 cP at 40°C.22,23 Table 3 compares the differences between Cerenol and PTMEG polyols.

Table 3

<table>
<thead>
<tr>
<th>Polyol</th>
<th>Cerenol 2000</th>
<th>PTMEG 2000</th>
</tr>
</thead>
<tbody>
<tr>
<td># of C in backbone</td>
<td>C3</td>
<td>C4</td>
</tr>
<tr>
<td>$T_g$ (°C)</td>
<td>-77</td>
<td>-85</td>
</tr>
<tr>
<td>$T_m$ (°C)</td>
<td>17</td>
<td>27</td>
</tr>
<tr>
<td>Viscosity at 60°C (cP)</td>
<td>340</td>
<td>575</td>
</tr>
<tr>
<td>Density (g/mL)</td>
<td>1.02</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Cerenol (C3 polyols) fill the gap between PTMEG (C4 polyols) and PEG/PPG (C2 polyols). Shown below in Figure 15 are the chemical structures of Cerenol and PTMEG. This research focused on the investigation of reaction extrusion of Cerenol based TPUs and PTMEG based TPUs, and defined the optimal formulations and processing conditions for TPUs with three different hardness levels of 70A, 85A and 50D. The research also analyzed reaction kinetics, and numerous thermo-mechanical properties of the fabricated TPUs.
Figure 15. Chemical structure of (a) Cerenol and (b) PTMEG.

3.4 Experimental

3.4.1 Materials

Polytrimethylene ether glycol (1000 MW and 2000 MW) Cerenol, was provided by DuPont. Polytetramethylene ether glycol (1000 MW and 2000 MW), PTMEG, was purchased from Everchem Specialty Chemicals. Methylene diphenyl 4,4’-diisocyanate (MDI, 250.26 g/mol), Lupranate MS, was purchased from BASF. 1,4-butanediol (BD, 90.12 g/mol), Reagentplus 99%, was purchased from Sigma-Aldrich. Dibutyltin dilaurate (DBTDL, 631.56 g/mol), 98%, was used as a catalyst and purchased from Pfaltz & Bauer. Irganox 1010 was used as an anti-oxidizing agent and purchased from Ciba USA. All materials were used as received.

3.4.2 TPU Reaction

Aside from Cerenol, the reactants used in this research were selected because they are the most commonly used reactants for the synthesis of high performance TPUs. Figure 16 shows the modified TPU reaction using Cerenol polyol. To begin, excess MDI having isocyanate moieties was reacted with BD having alcohol moieties. This results in the formation of the TPU hard-block with isocyanate moieties. The soft-block, Cerenol (shown), having alcohol moieties,
reacts with the hard-block to form high MW TPU. DBTDL was used as a catalyst to speed up the reaction, and Irganox was used as an anti-oxidizing agent.

![Chemical Reaction Diagram](image)

**Figure 16.** Reaction of hard-block formation followed by the addition of the Cerenol soft-block.

### 3.4.3 Reaction Extrusion

As discussed in Chapter II, a twin screw extruder can be readily modified through screw design and screw length to incorporate raw material metering, devolatilization, blending, residence reaction time, etc. For example, well-metered liquids, solids, and catalysts can be introduced into the reactor...
sequentially as materials are transported along the process, and the system is quite flexible for incorporating any materials into the reactor in prescribed quantities. Since the reactor screw is a highly efficient mixer, multiple reactions can be sequenced within a single reactor as required for the process. Finally, adjusting chemical formulations can be accomplished quickly and efficiently “on the fly” enabling numerous chemical formulations to be accomplished in a single set-up and experiment.

A Prism TSE-16-TC intermeshing co-rotating twin screw extruder (L/D ratio = 25) was used as the continuous polymer reactor in this research. The screw configuration is shown in Figure 17. Multiple screw iterations were evaluated before settling on the current, optimal configuration. Forward feeding screws at the feed zone were used to transport reactants away from the feed zone to prevent material build up. Next, a large kneading section was used to mix the material, and to create an area of high shear and pressure. Two additional kneading sections were added to ensure that the reaction was advancing, and that TPU was building MW and viscosity. Intermediary forward feeding screws were used to guarantee that material would not stagnate and degrade. In the last kneading zone, a reverse element was used to increase the residence time, and to create a melt seal to allow material to flow smoothly through the die.
3.4.4 Feeding of the Reactants

The feeding setup of the reactants is depicted in Figure 18. BD and polyols were premixed together with 3000 ppm Irganox 1010 based on total TPU weight in a 4 L reactor. Irganox 1010 was used to prevent oxidation and to maintain clarity of the TPU. 2000 MW Cerenol or PTMEG was used to fabricate 70A samples. 1000 MW Cerenol or PTMEG was used to fabricate 85A and 50D samples. The BD/polyol reactor was heated to 100°C to decrease viscosity of the blend to help with pumping. MDI was heated in a 3 L reactor at 75°C. The BD/polyol mixtures were pumped into the extruder using a Masterflex 77521-40 peristaltic pump. MDI was pumped into the extruder using a Masterflex 77521-50 peristaltic pump. Both pumps were placed in a 60°C hotbox, which was heated by a MHT 750VT Heat Gun controlled by a Digi-Sense Temperature Controller. Masterflex Viton L/S 16 tubing with 3.1 mm inside diameter was used to convey the reactants. All tubing were wrapped with BriskHeat Heating Tape powered by

---

**Figure 17.** Screw design used for TPU synthesis.

<table>
<thead>
<tr>
<th>Utilized Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Screw, L=1/D</td>
</tr>
<tr>
<td>Half Feed Screw, L=1/D/2</td>
</tr>
<tr>
<td>Mixing Element 90° Offset, L=1/D/4</td>
</tr>
<tr>
<td>Extrusion Screw, L=1.5D</td>
</tr>
<tr>
<td>Reverse Half Feed Screw, L=1/D/2</td>
</tr>
<tr>
<td>Mixing Element 0° Offset, L=1/D/4</td>
</tr>
</tbody>
</table>
transformers supplying 40 volts, which heated the tubing to approximately 80°C. A Razel R-100E Syringe Pump was used to inject DBTDL catalyst, which was diluted with the respective polyol being used. All reactants were fed into the first feeding port of the extruder to maximize residence time. The catalyst was pumped through a needle that was inserted into the BD/polyol flow tube just before the feeding port. Both BD/polyol and MDI pumps were calibrated prior to each run to ensure that the proper amount of reactants was being pumped.

*Figure 18. Feeding setup of the reactants.*

Controlling and optimizing critical process variables is a complex process in the twin screw extruder continuous polymer reactor. Further, reproducing desirable MWs and thermo-mechanical properties from the polymers using this system was a challenge. Variables associated with the process included the NCO/OH ratio, hard-block content, throughput, extruder zone temperatures, screw design, and screw speed. All these variables were tuned to obtain the TPUs obtained in this study.
3.4.5 Experimental Analysis

Numerous analytical techniques were used to analyze the reactants, the chemical reaction, and the resultant TPUs that were formed by the reaction. The section below describes these techniques.

3.4.5.1 Differential Scanning Calorimetry

A TA DSC Q200 was used to study reaction kinetics, glass transition temperatures, and melting temperatures. Differential scanning calorimetry (DSC) was run on polyols, reactant mixtures, and TPUs. 3-5 mg samples were deposited into aluminum DSC pans. Heating and cooling rates were usually set at 20°C/min. Data were analyzed using Universal Analysis 2000 software.

3.4.5.2 Thermogravimetric Analysis

The heat weight loss behaviors of polyols and TPUs were analyzed using a TA TGA Q50 Thermogravimetric Analyzer (TGA) in a nitrogen atmosphere. The heating and cooling rate was usually set at 10°C/min and nitrogen flow rate at 20 cc/min. Data were analyzed using Universal Analysis 2000 software.

3.4.5.3 Hardness Test

All extruded TPU samples were compression molded into 4mm disks at 180°C and 3500 PSI for 5 minutes. The disks were then measured with either Gardco 408 Type A or 409 Type D durometers. At least five measurements were recorded for five samples from each TPU formulation.
3.5 Results

3.5.1 DSC of Cerenol and PTMEG Polyols

Cerenol exists as a clear liquid at room temperature. However, PTMEG has a white waxy form at room temperature. 1000 and 2000 MW samples of Cerenol and PTMEG were analyzed using DSC to explain this trait. Samples were cooled at 20°C/min from room temperature to -90°C, held for 3 minutes, then heated at 20°C/min to 150°C. Figures 19 and 20 show DSC curves of Cerenol and PTMEG, respectively.

During the cooling cycle, Cerenol exhibited crystallization peaks around -30°C, and T_g of -77°C for Cerenol 1000 and -74°C for Cerenol 2000. PTMEG exhibited crystallization peaks around 0°C. Because of the capability of the DSC, the T_g of PTMEG could not be observed. The reported T_g of PTMEG is around -85°C.

During the heating cycle, Cerenol exhibited a melting point of 15°C for Cerenol 1000 and 18°C for Cerenol 2000. PTMEG 1000 had a melting point of 23°C, while PTMEG 2000 had a melting point of 25°C. PTMEG containers had to be heated in order to pour out the polyols. Cerenol on the other hand poured readily. Cerenol is easier to handle and process because it is in liquid form at room temperature and has lower viscosity than PTMEG at any temperature. Cerenol and PTMEG melting points were in line with published values.
Figure 19. DSC curves of 1000 and 2000 MW Cerenol.

Figure 20. DSC curves of 1000 and 2000 MW PTMEG.
3.5.2 DSC Reaction Kinetics

One of the goals of this research was to evaluate the use of Cerenol as a drop-in replacement for conventional polyether polyols. For Cerenol to be utilized in such a manner, the reaction kinetics of Cerenol must be similar to those of PTMEG. DSC was used to analyze the reaction kinetics of Cerenol TPUs and PTMEG TPUs.

Varying TPU formulations with an NCO/OH ratio of 1.03, and a hard-block content of 8.77% were made. No catalyst was used for initial analysis. The polyol content was adjusted accordingly using 1000 MW Cerenol or PTMEG. Formulations were quickly mixed in an ultrasonic ice water bath, and frozen for further isothermal reaction analysis. Around 3-5 mg samples were placed into aluminum DSC pans and isothermally reacted at various temperatures. Nitrogen flow rate was set at 20 cc/min. The samples were heated at 60°C/min to reaction temperatures and held until the reaction was completed. Reaction kinetics were analyzed based on the Avrami equation as:

\[ X_c = 1 - \exp(-kt^n) \]  \hspace{1cm} (19a)

\[ \ln[-\ln(1 - X_c)] = \ln k + n \ln t \]  \hspace{1cm} (19b)

where \( X_c \) is the reaction conversion, \( k \) is a reaction rate constant, \( t \) is the reaction time, and \( n \) is another parameter related to the reaction mechanism. The 100% conversion threshold was determined from the total heat exotherm measured under isothermal conditions at 250°C using DSC. Subsequent conversions were compared against the threshold by using the area under the curve.
Figures 21 and 22 present the % conversion versus reaction time of 1000 MW Cerenol and PTMEG TPUs, respectively. The results showed that at temperatures above 180°C, 95% conversion could be achieved in less than five minutes. As reaction temperatures increased, % conversion for a given period of time also increased. Of main importance, Cerenol and PTMEG TPUs performed similarly across the temperature range with the time to 95% conversion of both polyol TPUs deviating within a minute of each other.

*Figure 21. TPU % conversion versus time at various reaction temperatures of BD/Cerenol 1000 = 8.77%, no catalyst, and NCO/OH = 1.03*
Figure 22. TPU % conversion versus time at various reaction temperatures of BD/PTMEG 1000 = 8.77%, no catalyst, and NCO/OH = 1.03.

Reaction rate constants were also analyzed for the same formulations. Figure 23 shows these results. The reaction rate constants increased with increasing temperature. Further, the reaction rate constants for Cerenol and PTMEG were quite similar, from 120-220°C.
Figure 23. Reaction rate constant and time to 95% conversion versus reaction temperature of 1000 MW Cerenol and PTMEG TPUs. NCO/OH ratio was 1.03, BD/Polyol ratio was 8.77%, and no catalyst.

The effect of catalyst and temperature on the reaction rate constant of Cerenol and PTMEG is shown in Figure 24. The catalyst level was varied at 40 ppm or 100 ppm. At 40 ppm, Cerenol reacted at a slightly faster rate than PTMEG. At 100 ppm, PTMEG reacted at a slightly faster rate than Cerenol. At higher catalyst levels (>100 ppm) and higher reaction temperatures (>120°C), the reaction advanced so quickly that it was hard to measure in the DSC. Considering DSC experiment error, there was no obvious difference between Cerenol and PTMEG TPU reaction rates.
3.5.3 Isocyanate-Hydroxyl Ratio Effect

As previously discussed, a specific advantage for utilizing reaction extrusion in an extruder reactor is the opportunity to modify polymer formulations in real-time during a reaction experiment. This flexibility provides a unique advantage over wet chemistry when conducting reactions since reaction variables can be adjusted during experimentation to formulate multiple polymers during a single run. TPU polymerization reactions can be monitored in the extruder by observing measurable outputs incorporated into the process. Exotherms associated with the chemical reaction in specific zones can be observed as an increase in material temperature using melt-thermocouples in
specific zones of the reactor. Similarly, the torque and die pressure that are measured by the extruder can be used as indicators of the extent of reaction and the formation of high MW TPU.

To determine the optimal NCO/OH ratio, a BD/Cerenol (1000 MW) ratio of 8.77% with a catalyst level of 250 ppm was used. The extruder zone temperature profile was set at 80-140-180-180-180°C from feeding port to die, and screw speed was set at 250 rpm. Total throughput was 1.65 lbs/hr. The BD/Cerenol mixture was pumped at a constant rate and MDI pumping rate was varied to obtain various NCO/OH ratios. Both torque and pressure responded within a minute of any change to the NCO/OH ratio. Figure 25 shows the effect of NCO/OH ratio on extruder torque and die pressure. As previously discussed, previous research has shown the optimal NCO/OH ratio is between 1.01-1.05. Maximum torque and die pressure was observed at an NCO/OH ratio of 1.03. Outside of the 1.01-1.05 range, torque and die pressure dropped off significantly. The TPU strands that were being extruded also looked clearer when the NCO/OH ratio was 1.03. When the NCO/OH ratio deviated from this value (either above or below), the strands became translucent.
Figure 25. NCO/OH ratio effect on extruder torque and die pressure.

Figure 26 shows the effect of NCO/OH ratio on sample hardness. NCO/OH ratio of 0.95 showed the highest hardness, 81A. However, the TPU was translucent at this ratio, which is an undesirable quality for manufacturing TPUs. Translucency disappeared after NCO/OH ratio was increased to greater than 1.01. Hardness was approximately the same, 75-77A, for NCO/OH ratios 1.01-1.11. After analyzing extruder torque, die pressure, translucency, and hardness, an NCO/OH ratio of 1.03 was deemed to be the optimal NCO/OH ratio for the given TPUs in this research.
Figure 26. NCO/OH ratio effect on Shore A hardness.

3.5.4 Formulation Determination

3.5.4.1 Wet Chemistry Formulation

Prior to extrusion, TPUs were synthesized through wet chemistry techniques to determine the approximate hard-block content to target the three hardness levels: 70A, 85A, and 50D. The following is a typical procedure for synthesizing a TPU with an NCO/OH ratio of 1.03 and a hard-block content of 12%. TPU hard-block was initially formed by adding 4.72 g of MDI (1.887x10^{-2} mol), 1.20 g of 1,4-butanediol (1.332x10^{-2} mol), and 0.042 g of DBTDL (6.707x10^{-5} mol) to 100 mL of toluene in a 500 mL round bottom flask. The hard-block solution was heated at 50°C in an oil bath and mechanically stirred for 10
minutes. These conditions provide adequate time for the hard-block to form prior to precipitation. 10 g ($5 \times 10^{-3}$ mol) of Cerenol (2000 MW) was separately dissolved in 100 mL of toluene in a 250 mL beaker. The soft-block solution was then added to the hard-block solution and stirred for approximately 24 hours to complete the reaction. Toluene was removed by rotary evaporation, and the resultant polymer was dissolved in chloroform and poured into a 300 mL PTFE dish. The dish was then placed in a room temperature vacuum oven to remove residual chloroform. Samples for hardness testing were stamped out of the resultant TPUs.

It is easy to see why the continuous polymer extrusion method is the preferred choice for large-scale production of TPUs. The wet chemistry method of producing TPUs is a long, energy intensive process requiring additional reactants and hazardous solvent disposal. By using a twin screw extruder, TPUs can be made in one continuous process within a few minutes, as opposed to wet chemistry, which requires multiple steps and requires a long period of time.

3.5.4.2 Extrusion Formulation

While wet chemistry formulation is useful to approximate the hard-block content necessary to target the different hardness levels, further evaluation was required on the extruder to zero in the exact formulation. Reactions occur much faster and in much smaller quantities, and thus present a different set of challenges. The approach to narrow down the hard-block content was to generate curves to predict the specific hardnesses: 70A, 85A, and 50D.
For 70A, hard-block content was varied from 3% up to 8% using 2000 MW Cerenol and PTMEG. Figure 27 shows the effect of hard-block content on the hardness of both Cerenol and PTMEG TPUs. For 85A and 50D, the hard-block content was varied from 4% up to 30% using 1000 MW Cerenol and PTMEG. Figure 28 shows the effect of hard-block content on the hardness of both Cerenol and PTMEG TPUs. The NCO/OH ratios were set at 1.03 for all samples.

Figure 27. TPU hardness versus hard-block content of 2000 MW Cerenol and PTMEG TPUs targeting 70A hardness.
After hardness evaluation of all TPUs samples, curves were generated to predict the hard-block content for the specified hardnesses. For Cerenol TPUs, 70A required 6.0% hard-block, 85A required 12.6% hard-block, and 50D required 25.7% hard-block. For PTMEG TPUs, 70A required 5.2% hard-block, 85A required 11.0% hard-block, and 50D required 21.5% hard-block. Cerenol TPUs required more hard-block than their PTMEG counterparts.

3.5.5 Extrusion

Extrusion of TPUs was performed as described earlier in this chapter. Table 4 shows the formulations and extrusion processing conditions that were used to synthesize the TPUs. 3000 ppm Irganox 1010 anti-oxygen agent was used in all formulations based on total TPU weights. Screw speed was set at 250
RPM and total throughput was set at 3.3 lbs/hr for all samples. The extruder had five heating zones that could be adjusted to a desired temperature. The temperatures provided in the table are for the last three zones, including the die. The feeding port was cooled by circulated water to avoid early reaction, which could potentially block flow. The first two zone temperatures were maintained at 100°C and 140°C for all conditions. The temperature profile from feeding port to die was 100-140-180-180-180°C for 70A samples, 100-140-190-190-190°C for 85A samples, and 100-140-200-200-200°C for 50D samples. With increasing hardness, higher extruder zone temperatures were necessary to feed higher viscosity, higher modulus material. Extruded polymer strands were required to possess high optical quality, and were quickly quenched in a water bath and pelletized. The pellets were then post cured at 60°C for 12 hours.

Table 4

*TPU hardness versus hard-block content of 1000 MW Cerenol and PTMEG*

*TPUs targeting 85A and 50D hardness*

<table>
<thead>
<tr>
<th>Polyol</th>
<th>Hardness</th>
<th>BD/polyol (%)</th>
<th>Irganox 1010 (ppm)</th>
<th>Screw Speed (rpm)</th>
<th>Temp. (°C)</th>
<th>Flow Rate (lbs/hour)</th>
<th>Catalyst (ppm)</th>
<th>Torque (N*m)</th>
<th>Pressure (PSI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerenol 70A</td>
<td>6.0</td>
<td>3000</td>
<td>250</td>
<td>180</td>
<td>5.9</td>
<td>1400</td>
<td>20</td>
<td>190</td>
<td></td>
</tr>
<tr>
<td>Cerenol 85A</td>
<td>12.6</td>
<td>3000</td>
<td>250</td>
<td>190</td>
<td>6.6</td>
<td>460</td>
<td>18</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>Cerenol 50D</td>
<td>25.7</td>
<td>3000</td>
<td>250</td>
<td>200</td>
<td>6.6</td>
<td>266</td>
<td>18</td>
<td>190</td>
<td></td>
</tr>
<tr>
<td>PTMEG 70A</td>
<td>5.2</td>
<td>3000</td>
<td>250</td>
<td>180</td>
<td>6.6</td>
<td>1400</td>
<td>21</td>
<td>260</td>
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<tr>
<td>PTMEG 85A</td>
<td>11.0</td>
<td>3000</td>
<td>250</td>
<td>190</td>
<td>6.6</td>
<td>460</td>
<td>18.8</td>
<td>180</td>
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</tr>
<tr>
<td>PTMEG 50D</td>
<td>21.5</td>
<td>3000</td>
<td>250</td>
<td>200</td>
<td>6.6</td>
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</tbody>
</table>
The catalyst level had to be increased with decreasing hardness/hard-block content. This is because the kinetics of the soft-block, polyol, was much slower than that of the hard-block, MDI and BD. At lower hard-block content, more soft-block needed to be reacted and thus required higher catalyst level to build MW and viscosity. At low catalyst levels, the unreacted, low viscosity TPU mixtures would back up into the feeding port, and exhibit low extruder torque and die pressure. For 70A TPUs, the catalyst was diluted in 2000 MW Cerenol or PTMEG at 40% concentration. For 85A TPUs, the catalyst was diluted in 1000 MW Cerenol or PTMEG at 20% concentration. For 50D TPUs, the catalyst was diluted in 1000 MW Cerenol or PTMEG at 10% concentration. TPUs with higher hardness were produced at higher temperatures. Otherwise, pressure would build up at the die causing a potentially hazardous situation. A ten-degree increase in temperature was adequate for each hardness step.

3.6 TPU Evaluation

3.6.1 DSC Evaluation

DSC analysis was performed on extruded TPU samples. Two heating runs were performed on all samples. The samples were heated from room temperature to 250°C at 20°C/min, held for 3 minutes, then cooled to -75°C at 20°C/min, held for 3 minutes, then heated back up again to 250°C at 20°C/min.

Figure 29 shows the first heat scan DSC curves of Cerenol and PTMEG TPUs. All TPUs showed melting peaks between 100-140°C, which disappeared in the second heating cycle. This may be because of the quenching effect of the polymer melt through the ice water bath post extrusion. 70A samples only
showed small melting peaks. With increasing TPU hardness, the crystal fusion enthalpy increased indicating higher crystallinity. For 85A and 50D samples, PTMEG TPUs exhibited higher $T_m$s than Cerenol TPUs. During the second scan, Figure 30, all TPUs showed obvious $T_g$s. With increasing TPU hardness, $T_g$ also increased.

*Figure 29*. First heating scan DSC curves of Cerenol and PTMEG TPUs.
Figure 30. Second heating scan DSC curves of Cerenol and PTMEG TPUs.

3.6.2 TGA Evaluation

Figure 31 shows the first derivative curve of TGA analysis for the TPUs. All samples decomposed in two steps. The first decomposition began around 280°C while the second decomposition began around 380°C. The respective 85A and 50D Cerenol and PTMEG TPUs performed similarly, while there was disparity between the 70A Cerenol and PTMEG TPUs. With increasing hardness, the first decomposition weight loss increased. This is shown in Figure 32. Further, Cerenol and PTMEG TPUs showed similar weight loss behavior in the first decomposition. In the second decomposition, Cerenol TPUs demonstrated higher decomposition temperatures than PTMEG TPUs.
Figure 31. First derivative TGA of Cerenol and PTMEG TPUs.

Figure 32. TGA % weight loss of Cerenol and PTMEG TPUs.
3.6.3 Mechanical Testing Evaluation

Mechanical testing was performed independently using various ASTM standards at the Mississippi Polymer Institute:

- D412 Tensile Strength and Ultimate Elongation
- D790 Flex Fatigue
- D624 Die C Tear Strength
- D470 Split Tear Strength
- D2240 Durometer
- D575 Compression

Table 5 shows the mechanical properties of the TPUs. Cerenol TPUs showed slightly lower tensile strength but higher compression strength than PTMEG TPUs. Both TPUs had comparable tear strength.

Table 5

<table>
<thead>
<tr>
<th>Description</th>
<th>Test Method</th>
<th>Units</th>
<th>Cerenol 50D</th>
<th>PTMEG 50D</th>
<th>Cerenol 85A</th>
<th>Cerenol 70A</th>
<th>PTMEG 70A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
<td></td>
<td>lb/in²</td>
<td>4002.6</td>
<td>4647.4</td>
<td>5169.5</td>
<td>2173.4</td>
<td>2733.3</td>
</tr>
<tr>
<td>Ultimate Elongation</td>
<td></td>
<td>%</td>
<td>689</td>
<td>952</td>
<td>1773</td>
<td>2154</td>
<td>2166</td>
</tr>
<tr>
<td>Tensile Strength at 50%</td>
<td>ASTM D412, Die C, 20 in/min</td>
<td>lb/in²</td>
<td>1067.8</td>
<td>909.84</td>
<td>446.4</td>
<td>208.7</td>
<td>208.4</td>
</tr>
<tr>
<td>Tensile Strength at 100%</td>
<td></td>
<td>lb/in²</td>
<td>1419.8</td>
<td>1183.7</td>
<td>625.6</td>
<td>315.4</td>
<td>316</td>
</tr>
<tr>
<td>Tensile Strength at 300%</td>
<td></td>
<td>lb/in²</td>
<td>2181.7</td>
<td>1852</td>
<td>922.9</td>
<td>507.9</td>
<td>514.9</td>
</tr>
<tr>
<td>Flexural Strength</td>
<td>ASTM D790, 0.053 in/min</td>
<td></td>
<td>9508.4</td>
<td>7763.4</td>
<td>2993.4</td>
<td>1292.3</td>
<td>1446.4</td>
</tr>
<tr>
<td>Tear Strength</td>
<td>ASTM D624, Die C</td>
<td>lb/in</td>
<td>671.1</td>
<td>596</td>
<td>408</td>
<td>347.3</td>
<td>331.5</td>
</tr>
</tbody>
</table>
Table 5 (continued).

<table>
<thead>
<tr>
<th>Description</th>
<th>Test Method</th>
<th>Units</th>
<th>Cerenol 50D</th>
<th>PTMEG 50D</th>
<th>Cerenol 85A</th>
<th>Cerenol 70A</th>
<th>PTMEG 70A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Split Tear Strength</td>
<td>ASTM D470, 20 in/min</td>
<td></td>
<td>187</td>
<td>194.1</td>
<td>130.4</td>
<td>101.7</td>
<td>101.3</td>
</tr>
<tr>
<td>Hardness</td>
<td>ASTM D2240</td>
<td>Scale D</td>
<td>49.7</td>
<td>49.1</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Scale A</td>
<td>—</td>
<td>—</td>
<td>84.8</td>
<td>69.6</td>
<td>72.07</td>
</tr>
<tr>
<td>Compression Stress at 2%</td>
<td></td>
<td></td>
<td>285.7</td>
<td>161</td>
<td>120.2</td>
<td>55.6</td>
<td>45.8</td>
</tr>
<tr>
<td>Compression Stress at 5%</td>
<td></td>
<td></td>
<td>522.9</td>
<td>423.2</td>
<td>244.3</td>
<td>116.3</td>
<td>115.1</td>
</tr>
<tr>
<td>Compression Stress at 10%</td>
<td></td>
<td></td>
<td>2433.2</td>
<td>2353.8</td>
<td>771.1</td>
<td>374</td>
<td>441.9</td>
</tr>
<tr>
<td>Compression Stress at 15%</td>
<td></td>
<td>lb/in²</td>
<td>2780.6</td>
<td>2741.8</td>
<td>960.8</td>
<td>451.4</td>
<td>561</td>
</tr>
<tr>
<td>Compression Stress at 20%</td>
<td></td>
<td></td>
<td>3152.7</td>
<td>3153.2</td>
<td>1162.7</td>
<td>538.1</td>
<td>690</td>
</tr>
<tr>
<td>Compression Stress at 25%</td>
<td></td>
<td></td>
<td>3566.5</td>
<td>3606.3</td>
<td>1380.4</td>
<td>635.9</td>
<td>836.2</td>
</tr>
<tr>
<td>Compression Stress at 50%</td>
<td></td>
<td></td>
<td>7425.3</td>
<td>8078.8</td>
<td>3332</td>
<td>1684.7</td>
<td>2335.5</td>
</tr>
</tbody>
</table>

3.7 Discussion

Initial DSC analysis indicated that Cerenol and PTMEG exhibited similar reaction kinetics. At temperatures above 120°C and a minimum of 40 ppm catalyst, the reaction advanced so quickly that it could not be measured with the DSC. This was further reinforced during reaction extrusion, where reactions occur even faster. For a given hardness, regardless of whether Cerenol or PTMEG was used as the soft-block, the TPU required the same processing conditions: screw speed, barrel temperatures, throughput, and catalyst level.
Further, they had similar extruder feedback in the form of extruder torque and die pressure. This indicates that Cerenol polyols can be readily adapted to current processing techniques used to manufacture PTMEG TPUs. However, it is important to note that Cerenol TPUs required higher hard-block content to obtain the same hardness level as PTMEG TPUs.

Shown in Table 6 are the $T_g$'s of Cerenol and PTMEG polyols and their respective TPUs based on DSC data. Cerenol polyols did not crystallize in the cooling cycle leaving all the molecules in an amorphous state. Thus, their observed $T_g$'s were prominent at extremely low temperatures, -75-77°C. PTMEG polyols, however, did crystallize in the cooling cycle. Thus, they had much higher $T_g$'s compared to Cerenol polyols. When Cerenol and PTMEG polyols were used to form the soft-block of TPUs, they continued to exist in an amorphous state and did not exhibit melting peaks. Thus, both Cerenol and PTMEG TPUs showed obvious $T_g$'s with Cerenol TPUs exhibiting lower $T_g$'s than their PTMEG TPU counterparts. Cerenol TPUs also showed higher $T_g$'s than their soft-block polyols because the crystallized hard-block units restricted the motion of the polyol soft-block molecules. Cerenol TPUs also had slightly higher hard-block content. PTMEG polyols had lower $T_g$'s than when incorporated into TPUs. This is probably because the polyols in their pure state crystalize sooner and consequently, have more restriction on molecular motion than the hard-block in their TPUs.
Table 6

Glass transition temperatures of TPU and polyols measured by DSC

<table>
<thead>
<tr>
<th>TPU</th>
<th>Polyol Type</th>
<th>Polyol Tg (°C)</th>
<th>TPU Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerenol 70A</td>
<td>Cerenol 2000</td>
<td>-75</td>
<td>-58</td>
</tr>
<tr>
<td>Cerenol 85A</td>
<td>Cerenol 1000</td>
<td>-77</td>
<td>-39</td>
</tr>
<tr>
<td>Cerenol 50D</td>
<td>Cerenol 1000</td>
<td>-77</td>
<td>-31</td>
</tr>
<tr>
<td>PTMEG 70A</td>
<td>PTMEG 2000</td>
<td>-31</td>
<td>-65</td>
</tr>
<tr>
<td>PTMEG 85A</td>
<td>PTMEG 1000</td>
<td>-9</td>
<td>-12</td>
</tr>
<tr>
<td>PTMEG 50D</td>
<td>PTMEG 1000</td>
<td>-9</td>
<td>6</td>
</tr>
</tbody>
</table>

All Cerenol TPU showed narrower Tgs than PTMEG TPU. For 85A and 50D samples, Cerenol TPU had much lower Tg than PTMEG TPU. In Cerenol polyols, 50% of the C-O bonds are flexible. In PTMEG polyols, 40% of the C-O bonds are flexible. The higher percentage of flexible C-O bonds in Cerenol polyols makes them crystallize at a lower rate than PTMEG polyols leading to lower Tg for Cerenol TPU.

Figure 33 shows the TGA of Cerenol and PTMEG polyols, and the MDI-BD hard-block. The decomposition peak of the hard-block is around 325°C.

Table 7 summarizes the TGA of both TPU and polyols. The first decomposition peaks of the TPU are wide; therefore, a temperature range is given. These decomposition peaks are close to the hard-block decomposition temperature. The weight loss of the first decomposition peak increased with increasing hard-block. Thus, the first decomposition peak was assigned to the decomposition of the hard-block of the TPU. The second decomposition peaks were sharper and
closer to those of the polyols. The weight loss associated with these peaks decreased with increasing hard-block. Thus, the second decomposition peak was assigned to the decomposition of the soft-blocks of the TPUs. Both Cerenol and PTMEG TPUs had similar first decomposition peak temperatures. However, Cerenol TPUs showed higher second decomposition peak temperatures than PTMEG TPUs.

Figure 33. TGA of polyols and MDI-BD hard-block.
Table 7

TGA data of polyols and TPUs

<table>
<thead>
<tr>
<th>TPUs</th>
<th>First Decomposition Peak (°C)</th>
<th>Second Decomposition Peak (°C)</th>
<th>Polyol Decomposition Peak (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerenol 70A</td>
<td>314-349</td>
<td>440</td>
<td>404</td>
</tr>
<tr>
<td>Cerenol 85A</td>
<td>366</td>
<td>430</td>
<td>397</td>
</tr>
<tr>
<td>Cerenol 50D</td>
<td>323-351</td>
<td>424</td>
<td>397</td>
</tr>
<tr>
<td>PTMEG 70A</td>
<td>320-357</td>
<td>416</td>
<td>385</td>
</tr>
<tr>
<td>PTMEG 85A</td>
<td>326-361</td>
<td>420</td>
<td>401</td>
</tr>
<tr>
<td>PTMEG 50D</td>
<td>327-3357</td>
<td>416</td>
<td>401</td>
</tr>
</tbody>
</table>

3.8 Conclusion

TPUs based on both Cerenol and PTMEG polyols were successfully fabricated using a “one-shot” continuous polymer reactor. DSC studies showed that the two kinds of polyols had similar reaction kinetics with the hard-block. Cerenol and PTMEG TPUs were synthesized with almost identical reaction extrusion conditions to make the same hardness TPUs. Cerenol TPUs required a slightly higher hard-block content to obtain the same hardness as PTMEG TPUs. Cerenol and PTMEG TPUs demonstrated similar T_m's. However, Cerenol TPUs showed lower T_g's and higher thermal degradation temperatures than PTMEG TPUs. Based on reaction kinetics and the capability to use the same processing conditions as PTMEG TPUs, Cerenol could be used as a drop in replacement for existing polyols in TPU processes.
REFERENCES


27. Sunkara, H. B.; Parmpi, P. There is disclosed a process for preparing polytrimethylene ether glycol by acid catalyzed polycondensation of a diol (1,3-propanediol), purification, neutralization with a water-insoluble base (calcium hydroxide) and contacting with filter aid (diatomite, perlite and cellulose); avoids hydrolysis and yet provides product substantially free of catalyst derived end groups. E.I. DuPont De Nemours And Company assignee. Patent 7,074,969. 2006.


CHAPTER IV
PREPREG EPOXY MATRIX PREPOLYMERS FROM CONTINUOUS POLYMER REACTOR DESIGN

4.1 Abstract

Continuous polymer reactor designs were used to synthesize and partially cure two commercially used prepreg epoxy matrix prepolymers (prepolymers): 8281 and 5208. 828 and 5208 are epoxy systems widely used in the aerospace industry. 8281, a variant of 828, consists of two components: a diglycidyl ether of bisphenol A (DGEBA) variant and 4,4’-diaminodiphenylsulfone (44DDS). 5208 consists of three components: 44DDS, N, N, N’, N’-tetraglycidyl-4,4’-diaminodiphenylmethane (TGDDM), and 4-[2-(4-hydroxyphenyl) propan-2-yl] phenol (SU-8). These prepolymeres were first examined in batch reactors to analyze cure kinetics, and to obtain target glass transition temperatures ($T_g$). The target $T_g$ was identified via differential scanning calorimetry as the temperature at which the prepolymer should be partially cured to in order to successfully process into prepreg. Target $T_g$s were approximately 5°C for both prepolymeres. Reactive extrusion was then performed at varying processing conditions to obtain the target $T_g$s. The results showed that target $T_g$s could be achieved at extruder temperatures of 200°C for 8281 and 150°C for 5208. A comparison of the batch and continuous reactor prepolymeres showed that there was no difference in cured epoxy DMA properties such as $T_g$, and storage and loss modulus. It was concluded that 8281 and 5208 prepolymeres could be partially cured via continuous polymer reactor design to make prepolymer suitable for prepreg.
4.2 Introduction

4.2.1 Prepreg

Prepregs are composite construction materials used in the aerospace industry for the manufacturing of advanced and high-performance composite parts and structures. Prepregs consist of carbon fiber preimpregnated with a matrix prepolymer, usually a thermoset epoxy.\textsuperscript{1,2} When compared to other carbon fiber reinforced composite manufacturing techniques, prepregs have more even resin distribution and a relatively fixed fiber to resin ratio (generally 67:33 fiber to resin weight percent ratio). The fiber to resin ratio helps control the final physical properties of the composite.

The production of prepregs begins with bare carbon fiber tows. Each tow consists of thousands of carbon fiber filaments grouped together. Multiple tows are pulled together in a flat sheet, and sandwiched between papers coated with partially cured (or B-staged) prepreg epoxy matrix prepolymer (prepolymer). The prepolymer is B-staged to increase viscosity and MW to promote processability and handleability of the prepreg. The carbon fiber, prepolymer, and paper then pass through sets of heated rollers. The heat and pressure of the rollers spreads the fibers within each tow and forces the prepolymer between individual filaments. The consolidated prepreg is then quickly chilled to prevent further curing of the resin.\textsuperscript{3}

To make a part, prepreg is cut to the necessary ply (individual layer of prepreg or lamina) shapes and sizes needed to form a part against a mold surface. Prepregs can be used to create composite parts that have intricate
designs. Parts can consist of a few plies to hundreds of plies. The laid up prepreg and mold are then vacuum bagged and autoclaved to completely cure the part.

4.2.2. B-staging Prepreg

One of the key features to producing high quality prepreg is to control the prescribed extent of cure of the prepolymer. As mentioned earlier, B-staging the prepolymer increases viscosity and MW of the prepolymer and allows for easier processing and handleability of the prepreg. A certain level of tack must be obtained to provide appropriate lamina adhesion during the lay-up process. Although there is no quantitative assessment for this property, it is said to be “tacky but not sticky.” To further evaluate this property, this research aimed to quantitatively define this property by measuring changes in the glass transition temperature ($T_g$) and viscosity of the prepolymers being studied. A low B-stage level corresponds to a prepreg with a high level of tack, and makes handleability hard when laying up parts. Excessive flash can lead to porosity and void defects in the composite part. Conversely, a high B-stage level corresponds to a prepreg with a low level of tack, which can lead to prepreg consolidation issues. The handling, storage, and mechanical life of the prepreg can also be reduced. Thus, the appropriate level of B-staging and tack is a necessity for manufacturing high-quality prepreg.

4.3 Background

4.3.1 Prepolymer Chemistry

The matrix phase, prepolymer, of carbon fiber reinforced composites is typically formed from epoxy resins in step-growth polymerization reaction with
multifunctional amines. In the first step, primary amines react with epoxies to form epoxy moieties that contain secondary amines. Secondary amines then react with subsequent epoxies to form a crosslinked network. When cured, the resin forms a three-dimensional polymer network with large MWs. The previous chapter discussed thermoplastics. Thermoplastics are held together by intermolecular interactions. When heated above their T_g s, thermoplastics melt. Epoxies however are thermoset polymers. Thermoset polymers actually form chemical bonds with other chains to create a three-dimensional polymer network. Thus, once reacted, a thermoset cannot melt and can only degrade at high temperatures.^[4]

4.3.2 Prepolymer via Batch Process

Currently, prepolymer are reacted in batch reactors. Epoxies and amines are heated at high temperatures over long periods of time to dissolve the amines and initiate the cure reaction. Once the prepolymer is advanced to its prescribed oligomeric MW and viscosity, it is discharged from the batch reactor, quenched, and stored in freezers for indefinite periods of time in order to slow kinetics, minimize continued reaction, and maintain target MW. After some period of time in sub-ambient storage, the prepolymer is re-heated above its T_g, discharged onto film lines, further heated, and then converted to thin films used in prepreg manufacturing.

Although widely used, there are several limitations with the batch process. Epoxy-amine reaction kinetics can be extremely difficult to control, and are time and energy consuming. The reaction is very exothermic, especially in large batch
reactors, and can become a runaway reaction, which is extremely dangerous. Furthermore, since the reaction continues to advance whenever heated, B-staging level is varied leading to inconsistent batch-to-batch prepolymer.

Prepolymers also continue to react even at cold temperatures; thus, their viscosity is constantly changing. These changes can cause variations in prepreg and consequently in the final cured composite structure. Therefore, a continuous polymer reactor design was investigated to produce prepolymer more efficiently with reduced variation of curing conversion.

4.3.3 Prepolymer via Continuous Polymer Reactor Design

The previous chapter focused on the extrusion of TPUs, a thermoplastic material that is melt-processable. However, prepolymer are generally thermoset polymers as explained earlier. There is limited use and research on the reaction extrusion of prepolymer systems. Review of the scientific literatures has revealed a significant gap of knowledge for the continuous reactive extrusion of prepolymer. Only the research conducted by Titier and co-workers has demonstrated the possibility of reacting epoxies with amines via reaction extrusion. We envision using continuous reactors to prepare prepolymer integrated directly onto prepreg film lines, which will substantially reduce the energy and the variation in the production of these materials. In short, this research provides excellent opportunities to improve energy-efficient processing techniques with enhanced reaction control, improved reproducibility, and safety compared to processes currently used in industry.
Twin screw extruders can be exceptional prepolymer reactors because reactions can be precisely controlled. Prepolymer can be obtained minutes after introducing epoxies and amines at the beginning of the barrel. The screws are intermeshed together allowing for the screw surfaces to slide past each other constantly removing any polymer that is stuck to the screw. As a result, reactions occur in small quantities between the two screws minimizing exothermic reaction energy.⁹

**Scope of Research**

The research presented in this chapter consists of two prepolymer systems: 8281 and 5208. For brevity, 8281 will refer to the DGEBA and 44DDS mixed prepolymer. 5208 will refer to the TGDDM, SU-8 and 44DDS mixed prepolymer. Both prepolymer systems are widely used in the aerospace industry in the manufacturing of high-performance prepreg. The viability of reacting 8281 prepolymer was first investigated on a lab-scale extruder. Next, scaled-up reaction extrusion of 5208 was investigated using an industrial size extruder.

**4.4 Continuous Polymer Reactor Design of 8281**

**4.4.1 8281**

8281 prepolymer, a variant of 828, consists of two components: a diglycidyl ether of bisphenol A (DGEBA) variant, and 4,4’-diaminodiphenylsulfone (44DDS). Shown below in Figure 34 are the chemical structures of 8281 epoxy and 44DDS amine, respectively. When crosslinked, 8281 exhibits good mechanical and adhesive properties, good dimensional stability, and has high dielectric and chemical resistance. 8281 has been used in
applications such as prepolymer, adhesives, electrical encapsulants, molding compounds, tool compounds, and many construction end uses.\textsuperscript{10-12}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{image1}
\caption{Representation of 8281 (a) and 44DDS (b). 8281 has a functionality of 2 while the 44DDS has a functionality of 4.}
\end{figure}

4.4.2 Experimental

Materials

The following materials were used as received: 4,4’-diaminodphenylsulfone (44DDS, Royce Chemical Corp., MW = 248.28 g/mol, Amine Equivalent Weight = 62.07), and EPON Resin 8281/DGEBA (8281, Hexion Specialty Chemical, MW = 380 g/mol, Epoxy Equivalent Weight = 190). The 8281 prepolymer formulation contained 73.4 wt% DGEBA and 24.6 wt% 44DDS. This corresponded with a 1:1 ratio of functional epoxies and amines.
Batch Reaction Synthesis of 8281

Prior to reaction extrusion, batch reactions of 8281 prepolymer were synthesized to determine the approximate temperatures necessary to obtain a target B-staged prepolymer. 8281 was heated and stirred in an 85°C oil bath and vacuum was applied to evacuate any bubbles. The temperature was increased to 100°C, and 44DDS was added. The temperature was then increased 5°C every 10 minutes to 120°C. 44DDS completely dissolved into 8281 at 120°C. The prepolymer was allowed to B-stage at 120°C until prescribed curing conversion was reached. Aliquots of the prepolymer were taken at different curing times and frozen immediately to determine appropriate B-staging level. The samples were analyzed using differential scanning calorimetry (DSC) to determine the T_g. The temperature at which the reaction occurred and the time taken for the reaction to occur were then used as starting parameters for reaction extrusion. The resultant batch prepolymer was also cast into silicone molds, and cured for dynamic mechanical analysis (DMA) and mechanical testing.

Continuous Polymer Reactor Design of 8281

Reaction extrusion was performed using a Prism TSE-16-TC intermeshing co-rotating twin screw extruder (L/D ratio = 25). A mixture of 8281 and 44DDS was pumped into the first feed port of the extruder. Screw speed was set at 150 rpm with a throughput of 18 g/min. The temperatures of the last four zones of the extruder were increased to advance the reaction of the resin. After temperatures were stabilized for each condition, a sample of the extrudate was captured and immediately frozen for later analysis. In addition to varying extruder temperature
zones, screw speed and throughput were also varied in order to perform a design of experiments (DOE) analysis to determine which extruder variables had the greatest effect on B-staging level.

8281 and 44DDS were premixed at 80°C in a 4 L glass reactor. Because 44DDS was in a powder form, the feeding equipment for the lab-scale extruder was unable to feed 44DDS. Thus, 44DDS and 8281 were premixed together. Analyses were performed to ensure that the prepolymer would not B-stage prematurely. The assumption was that the prepolymer would only B-stage a small degree at 80°C.

The premixed prepolymer was pumped into the extruder using a Masterflex 77521-40 Peristaltic Pump. The pump was placed in a 60°C hotbox, which was heated by a MHT 750VT Heat Gun controlled by a Digi-Sense Temperature Controller. Masterflex Viton L/S 16 tubing with 3.1 mm inside diameter was used to convey the premix. All tubing were wrapped with BriskHeat Heating Tape powered by transformers supplying 40 volts, which heated the tubing to approximately 80°C. Heating of the lines and pump was required to decrease the viscosity of the prepolymer so that it would pump efficiently.

The extruder screw design is show below in Figure 35. Unlike the TPU screw design, the current screw design did not incorporate reverse elements. This was done to minimize residence time to a certain extent such that gelation would not occur in the extruder. The screw had three kneading sections and a long die section to insure that there was no prepolymer buildup in the extruder.
Figure 35. 8281 prepolymer screw design consisting of three kneading sections.

**Differential Scanning Calorimetry**

DSC was performed on the prepolymer to determine the $T_g$ of various samples. DSC was conducted on a TA DSC Q200. The cooling and heating rate was set at 5°C/min with a temperature scan from -50°C to 100°C under nitrogen atmosphere. $T_g$ was read at the midpoint of the glass transition step.

**Near-Infrared Reflectance Spectroscopy Analysis**

Near-infrared reflectance spectroscopy (NIR) in transmission mode was recorded using a Thermo Scientific Nicolet 6700 FT-IR in the range of 4000-8000 cm$^{-1}$. A white light source was used in conjunction with a KBr beam splitter and a DTGS KBr detector. Samples were prepared by sandwiching prepolymer mix between glass slides with a 0.8 mm Teflon washer used as a spacer. The reaction progressed according to varying curing prescriptions in a Simplex Scientific Heating Cell where 16 scans at 4 cm$^{-1}$ resolution were acquired every 10 minutes during cure.
Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was conducted on cured samples to analyze the T\textsubscript{g}, and storage and loss modulus of samples. Samples were cured using a Thermo Scientific Lindberg Blue M Programmable Oven. The cure cycle consisted of holding at 125°C for five hours, and post curing at 200°C for two hours. DMA was conducted using a TA DMA Q800. Testing was performed in tension with a strain of 0.05%. The temperature was ramped from 30°C to 350°C at 3°C/min.

Mechanical Testing

Tensile testing procedures followed ASTM Standard D-638-10. Type IV dog bone shaped tensile specimens were cast and cured. Specimens were strained at a displacement controlled test rate of 0.05 in/min on an MTS Insight electromechanical universal test frame equipped with mechanical wedge grips. Displacement was measured by a linear variable differential transformer and load was measured using a MTS 10 kN load cell. Data were collected at a sampling rate of 10 Hz using MTS Testworks software.

4.4.3 8281 Results and Discussion

8281 Batch Reaction Analysis

DSC curves for batch samples are displayed in Figure 36. The data were vertically shifted to arrange the curves in order of reaction time. The reaction time was the time after which 44DDS dissolved in 8281. T\textsubscript{g} increased with increasing reaction time starting with a T\textsubscript{g} of 0.5°C for a reaction time of 0 minutes. The target T\textsubscript{g} was evaluated by the “tacky but not sticky” peel method. Batch aliquots
were applied on release paper to determine their tackiness. It was determined that the optimal $T_g$ was around 5°C for a reaction time of 20 minutes.

![Partial DSC plots of the batch reaction.](image)

**Figure 36.** Partial DSC plots of the batch reaction.

It is important to note the challenge in stopping a reaction after 20 minutes at the optimal prepolymer B-stage level. At 120°C, the prepolymer continued to B-stage and by an hour had advanced to a $T_g$ of 15°C. The large batches synthesized in the composites industry would be hard to cool down so quickly; thus, one can expect the prepolymer to continue to advance prior to prepregging. The continuing advancement of B-stage level leads to intra-batch and batch-to-batch variation in the prepolymer.

**8281-44DDS Extrusion Premix**

As described earlier, due to feeding limitations of the lab-scale extruder, 8281 and 44DDS had to be premixed prior to being fed into the extruder. 8281 and 44DDS were premixed at 80°C. It was hypothesized that at 80°C, 44DDS
would not completely dissolve and that the reaction would not advance significantly. Samples were tested in one-hour increments to determine the B-staging level of the prepolymer. Figure 37 shows the advancement of $T_g$ at 80°C. Even after 6 hours, the $T_g$ of the prepolymer was only -6°C. Thus, it was determined that the premix did not assist the reaction extrusion process.

Figure 37. Plot showing progression of $T_g$ of 8281-44DDS premix held at 80°C prior to reaction extrusion.

NIR also showed that there was little reaction when holding the premix at 80°C for extended periods of time. Figure 38 shows the NIR absorbance of 8281-44DDS premix held at 80°C for twelve hours. The absorption peak at 4962-5129 cm$^{-1}$, 6504-6805 cm$^{-1}$, and 4493-4568 cm$^{-1}$ corresponds to the primary amine overtone, the primary amine-secondary amine combination, and the primary amine-epoxy overlap, respectively. The peak intensities, reflecting the concentration of the corresponding functional groups decreases only slightly over
12 hours. This is in agreement with previous $T_g$ measurements, which show only a slight increase in $T_g$ over time at 80°C.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure38}
\caption{NIR of 8281-44DDS premix at initial scan and after 12 hours.}
\end{figure}

8281 Continuous Polymer Reactor DOE

A fractional factorial DOE was performed to determine the effect of extruder variables on the B-staging level of 8281 prepolymer. Table 8 shows the reaction conditions of each run. Each variable had a high and a low setting. Extruder zone temperatures were set at 100°C or 200°C, throughput at 18 g/min or 26 g/min, and screw speed at 100 rpm or 200 rpm. Figure 39 displays these results. All variables had a significant effect on the $T_g$ of the prepolymer. However, zone temperatures had the greatest effect on $T_g$. The kinetics of the epoxy-amine reaction are faster at higher temperatures; thus, the prepolymer was B-staged to a higher level with increasing barrel temperatures.
Table 8

**DOE of 8281 extrusion variables**

<table>
<thead>
<tr>
<th>Run</th>
<th>Temperature (°C)</th>
<th>Screw Speed (rpm)</th>
<th>Throughput (g/min)</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>100</td>
<td>26</td>
<td>-4.42</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>200</td>
<td>18</td>
<td>-5.59</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>100</td>
<td>18</td>
<td>-0.16</td>
</tr>
<tr>
<td>4</td>
<td>200</td>
<td>200</td>
<td>26</td>
<td>1.88</td>
</tr>
</tbody>
</table>

![Bar chart showing variable coefficients of 8281 DOE.

Figure 39. Variable coefficients of 8281 DOE.]

8281 Continuous Polymer Reactor Design Analysis

Prepolymer could readily be B-staged using a continuous polymer reactor design. As determined by the DOE, extruder zone temperatures had the greatest
effect on the T<sub>g</sub> of the prepolymer. Thus, throughput and screw speed were set at 18 g/min and 150 rpm for all runs. The first zone temperature was set at 90°C, while the other four zones' temperatures were increased to B-stage the prepolymer. Table 9 details the run conditions for each of the extrusion runs.

Table 9

8281 Continuous polymer reactor trials

<table>
<thead>
<tr>
<th>Condition</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Through put (g/min)</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
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<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Screw speed (rpm)</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>Zone 1 (°C)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>Zones 2-5 (°C)</td>
<td>100</td>
<td>110</td>
<td>120</td>
<td>130</td>
<td>140</td>
<td>150</td>
<td>160</td>
<td>170</td>
<td>180</td>
<td>190</td>
<td>200</td>
<td>210</td>
<td>220</td>
<td>230</td>
</tr>
<tr>
<td>Tg (°C)</td>
<td>-8.68</td>
<td>-7.94</td>
<td>-1.38</td>
<td>0.00</td>
<td>0.39</td>
<td>0.63</td>
<td>1.10</td>
<td>1.04</td>
<td>1.88</td>
<td>2.25</td>
<td>4.97</td>
<td>10.70</td>
<td>14.96</td>
<td>41.46</td>
</tr>
</tbody>
</table>

DSC Analysis of Extruded 8281 Prepolymer

DSC analysis showed that T<sub>g</sub> of the prepolymer and the B-stage level could be significantly increased using the extruder. Partial DSC plots of 8281 prepolymer are show in Figure 40. The vertical scale has been adjusted to order the plots by increasing time. T<sub>g</sub> increased from -9°C at 100°C barrel temperatures to over 40°C at 230°C barrel temperatures. 8281 even reached its gel point at temperatures above 230°C, and seized up the screws within the barrel. 44DDS dissolved into 8281 at 110°C. The optimal T<sub>g</sub> of the prepolymer as determined through the “tacky but not sticky” peel method, 5°C, was obtained via a barrel temperature of 200°C.
Figure 40. Partial DSC plots 8281 prepolymer extrudate at various extruder barrel temperatures.

DMA of Cured 8281 Prepolymer

DMA was performed on cured 8281 prepolymer. Both batch and extrusion prepolymer were obtained from conditions when 44DDS dissolved into 8281, and from conditions that resulted in an optimally B-staged prepolymer (T_g = -5°C). Batch prepolymer was obtained when 44DDS dissolved into 8281 at 120°C and also after 25 minutes of B-staging. Extrusion prepolymer was obtained at 110°C when 44DDS dissolved into 8281 and also at 200°C. The DMA curves of the cured samples are show in Figure 41. All samples exhibited similar cured T_g values between 203°C and 208°C. Further, the tan delta curves were similar, while extruder prepolymer samples had a slightly higher storage modulus.
Figure 41. DMA of cured 8281 prepolymer.

Mechanical Testing of Cured 8281 Prepolymer

Mechanical testing was also conducted to compare the properties of fully cured 8281 prepolymer from the batch method and continuous polymer reactor method. The results are shown in Table 10. Both sets of cured samples exhibited similar modulus, peak stress, and strain at break. The resultant tensile properties were thus unaffected by the method used to make prepolymer.

Table 10

Mechanical testing of 8281

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tensile Modulus (MPa)</th>
<th>Peak Stress (MPa)</th>
<th>Strain at Break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch Reactor</td>
<td>2992 ± 111</td>
<td>74 ± 9</td>
<td>4.6 ± 1.0</td>
</tr>
<tr>
<td>Continuous Reactor</td>
<td>3018 ± 5</td>
<td>72 ± 10</td>
<td>4.5 ± 1.3</td>
</tr>
</tbody>
</table>
**8281 Discussion**

To establish the proper level of B-staging, batch 8281 prepolymer was first synthesized. Using the “tacky but not sticky” peel method, it was established that 8281 prepolymer had to be reacted at 120°C for 20 minutes in order to reach the optimal B-stage level.

Reaction extrusion of 8281 prepolymer was challenging. Because of the limitations of the reactor design, 8281 and 44DDS had to be premixed. However, the premix had little to no advancement in B-stage level because it was kept at 80°C. A DOE showed that extruder zone temperatures had the greatest effect on B-staging level ($T_g$). Thus, extruder barrel temperature was increased to B-stage the prepolymer. 44DDS dissolved into 8281 at 110°C, and reached optimal B-stage level at 200°C.

The optimal B-stage level was identified as a prepolymer having a $T_g$ of 5°C. DMA analysis showed that regardless of the extent of cure, cured 8281 samples exhibited similar cured $T_g$s between 203-208°C. They also exhibited similar storage and loss modulus. Mechanical testing revealed that resultant tensile properties were unaffected by the method used to synthesize prepolymers. 8281 prepolymer was successfully processed using a continuous polymer reactor design. The next section will discuss the use of an industrial size extruder to obtain 5208 prepolymer.
4.5 Continuous Polymer Reactor Design of 5208

4.5.1 5208

5208 consists of three components: 44DDS, N, N, N’, N’-tetraglycidyl-4, 4’-diaminodiphenylmethane (TGDDM), and 4-[2-(4-hydroxyphenyl) propan-2-yl] phenol (SU-8). Shown below in Figure 42 are the chemical structures of 44DDS, TGDDM, and SU-8. TGDDM and 44DDS form the foundation of many commercial products. 13 5208 prepolymer is usually combined with T300 fiber, which is an intermediate modulus and intermediate strain-to-failure carbon fiber. This prepreg system has been used in many high performance applications. Boeing, Douglas Aircraft Company, and Lockheed all participated in a National Aeronautics and Space Administration (NASA) Aircraft Energy Efficiency Program in the 1970s, which was geared towards designing and building the first composite components for a commercial transport aircraft. The common thread was the use of T300/5208. Through the program, smaller components were first produced, such as Lockheed L-1011 fairing panels, Boeing B-737 spoilers, and Douglas DC-10 aft pylon skins and upper aft rudders. Larger components were then manufactured, such as the Boeing B-727 elevator, Boeing B-737 horizontal stabilizer, Douglas DC-10 vertical stabilizer, and Lockheed L-1011 aileron. T300/5208 has since then been used to manufacture primary and secondary structures, and control surfaces for many commercial transport aircraft. It also serves as the material for some of the primary structures of the B-2 stealth bomber. 14
4.5.2 Experimental

Materials

The following materials were used as received: 4,4'-diaminodphenylsulfone (44DDS, Royce Chemical Corp., MW = 248.28 g/mol, Amine Equivalent Weight = 62.07), N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM/MY721, Huntsman, MW = 444-468 g/mol, Epoxide Equivalent Weight = 111-117), and 4-[2-(4-hydroxyphenyl)propan-2-yl]phenol (SU-8, Momentive, MW = 1736 g/mol, Epoxide Equivalent Weight = 217).

Figure 42. Structures of (a) 44DDS, (b) TGDDM, and (c) SU-8.
5208

The formulation of 5208 consists of 20.9 wt % 44DDS, 65.9 wt % TGDDM, and 13.2 wt % SU-8.\textsuperscript{9,10,12} SU-8 is added to improve the thermal and mechanical properties of the system. Using their respective weight percentages, this composition corresponds to an amine-epoxy ratio of approximately 0.60.\textsuperscript{13}

**Batch Reaction Synthesis of 5208**

Batch reaction was performed to determine reaction kinetics and appropriate curing levels of 5208 prepolymer. TGDDM and SU-8 were heated and stirred in an 85°C oil bath. Vacuum was applied to evacuate any bubbles. The temperature was increased to 100°C, and 44DDS was added. The temperature was then increased 5°C every 10 minutes to 120°C. 44DDS completely dissolved into 5208 at 120°C. The prepolymer was allowed to cure at 120°C until prescribed curing conversion was reached. Aliquots of the prepolymer were taken at different curing times to determine appropriate B-staging level, $T_g$, and viscosity. The resultant prepolymer was also cast into silicone molds and cured for mechanical analysis.

**Continuous Polymer Reactor Design of 5208**

5208 prepolymer was produced using a Coperion ZSK 26mm MEGA compounder with a 36:1 L/D ratio. This extruder was an industrial scale extruder with higher modularity than the Prism TSE-16-TC extruder. The twin screw extruder had intermeshing co-rotating screws with 10 barrel zones. The general setup of the continuous reactor is shown in Figure 43. TGDDM and SU-8 were
preheated at 85°C in a 10L reactor and stirred using a variable speed 1/5 HP Lightnin Mixer. The two epoxies could be mixed together as no reaction would take place because there was no amine in the reactor. The unreacted epoxies were pumped into an injection port in Zone 1 of the extruder using a Zenith B-9000 Size D Chemical Gear Pump equipped with a Proline Promass 83A Flow Meter.

**Figure 43.** Continuous polymer reactor design for 5208.

Unlike the Prism TSE-16-TC extruder, the ZSK was able to feed 44DDS separately. 44DDS was metered using an Accurate ProFlex C-500 Gravimetric Feeder. The feeder fed 44DDS into the hopper of a ZSB-25mm Side Stuffer, which conveyed 44DDS into the side of a Zone 2 combi-barrel.

A Nash-Elmo Industries GmbH 2BL2061-1AH50-4A Vacuum Pump was used to apply vacuum at Zone 9 to remove any moisture from the prepolymer. A Zenith PEP II Size D Chemical Gear Pump was used to meter the prepolymer melt through the die and to form a melt seal to pull vacuum. The curing level of
the prepolymer was controlled using key extrusion parameters such as screw configuration, barrel temperature, screw speed, and throughput. As before, aliquots of prepolymer were taken at the end of the extruder and the resultant prepolymer was cast into silicone molds for analysis.

The screw configuration is shown in Figure 44. Forward feeding screws were used to transport the epoxy premix and 44DDS away from the feed zone. A kneading section with a reverse element was used to mix the prepolymer, and to create an area of high shear and pressure. Two additional kneading sections were added to ensure that the reaction was advancing, and that the prepolymer was B-staging. Intermediary forward feeding screws were used to guarantee that the prepolymer would not stagnate, degrade, or gel. In the last kneading zone, a reverse element was used to increase the residence time, and to create a melt seal to pull vacuum and to allow material to flow smoothly through the die.

Figure 44. 5208 prepolymer screw design consisting of three kneading sections.

Experimental Analyses of 5208

Numerous analytical techniques were used to analyze the prepolymer, and cured 5208. DSC, DMA, NIR, and mechanical testing were performed as described earlier in this chapter.
Curing Procedure for 5208

A Thermo Scientific Lindberg Blue M Programmable Oven was used for curing 5208 prepolymer. The cure cycle consisted of holding at 125°C for 5 hours, and post curing at 225°C for 2 hours.

Viscosity of 5208

The viscosity was measured using a Brookfield CAP2000 HT viscometer with a #6 spindle at 85°C and 200 rpm (667 s⁻¹ shear rate). Viscosity measurements were performed on batch and extrusion 5208 prepolymer.

4.5.3 5208 Results and Discussion

5208 Batch Reaction Analysis

Batch reaction of 5208 was performed to determine reaction kinetics and appropriate cure levels of 5208 prepolymer for prepreg use. When the prepolymer starts to cure, the $T_g$ increases as a function of curing conversion. As previously described, in order to determine and quantitatively describe the optimal cure levels of 5208 prepolymer, the $T_g$ was measured by DSC. Shown below in Figure 44 is a plot of $T_g$ as a function of curing time for 5208 prepolymer B-staged in a batch at 120°C. Based on our experience of prepreg manufacturing and using the “tacky but not sticky” peel method, it was determined that 5208 prepolymer reached its optimal processing level at one hour, equivalent to a $T_g$ of 3.40°C. Thus, after one hour of B-staging at 120°C, the prepolymer has good tackiness, viscosity, and processability. After about 6 hours, the resin lost its processability due to the high viscosity of the system and lack of tackiness ($T_g =$
13.31°C). Further, 5208 prepolymer reached its gel point after 9 hours at which point the $T_g$ was 24.9°C. This leads to the conclusion that the processing window of 5208 prepolymer is no more than 6 hours at 120°C with the optimal B-staged prepolymer synthesized after one hour. The $T_g$ of epoxy prepolymer should be maintained between 3.40°C and 13.31°C.

![Graph showing glass transition temperature as a function of reaction time](image)

**Figure 45.** Plot of $T_g$ as function of curing time for 5208 in batch.

NIR was also used to track the reaction in real-time through monitoring the changes in concentration of the functional groups. Figure 45 shows the NIR spectra of a simulated 5208 prepolymer in a batch reaction. The absorption peaks at 4962-5129 cm$^{-1}$, 6504-6805 cm$^{-1}$, and 4493-4568 cm$^{-1}$ correspond to the primary amine overtone, the primary amine-secondary amine combination,
and the primary amine-epoxy overlap, respectively. The peak intensity, reflecting the concentration of corresponding functional group decreases with increasing curing time. The primary amine peak at 4962-5129 cm\(^{-1}\) almost disappears after 9 hours when the reaction starts to gel. This is in agreement with previous \(T_g\) measurements.

![NIR of a simulated 5208 prepolymer batch reaction](image)

**Figure 46.** NIR of a simulated 5208 prepolymer batch reaction.

5208 Continuous Polymer Reactor Design Analysis

By studying the properties of epoxy prepolymer at varying curing levels, the reaction time for the target 5208 prepolymer was between 1 to 6 hours at 120°C. However, in a continuous polymer reactor, the reaction/residence time is usually around 1 to 5 minutes. In order to accelerate this reaction in a continuous
reactor with this technical limitation, the reaction temperature must be increased to accelerate cure kinetics. The throughput was kept constant at 5.74 kg/hr. Extruder screw speed was set at 200 rpm. Figure 46 shows the $T_g$ of 5208 prepolymers that were produced at different extruder processing temperatures. When operating at 150°C, the extruded samples formed a transparent solution indicating that 44DDS fully dissolved into epoxy. The $T_g$ of the prepolymer was 4.96°C at this point, which implies that a desired curing conversion was obtained. To determine the upper processing temperature limit, extruder temperatures were adjusted accordingly to increase prepolymer curing level. At 220°C, the $T_g$ was 7.95°C. For processing temperatures greater than 220°C, a large increase in viscosity was observed leading to inadequate transport in the extruder. The prepolymer residual time was too long and gelation was observed.
Figure 47. Plot of Tg as a function of barrel temperature for 5208 in continuous reactor.

5208 Continuous Polymer Reactor DOE

A DOE was performed to study the effect of critical processing conditions on prepolymer $T_g$. Shown in Table 11 is the setup of the DOE and the resultant $T_g$s. Statistical analysis showed that barrel temperature was the most crucial factor that affected the $T_g$ of 5208 prepolymer. Screw speed, throughput, and the interaction between variables had no effect on the $T_g$ of extruded prepolymer. In batch reactors, once the amine was solubilized, the prepolymer could react for a given amount of time. However, in an extruder, reaction time is restricted by the residence time (time it takes for polymer melt to pass through the extruder), which in turn is determined by the processing parameters. The residence time
only changed slightly at different throughputs and screw speeds used in this DOE (several seconds). Since residence time was so short, it was hypothesized that the prepolymer $T_g$ and B-stage level could only be efficiently affected by barrel temperature.

Table 11

**DOE of 5208 extruder processing conditions**

<table>
<thead>
<tr>
<th>DOE #</th>
<th>Screw Speed (rpm)</th>
<th>Throughput (kg/hr)</th>
<th>Barrel T ($^\circ$C)</th>
<th>$T_g$ ($^\circ$C)</th>
<th>Factor Name</th>
<th>Coeff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200</td>
<td>5.74</td>
<td>150</td>
<td>4.4</td>
<td>Const.</td>
<td>5.87</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
<td>5.74</td>
<td>220</td>
<td>7.3</td>
<td>A Screw Speed</td>
<td>-0.02</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>8.61</td>
<td>150</td>
<td>4.1</td>
<td>B Throughput</td>
<td>-0.13</td>
</tr>
<tr>
<td>4</td>
<td>200</td>
<td>8.61</td>
<td>220</td>
<td>7.8</td>
<td>C Barrel T</td>
<td>1.84</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>5.74</td>
<td>150</td>
<td>4.0</td>
<td>AB Interaction</td>
<td>-0.18</td>
</tr>
<tr>
<td>6</td>
<td>300</td>
<td>5.74</td>
<td>220</td>
<td>8.3</td>
<td>AC Interaction</td>
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<td>8.61</td>
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<td>300</td>
<td>8.61</td>
<td>220</td>
<td>7.5</td>
<td>ABC Interaction</td>
<td>-0.13</td>
</tr>
</tbody>
</table>

**5208 Viscosity**

The viscosities of prepolymer samples from batch and reaction extrusion were analyzed. The results are displayed in Figure 47. 5208 prepolymer extruded at varying temperatures is shown on the left axis and 5208 prepolymer from batch reaction at different times at 120°C is show on the right axis. The viscosity is shown on the x-axis. Although the optimal $T_g$ was achieved with the continuous
polymer reactor, the viscosities of the extruded prepolymer were much lower than that of batch prepolymer. From previous experience with prepregging, once prepolymer reaches a viscosity of 100 cP it can be readily prepregged. Thus, even though extruded prepolymer did not obtain as high a viscosity as batch prepolymer, it still met the minimum viscosity criteria for prepregging.

Figure 48. Viscosity (cP) of extrusion and batch 5208 prepolymer.

DMA was used to compare cured prepolymer prepared by the batch reactor and the continuous reactor. The results are shown in Figure 48. As expected, the $T_g$ of optimally B-staged and then fully cured samples was around 265°C. However, the storage modulus of 5208 extruded prepolymer was slightly higher than batch prepolymer at low temperatures. The results of DMA proved
that the properties of 5208 prepolymer produced by the two methods are almost identical.

![Plot of storage modulus and loss modulus of cured 5208 prepolymer.](image)

**Figure 49.** Plot of storage modulus and loss modulus of cured 5208 prepolymer.

**5208 MTS**

**Mechanical Testing of Cured 5208 Prepolymer**

Mechanical testing was also conducted to compare the properties of fully cured 5208 prepolymer from the batch method and continuous polymer reactor method. The results are shown in Table 12. Tensile modulus was about 8% higher for batch prepolymer. However, cured extruded prepolymer exhibited similar peak stress, and elongation at break as cured batch prepolymer.
Table 12

Mechanical testing of 5208

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tensile Modulus (MPa)</th>
<th>Peak Stress (MPa)</th>
<th>Strain at Break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch Reactor</td>
<td>1662 ± 49</td>
<td>72 ± 17</td>
<td>5.7 ± 1.9</td>
</tr>
<tr>
<td>Continuous Reactor</td>
<td>1542 ± 5</td>
<td>71 ± 18</td>
<td>5.8 ± 2.0</td>
</tr>
</tbody>
</table>

5208 Discussion

To establish the proper level of B-staging, batch 5208 prepolymer was first synthesized. Using the “tacky but not sticky” peel method, it was established that 5208 prepolymer had to be reacted at 120°C for one hour in order to reach the optimal B-stage level.

Reaction extrusion of 5208 prepolymer was accomplished with separate epoxy and amine feeds. This was more desirable as there was no prepolymer reaction prior to extrusion. A DOE showed that only extruder zone temperatures had an effect on B-staging level ($T_g$). 44DDS dissolved into 5208 at 150°C, which also resulted in the optimal B-stage level prepolymer.

The optimal B-staged 5208 prepolymer had a $T_g$ of 5°C and a viscosity above 100 cP. DMA analysis showed that regardless of the extent of cure, cured 5208 samples exhibited similar cured $T_g$ of approximately 265°C. They also exhibited similar storage and loss modulus.
4.6 Conclusion

Continuous polymer reactors provide increased reaction control, improved reproducibility, and good safety compared to conventional batch processes. The continuous polymer reactor designs in this study were able to successfully synthesize optimal 8281 and 5208 prepolymer. We envision the use of continuous polymer reactors integrated directly onto prepreg film lines, which can substantially reduce the energy used in the manufacture of these materials. Intra-batch and batch-to-batch variation could be reduced leading to uniform prepreg with controlled handling, storage, and mechanical life. New epoxy-amine prepolymer could also be prepared otherwise limited by the batch reaction process.
REFERENCES


CHAPTER V
RECOMMENDED FUTURE WORK

The work presented in this dissertation has demonstrated that continuous polymer reactor designs can be successfully used to produce TPUs and prepolymers. The modularity of twin screw extruders provides the framework for performing a multitude of chemical reactions in an extruder. Future work can further advance the understanding of these systems and polymers.

The high renewable content TPUs that were produced in this research consisted of Cerenol based TPUs. Even higher renewable content TPUs could be synthesized using Susterra as the hard-block diol. Susterra is the raw material that is polymerized to form Cerenol. Hard-block content and the MW of the soft-block were varied to produce 70A, 85A, and 50D hardness TPUs. Developing a better curve for estimating hardness can prove useful for manufacturing TPUs with a specific hardness. Further, because of the size and the length of the extruder, a high catalyst level was used to advance the reaction. Catalysts are expensive, toxic, and lower thermo-mechanical properties; thus, lowering the catalyst level can provide improved TPUs.

8281 and 5208 were successfully B-staged to optimized levels using continuous polymer reactor designs. Further evaluation on other high performance prepolymer, such as 3900, would be of great value. 3900 is a highly toughened prepolymer used in many commercial primary structures. The work by Cheng et. al, which followed the work in this dissertation, has already proven that thermoplastic tougheners can be readily incorporated into
prepolymers using continuous polymer reactor design.\textsuperscript{1} Further work could focus on separately feeding 8281 and 44DDS into the extruder. Due to feeding limitations of the lab-scale extruder, 8281 and 44DDS had to be premixed together. The DOEs on prepolymers highlighted that barrel temperature had the most significant effect on the B-staging level of prepolymers; thus, temperature was increased to obtain the desired B-stage level. The issue that arises from this is that the prepolymer melt is too hot to be directly employed onto a prepreg line. Consequently, an additional cool-down step is necessary to yield a functional prepolymer.

A Prism TSE16-TC extruder was used to manufacture TPUs and 8281. Although efficient, this extruder is a lab-scale extruder so care must be taken when scaling-up to a larger extruder. There are many theories and methods that can be applied when scaling-up, but optimizing the process will require additional work and prior knowledge should only be used as a starting point. The work presented in this dissertation can be of benefit in the manufacturing of renewable sourced TPUs, and prepolymers.
REFERENCES