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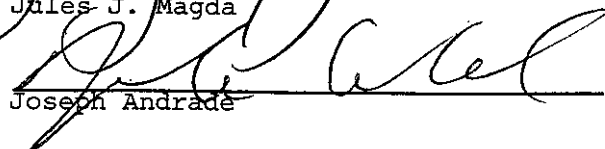
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RELATIONSHIPS BETWEEN THE MECHANICAL  
PROPERTIES OF THERMOPLASTIC  
POLYURETHANE ELASTOMERS  
AND THE STRUCTURE OF THE  
DIISOCYANATE UNIT

by

George R. Wallace, III

A thesis submitted to the faculty of  
The University of Utah  
In partial fulfillment of the requirements for the degree of

Master of Science

Department of Chemical and Fuels Engineering

The University of Utah

June 1998

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**SUPERVISORY COMMITTEE APPROVAL**

of a thesis submitted by

George R. Wallace, III

This thesis has been read by each member of the following supervisory committee  
and by majority vote has been found to be satisfactory.

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## FINAL READING APPROVAL

To the Graduate Council of the University of Utah:

I have read the thesis of George R. Wallace, III in its final form and have found that (1) its format, citations and bibliographic style are consistent and acceptable; (2) its illustrative materials including Figures, tables, and charts are in place; and (3) the final manuscript is satisfactory to the supervisory committee and is ready for submission to The Graduate School.

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## ABSTRACT

Structure versus property relations were investigated in several thermoplastic polyurethanes. Specifically, samples in the hardness range of 92-95 Shore A were prepared through polymerization of p-phenylenediisocyanate (PPDI), 3,3'-dimethyl-4,4'-diphenyldiisocyanate (TODI), or diphenylmethane-4,4'-diisocyanate (MDI) with 1,4-butanediol and a 2000 molecular weight polycaprolactone polyol to explore relationships between the mechanical properties of thermoplastic polyurethane elastomers and the structure of the diisocyanate unit. The three thermoplastic polyurethane elastomers (TPUs) possessed mechanical and dielectric properties that differed significantly from one another. In general, the elastomer containing the diisocyanate with the fewest degrees of freedom and the least steric hindrance possessed superior mechanical properties. In conjunction with this, a relationship was found to exist between the diisocyanate unit and the molar ratio of diisocyanate to polyol required in synthesizing a TPU of the target hardness. This relationship reflects the inter-chain proximity of the diisocyanate units within the hard segment domain that is governed not only by steric factors but also by the degrees of rotational freedom of the diisocyanate unit.

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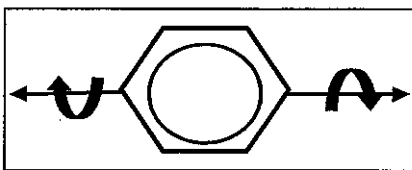
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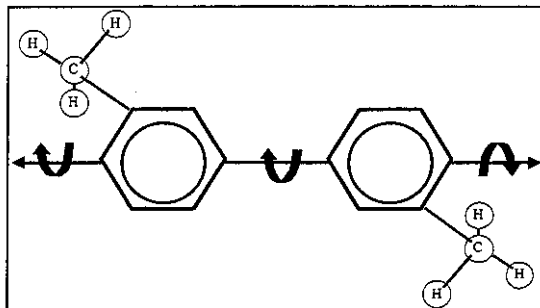
## CHAPTER 1

### INTRODUCTION

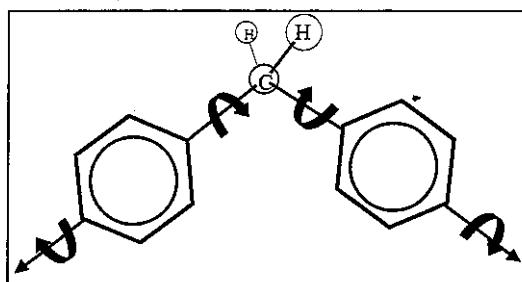
Thermoplastic polyurethanes (TPUs) have achieved an important place in elastomer technology. This is by virtue of the fact that such elastomers combine desirable mechanical properties with the ability to be reversibly melted and thus processed by conventional plastics thermoforming techniques. Because of the wide variety of chemical structures available for use in TPUs, it is important to achieve some understanding of how these structures affect the end-use properties. In the present work, a structure versus property study is carried out that involves several TPUs. Specifically, samples in the hardness range of 92-95 Shore A were prepared through polymerization of p-phenylenediisocyanate (PPDI) (Figure 1), 3,3'-dimethyl-4,4'-diphenyldiisocyanate (TODI) (Figure 2), or diphenylmethane-4,4'-diisocyanate (MDI) (Figure 3) with 1,4-butanediol and a 2000 molecular weight polycaprolactone polyol



**Figure 1. PPDI Two Degrees of Rotational Freedom**



**Figure 2. TODI Steric Groups and Three Degrees of Rotational Freedom**



**Figure 3. MDI Steric Groups and Four Degrees of Rotational Freedom**

to explore relationships between the mechanical properties of thermoplastic polyurethane elastomers and the structure of their diisocyanate unit. The work that follows shows a dependence upon and correlation between the measured stress-strain properties, dynamic relaxation spectra, and dielectric relaxation spectra of the TPU and the diisocyanate employed in its manufacture. In general, the elastomer containing the diisocyanate with the fewest degrees of conformational freedom and the least steric hindrance will possess superior properties.

In conjunction with this, a relationship will be shown to exist between the diisocyanate unit and the molar ratio of diisocyanate to polyol required in synthesizing a TPU of the target hardness. This relationship will be shown to reflect the inter-chain

proximity of the diisocyanate units within the hard segment domain, which is governed not only by steric factors but also by the degrees of rotational freedom of the diisocyanate unit.

## CHAPTER 2

### BACKGROUND INFORMATION

#### 2.1 Polyurethane Chemistry

Polyurethane chemistry has been studied in detail since its discovery by Otto Bayer in 1937<sup>1</sup>. Volumes that chronicle this body of work well are those by Oertel<sup>2</sup>, Hepburn<sup>3</sup>, the series by Frisch and Reegen<sup>4</sup>, and that of Buist and Gudgeon<sup>5</sup>. The urethane reaction is a polyisocyanate polyaddition reaction, rather than an olefinic or a polycondensation reaction, which were well known at the time of the discovery of urethane chemistry. The inventors saw a myriad of uses for this new technology, and they were right. Today, urethanes are used in almost all facets of our lives, from cushioning in our chairs, padding in our shoes, insulation in our homes, and hoses in our automobiles to implants in our bodies. The applications for urethane chemistry seem endless. The particular field of urethane chemistry that is the focus of this thesis is that of thermoplastic polyurethane elastomers (TPU), or solid, nonporous, urethanes that may be shaped by heat, pressure, and time. These urethanes are produced by polymerizing at least one component from each of the three following sets of materials: long chain polyol with molecular weight of between 500 and 5000 and at least two reactive –OH groups, short chain polyol with molecular weight of between 50 and 500 and at least two reactive –OH groups, and diisocyanate with at least two

reactive  $-NCO$  groups. The properties of the finished TPU are, of course, impacted both by the ratio of one component to the next, as well as by the choice of components. The particular focus of this thesis is TPUs that are used in the manufacture of hydraulic and pneumatic seals. As will be discussed below, many researchers have examined the influence of varying ratios and differing monomers has on the properties of the finished TPU.

### 2.1.1 Polyols

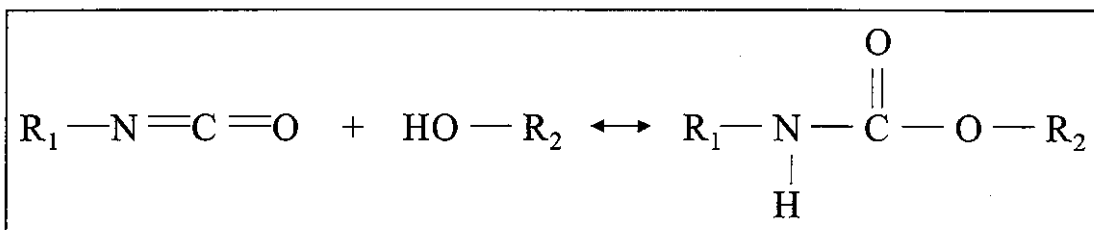
Polyols used in TPU polymerization are generally grouped into two categories, polyethers and polyesters. Polyethers are also called polyalkylene glycols or polyalkylene oxides. Polyethers contain the  $-O-CH_2-$  group as the repeat unit in the chain. Their use in thermoplastic urethanes is typically limited to polyethers that are linear and difunctional. Branching or trifunctionality leads to covalent cross-linking, which is not reversible at moderate heats, and thus to a thermoset resin. Polyethers impart good hydrolysis resistance to urethanes, as well as good resistance to acids and bases. However, urethanes based on polyether chemistry tend to swell when exposed to mineral oils such as hydraulic fluid. Accordingly, the TPUs examined in this thesis were based on polyester chemistry, which yields TPUs that do not swell significantly when exposed to mineral oils. Polyesters contain the  $-O-CO-$  group as the repeat unit in their chain. The particular polyol of interest in this work is polycaprolactone. Polycaprolactone is made by the polymerization of  $\epsilon$ -caprolactone in the presence of a glycol initiator, such as ethylene glycol. TPUs based on polycaprolactone chemistry typically possess a lower glass-transition temperature

( $T_g$ ) than regular polyesters, as well as better hydrolysis resistance, with only minor sacrifices to compatibility with mineral oils.

### 2.1.2 Chain Extenders

Chain extenders or crosslinkers are low molecular weight, multifunctional compounds that react with the  $-NCO$  groups of diisocyanates. Chain extenders are categorized as either alcohols or amines. Amines contain the reactive  $-NH$  group, which, upon reaction with the  $-NCO$  group, yields a urea. Polyureas are typically thermoset polymers; however, in some cases, the combination of an aliphatic diisocyanate with a hindered aliphatic amine will yield a melt processable polyurea. This work focuses on polyurethanes produced through the reaction of short chain alcohols and polycaprolactones with diisocyanates. Alcohols contain the reactive  $-OH$  group, which, upon reaction with the  $-NCO$  group, yields a urethane group (Figure 4).

The chain extender used to produce the TPUs studied in this thesis is 1,4-butanediol (1,4-BD or BDO). Other chain extenders commonly used in the industry are ethylene glycol, 1,6-hexanediol, bis- (hydroxyethyl) hydroquinone (HQEE), 1,4-cyclohexanedimethanol (CHDM), glycerol, 1,3-propanediol, and trimethylol propane



**Figure 4. The Urethane Reaction**

(TMP). The effect of varying the chain extender on the final properties of the TPU is well documented in the literature<sup>6,7</sup>.

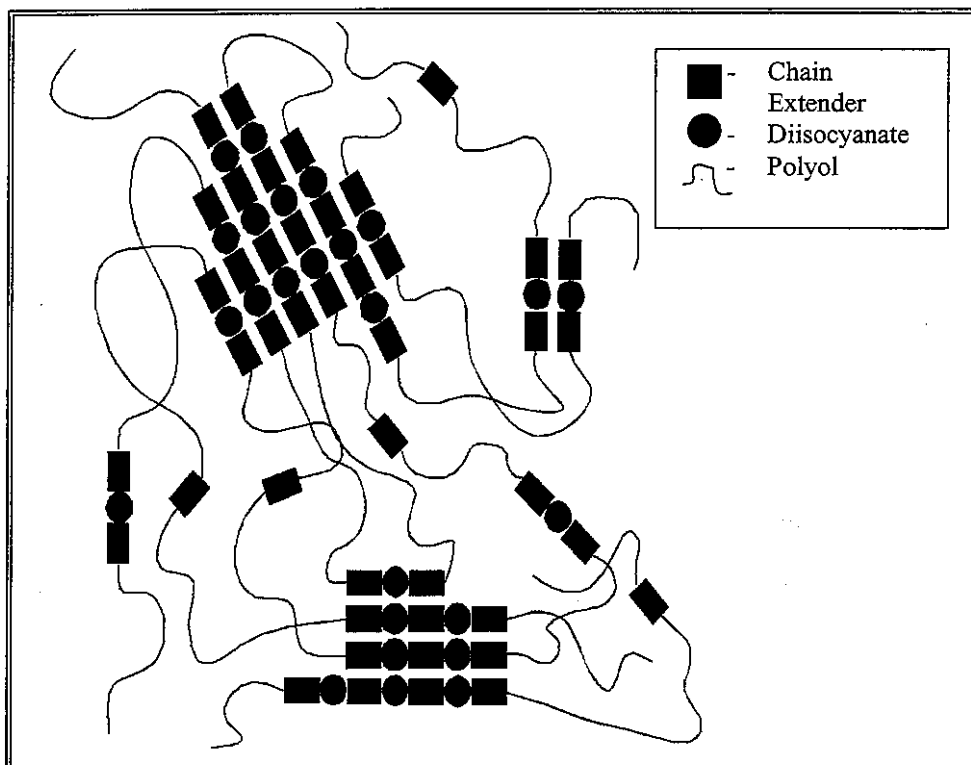
### 2.1.3. Diisocyanates

The extremely reactive  $-NCO$  group of the diisocyanate is the basis of polyurethane chemistry. Diisocyanates are typically produced through phosgenation of the corresponding diamine. Alternate routes to diisocyanate include modified Hoffmann degradation and alkylation of alkali cyanates. Diisocyanates are typically grouped by aromaticity; thus, there are aromatic diisocyanates and aliphatic diisocyanates. Typically, the aliphatic diisocyanates are used in the coatings industry for their superior ultraviolet resistance. The elastomer industry typically uses the aromatic diisocyanates due to the superior properties they lend to polyurethanes. The most widely used aromatic diisocyanate is diphenylmethane-4,4'-diisocyanate (MDI) (Figure 3), followed by Toluene diisocyanate (TDI) which is commonly used as a mixture of the 2,4 and 2,6-isomers. 1,5-Naphthalene diisocyanate (NDI) is commonly used in high performance elastomers. TDI and NDI both yield thermoset polyurethanes and thus were not studied in this work. The two remaining aromatic diisocyanates are *para*-phenylenediisocyanate (PPDI) (Figure 1) and 3,3'-dimethyl-4,4'-diphenyldiisocyanate (TODI) (Figure 2). One other diisocyanate of interest is Trans-cyclohexane 1,4-diisocyanate (CHDI). CHDI is a cyclic rather than aromatic diisocyanate. Although CHDI does impart superior properties to TPUs<sup>8</sup>, it is not commercially available at this time and was not studied. TODI is not commonly cited in the literature<sup>9</sup>, as it has been used entirely by its manufacturer for many years. The

Disogrin elastomers of the Freudenberg-NOK conglomerate are based on TODI in combination with various polyols and chain extenders. PPDI has been known since 1913<sup>10</sup> and the literature contains many documented studies of this monomer in thermoplastic and thermoset polyurethanes<sup>11</sup>.

#### 2.1.4 Morphology

The morphology of polyurethanes is widely discussed in the literature<sup>2-5</sup>. The commonly accepted view of polyurethane morphology is that depicted in Figure 5, wherein the polyurethane consists of discrete hard and soft domains.



**Figure 5. Thermoplastic Urethane Elastomer Chain Organization**

The hard domains or segments consist of the chain extender and diisocyanate monomers and give the polyurethane its elastomeric properties. In Voight or Maxwell<sup>12,13</sup> models, the hard domains correlate to the spring, whereas the soft domains correlate to the dashpot. The soft domains consist of the long chain polyols and give the elastomer its flexibility and plastic properties. The hard domains are thought to phase separate from the soft domains through hydrogen bonding. Kazmierczak et al<sup>14,15</sup> have studied the morphology of PPDI-based TPUs in detail using differential scanning calorimetry (DSC), Small-angle x-ray scattering (SAXS), wide-angle x-ray scattering (WAXS), dynamic mechanical analysis (DMA), and electron microscopy. Spathis et al.<sup>16</sup> examined the effect of varying the NCO/OH ratio on polyurethane morphology. Vallance and Cooper<sup>17</sup> measured polarization to study polyurethane morphology. Christenson et al<sup>18</sup> correlated physical properties of urethanes to morphology. Tingey<sup>19</sup> studied interfacial properties of polyurethanes in biomedical applications. All of these authors have concluded that the morphology of the urethane polymer has a dramatic impact its physical properties.

## 2.2 Dynamic Mechanical Thermal Analysis (DMTA)

One method of evaluating a polymer's dynamic characteristics is to impose a cyclic strain upon a sample and measure the stress required to impose such a strain across a large temperature range. This is discussed in detail by Ferry<sup>20</sup> and McCrum<sup>21</sup>. In the case of Figure 6, stress was applied to polymer samples across temperatures ranging from  $-150^{\circ}\text{C}$  to  $190^{\circ}\text{C}$ . The stress, which is known as a dynamic modulus,  $G^*(\omega)$  (Shear) or  $E^*(\omega)$  (Tensile), was measured and some of its components were

plotted against temperature. The two governing equations, in which G may be substituted for E, are:

$$E^* = E' + i E''$$

$$\tan \delta = E'' / E'$$

Significant features of a shear or tensile modulus plot (Figure 6) include the location of low temperature downturn, which is associated with the glass transition temperature of the polymer. The location on the temperature axis of the high temperature downturn is associated with softening of the hard segment domains. The magnitude of the modulus is associated with the 'stiffness' of the material. The width

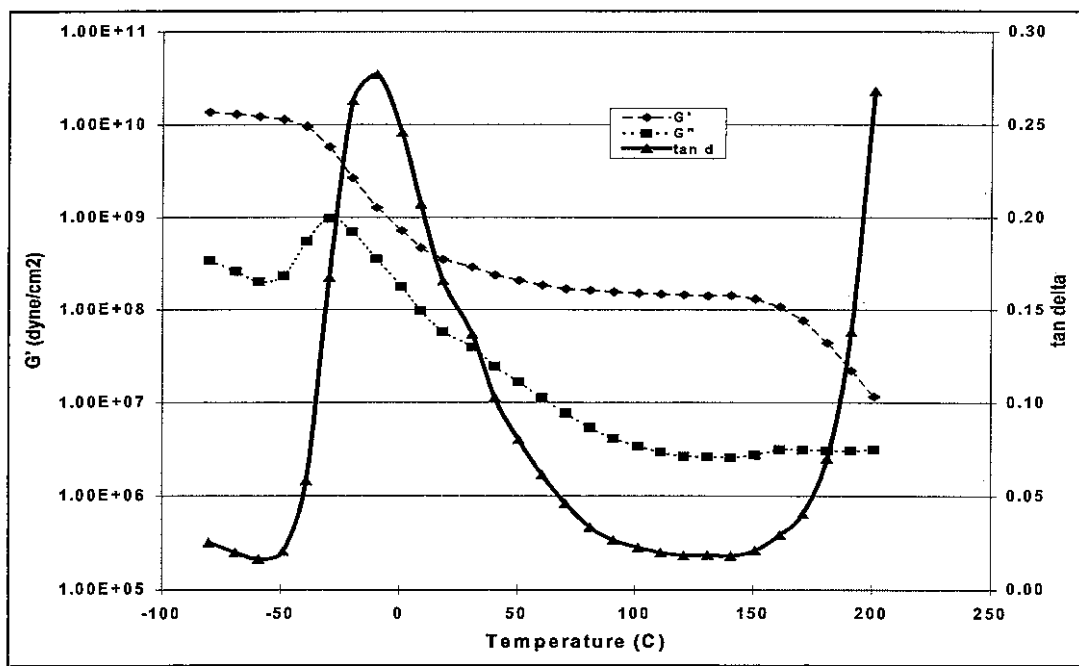


Figure 6. Mechanical Loss Factors and Shear Moduli vs. Temperature at 1 Hz

of the constant modulus plateau demonstrates over what temperature range the polymer maintains a constant modulus.

When a polymer is stressed, two different things happen to the force imposed on the sample. Some of the force is stored in the sample and may be converted directly back into force. The rest of the force is converted into heat and is either slowly dissipated to the environment or felt as a temperature increase in the polymer. For example, upon stretching a rubber band, some of the force supplied to stretch the rubber band is stored as tension and some of the force is converted to heat. The stored energy is responsible for making the rubber band snap back to its original shape, whereas the energy converted to heat is responsible for raising the temperature of the rubber band.

With this analogy, the storage modulus,  $G'(\omega)$  or  $E'(\omega)$ , is that portion of the dynamic modulus which is responsible for making the sample snap back to its original shape. In other words, the storage modulus is that portion of the dynamic modulus that is converted directly back into force upon removal of the applied stress. In a cyclic deformation, the work associated with the storage modulus is reversible and is equal to zero over a complete cycle.

The loss modulus,  $G''(\omega)$  or  $E''(\omega)$ , is that portion of the dynamic modulus which is responsible for converting force into heat. In a cyclic process, the work associated with the loss modulus is not reversible and does not equal zero over a complete cycle. The magnitude of the loss modulus is typically much less than that of the dynamic modulus. However, loss modulus is related to energy absorbed by the sample as heat. In a cyclic process, heat build up may be very fast if the magnitude of the loss

modulus is high. A difference of one order of magnitude in loss modulus at the application temperature is quite significant for materials in cyclic applications. Demarest and Moore<sup>22</sup> have derived a relationship between rebound resilience and loss and storage modulus.

The tangent delta,  $\tan \delta$ , of a sample is the ratio of its loss modulus to its storage modulus. This translates to a measurement of the ratio of the energy absorbed by the sample as heat to the energy used by the sample to return to its original shape. Tangent delta plots are useful in presenting information about both storage modulus and loss modulus on a single plot. Significant features of a tangent delta plot (Figure 6) include the location of the low temperature maximum, which is associated with the glass transition temperature of the polymer. Also significant is the area under the low temperature maximum, where smaller areas are associated with better separation of the hard and soft phases of a TPU sample as well as less of the hard phase being involved in the glass transition. The magnitude of tangent delta across the application temperature, which is proportional to the ratio of energy absorbed as heat by the sample to energy returned as movement of the sample. Also significant is the location of the high temperature upturn, which is associated with softening of the polymer. Very low temperature  $\gamma$  and  $\beta$  transition peaks are associated with reordering of the hard segment domains<sup>21</sup>.

### 2.3 Dielectric Thermal Analysis (DETA)

Dielectric thermal analysis (DETA or DEA) is analogous to DMTA in that an electric field is used as a stress, and charge displacement is measured as strain. This

has been shown in detail by Boyd<sup>23</sup>, McCrum et al.<sup>21</sup> and Ferry<sup>20</sup>. McCrum et al.<sup>21</sup> has demonstrated methods of measurement. Polyurethanes, being block copolymers with substantial hydrogen bonding in the hard segment phase, respond well to dielectric thermal analysis. Schönhals and Schlosser<sup>24</sup> have attempted to fit shape parameters to polyurethane dielectric-relaxation spectra, and Murthy and Sobhanadri<sup>25</sup> have studied several polyurethane elastomers using electrical methods. Figure 7 shows the response of TPU over varying temperatures and frequencies.

In DETA, the permittivity,  $\epsilon'$ , represents the amount of alignment of the dipoles to an electric field.  $\epsilon'$  is low for polymers at low temperatures and highly cross-linked polymers because the molecules are frozen in place and the dipoles are not able to

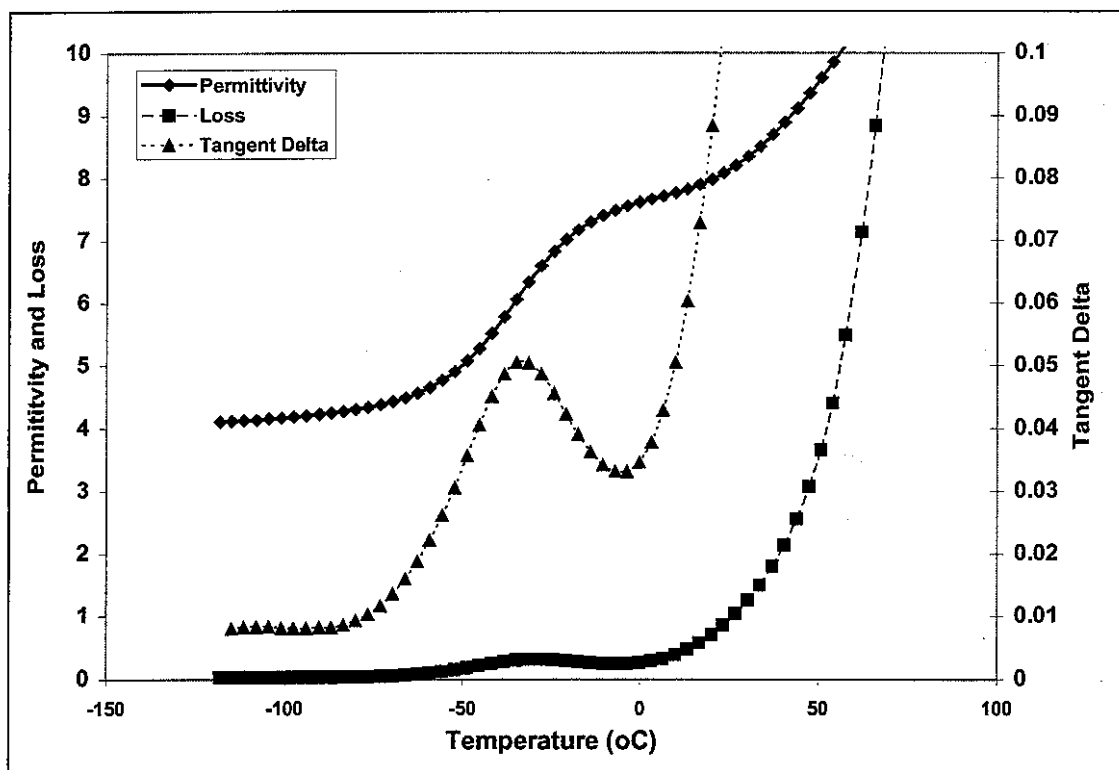


Figure 7. DEA Curve for TPU at 1 Hz

move and align themselves with the electric field. The loss factor,  $\epsilon''$ , measures the amount of energy required to align the dipoles in the polymer chain. As with DMTA, the dielectric tangent delta,  $\tan \delta_\epsilon$ , is the ratio of  $\epsilon''$  to  $\epsilon'$ .

## CHAPTER 3

### EXPERIMENTAL

#### 3.1 Polymerization Details

Thermoplastic polyurethanes were formulated using 2000 molecular weight polycaprolactone and 1,4-butanediol with MDI, TODI, and PPDI to yield samples ranging from 93 to 95 Shore-A hardness. I employed an iterative procedure to generate the batches that were studied in this work; thus several batches were produced prior to the batches that exhibited the desired hardnesses. Each sample was produced by preparing a prepolymer from reaction of flaked diisocyanate with polycaprolactone polyol preheated to 100-110°C. Upon completion of the prepolymer reaction, the polymerization was completed by chain extension with BDO. Specifics are presented in Table 1. The weight given represents the total weight of that component added to the reactor. The measurement designated as 'equivalents' is defined as the number of reactive sites on the monomer times the weight of the monomer in the sample divided by the molecular weight of the monomer. The number of equivalents of diisocyanate exceeds the number of equivalents of diol to some extent in all three cases. This is common practice in the polyurethane industry and is referred to as the 'percent theory' or 'isocyanate index' of the resultant polyurethane.

**Table 1. Formulation Data**

Compound →	MDI TPU	TODI TPU	PPDI TPU
PCL (2000 MW) Equivalents / Weight (g)	1.0 / 1000	1.0 / 1000	1.0 / 1000
1,4-butanediol Equivalents / Weight (g)	4.4 / 198	3.0 / 135	1.7 / 76.5
Diisocyanate Equivalents / Weight (g)	5.83 / 725	4.45 / 588	2.92 / 233

The excess diisocyanate reacts with moisture in the air and with itself to form a small amount of cross-linking in the polyurethane matrix.

Reacting mixtures were mixed vigorously before being cast into 1-inch slabs as they gelled. The samples were then cured for 30 minutes at 125°C. The resulting slabs were allowed to age at 25°C and 20% relative humidity for 7 days prior to granulation. The granulated samples were dried 16 hours at 190°F prior to the injection molding of test specimens. After molding, the test specimens were annealed at 125°C for 16 hours. The samples were then allowed to age at 25°C and 20% relative humidity for a minimum of 10 days prior to testing.

### 3.2 Physical Testing Details

Stress-strain values and tensile retention values at elevated temperatures were performed using an Instron environmental tensile chamber. Specimens were conditioned and tested at room temperature, 100°C, 130°C, and 150°C. Values of the moduli at 100% strain and 300% strain were also recorded throughout the testing.

Vicat softening points were determined for each compound according to ASTM method D-1525-91 using a VICAT/CSI unit with a 1-mm<sup>2</sup> needle. Failure was defined at 1-mm of penetration.

Heat deflection temperature values were measured via ASTM method D648-82/88 using CSI model HDV3 instrumentation. Samples were die cut and conditioned according to ASTM D-618. Temperature rise rates of 120 °C/hour were employed.

Dynamic test data were measured under tensile mode using Rheometrics RSA II instrumentation. Similar comparison data were generated under dynamic torsional mode using Rheometrics RVE-S equipment. The analyses were carried out by Dr. Kenneth Beardsley at Uniroyal Chemical Company.

Dielectric test data were measured using a TA-2950 Dielectric Spectrometer. The frequency range covered was 0.1 Hz to 100 kHz. The temperature range covered was -120°C to 200°C. The analyses were carried out by Dr. John Coburn at DuPont Chemical Company.

## CHAPTER 4

### RESULTS AND DISCUSSION

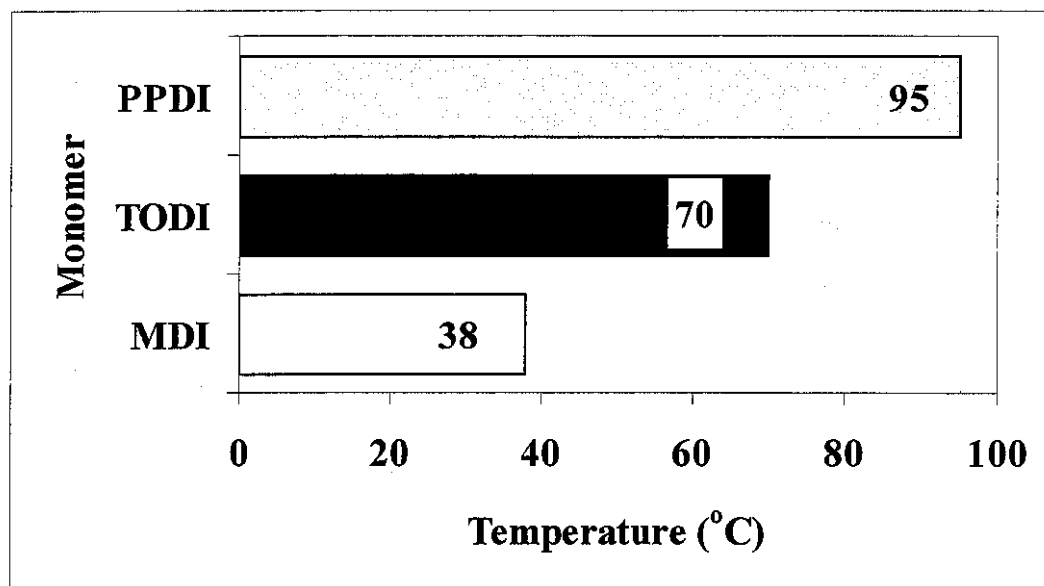
#### 4.1 Theoretical Considerations

Structural variations differentiate the PPDI, TODI, and MDI monomeric structures. Examination of the basic MDI structure (Figure 3) indicates a conformational preference about the methylene moiety that forces the benzene rings into two separate planes. The skewed planarity coupled with steric hindrances generated by the methylene group produce inefficient hard segment stacking within the phase separated hard segment domains.

Similar steric hampering is revealed upon examination of the TODI molecular structure (Figure 2). The rotational freedom about the phenyl-phenyl bond is not forced out of planarity by the methyl groups, but they do generate a significant impediment to hard segment stacking in the hard segment domain. A priori, it would appear that these interactions have a smaller impact on the TODI hard segment domains than the combination of methyl interference and nonplanarity in the MDI hard segment phases. The PPDI structure (Figure 1) possesses no pendant methyl groups to interfere with stacking, and as it consists of only a single benzene ring, it is always planar. This allows the adjacent polymer chains of the PPDI TPU to stack more efficiently than those of the MDI or TODI based urethanes. The stacking

efficiency allows for stronger hydrogen bonding. The 'tightness' of the PPDI hard segment phase not only provides the finished TPU with greater temperature resistance but also minimizes the loss of input mechanical energy that is used to rearrange the hard segment semicrystalline structure. This is shown dramatically in Figure 8, which relates the melting point of the monomeric diisocyanate to its degrees of rotational freedom. The impact of the diisocyanate structure on the static, dynamic, and dielectric properties of corresponding thermoplastic polyurethane samples will be shown by the data that follows.

Figures 9 and 10 show that the required ratio of hard segment (Diisocyanate and 1,4-BD) to soft segment (PCL) decreases significantly for the preparation of a 93 Shore-A TPU based on TODI versus the ratio required to prepare a 93 Shore-A MDI based TPU. Furthermore, the decrease is even greater when formulating a 93 Shore-A TPU based on PPDI. The progression of this ratio illustrates the increase in hard



**Figure 8. Monomeric Diisocyanate Melting Points**

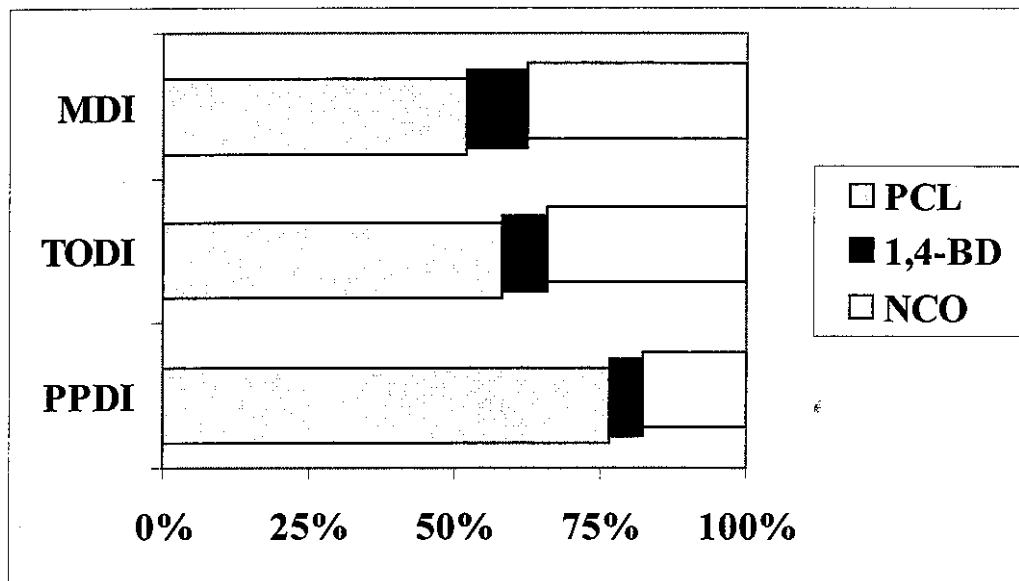


Figure 9. Component Proportions (% by Weight)

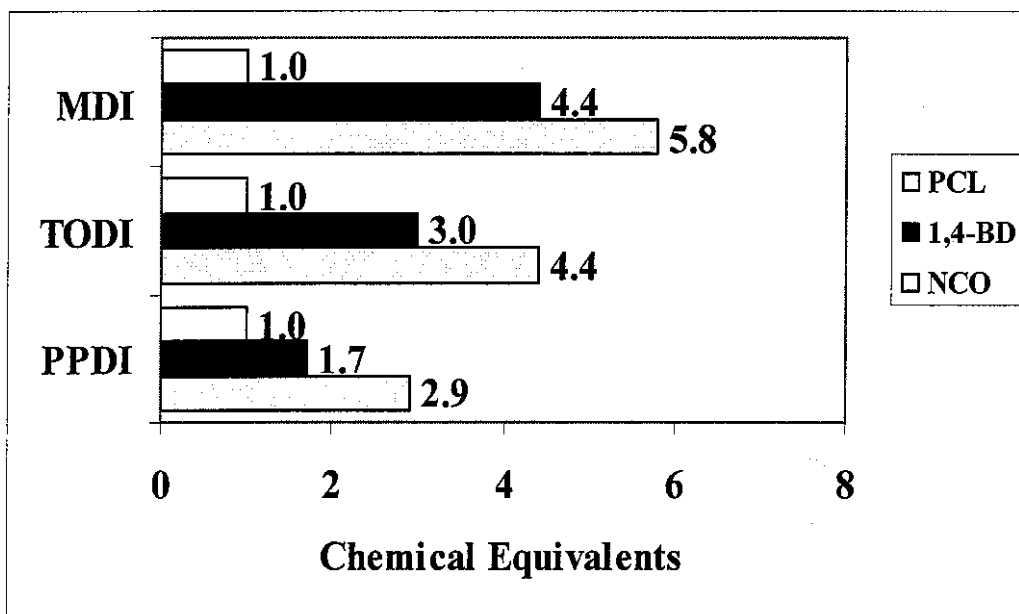


Figure 10. Chemical Equivalents

segment stacking efficiency. This is due to the minimal steric obstruction of the PPDI based hard segment, the slightly greater obstruction of the TODI based hard segment, and the even greater obstruction of the MDI based hard segment. This trend also serves to offset the high price of the PPDI monomer.

#### 4.2 Stress-Strain Properties

Original physical properties, measured at room temperature, of TPU samples based on the three diisocyanates studied are presented in Table 2. All three compounds exhibit excellent properties and fall within narrow hardness ranges with respect to both the Shore A and Shore D scales.

**Table 2. Original Physical Properties at Room Temperature**

<b>Compound → Property ↓</b>	<b>MDI TPU</b>	<b>TODI TPU</b>	<b>PPDI TPU</b>	<b>ASTM Test</b>
<b>Hardness (A/D)</b>	93 / 50	95 / 51	93 / 48	D2240
<b>Ultimate Tensile (psi)</b>	8130	7830	8510	D412
<b>Modulus at 100% Elongation (psi)</b>	1600	2180	2140	D412
<b>Modulus at 300% Elongation (psi)</b>	2350	3270	2860	D412
<b>Ultimate Elongation (%)</b>	450	450	650	D412
<b>Taber Abrasion, 1000g load / H-18 Wheel (mg loss/5000 cycles)</b>	50	250	90	D1044
<b>NBS Abrasion Index</b>	1500	1200	1400	D1630
<b>Compression Set (%)</b>				
70 hours @ 70°C	26.0	29.8	23.9	D395
70 hours @ 100°C	<b>51.0</b>	<b>49.1</b>	<b>33.3</b>	
<b>Bayshore Rebound (%)</b>	<b>34</b>	<b>45</b>	<b>66</b>	D2632

The initial test results highlight two areas that reflect the impact of hard segment domain stacking efficiency on the properties of the TPU sample. First, the compression set test at 100°C yields a value for the PPDI-based sample that is approximately one third lower than the results for the MDI- and TODI-based samples. This is because the TODI- and MDI-based hard segment domains have gone through conformational rearrangements during their exposure to strain at an elevated temperature. The PPDI-based hard segment domain is unable to change conformation, and, therefore, exhibits a much lower compression set value. Second, the Bayshore rebound resilience results show a trend from low for the MDI-based sample to high for the PPDI-based sample. This trend reflects the increase in hard segment ‘tightness’ of the samples, which minimizes the amount of mechanical energy that when input to the system is lost to rearrangement of the hard segment semicrystalline structure.

The Vicat softening point of 198°C that was measured for the PPDI-based sample (Figure 11) reflects the ability of the PPDI-based hard segment to maintain its

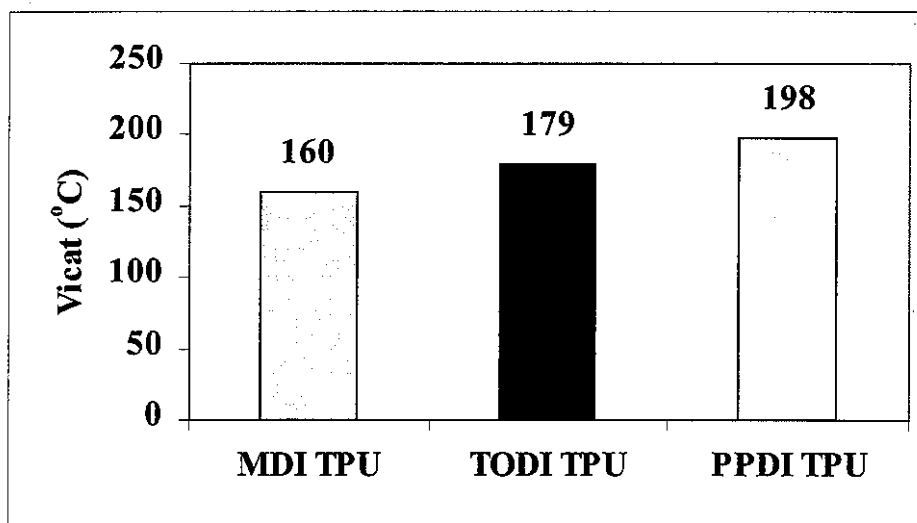


Figure 11. Vicat Softening Points

integrity at higher temperatures than those based on TODI or MDI. Similarly, the PPDI heat deflection value (Figure 12) shows a slight advantage over the TODI-based sample but shows a pronounced improvement over the corresponding MDI-based sample. Furthermore, the stress-strain values at elevated temperatures (Figures 13-15) continue to reflect the ability of the PPDI based hard segment domains to retain their integrity better than their TODI and MDI counterparts at elevated temperatures. This is due to the increased proximity of the polymer chains in the hard segment phase and, therefore, stronger hydrogen bonding, allowed by the simplicity of the PPDI monomer. The stress-strain values are shown here as percent retention of room temperature values.

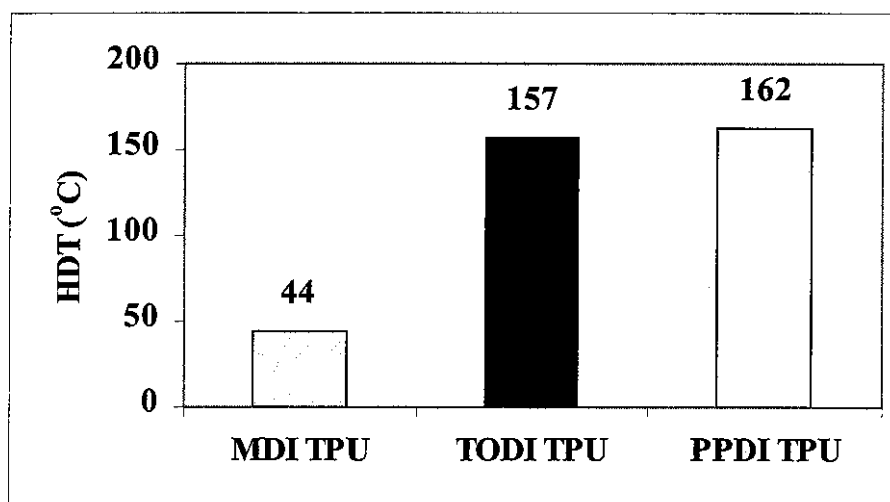
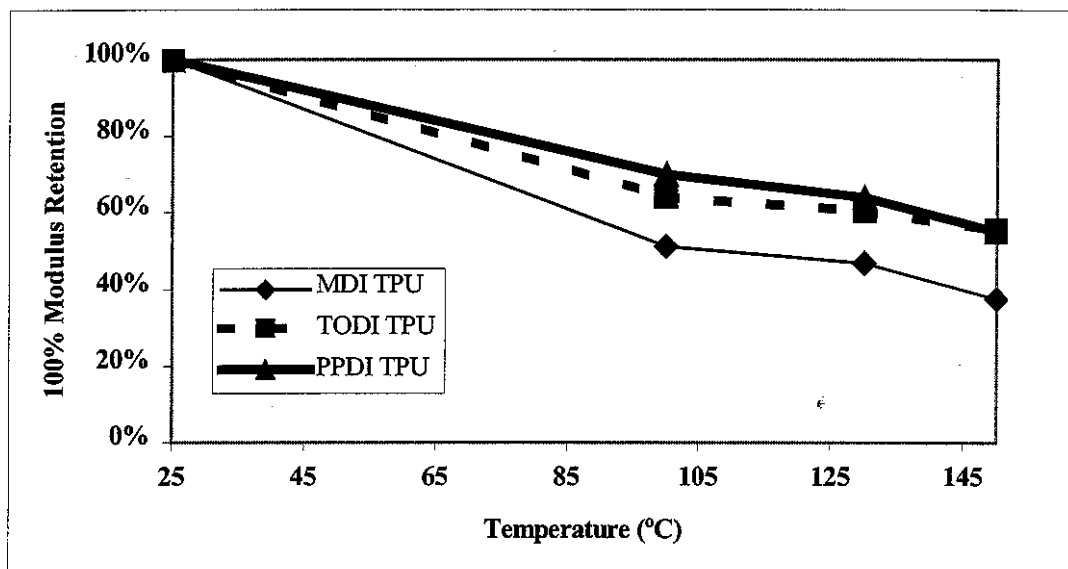
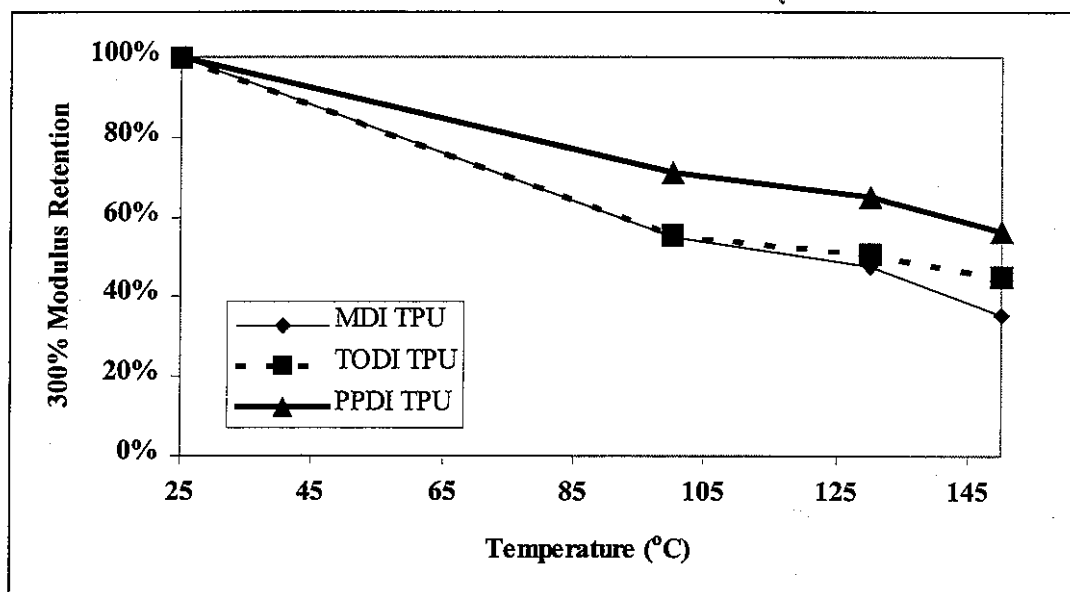


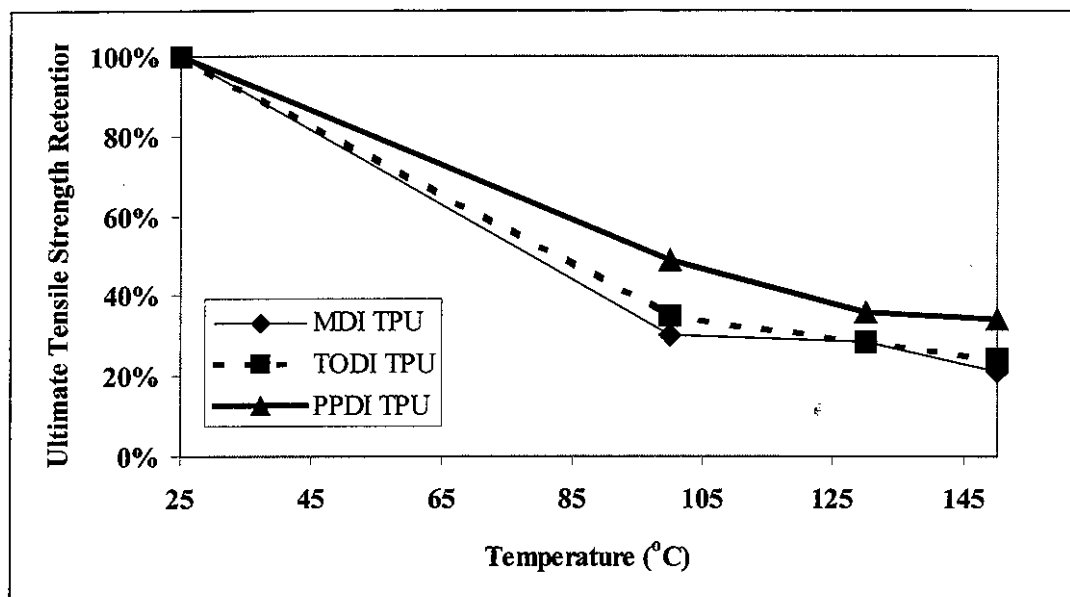
Figure 12. Heat Distortion Temperatures (°C)



**Figure 13. Modulus Retention at 100% Elongation**



**Figure 14. Modulus Retention at 300% Elongation**



**Figure 15. Ultimate Tensile Strength Retention**

#### 4.3 Dynamic Relaxation Spectra

Figures 16 and 17 depict the tensile storage moduli  $E'$  and the shear storage moduli  $G'$  respectively for the TPU samples prepared from the three diisocyanates under investigation. The moduli of the TODI- and PPDI-based samples remains more or less constant over the temperature range of approximately 25°C to 150°C in both shear and tensile test modes. In contrast to this, the MDI-based sample has no region of constant modulus in either mode. This constant modulus plateau denotes a region of temperature wherein the hard segment domains of the polymer sample maintain their integrity. The downturn of the modulus at high temperatures is associated with dissociation of the hard segment domains in the TPU sample. It is interesting to note the correspondence of the location of the high temperature downturn on the temperature axis to that of the heat distortion temperatures shown in Figure 12.

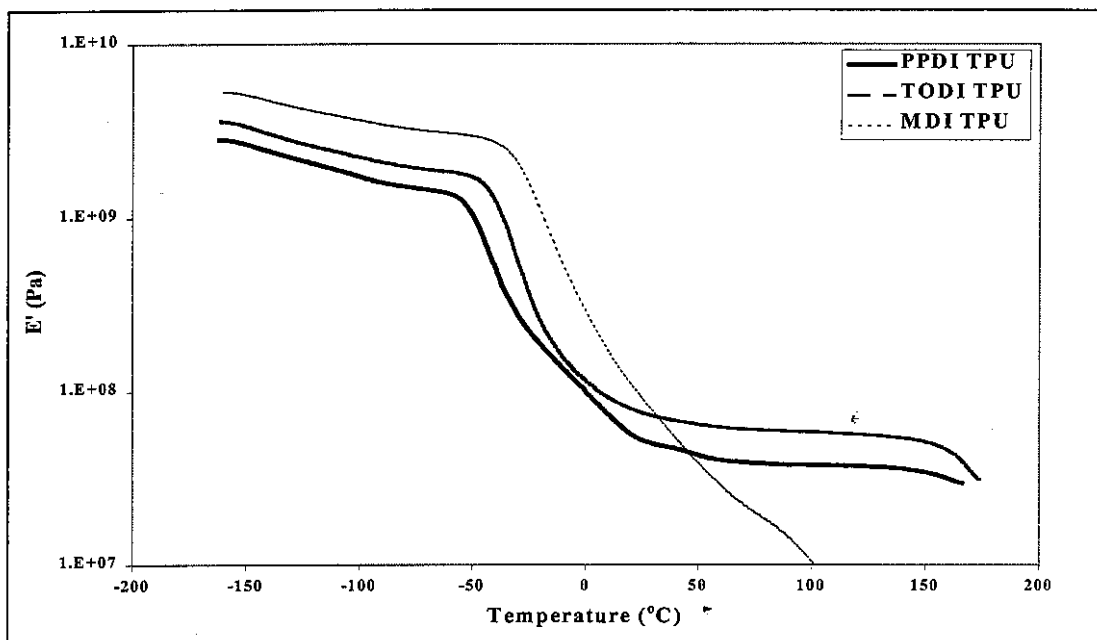


Figure 16. Tensile Storage Modulus at 1 Hz

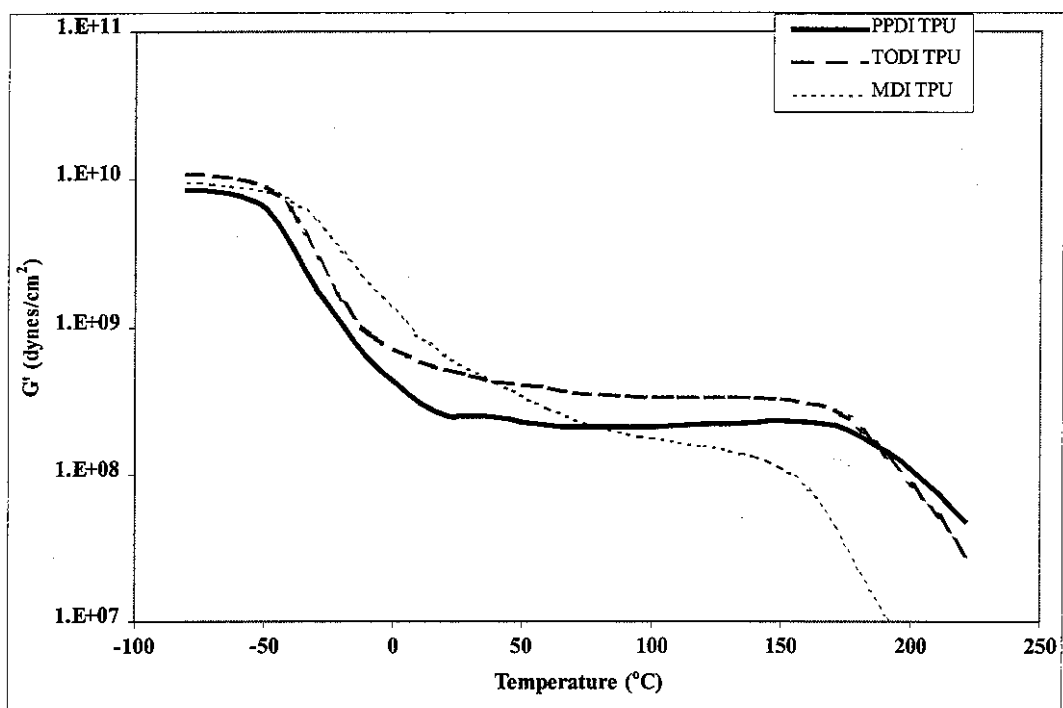


Figure 17. Shear Storage Modulus at 1 Hz

The tensile loss moduli  $E''$  and the shear loss moduli  $G''$  data (Figures 18 and 19 respectively) reflect both the efficiency of the hard segment stacking of the TPU samples and the impact of stacking efficiency on phase separation. First, the value of the loss modulus of the PPDI-based sample is lower than that of the other two samples at all points in the temperature range. This is due, again, to the 'tightness' of the PPDI-based hard segment domains, which do not absorb mechanical energy to change conformation. Second, the location of the low temperature maxima, which are associated with  $T_g$ , in both modes of measurement progress from the PPDI-based sample at the lowest temperature, the TODI-based sample in the middle, and the MDI-based sample at the highest temperature. This is due to greater phase separation allowed by the efficient stacking of the PPDI-based hard segment, which yields less

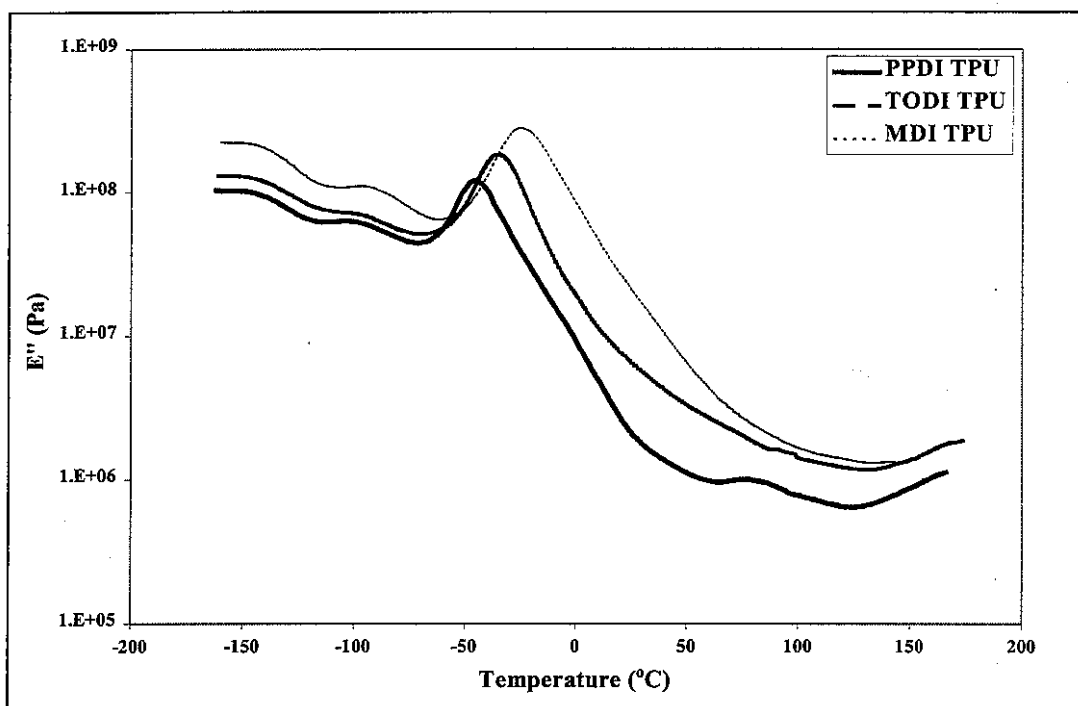


Figure 18. Tensile Loss Modulus at 1 Hz

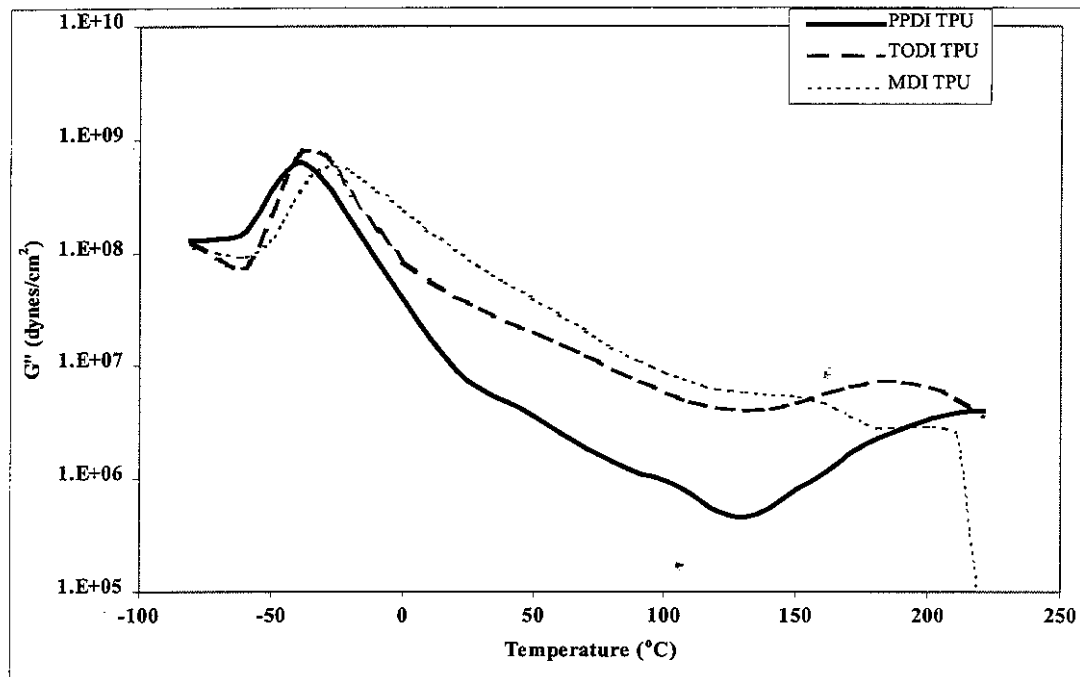


Figure 19. Shear Loss Modulus at 1 Hz.

participation of the hard segment in the glass transition, and thus transition at a lower temperature.

Significant features of the  $\tan \delta$  data presented for tensile and shear test modes (Figures 20 and 21 respectively) are reflections of the storage and loss moduli data already presented. The location of the low temperature maxima, associated with  $T_g$ , reflects the tightness of the packing of the hard segment domains. Again, the hard segments based on PPDI show as the tightest, followed by those based on TODI, and finally those based on MDI. The area under the low temperature maxima reflects the degree of phase separation of the soft and hard phases, there being less area under the curve due to greater phase separation. Again, the PPDI-based hard segments display greater cohesion than the TODI and MDI counterparts. The magnitude of  $\tan \delta$  across

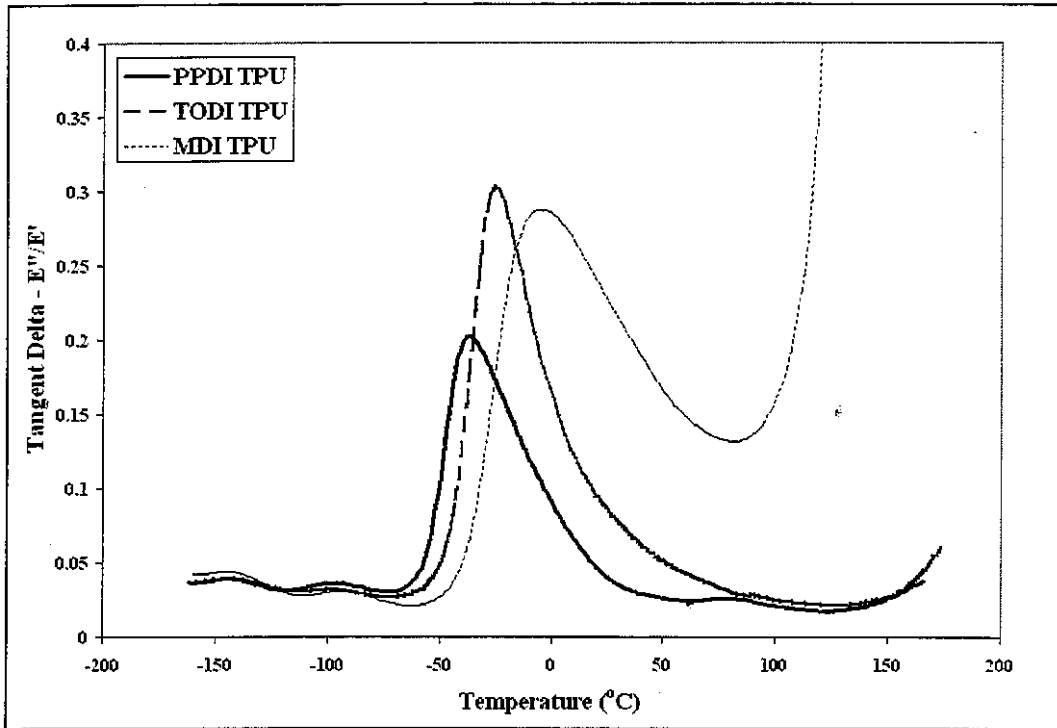


Figure 20. Tensile Tangent Delta at 1 Hz

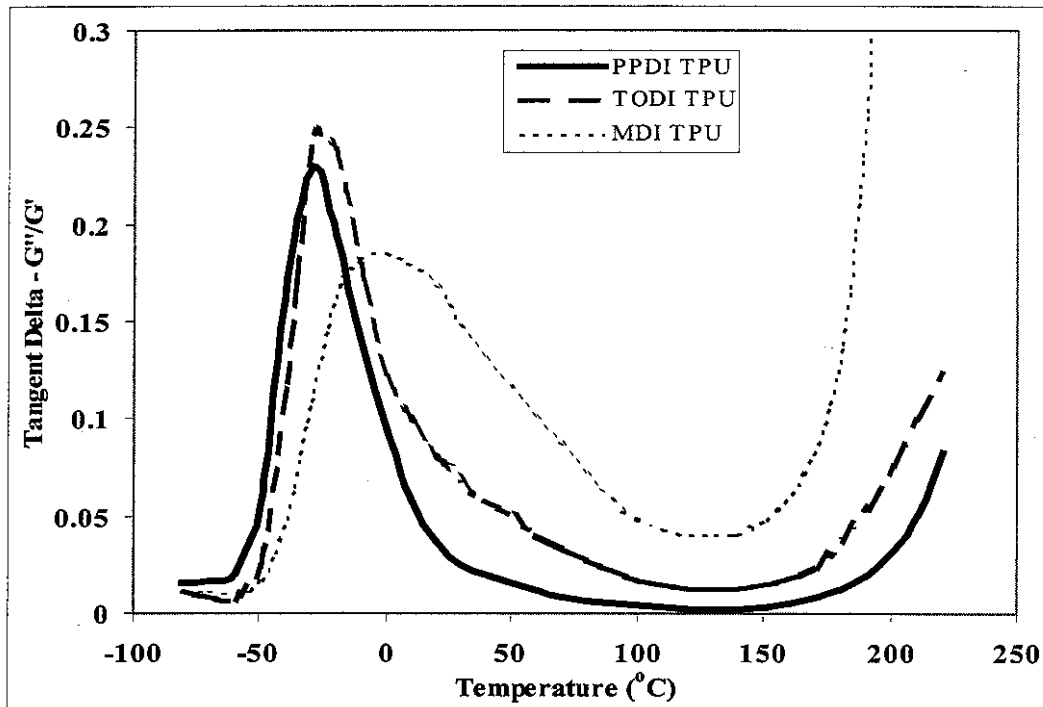


Figure 21. Shear Tangent Delta at 1 Hz

the application temperature range is a reflection of the percentage of mechanical energy that is absorbed by the TPU sample. The hard segments based on TODI and MDI absorb mechanical energy while undergoing conformational changes, and this is reflected in the Figures as higher values of  $\tan \delta$ . Finally, the location of the high temperature upturns show the ability of the PPDI-based hard segments to maintain their cohesiveness at higher temperatures than the hard segments based on TODI and MDI. This is because the PPDI-based hard segments have less steric interference, are able to pull more closely together, and thus have a greater ability to hydrogen bond. The relationships maintain throughout the frequency range tested, as illustrated in Figure 22. The next three Figures (Figures 23 through 25) are included for reference and depict the individual samples'  $\tan \delta$  values across the frequency range of 1- to 20 Hz.

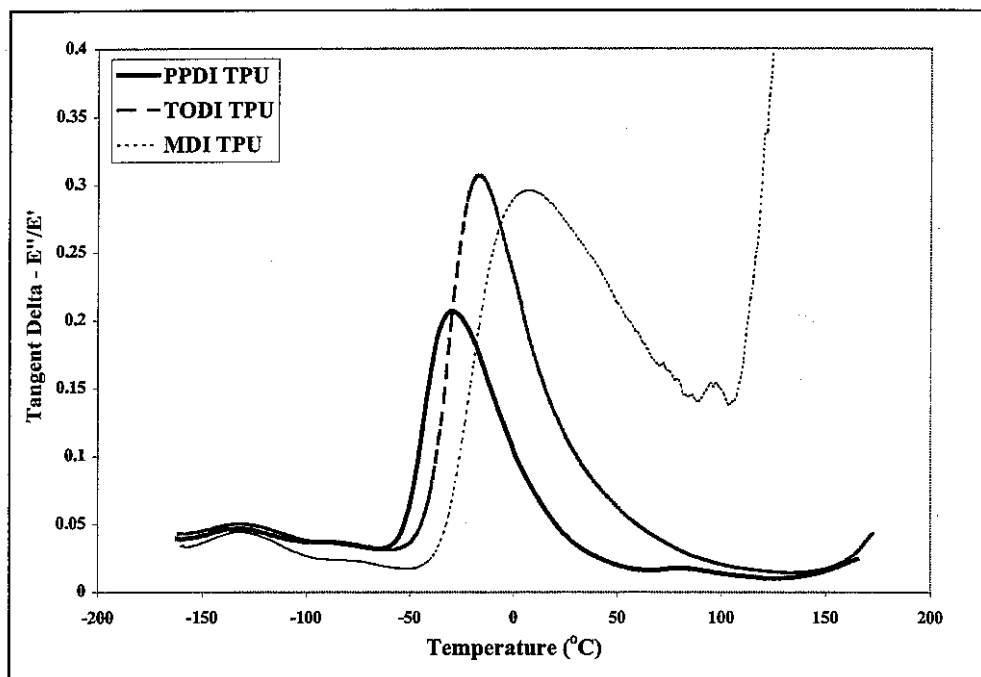


Figure 22. Tensile Tangent Delta at 20 Hz

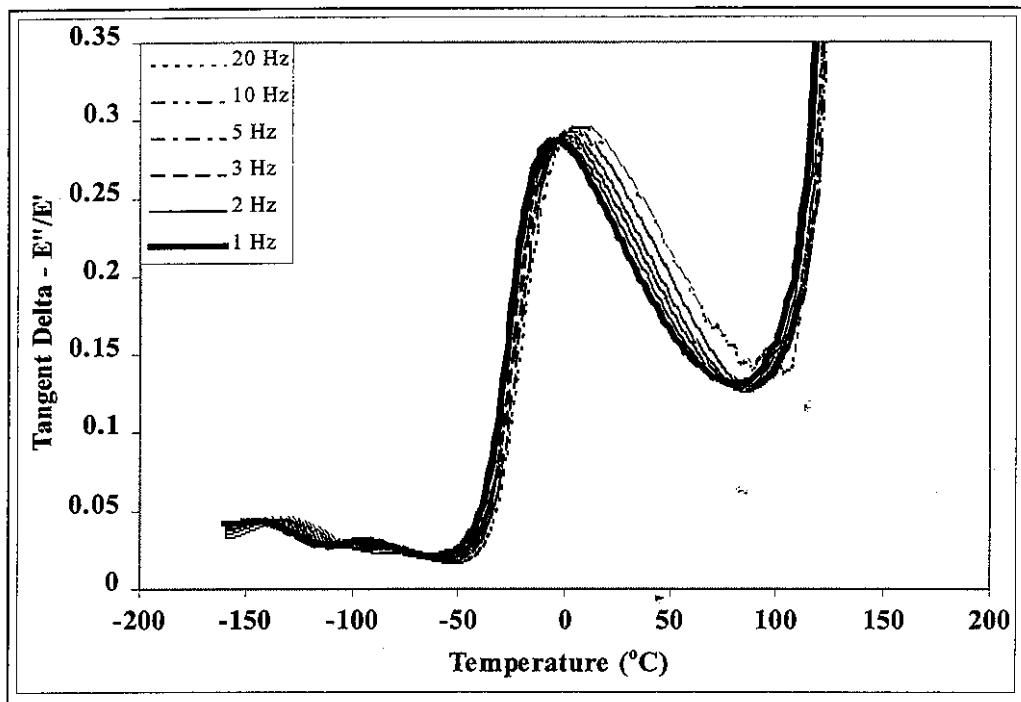


Figure 23. Tensile Tangent Delta for MDI TPU – Multiplexed

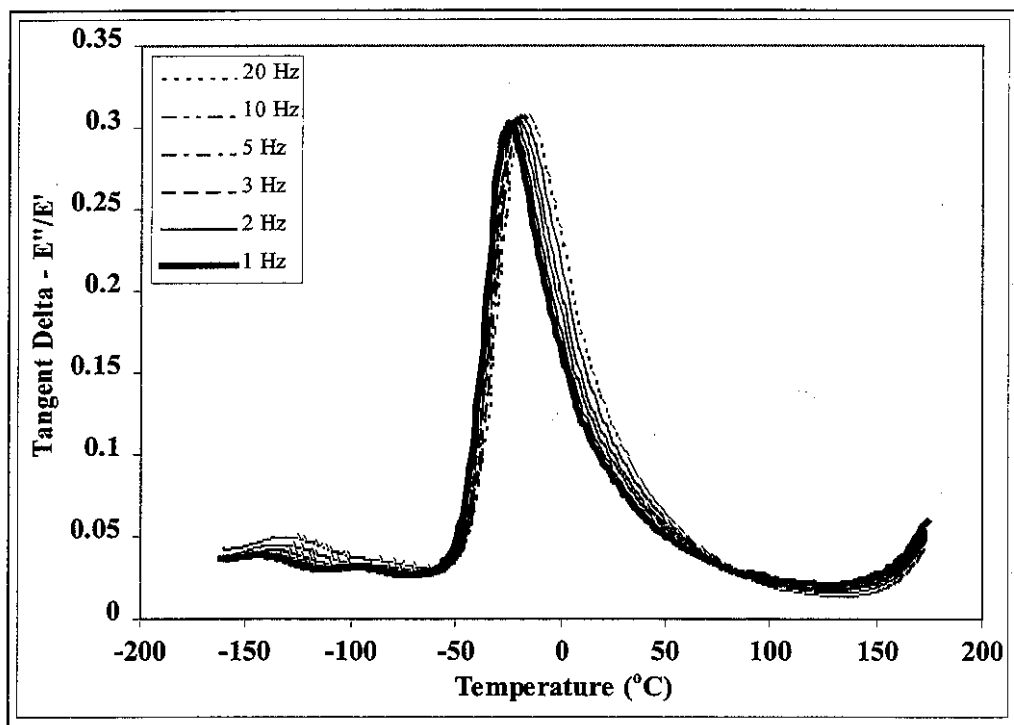


Figure 24. Tensile Tangent Delta for TODI TPU – Multiplexed

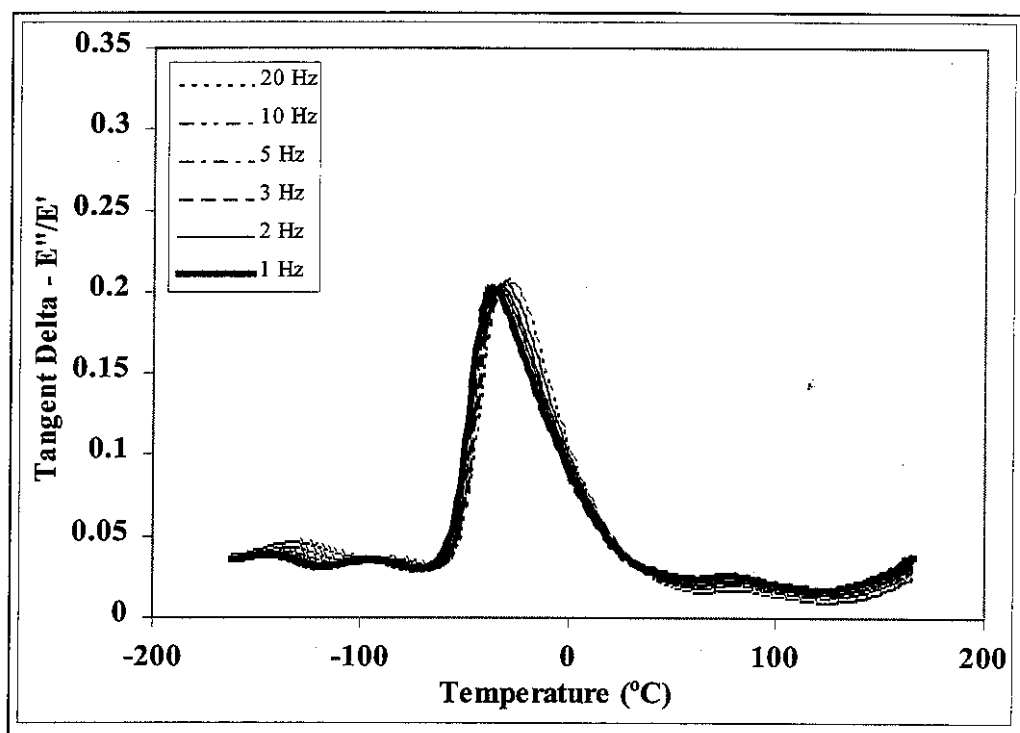


Figure 25. Tensile Tangent Delta for PPDI TPU – Multiplexed

#### 4.3 Dielectric Relaxation Spectra

Trends similar to those shown by DMTA in section 4.2 are evident in the dielectric thermal analysis spectra presented below. At 0.1 and 1 Hertz (Figures 26 and 27, respectively), we again see the characteristic curves showing the PPDI-based hard segment as that possessing the tightest packing, followed by those based on TODI and MDI, in that order. The location of the low temperature maxima,  $T_g$ , reflects the tightness of the packing of the hard segment domains. The hard segment domains based on PPDI show as the tightest, followed by those based on TODI, and finally those based on MDI. The area under the low temperature maxima reflects the degree of phase separation of the soft and hard phases, there being less area under the curve due to greater phase separation. Again, the PPDI-based hard segments display

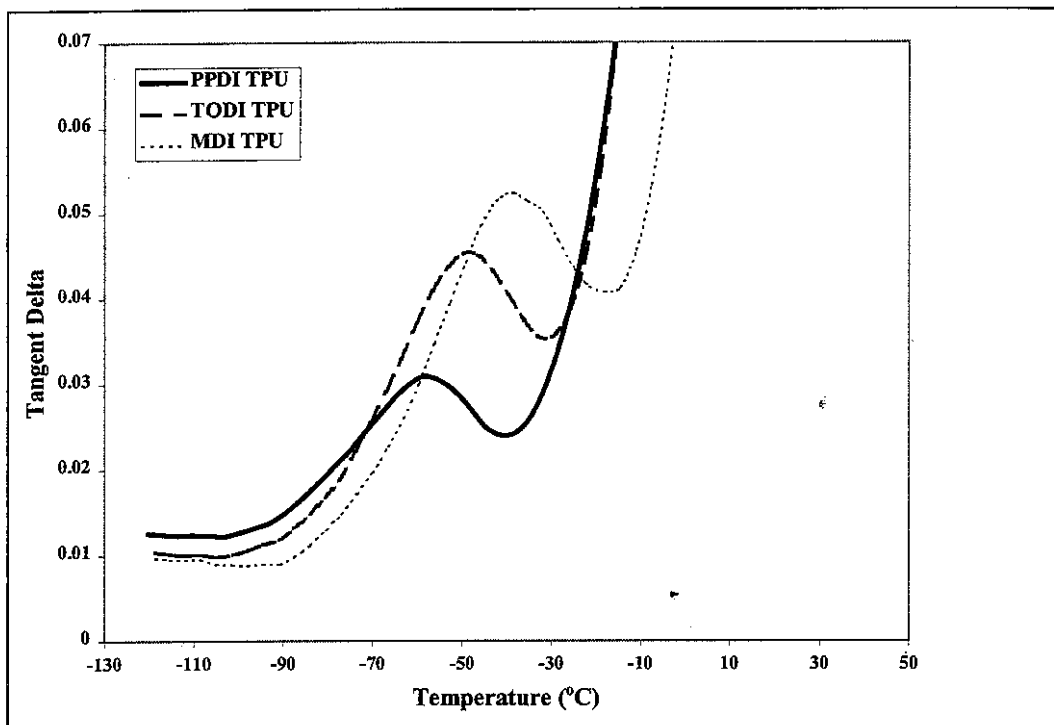


Figure 26. Dielectric Tangent Delta at 0.1 Hz

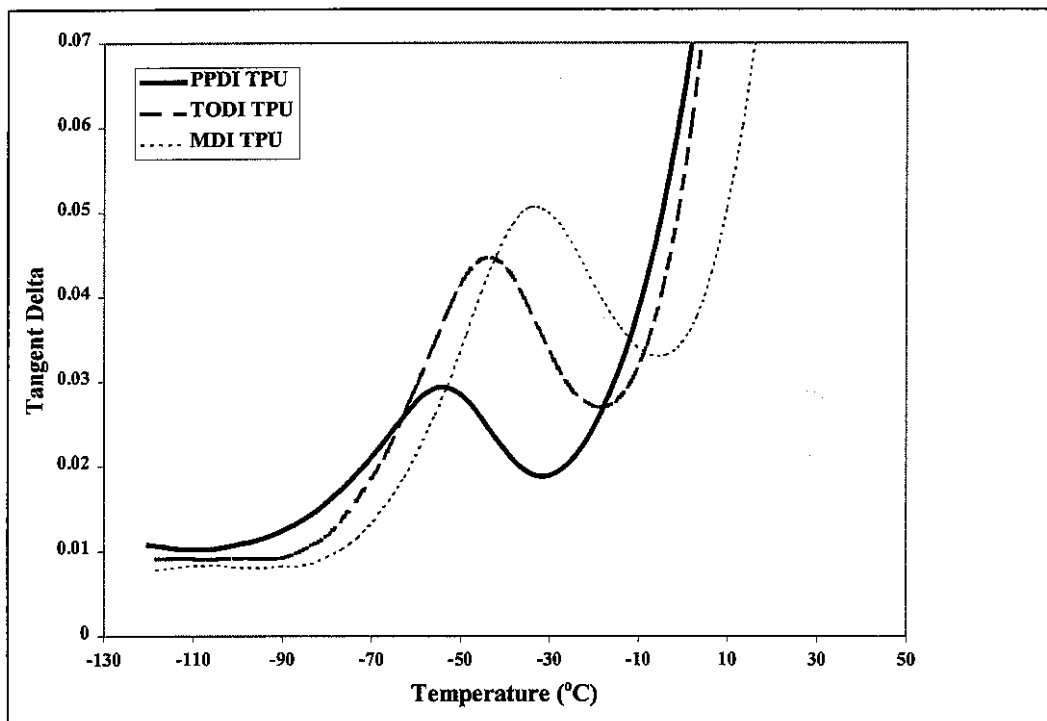


Figure 27. Dielectric Tangent Delta at 1 Hz

greater cohesion than the TODI and MDI counterparts. It should be noted here that the upturn of the  $\tan \delta_e$  values at temperatures greater than  $T_g$  is not a result of dissociation of the hydrogen bonding in the hard segment phase, as is the case in the DMTA curves presented earlier. Rather, this upturn is due to conductance loss, i.e. the presence of D.C. conductance<sup>18,24</sup>. Examination of the curves generated at 100,000-Hertz (Figure 28) reveals the same trends. In fact, the curves themselves are very similar to the DMTA curves generated from 1- to 20-Hertz. The next three Figures (Figures 29 through 31) are included for reference only and depict the individual samples'  $\tan \delta_e$  values across the frequency range of 0.1- to 100,000 Hz.

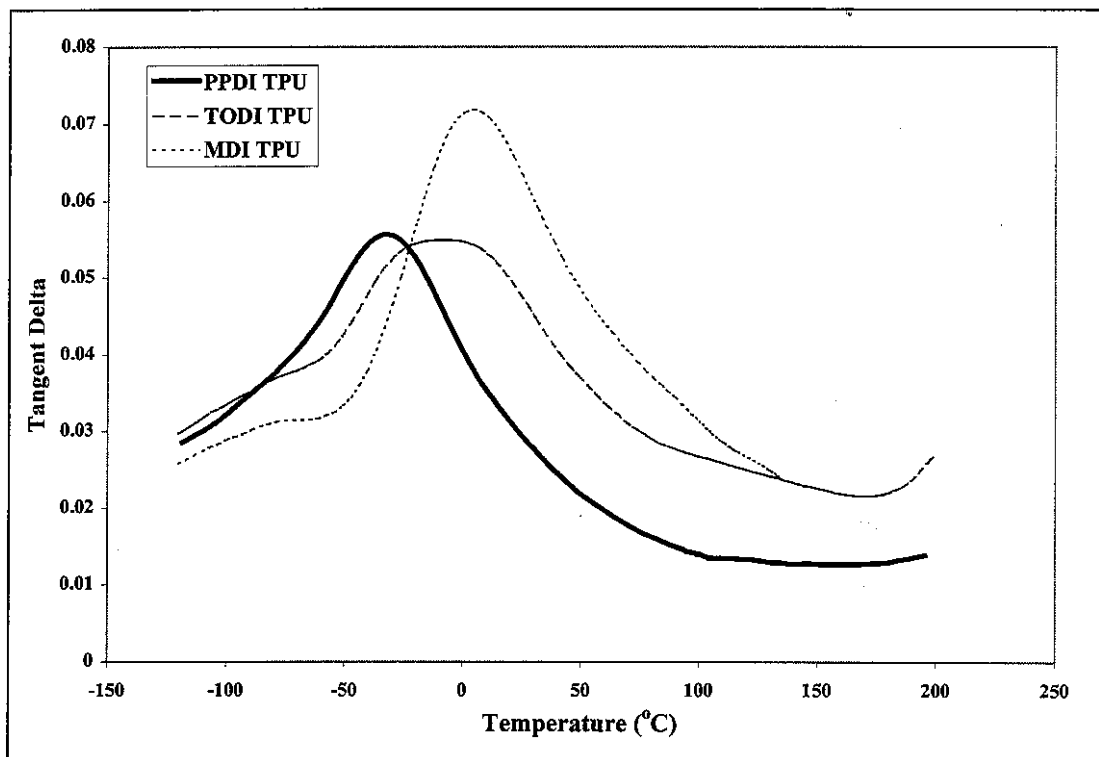


Figure 28. Dielectric Tangent Delta at 100,000 Hz

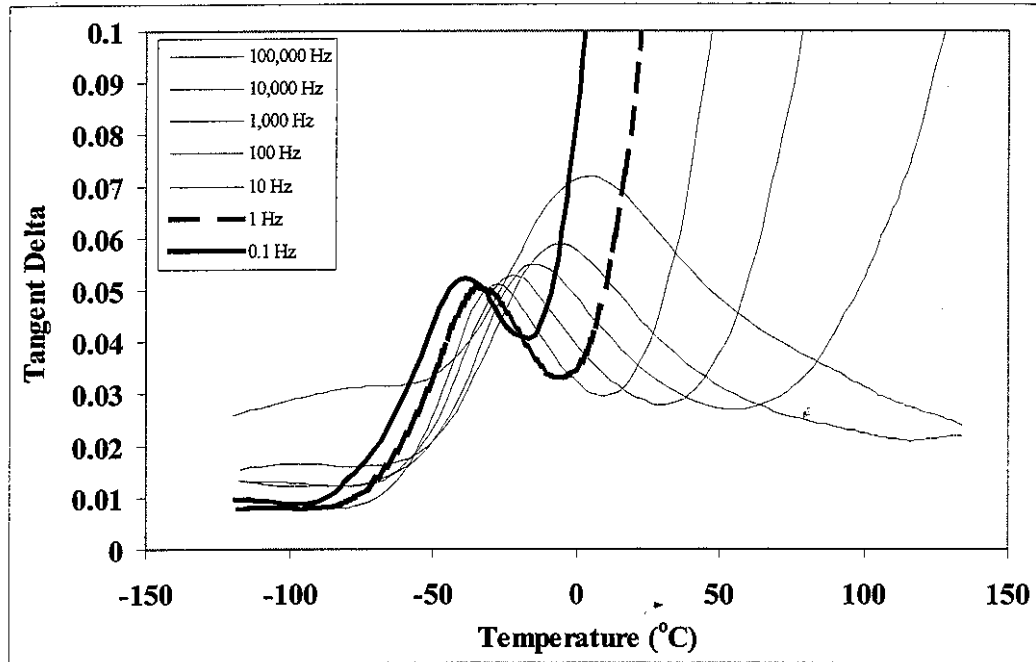


Figure 29. Dielectric Tangent Delta for MDI TPU – Multiplexed

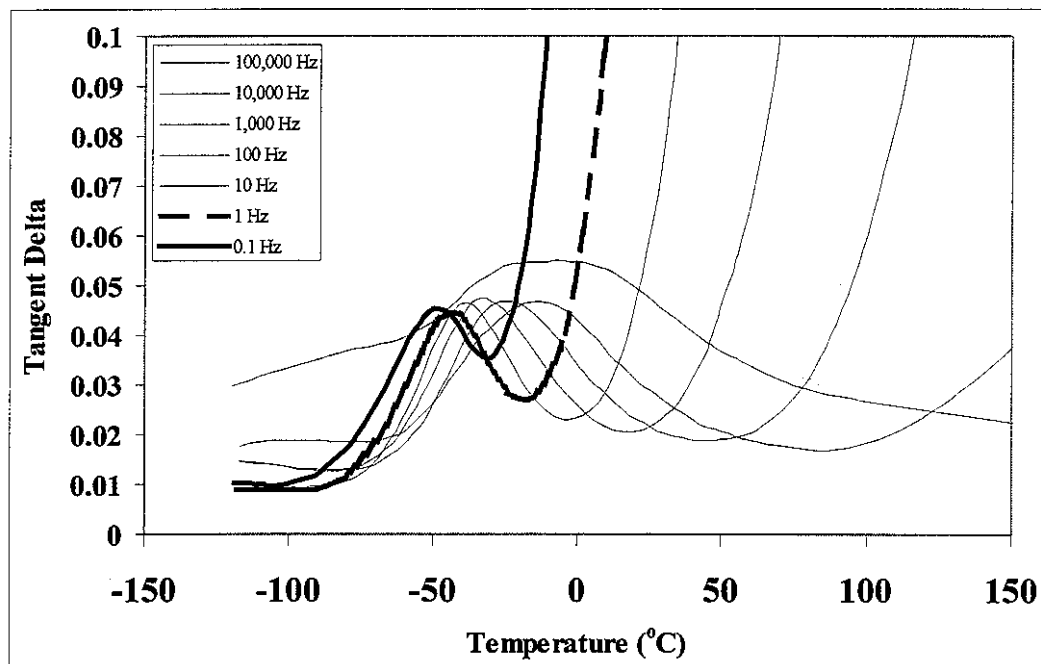
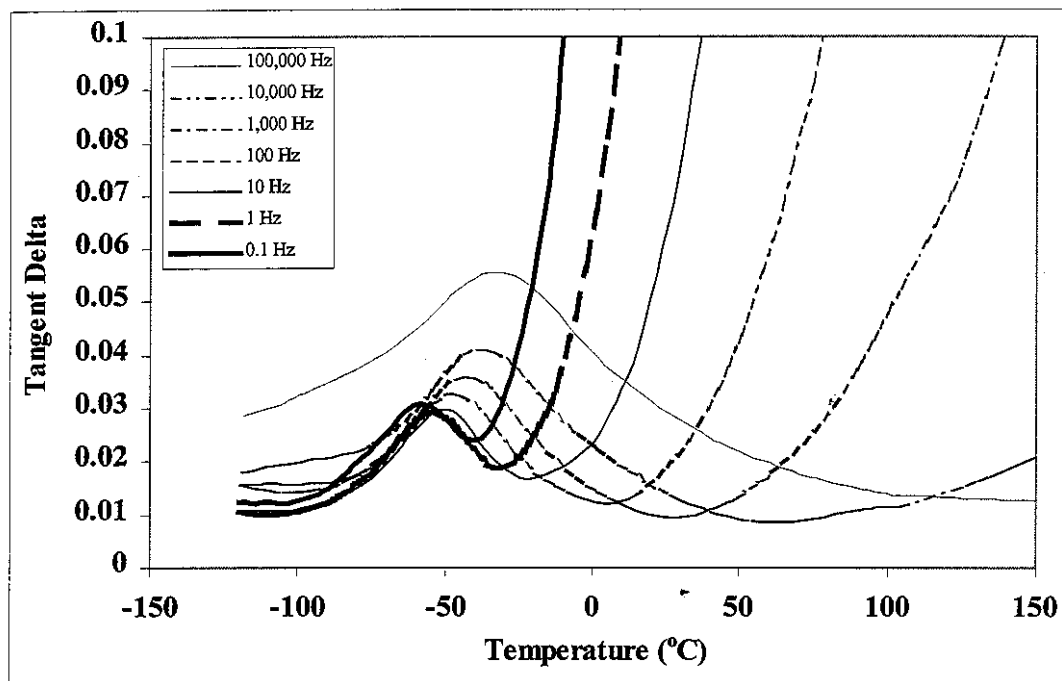


Figure 30. Dielectric Tangent Delta for TODI TPU – Multiplexed



**Figure 31. Dielectric Tangent Delta for PPDI TPU – Multiplexed**

The final two Figures (Figures 32 and 33) are “loss maps” of the data. These Figures depict the temperature of the maximum of the loss factor (tangent delta in Figure 32 or loss values in Figure 33) versus the frequency at which the loss factor was measured. These plots show the correspondence between the dielectric and mechanical data. Figure 32 shows that the mechanical  $\tan \delta$  is displaced far to high temperature from the dielectric  $\tan \delta$ . This is due to the effect in the mechanical case of the large drop in  $E'$  or  $G'$  with increasing temperature displacing the maximum in the ratio  $E''/E'$  or  $G''/G'$  to higher temperature than for  $E''$  or  $G''$  separately. Figure 33 demonstrates that plotting the temperature of the  $E''$  and  $e''$  maxima generates a much closer correlation.

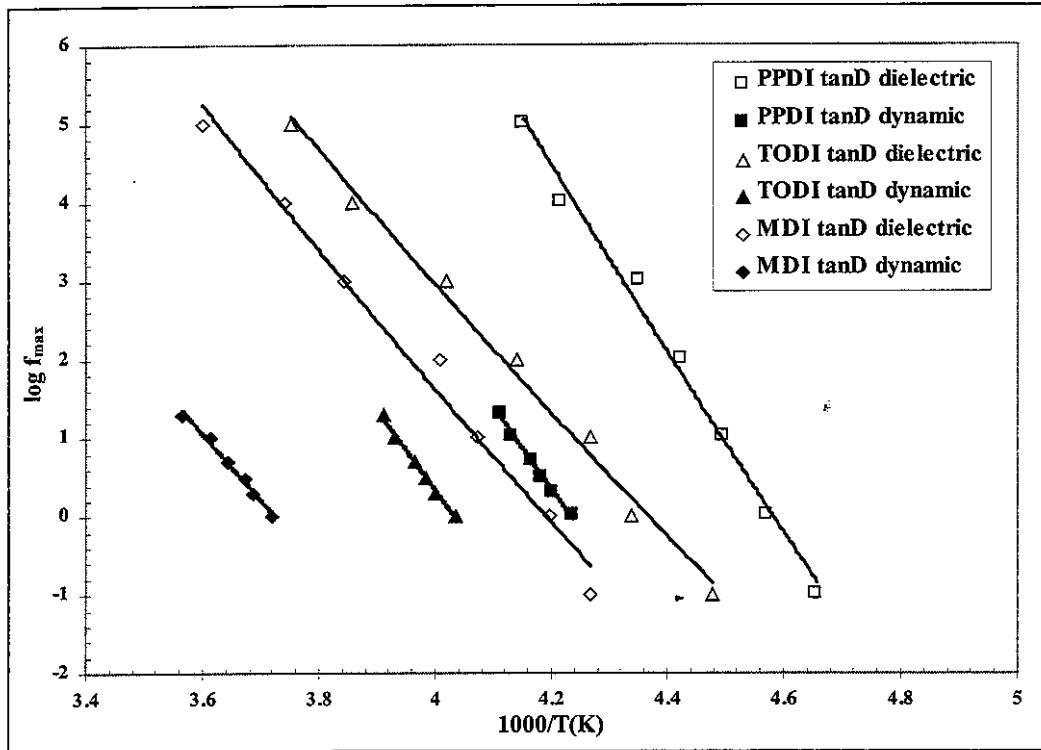


Figure 32. Loss Map of Tangent Delta vs. Temperature

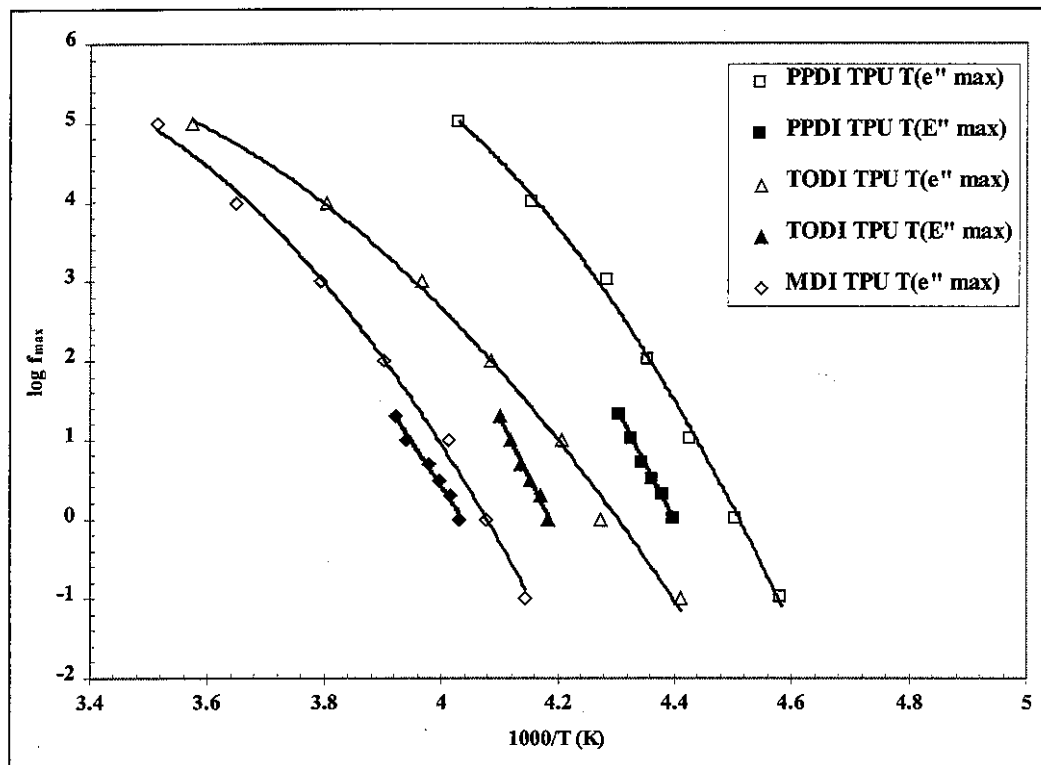


Figure 33. Loss Map of Loss Factor vs. Temperature

## CHAPTER 5

### SUMMARY

Thermoplastic polyurethanes (TPUs) have achieved an important place in elastomer technology. This is by virtue of the fact that such elastomers combine desirable mechanical properties with the ability to be reversibly melted and thus processed by conventional plastics thermoforming techniques. Because of the wide variety of chemical structures available for use in TPUs, it is important to achieve some understanding of how these structures affect the end-use properties. In the present work, a structure versus property study is carried out that involves several TPUs. Specifically, samples in the hardness range of 92-95 Shore A were prepared through polymerization of p-phenylenediisocyanate (PPDI), 3,3'-dimethyl-4,4'-diphenyldiisocyanate (TODI), or diphenylmethane-4,4'-diisocyanate (MDI) with 1,4-butanediol and a 2000 molecular weight polycaprolactone polyol to explore relationships between the mechanical properties of thermoplastic polyurethane elastomers and the structure of the diisocyanate unit. The three thermoplastic polyurethane elastomers possessed mechanical and dielectric properties that differed significantly from one another. In general, the elastomer containing the diisocyanate with the fewest degrees of freedom and the least steric hindrance possessed superior mechanical properties. In conjunction with this, a relationship was found to exist

between the diisocyanate unit and the molar ratio of diisocyanate to polyol required in synthesizing a TPU of the target hardness. This relationship reflects the inter-chain proximity of the diisocyanate units within the hard segment domain that is governed not only by steric factors but also by the degrees of rotational freedom of the diisocyanate unit.

Essentially, the inter-chain proximity within the hard segment domains allows the adjacent polymer chains of the PPDI-based TPU to stack more efficiently than those of the MDI- or TODI- based urethanes. The stacking efficiency allows for stronger hydrogen bonding and hence greater cohesive energy in the hard segment phase. The 'tightness' of the PPDI hard segment phase not only provides the finished TPU with greater temperature resistance but also minimizes the loss of input mechanical energy that is used to rearrange the hard segment semicrystalline structure. The impact of the diisocyanate structure on the static, dynamic, and dielectric properties of corresponding thermoplastic polyurethane samples was shown as significant.

In conclusion, the inherently simple structure of p-phenylenediisocyanate allows for the preparation of thermoplastic polyurethanes that display exceptional high temperature stability. More notably,  $\tan \delta$  measurements indicate that PPDI-based thermoplastic polyurethanes are capable of redefining the role that thermoplastic polyurethane technology will play in the future. PPDI-based thermoplastic polyurethanes are beginning to make inroads into high stress dynamic applications where previously only thermoset materials were able to perform. Some of these

dynamic applications include high load wheels, diaphragms, high impact bumpers, and hydraulic seals.

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