Polyurethane Division

The Society of the Plastics Industry, Inc.

POLYURETHANES EXPO '96

International Technical Conference & Exposition

Where Technology Pays Off

October
20–23
1996

Proceedings of the Polyurethanes EXPO '96 • Sponsored by the SPI Polyurethane Division

Bally's Casino & Hotel
Las Vegas, Nevada

Para-Phenylenediisocyanate (PPDI) Based Thermoplastic Polyurethanes Provide High Thermal Stability and Excellent Power Loss Properties

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ABSTRACT

Thermoplastic polyurethanes based on p-phenylenediisocyanate (PPDI) increase the application temperature range of the thermoplastic family of polyurethanes to well beyond that of traditional diphenylmethane- 4, 4'-diisocyanate (MDI) and 3, 3'- dimethyl - 4, 4'- diphenyldiisocyanate (TODI) based formulations. The absence of sterically hindering pendant moieties on the PPDI molecule, as well as its symmetrical nature, provide this simple diisocyanate with exceptional efficiency in hard segment stacking and phase separation. Stoichiometrically, lower molar ratios of isocyanate to polyol are required for PPDI systems as compared with similar MDI and TODI formulations having comparable hardnesses and modulus properties. This trend reflects the relatively low level of steric influences and relatively high degree of stacking efficiency inherent in the p-phenylene structure. These attributes render highly resilient PPDI based thermoplastic polyurethane materials excellent for use in applications requiring minimal power loss and superior thermal stability. In the present work, thermoplastic polyurethane compounds representing MDI, TODI and PPDI formulations in a hardness range of 92-95 Shore A and prepared from conventional polycaprolactone polyol and 1, 4 - butanediol were evaluated with respect to Stress-Strain and Compression Set properties, Vicat softening, Rheometrics data, and Power Loss determination. The test data presented illustrate that PPDI based thermoplastic polyurethanes possess unique dynamic properties and increased thermal stability that will expand thermoplastic polyurethane use in critical engineering applications. PPDI technology is playing an ever increasing role in hydraulic sealing applications, where thermal stability and compression set resistance of the sealing material are major engineering concerns. In addition, high performance PPDI based thermoplastic polyurethanes are finding increased use in other demanding mechanical applications traditionally limited to thermoset materials, where exceptionally high Bashore resilience and minimal hysteretic power consumption are of primary importance. These dynamic applications include, but are not limited to, bumpers, mechanical couplings, and wheels.

INTRODUCTION

Many new chemical innovations have been added to the polyurethane formulator's repertoire during the last several decades. A majority of these innovations have included commercialization of numerous new chain extenders, as well as an occasional new polyol soft segment. All have enhanced the diversification of polyurethane technology. Seldom, however, has the polyurethane formulator been given an opportunity to explore the realm of a newly commercialized diisocyanate. The introduction of DuPont's Hylene® PPDI (p-phenylenediisocyanate) in the early 1990's opened such a window of exploration to the polyurethane technologist.

Much of the current commercial work involving PPDI has centered around cast technology. Parker-Hannifin Corporation's Packing Division, being principally an injection molding concern, set out early on to explore the potential for PPDI use in the thermoplastic polyurethane (TPU) arena. We have found that the PPDI based hard segment coupled with polycaprolactone polyols renders TPU compounds having heat stabilities and hysteretic properties that in most cases improve upon those properties exhibited by TPU formulations based on the more traditional diisocyanates; diphenylmethane - 4,4' - diisocyanate (MDI) and 3, 3'- dimethyl - 4, 4' -diphenyldiisocyanate (TODI). During this presentation we will focus our discussions around three similar formulations based on MDI, TODI, and PPDI. All formulations used polycaprolactone (PCL, 2000 molecular weight) for the soft segment and 1,4 - butanediol (BDO) for the chain extender. The three experimental TPU formulations yielded Shore hardnesses ranging between 93A and 95A. We will examine and compare various static and dynamic properties of each polymer and the impact of temperature on the respective polymers.

THEORETICAL CONSIDERATIONS

Before examining any data, let us look at some theoretical considerations. Structural variations in the steric factors and the internal degrees of rotational freedom differ-

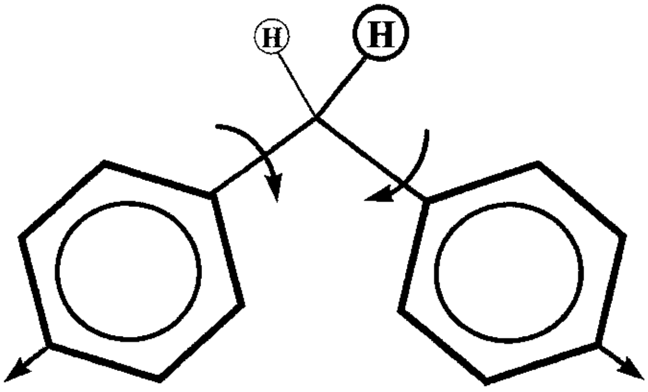

Figure 1. MDI: Degrees of Freedom & Steric Groups

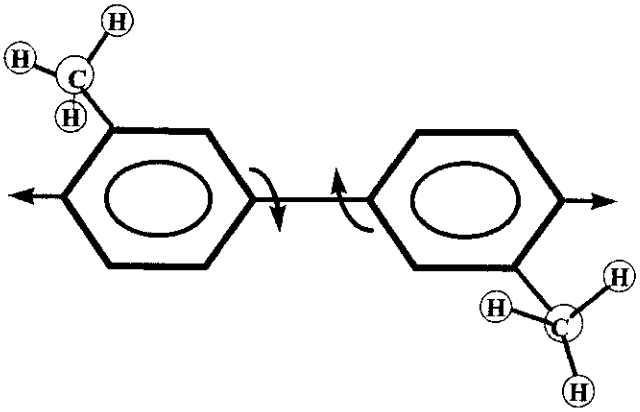

Figure 2. TODI: Degrees of Freedom & Steric Groups

entiate the MDI, TODI, and PPDI monomeric structures. Examination of the basic MDI structure (Figure 1) indicates a degree of rotational preference about the methylene moiety due to steric phenyl hydrogen interactions. This forces the two benzene rings into separate planes. This nonplanar conformational preference coupled with steric interference from the methylene hydrogen atoms promotes inefficient hard segment stacking within the finished polymer. Likewise, examination of the TODI molecular structure (Figure 2) illustrates rotational freedom about the phenyl-phenyl bond as well as steric interactions associated with the pendant methyl groups attached to the phenyl rings. These interactions intuitively appear to have lesser impact due to the planar/linear nature of TODI, when compared to the hingelike methylene structure associated with the MDI molecule. The PPDI structure, as indicated in Figure 3, possesses minimal interactions and provides maximum phenyl stacking efficiency. The effects of these features are illustrated in Figure 4, wherein the monomeric melting points are shown to increase with decreasing rotational degrees of freedom and lower steric interactions. These structural trends are also reflected in the static and dynamic properties exhibited by corresponding TPU formulations, as will be demonstrated in the data presented below.

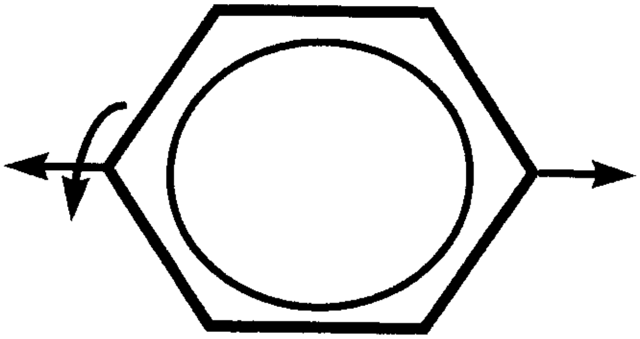

Figure 3. PPDI: Degrees of Freedom

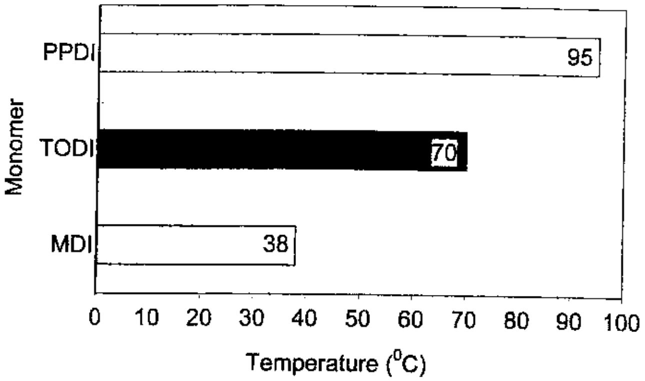

Figure 4. Monomeric Diisocyanate Melting Points

Table 1. Formulation Data

Compound >	MDI TPU	TODI TPU	PPDI TPU
PCL (2000 mw) Equivalents/Weight	1.0 / 1000	1.0 / 1000	1.0 / 1000
1,4 - butanediol Equivalents/Weight	4.4 / 198	3.0 / 135	1.7 / 76.5
Diisocyanate Equivalents/Weight	5.83 / 725	4.45/ 588	2.92 / 233
Prepolymer Temp. (⁰C)	85-90	85-90	85-90

PROCESSING PARAMETERS

MDI, TODI and PPDI injection moldable TPUs were formulated using 2000 molecular weight polycaprolactone and 1,4 - butanediol to yield materials between 93 to 95 Shore A hardness. Each compound was produced via prepolymer preparation by reaction of flaked diisocyanate with polycaprolactone polyol preheated to 100-110°C followed by chain extension with BDO. Specific conditions are presented in Table 1. Reaction mixtures were cast into one inch slabs which were annealed for thirty minutes at 125°C. The resulting polymer slabs were allowed to age at ambient conditions for seven days prior to granulation. The granulated compounds were oven dried for 16 hours at 190°F prior to injection molding of test specimens. Test specimens were annealed at 125°C for 16 hours then allowed to age under ambient conditions for a minimum of ten days prior to testing.

The required proportion of hard segment (Diisocyanate & BDO) to soft segment (PCL) decreases significantly for the preparation of TPUs of similar hardness as the formulation progresses from the MDI based compound to the TODI based material (Figures 5 & 6). This decrease

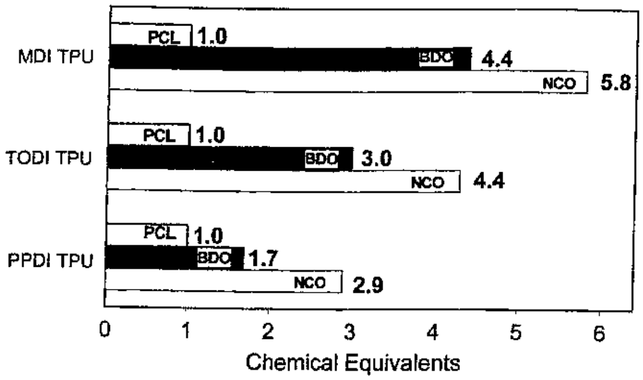

Figure 5. *Stoichiometry (by Chemical Equivalents)*

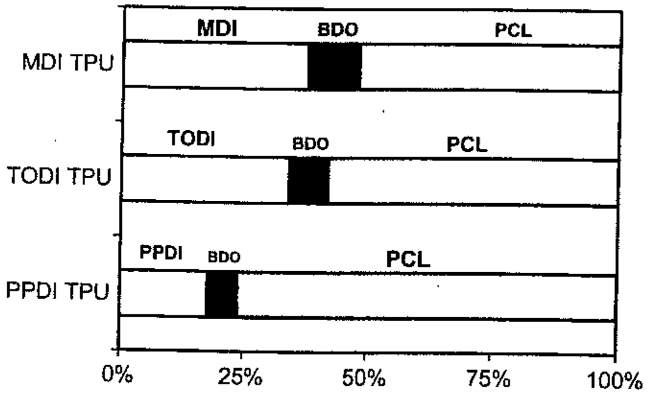

Figure 6. *Component Proportions (% by Weight)*

becomes even more significant in formulating PPDI based TPUs. The minimal amount of PPDI required to achieve a 93A TPU illustrates an increase in hard segment stacking efficiency and enhanced virtual crosslinking within the polymer. This trend also serves to offset the high price of the PPDI monomer.

TEST RESULTS

Basic physical properties for the three TPUs are presented in Table 2. All three compounds exhibit excellent tensile properties and fall within narrow hardness ranges with respect to Shore A and Shore D scales.

Based on initial test results two key areas where the PPDI based TPU shows significant advantage include compression set properties and Bashore resilience. The compression set values imply that the PPDI based material will serve well in high temperature applications. As well, since Demarest and Moore[1] have illustrated a relationship between rebound resilience and DMTA data, additional testing was performed to better define the relative temperature resistance and dynamic characteristics of these three materials.

Table 2. *Original Physical Properties @ R.T.*

Compound > Property	MDI TPU	TODI TPU	PPDI TPU	ASTM No.
Hardness (A/D)	93 / 50	95 / 51	93 / 48	D2240
Tensile strength (psi)	8130	7830	8510	D412
100% Modulus (psi)	1600	2180	2140	D412
300% Modulus (psi)	2350	3270	2860	D412
Elongation, %	450	450	650	D412
Taber Abrasion, 1000g load/H-18 Wheel mg loss/5000 cycles	48.5	244.4	89.5	D1044
NBS Abrasion Index	1547.4	1211.0	1392.7	D1630
Compression set, %				
70 hours @ 70^0 C	26.0	29.8	23.9	D395 b
70 hours @ 100^0 C	51.0	49.1	33.3	D395 b
Bashore Rebound, %	34	45	66	D2632

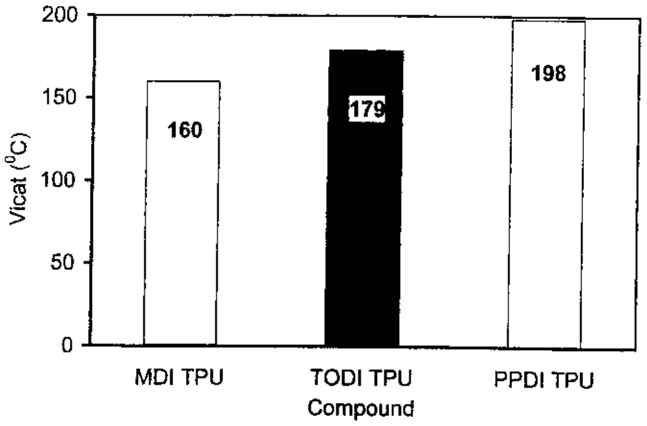

Figure 7. *Vicat Softening Points*

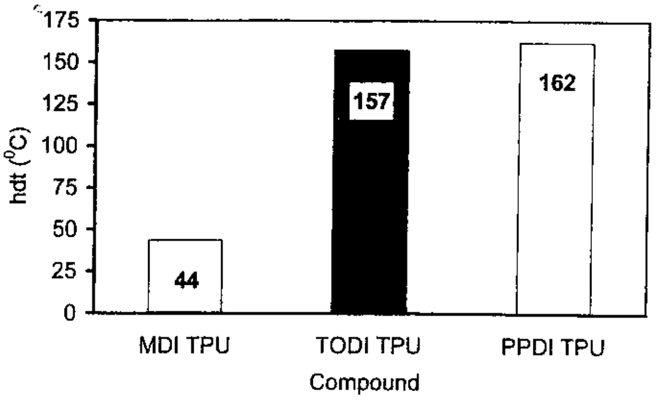

Figure 8. *Heat Distortion Temperatures (°C)*

Vicat softening points (Figure 7) were determined for each compound according to ASTM method D-1525-91 using a VICAT/CSI unit with a 1 mm^2 needle. Failure was defined at 1 mm penetration. Heat deflection temperature values (Figure 8) were also 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 in both sets of tests. The Vicat measurement of 198°C determined for the PPDI sample represents a significant improvement over the other two materials. The

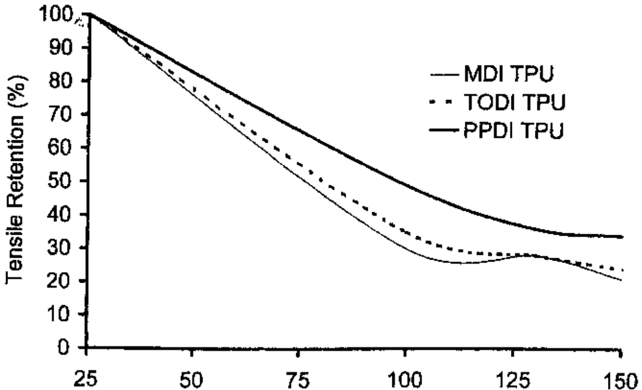

Figure 9. *Tensile Retention vs. Temperature*

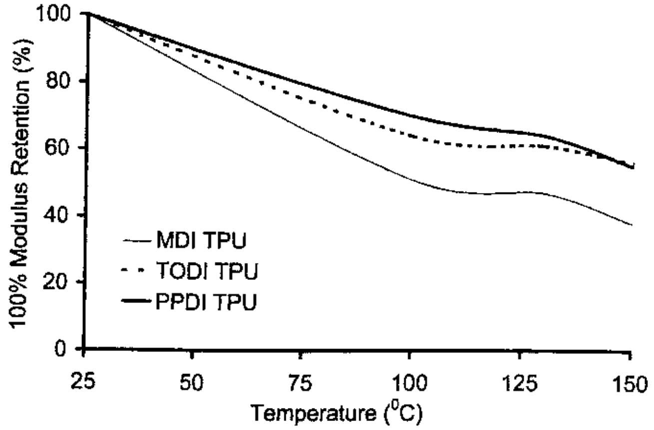

Figure 10. *100% Modulus Retention vs. Temperature*

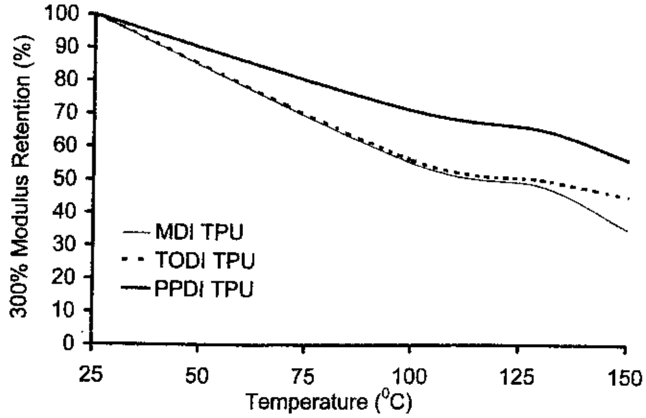

Figure 11. *300% Modulus Retention vs. Temperature*

PPDI heat deflection value indicates a marginal improvement over the TODI sample; but shows a pronounced advantage over the corresponding MDI compound.

Tensile retention values at elevated temperatures (Figure 9) were performed using an Instron environmental tensile chamber. Specimens were conditioned and tested at room temperature, 100, 130, and 150°C. Values for the 100% and 300% moduli were also recorded throughout testing (Figures 10 and 11). The resulting values continue to reflect the increased temperature stability of the PPDI based TPU over the corresponding MDI and TODI formulations.

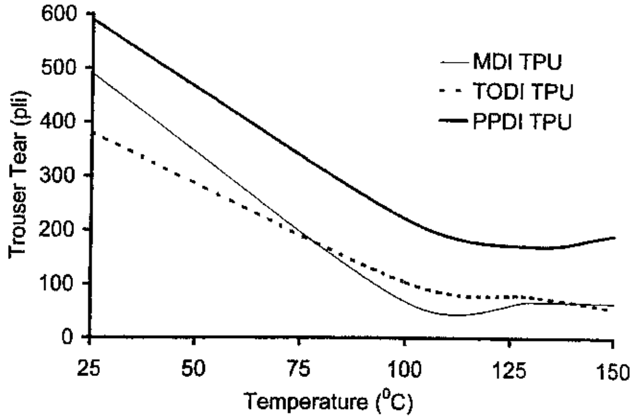

Figure 12. *Trouser Tear vs. Temperature*

Hot Trouser Tear values (Figure 12) were similarly established via ASTM D-1938 using the Instron environmental chamber. The samples were tested at room temperature, 100, 130, and 150°C. The original room temperature value of 590 pli measured for the PPDI based TPU shows an initial Trouser Tear advantage for this polymer under ambient conditions. This advantage is maintained throughout the temperature range studied.

DYNAMIC DATA

Our studies included Rheometric examination of the dynamic behavior of the three subject TPUs. Dynamic test data (Figures 13, 14 & 15) were measured under tensile mode using Rheometrics RSA II instrumentation. Similar comparison data (Figures 16, 17, 18 & 19) were generated under dynamic torsional mode using Rheometrics RVE-S equipment.

The Tensile Storage Moduli E' (Figure 13) and the Shear Storage moduli G' (Figure 16) for both the TODI and PPDI derived polymers retain stable plateaus between approximately 20°C and 175°C with crossover occurring at approximately 180°C. This defines a significantly wide temperature region wherein both polymers maintain consistent elastomeric integrity. The MDI based material, on the other hand, displays a continuous loss of storage modulus throughout the temperature range covered, signifying gradual loss in the elastic integrity of the polymer with increasing temperature.

The corresponding Tensile Loss Moduli E" and the Shear Loss Moduli G" data (Figures 14 and 17 respectively) display the PPDI derived compound as having a low temperature maximum occurring at lower temperatures than the corresponding maxima for the TODI and MDI polymers. This temperature value is associated with the glass transition temperature T_g of each material. Additionally, the lower E" and G" values obtained for the PPDI based compound over the standard application temperature range of between –30°C and 125°C indicate significantly lower heat build up associated with applied forces in application.

Significant features of the Tan δ data presented for both test modes (Figures 15 and 18) include: (1) the location of the low temperature maxima, again T_g related, (2) the surface area under the low temperature maxima, (3) the

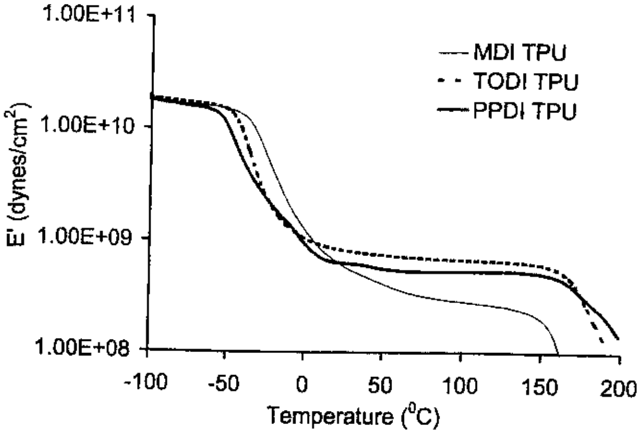

Figure 13. Tensile Storage Modulus (E') vs. Temperature

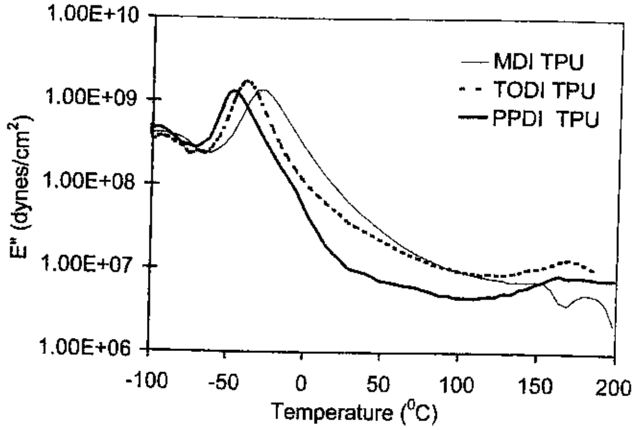

Figure 14. Tensile Loss Modulus (E") vs. Temperature

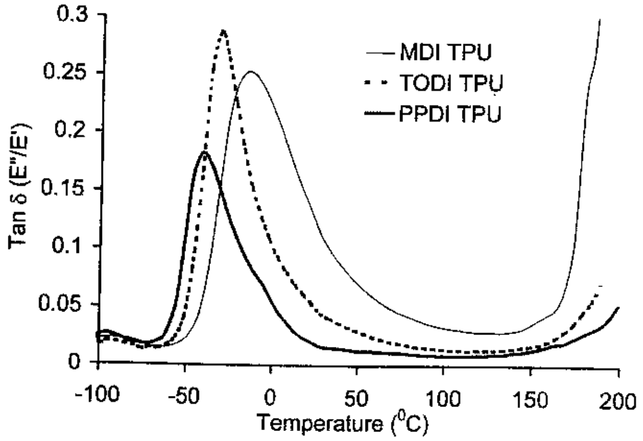

Figure 15. Tan δ (E"/E') vs. Temperature

magnitude of Tan δ across the application temperature range and (4) the location of the high temperature upturn. The test data indicate that the PPDI derived TPU has the lowest T_g of the three polymers. The small value of the PPDI Tan δ integral through T_g indicates more efficient phase separation and/or less hard segment involved in the glass transition. The low Tan δ values across the practical application range (–30°C-125°C) indicate a lower ratio of

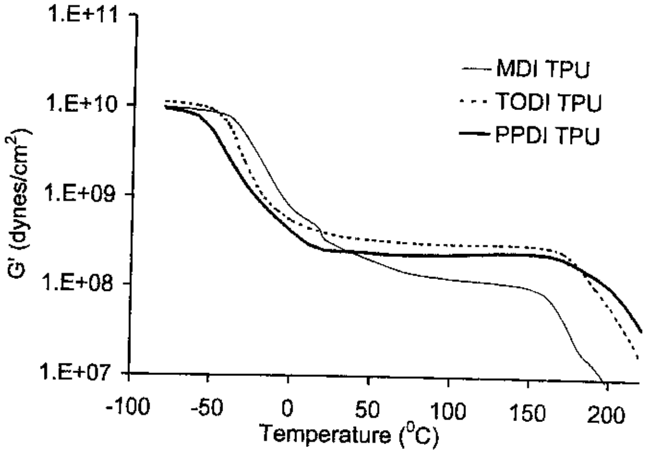

Figure 16. Shear Storage Modulus (G') vs. Temperature

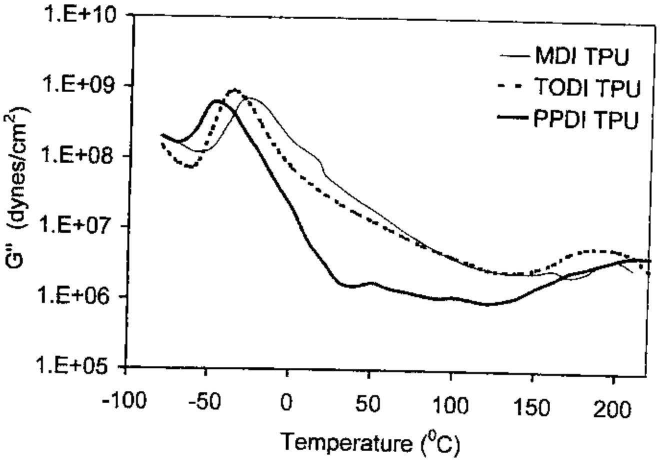

Figure 17. Shear Loss Modulus (G") vs. Temperature

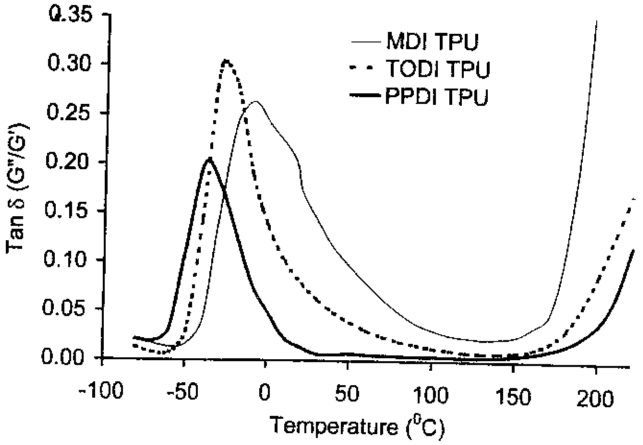

Figure 18. Tan δ (G"/G') vs. Temperature

energy absorbed as heat by the sample to energy returned as resilience by the sample. Finally, the higher temperature upturn of the Tan δ value verifies the higher softening temperature for the PPDI formulation.

Power loss data were determined from shear modulus data and is presented in Figure 19. The extremely low and

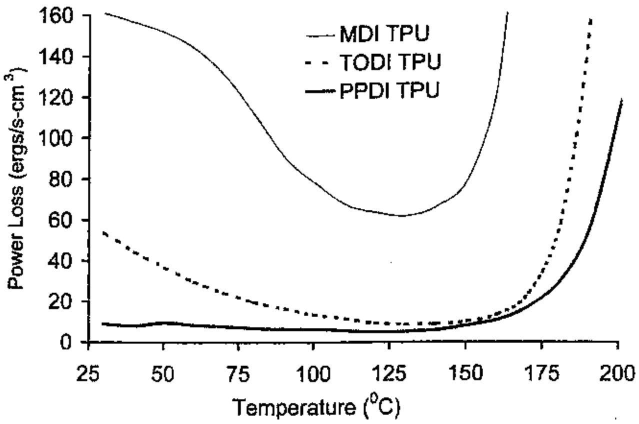

Figure 19. *Power Loss vs. Temperature*

Table 3. *Texus Flex Data*

Compound	Average Cycles to Failure
Test Data @ 30^0 Deflection @ 70^{0}C	
MDI TPU	215,000
TODI TPU	940,000
PPDI TPU	4,600,000*
Test Data @ 45^0 Deflection @ 70^{0}C	
MDI TPU	80,000
TODI TPU	470,000
PPDI TPU	4,510,000**

*None of the 6 samples failed; average cut growth =.13
**None of the 6 samples failed; average cut growth=.50

constant values produced by the PPDI based TPU illustrate significantly low heat absorption under cyclic loading. This single feature makes PPDI stand out as the hard segment of choice for engineering applications involving high cyclic loading.

TEXUS FLEX FATIGUE

Texus Flex data are included in Table 3. Tests were run at a 30° angle of deflection and a 45° angle of deflection. Both sets of data were generated at 70°C. The significant lack of cut growth within the PPDI based samples demonstrates the tenacious resistance that this material has to crack propagation.

A cautionary note should be made at this point. None of the formulation stoichiometries used in this study were optimized for fatigue resistance. Palinkas[2] has demonstrated the sensitive nature of Texus Flex results to variations in stoichiometry and to the chemical nature of the base polymer backbone. Therefore, the results acquired for the TODI and MDI based TPUs used in this study should not be used as benchmarks for other formulations produced from these specific diisocyanates. This does, however, raise an interesting challenge as to the full potential of PPDI in formulating the ultimate in a fatigue resistant polyurethane.

CONCLUSIONS

The inherently simple rigid chemical structure of DuPont's Hylene® PPDI (p-phenylenediisocyanate) allows the preparation of thermoplastic polyurethanes which exhibit extraordinary high temperature stability. The compression set, Vicat softening and tensile retention data verify that PPDI expands the high temperature performance of TPUs to well beyond traditional limits. More remarkably, the loss modulus, Tan δ and power loss measurements indicate that PPDI based materials are capable of redefining the role that TPU technology will play in future dynamic materials engineering technology. PPDI based TPUs are beginning to make inroads to dynamic applications where previously only thermoset materials dared to enter. Some of these dynamic applications include, but are not limited to, high load wheels, mechanical couplings, diaphragms, high impact bumpers, and seals.

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BIOGRAPHIES

Thomas L. Plummer

Tom Plummer served six years at Uniroyal in elastomers research and rubber compounding prior to joining Parker-Hannifin Corporation in 1981 as a research chemist. Mr. Plummer has served over ten years as Polymer Research Manager at Parker's Salt Lake City laboratory; Parker-Hannifin Corporation's main U.S. center for Thermoplastic Polyurethane research. He received his degree in organic chemistry from Wayne State University in 1974.

Val C. Comes

Val Comes earned his B.S.Ch.E. degree at the University of Utah in 1977. At present, he is the Chief Process Engineer for the Packing Division of Parker Hannifin Corporation and is an adjunct instructor at the Salt Lake Community College. He has spent more than 22 years with Parker in the development of polymers, products, and processes.

George R. Wallace

George Wallace earned his B.S. in Chemical Engineering from North Carolina State University in 1991. He is currently pursuing an advanced degree from the University of Utah, where he is studying relationships between the dielectric and mechanical relaxation spectra of thermoplastic polyurethane elastomers. He is simultaneously carrying out his responsibilities as a Process Engineer for Parker-Hannifin Corporation. His work at the Packing Division includes analyzing the effects of modifications to TPU chain structure on both injection molding operations and polymer physical properties.

James Chin

James Chin—Sr. Research Scientist, Uniroyal Chem. Co Incorp.; BCHE 63 Ohio State U.; spent more than 30 years in product/process R&D of polymers (ABS, thermoplastics, TPU, TPE, TPR, & liquid casting systems) with 20+ years of it in polyurethane polymers.

Joseph P. Haley

Joe Haley is a Technical Service Representative for DuPont Chemicals and supports products associated with polyurethane chemistry including Terathane, BDO, THF, Hylene® PPDI and TPE. He studied biology and chemistry at the University of Delaware.