

THE EFFECTS OF CBDO MONOMER ON THE THERMO/MECHANICAL PROPERTIES
OF POLYURETHANES

THESIS

Presented to the Graduate Council of
Texas State University-San Marcos
in Partial Fulfillment
of the Requirements

for the Degree

Master of SCIENCE

by

Megan L. Smith, B.A.

San Marcos, Texas
August, 2010

COPYRIGHT

by

Megan L. Smith

2010

ACKNOWLEDGEMENTS

I would like to thank my research advisor and chair of my committee, Dr. Chad Booth, as well as my committee members, Dr. Patrick Cassidy and Dr. Clois Powell for their guidance, support, and time they have willingly given me throughout my graduate career. Along with my committee members, I would like to thank the other members in my research group, Kristen Suprobo, Alisa Sokolova, Alberto Cisneros, and John Boatwright for the time they spent helping me in the lab. I would also like to thank our lab technician, Al Martinez for running my TGA, DSC, and DMA samples, Dr. Michelle Londa for being so generous to allow me to use some of her chemicals, and the Welch Foundation for funding my research during the summer of 2009.

This manuscript was submitted on May 21, 2010.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS.....	iv
LIST OF TABLES	vii
LIST OF FIGURES	viii
ABSTRACT.....	ix
CHAPTER	
1.0 INTRODUCTION	1
2.0 EXPERIMENTAL.....	9
2.1 Materials	9
2.2 Synthetic Methods	9
2.3 Characterization Methods	12
2.3.1 Thermogravimetric Analysis.....	12
2.3.2 Dynamic Mechanical Analysis	13
2.3.3 Dart Impact	13
3.0 RESULTS	14
3.1 Thermogravimetric Analysis.....	14
3.2 Dynamic Mechanical Analysis.....	14
3.3 Dart Impact	15
4.0 DISCUSSION.....	16
4.1 Thermogravimetric Analysis.....	16
4.2 Dynamic Mechanical Analysis.....	16
4.3 Dart Impact	17
5.0 CONCLUSIONS.....	19

APPENDIX A: TGA Data.....	20
APPENDIX B: DMA and DSC Data	24
REFERENCES	29

LIST OF TABLES

Table	Page
1. Calculated amounts of CBDO and PDO for each polymer in the 60% hard segment polyurethane system.....	10
2. The 10% Weight Loss Temperatures obtained from the TGA's of the polymer samples	13
3. The T_g and Storage Modulus at $-100\text{ }^\circ\text{C}$ and $0\text{ }^\circ\text{C}$ for each polymer sample .	14

LIST OF FIGURES

Figure	Page
1. General synthesis of a polyurethane	1
2. Structure of polypropylene glycol, a polyester polyol (A ⁶) and polyester tetrol, a polyester polyol (B ⁷)	3
3. Representation of the hard segments and soft segments making up a semi-crystalline polymer	3
4. The effect hard segment content has on the elastic modulus of a polymer	4
5. Structure of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO).....	5
6. Synthesis of CBDO	5
7. The CBDO containing co-polyterephthalate reported by Kelsey	6
8. The effect the percentage of CBDO has on the impact resistance and T _g values of terephthalate copolymers made with 1,3-PDO (squares) and 1,4-BDO (circles)	7
9. Proposed polyurethane synthesis	8
10. The effect percent nanocomposite has on the storage modulus of copolyterephthalates	16

ABSTRACT

THE EFFECTS OF CBDO MONOMER ON THE THERMO/MECHANICAL PROPERTIES OF POLYURETHANES

by

Megan L. Smith, B.A.

Texas State University-San Marcos

May 2010

SUPERVISING PROFESSOR: CHAD BOOTH

Research has shown that when 40% 2,2,4,4-tetramethyl-1,3-cyclobutane diol (CBDO) is incorporated into terephthalate copolyesters, an impact resistance of 1070 J/m is measured. Cycloaliphatic monomers, like CBDO, normally are not rigid enough to produce materials with high mechanical strength. It has been postulated that the cis isomer of CBDO makes kinks in the polymer structure, which help to absorb the force upon impact and thus, improve the impact resistance of the material. This project involves the synthesis of a series of polyurethanes using CBDO and 1,3-propanediol (PDO) monomers in varying ratios. Although some of the trends observed in the thermal analysis and impact data concur with those found in the copolyester research, high impact resistances were not observed in this system.

1.0 INTRODUCTION

Polyurethanes are commonly synthesized by the reaction of a diisocyanate (2,2, 2,4, or 4,4-methylene diphenyl diisocyanate (MDI), 2,4 or 2,6-toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), or naphthalene 1,5-diisocyanate (NDI)) with a diol (1,3-propanediol (PDO), 1,4-butanediol (BDO), ethylene glycol (EG), or 1,6-hexanediol (HDO)) (Figure 1).

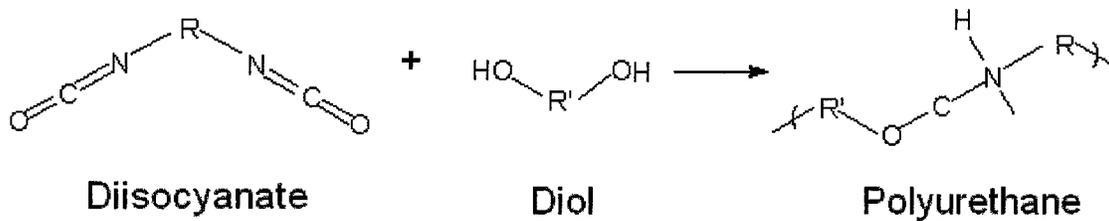


Figure 1: General synthesis of a polyurethane.

In most urethane systems, a catalyst(s) and polyol are added in addition to the monomers in Figure 1. Without the addition of the polyol, the polymer is typically brittle. Polyols, generally, are polyester or polyether based organic compounds that have at least one hydroxyl group attached at each end (Figure 2). The molecular weight of a polyol typically varies from 400 g/mol to 7000 g/mol. As the molecular weight of the polyol increases, the flexibility of the polymer increases. The mechanical properties of polyurethanes are dictated by the molecular weight of the polyol, the type of polyol used, and

the ratio of polyol, diisocyanate, and diol used. Catalysts such as triethylenediamine, dibutyl tin dilaurate, or bismuth octanoate are typically added to increase the rate of polymerization. The selected catalyst(s) serves as a good nucleophile in the system. Because the oxygen atom is electronegative, the electron density in the O-H bond is concentrated on the oxygen atom. The lack of the electron density being shared evenly between the oxygen and hydrogen atom causes the hydrogen atom to have a partial positive charge. The electrons from the catalyst are able to coordinate with the hydrogen atom to make the oxygen atom have a partial negative charge, causing it to be very reactive towards the electrophilic carbon atom on the isocyanate group.

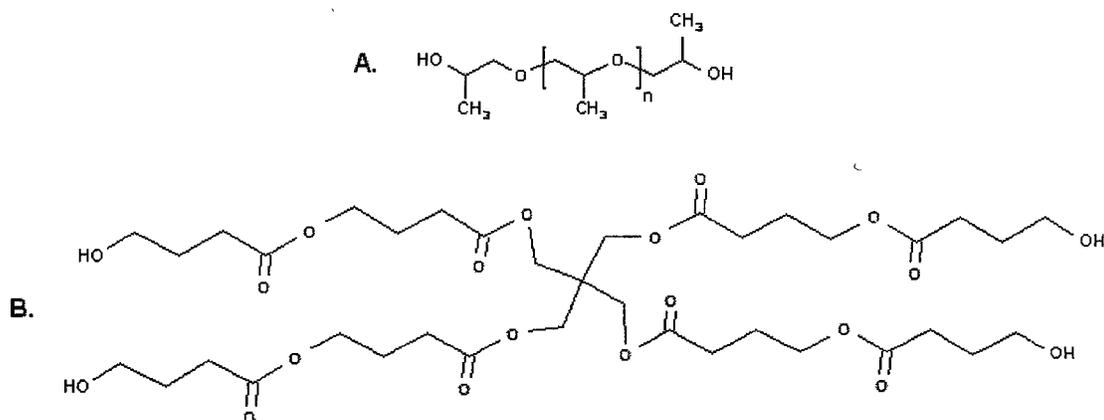


Figure 2: Structure of polypropylene glycol, a polyether polyol (A⁶) and polyester tetrol, a polyester polyol (B⁷).

The percentages of hard segment and soft segment in the polymer system are significant independent variables that, in addition to the polyol, affect the mechanical properties of the polymer⁵. Typically in polyurethanes, the polyol makes up the soft segment while the urethane linkages, produced

from the reaction of a diisocyanate with a diol, make up the hard segment (Figure 3)⁵. The hard segments of each polymer chain aggregate through hydrogen bonding to form hard segment domains. As the percent hard segment in a polymer system decreases, the likelihood of the chains aggregating also decreases. This decreases the number and amount of hard segment domains and makes the polymer softer and less elastic. Research shows that as the percent hard segment of hydroxyl-terminated polybutadiene based polyurethanes is increased, the storage modulus of elasticity is increased regardless of the compound making up the hard segment (PDO, BDO, HDO, or dihydroxy isopropyl-N-aniline (DHPA) (Figure 4)². The amount of order, structurally, in a polymer system dictates its overall mechanical properties.

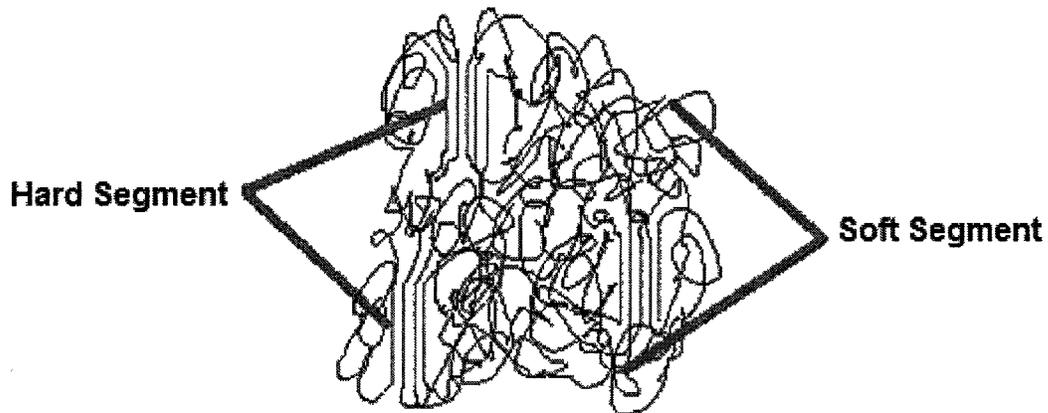


Figure 3: Representation of the hard segments and soft segments making up a semi-crystalline polymer.

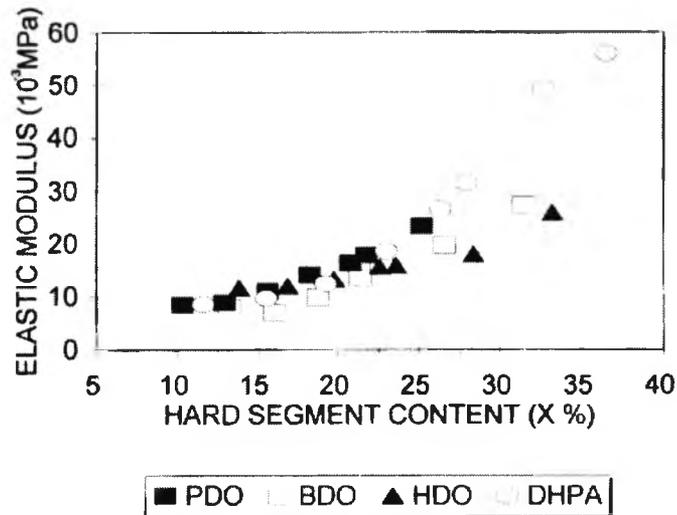


Figure 4²: The effect hard segment content has on the elastic modulus of a polymer.

Polyurethanes are unique because they are some of the most versatile of all polymeric materials. The mechanical properties of the polymer can be altered by changing one or more of the factors previously discussed (molecular weight of the polyol, type of polyol, *etc.*) to obtain the characteristics for a desired application. Polyurethanes can be synthesized, using the method discussed herein or alternate methods, to make foams (a more common application), elastomers, coatings, and adhesives. The applications of polyurethane foams include: mattresses, upholstered furniture, seat cushions, roofing, and insulation. The applications of elastomers include: forklift tires, skateboard wheels, automobile tires, and sporting goods².

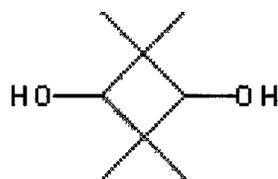


Figure 5: Structure of 2,2,4,4-tetramethyl-1,3-cyclobutanediol

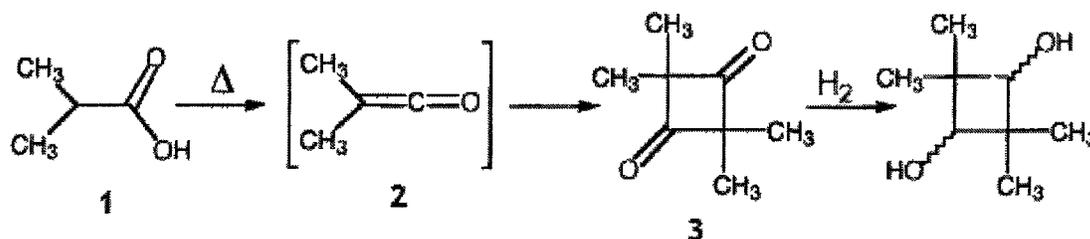


Figure 6¹: Synthesis of CBDO.

2,2,4,4-Tetramethyl-1,3-cyclobutanediol (CBDO) (Figure 5) is a unique aliphatic diol monomer that has gained much interest over the past decade. It is synthesized by pyrolysis of isobutyric acid (1) or isobutyric anhydride to form dimethylketene (2), which spontaneously dimerizes through an allowed 2 + 2 concerted addition to the cyclic diketone (3) (Figure 6)¹. When the p-orbitals in the C-C double bond of one ketene molecule are orthogonal to those in another ketene molecule, orbital interaction occurs. The p-orbital that is closest to the methyl groups in one ketene molecule overlaps suprafacial with the p-orbital closest to the oxygen atom in the other ketene molecule while the p-orbital from each molecule overlaps antarafacial resulting in the formation of the diketone. Hydrogenation of the cyclic diketone using ruthenium, nickel, or rhodium catalysts results in the formation of a cis/trans mixture of 2,2,4,4-tetramethyl-1,3-cyclobutanediol¹.

The incorporation of CBDO into the backbone of polyesters increases the rigidity of the system³. This observation is unusual because normally, when cycloaliphatic monomers are introduced into a polymer system, they do not have enough rigidity to produce polymers with high mechanical strength.

Bisphenol A polycarbonate, which has an impact resistance of approximately 850 J/m, has been used the past 40 years in military and civilian security and protection applications³. Research has shown that when CBDO is copolymerized into polyesters, high T_g 's (glass transition temperatures) and improved impact resistance is observed. In 2000, Kelsey from Shell Chemical Company reported a new polyester, that contained the CBDO monomer, (Figure 7) to have an impact resistance of 1080 J/m³.

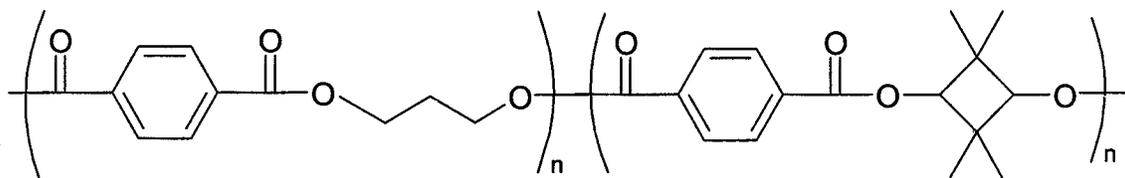


Figure 7³: The CBDO containing co-polyterephthalate reported by Kelsey.

Results from a study involving terephthalate copolymers containing CBDO and PDO show that as the CBDO mole content in the polymer increases, lower impact resistances and higher T_g values are observed (Figure 8)¹. Based on these data, the highest impact resistances are observed when the CBDO content in the polymer is below 60%¹. When the polymer contained approximately 40% CBDO, an impact resistance of 1070 J/m and a T_g value of 85 °C were observed¹.

Molecular models of the copolymer containing only the cis or trans isomer of CBDO show that the structures are very different³. The structure of the copolymer with only the trans isomer appears to be linear while that of only the cis isomer tends to be kinked³. It is believed that the kinks in the copolymer help to absorb impact, thus leading to a higher impact-resistant material³.

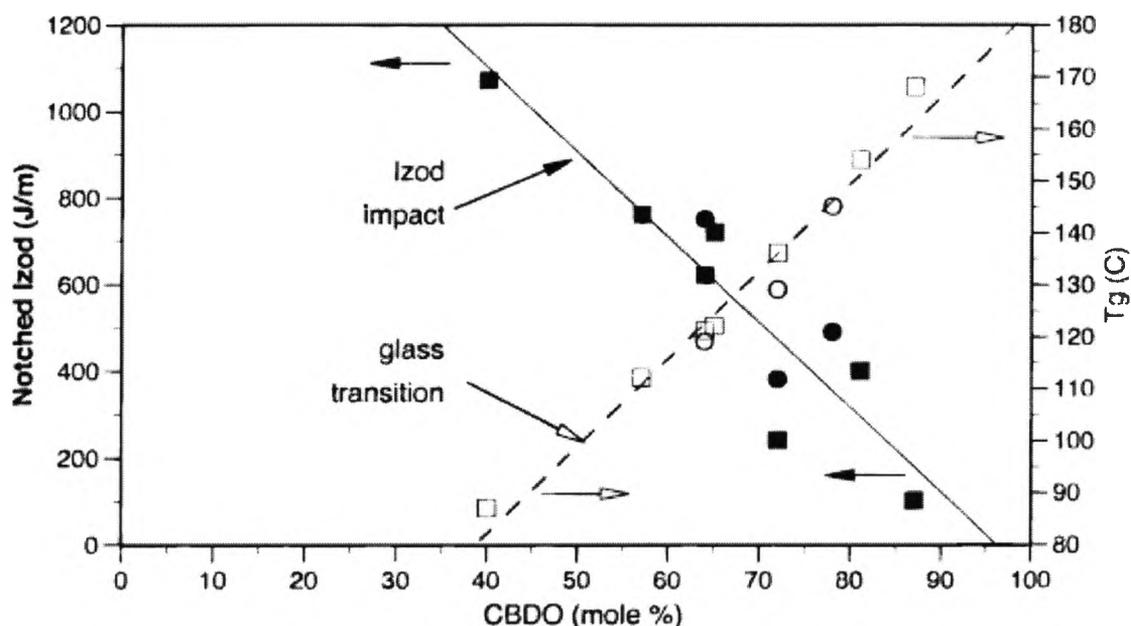


Figure 8¹: The effect the percentage of CBDO has on the impact resistance and T_g values of terephthalate copolymers made with 1,3-PDO (squares) and 1,4-BDO (circles).

The repeat unit of the polyurethanes to be synthesized in this research project is shown in Figure 9. A series of polyurethanes will be made using MDI, PDO, CBDO, polyol 1000 (polypropylene glycol, a polyether polyol with a molecular weight of 1000 g/mol), and triethylenediamine (TEDA). The percent hard segment *versus* soft segment for each polymer made in this series is 60%

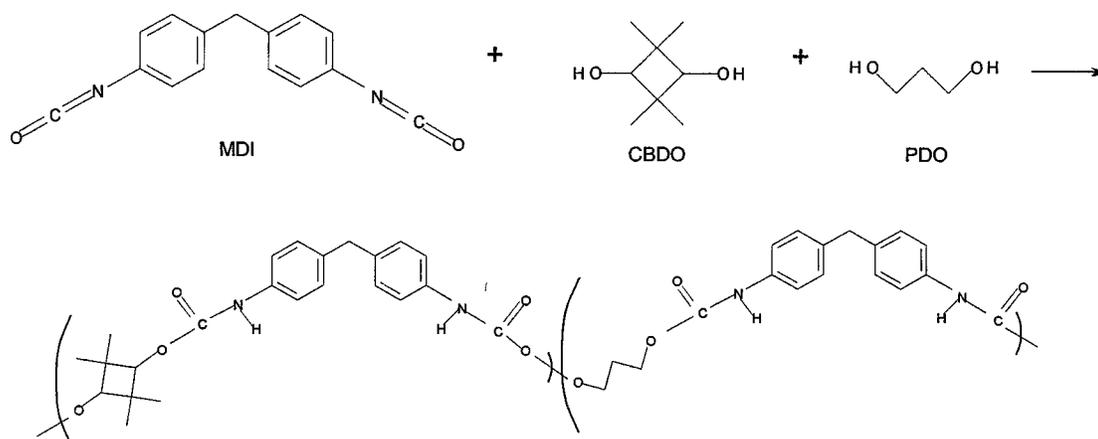


Figure 9: Proposed polyurethane synthesis.

(total diol content) to 40%. The amount of polyol used to synthesize each polymer will remain the same while the amount of CBDO relative to PDO will vary. The polymers to be made in the series are: 60% CBDO / 0% PDO, 40% CBDO / 20% PDO, 20% CBDO / 40% PDO, and 60% PDO / 0% PDO. The actual percent incorporation of CBDO and PDO in each polymer sample can be found by dividing 60% by the percentage of the component in the polymer sample. Each polymer will be characterized using thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). The impact resistance of each polymer will be measured using dart impact. If high impact resistance is observed in these polymers, they could potentially be incorporated into the materials used for low speed impact-resistant material applications.

2.0 EXPERIMENTAL

2.1 Materials

MDI (SUPRASEC 9651), polyol 1000 (JEFFOL PPG), and TEDA (JEFFCAT TD-33A) were donated by Huntsman Polyurethanes and were used without further purification. CBDO (cis/trans ratio of 46/54 and 98% purity) was purchased from TCI America and used as received. PDO was donated by Shell Chemical Company and used as received.

2.2 Synthetic Methods

Three different methods of polymerization were attempted during this research. The first method involved bulk polymerizations, the second method involved making an MDI-CBDO-MDI trimer, and the third method involved solution polymerizations. Although the first two methods were unsuccessful for different reasons, they provided useful information that helped establish the final method.

In the first method, calculated stoichiometric amounts of the reagents used for the polymerization (a mixture of 80% 2,4-TDI and 20% 2,2-TDI, polyol 1000, PDO, and TEDA) were weighed out in a drybox, mixed, and poured into a plastic container. Because most of the reagents used for the polymerization are sensitive to moisture, measurements were carried out in a drybox. Once

the container was removed from the drybox, it was put into a vacuum oven at 80 °C. The pressure in the vacuum oven was increased slowly until the maximum pressure of 30 KPa was reached. After most of the bubbling of the mixture subsided, the container was removed from the oven and placed into an oven at 80 °C for 24 hours to cure.

This method had two disadvantages that led it to be unsuccessful. All polymers made using this method suffered from bubble formation. Also, CBDO sublimes at 70 °C. Because temperatures of 80 °C were needed and used, CBDO was subliming, which led to a stoichiometric imbalance in the monomer ratio.

In the second method, an MDI-CBDO-MDI trimer was made using 4,4-MDI and CBDO. Calculated amounts of MDI and CBDO were weighed out and put into a glass vial containing a stir bar. The mixture was heated to 50 °C and stirred for approximately 24 hours or until all the CBDO was dissolved. The trimer was added to a stoichiometric amount of polyol 3800 and TEDA in a drybox. The mixture was stirred, poured into a plastic container, and removed from the drybox. The container was put into a vacuum oven at 80 °C. The pressure in the vacuum oven was increased slowly until the maximum pressure of 30 KPa was reached. Once bubbling of the mixture subsided, the container was removed from the vacuum oven and put into an oven at 80 °C for 24 hours to cure.

Although this method was successful in eliminating the bubble issue, a maximum of 50% CBDO could be incorporated into the polymers. The thermo/mechanical properties of polyurethanes containing higher percentages of CBDO were of interest.

In the final method, the materials needed for the polymerization were put into a chamber connected to the drybox with a moisture content of 14.3 ppm (dew point -72.0 °F). The chamber, connected to a vacuum pump and an argon tank, was degassed for approximately ten minutes and then filled with argon. This procedure was repeated once more. The chamber was then opened from the inside of the drybox and the components used for the reaction were weighed out and put into a three-neck, round-bottom flask containing a stir bar. Although the relative amounts of CBDO and PDO used to make the polymers varied, the following remained constant: 60 mL dry THF, 3.96 g (0.00989 mol) polyol, 3.00 g (0.00989 mol) MDI (with the addition of a 5% excess (3.15 g)), and 4 drops of TEDA. The THF was dried using benzophenone and sodium. The THF was allowed to reflux for at least one hour under argon before it was collected and used. The calculated amounts of CBDO and PDO required for each polymer in the series is shown in Table 1. Once all of the components were added to the flask, a septum was put into each neck to prevent moisture from entering the flask. The flask was then removed from the drybox. An adapter containing a thermometer was put into the left neck, a condenser into the middle neck, and a septum in the right neck. A balloon filled with argon was put onto the top of the condenser to allow the

polymerization to occur in an inert atmosphere. A heating mantle was used to gently reflux the mixture for approximately 28 hours at 70 °C. After 28 hours, the apparatus was disassembled and the polymer was precipitated by pouring the reaction mixture slowly into approximately 300 mL of methanol that was cooled by an icebath. The solution was constantly magnetically stirred. The precipitate was then filtered off and allowed to dry for approximately 24 hours. Once dry, the precipitate was dissolved in 65 °C THF and the solution was cast onto a Teflon plate. The average concentration of each solution was 0.52 g/mL. After 24 hours, the polymer was prepared for thermo/mechanical analysis. This method was successful because it kept the polymers bubble free and allowed 100% CBDO to be incorporated into the polymers.

Table 1: Calculated amounts of CBDO and PDO for each polymer in the 60% hard segment polyurethane system.

	CBDO	PDO
60% CBDO/0% PDO	0.86 g	0 g
40% CBDO/20% PDO	0.57 g	0.15 g
20% CBDO/40% PDO	0.30 g	0.29 g
0% CBDO/ 60% PDO	0 g	0.45 g

2.3 Characterization Methods

2.3.1 Thermogravimetric Analysis

The TGA's were measured on a TA Instruments Q50 thermal gravimetric analyzer. For each sample, the analysis was carried out with an air flow rate

of 60.0 mL/min from ambient temperature to 800.00 °C at 20.00 °C/min. The samples weighed between 4 and 6 mg. TGA data show the percent weight loss, or degradation, of a polymer sample as a function of temperature. These data determines the temperature range at which a polymer sample can be successfully used at for a desired application.

2.3.2 Dynamic Mechanical Analysis

The DMA's were measured on a TA Instruments Q800 dynamic mechanical analyzer using liquid nitrogen as the cooling gas. The data for each polymer sample were collected from -150.00 °C to 70.00 °C every 5.00 °C. A tensile configuration was used. DMA data show the T_g and storage modulus (the force required to stretch the sample 125%) as a function of temperature of a polymer sample. The DMA bars were 20 mm long. The width of each bar, ranging from 2-5 mm, was dependent on the thickness of the film (*i.e.* a thickness of 0.3 mm corresponds to a width of 3 mm).

2.3.3 Dart Impact

Impact data were obtained using a Qualitest dart impact tester equipped with either an eight or half-pound weight. The impact resistance of the 60% PDO / 0% CBDO polymer was obtained using an 8 pound weight, while a half-pound weight was used for the 40% PDO / 20% CBDO, 20% PDO / 40% CBDO, and 0% PDO / 60% CBDO polymer samples. The weights were dropped from calibrated distances, which are proportional to the amount of force applied to the sample.

3.0 RESULTS

3.1 Thermogravimetric Analysis

The decomposition temperature was identified as the temperature at which the material lost 10% of its mass. These values are shown in the table below.

Table 2: The 10% Weight Loss Temperatures obtained from the TGA's of the polymer samples.

Sample	10% Weight Loss Temperature
60% PDO / 0% CBDO	289 °C
40% PDO / 20% CBDO	288 °C
20% PDO / 40% CBDO	300 °C
0% PDO / 60% CBDO	301 °C

3.2 Dynamic Mechanical Analysis

Although DSC data was obtained, the T_g values could not be determined (Figure 19). The DMA $\tan \delta$ values were reported as the T_g 's for the polymer samples. The T_g and storage modulus at -100 °C and 0 °C of each polymer sample are shown in Table 3.

Table 3: The T_g and Storage Modulus at $-100\text{ }^\circ\text{C}$ and $0\text{ }^\circ\text{C}$ for each polymer sample.

Sample	T_g	Storage Modulus at $-100\text{ }^\circ\text{C}$	Storage Modulus at $0\text{ }^\circ\text{C}$
60% PDO / 0% CBDO	$7\text{ }^\circ\text{C}$	4458 MPa	168.2 MPa
40% PDO / 20% CBDO	$21\text{ }^\circ\text{C}$	4388 MPa	882.6 MPa
20% PDO / 40% CBDO	$34\text{ }^\circ\text{C}$	4160 MPa	1883 MPa
0% PDO / 60% CBDO	$28\text{ }^\circ\text{C}$	3078 MPa	1307 MPa

3.3 Dart Impact

The 60% PDO / 0% CBDO sample had an impact resistance of 40 in·lbs and the 40% PDO / 20% CBDO sample had an impact resistance of 7.5 in·lbs. The 20% PDO / 40% CBDO and 0% PDO / 60% CBDO samples failed when the minimum force was applied (0.5 in·lbs).

4.0 DISCUSSION

4.1 Thermogravimetric Analysis

As the percentage of PDO relative to CBDO in the polymer sample increased, the decomposition temperature (10% weight loss) decreased. It is believed that when the polymer sample is heated, the O-R bonds present in the sample cleave. An increased percentage of PDO in the polymer sample would increase the amount of O-R bonds cleaved, resulting in lower decomposition temperatures. Research supporting these results show that a 87/13 CBDO/PDO terephthalate copolymer has 5% weight loss temperatures of 417 °C and 392 °C while a 64/36 CBDO/PDO copolymer has 5% weight loss temperatures of 393 °C and 382 °C¹.

4.2 Dynamic Mechanical Analysis

Data in Figure 8 show that as the percentage of CBDO in the copolyester increased, the T_g also increased. With the standard deviation of the T_g values listed in Table 3 taken into account, this same trend holds true for this particular urethane system.

Other data show that as the percent nanocomposite (made with a CBDO containing copolyterephthalate and Cloisite 20A clay) in copolyterephthalates

increases, the storage modulus (*i.e.* stiffness) increases (Figure 10)⁴. This trend is not observed in the urethane system studied. As shown in Table 3, as the percent CBDO in the polyurethane increased, the storage modulus decreased at -100 °C.

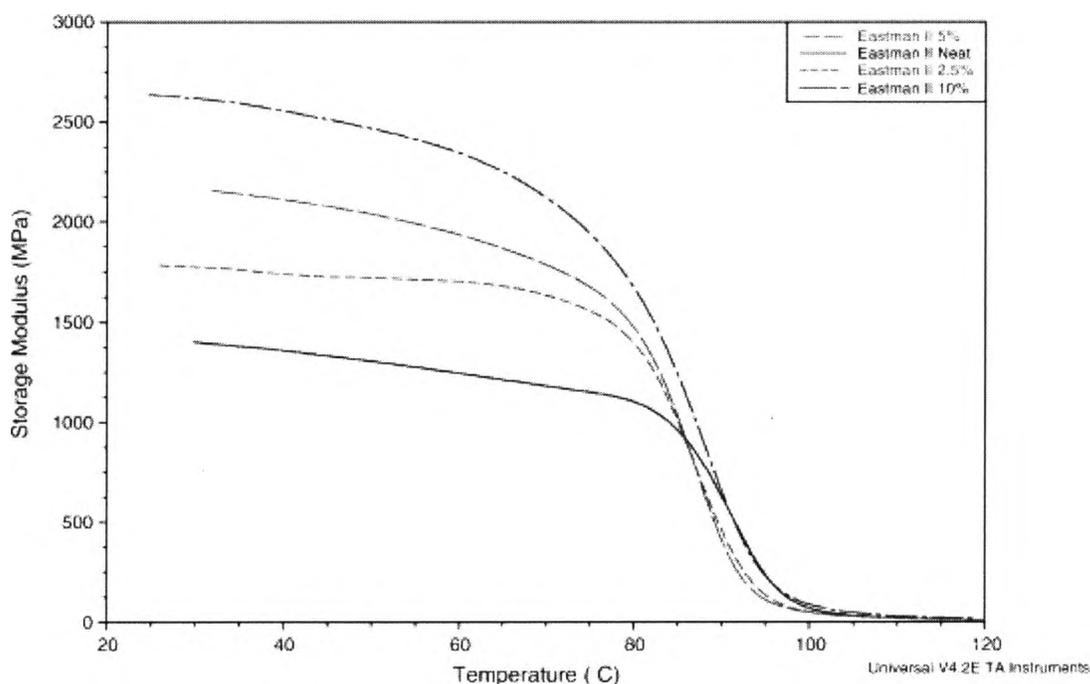


Figure 10⁴: The effect percent nanocomposite has on the storage modulus of copolyterephthalates.

4.3 Dart Impact

Data in Figure 8 also show that as the percentage of CBDO in the copolymer increased, the impact resistance decreased. Although data could not be collected on the two polyurethane samples containing 100% CBDO and 67% CBDO, the trend seems to hold true in this particular urethane system.

Because CBDO is rigid, general knowledge suggests that its incorporation into the backbone of a polymer chain would increase the brittleness (due to a

decrease in conformational flexibility) and thus, decrease the impact resistance. Although the copolyester work showed that the incorporation of CBDO into the backbone of this particular system resulted in high impact-resistant materials, this observation was not seen in the urethane system studied.

5.0 CONCLUSIONS

A series of polymers with varying ratios of CBDO to PDO were synthesized *via* solution polymerization techniques and characterized by TGA, DMA, and dart impact.

As the percent incorporation of CBDO increased, the 10% weight loss temperature increased. As previously mentioned, it is believed that the O-R bonds in the polymer sample cleave when the sample is heated. An increased percentage of PDO in the polymer sample results in a greater number of O-R bonds cleaved which results in lower degradation temperatures.

The incorporation of CBDO into the urethane system resulted in higher T_g values and lower impact resistances. These trends concur with those shown for the copolyester system in Figure 8. Although both of these trends were observed in the urethane system studied herein, high impact values were not obtained. As general knowledge suggests, the incorporation of a rigid monomer into the backbone of a polymer chain should increase the brittleness of the material, thus decreasing its impact resistance.

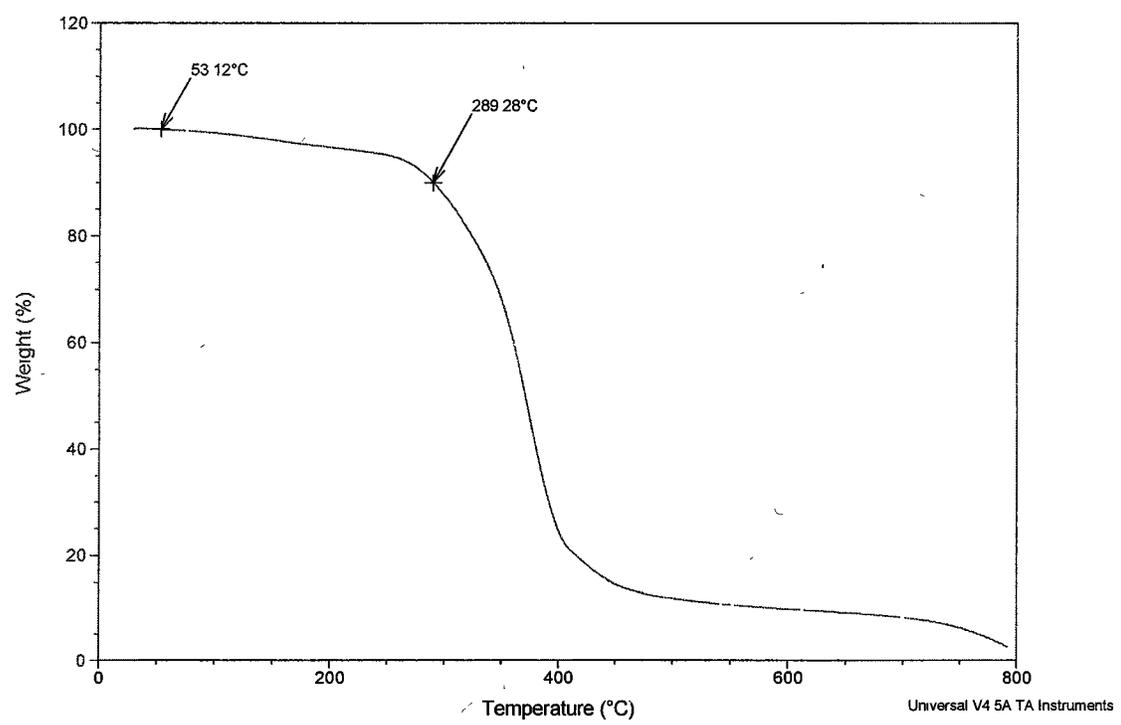
APPENDIX A

TGA Data

Sample PDO 60%_5 2mg
Size 5 1910 mg
Method Normal_Procedure

TGA

File T\TGA\Booth\Megan\PDO 60%_5 2mg
Operator Martinez
Run Date 24-Nov-2009 09 55
Instrument TGA Q50 V6 7 Build 203

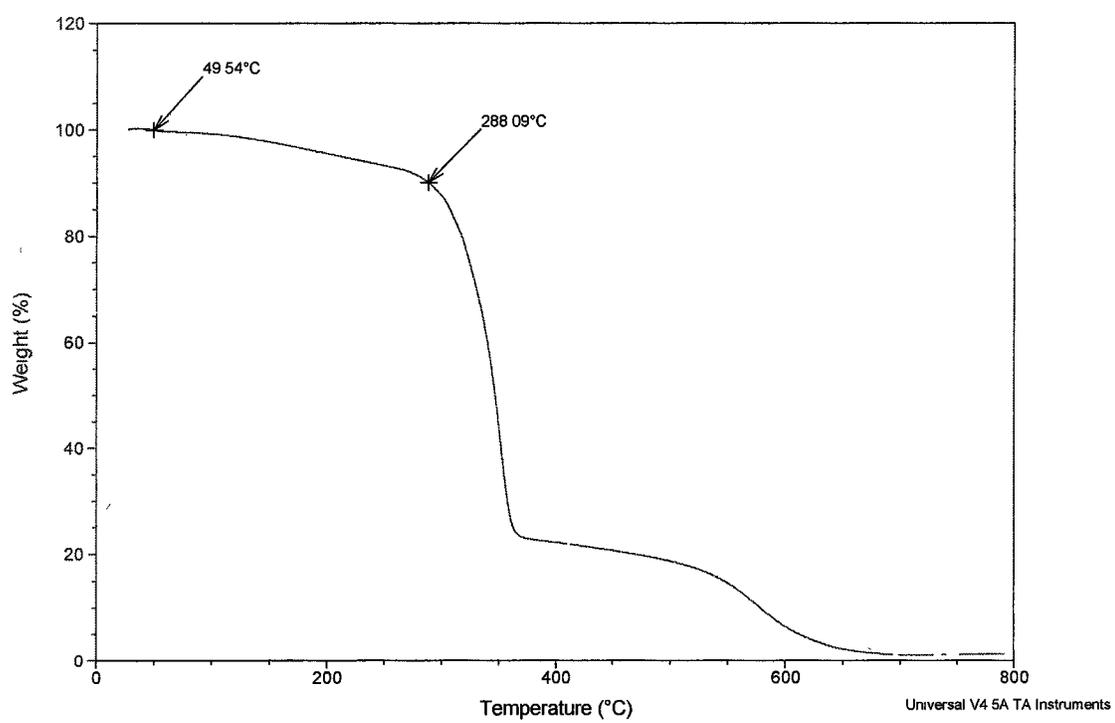


TGA of 60% PDO / 0% CBDO polymer.

Sample CBDO 20%_3 8mg
Size 3.7970 mg

TGA

File T \TGA\Booth\Megan\CBDO 20%_3 8mg
Operator Martinez
Run Date 22-Oct-2009 13:49
Instrument TGA Q50 V6.7 Build 203

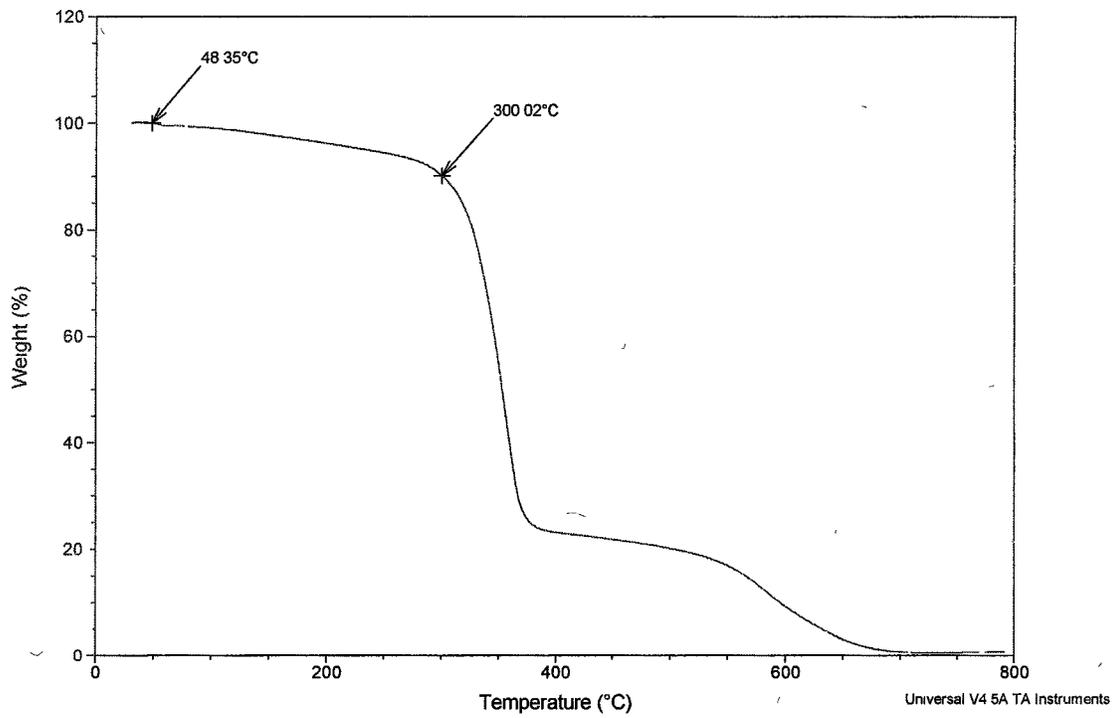


TGA of 40% PDO / 20% CBDO polymer.

Sample CBDO 40%_3 7mg
Size 3.7910 mg

TGA

File T \TGA\Booth\Megan\CBDO 40%_3 7mg
Operator Martinez
Run Date 22-Oct-2009 15:10
Instrument TGA Q50 V6.7 Build 203

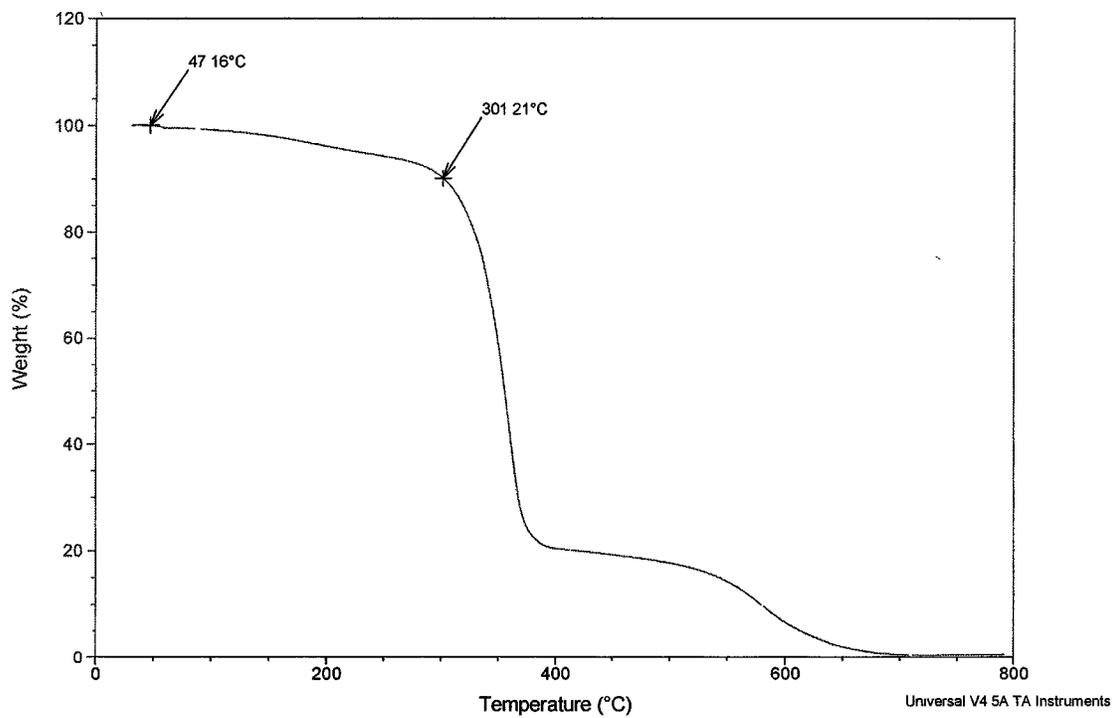


TGA of 20% PDO / 40% CBDO polymer.

Sample CBDO 60%_4 1mg
Size 4 1690 mg

TGA

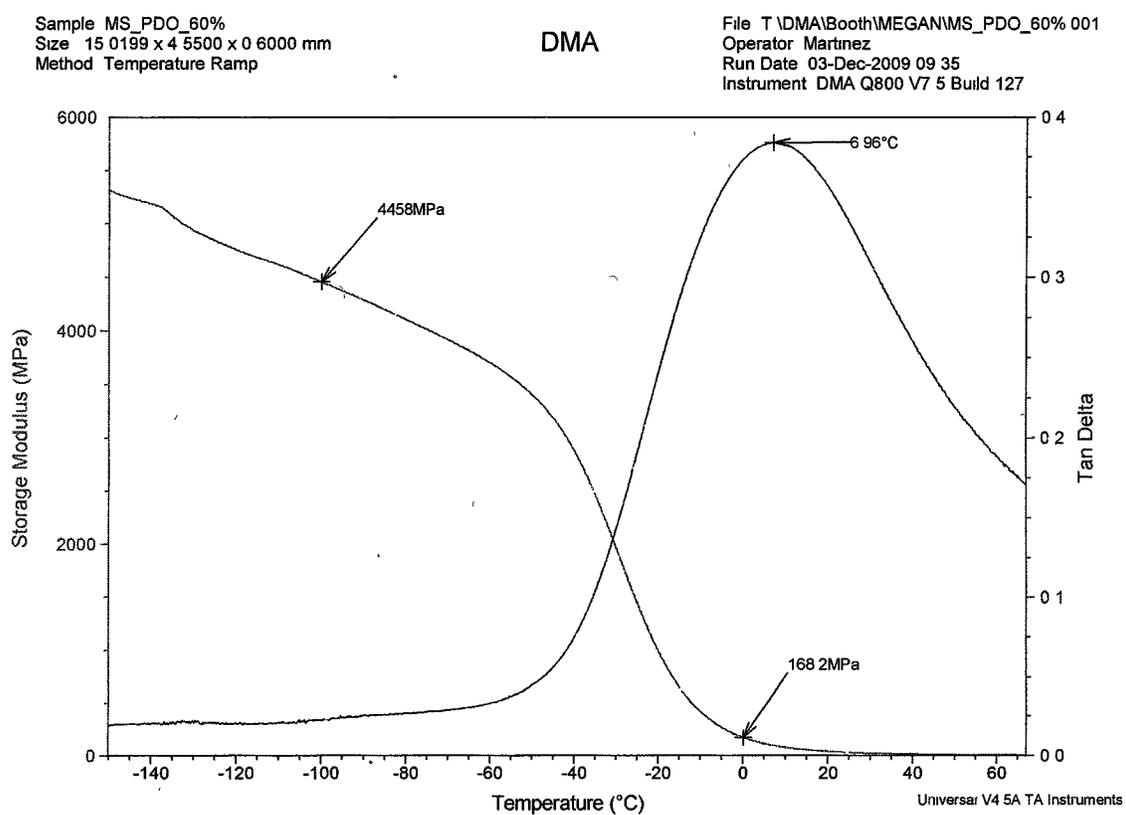
File T:\TGA\Booth\Megan\CBDO 60%_4 1mg
Operator Martinez
Run Date 22-Oct-2009 16 31
Instrument TGA Q50 V6 7 Build 203



TGA of 0% PDO / 60% CBDO polymer.

APPENDIX B

DMA and DSC Data

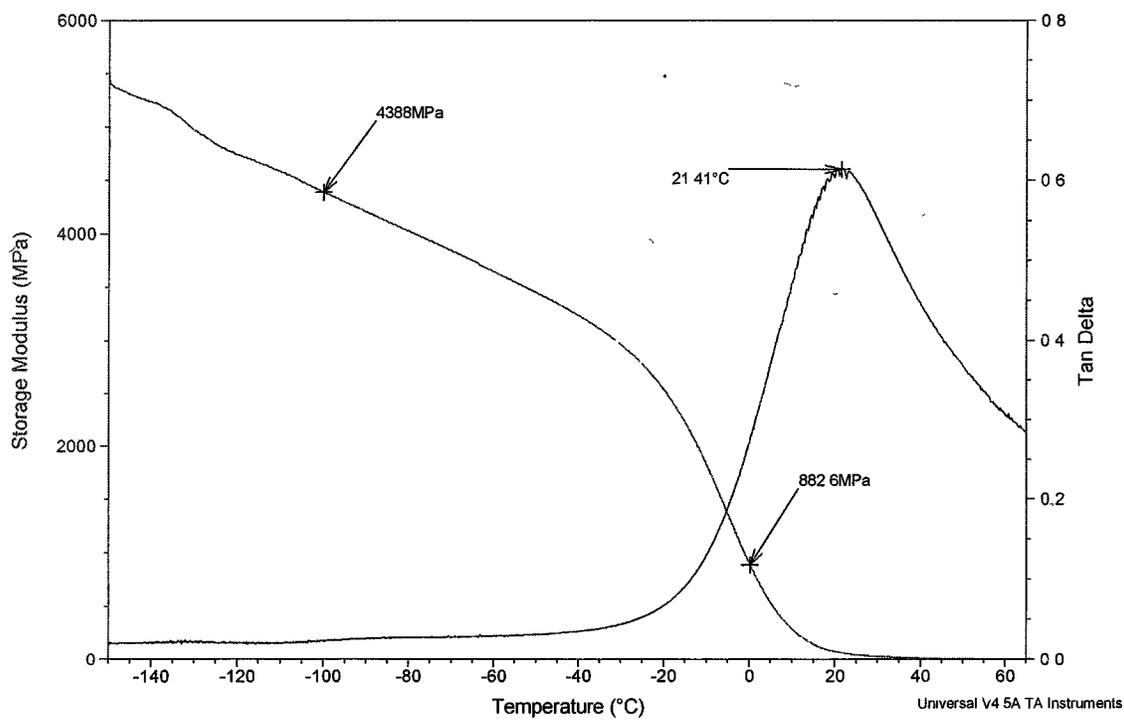


DMA of 60% PDO / 0% CBDO polymer.

Sample MS_CBDO_20%
Size 21 4133 x 6 4500 x 0 3300 mm
Method Temperature Ramp

DMA

File T:\DMA\Booth\MEGANMS_CBDO_20% 001
Operator Martinez
Run Date 02-Dec-2009 15 04
Instrument DMA Q800 V7 5 Build 127

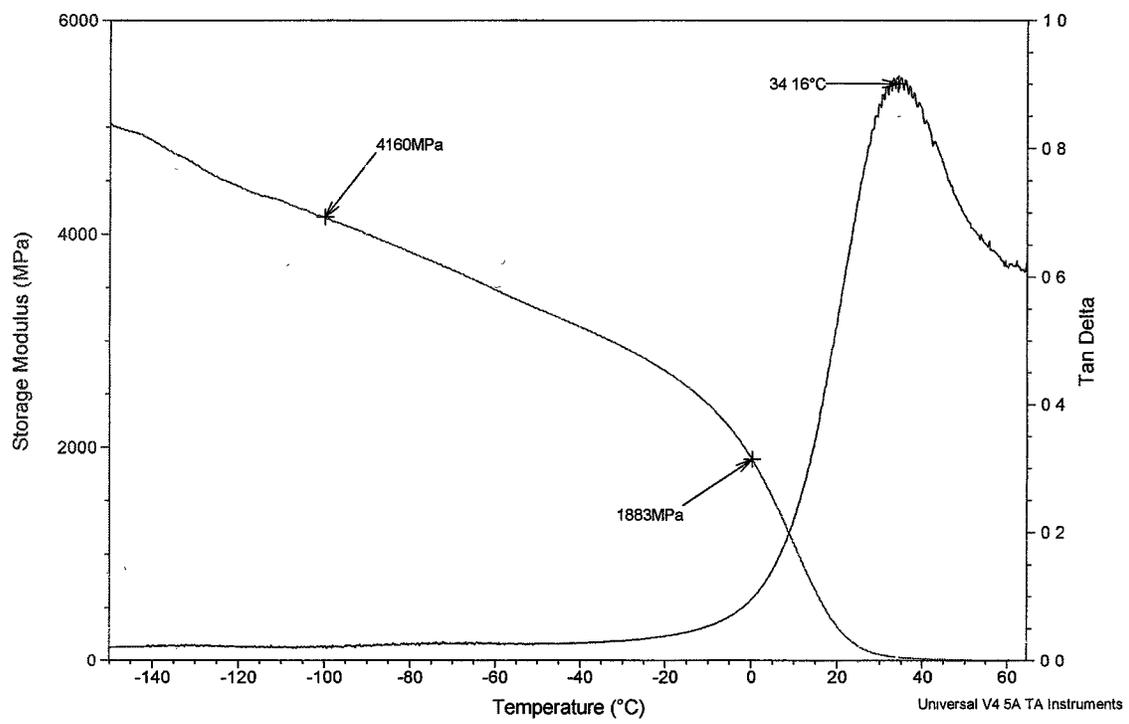


DMA of 40% PDO / 20% CBDO polymer.

Sample MS_CBDO_40%
Size 13 0184 x 3 5200 x 0 2000 mm
Method Temperature Ramp

DMA

File T:\DMA\Booth\MEGAN\MS_CBDO_40% 004
Operator Martinez
Run Date 03-Dec-2009 15 55
Instrument DMA Q800 V7 5 Build 127

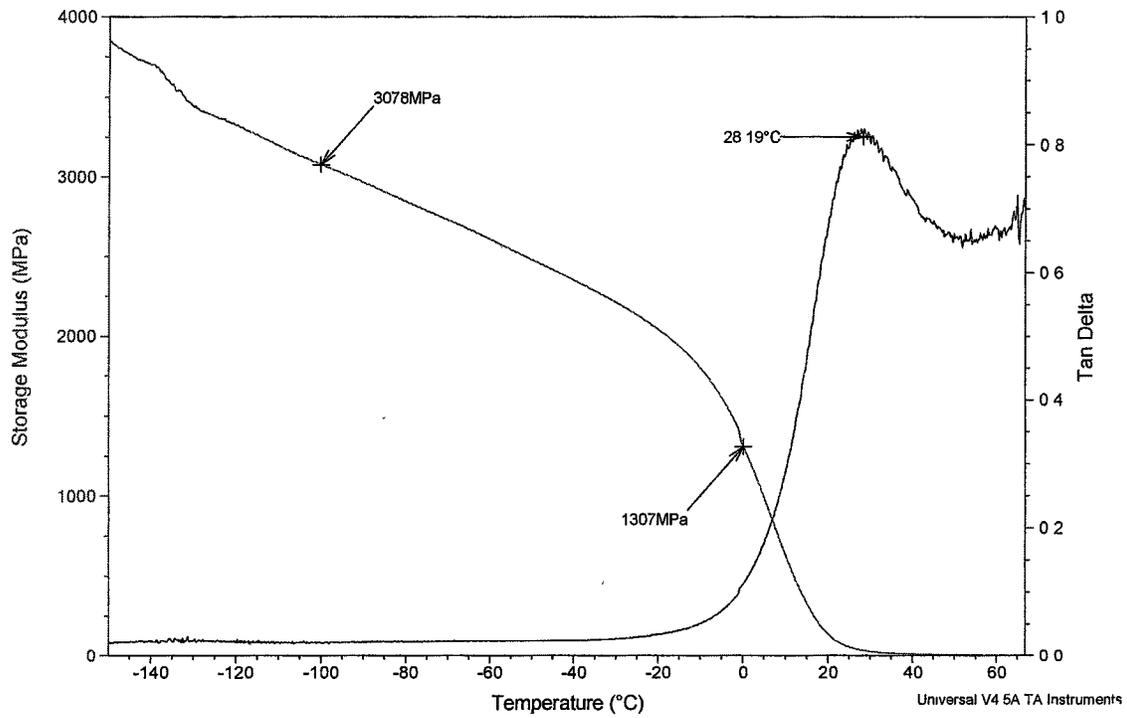


DMA of 20% PDO / 40% CBDO polymer.

Sample MS_CBDO_60%
Size 21 4266 x 4 9000 x 0 1200 mm
Method Temperature Ramp

DMA

File T:\DMA\Booth\MEGAN\MS_CBDO_60% 001
Operator Martinez
Run Date 02-Dec-2009 17 00
Instrument DMA Q800 V7 5 Build 127

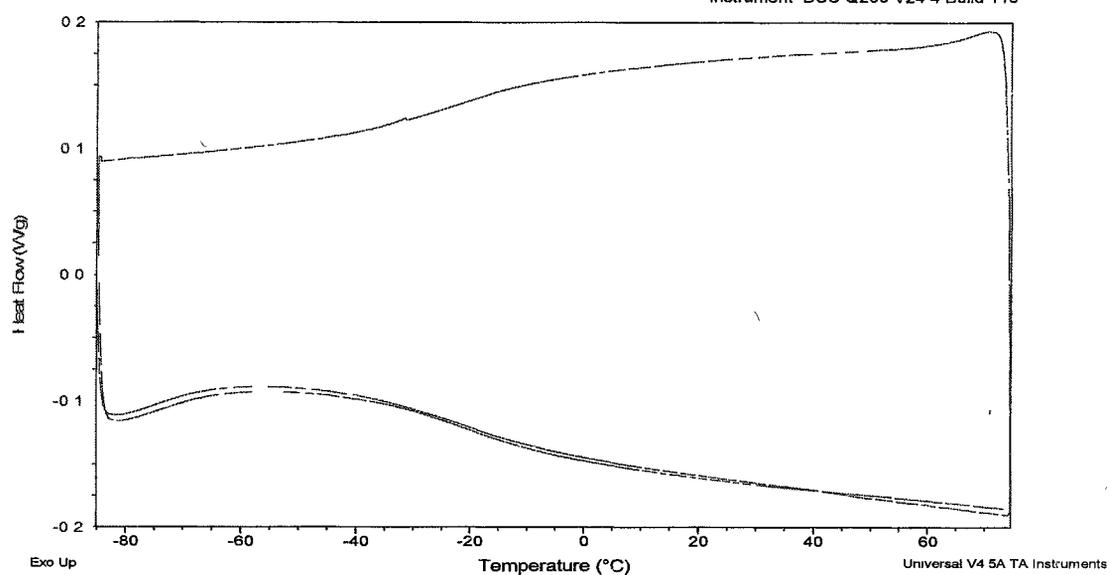


DMA of 0% PDO / 60% CBDO polymer.

Sample MS_CBDO_40%_5 4MG
Size 18 9000 mg
Method AI_Method_Megan

DSC

File T:\DSC\Booth\Megan\MS_CBDO_40%_5 4MH
Operator Martinez
Run Date 03-Dec-2009 16 41
Instrument DSC Q200 V24.4 Build 116



DSC of 20% PDO / 40% CBDO Polymer.

REFERENCES

- 1.) Kelsey, D.R., Scardino, B.M., Greowicz, J.S. & Chuah, H.H., (2000) *Macromolecules*. **33**, 5810-5818.
- 2.) Zawadzki, S.F. & Akcelrud, L., (1997) *Polymer International*. **42**, 422-428.
- 3.) Booth, C.J., Kindinger, M., McKenzie, H.R., Handcock, J., Bray, A.V. & Beall, G.W., (2006) *Polymer*. **47**, 6398-6405.
- 4.) Beall, G.W., Powell, C.E., Hancock, J., Kindinger, M., McKenzie, H.R., Bray, A.V. & Booth, C.J., (2007) *Applied Clay Science*. **37**, 295-306.
- 5.) Forschner, T.C., Gwyn, D.E., Sendijarevic, A., Jackson, P., Wang, J. & Frisch, K.C., *Corterra™ Polymers*.
- 6.) "Polypropylene glycol." Wikipedia. 2 Feb. 2010. 10 May 2010
http://en.wikipedia.org/wiki/Polypropylene_glycol.
- 7.) "Polyol." Wikipedia. 16 Apr. 2010. 10 May 2010
<http://en.wikipedia.org/wiki/Polyol>.

VITA

Megan L. Smith was born in Austin, Texas on October 17, 1985. She is the daughter of Leland and Angela Smith, the sister of Leland Smith II, and the granddaughter of Don and Clara Smith and Bernard and Gwen Meuth. After graduating from Smithville High School in May of 2004, she started college in August at Texas Lutheran University. In the summer of 2007, Megan did polyurethane and organoclay research at TLU. In March of 2008, during her senior year at TLU, she presented a poster about her research at the American Chemical Society national meeting in New Orleans, Louisiana. With her poster, she received a second place award in the polymer science division. In May of 2008, she received her Bachelor of Arts degree in Chemistry from TLU. In August of 2008, she entered the Graduate College at Texas State University-San Marcos. In the summer of 2009 and 2010 she received a Welch Foundation fellowship award. Megan was received the department of chemistry outstanding graduate student award during the 2009-2010 school year. In August of 2010, Megan received her Master's of Science degree in Chemistry from Texas State.

Permanent Address: P.O. Box 295

Luling, Texas 78648

This thesis was typed by Megan L. Smith.