

Effect of Aliphatic Diisocyanate and Aromatic Diisocyanate on the Properties of Castor Oil-Based Polyurethanes

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Abstract: The Study Deals The Effect Of Increasing NCO/OH Molar Ratio On The Physico-Mechanical Properties Of Isocyanate Terminated Polyurethane Prepolymer. The Prepolymer Was Prepared Using Castor Oil With Toluene-2,4-Diisocyanate And Hexamethylene Diisocyanate. The NCO/OH Molar Ratio Has Been Varied From 1.6 To 2.0. The Formation Of The Prepolymer Was Confirmed By Uv And FTIR Spectroscopy. To Investigate The Effect Of Increasing NCO/OH Molar Ratio On Mechanical Properties Of The Isocyanate Terminated Polyurethane Prepolymers. It Shows The Effect Of Increasing NCO/OH Molar Ratio On The Tensile Strength, Tensile Modulus And Percent Elongation Of The Polyurethane Film. The Results Reveal That The Curing Time Of The Prepolymer Decreased With Increase In NCO/OH Molar Ratio. When NCO/OH Molar Ratio Increased, The Tensile Strength Of The Polyurethane Film Increased, While Percent Elongation Decreased Due To Increase In Hard Segment Content. The Swelling Data Of PU films With Different NCO/OH Molar Ratios Are Illustrated . PU film Demonstrated The Maximum Swelling Coefficient Value In Tetrahydrofuran (THF) As Compared With Other Solvent. The Thermal Stabilities Of These PUs Were Confirmed By Thermal Analysis Techniques (TG/DTA).

Keywords : Polyurethane, Isocyanate, FT-IR, TG, DTA, Tensile Strength

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I. Introduction

Bio-Based Materials Are Now Receiving Considerable Attention In The Promotion Of Sustainable Chemistry In The Production Of Materials By Its Replacement Of Petroleum-Derived Raw Materials In The Production Of Different Products Needed In Various Industries ^[1]. The Shift To A More Green Way Of Chemistry Is Due To The Increasing Concerns About The Environment And A Shift To A More Sustainable Engineering Are Pushing Scientist And Engineers To Research New Ways To Better Understand Renewable Resources And How Can They Be Used Efficiently In The Conversion Of Raw Materials To Products ^[2]. Polyurethanes, Which Are Usually Produced Using Di-Isocyanate Is One Of The Materials Receiving Intensive Studies Today Due To Their Potential In Being Used In Different Fields Such As Biomedical Engineering And Tissue Engineering. These New Polyurethanes Which Uses Materials Derived From Vegetable Oils Like Canola Oil, Castor Oil, Etc. Can Be Used As A Scaffold In Which Isolated Cells May Be Seeded Into Which Allows The Cells To Grow And Proliferate Until It Forms A Tissue Construct Which Can Then Be Implanted Back To The Patient ^[3]. These New Polyurethanes May Exhibit The Ability To Biodegrade, Has Excellent Mechanical, Chemical, And Thermal Properties, And Has High Wear Resistance And Good Blood And Tissue Compatibility ^[4]. Thus, The Goal For The Next Generation Development Of Bio-Based Polyurethanes Is To Develop A Material Which Minimizes The Side Effect Of Diisocyanate Which Is Toxic And To Enhance Traits Which Can Improve The Efficiency Of The Produced Product.

In The Present Work We Have Attended To Utilize The Castor Oil For The Synthesis Of Polyurethane. It Was Further Reacted With Toluene Diisocyanate And Hexamethylene Diisocyanate In Different Ratio To Develop A Series Of Polyurethane. The Synthesized Polyurethanes Were Tested For The Evaluation Of Their Chemical, Mechanical, Thermal Properties.

II. Experimental

Required Materials

Castor Oil Was Obtained From The Local Market, Toluene 2,4 Diisocyanate With The Commercial Name Of TDI (Mw=174.16), The Hexamethylenediisocyanate With The Commercial Name Of HMDI (Mw=168.19) And The Catalyst Stannous Octoate With The Commercial Name Of Tin (II) 2ethylhexanoate (Mw=405.12) Provided By Sigma- Aldrich Company.

III. Material And Methods

Synthesis Of Polyurethane With TDI

A Three-Necked Round-Bottomed Flask, Equipped With A Mechanical Stirrer, Thermometer And Nitrogen Gas Inlet, Was Used For Preparation Of The Polyurethane. The Reaction Vessel Was Flushed With Nitrogen And Charged With Castor Oil And TDI, In Order To Maintain NCO/OH Ratio 1.6 And Stannous Octoate 0.25wt % (With Respect To The Castor Oil And The Isocyanate) Was Stirred For 1 Hr At 45°C. The Polymer Mixture Resulted A Viscose Solution And It Was Poured Out Onto A Glass Plate Of 2mm Thickness. The Plate Was Put In A Vacuum Oven At 100°C, For 24 Hours To Get Dried. Following The Above Procedure, The Other Polyurethanes (Tpus) With Varying NCO/OH Were Prepared ^[5].

Synthesis Of Polyurethane With HMDI

A Three Necked Round Bottomed Flask, Equipped With A Mechanical Stirrer, Thermometer And Nitrogen Gas Inlet, Was Used For Preparation Of The Polyurethane. The Reaction Vessel Was Flushed With Nitrogen And Charged With Castor Oil And HMDI, In Order To Maintain NCO/OH Ratio 1.6 And Stannous Octoate 0.25wt % (With Respect To The Castor Oil And The Isocyanate) Was Stirred For 1 Hr At 45°C. The Polymer Mixture Resulted A Viscose Solution And It Was Poured Out Onto A Glass Plate Of 2mm Thickness. The Plate Was Put In A Vacuum Oven At 100°C, For 24 Hours To Get Dried. Following The Above Procedure, The Other Polyurethanes (Hpus) With Varying NCO/OH Were Prepared ^[6].

Characterization Methods

Infrared Spectra:

Infrared Spectra Of The PPU In Kbr Pellets Were Obtained From Shimadzu FTIR 4200 Series Spectrophotometer. Whereas In Case Of PPU, Being A Liquid, A Thin Film Was Cast Over The Nacl Block And Its FTIR Was Recorded.

Mechanical Properties:

The Tensile Strength And Elongation At Break Were Measured At Room Temperature Using Instronhouns-Field Universal Testing Machine Model 4204 As Per ASTM D-638 Method ^[7,8].

Swelling Behaviour

Swelling Measurements Of The Synthesized Polyurethanes Were Performed At Room Temperature Using Five Different Solvents (N-Pentane, Cyclohexane, Toluene, Thf and N-Propanol Water). Test Samples For Swelling Experiments Were Squares, Cut From The Cast Films, Weighing About 0.2 G. The PU Samples Were Immersed In Solvent. Periodically, These Specimens Were Removed From The Solvent And Weighed After Removal Of The Excess Of Solvent From The Sample Using Filter Paper. This Was Repeated Until Constant Weight (Equilibrium Swelling). The Average Value Of Three Parallel Swelling Experiments In Every Solvent For Each Sample Was Used. The Swelling Degree, Q, Was Calculated Using Gravimetric Method:

$$Q = \frac{M - M_0}{M_0}$$

Where M And M₀ Are The Sample Weights After And Before Swelling, Respectively ^[9].

Thermal Properties

In The Present Work, TGA/DTA Studies Were Carried Out Using SDT Q 600V 8.3 Build 101 Instrument At The Heating Rate Of 10 C/Min From Ambient To 800 C In Nitrogen Atmosphere Using 2-5 Mg Of The Sample ^[10].

IV. Results And Discussion

The Polyurethane Prepolymer Obtained From Castor Oil And TDI Were Characterized According To Following Reports.

Infrared Spectroscopy

Infrared Spectroscopy Of Tpus

Fig. 1a Shows The IR Spectra's Of Castor Oil. Fig 1 B, C, D, Shows The Synthesized Prepolymers At Different NCO/OH Molar Ratio. All The Synthesized Prepolymer Shows The Characteristics Absorption Bands Of Polyurethanes Except In The Peak Associated To Ncostretching Which Shows Higher Absorption Area In Case Of Higher NCO/OH Molar Ratio. It Was Observed That All The Prepolymers Possess The Following Characteristic Absorption Bands, Urethane NH Stretching At 3343-3321cm⁻¹, Bending At 1531-1528cm⁻¹,

Methylene Or Alkyl Group At 2974 cm^{-1} , Carbonyl Group At $1727\text{-}1730\text{ cm}^{-1}$ And C-O-C Stretching At $1025\text{-}1044\text{ cm}^{-1}$. The Strong Characteristic Absorption Peak At $2272\text{ - }2275\text{ cm}^{-1}$ Is Associated With NCO Stretching. Presence Of NCO Stretching And All The Above-Mentioned Peaks Indicate Formation Of Isocyanate Terminated Polyurethane Prepolymer. FT-IR Spectra Of The Different Prepolymers Show NCO Stretching Band And The Same Peak Does Not Present The Castor Oil. It Confirms The Formation Of Prepolymers Through The FT-IR Data.

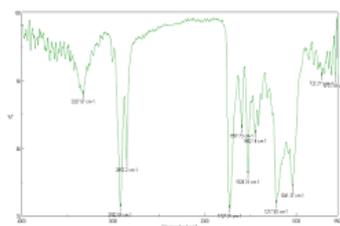


Fig.1a Castor oil

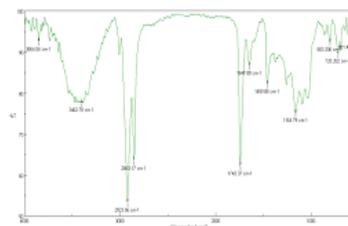


Fig.1b Prepolymer (1.6)

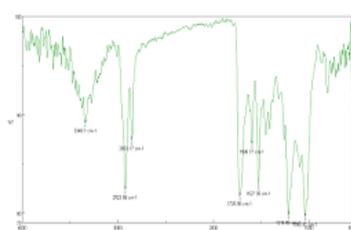


Fig. 1c Prepolymer (1.8)

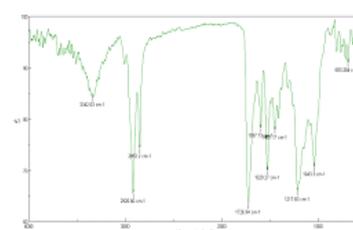


Fig 1d Prepolymer (2.0)

Figure FT-IR Spectrum OF TPUS

Infrared Spectroscopy Of Hpus

The Occurrence Of Urethane Bond Between HMDI And Castor Was Determined By Fourier Transform Infrared (FTIR) Spectroscopy. The IR Spectra Of The Castor Oil And PU Films Are Shown. The Peak At The Wave Number Around 1535 cm^{-1} Is Indicative Of Urethane Linkage (C-N-H) Formation In All Of The Synthesized PU Samples. In Addition, Vibration Peak Found At 3300 cm^{-1} Corresponds To The Amide N-H Stretching In Urethane. The Peak At 1730 cm^{-1} Which Is Attributed To The Ester Carbonyl (C=O) Stretching Of Castor Oil And Urethane Carbonyl. The Bands Between 2925 cm^{-1} And 2931 cm^{-1} Are Attributed To The Methylene (CH₂) Asymmetric And Symmetric Stretching Vibration Of The Hydrocarbon Chain Of Castor Oil And HMDI.

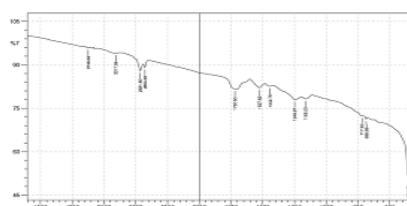


Fig FT-IR HPU 1

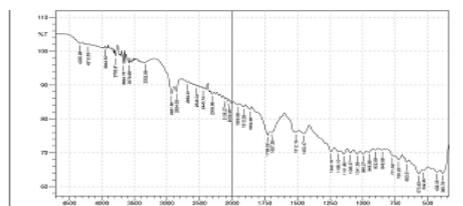


Fig FT-IR HPU 2

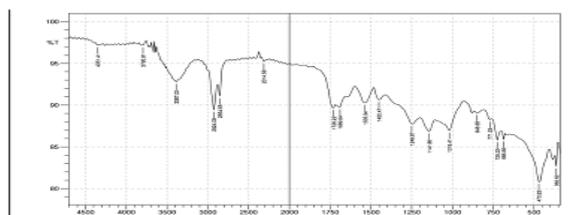


Fig FT-IR HPU 3

Figure FT-IR Spectrum Of HPUS

Mechanical Properties

To Investigate The Effect Of Increasing NCO/OH Molar Ratio On Mechanical Properties Of The Isocyanate Terminated Polyurethane Prepolymers. It Shows The Effect Of Increasing NCO/OH Molar Ratio On The Tensile Strength, Tensile Modulus And Percent Elongation Of The Polyurethane Film. It Was Observed That On Increasing The NCO/OH Molar Ratio, The Tensile Strength And Tensile Modulus Of The Polyurethane Film Increases Whereas The Percent Elongation Decreases. This May Be Due To The Fact That, With Increasing NCO/OH Molar Ratio, Hard Segment Content Of The Polymer Increases. More Hard Segments Allow More Effective Intermolecular Hydrogen Bonding Between The Segments. This Tends To Increase The Tensile Strength And Tensile Modulus And Also Decreases The Percent Elongation Of The Polyurethane Film With Increase In NCO/OH Molar Ratio. This Tends To Increase The Tensile Strength And Tensile Modulus And Also Decreases The Percent Elongation Of The Polyurethane Film With Increase In NCO/OH Molar Ratio, Which Also Supports The Above Discussed Results ^[11].

Table Data On Mechanical Properties Of Tpus

Sample Code	Tensile Strength(Mpa)	Elongation At Break(%)	Tensile Modulus(Mpa)
TPU 1	1.40	115	.7157
TPU 2	1.701	95	.5714
TPU 3	2.07	86.22	.4361

Table Data On Mechanical Properties Of Hpus

Sample Code	Tensile Strength(Mpa)	Elongation At Break(%)	Tensile Modulus(Mpa)
HPU 1	1	80.3448	1.2740
HPU 2	1.5	67.8494	.6765
HPU 3	2	40.4744	.1235

Swelling Behaviour

This Observation Can Be Explained On The Basis That A Three Dimensional Network Was Formed By The Reaction Between The OH Groups In CO And -NCO Groups In Di Isocyanates Resulting In An Increase In Degree Of Crosslinking. This Might Be Due To The Presence Of More NCO Groups That Participate In Crosslinking Reactions. The Swelling Data Of PU films With Different NCO/OH Molar Ratios Are Illustrated . PU film Demonstrated The Maximum Swelling Coefficient Value In Tetrahydrofuran (THF) As Compared With Other Solve.

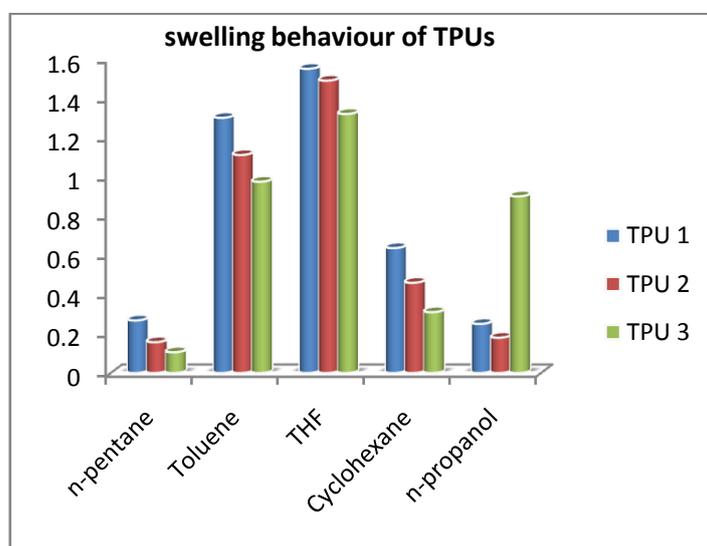


Figure Swelling Behaviour Of TDI Based Polyurethane (Tpus)

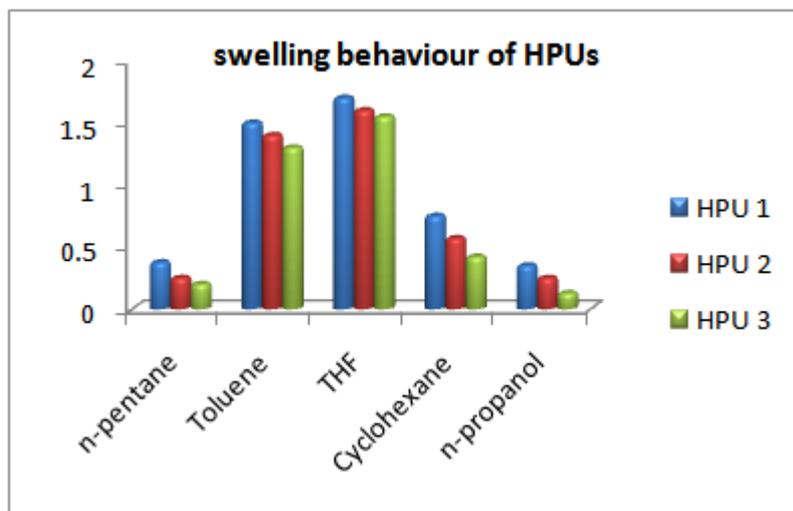


Figure Swelling Behaviour Of HMDI Based Polyurethane (Hpus)

Thermo Gravimetric Analysis

The TGA Curves Of Polyurethanes Show That These Polyurethanes Decompose In Two Or Three Distinct Stages. As Can Be Seen From The Thermograms, All The Polyurethane Samples, Regardless Of The Chain Length Of Polyol Used, Undergo Spontaneous Decomposition Around 270°C. Once The Degradation Has Started, Weight Loss Is Rapid. The Initial Weight Loss (About 5%) Up To 250 ° C Is Attributed To The Moisture Retained In The Sample. The First Break Of The TG Curves Around 270 ° C Is Due To The Decross Linking Or Post Curing Process. The Second Break Around 350 ° C-400 ° C Indicates The Decomposition Of Polyurethane Moiety Of The Compound. And The Last Break Around 500 ° C Is Due To Disintegration Of The Resin Moiety Into Simpler Molecules. Corcuera Et Al^[12] Reported That The Thermal Stability Of PU Is Related To The Structure, Chemical Composition And Molar Ratio Of The Hard Segment And Soft Segment.

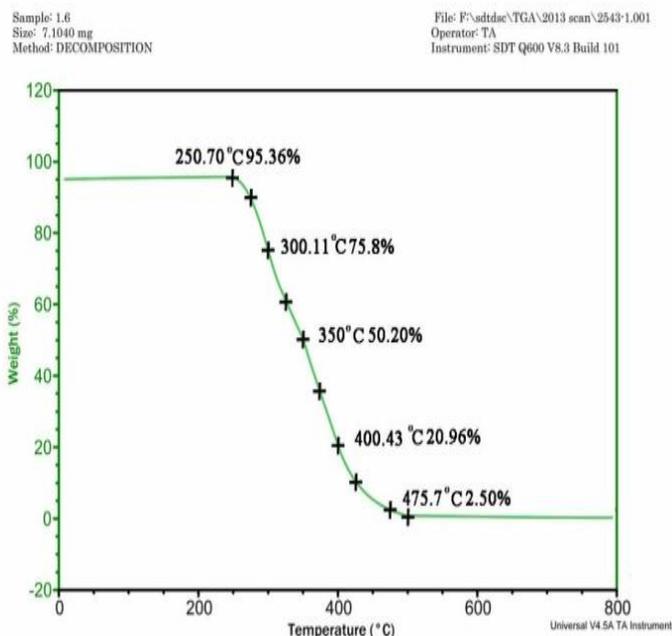


Figure Thermo Gravimetric Analysis Of TPU 3

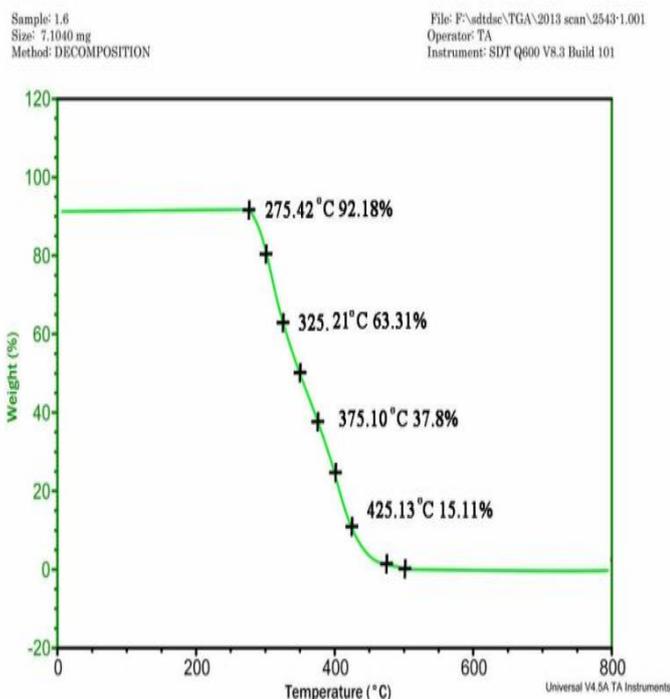


Figure Thermo Gravimetric Analysis Of HPU 3

Table Percentage Of Mass Loss Of Pus At Various Temperatures (0° C)

PU Code	% Weight Loss At Various Temperatures ° C						
	200	250	300	350	400	450	500
TPU 3	0	05	25	50	80	90	99
HPU 3	0	2.76	20	48	75	88	98

Differential Thermal Analysis Data Of Polyurethanes

The DTA Curves Of Polyurethanes Do Not Show Any Endothermic Peak For Softening. But Two Exotherms Are Invariably Seen In All The Cured Polyurethanes. The First Exotherm Is Relatively Weak And The Second Exotherm Is Strong In All The Four Polyurethanes. The First Exotherm Is Due To The Cleavage Of Allophanate Linkages At Low Temperatures. All The Three Exotherms Of The Urethane Function With HMDI (Hpus) Occurs At Higher Temperature And Thus Posses Higher Degradation Temperature In Comparison With That Of The Urethane Function With TDI (Tpus).

DTA Data Of Pus

PU Code	Exotherm ° C		
	First	Second	Third
TPU 3	282	374	418
HPU 3	323	386	425

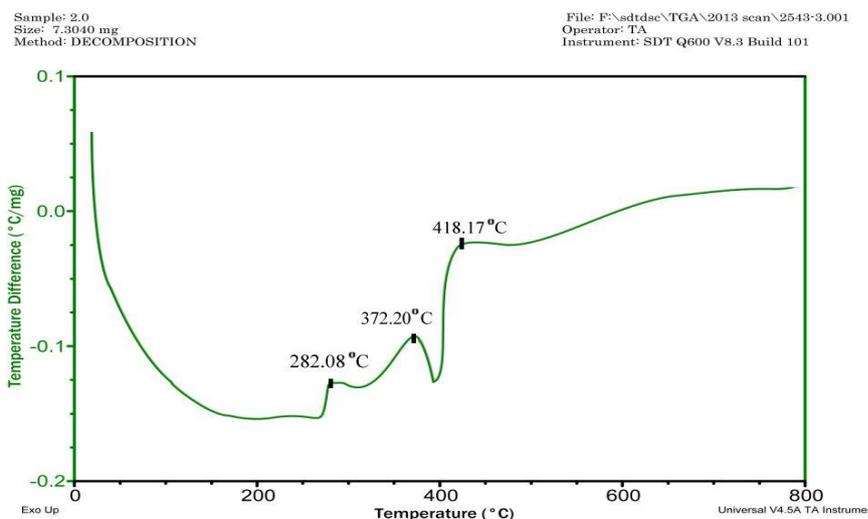


Figure Differential Thermal Analysis Data Of Of TPU

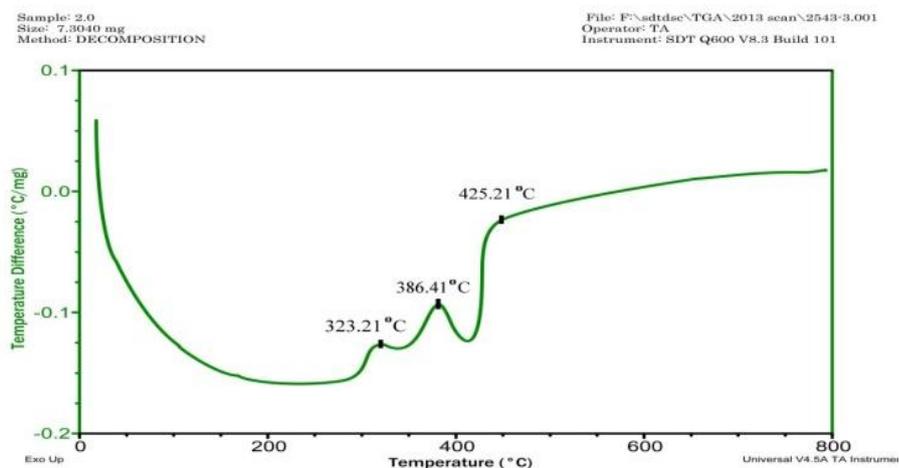


Figure Differential Thermal Analysis Data Of HPU

V. Conclusion

The Attractiveness Of Polyurethanes For Medical Implants Is Largely Due To Their Excellent Mechanical Properties And Relatively Good Process Ability. They Exhibit High Tensile Strength And Elongation At Break. Their Chemical Make-Up Also Offers Substantial Opportunities For Synthetic Polymer Chemists To Tailor Structure To Meet Specific Property Requirements. However, During The Last 15 Years Several Research Groups Have Focused On Developing Improved Polyurethanes With Chemistries That Achieve A Combination Of Good Mechanical Properties, Process Ability, And Resistance To Degradation. The Hard Segment Chemical Structure And Content Significantly Influence The Bio Stability Of Polyurethanes. Several Researchers Have Reported That Polyurethanes Based On Aromatic Diisocyanates Are More Biostable Than Their Aliphatic Counterparts. In This Present Work, Polyurethanes Were Synthesized From Castor Oil

And Two Different Isocyanates- Toluene Diisocyanate And Hexamethylene Diisocyanate-With Stannous Octoate As A Catalyst. A Systematic Investigation Of Physical And Mechanical Properties And Thermal Stability Of The Corresponding Products Enables Us To Conclude On The Important Contribution Of The Nature Of The Diisocyanate. Concerning These Properties; TDI Is More Reactive Than HDI Because Of The Electron Withdrawing Effect Of The Aromatic.

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