

# Thermal Behavior of Cast Polyurethane Elastomers

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## Synopsis

Thermal properties like glass transition temperature ( $T_g$ ), initial decomposition temperature (*idt*), integral procedural decomposition temperature (*ipdt*), and temperature at various % weight loss of a number of polyurethane systems are reported in this paper. Glass transition temperature was determined on TMA, and other thermal properties were determined by thermogravimetry. The experiments were designed to understand various factors such as length of chain extender moiety, flexibility of chain extender units by substitution of ether link in the diol chain, nature of bonds (unsaturation) in the extender unit, and nature of diisocyanates.

## INTRODUCTION

Most polymers are either completely amorphous or have an amorphous-like component even if they are crystalline. Such materials are hard, rigid glasses below a temperature known as the glass transition temperature ( $T_g$ ). Above this temperature, polymers are soft and flexible and elastomeric in appearance. Mechanical properties show profound changes in the region of the glass transition, and, therefore,  $T_g$  can be considered the most important material characteristic of a polymer. Many properties change rapidly with temperature in the glass transition region. These properties include coefficient of thermal expansion,<sup>1</sup> heat capacity,<sup>2</sup> refractive index,<sup>3</sup> mechanical damping,<sup>4</sup> nuclear magnetic resonance behavior, and electrical properties.<sup>5</sup> The ability to determine and interpret  $T_g$  of polymers is an important characterization capability, since  $T_g$  values have been used as a primary basis or a key component for properties such as product uniformity, quality control, polymer identification, structural aspects, plasticizer efficiency, degree of curing, blend compatibility, phase composition, etc.<sup>6</sup>

Thermogravimetry has been used for many years to study the degradation process in polymers. Numerous papers on structure-thermal property relationship, mechanism of thermal degradation have been reported.<sup>6</sup> Thermal study of polymers mainly deals with deterioration of mechanical properties with temperature. The deterioration in properties is a result of cleavage of thermally weak bonds. Sometimes toxicity of degradation products of polymers is also studied. Another important application of thermogravimetry is in elucidation of kinetics of degradation.

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TABLE I  
List of Low Molecular Weight Diols

Designation	Structure	Source
Ethanediol	$\text{HO}-(\text{CH}_2)_2-\text{OH}$	Emerk
Propanediol	$\text{HO}-\overset{\text{CH}}{\underset{ \text{H}_3}{\text{C}}}-\text{CH}_2-\text{OH}$	Sarabhai Chemical
1,4-Butanediol	$\text{HO}-(\text{CH}_2)_4-\text{OH}$	BDH (u.K.)
1,5-Pentanediol	$\text{HO}-(\text{CH}_2)_5-\text{OH}$	BDH
1,6-Hexanediol	$\text{HO}-(\text{CH}_2)_6-\text{OH}$	Fluka AG
1,4-Butenediol	$\text{HO}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{OH}$	Merk
1,4-Butynediol	$\text{HO}-\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_2-\text{OH}$	Fluka AG
Di(ethylene glycol)	$\text{HO}-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-\text{OH}$	Sarabhai Chemical
Poly(ethylene glycol)	$\text{HO}-(\text{CH}_2-\text{CH}_2-\text{O})_n-\text{OH}$ $n = 0-9$	BDH

TABLE II  
List of Diisocyanates Used as Hard Segments in the Polyurethane Synthesis

Designation	Notes	Source
2,4-Toluene diisocyanate (TDI)	80% 2,4- and 20% 2,6-isomeric mixture	Fluka AG
Diphenyl methane diisocyanate (MDI)	Mixture of di- and triisocyanates, dark brown viscous liquid	E. Merk
1,6-Hexamethylene diisocyanate (HDI)	Colorless liquid, 98%	Aldrich
Isophoron diisocyanate (IPDI)	Colorless liquid, —NCO content 37.6% by weight	Chemisch
Trimethyl hexamethylene diisocyanate (TMDI)	Colorless liquid, > 99% pure, 2,2,4- and 2,4,4-isomeric mixture (1 : 1)	Chemisch

Polyurethane block polymers are a family of elastomeric materials whose chains are composed of alternating low glass transition (soft) segments generally formed by polyethers and polyesters and more rigid polar urethane (hard) segments formed from the extension of a diisocyanate with a low molecular weight diols. In this paper the influence of various factors on  $T_g$  and thermal stability of cast polyurethanes is reported.

## EXPERIMENTAL

**Materials.** Polyester polyols, diols, and diisocyanates used in the synthesis of polyurethanes are reported in Tables I, II, and III. The structure of diisocyanates is shown in Figure 1.

TABLE III  
 Polyols and Their Characteristics Used for the Synthesis of Polyurethane Elastomers

No. Polyol	Appearance	Acid no.	Hydroxy no.	MW (VPO)	MW (End group)
1. Polyethylene-co-propylene adipate (PEPA)	Viscous liquid, light yellow	2.24	53 ± 2	2200	2050
2. Polyethylene adipate (PEA)	White waxy, solid	3.5	34 ± 1	3075	3200
3. Polypropylene adipate (PPA)	Viscous liquid, yellow color	4.1	27 ± 1	4000	4150
4. Polydiethylene adipate (PDEA)	Viscous liquid, light yellow	2.13	63 ± 2	1750	1600
5. Polyhexylene-co-neopentylene adipate (PHNA)	Viscous liquid, colorless	< 2	105	—	1100
6. Castor oil (I.P.) (CO)	Viscous liquid, yellow color	—	—	—	930

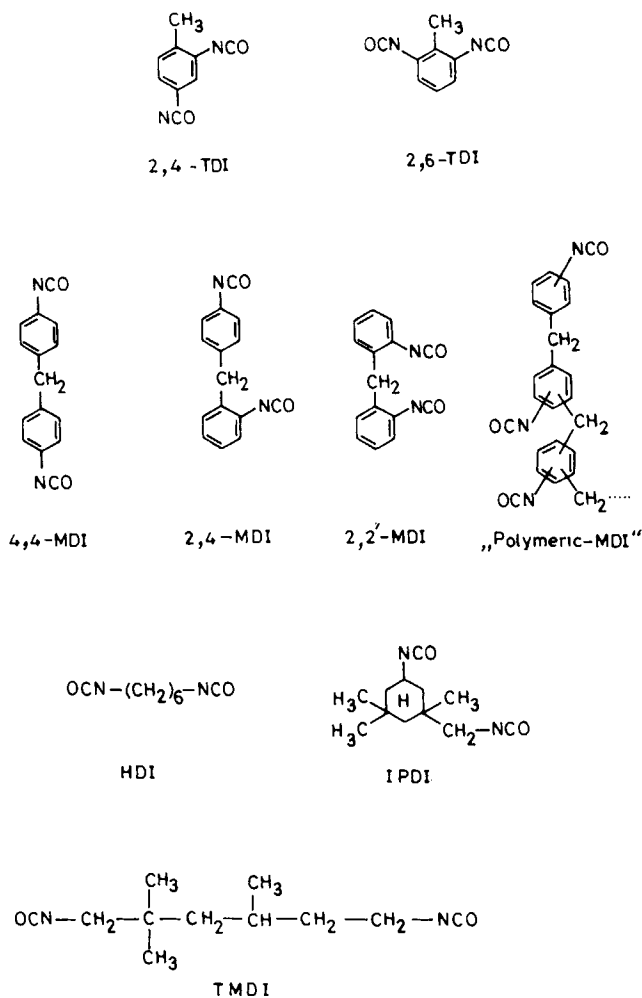


Fig. 1. Structure of diisocyanates.

Polyester polyols were synthesized by condensation method and the detail procedure is described in our earlier paper.<sup>7</sup>

**Polyurethane Synthesis.** Prepolymer was obtained by the reaction of polyester polyol and diisocyanates. Diisocyanate was added in excess. The mix was stirred continuously for 0.5 h at 55–60°C. The prepolymer was then reacted with glycol chain extenders. The mixture was stirred continuously for 15 min. The mix was degassed after becoming viscous and was poured onto a stainless steel die (coated with a silicon mold releasing agent). The sheets were cured in oven at 100°C for 24 h, which were subjected to characterization after proper conditioning. The molar proportion of polyester : diisocyanate : chain extender is 1 : 3.2 : 2 in all the systems.

**Measurements.** Thermomechanical analyzer (TMA) was used to detect glass transition temperature ( $T_g$ ) of the elastomers.<sup>8</sup> The specimen (circular, about 8 mm in diameter and about 2 mm thick) was placed in a quartz tube. The tube was surrounded by a minifurnace. A quartz probe was used, one end

of which rests on the sample and the other being connected to an LVDT detector. In the beginning, the probe was lifted up, and the sample was cooled down sufficiently using liquid nitrogen. The specimen became hard, and the probe (sharp end) was then placed on the sample. The sample tube was heated at a uniform rate (8°C/min) using a temperature programmer. At the glass transition temperature, the sample softened, and the quartz probe penetrated into the sample. This displacement of the probe was sensed by the LVDT detector. The temperature of the sample was measured by the thermocouple. The output of LVDT ( $\Delta L$ ) and thermocouple was recorded on a two-pen strip-chart recorder. The inflection point on the  $\Delta L$  vs. temperature plot was taken as  $T_g$  of the sample.

Thermogravimetric analysis (TGA) was carried out on DT-30 (Shimadzu Corp., Japan) thermobalance. The primary thermograms of % weight loss as a function of temperature were recorded, in nitrogen atmosphere. The temperature was scanned from ambient to 500°C. Using this data, thermal stability of polymeric materials was studied by considering following aspects, viz., (i) initial decomposition temperature (*idt*), (ii) integral procedural decomposition temperature (*ipdt*), (iii) temperature at various % weight losses, and (iv) energy of activation ( $E_a$ ).

Integral procedural decomposition temperature (*ipdt*) can be obtained from the summation of the whole shape of the normalized data curve. This method involves the integration of the primary thermograms on the basis of total experimentally accessible temperature range and calculating an integrated volatilization temperature based on the residual weight fraction. *ipdt* was calculated over the range of temperature 25–500°C. The area under the primary thermograms  $A_1$  and the total area  $A_2$  in this temperature range was determined in each case. *ipdt* was calculated as follows:

$$ipdt = (T_f - T_s)A + T_s$$

where  $T_f$  = final decomposition temperature,  $T_s$  = starting temperature, and  $A = \text{area } A_1 / \text{area } A_2$ .

Energy of activation ( $E_a$ ) was studied by the method involving maximization of rate. This method emphasizes the position of parameters. Following expression was used<sup>9</sup>:

$$\log Rt = \log A + (E/R) \left[ (W_m/R_m T^2 m) \log W - (1/2.303T) \right]$$

In this equation  $W_m$ ,  $R_m$ , and  $T_m$  are the weight of active material remaining, the slope, and the temperature, respectively, at the inflection point on the primary thermogram.  $R_i$  is the rate of decomposition and is equal to  $-dw/dt$ . The plot of  $\log Rt$  vs.  $[(W_m/R_m T^2 m) \log W - 1/2.303T]$  gives a straight line. The points were fitted using the least square fitting, to obtain the slope and the intercept of the line. From the slope,  $E_a$  was calculated.

## RESULTS AND DISCUSSION

Glass transition temperature of various polyurethanes as determined on TMA are reported in Table IV. Number of polyurethanes were synthesized by

TABLE IV  
Glass Transition Temperature [ $T_g$  ( $^{\circ}\text{C}$ )] of Various PUs (Polyester/TDI/Diol Systems)

Diol chain extender	Various polyesters			
	PEPA	PEA	PPA	PDEA
Ethanediol	-24.0	-24.5	-35.0	-24.5
Propanediol	-26.5	-27.5	-38.0	-26.0
1,4-Butanediol	-29.0	-29.0	-39.5	-26.0
1,5-Pentanediol	-31.5	-29.5	-41.0	-28.0
1,6-Hexanediol	-33.0	-31.0	-41.5	-31.0

using various polyester polyols, 2,4-toluene diisocyanate, and a homologue series of diols. Table IV presents the  $T_g$ 's of polyurethanes correlated with number of methylene carbons present in the extender. In general, it was observed that glass transition temperature decreased with increasing methylene groups in the extender for all polyester-extender system. The decrease in  $T_g$  from ethanediol extended polyurethane to the hexane-diol-extended polyurethane, was marginal (6–9 $^{\circ}\text{C}$ ). The lowering of  $T_g$  can be explained on the basis of polarity as well as chain flexibility imparted in the polyurethane by the extender. Decrease in polarity causes a decrease in  $T_g$ .<sup>10</sup> The polarity of diols decreases with increasing number of methylene sequences between the two polar hydroxyl groups. Also additional flexibility in the polyurethanes is imparted by increasing number of methylene sequences of extender. This additional flexibility reduces restrictions on mobilities of hard segments which is comprised of the diisocyanate and diol.

Although the overall effect of increasing methylene groups in diol resulted in lowering the  $T_g$ , polyurethanes synthesized from various polyesters showed different values of  $T_g$ 's (Table IV).  $T_g$ 's shown by polypropylene-adipate-based polyurethanes were found to be the lowest, probably due to higher molecular weight, which offers higher flexibility to the PU network. Considering flexibility of the —C—O—C bond, the  $T_g$ 's of polydiethylene-adipate-based polyurethanes were expected to be much lower, contrary to the observation. This can be accounted for by the lower molecular weight of the parent polymer (PDEA). Reaction of the lower molecular weight of the polyester in the synthesis of PU results in a decrease in the ratio of soft core to hard core.

To study the thermal stability of PUS, the PEPA/TDI/diol system was selected. The results are reported in Table V. It was observed that the structure of diol had very little influence on the thermal stability of polyurethanes. Among the polymers, butanediol-extended PU showed the highest values of energy of activation as well as *ipdt* index. The *ipdt*, as proposed by Doyle,<sup>11</sup> is a comprehensive index of thermal stability, which places all materials on a common basis and provides the most valid comparison of thermal stability of different polymeric materials.

Table VI shows the effect of increasing unsaturation in the diol. The increase in  $T_g$  can be explained on the basis of restrictions on the mobilities of polyurethane imposed by  $\text{SP}^2$  and  $\text{SP}$  hybridized bondings from the diol moieties. Also the reactivity increases from butanediol to butynediol towards polyurethane reactions.<sup>12</sup>

TABLE V  
Thermal Behavior of Polyurethanes (PEPA/TDI/Diol System)

Diol chain extender	<i>idt</i> (°C)	Temperature at % wt loss				<i>ipdt</i> (°C)	Residue at 500°C (%)	$E_a$ (kcal)
		10	30	50	70			
Ethanediol	224	260	330	358	392	351	3.0	19.8
1,2-Propanediol	222	260	328	352	390	354	—	14.0
1,4-Butanediol	228	265	335	368	390	365	3.0	21.3
1,5-Pentanediol	230	280	330	360	390	353	2.0	17.0
1,6-Hexanediol	240	280	362	362	395	358	3.0	17.2

TABLE VI  
Glass Transition Temperature of Various PUs [ $T_g$  ( $^{\circ}$ C)]  
(Polyester/TDI/Diol Systems): Unsaturation Effect

Diol chain extender	Various polyesters				
	PEPA	PEA	PPA	PDEA	PHNA
1,4-Butanediol	-29.0	-29.0	-39.5	-26.0	-8.0
1,4-Butene-2-diol	-26.5	-26.0	-37.0	-25.0	-5.0
1,4-Butyne-2-diol	-23.0	-21.5	-33.5	-19.5	-1.0

The data on thermogravimetric analysis based on unsaturated diols is reported in Table VII. The thermal stability of polyurethanes was found to increase with increasing unsaturation in the diol extenders, since the bond dissociation energies increase with unsaturation<sup>13</sup> as follows:

Nature of bond	Bond dissociation energy (kJ/mol)
HC $\equiv$ CH	712
H <sub>2</sub> C=CH <sub>2</sub>	523
RCH <sub>2</sub> -CH <sub>2</sub> R	327

The effect of chain flexibility imparted by the ether link in the diol chain on  $T_g$  is reported in Table VIII. Substitution of a methylene group by an oxygen atom (referring to the case of 1,5-pentanediol and diethylene glycol) did not result in lowering the  $T_g$  despite higher flexibility offered by the —C—O—C— bond. However, when the number of the —C—O—C— bond in the extender increased, the  $T_g$  was found to be lowered, as in the case of poly(ethylene glycol) (PEG 400). The thermal stability was observed to be more or less similar in the case of polyurethanes extended by pentanediol, diethylene glycol, and PEG (400).

The effect of diisocyanate structure on chain mobility ( $T_g$ ) is studied using various diisocyanates such as TDI, MDI, HDI, IPDI, and TMDI, and various polyols such as PEPA-I, PEA, PPA, PDEA, PHNA, and castor oil. In all these recipes the chain extender used was butanediol. Table IX reports magnitudes of  $T_g$ 's of various polyurethanes. It was generally observed that irrespective of nature of backbone polyol, the maximum and minimum  $T_g$ 's were found in MDI- and HDI-based polyurethanes. Also  $T_g$ 's due to TDI- and IPDI-based polyurethanes were closely located, the latter invariably occurring at lower temperature than the former. The higher  $T_g$  exhibited by MDI-based PU can be attributed to the higher functionality of MDI (Fig. 1), which in turn provides sites for crosslinking, thereby increasing the  $T_g$ . The  $T_g$ 's of IPDI- and TDI-based polymers were closely located because of two factors, viz., cyclic structure of the diisocyanate and presence of crosslinking site (—NCO group) on the cyclohexyl ring. The  $T_g$ 's of HDI-based polyurethane were the lowest because of the presence of a purely aliphatic network and the absence of a rigid structure in the backbone. The  $T_g$ 's of TMDI-based polymers were considerably lower but higher than HDI-based polyurethane. TMDI has three pendent methyl groups; out of the three, two are attached onto the same



TABLE VII  
Thermal Behavior (PHNA/TDI/Diol System): Unsaturation Effect

Diol chain extender	<i>idt</i> (°C)	Temperature % wt loss			<i>ipdt</i> (°C)	Residue at 500°C (%)
		10	30	50		
1,4-Butanediol	240	315	345	370	382	5.0
1,4-Butene-2-diol	260	310	354	384	388	6.0
1,4-Butyne-2-diol	268	322	364	395	394	13.0
		(PEPA/TDI/diol system)				
1,4-Butanediol	228	275	315	358	365	3.0
1,4-Butene-2-diol	235	280	328	370	378	4.0
1,4-Butyne-2-diol	230	280	345	375	388	3.0
						21.3
						27.1
						31.7

TABLE VIII  
Glass Transition Temperature of Various PUs [ $T_g$  ( $^{\circ}\text{C}$ )]  
(Polyester/TDI/Diol Systems)

Diol chain extender	Various polyesters			
	PEPA	PEA	PPA	PDEA
1,5-Pentanediol	-31.0	-29.5	-41.0	-28.0
Diethylene glycol	-30.0	-29.5	-39.3	-26.0
Polyethylene glycol	-38.0	-37.5	-43.0	-34.5

TABLE IX  
Glass Transition Temperature [ $T_g$  ( $^{\circ}\text{C}$ )] of Various PUs  
(Polyester/Diisocyanate/BD System)

Diisocyanate used	Various polyesters					
	PEPA	PEA	PPA	PDEA	PHNA	CO
TDI	-29.0	-29.0	-39.5	-14.5	-8.0	-14.5
MDI	-13.5	-17.0	-34.0	-12.0	-2.0	-2.0
HDI	-42.0	—	-48.0	-44.0	-50.0	-39.0
IPDI	-34.0	-31.5	-39.0	-20.0	-14.0	-17.5
TMDI	—	35.0	—	—	-38.0	-36.0

carbon atom which contributes towards the symmetry of the molecule but the third one (methyl group) disturbs the symmetry. Generally, existence of a pendent group increases the  $T_g$  substantially, as observed in the case of polyethylene ( $T_g = -120^{\circ}\text{C}$ ) and polypropylene ( $T_g = -10^{\circ}\text{C}$ ).

The thermogravimetric analysis data of polyurethanes based on various diisocyanates are reported in Table X. It was observed that the thermal stability of MDI- and TMDI-based polymers was the highest and the lowest, respectively. The general order of thermal stability due to diisocyanates was found to be as follows: MDI > TDI > IPD > HDI > TMDI. The observation was based on the *idt* and *ipdt* values of the polymers (Table X). Actually, the thermal stabilities of TDI- and MDI-based polyurethane should have been nearly equal as both of them had thermally stable aromatic nuclei in their structure. However, there was a considerable difference between the thermal stabilities of the two polymers. The highest thermal stability imparted by MDI can be accounted for by its higher functionality which causes higher degree of crosslinking.

The IPDI-based PU showed lower thermal stability compared to TDI-based polymers. This can be explained on the basis of two factors: (i) One of the isocyanate groups in IPDI is not attached directly to the cyclic ring and (ii) the absence of electron cloud over cyclohexyl ring.

The least thermal stability shown by TMDI-based polyurethane was due to the presence of pendent group in the diisocyanate. Hansen and co-workers<sup>14</sup> have illustrated the effect of pendent group on thermal stability.

TABLE X  
Thermal Behavior of Various PU Systems: Diisocyanate Effect

Diisocyanate used	<i>idt</i> (°C)	Temperature at % wt. loss			<i>ipdt</i> (°C)	Residue at 500°C (%)	$E_a$ (kcal)
		10	30	50			
PEPA/diisocyanate/BD system							
TDI	275	318	356	390	410	12.0	31.6
MDI	280	322	380	410	460	25.0	35.0
HDI	260	310	350	378	400	0.0	20.0
IPDI	263	312	350	385	405	5.5	25.3
TMDI	258	310	345	370	390	—	—
PHNA/diisocyanate/BD system							
TDI	240	315	345	370	395	6.0	—
MDI	270	315	370	410	450	24.0	—
HDI	220	295	330	345	375	1.0	—
IPDI	215	300	330	365	395	5.0	—
TMDI							
PPA/diisocyanate/BD system							
TDI	280	330	377	393	405	7.5	18.3
MDI	282	340	392	406	412	13.0	25.0
HDI	270	305	368	380	392	4.0	11.2
PEA/diisocyanate/BD system							
TDI	255	325	380	420	444	7.0	23.0
MDI	282	337	397	434	456	24.0	29.4



## CONCLUSION

Polyurethanes based on  $\alpha,\omega$ -homologue series of saturated diols show decreasing  $T_g$  with the higher member of the series, i.e.,  $T_g$  decreased from ethanediol- to hexanediol-extended polymers. In the case of the unsaturation effect, the  $T_g$  was found to increase from butanediol- to butynediol-extended polyurethanes. Incorporation of the ether link in the extender moiety did not show significant changes in the thermal properties of polyurethanes. The order of thermal stability of polyurethanes based on various diisocyanates is as follows:

MDI > TDI > IPDI > HDI > TMDI

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