

UrethHall[®] Comparison to Adipates

Introduction

Polyester polyols for urethanes have been available for many years and have served the industry by offering outstanding tensile strength, tear strength, solvent resistance, UV resistance and flexibility. Over this time, however, formulators have been limited by the polyester polyols available and have had to formulate around these limitations to solve existing problems.

Objective and scope

The purpose of this paper is to compare and contrast currently available polyols to newly available polyester polyols, to present a comprehensive battery of tests allowing for easy evaluation of alternative technologies and to establish the role of the isocyanate in the choice of polyester polyols for various properties. It is important to note that the formulations were not optimized for any particular performance property. Rather, they were designed to determine at equivalent loadings (stoichiometry) what differences could be noted in the prepolymer and Thermoplastic Polyurethane (TPU) general physical and performance properties.

The linear systems used in these evaluations can, in fact, be processed either as cast elastomers or as TPUs. The TPU process was chosen in order to avoid potential experimental difficulties with viscosity and rapid gel times that could make it difficult to prepare void-free specimens. It is our belief that the results obtained here accurately reflect the results one would obtain in either a TPU or castable part prepared with these recipes.



Experimental procedure of prepolymers and TPUs

<u>Apparatus</u>:

- Vacuum autoclave equipped with dry ice trap and vacuum pump capable of 29 inches of H₂O or better vacuum.
- Variable speed overhead stirrer capable of 0–50 rpm.
- 1l Ball[®] jar reactor equipped with stirrer, thermometer, N₂ inlet, and installed in a temperature controlled oven and operated with a fume hood.
- 500 ml Erlenmeyer filtration flask with 70 mm Buchner funnel and #1 analytical filter paper for hot filtering 4,4 diphenylmethane diisocyanate (MDI).
- Gloves, goggles and 3M activated carbon type respirator mask.
- 3-blade propeller type stirrer.
- 8" x 11" Teflon[®] coated baking pans.
- % NCO apparatus per ASTM D2572-80.
- Top loading balance/scale with capacity of at least 2500 g
- 80 mm long stem funnel cut to 5".
- Brookfield viscometer equipped with #4 spindles and set for 6 rpm.

Reagents:

- MDI Bayer Mondur[®] M (freshly filtered)
- 1,4 butanediol DuPont (vacuum dried at 40°C and stored over molecular sieves).
- Polyols as indicated, vacuum dried at 80°C for >2 h.
- Hylene® para-phenylene diisocyanate (PPDI) DuPont
- % NCO apparatus and reagents per ASTM D2572-80.

Procedure:

- 1. Approximately 500 g of polyol at 80 °C was weighed directly into the pre-dried 11 Ball® jar reactor assembly.
- 2. The reactor assembly was placed in a heating oven, equipped with an N₂ blanket and fitted to a stirring motor and allowed to come to equilibrium with the 80°C oven.
- The teactor assembly was removed from the oven and either RT granulated PPDI or freshly filtered 60°C MDI was quickly weighed into the reactor, and the reactor was closed and reinstalled into the oven. N₂ sweep and stirring were commenced immediately.
- 4. The prepolymer was allowed to react for 90 minutes in the case of PPDI and 120 minutes in the case of MDI. The reaction was maintained at 80°C, except that the temperature rose to approximately 90–100°C upon initial exotherm.
- 5. The reactor was removed from the oven and the stirrer assembly was removed. The vessel was quickly swept with N₂, sealed and stored for 12 hours at 50°C.



- 6. The prepolymer was sampled for percent NCO and analyzed per ASTM D2572-80.
- 7. TPUs were prepared as 600 g batches. The 80°C prepolymer was weighed into a 11 disposable beaker. BDO was added and the mixture was stirred vigorously until it began to thicken. The mixture was poured into dried Teflon® pans, covered with aluminum foil and placed in the oven at 150°C for two hours. The polymer was post-cured for 12 hours at 70°C.
- 8. The TPU was cut into approximately 1" squares, sealed in a glass jar and stored. Samples were vacuum dried at 80°C for two hours prior to compression molding.

Polyol discussion

In this study, a series of polyester polyols that varied in terms of glycol component and acid backbone were tested. The polyester polyols studied with MDI were made with ethylene glycol, 1,4 butanediol, 1,6 hexanediol and 2-methyl-1,3-propanediol, while the acid moieties were hexanedioic acid (traditional adipate technology) and pentanedioic acid (UrethHall® polyester technology). In the PPDI study, the polyols were derived from 1,4 butanediol, while the acid moieties were hexanedioic acid acid.

Polyol physical properties

Polyester polyols whose backbones are based on pentanedioic acid have unique properties when compared to their adipic acid counterparts. Most notable is the fact that the pentanedioic acid backbone polyesters are all liquid at room temperature, whereas their adipate counterparts are opaque solids if a branched glycol is not used as evidenced in Table I. Thus, the UrethHall® polyester technology offers a polyol that is more readily processable, lower in viscosity and fluid and pourable at room temperature (*Fig. 1, 2*). If the UrethHall® polyol should become frozen, the heat of fusion required to return it to a liquid state is substantially lower than that of an adipate, thereby reducing energy costs and process times.

Tight manufacturing specifications for the UrethHall[®] polyesters provide greater lot-to-lot consistency and better urethane performance and processing. Low acid values on the UrethHall[®], usually 0.30 maximum, compared to standard adipates, usually 0.50– 1.00 maximum, contribute to greater hydrolytic stability of the urethane (Figs. 3, 4). Together with the liquid nature of UrethHall[®] polyesters, the low moisture values on the polyols (0.05 percent maximum) reduce gassing problems and the need for higher curative levels.

Prepolymer discussions

MDI prepolymer composition

The mole ratios of the MDI/polyol were held at 3.86/1.00 throughout the experiments. Likewise, the total NCO/OH mole ratio was held at 1.03/1.00 (i.e., 97 percent stoichiometry), which is typically optimal for an MDI-based TPU.



PPDI prepolymer compositions

The mole ratios of the PPDI/polyol were held at 2.06/1.00 throughout the experiments. The total NCO/OH mole ratio was held at 1.05/1.0 (95 percent stoichiometry). While it would seem desirable to compare MDI and PPDI at the same stoichiometry, previous experience has shown that although 1.03 is optimal for MDI, it is deficient for PPDI.

Prepolymer physical properties

PPDI vs. MDI

It is generally known that PPDI produces higher viscosity prepolymers than either MDI or TDI. This was extremely evident in the adipate controls where prepolymer viscosities were extremely high (Table I; Figs. 5, 6).

UrethHall[®] vs. Adipate

The PPDI/UrethHall[®] prepolymers had a significantly lower viscosity compared to the controls. This trend was evident through the MDI system as well but not so dramatic as with PPDI. In either case, the UrethHall[®] technology potentially offers the formulator a prepolymer that is much easier to process and thus more cost effective (Table I; Figs. 5, 6).

TPU discussions

TPU physical properties

General

All the polyol and isocyanate systems prepared in this study provided good to excellent tensile and tear strengths as 80-85A durometer TPUs (Table II; Figs. 7, 8).

PPDI vs. MDI

The 100 percent modulus of the PPDI system was a little lower than with MDI (see Table II; Fig. 9). Among the PPDIs, the butylene adipate was the stiffest, followed by the butylene UrethHall[®]. This appears to have been caused by the crystallization of the butylene adipate soft segment. In contrast, the butylene UrethHall[®] soft segment remained fully amorphous. PPDI also appears to provide superior tear strength when compared to MDI in these systems (Table II; Fig. 8).

UrethHall[®] vs. Adipate



As stated earlier, the UrethHall[®] technology offers the advantage of a more fully amorphous soft segment in PPDI TPUs compared to the crystalline nature of the adipate soft segment yielding improved 100 percent modulus. The slightly lower tear and tensile strengths of the UrethHall[®] TPUs when compared to the adipate controls are, nonetheless still good for an 80-85 Shore A unoptimized system. As tear strength is generally related to NCO content, a slight adjustment in the isocyanate content is suggested for improved properties (see Table II; Figs. 7, 8, 9, 10.)

TPU dynamic properties

PPDI vs. MDI

The dynamic mechanical analysis data (Table III; Figs.11, 12, 13) shows the following results: PPDI systems exhibit dramatically superior resilience when compared to those utilizing MDI, as evidenced in the lower loss tangent for PPDI. PPDI also provides greater phase separation than MDI, as indicated by its much lower glass transition (Tg) (Table III; Fig. 11). The Tg is measured as the tan delta peak temperature (Table III; Fig. 12). It is at this temperature that the soft segment chains are free to move and are able to reduce the stress that was initially applied. The PPDI systems also exhibit dramatically better percent Bashore rebound results than MDI systems, nearing the 70–100 percent improvement range (Table IV; Fig. 14). PPDI-based urethanes exhibit superior cut growth resistance with negligible cut growth in over 1MM cycles compared to the best MDI system tested at 341.

UrethHall[®] vs. Adipate

The DMTA data indicates that with MDI systems, the adipates yield slightly lower Tgs and higher resilience than the UrethHall[®]. However, the opposite is true with PPDI systems.

TPU thermomechanical properties

PPDI vs. MDI

The PPDI systems provide substantially higher vicat softening points than MDI systems (see Table IV; *Fig. 15.*) PPDI provides a very small improvement in percent compression set over MDI (Table IV; *Fig. 16*). Percent compression set can usually be improved by increasing the isocyanate/polyol mole ratio in favor of the isocyanate.

UrethHall® vs. Adipate

The ethylene UrethHall[®] had a 43° higher vicat softening point than the ethylene adipate in the MDI system. The butylene adipate had a 6° higher vicat softening point than the butylene UrethHall[®] in the MDI system. However, the butylene UrethHall[®] had a 6° higher vicat softening point than the butylene adipate in the PPDI system. It is difficult to draw any sound general conclusions in regards to these properties and why the fluctuations are occurring (see Table IV; Fig. 15).



Hydrolytic stability

General

Micro dumbbells were aged in water at 100°C, samples were withdrawn periodically, equilibrated and then tested. The test is designed to be so severe that it accelerates the degradation of TPU and destroys its integrity before 200 hours. All polyols chosen were below a 0.30 acid value so that the acid value would not have an impact on the rate of hydrolysis. It had been previously determined that polyol acid values of 0.50 or less are necessary to reliably test the hydrolytic stability of the urethane versus acid catalyzed degradation of the polyester.

PPDI vs. MDI

Comparing PPDI versus MDI in a butylene UrethHall[®] system, MDI seems to be significantly better than PPDI. This is most likely related to the substantially higher weight percent polyester in the PPDI system (see Figs. 3, 4.).

UrethHall[®] vs. Adipate

Comparing the butylene UrethHall[®] versus the butylene adipate in MDI systems, substantial improvement in the hydrolytic stability of the TPU with the UrethHall[®] polyol is clearly evident (Figs. 3, 4). This surprising result is fully reproducible and has been verified in related systems.

Oil resistance

General

The TPU coupons are weighed, immersed in ASTM #3 oil for 48 hours at 70°C and then reweighed for percent change, per ASTM D-471.

PPDI vs. MDI

MDI appears to have slightly better oil swell properties than PPDI in both the UrethHall[®] and adipate TPUs (Table IV; *Fig. 17*).

UrethHall® vs. Adipate

The UrethHall[®] TPUs consistently show lower oil swells than the adipates in both isocyanate systems, as well as versus different glycol-based polyols. These differences can be substantial, of the order of 300 percent improvement in the ethylene glycol systems (Table IV, Fig 17).



Conclusions and recommendations

General

Although the formulations were not optimized for performance properties, the objectives of producing representative prepolymers and TPUs were met. A comprehensive series of tests were performed in order to compare and contrast the physical and performance properties of the urethane systems. All the polyester polyols readily produced high polymer TPUs.

PPDI systems

The high viscosity of these systems make them more difficult to handle than the MDI systems. The UrethHall[®] technology definitely helped to reduce the viscosity of PPDI prepolymers to the point where they are manageable. Some examples of successful applications for PPDI systems might include industrial tires, rollers and vibration and sound dampeners.

The PPDI systems should be of value where superior resilience is required, as evidenced by the Bashore rebound and the dynamic property measurements. PPDI systems are also recommended with high upper load bearings for continuous high temperatures, as evidenced by the high vicat softening point. Low part deformation under load is evidenced by the good compression set. Excellent tear strength and cut growth resistance (Ross Flex) provide another indication of relative toughness when PPDI is used versus MDI. However, MDI or TDI elastomers may prove more successful than PPDI in high moisture or high ASTM #3 oil environments.

MDI Systems

MDI systems offer good to excellent overall polyurethane physical and dynamic properties. They provide better hydrolytic stability and oil immersion properties than PPDI. The prepolymers and TPUs made with MDI are much easier to process than PPDI. Some examples of successful applications for MDI systems could include oil seals and gaskets, oil pipeline pigs and printing rolls.

Polyols

The UrethHall[®] polyesters with their "fluid and pourable at room temperature" viscosity, lower heat of fusion and tighter manufacturing specifications have advantages over their linear glycol adipate counterparts. These properties carry over to the MDI and PPDI prepolymers, providing lower viscosity prepolymers that are easier to handle and process. Manufacturing and fabrication is facilitated by reduced gassing problems and greater lot-to-lot consistencies. As a result, energy costs and processing times can be reduced when utilizing UrethHall[®] polyesters versus traditional adipate polyols.

The UrethHall[®] technology definitely is the best polyol choice for PPDI systems. The UrethHall[®] polyesters provide prepolymer PPDI viscosities that are readily processable when compared to the PPDI–adipate viscosities that exceeded 100,000 cps at 70°C. The UrethHall[®] technology also offers a PPDI TPU that has a more fully amorphous soft segment compared to the semi-crystalline adipate soft segment. This



yields improved 100 percent modulus properties and improved polyurethane dynamic performance.

In MDI systems, the adipates have slightly higher tensile strengths/tear strengths than the UrethHall[®] polyesters. However, this was in unoptimized systems. Simple reformulation by increasing the percent hard segment could improve these properties while maintaining the advantages of UrethHall[®] polyesters, namely, their pourable nature, lower prepolymer viscosity, improved oil swell and hydrolytic stability.

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TABLE I

Polyol/prepolymer properties

			Polyol			Prepoly	mer
Polyol	Isocyanate	Sample TPU	Acid No	OH No	Visc. at 25°C, cps	% NCO	cps at 70°C
Ethylene Adipate 4,000	MDI		2060	0.32	54.0	solid	7.16
Ethylene UrethHall®	MDI	2050	0.22	55.4	17,800	7.87	2,400
Butylene Adipate	MDI	4060	0.24	56.2	solid	7.64	5,000
Butylene UrethHall®	MDI	4050	0.20	54.8	9,500	7.60	4,000
Branched Butylene Adipate	MDI	4060A	0.11	63.8	15,100	6.94	4,000
Branched Butylene	MDI	4050A	0.12	55.0	21,600	7.40	3,500
UrethHall [®]							
Hexylene UrethHall®	MDI	6050	0.25	57.1	7,000	7.49	2,500
Hexylene UrethHall®	PPDI	6050	0.25	57.1	7,000	3.14	75,000
Butylene Adipate	PPDI	4060	0.24	56.2	solid	3.54	>100,000
Butylene UrethHall®	PPDI	4050	0.20	54.8	9,500	3.98	18,000



TABLE II

TPU Properties

Polyol	Isocyanate	Sample TPU	T.S. (psi)	Mod. (psi) 50%/100 %	%UE	Die C Tear (PLI)	Shore A Hardnes s
Ethylene Adipate	MDI	2060	7,040	480/740	635	490	80
Ethylene UrethHall®	MDI	2050	5,040	570/950	600	425	81
Butylene Adipate	MDI	4060	8,390	420/850	500	470	87
Butylene UrethHall®	MDI	4050	6,960	380/780	520	440	85
Branched Butylene	MDI	4060A	6,505	315/730	600	380	80
Adipate							
Branched Butylene	MDI	4050A	6,385	325/715	540	335	85
UrethHall®							
Hexylene UrethHall®	MDI	6050	7,335	340/720	520	380	82
Hexylene UrethHall®	PPDI	6050	7,235	475/980	665	500	85
Butylene Adipate	PPDI	4060	8,340	465/890	720	690	82
Butylene UrethHall®	PPDI	4050	8,600	475/960	615	483	83

TABLE III

DMTA TPU Properties

Polyol	Isocyanate	Sample TPU	Tg E'Onse t	Tg tan δ	tan δ 25°C	Soften Pt. °C	Breadth of Trans.
Ethylene Adipate	MDI	2060	-23	-4	0.10	114	45
Ethylene UrethHall®	MDI	2050	-24	-4	0.13	139	43
Butylene Adipate	MDI	4060	-31	-12	0.10	115	45
Butylene UrethHall®	MDI	4050	-31	-6	0.12	114	46
Branched Butylene Adipate	MDI	4060A	-29	-8	0.15	89	46
Branched Butylene	MDI	4050A	-22	-2	0.18	99	43
UrethHall®							
Hexylene UrethHall®	MDI	6050	-28	-7	0.13	108	41
Hexylene UrethHall®	PPDI	6050	-38	-26	-0.04	110	30



Butylene Adipate	PPDI	4060	-36	-22	0.05	110	67
Butylene UrethHall®	PPDI	4050	-38	-27	0.05	120	35

TABLE IV

TPU Properties - Cont'd

Polyol	Isocyanate	Sample TPU	Vicat Sft. Pt.	DMT A Sft. Pt.	ASTM #3 48 h/70 °C Swell %	Bashore Rebound	% Compr. 22 h/70°C
Ethylene Adipate	MDI	2060	95	114	1.3	26	63.3
Ethylene UrethHall®	MDI	2050	133	139	0.5	26	54.2
Butylene Adipate	MDI	4060	131	115	3.0	40	43.5
Butylene UrethHall®	MDI	4050	126	114	2.1	36	51.3
Branched Butylene Adipate	MDI	4060A	101	89	3.3	24	49.4
Branched Butylene	MDI	4050A	98	99	2.5	19	54.8
UrethHall®							
Hexylene UrethHall®	MDI	6050	109	108	4.2	34	54.7
Hexylene UrethHall®	PPDI	6050	156	101	6.1	68	46.8
Butylene Adipate	PPDI	4060	166	110	4.5	63	41.5
Butylene UrethHall®	PPDI	4050	170	120	3.6	68	50.0



POLYESTER VISCOSITY

Temperature Dependence - Linear Glycols



<u>FIG</u>. 1

POLYESTER VISCOSITY







HALLSTAR

HYDROLYTIC STABILITY



<u>FIG</u>. 3

HALLSTAR

HYDROLYTIC STABILITY



--- 4050, AV 0.10 --- 4060, AV 0.20 --- 4060, AV 0.30

<u>FIG.</u> 4

HALLSTAR

PREPOLYMER VISCOSITIES



■ XX60-55 □ XX50-55

<u>FIG</u>. 5

PREPOLYMER VISCOSITIES Glycols and Isocyanates



■ XX60-55 ■ XX50-55



TENSILE STRENGTH Glycols and Isocyanates 10 8 Tensile (M psi) 6 4 2 0 EG BG HG **MPDiol NPG** BG 6050 MDI MDI MDI MDI MDI PPDI PPDI

■ XX60-55 □ XX50-55

<u>FIG</u>. 7

DIE C TEAR Glycols and Isocyanates







■ XX60-55 ■ XX50-55

<u>FIG</u>. 9

50% MODULUS Glycols and Isocyanates



■ XX60-55 ■ XX50-55





■ XX60-55 ■ XX50-55

<u>FIG</u>. 11







■ XX60-55 ■ XX50-55

<u>FIG</u>. 13

% BASHORE REBOUND Glycols and Isocyanates



<u>FIG</u>. 14



VICAT SOFTENING POINT

Glycols and Isocyanates



■ XX60-55 □ XX50-55

<u>FIG</u>. 15



<u>FIG</u>. 16





ASTM # 3 OIL SWELL

<u>FIG</u>. 17

% ELONGATION Glycols and Isocyanates



■ XX60-55 □ XX50-55



Materials Studied

ISOCYANATES

POLYOLS

4,4'-diphenylmethane diisocyanate, MDI

para-phenylene diisocyanate, PPDI

CHAIN EXTENDER

1,4 - butanediol

Formulated to comparable hardness

2060-55 Ethylene Glycol Adipate-Control

- 4060-55 1,4-Butylene Adipate-Control
- XX50-55 UrethHALL Polyesters
 - Ethylene, XX = 20 Neopentyl, XX = 50
- 1,4 Butylene, XX = 40 1,6-Hexylene, XX=60

4050A, 4060A from 2-Methyl-1,3, Propanediol, MPDiol

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Supported work with PPDI

Arco

Supported work with MPDiol

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Nomenclature

<u>XX60</u>	XX = number of carbons in glycol
	2060 is an ethylene glycol
<u>20YY</u>	YY = number of carbons in primary diacid component
	2060 is primarily adipic acid
<u>2060-ZZ</u>	ZZ = hydroxyl value
	2060-55 is 55 OH, ca. 2000 M.W.