MDI-Based Polyurethane Elastomers Using Di-(2-hydroxyethyl) Disulfide as a Curative

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ABSTRACT

Di-(2-Hydroxyethyl) disulfide (DiHEDS) has a similar structure to 1,4-butanediol (BDO) except that there are two sulfur atoms in the middle of the molecule. This paper gives an overview of MDI-based elastomer properties using DiHEDS versus BDO. Physical and thermal mechanical elastomer properties are presented.

The main objective of this study is determining the stoichiometry of an MDI-based elastomers using x-ray fluorescence (XRF). Traditionally, only TDI-based systems make use of measuring stoichiometry by XRF, due to the curatives containing chlorine or sulfur atoms. In this paper, the sulfur content of MDI elastomers cured with DiHEDS was determined using XRF. A study is given showing the accuracy of predicting the stoichiometry from these sulfur values.

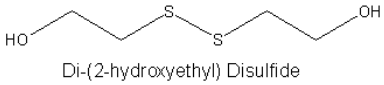
INTRODUCTION

Polyurethane elastomers based on toluene diisocyanate (TDI) are typically cured with diamines. The diamines used most often have an element such as chlorine or sulfur on them which can be measured by a technique called x-ray fluorescence (XRF). In XRF, a sample is bombarded with x-rays, exciting the atoms in the sample and causing them to emit unique and distinguishable radiation back to a detector which can measure the amount of an element of interest. This measurement can be used to calculate the stoichiometry of the polyurethane sample if the %NCO is known.

Since MDI-based elastomers are usually cured with BDO or another diol, XRF cannot be used for calculating the stoichiometry of a part. There are no elements in the molecule to analyze. A mainstream XRF is effective at detecting elements starting from sodium and up to uranium on the periodic table. So, for MDIs, the only way to make sure the ratio was correct when casting with a meter, mix, and dispense machine is to calibrate very well and often. This still gives no way to check the final parts, though.

In a paper given in 2009 at the PMA, it was shown that compression set could be used to predict stoichiometry of a cast part [1]. However, the time before measuring the compression set was a minimum of three days, which in production is a very long time to wait. With XRF, a measurement can be made as soon as the sample cools after demold. That short of an analysis time could be advantageous so adjustments to a casting process could be made before many parts are cast or sent to customers. It would also be good for quality control by periodically checking samples to track variability and accuracy of stoichiometry.

Di-(2-Hydroxyethyl) disulfide is a diol that contains two sulfur atoms bonded together with one hydroxyethyl group attached to each sulfur (Fig. A). So basically it is BDO with a disulfide



Di-(2-hydroxyethyl) Disulfide

1,4 Butanediol

Figure A

group in the middle, making it approximately 41.6% sulfur by weight. It is a low viscosity liquid and its properties are shown in Table 1. It is a somewhat toxic material in that it causes moderate skin irritation and can cause serious damage to the eyes. The equivalent weight is 77 g/eq, making it a little less sensitive than BDO to ratio changes if weights or %NCO is off.

Table 1. Properties of DiHEDS and BDO

	DiHEDS	BDO
Appearance	Clear liquid	Clear liquid
Color	Pale yellow	Water-white
Freezing Pt.	<41°F	64°F
Water Solubility	Miscible	Miscible
Density (20°C)	1.253 g/mL	1.017 g/mL
Viscosity (20°C)	50cP	70 cP (25°C)
Equivalent Wt.	77 g/eq	45 g/eq

Upshaw, et. al. [2] showed that DiHEDS could be a replacement for BDO in MDI-based elastomers. Their research showed that chemical resistance to highly polar organic compounds/solvents is greatly improved in an MDI-polycaprolactone elastomer (Table 2). Other sulfur-containing polymers have shown similar trends, especially in sealants. The focus of this paper, however, is to show that the sulfur atoms in DiHEDS can be used to calculate the stoichiometric ratio (OH:NCO) in an elastomer.

Table 2. Chemical Resistance - BDO vs. DiHEDS

Elastomer Makeup		
Prepolymer	MD-PCL	MDI-PCL
Curative	BDO	DiHEDS
Shore A	90	86
Chemical Resistance: %Wt. gain (1 day)		
Water	0.70%	0.50%
Sulfuric Acid (30%)	0.40%	0.30%
Methanol	10%	8%
Toluene	27%	25%
Isopropanol	11%	6%
MEK	240%	115%
Glacial Acetic Acid	62%	31%
Skydrol LD-4	115%	42%
Chemical Resistance: %Wt. gain (1 week)		
Water	0.90%	0.80%
Sulfuric Acid (30%)	0.60%	0.30%
Methanol	19%	16%
Toluene	44%	43%
Isopropanol	22%	14%
MEK	Destroyed	120%
Glacial Acetic Acid	132%	76%
Skydrol LD-4	Destroyed	150%

A thorough evaluation of processing, physical properties, and thermomechanical properties on the DiHEDS-cured elastomers was done to investigate its similarity to BDO, followed by an XRF study to assess the accuracy of determining the stoichiometry by way of percent sulfur. The studies revealed that DiHEDS is similar to BDO and that XRF is a viable tool for determining stoichiometry in these elastomers.

EXPERIMENTAL

To evaluate the DiHEDS versus BDO, 6”x6” plaques of each were cast with a variety of off the shelf MDI prepolymers. Two polyester-based prepolymers and two PTMEG-based prepolymers were selected. The polyesters had nominal %NCOs of 6.6% (labeled as E1) and 8.15% (labeled as E2) and the PTMEGs had nominal NCOs of 7.25% (labeled as T1) and 8.5% (labeled as T2). The stoichiometry (OH:NCO) targeted for each casting was 97% (NCO/OH index of 103%). It will be the practice in this paper to use stoichiometry from here on. In order to compare the processing of the DiHEDS and BDO, each was cast with and without catalyst. The catalyst used was Dabco® 33LV, a tertiary amine. The amount of catalyst was adjusted to give a potlife of around 5-8 minutes with BDO. The casting conditions were as follows: the prepolymers were heated to 190-200°F, the curatives were at ambient, and the mold temperature was 212°F. The parts were cured for approximately 16 hours at 212°F and left to condition at ambient for 4 weeks before testing. The tests ran on the conditioned plaques are in Table 3. Dynamic mechanical analysis was also run using a 3-point bending apparatus in a constant strain mode at a frequency of 1 Hz.

For the XRF evaluation, only the 6.6% NCO polyester (E1) and the 7.25% NCO PTMEG (T1) were used. Button samples (cylinders with an area of ~1in^2 on the face) that had varying known stoichiometries were cast at the same conditions as above to use as the XRF calibration standards.

Table 3. ASTM Methods used for Testing

Tensile properties	D412
Die C tear	D624
Split tear	D1938
Compression Set	D395, Method B
Rebound	D2632

The XRF testing consisted of setting up a method for the polyether and the polyester for measuring sulfur, running blanks and the calibration standards we cast, and then running some blind samples. The XRF used was a Spectro Phoenix II, which uses indirect excitation and an x-ray tube as its source of x-rays.

RESULTS AND DISCUSSION

Processing Differences

One major difference in the diols was the potlife. With the DiHEDS, the potlife was much longer. In most cases, it was at least twice as long, whether catalyzed or not (Table 4). The uncatalyzed specimens had potlives greater than 20 minutes. Looking at T1, the addition of three times as much catalyst finally gave a potlife of less than what it was with BDO. The longer potlife makes sense since sulfur is a fairly electronegative element and it would have a tendency to lower the reactivity of the hydroxyls in the same manner as the chlorine atoms in MBOCA do. Unfortunately, the long potlives caused imperfect samples with cracks and/or flakes in the elastomer that lead to low tensile and elongation values.

Table 4. Processing Differences between BDO/DiHEDS

Pre-polymer	Catalyst (drops)	Approx. Potlife (mins.)	
		BDO	DiHEDS
T1	--	12	>35
T1	4	5	12
T1	12		4
T2	--	9	23
T2	3	5	9
E1	--	20	48
E1	3	6	9
E2	--	n.d	n.d.
E2	2	5	45

E1 = 6.6% NCO MDI-Polyester
E2 = 8.15% NCO MDI-Polyester
T1 = 7.25% NCO MDI-PTMEG
T2 = 8.5% NCO MDI-PTMEG

Physical Properties

The tensile, tear, and compression properties of the elastomers can be found in Appendix A. All the DiHEDS-cured materials had slightly higher hardness compared with their BDO analogs. This is probably due to the higher MW of DiHEDS versus BDO resulting in a higher hard segment content. The DiHEDS samples also exhibited slightly lower rebounds and increased compression set with all the prepolymers. Many of the samples had abnormalities in them, which is why some of the tensile strengths and elongations are much lower than the BDO cured materials, which also had some abnormalities. This made it hard to find any trends between the two curatives.

Two extra sets (T1 & E1) of materials were cast with higher levels of catalyst, since in our experience, MDI based elastomers are physically and aesthetically better when catalyzed to have a short potlife. The test specimens for these looked much better and had no cracking or flaking. The physical properties were much higher and are compared to previous test data when cast with BDO in Table 5.

From this data, it can be seen that the DiHEDS cured elastomers provide similar tensile and tear strength to the BDO cured materials. The compression set with E1 was almost identical, but with the PTMEG (T1), the value was significantly higher (30% vs. 15%), though 30% is still a good value. The same was true of the elongation with T1. One theory for this may be that the MDI-DiHEDS hard segment is a little

Table 5. Physical Properties - DiHEDS vs. BDO: Higher Catalyst Level

Prepolymer	T1	T1	E1	E1
Curative	DiHEDS	BDO*	DiHEDS	BDO*
Shore Hardness	92A	90A	88A	85A
Tensile, psi	4975	4100	5628	5620
100% Modulus, psi	1041	1250	838	800
300% Modulus, psi	1689	2450	1636	1690
Elongation, %	538	430	589	585
Die C Tear, pli	394	410	458	500
Split Tear (avg.), pli	110	90	241	220
Rebound, %	58	66	28	32
Compression Set, %	30	15	34	32

*Values from previous tests

more flexible in the polyether due to some type of phase mixing or compatibility issue. Another theory may be that the hard segment is less ordered or less crystalline than an MDI-BDO hard segment. The DMA curves also illustrate this small difference in the hard segment, as can be seen in the next section.

Dynamic Mechanical Analysis

Figures B and C show the storage modulus and tan delta curves for T1 and E1 cured with BDO and DiHEDS. Both of the DiHEDS samples match their BDO analogs very closely. The region where the glass transition or brittle point occurs is approximately -75°C for T1 cured with BDO and -70°C with the DiHEDS. For E1, the polyester, the brittle point is at approximately -20°C with BDO and -20°C with DiHEDS.

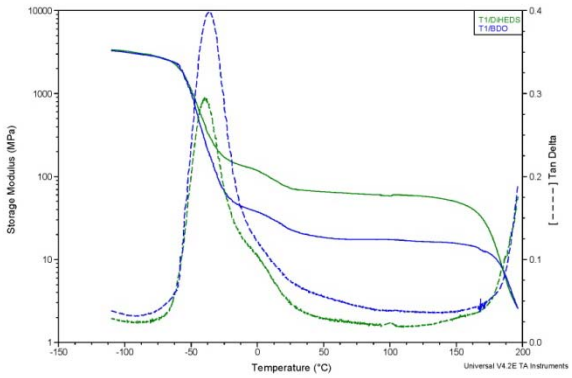


Figure B. DMA curves for T1 (Blue=BDO, Green=DiHEDS)

The storage modulus for the T1 and E1 was higher for the DiHEDS than with BDO, which makes sense since the hardness was a little higher. The softening (melting) point of the hard segment for T1 was approximately 175°C with BDO, but only 166°C with the DiHEDS. At least with the PTMEG, it appears that just as observed with compression set and elongation, the hard segment formed with DiHEDS is not quite as phase separated or as ordered. These slight differences are not necessarily going to make a difference in performance, however, field testing or dynamometer testing would be the way to confirm this.

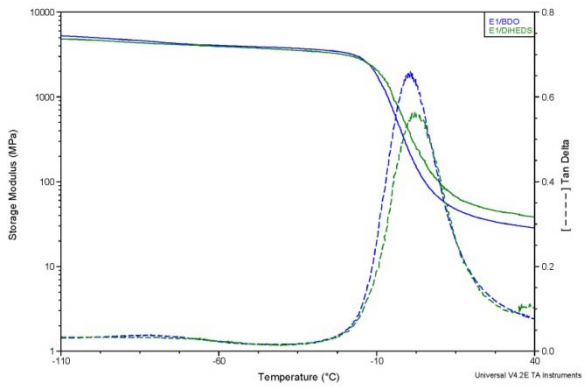


Figure C. DMA curves for E1 (Blue=BDO, Green=DiHEDS)

XRF Analysis

The ability to accurately predict the amount of sulfur in the DiHEDS elastomers was ultimately our goal if the elastomers produced had comparable properties to BDO. Since the properties were comparable, the next step was to create methods on the XRF analyzer to measure the sulfur content. Standards were cast at stoichiometries ranging from 85% to 105% in increments of five, again using E1 and T1. This range represents the typical processing range of an MDI with a cushion on either end.

After the method was created, four blind (unknown to the analyzer) samples of each were cast and analyzed on the XRF. The data is in Table 6. When running XRF samples, it is our protocol to run a standard side-by-side with an unknown to develop an adjustment factor, since variables such as temperature can influence the XRF to drift very slightly from calibration. By running the known sample, this drift can be factored out. In this case, multiple known samples were analyzed, drift factors calculated, and an average was used.

The predicted stoichiometries on the samples were fairly close to the actual values. Other studies we have previously done using MBOCA, which contains chlorine, have had percent errors of 1.0-1.5%, on average. The average percent error for T1 was -1.88% and for E1 the average was -2.26%. The error is higher, but for most systems, knowing the stoichiometry within 2% would be acceptable.

For a more direct comparison on XRF accuracy, a blind sample study was done on a TDI-based elastomer also cured with a sulfur containing curative. A standard low free TDI/PTMEG prepolymer cured with Ethacure

300 (another sulfur containing diamine) was chosen for the study. The results are in Table 7. The percent error for the TDI-based system was -0.69%. This is almost three times lower percent error, showing slightly better accuracy with a TDI-Ethacure 300 system.

Table 6. XRF Predictions - MDI-DiHEDS

Sample	%Sulfur	Stoichiometry		Difference	%Difference
		Predicted	Actual		
T1-A	4.491	0.898	0.886	-0.0120	-1.35%
T1-B	5.315	1.087	1.066	-0.0208	-1.95%
T1-C	4.852	0.980	0.964	-0.0158	-1.64%
T1-D	4.625	0.928	0.905	-0.0233	-2.57%
					Avg.=-1.88%
E1-A	4.836	1.079	1.060	-0.0187	-1.77%
E1-B	4.173	0.914	0.892	-0.0224	-2.51%
E1-C	4.293	0.944	0.923	-0.0206	-2.24%
E1-D	4.586	1.016	0.991	-0.0250	-2.53%
					Avg.=-2.26%

Table 7. XRF Predictions - LFTDI-PTMEG-Ethacure 300

Sample	%Sulfur	Stoichiometry		Difference	%Difference
		Predicted	Actual		
A	4.014	1.016	1.017	0.0009	0.09%
B	3.691	0.922	0.911	-0.0115	-1.26%
C	3.952	0.998	0.993	-0.0048	-0.48%
D	3.813	0.958	0.946	-0.0116	-1.22%
E	4.031	1.021	1.015	-0.0060	-0.59%
					Avg.=-0.69%

CONCLUSION

DiHEDS is a molecule that is similar to 1,4 butanediol in structure. When curing MDI-based prepolymers with DiHEDS, it was shown that the physical and dynamic properties of the elastomers compare very well with BDO cured MDIs. Since there are sulfur atoms in DiHEDS, XRF can be used to calculate back to the stoichiometry of the elastomer, and it was demonstrated that the error is only around 2%. Overall, DiHEDS could be used as a good replacement for BDO with the added advantages of better chemical resistance to highly polar organic compounds/solvents and the ability to check stoichiometry on cast parts.

REFERENCES

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Appendix A. Physical Properties - DiHEDS vs. BDO

Prepolymer	T1	T1	T1	T1	T2	T2	T2	T2
Curative	BDO	DiHEDS	BDO	DiHEDS	BDO	DiHEDS	BDO	DiHEDS
Catalyst	yes	yes	no	no	yes	yes	no	no
Shore A Hardness	87A	90A	88A	92A	91A	94A	91A	94A
Tensile Strength, psi	3014	1860	3010	1098	1517	1175	1464	1429
100% Modulus, psi	904	923	1031	931	1200	1208	1179	1082
300% Modulus, psi	1739	1533	1996	-	-	-	-	205
Elongation, %	444	369	369	203	173	105	172	237
Die C Tear, pli	458	413	437	372	541	452	483	365
Split Tear (avg.), pli	87	76	70	72	89	112	85	101
Rebound	65	59	67	59	64	58	64	58
Compression Set	17	31			19	24		
Comment	flakes	bubbly	cracks	bubbly	cracks	flakes	bubble	bubbly

Prepolymer	E2	E2	E2	E2	E1	E1	E1	E1
Catalyst	yes	yes	no	no	yes	yes	no	no
Curative	BDO	DiHEDS	BDO	DiHEDS	BDO	DiHEDS	BDO	DiHEDS
Shore Hardness	91A	92A	93A	92A	82A	85A	82A	85A
Tensile, psi	6232	464	5565	1226	5603	4725	7068	5112
100% Modulus, psi	1151	-	1294	1073	739	646	760	669
300% Modulus, psi	2607	-	2620	575	1627	1273	1701	1298
Elongation, %	477	12	438	152	538	570	580	570
Die C Tear, pli	545	361	576	462	482	386	499	376
Split Tear (avg.), pli	208	122	220	153	175	164	183	145
Rebound	50	41	52	40	36	26	36	30
Compression Set	16	30			22	26		
Comment		cracks		bubbly				dimpled