

**Progress in Chain Extender Evaluation  
for Polyurethanes Derived from  
Hydroxyl-Terminated  
Polybutadiene Resins**

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## ABSTRACT

Chain extender plays a significant role in enhancing the final mechanical properties of polyurethanes derived from hydroxyl-terminated polybutadiene (HTPB) and 4,4'-methylenebis(phenyl isocyanate) (MDI). Conventionally, N, N-diisopropanol aniline (DIPA) and 2-ethyl-1,3-hexanediol (EHD) are recommended for their compatibility and physical property enhancement of the polyurethane elastomer. By comparison, 1,4-butanediol (BDO), widely employed in polyurethanes based on polyether or polyester polyols, is not a good choice owing to its poor compatibility with HTPB resins. A systematic screening of both aromatic and aliphatic diols as potential chain extenders in standard HTPB-based polyurethane formulations has been carried out. Although a good correlation could not be drawn between the diol structure and mechanical performance, two new aliphatic diols were notable for their superior performance.

## INTRODUCTION

Polyurethanes based on polybutadiene polyols are known for excellent hydrophobicity, hydrolytic and chemical resistance, electrical insulation properties, and low-temperature flexibility [1-3]. Similar to other polyurethanes, the gum stock formulations based on neat HTPBs and stoichiometric amounts of diisocyanates usually possess inferior mechanical properties. Incorporating chain extenders, such as diols of low molecular weight, in the gum stock formulas enhances the elastomeric properties of the resulting polyurethanes, because the small diols react with diisocyanates and form hard domains to serve as the physical crosslink for the polyurethane systems. Traditionally, 1, 4-butanediol is one of the most important chain extenders used in commercial polyurethane elastomers based on polyether or polyester polyols. Since HTPBs have a completely non-polar backbone structure, many chain extenders designed for polyether or polyester polyols were proven to be unsuitable for the HTPB-derived polyurethanes. The poor compatibility between the chain extenders and the non-polar nature of the polybutadiene backbone was attributed to be the root cause.

Two types of HTPB resins are available commercially. Poly bd<sup>®</sup> resins are radically polymerized products,

having about 2.5 hydroxyl functionalities [4]. Krasol<sup>®</sup> LBH and LBH-P polybutadiene diols are anionically polymerized products with a very narrow molecular-weight distribution, each containing no species with a functionality higher than 2.0 [4]. We have shown in previous publications that 2-ethyl-1,3-hexanediol and N,N-diisopropanol aniline (Voranol<sup>®</sup> 220-530) were excellent chain extenders [1,5] for the polyurethanes derived from either Poly bd or Krasol resins. Because of recurring supply issues, we initiated a search for alternative chain extenders suitable for the polyurethane system based on HTPB resins. The report describes our preliminary findings.

## EXPERIMENTAL

### Materials

Poly bd and Krasol resins were obtained from Cray Valley Co. Chain extenders 2-ethyl-1,3-hexanediol (EHD), 1,3-butanediol (1,3-BG), 2-butyl-2-ethyl-1,3-propanediol (BEPG), and 2,4-diethyl-1,5-pentanediol (PD-9) were sampled from Kyowa Hakko U.S.A. Inc. Hydroquinone bis(2-hydroxyethyl) ether, N-phenyldiethanolamine, 4,4'-methylenebis(phenyl isocyanate) (MDI), dibutyltin dilaurate (DBTDL), 1,6-hexanediol, and 2,2,4-trimethyl-1,3-pentanediol (TMPD) were purchased from Aldrich. HER<sup>™</sup> HP, i.e., resorcinol di(2-hydroxyethyl)ether was kindly given to us by Indspec Chemical Corporation. All the materials were used in the reaction as is, without further purification.

### Preparation of Polyurethanes

#### Lab Procedure:

##### One-Shot Procedure

To a four-necked resin kettle was added Krasol LBH-2000 resin, followed by degassing and dehydrating at 85°C *in vacuo* (<10 mmHg) for 1.5 hrs. Diisocyanate MDI flakes and solid chain extenders (CE) were melted in an oven right before usage. To a centrifuge cup were then charged liquid Krasol resin, MDI, CE, and DBTDL catalyst. The mixture was homogenized in a SpeedMixer<sup>™</sup> (model DAC 150), then poured onto a hot metal mold. The sample was initially cured in an oven at 110°C for 3.5 hrs, and then at 65°C overnight. The sample was further aged one week at room

temperature to ensure complete curing before the testing of physical properties was performed.

#### Prepolymer Procedure

To a four-necked resin kettle was charged MDI flakes. The kettle was heated with stirring to melt the MDI under nitrogen. To the kettle containing liquid MDI was added warm (65°C) Krasol LBH 2000 resin. The reaction was held at 75°C for 1.5 hrs to form the prepolymer, which was then degassed at 75°C *in vacuo*. To a centrifuge cup were then charged the prepolymer, liquid CE, and DBTDL catalyst. The mixture was homogenized in a SpeedMixer™ (model DAC 150), then poured onto a hot metal mold. The sample was initially cured in an oven at 110°C for 3.5 hrs, and then at 65°C overnight. The sample was further aged one week at room temperature to ensure complete curing before the testing of physical properties was performed.

#### Characterization and Testing

An Instron Materials Tester (model 4301) was used for measuring physical properties of polyurethane sheets at 22.2°C (72°F) and 60% relative humidity. Tensile strength, elongation and modulus (at 50% strain) were obtained by following the ASTM D 412 protocol. Tear strength was determined by following the ASTM D 624 protocol. For each sample four or five specimens were tested and an average value was reported. Sample hardness was determined with a

Round Shore Durometer Type A or Type D at room temperature.

## RESULTS AND DISCUSSION

A few diols of low molecular weight were selected as potential chain extenders, including aromatic and aliphatic ones. Examining the compatibility of the diols with HTPB resins at various temperatures serves as the initial screening before incorporating them in polyurethane formulations. Two preparative procedures, namely, one-shot and prepolymer, were used to make the polyurethane sheets. The hard domain contents in the polyurethane sheets were set at 30, 35, 40 and 45% for monitoring the concentration effect of the chain extenders on physical properties. As to HTPB resins, both Krasol LBH 2000 and Poly bd R45HTLO resin were examined.

#### Aromatic Diols As Chain Extenders

The compatibility of three aromatic chain extenders with Krasol LBH 2000 resin was evaluated and the results are listed in Table 1. It is conceivable that the aromatic chain extenders selected have extremely poor compatibility with the Krasol resin. We managed to evaluate 1,3-bis(2-hydroxy ethoxy) benzene and N-phenyldiethanolamine in a prepolymer procedure, hoping that pre-reacting of the diols with MDI would mitigate the compatibility issue. Unfortunately, with the 30%, 35% and 40% hard domain contents, the polyurethanes derived from both chain extenders were inferior to the controls containing EHD. Thus, they were not evaluated further.

Table 1. Compatibility of Aromatic Chain Extenders (CE) with Krasol LBH 2000 Resin

Chemical name	Wt ratio of CE / LBH- 2000	Miscibility and solubility	
		@ 23°C	@ 110°C
1,3-bis(2-hydroxy ethoxy) benzene, (HER™ HP)	3.2 / 10.0	Two phases (liquid, solid)	Two liquid phases
Hydroquinone bis(2-hydroxyethyl) ether	3.2 / 10.0	Two phases (liquid, solid)	Two phases (liquid, solid)
N-phenyldiethanolamine	3.0 / 10.0	Two phases (liquid, solid)	Two liquid phases

### Aliphatic Diols As Chain Extenders

These aliphatic diol candidates were chosen based on their commercial availability and significant hydrocarbon moiety in the molecules. They were

submitted for compatibility testing with Krasol LBH 2000 resin and the results are listed in Table 2. There is no strong distinction based on compatibility to favor any one chain extender over the others. Thus, they were all tested in the polyurethane formulations.

Table 2. Compatibility of Aliphatic Chain Extenders (CE) with Krasol LBH 2000 Resin

Chemical name	Wt ratio of CE / LBH- 2000	Miscibility and solubility	
		@ 23°C	@ 110°C
1, 6 - hexanediol	3.0 / 10.0	Two layers	Two layers
2, 2, 4 – trimethyl-1, 3–pentanediol (TMPD)	3.2 / 10.0	Soluble	Soluble
2-ethyl-1,3-hexanediol (EHD)	Any ratio	Soluble	Soluble
1,3-butanediol (1,3-BG)	2.0 / 10.0	Intensely cloudy	Cloudy
2-butyl-2-ethyl-1,3-propanediol (BEPG)	3.0 / 10.0	Partial BEPG crystallized	Clear, homogeneous
2,4-diethyl-1,5-pentanediol (PD-9)	3.0 / 10.0	Cloudy, heterogeneous	Lightly cloudy, no separation

The chain extender 1,6-hexanediol turned out to be too incompatible with the Krasol resin in the one-shot process. The approach was abandoned. Similarly, the chain extenders 1,3-butanediol and PD-9 yielded parts of low hardness, tensile strength, and modulus compared with those made using EHD in the one-shot process. Although the prepolymer procedure in general mitigated the compatibility issue to a certain degree, the polyurethane parts made by using 1,6-hexanediol, 1,3-butanediol or PD-9 were still not on a par with the materials containing EHD. On the other hand, the chain extenders TMPD and BEPG yielded excellent polyurethane parts with the hard domain contents ranging from 30 to 45%.

The formulations and physical properties of the polyurethanes having hard domain contents of 30% are listed in Tables 3 and 4, which employ Krasol LBH 2000 and Poly bd R45HTLO resin, respectively, along with three outstanding chain extenders. Since the polyurethanes derived from Krasol resin and 4,4'-MDI should be thermoplastic in nature (Table 3), they have better elongation, tear resistance and tensile strength than those crosslinked polyurethanes derived from Poly bd resin and Isonate 143L (Table 4). However, the differences in physical properties between those derived from Krasol and Poly bd resin (Tables 5 and 6, respectively) are not as significant when the hard domain contents reach 45%.

Table 3. Krasol Resin-Derived Polyurethanes Having 30% Hard Domain Contents

	1	2	3	4	5	6
Krasol LBH 2000L, g	100	100	100	100	100	100
2-ethyl-1,3-hexanediol, g	11.69	---	---	11.69	---	---
2-butyl-2-ethyl-1,3-propanediol, g	----	12.45	---	----	12.45	---
2,2,4-trimethyl-1,3-pentanediol, g	---	---	11.46	---	---	11.46
4,4'-methylene bis(phenyl isocyanate), g	31.11	30.56	31.14	31.11	30.56	31.14
20% DBTDL solution in dibutyl phthalate(DBP), drop(s)	2	1	2	1	2	2
Hard segment content, wt. %	29.97	30.08	29.87	29.97	30.08	29.87
Equivalent ratio of LBH/MDI/chain extender	1/2.8/1.8	1/2.75/1.75	1/2.7/1.7	1/2.8/1.8	1/2.75/1.75	1/2.7/1.7
<b>Procedure in synthesis</b>	One shot			Prepolymer		
<b>Physical Property</b>						
Hardness (shore A) at 23°C	79	79	80	82	80	79
Tensile strength, psi	1106	1300	1650	2139	2147	1263
Modulus, psi	438	434	418	518	491	404
Elongation at break, %	216	315	511	440	465	553
Tear resistance, lbf/in	308	305	313	334	312	283

Table 4. Polybd Resin-Derived Polyurethanes Having 30% Hard Domain Contents

	1	2	3	4	5	6
Polybd R45 HTLO, g	100	100	100	100	100	100
2-ethyl-1,3-hexanediol, g	11.62	----	----	11.62	----	----
2-butyl-2-ethyl-1,3-propanediol, g	----	11.30	---	----	11.30	---
2,2,4-trimethyl-1,3-pentanediol, g	----	----	10.62	----	----	10.62
Isonate 143L	32.86	32.27	32.86	32.86	32.27	32.86
20% DBTDL solution in DBP, drop(s)	3	4	3	2	1	1
Hard segment content, wt. %	30.31	30.34	30.31	30.31	30.34	30.31
Equivalent ratio of R45HTLO / Isonate143L / CE	1 / 2.75/1.75	1/2.7/1/7	1/2.75/1.75	1 / 2.75/1.75	1/2.7/1.7	1/2.75/1.75
<b>Procedure in synthesis</b>	One shot			Prepolymer		
<b>Physical property</b>						
Hardness (shore A) at 23°C	81	79	80	79	78	81
Tensile strength, psi	946	874	868	844	712	809
Modulus, psi	450	425	458	449	355	454
Elongation at break, %	195	197	181	177	193	164
Tear resistance, lbf/in	213	203	191	189	142	175

Table 5. Krasol Resin-Derived Polyurethanes Having 45% Hard Domain Contents

	1	2	3	4	5	6
Krasol LBH 2000L, g	100	100	100	100	100	100
2-ethyl-1,3-hexanediol, g	26.30	---	---	26.30	---	---
2-butyl-2-ethyl-1,3-propanediol, g	----	27.75	---	----	27.75	---
2,2,4-trimethyl-1,3-pentanediol, g	---	---	26.28	---	---	26.28
4,4'-methylene bis(phenyl isocyanate), g	56.11	54.45	56.51	56.11	54.45	56.51
20% DBTDL solution in DBP, drop(s)	3	3	2	3	3	1
Hard segment content, wt. %	45.20	45.12	45.29	45.20	45.12	45.29
Equivalent ratio of LBH/MDI/chain extender	1/5.05/4.05	1/4.9/3.9	1/4.9/3.9	1/5.05/4.05	1/4.9/3.9	1/4.9/3.9
<b>Procedure in synthesis</b>	One shot			Prepolymer		
<b>Physical Property</b>						
Hardness (shore A) at 23°C	91	93	94	95	96	95
Tensile strength, psi	2153	2049	2181	3503	3458	2999
Modulus, psi	1104	1145	1439	1565	1512	1702
Elongation at break, %	179	193	173	351	365	368
Tear resistance, lbf/in	429	440	535	534	544	572

Table 6. Polybd Resin-Derived Polyurethanes Having 45% Hard Domain Contents

	1	2	3	4	5	6
Polybd R45 HTLO, g	100	100	100	100	100	100
2-ethyl-1,3-hexanediol, g	23.67	----	-----	23.67	----	-----
2-butyl-2-ethyl-1,3-propanediol, g	----	23.36	---	----	23.36	---
2,2,4-trimethyl-1,3-pentanediol, g	----	----	23.67	----	----	23.67
Isonate 143L	58.56	57.96	58.56	58.56	57.96	58.56
20% DBTDL solution in DBP, drop(s)	4	4	4	1	1	1
Hard segment content, wt. %	45.12	44.94	45.12	45.12	44.94	45.12
Equivalent ratio of R45HTLO / Isonate143L / CE	1 / 4.9 / 3.9	1/4.85/3.85	1 / 4.9 / 3.9	1 / 4.9 / 3.9	1/4.85/3.85	1 / 4.9 / 3.9
<b>Procedure in synthesis</b>	One shot			Prepolymer		
<b>Physical property</b>						
Hardness (shore A) at 23°C	95	96	97	92 - 93	96 - 97	96 - 97
Tensile strength, psi	2617	2780	3326	3032	2622	2580
Modulus, psi	1384	1427	1565	1500	1385	1406
Elongation at break, %	216	246	290	271	235	238
Tear resistance, lbf/in	422	431	487	446	450	465

Based on the limited examples above, it is noted that the good chain extenders, namely, EHD, BEPG, and TMPD are completely soluble in HTPB resins (Table 1). The solubility criterion seems to be a necessary condition for the chain extenders to have before further examining the mechanical properties of the polyurethanes derived from them and HTPB resins. Needless to say, the molecular weight of the chain extenders cannot be excessively large to disrupt the hard domain formation through hydrogen bonding. Interestingly, EHD was found not to be a suitable chain extender any longer when HTPB resins were blended with polyether polyols, such as polypropylene glycol (PPG) and polytetramethylene glycol (PTMEG), to make polyurethane copolymers. BDO turned out to be outstanding again in those polyol blends [5]. Similarly, BDO is a better chain extender than EHD for the polyurethane block copolymers derived from HTPB and polyester polyols [6] regarding the mechanical properties enhancements.

## CONCLUSIONS

In addition to the two classic chain extenders, namely, N,N-diisopropanol aniline and 2-ethyl-1,3-hexanediol, recommended for the polyurethane systems derived from hydroxyl-terminated polybutadienes, two more aliphatic diols are identified through extensive testing for the same utility. These two new chain extenders, 2-butyl-2-ethyl-1,3-propanediol and 2,2,4-trimethyl-1,3-pentanediol are not only miscible with hydroxyl-terminated polybutadienes, but also enhance the mechanical properties in the HTPB-derived polyurethanes, as well as the benchmark 2-ethyl-1,3-hexanediol chain extender.

## REFERENCES

1. "Cray Valley Products for Urethane Elastomers," *Cray Valley Technical Bulletin* No. 1560, Cray Valley Co., 08/05.
2. Pytela, J., M. Sufcak, J. Cermak, and J. G. Drobny. 1998. "Novel Isocyanate Prepolymers Based on Polybutadiene Diols for Composite Binders and Cast Elastomers," *Proceedings of the Polyurethanes EXPO98*, Dallas, September 1998, pp. 563
3. Pytela J. and M. Sufcak. 2000. "Polybutadiene-Urethane Elastomers with Outstanding Resistance to Aggressive Aqueous Media," UTECH 2000 Conference, The Hague, The Netherlands, March 2000. *Conference Proceedings, Coatings, Adhesives, Sealants and Elastomers Session*, Paper 9.
4. "Hydroxyl Terminated Polybutadiene Resins and Derivatives - Poly bd and Krasol," *Cray Valley Technical Bulletin* No. 3151, Cray Valley Co., 06/07.
5. Chao, H. S., J. Pytela, N. Tian, and J. Murphy. 2005. "Thermoplastic Polyurethanes (TPUs) Derived from Hydroxyl-Terminated Polybutadienes (Krasol®)" API 2005 Polyurethanes Technical Conference and Trade Fair, October 17-19, 2005.
5. Pytela J. and M. Sufcak, 1997. "New Anionic Polybutadiene Diols for Polyurethane Systems," *Proceedings of the Polyurethanes World Congress 1997*, Amsterdam, The Netherlands, September 1997, pp. 704.
6. Chao, H. S., and N. Tian, 2007 "Preparation and Property Evaluation of Thermoplastic Polyurethanes (TPUs) Based on Polybutadiene and Polyester Polyols" Polyurethanes 2007 Technical Conference, September 24-26, 2007.