

**Polyurethane Elastomers Derived from  
Krasols<sup>®</sup> and Hydrogenated Krasols<sup>®</sup>  
and Their Weathering and Thermal  
Aging Properties**

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## ABSTRACT

Hydroxyl-terminated polybutadiene (HTPB) resins occupy a unique position among the commercially available polyols. This class of materials may be used to prepare polyurethane elastomers that are characterized by low temperature flexibility, hydrophobicity and hydrolytic stability. Due to the hydrocarbon nature of the polymer backbone, these elastomers also possess extremely low dielectric constant, dissipation factor, and MVTR (moisture vapor transmission rate) properties.

Depending on the hydroxyl functionality and backbone microstructure, namely, the 1,2-vinyl, 1,4-cis, or 1,4-trans distribution of each repeating unit, the HTPB-derived polyurethane elastomers can have a wide range of physical properties including glass transition temperature and viscosity.

The effects of the weathering and thermal aging process on the performance of the HTPB- and hydrogenated HTPB resin-based polyurethanes products were examined.

## INTRODUCTION

Cray Valley's Poly bd<sup>®</sup> resins, a series of hydroxyl-terminated polybutadiene liquid resins, are used worldwide in adhesives, sealants, and electrical applications due to their low glass transition temperatures (-75°C), hydrophobicity, acid-base resistance, and excellent dielectric properties.

The Poly bd<sup>®</sup> resins are made by radical polymerization using hydrogen peroxide initiator and have only about 20% 1,2-vinyl moiety. Although these resins have a predominantly linear backbone structure, they also contain a small portion of branched polymers resulting from the radical polymerization process. Thus, the commercial product has a hydroxyl functionality of 2.4-2.6 per chain on average. This branched structure occasionally imposes limitations on customers' processes or product performance especially when they seek design flexibility between thermoplastic and thermoset properties.

Depending on the hydroxyl functionality and backbone microstructure, namely, the 1,2-vinyl,

1,4-cis, or 1,4-trans distribution of each repeating unit, the HTPB-derived polyurethane elastomers can have a wide range of physical properties including glass transition temperature. To offer more choices and flexibility in the hydroxyl-terminated polybutadiene resin product line, Krasol<sup>®</sup> HTPBs and several new Poly bd<sup>®</sup> LF grades with lower average hydroxyl functionality of 1.9-2.3 were introduced. The Krasol<sup>®</sup> LBH (secondary alcohol termination) and LBH-P (primary alcohol termination) resins are linear diols with an average of 1.9 hydroxyl groups per chain and no species with functionality higher than two. They are made by anionic polymerization and have approximately 65% 1,2-vinyl structure. The di-functional Krasol<sup>®</sup> resins can be used to prepare thermoplastic polyurethane elastomers. Also, the isocyanate-capped prepolymers derived from Krasol<sup>®</sup> LBH resins, as anticipated, have lower viscosity and better stability than those based on the Poly bd<sup>®</sup> resins.

We would like to report some new advancements made with the Krasol<sup>®</sup> HTPB resins.

## RESULTS AND DISCUSSIONS

### Effect of Chain Extenders on the Physical Properties of Krasol<sup>®</sup> Resins-Derived Polyurethane Elastomers

Chain extenders are known to improve the physical properties of polyurethanes by creating hard domains in the elastomers. Because of the incompatibility of many common short chain diols with hydroxyl-terminated polybutadienes, the current study was limited to two compounds, 2-ethyl-1,3-hexanediol (EHD) and N, N-diisopropanolamine (DIPA). The chain extender content was systematically altered to probe its effect on the physical properties of the resulting polyurethanes and then to compare the performance of these two chain extenders.

The polyurethanes were prepared by using Krasol<sup>®</sup> LBH-P 2000 resin and Isonate 143L with a one-shot process. The physical properties of the resulting polyurethanes using EHD as the chain extender are shown in Table 1. The pot life and gel

time do not appear to have any correlation with the hard segment content or the amount of chain extender. However, the hardness, tensile strength, modulus, and tear strength all increased consistently with the increase of the hard segment or chain extender content of the polyurethanes. The elongation at break decreased with the increase of

hard segments. Interestingly, the resilience and compression set properties at room and an elevated temperature did not vary much with the increase of the hard segment contents. The softening temperature ( $T_s$ ) and glass transition temperature ( $T_g$ ) are also reported for all the polyurethane compositions.

**Table 1: Effect of EHD Chain Extender on the Physical Properties of One-Shot Polyurethane Elastomers**

	1	2	3	4	5	6	7	8	9
<b>Elastomer composition</b>									
LBH-P 2000 (1) (pbw)	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Isonate M143 (2) (pbw)	13.44	16.40	21.34	26.89	33.61	40.74	49.79	59.75	71.90
EHD (3) (pbw)	0.00	1.42	3.80	6.46	9.70	13.12	17.48	22.27	28.10
DBTL, 10 % sol. (pbw)	0.06	0.06	0.08	0.08	0.10	0.10	0.10	0.12	0.12
Hard segment (%)	11.85	15.12	20.09	25.01	30.22	35.01	40.22	45.06	50.00
(1)/(2)/(3) equiv. ratio	100/105/0	82/105/18	63/105/37	50/105/50	40/105/60	33/105/67	27/105/73	23/105/77	19/105/81
<b>Processing characteristics</b>									
Pot life (min)	5	9	6	10	5	7	10	8	8
Gel time (min)	6	10	7	11	6	9	11	9	9
<b>Elastomer properties</b>									
Hardness (Shore A)	37.0	46.5	52.3	64.3	68.5	74.3	77.3	81.2	81.8
Tensile strength (MPa)	2.4	3.0	4.3	8.4	12.1	17.3	17.8	18.5	20.6
Elongation (%)	309	253	217	273	231	268	234	176	151
Modulus 100 (MPa)	1.16	1.59	2.47	3.97	7.13	10.18	13.13	15.54	19.38
Tear strength (kN/m)	14	16	23	42	56	62	71	85	95
Resilience/Rebound (%)	-	45.6	50.3	46.8	45.9	45.6	46.2	50.1	53.0
Compression set (%), 72h@23°C	-	58	32	60	53	53	53	55	57
Compression set (%), 22h@70°C	-	78	63	77	73	76	76	89	93
$T_s$ (°C)	95	114	122	103	120	66; 107	67; 108	74; 106	69
$T_g$ (°C)	-38	-37	-36	-36	-35	-35	-36	-36	-36

Similar trends were observed with chain extender DIPA (Table 2) with respect to hardness, tensile strength, modulus, and tear strength. The elongation at break again decreased with the amount of hard segments in the polyurethanes, but the data do not

follow a strictly linear relationship. The room temperature compression set showed significant improvement for the polyurethanes with the higher amount of DIPA chain extender. This phenomenon was not observed with EHD-containing polyurethanes (Table 1).

**Table 2: Effect of DIPA Chain Extender on the Physical Properties of One-Shot Polyurethanes**

	1	2	3	4	5	6	7	8
<b>Elastomer composition</b>								
LBH-P 2000 (1) (pbw)	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Isonate M143 (2) (pbw)	16.01	20.37	25.22	30.91	37.40	44.98	53.99	64.79
DIPA (3) (pbw)	1.76	4.76	8.10	12.01	16.48	21.69	27.89	35.32
DBTL, 10 % sol. (pbw)	0.04	0.04	0.05	0.07	0.10	0.12	0.12	0.15
Hard segment (%)	15.09	20.09	25.00	30.03	35.01	40.00	45.02	50.03
(1)/(2)/(3) equiv. ratio	84/105/16	66/105/34	53/105/47	44/105/56	36/105/64	30/105/70	25/105/75	21/105/79
<b>Processing characteristics</b>								
Pot life (min)	7	8	6	7	5	6	8	5
Gel time (min)	8	9	7	8	6	8	9	6
<b>Elastomer properties</b>								
Hardness (Shore A)	43.8	48.2	65.0	67.5	69.8	80.0	86.3	85.5
Tensile strength (MPa)	3.1	5.2	9.1	12.6	14.5	18.3	19.0	20.5
Elongation (%)	208	330	300	329	260	279	217	187
Modulus 100 (MPa)	1.85	1.99	4.11	6.31	9.18	12.32	15.36	18.19
Tear strength (kN/m)	20	29	49	60	76	84	92	108
Resilience/Rebound (%)	-	47.5	47.9	46.4	46.1	46.6	46.9	47.7
Compression set (%), 72h@23°C	-	57	50	55	45	26	30	28
Compression set (%), 22h@70°C	-	88	76	89	84	84	81	86
Ts (°C)	108	93	67,99	64	69	73	79	64
Tg (°C)	-37	-38	-36	-35	-34	-37	-38	-38

In addition, at a fixed hard segment content, the property changes resulting from molecular weight and microstructure variations of the HTPB component were investigated. These results are shown in Table 3.

The elastomer hardness varied little with different molecular weights of Krasol® resins. Tensile strength, modulus, and tear properties decreased with increasing Krasol® resin molecular weight. The rebound and room temperature compression set properties appeared to favor higher Krasol® molecular weight. The polyurethane derived from the Poly bd® resin yielded a harder material and had much better compression set at an elevated temperature due to its branched structure.

**Table 3: Physical Properties Changes of One-Shot Polyurethanes Caused by Molecular Weight and Microstructure Variations**

LBH-P 2000 (pbw)	100.00				100.00			
LBH-P 3000 (pbw)	-	100.00	-	-	-	100.00	-	-
LBH-P 5000 (pbw)	-	-	100.00	-	-	-	100.00	-
Poly bd R45HTLO (pbw)	-			100.00	-			100.00
Isonate M143 (pbw)	40.74	39.78	38.43	40.88	37.40	36.16	34.45	37.51
EHD (pbw)	13.12	14.15	15.51	13.09	-	-	-	-
DIPA (pbw)	-	-	-	-	16.48	17.76	19.46	16.41
DBTL, 10 % sol. (pbw)	0.10	0.10	0.10	0.20	0.10	0.10	0.10	0.20
Hard segment (%)	35.01	35.04	35.04	35.05	35.01	35.03	35.03	35.03
<b>Elastomer properties</b>								
Hardness (Shore A)	74.3	75.8	70.7	82.2	69.8	74.2	69.2	81.2
Tensile strength (MPa)	17.3	15.7	10.7	10.1	14.5	14.6	12.0	11.8
Elongation (%)	268	254	176	155	260	306	252	209
Modulus 100 (MPa)	10.18	8.54	5.94	8.16	9.18	8.32	6.03	7.48
Tear strength (kN/m)	62	51	48	48	76	61	49	48
Resilience/Rebound (%)	45.6	54.3	66.3	53.6	46.1	53.3	64.2	53.5
Compression set (%), 72h@23°C	53	29	19	35	45	27	34	31
Compression set (%), 22h@70°C	76	78	64	31	84	86	75	43
Ts (°C)	66; 107	116	112	167	69	71	104	167
Tg (°C)	-35	-37	-47	-74	-34	-38	-44	-74

Thermal Aging and Weathering Study on Polyurethanes Derived from Krasol® HTPB Resins and Hydrogenated Krasol® HTPB Resins

The polyurethane samples derived from Krasol® LBH-P 3000 resin or its hydrogenated derivative,

Krasol® HLBH-P 3000 and either aromatic (Suprasec MPR) or aliphatic (Desmodur W) isocyanate along with different amounts of antioxidant and UV absorbers (UVA) were prepared (Table 4) for both thermal aging and weathering studies.

**Table 4: Sample Formulations for Thermal Aging and Weathering Studies**

Sample No.			1	2	3	4	5	6	7	8	9	10
	Component (pbw)	(mmol/g)										
Polyol (1)	LBHP 3000	0.665	100.00	100.00	100.00	100.00	-	-	-	-	-	-
	HLBHP 3000	0.690	-	-	-	-	100.00	100.00	100.00	100.00	100.00	100.00
Stabilizer	Tinuvin B75	-	-	2.33	-	2.36	-	-	2.36	-	-	2.35
	Irganox 1520	-	-	-	-	-	-	0.23	0.23	-	0.23	0.23
Extender (3)	EHD	13.353	13.64	13.64	13.64	13.64	14.15	14.15	14.15	13.56	13.56	13.56
Crosslinker (4)	Glycerol	32.570	1.24	1.24	1.24	1.24	1.29	1.29	1.29	1.15	1.15	1.15
Isocyanate (2)	Suprasec MPR	7.992	37.99	37.99	-	-	39.41	39.41	39.41	-	-	-
	Desmodur W	7.620	-	-	39.84	39.84	-	-	-	39.62	39.62	39.62
Catalyst	DBTL 10 %	0.000	-	-	0.20+	0.20+	-	-	-	0.20+	0.20+	0.20+
	DBTL 0.3 %	0.000	0.20	0.20	-	-	0.20	0.20	0.15	-	-	-
<b>Formulation parameters</b>												
	Procedure		prepolymer		prepolymer		prepolymer			prepolymer		
	Hard segment (%)		34.59		35.37		35.42			35.20		
	Stoichiometry (1)/(2)/(3)/(4)		23/105/63/14		23/105/63/14		23/105/63/14			24/105/63/13		
<b>Processing characteristics</b>												
	Pot life (min)		32	31	21	19	12	20	14	20	-	-
	Gel time (min)		40	36	24	24	17	22	18	26	-	-

**POLYURETHANES – THERMAL AGING**

Test conditions for the aging study included dry heat in the dark at 80 °C for 1, 5, 10, 20, and 30 days. It should be noted, that the experiments were carried out in such a way to protect the samples from light. However, for some operations such as polyurethane synthesis in glass vessel, demolding of cured samples, and opening the oven to withdraw the samples, a short contact with light was inevitable.

The aging effect was monitored by measuring mechanical properties including tensile strength,

elongation at break, modulus @ 100 % elongation, tear strength, resilience/rebound, color changes (color difference, yellowing index) and thermal characteristics, i.e., softening temperature, Ts. The glass transition temperature (Tg) values were determined only for the samples before thermal aging.

The summary of results is given in Table 5. The designation of the samples consists of two numbers indicating the formulation and the exposure time in the aging test. For example, sample 5-20 refers to elastomer 5 in Table 4 after 20 days of aging.

**Table 5: Physical Properties of Thermal Aging Samples**

<b>Sample No.</b>	<b>1-0</b>	<b>1-1</b>	<b>1-5</b>	<b>1-10</b>	<b>1-20</b>	<b>1-30</b>	<b>2-0</b>	<b>2-1</b>	<b>2-5</b>	<b>2-10</b>	<b>2-20</b>	<b>2-30</b>
Tensile strength (MPa)	15.7	15.4	14.1	14.4	12.8	13.1	16.8	16.1	13.0	13.8	13.5	13.5
Elongation (%)	250	223	211	217	179	179	227	220	183	198	205	202
Modulus 100 (MPa)	8.5	8.2	8.0	7.4	8.0	8.1	8.4	8.2	7.7	8.0	7.8	7.7
Tear strength (kN/m)	45	43	43	40	40	42	46	46	41	40	42	44
Resilience/rebound (%)	60.8	60.2	59.7	60.3	60.0	60.0	60.5	60.4	60.0	60.0	59.6	59.5
Compression set, 72h@23°C	17	22	22	21	24	21	19	23	21	23	24	23
Compression set, 24h@70°C	39	25	20	23	19	21	34	22	22	23	19	17
Hardness (Shore A)	74.7	74.5	74.1	73.7	74.1	75.4	73.1	73.7	72.8	71.7	72.2	73.0
Ts (°C)	166	-	165	170	169	168	162	-	163	168	165	168
Tg (°C)	-40	-	-	-	-	-	-39	-	-	-	-	-
Delta E	0.00	1.63	2.10	3.73	5.71	9.01	0.00	1.44	1.51	2.50	3.11	5.30
Yellowing Index	0.0	0.5	2.5	5.5	9.2	14.8	3.5	5.3	6.1	7.5	8.9	12.5

<b>Sample No.</b>	<b>3-0</b>	<b>3-1</b>	<b>3-5</b>	<b>3-10</b>	<b>3-20</b>	<b>3-30</b>	<b>4-0</b>	<b>4-1</b>	<b>4-5</b>	<b>4-10</b>	<b>4-20</b>	<b>4-30</b>
Tensile strength (MPa)	14.0	13.8	15.7	14.2	13.5	13.3	13.4	13.8	15.7	14.4	13.8	13.0
Elongation (%)	311	301	314	290	289	258	381	420	332	299	286	288
Modulus 100 (MPa)	6.1	6.3	6.4	6.5	6.7	6.5	5.6	5.2	5.8	6.1	6.1	5.8
Tear strength (kN/m)	44	43	44	49	46	45	43	43	44	45	45	44
Resilience/rebound (%)	43.2	43.8	43.5	43.5	44.4	42.7	44.3	43.2	42.6	43.3	43.7	43.3
Compression set, 72h@23°C	41	46	36	38	36	48	43	40	34	40	42	40
Compression set, 24h@70°C	41	28	41	29	32	31	35	48	34	35	31	36
Hardness (Shore A)	75.4	77.4	78.0	77.6	76.2	75.5	73.9	75.8	76.6	75.5	73.0	70.4
Ts (°C)	141	-	144	145	156	159	140	-	144	151	148	151
Tg (°C)	-39	-	-	-	-	-	-40	-	-	-	-	-
Delta E	0.00	1.15	1.71	2.49	4.25	5.86	0.00	1.49	1.07	1.50	1.58	2.40
Yellowing Index	2.4	3.5	4.9	6.3	10.4	11.4	4.2	4.9	4.7	6.0	7.3	7.8

<b>Sample No.</b>	<b>5-0</b>	<b>5-1</b>	<b>5-5</b>	<b>5-10</b>	<b>5-20</b>	<b>5-30</b>	<b>6-0</b>	<b>6-1</b>	<b>6-5</b>	<b>6-10</b>	<b>6-20</b>	<b>6-30</b>
Tensile strength (MPa)	17.7	16.6	16.1	16.8	17.7	17.9	17.8	18.2	18.2	18.0	19.3	16.1
Elongation (%)	246	233	212	226	235	235	251	249	251	245	243	241
Modulus 100 (MPa)	11.1	10.1	10.8	10.3	10.5	10.7	9.3	9.3	9.1	9.3	9.5	8.8
Tear strength (kN/m)	49	47	44	45	47	52	49	45	47	47	48	46
Resilience/rebound (%)	57.3	57.2	58.8	59.1	59.1	60.3	58.9	57.5	59.7	59.0	59.6	59.7
Compression set, 72h@23°C	33	36	22	18	23	24	23	24	20	25	23	20
Compression set, 24h@70°C	35	45	33	34	26	25	48	36	35	27	33	21
Hardness (Shore A)	72.0	73.1	73.7	72.9	73.5	73.5	73.1	74.2	74.1	74.2	74.1	73.8
Ts (°C)	157	-	160	161	163	161	159	-	162	161	162	165
Tg (°C)	-49	-	-	-	-	-	-48	-	-	-	-	-

Sample No.	7-0	7-1	7-5	7-10	7-20	7-30	8-0	8-1	8-5	8-10	8-20	8-30
Tensile strength (MPa)	17.1	15.2	16.8	17.6	17.7	17.3	19.2	17.5	17.7	17.8	16.1	18.1
Elongation (%)	236	187	212	238	244	238	462	389	350	347	311	339
Modulus 100 (MPa)	10.7	10.2	10.6	9.6	10.1	10.1	7.1	6.8	7.5	7.8	7.3	7.1
Tear strength (kN/m)	47	46	43	44	42	48	50	52	52	51	49	51
Resilience/rebound (%)	57.9	57.8	58.2	58.7	58.9	60.3	48.6	48.0	47.4	47.3	48.7	47.4
Compression set, 72h@23°C	29	33	25	21	26	21	39	40	39	33	32	36
Compression set, 24h@70°C	53	48	40	30	23	24	56	62	55	53	45	42
Hardness (Shore A)	72.6	73.4	73.9	74.2	74.1	74.4	69.9	73.0	73.6	74.1	74.1	74.2
Ts (°C)	161	-	164	163	163	162	75	143	144	139	143	143
Tg (°C)	-50	-	-	-	-	-	-48	-	-	-	-	-

Sample No.	9-0	9-1	9-5	9-10	9-20	9-30	10-0	10-1	10-5	10-10	10-20	10-30
Tensile strength (MPa)	15.5	14.2	17.1	18.2	17.7	18.0	16.8	15.7	17.0	15.9	15.6	16.3
Elongation (%)	500	358	377	377	329	359	459	410	352	318	311	336
Modulus 100 (MPa)	7.0	6.8	7.2	7.6	7.3	6.8	6.8	6.6	6.9	7.3	7.0	6.4
Tear strength (kN/m)	52	52	53	52	49	49	51	49	50	49	47	47
Resilience/rebound (%)	47.6	47.9	48.0	48.0	49.0	47.9	47.7	46.8	47.3	47.7	48.9	47.6
Compression set, 72h@23°C	42	41	24	34	28	34	43	40	39	36	32	36
Compression set, 24h@70°C	68	58	55	53	54	38	71	61	48	49	42	38
Hardness (Shore A)	69.3	72.9	74.5	73.5	74.1	75.1	68.8	70.9	73.2	73.4	71.4	73.7
Ts (°C)	71	56	141	141	143	141	75	142	148	148	143	145
Tg (°C)	-47	-	-	-	-	-	-46	-	-	-	-	-

Mechanical properties such as tensile strength, modulus at 100% elongation (modulus 100), tear strength and resilience/rebound did not show a dramatic change during aging. Nevertheless, it appears that in many cases the properties reached their final value after 1 to 5 days of aging. This effect was more obvious on elongation and on properties measured on disk specimens (Shore hardness, compression set). These data suggest that the samples were not completely cured.

The compression set at 70 °C improved after 5 days aging for most samples. An interesting trend was observed for compression set at 23 °C. The maximum value for most of the elastomers was found after 1 day aging. Although no simple explanation is evident one can speculate that time-dependent recrystallization of hard segments might be involved.

The determination of compression set was based on the measurement of residual deformation of a test specimen 30 min after removal from the compression device (cf. ISO 815, ASTM D 395). It was found that in the case of determination at 70 °C the deformation was permanent (measurement several days after removal gave the same results), while in the case of test at 23 °C the specimens almost completely recovered within 5-7 days.

The other main objective of the study was to determine aging characteristics of polyurethanes based on the hydroxyl-terminated polybutadiene Krasol LBH-P resin versus hydroxyl-terminated polyolefin, Krasol HLBH-P (hydrogenated polymer). The set of ten different formulations provided indications of the role of diisocyanate (aromatic versus aliphatic), and the role of stabilizer.



### **THE ROLE OF POLYOL (UNSATURATED POLYBUTADIENE VERSUS HYDROGENATED ANALOG)**

The elastomers prepared from hydrogenated polyol exhibited somewhat better mechanical properties (tensile strength, modulus 100, tear strength) than those from unsaturated precursor, but their higher compression set at 70 °C was certainly a deficiency.

The elastomers based on hydrogenated polymer had significantly lower glass transition temperatures compared to those based on LBH-P (-46 to -50 °C versus -38 to -40 °C).

The  $T_s$  values were between 140 and 170 °C for most of the formulations and did not change after aging. The only exception was elastomers 8 to 10 based on hydrogenated polyol and aliphatic isocyanate. The TMA curve of these elastomers before aging exhibited two softening points, the first being rather low. After 1 to 5 days aging the first softening point disappeared and the TMA curve typical for all the formulations was obtained. This observation can be attributed to post-cure of the elastomer during the first days of aging. The samples 8 to 10 showed no signs of melting or deformation in the oven, however, the disks did stick slightly to the polypropylene pad.

### **THE ROLE OF ISOCYANATE (AROMATIC VERSUS ALIPHATIC)**

The elastomers were synthesized using either aromatic (MDI, Suprasec MPR) or aliphatic diisocyanate (hydrogenated MDI, H<sub>12</sub>MDI, Desmodur W). The results show the effect of diisocyanate on polyurethane aging as follows:

Regarding mechanical properties, aliphatic isocyanate markedly increased elongation at break. Also the Shore hardness was slightly higher but only for elastomers based on Krasol® LBH-P polybutadienes. Aromatic isocyanate, on the other hand, significantly improved resilience/rebound and compression set (both at 23 and 70 °C), and slightly increased modulus 100.

As for the thermal characteristics, elastomers prepared from an aromatic isocyanate exhibited

somewhat a higher softening temperature.  $T_g$  values were not affected by the nature of isocyanate.

The effect of isocyanate on the color change was not as obvious as expected, however a positive effect of aliphatic isocyanate on the color stability could be detected.

### **THE ROLE OF STABILIZERS**

Krasol® LBH-P resin contained Irganox 1520 as part of the production requirement, while the hydrogenated polymer Krasol® HLBH-P resin contained no stabilizer. The effect of addition of Tinuvin B75 (and, in the case of hydrogenated polymer, also Irganox) on the stability of elastomers was studied.

The addition of stabilizers had no significant effect on mechanical and thermal properties of the elastomers.

The data obtained from measuring the color changes allow us to discuss the role of stabilization in the case of polyurethanes prepared from the Krasol® LBH-P resins (formulations 1 to 4). The highest change in color was found for MDI based elastomers without Tinuvin; the best color stability was exhibited by polyurethanes containing an aliphatic isocyanate and stabilized with Tinuvin B75.

### **POLYURETHANE WEATHERING**

In many aspects, the effect of weathering was different from that of aging in the oven. Significant changes in elastomer properties were observed (Table 6). Each sample was placed in the QUV Accelerated Weathering Tester for accelerated weathering testing. The samples were examined after 333, 666, and 1000 hours of exposure, respectively. The designation of the samples consists of two numbers indicating the formulation and the exposure time in the weathering test. For example, sample 5-666 refers to elastomer 5 in Table 4 after 666 hours of accelerated weathering.

Sample 1 (Krasol® LBH-P and an aromatic isocyanate with no Tinuvin) had a large loss of elongation, pronounced deterioration of tensile and

tear strength, and increase in hardness with high color change. The Ts remained unchanged. Sample 2, which contained stabilizer, showed smaller changes in tensile, elongation and color (but more pronounced compared to the thermal aging in the oven); The Ts, hardness and tear strength remained unchanged. Sample 3 (Krasol<sup>®</sup> LBH-P and an aliphatic isocyanate without Tinuvin) was already brittle after 330 hours in the QUV tester with complete loss of elongation, and dramatic increase in hardness and Ts. These changes can be attributed to the sample's total transparency which let UV light penetrate deep into the material. The elastomers based on an aromatic isocyanate, such as Sample 1, were translucent and did not deteriorate as fast compared to Sample 3. The color change for Sample 3 was less than that for samples with an aromatic isocyanate, but higher than evidenced in the thermal aging test. Sample 4 (same as Sample 3, but with Tinuvin) presented less change in tensile, elongation, hardness and Ts than Sample 3, while tear strength and color were almost unchanged. All the improvements were mainly due to the presence of stabilizer. For Samples 5 to 7

(based on Krasol<sup>®</sup> HLBH-P and an aromatic isocyanate), the changes in mechanical properties were not dramatic after weathering, but were more pronounced than those in the aging test. For Samples 8 and 9 (based on Krasol<sup>®</sup> HLBH-P and an aliphatic isocyanate without Tinuvin) the surface degraded in a manner similar to a material of incomplete curing. The softening temperature (Ts) remained low with no property improvement, which could be attributed to post-cure, was observed (contrary to aging in oven). Deterioration of all the mechanical properties was observed. However, the presence of an aliphatic isocyanate resulted in lower color changes after weathering. Sample 10 (based on Krasol<sup>®</sup> HLBH-P and an aliphatic isocyanate with Tinuvin) showed no surface degradation, but its softening temperature (Ts) increased during the weathering (similar to aging in oven) with low color changes. Among all the samples tested, Sample 10 had the best performance in the weathering test. The presence of Tinuvin in a polymer completely derived from aliphatic components apparently protected well the material from degradation.

**Table 6: Physical Properties of Weathered Samples**

Sample No.	1-000	1-333	1-666	1-1000	2-000	2-333	2-666	2-1000
Tensile strength (MPa)	16.3	5.2	3.1	5.7	15.1	10.6	9.5	8.5
Elongation (%)	243	61	22	67	205	175	140	121
Modulus 100 (MPa)	8.55	-	-	-	8.48	6.86	7.31	7.21
Tear strength (kN/m)	47	24	20	20	45	43	43	40
Hardness (Shore A)	74.7	79.9	83.6	83.6	73.1	72.5	74.6	74.5
Ts (°C)	160	163	165	163	161	174	161	163
Delta E	0.00	36.49	46.09	43.49	0.00	21.64	27.89	30.86
Yellowing Index	-0.2	63.6	79.5	75.2	3.5	37.5	49.2	54.5

Sample No.	3-000	3-333	3-666	3-1000	4-000	4-333	4-666	4-1000
Tensile strength (MPa)	14.2	5.8	6.2	4.7	13.6	10.4	10.2	9.2
Elongation (%)	314	2	2	1	391	255	187	185
Modulus 100 (MPa)	6.09	-	-	-	5.65	5.55	5.88	6.13
Tear strength (kN/m)	44	28	22	-	44	44	45	45
Hardness (Shore A)	75.4	89.8	93.0	90.8	73.9	73.4	74.1	76.0
Ts (°C)	153	230	219	285	150	159	155	-
Delta E	0.00	8.86	14.26	17.09	0.00	1.51	1.63	2.40
Yellowing Index	2.4	15.5	23.4	27.4	4.2	6.7	6.7	7.3

Sample No.	5-000	5-333	5-666	5-1000	6-000	6-333	6-666	6-1000	7-000	7-333	7-666	7-1000
Tensile strength (MPa)	17.8	11.6	12.4	12.2	17.9	11.7	13.9	10.7	17.3	11.3	12.7	11.0
Elongation (%)	248	131	156	164	249	145	214	147	235	115	166	118
Modulus 100 (MPa)	11	10	10	9	9.46	8.92	8.06	8.32	10.58	10.28	9.50	9.88
Tear strength (kN/m)	50	43	47	48	48	45	45	44	47	46	43	44
Hardness (Shore A)	72	69	78	73	73.1	73.6	71.6	73.4	72.6	76.6	77.6	78.4
Ts (°C)	157	154	156	131	159	159	153	153	161	159	159	164

Sample No.	8-000	8-333	8-666	8-1000	9-000	9-333	9-666	9-1000	10-000	10-333	10-666	10-1000
Tensile strength (MPa)	18.8	9.5	9.5	7.8	15.6	9.9	8.0	8.3	16.6	13.0	12.2	13.4
Elongation (%)	470	236	214	205	456	186	221	198	459	196	172	228
Modulus 100 (MPa)	7.11	5.36	5.65	4.74	7.08	6.78	4.89	5.42	6.90	8.00	8.29	7.64
Tear strength (kN/m)	51	40	34	29	52	42	31	29	50	49	49	48
Hardness (Shore A)	69.9	65.1	62.4	62.9	69.3	67.5	63.1	61.9	68.8	72.0	71.6	72.1
Ts (°C)	75	43	43	-	71	45	-	-	75	-	-	-

## CONCLUSION

Both chain extenders EHD and DIPA improved the physical properties of the polyurethane elastomers derived from Krasol® LBH-P 2000 and Isonate 143M as a result of the increase in hard domain content. There was no significant difference in performance between the two chain extenders.

For each formulation tested, no significant degradation in physical properties was observed for either Krasol® or hydrogenated Krasol® HTPB resins with or without stabilizers during the course of thermal aging at 80°C although some color change at the surface was apparent. Some property improvement observed during aging test can be attributed to the advancement of curing. As anticipated, the polyurethanes made from hydrogenated Krasol® HLBH-P and aliphatic diisocyanate had the best performance in weathering, especially in the presence of a certain amount of antioxidant and UV stabilizers.

## EXPERIMENTAL

### Chain Extender Study

Krasol® polybutadiene diols were used as received, containing about 0.15 % Irganox 1520 antioxidant. Poly bd® R-45HTLO resin was stabilized prior to use by adding 0.18 % Irganox 1520 antioxidant. EHD and DIPA were dried under vacuum to a water content below 0.03 %. DBTL catalyst was diluted with paraffinic oil Marcol 82 prior to use.

The polyurethane elastomer samples were prepared as follows:

The synthesis was performed in a 200 ml glass vessel equipped with an agitator and a vacuum inlet. The vessel was charged with the components in the following order: Polybutadiene polyol, EHD or DIPA (DIPA preheated to 80 °C), isocyanate and catalyst. After each addition the content was mixed thoroughly and degassed using vacuum. The resulting homogeneous mixture was poured into molds. The cure was done at 100°C for 20 h, after demolding the elastomers were post-cured 3-4 weeks at ambient temperature.

### Sample Preparation for Thermal Aging and Weathering Study

The synthesis of the polyurethane elastomers was performed using a prepolymer procedure. In the first step, the Krasol® polyol was reacted with a diisocyanate at 80 °C for 1 h to yield a prepolymer. The synthesis was performed in a 4 l or 6 l glass reactor with an agitator and a nitrogen inlet. The reaction of Krasol® with MDI proceeded without catalyst, while with H<sub>12</sub>MDI the addition of DBTL was needed. In total, four different prepolymer products were prepared, each being synthesized in one 3-5 kg batch (Table 4).

The polyurethane elastomers were prepared in a 200 ml glass vessel equipped with an agitator and

a vacuum inlet. The vessel was charged with the components in the following order: prepolymer (preheated to 60-80 °C), Irganox 1520 (if applicable), EHD (with/without Tinuvin stabilizer), glycerol and catalyst. After each addition the content was mixed thoroughly and degassed using vacuum. The resulting homogeneous mixture was poured into molds. Two types of molds were used to obtain sheets (130x130x2 mm) or cylindrical disk specimens (12.5 mm thickness, 29 mm diameter). From one batch of the polyurethane, 4 sheets or 12 disk specimens were cast. The cure was done at 100 °C for 20 h, after de-molding the elastomers were post-cured at least 3 weeks at ambient temperature in the dark.

### **DETERMINATION OF ELASTOMER PROPERTIES**

Physical and mechanical properties of elastomers were evaluated by the following test methods:

1. Tensile stress-strain properties (ISO 37)
2. Tear strength (ISO 34)
3. Compression set (ISO 815)
4. Rebound resilience (ISO 4662)
5. Color (ASTM D1925 modified, reflectance measurements).
6. Shore hardness (ISO 868).

The glass transition temperature and the softening temperature of the polyurethanes were measured by thermomechanical analysis (TMA) using TMA-CXO4R analyzer (Intertec Ltd., Czech Republic).

### **THERMAL AGING TEST**

The aging of polyurethane elastomers was carried out in an oven at 80 °C in the dark for 1, 5, 10, 20 and 30 days. The cured samples of elastomers of each formulation were prepared for the test as follows:

The sheets (130x130x2 mm) were cut to pieces of either 32x130x2 mm (allowing die-cutting of one specimen for the determination of tensile properties) or 43x130x2 mm (for tear strength). These samples were used also for the determination of color and T<sub>g</sub>, T<sub>s</sub>.

From this “pool”, the samples were selected at random for the aging test to minimize the effect of batch-wise synthesis of the elastomer.

A hole of 5 mm diameter was cut near the edge of the elastomer piece so that the samples could be hung up in the oven using a wire (diameter ca. 4 mm). After the aging, the samples were withdrawn from the oven, die-cut and their properties measured according to the standard methods.

The disks prepared for each formulation were also selected at random for the aging test. They were placed on a polypropylene pad and put in the oven. The disks were used to determine resilience/rebound, compression set and Shore hardness.

### **WEATHERING STUDY**

QUV Accelerated Weathering Tester (model QUV/Spray) from Q Panel Lab Products was used for the accelerated weathering test. The samples were from the same batches as those made for thermal aging test.

### **PARAMETERS**

Set temperature (°C): 50

Actual Irradiance: UVA 340 lamps at 0.63 W/m<sup>2</sup>/nm at the calibration wavelength 340 nm.

Program: One cycle will be 2 hrs: 119 minutes UV at 50 °C, 1 minute UV + water spray. Positions of sample panel would be changed every 111 hrs.

Sample panels had been placed on the racks in QUV Tester for 333, 666, and 1000 hours duration, respectively, before physical tests were made on those weathered samples.