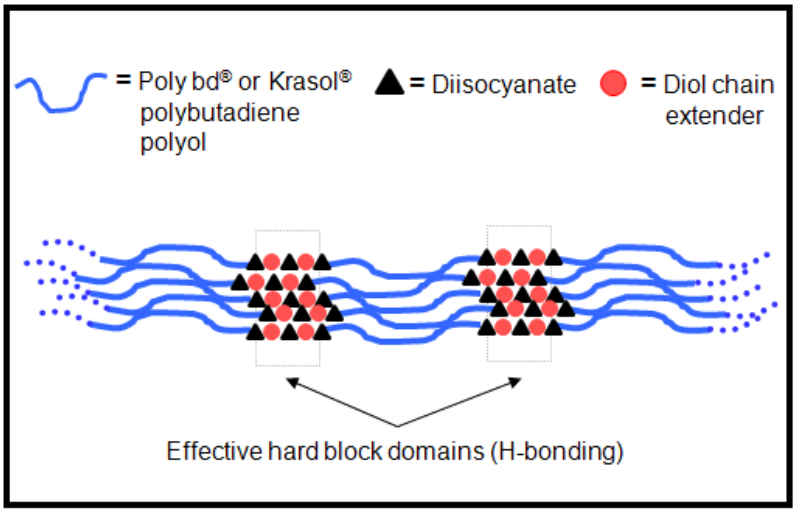
TECHNICAL UPDATE

CRAY VALLEY
Hydrocarbon Specialty Chemicals

Polyurethanes Based on Cray Valley's Hydroxyl-Terminated Polybutadiene Resins Derive Improved Performance from New Chain Extenders



Polyurethane Structure

Target Markets

- Adhesives
- Sealants
- Potting compounds
- Coatings

Additional Information

MSDS/TDS: Poly bd® R45HTLO, Krasol LBH® 2000

Description

Incorporating chain extenders, such as low molecular weight diols, in gum stock formulas enhances the elastomeric properties of the resulting polyurethanes. This is because the small diols react with diisocyanates to form hard domains that serve as physical crosslinks for the polyurethane systems. Traditionally, 1, 4-butanediol

has been one of the most important chain extenders used in commercial polyurethane elastomers based on polyether or polyester polyols. Since Poly bd® and Krasol® hydroxyl-terminated polybutadiene (HTPB) resins have a completely non-polar polybutadiene backbone, a different set of chain extenders are required. We have been recommending 2-ethyl-1,3-hexanediol (EHD) as the chain extender for polyurethanes derived from Poly bd and Krasol resins. Based on recent work, two new chain extenders are available to provide customers with more choices.

Evaluation Results

The chain extenders 2, 2, 4-trimethyl-1, 3-pentanediol (TMPD) and 2-butyl-2-ethyl-1,3-propanediol (BEPG) are soluble in Krasol resins and yield excellent polyurethane parts with the hard domain contents ranging from 30 to 45%. As shown in Table 1, their compatibilities are similar to those of the benchmark chain extender, EHD.

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

Chemical Name	Wt. Ratio of CE/Krasol LBH 2000	Miscibility and Solubility	
		@ 23 °C	@110 °C
2-ethyl-1,3-hexanediol (EHD)	Any ratio	Soluble	Soluble
2,2,4-trimethyl-1,3-pentanediol (TMPD)	3.2/10.0	Soluble	Soluble
2-butyl-2-ethyl-1,3-propanediol (BEPG)	3.0/10.0	Partial BEPG crystallized	Clear, homogeneous

The formulations and physical properties of the polyurethanes having hard domain contents of 30% are listed in Tables 2 and 3. These tables feature Poly bd R45HTLO and Krasol LBH 2000 resins, respectively, and illustrate the impact of three outstanding chain extenders. Since the polyurethanes derived from Krasol resin and 4,4'-methylenebis (phenyl isocyanate) 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 2). However, the differences in physical properties between polyurethanes derived from Krasol and Poly bd resins are not as significant when the hard domain contents reach 45%.

Table 2. Poly bd Resin-Derived Polyurethanes Having 30% Hard Domain Contents

	1	2	3	4	5	6
Poly bd® R45HTLO, g [1]	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, g [2]	32.86	32.27	32.86	32.86	32.27	32.86
20% dibutyl tin dilaurate (DBTDL) solution in dibutyl phthalate (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 Poly bd R45HTLO/Isonate 143L/CE	1.00/ 2.75/ 1.75	1.00/ 2.70/ 1.70	1.00/ 2.75/ 1.75	1.00/ 2.75/ 1.75	1.00/ 2.70/ 1.70	1.00/ 2.75/ 1.75
Procedure in synthesis	One-shot			Prepolymer		
Physical properties						
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

1. Poly bd® is a registered trademark of Cray Valley, Inc.
2. Isonate® is a registered trademark of Dow Chemical.

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

	1	2	3	4	5	6
Krasol® LBH 2000, g [3]	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) (MDI), g	31.11	30.56	31.14	31.11	30.56	31.14
20% dibutyl tin dilaurate (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 Krasol LBH 2000/MDI/CE	1.00/ 2.80/ 1.80	1.00/ 2.75/ 1.75	1.00/ 2.70/ 1.70	1.00/ 2.80/ 1.80	1.00/ 2.75/ 1.75	1.00/ 2.70/ 1.70
Procedure in synthesis	One-shot			Prepolymer		
Physical properties						
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

3. Krasol® is a registered trademark of Cray Valley, Inc.

Conclusions

Since the viable chain extenders, e.g., EHD, BEPG, and TMPD, are completely soluble in HTPB resins (Table 1), it seems that this is a reasonable pre-condition to their evaluation in polyurethanes derived from HTPB resins. In addition, the molecular weight of the chain extenders should not be excessively large as to disrupt hard domain formation through hydrogen bonding. Like the classic EHD, the new chain extenders enhance the mechanical properties of the HTPB-derived polyurethanes to offer formulators more choices.

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