TECHNICAL UPDATE

CRAY VALLEY
A BRAND OF TOTAL

Blending of Hydrogenated Krasol™ and Hydroxyl-Terminated Polybutadiene Polyols for Thermal Stability Improvement

Benefits

- Thermal stability
- Hydrophobicity
- Easy handling
- Excellent dielectric constant

Suggested Applications

- Electric potting compounds
- Thermally stable sealants

Additional Information

SDS: Poly bd® R45HTLO, Krasol™ LBH-P 2000, Krasol HLBH-P 2000 Resin

Description

Polyurethanes based on hydroxyl-terminated polybutadienes (HTPB) are known for excellent hydrophobicity, hydrolytic and chemical resistance, electrical insulation properties, and low-temperature elasticity. However, the unsaturation of the HTPB backbone is susceptible to oxidation and can result in poor aging characteristics of the final products. Hydrogenated hydroxyl-terminated polybutadienes possess the beneficial characteristics of the HTPBs as well as excellent oxidative stability.

This report summarizes the results of the mechanical and thermal properties trends of polyurethanes based on the blends between standard HTPBs and hydrogenated HTPBs.

Liquid hydroxyl-terminated polybutadienes are not always compatible with their hydrogenated counterparts depending on the backbone microstructure and functionalities. Polyurethanes were prepared from the mixture of both polyols in various weight ratios and liquefied methylenebenzene diisocyanate (MDI). The physical properties and morphology of the resulting polyurethanes were evaluated according to the polyol compositions. The purpose of employing two polyols is to reduce the tendency of urethanes made solely with unsaturated polybutadiene polyols to crosslink at elevated application temperature.

Blends Between Poly bd® R45HLTO and Krasol™ HLBH-P 2000 Resins

Poly bd® R45HTLO resin, a hydroxyl-terminated polybutadiene, is not compatible with hydrogenated Krasol™ HLBH-P 2000 resin. Five compositions ranging from pure polyols to turbid mixtures were submitted for reaction with liquefied MDI (Isonate 143L) for polyurethane formation, and their tensile properties were evaluated and reported (Table 1).

Formulas and Mechanical Properties

Table 1: Polyurethane formulas based on polyol blends of Poly bd R45HTLO and Krasol HLBH-P 2000 resin.

Series A	1	2	3	4	5
Poly bd R45HTLO	0	25	50	75	100
Krasol HLBH-P 2000	100	75	50	25	0
Isonate 143L	12.83	12.69	12.55	12.41	12.26

Physical Properties of PU					
Hardness, shore A	52	51	50	49	50
Modulus, psi	96	138	112	157	36
Tensile strength, psi	489	458	248	188	162
Elongation at break, %	894	455	321	138	97
Tear resistance, lbf/in	104	83	45	39	25

Having a lower amount of linear component (e.g., Krasol HLBH-P 2000 resin) in the starting polyol mixture, the tensile strength, elongation and tear resistance of the resulting polyurethanes are reduced. However, the modulus varies and the hardness stays relatively constant.

DSC, TEM and TGA Analysis of Incompatible Polyol Blends and Polyurethanes Made Therefrom

The glass transition temperatures of the individual polyols and their mixtures from the formulas in Table 1 were obtained by differential scanning calorimetry (DSC) analysis (Figure 1). The glass transition temperatures of the polyurethanes derived from those five formulas were measured as well (Figure 2), and the results were tabulated (Table 2).

The glass transition of polyurethanes derived from the incompatible polyol mixture is rather broad. The significant domain separation is confirmed by transmission electron microscopy (TEM) analysis (Figure 2) of sample A-3, with the polyurethane from hydrogenated Krasol resin as dispersed phase, which was not stained.

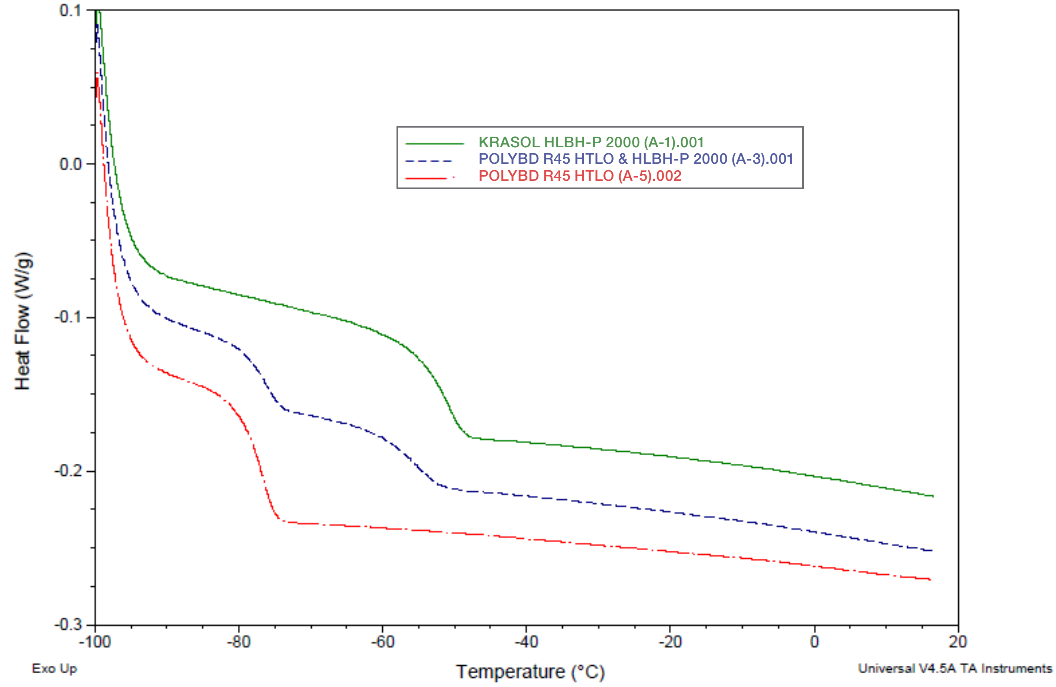

Figure 1: Differential scanning calorimetry (DSC) analysis of polyol blends.

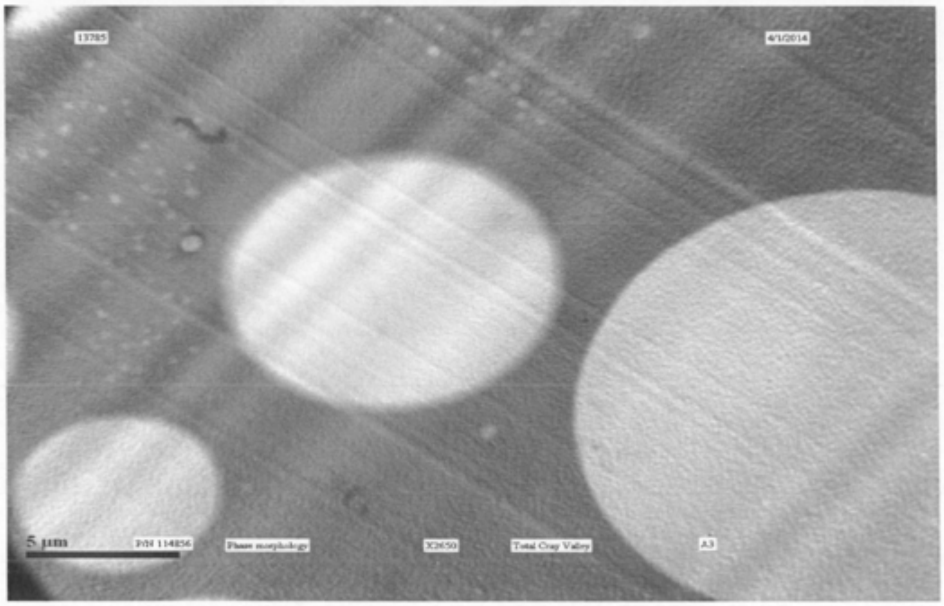

Figure 2: Transmission electron microscopy (TEM) image of the polyurethane derived from Poly bd R45HTLO/Krasol HLBH-P 2000 50/50 blend.

Table 2: Glass transition temperatures of polyol blends and polyurethanes made therefrom.

Series A	1	2	3	4	5
Poly bd R45HTLO	0	25	50	75	100
Krasol HLBH-P 2000	100	75	50	25	0
Tg, °C of polyol blends	-50.5	-76.9 / -55.4	-76.0 / -54.1	-76.4 / -54.0	-76.5
Tg, °C of cured PU	-41.2	-44.7	-63.1	-69.7	-71.2

Thermogravimetric analysis (TGA) (Figure 3) of samples A-1, A-3 and A-5 shows that the polyurethane containing only Poly bd resin takes in oxygen at an elevated temperature. Further, A-3, having 50% Krasol HLBH polyol, absorbs less oxygen as expected at an even higher temperature than A-1. The results suggest that blending hydrogenated Krasol polyol may delay the thermal aging effect compared to using neat Poly bd resin.

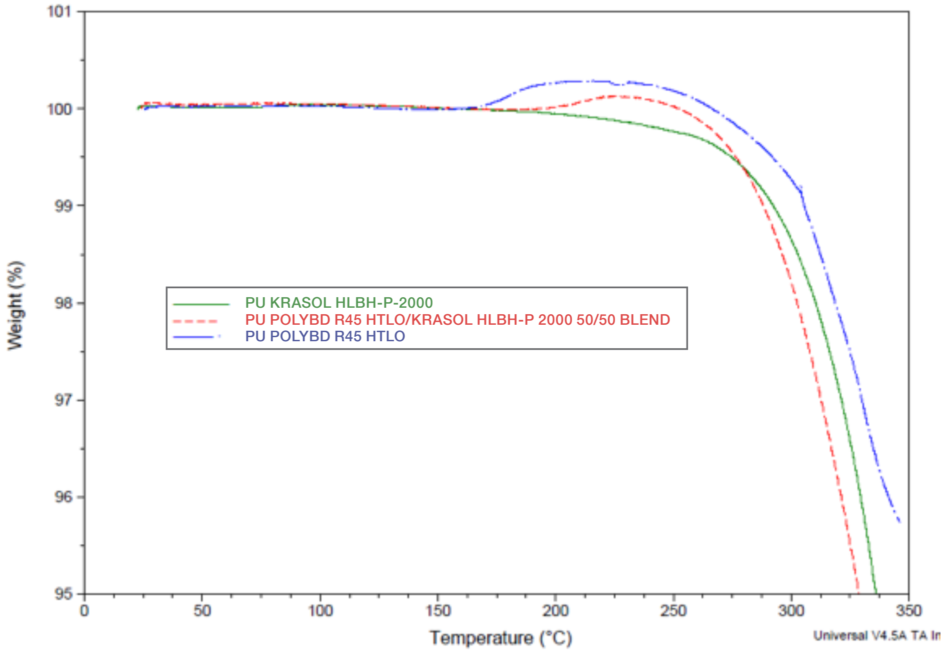

Figure 3: Thermogravimetric analysis (TGA) of the polyurethanes derived from Poly bd R45HTLO, Poly bd R45HLTO/Krasol HLBH-P 2000 (50/50) and Krasol HLBH-P 2000 resins.

Blends Between Krasol LBH-P 2000 and Krasol HLBH-P 2000 Resins

Krasol LBH-P 2000 resin, a standard hydroxyl-terminated polybutadiene, is completely miscible with hydrogenated Krasol HLBH-P 2000 resin. Five compositions ranging from pure polyols to homogeneous mixtures were submitted for reaction with liquefied MDI (Isonate 143L) to form polyurethanes, and their tensile properties were evaluated and reported (Table 3).

Formulas and Mechanical Properties

Table 3: Polyurethane formulas based on polyol blends of Krasol LBH-P 2000 and HLBH-P 2000 resin.

Series B	**1**	**2**	**3**	**4**	**5**
Krasol LBH 2000	0	25	50	75	100
Krasol HLBH-P 2000	100	75	50	25	0
Isonate 143L	12.83	12.98	13.13	13.27	13.43

Physical Properties of PU					
Hardness, shore A	51	49	49	50	49
Modulus, psi	115	107	113	103	112
Tensile strength, psi	861	705	746	566	549
Elongation at break, %	950	836	756	727	701
Tear resistance, lbf/in	88	81	89	72	78

Since both Krasol polyols are linear and miscible, the mechanical properties, such as hardness, modulus and tear resistance of the polyurethanes from the blends do not vary much. Only tensile strength and elongation gradually decrease as the Krasol LBH 2000 content increases in the compositions.

DSC, TEM and TGA Analysis of Homogeneous Polyol Blends and Polyurethanes Made Therefrom

The glass transition temperatures of the individual polyols and their homogeneous mixtures were obtained by DSC analysis (Figure 4). The glass transition temperatures of the polyurethanes derived from those five formulas were measured as well, and the results are listed in Table 4.

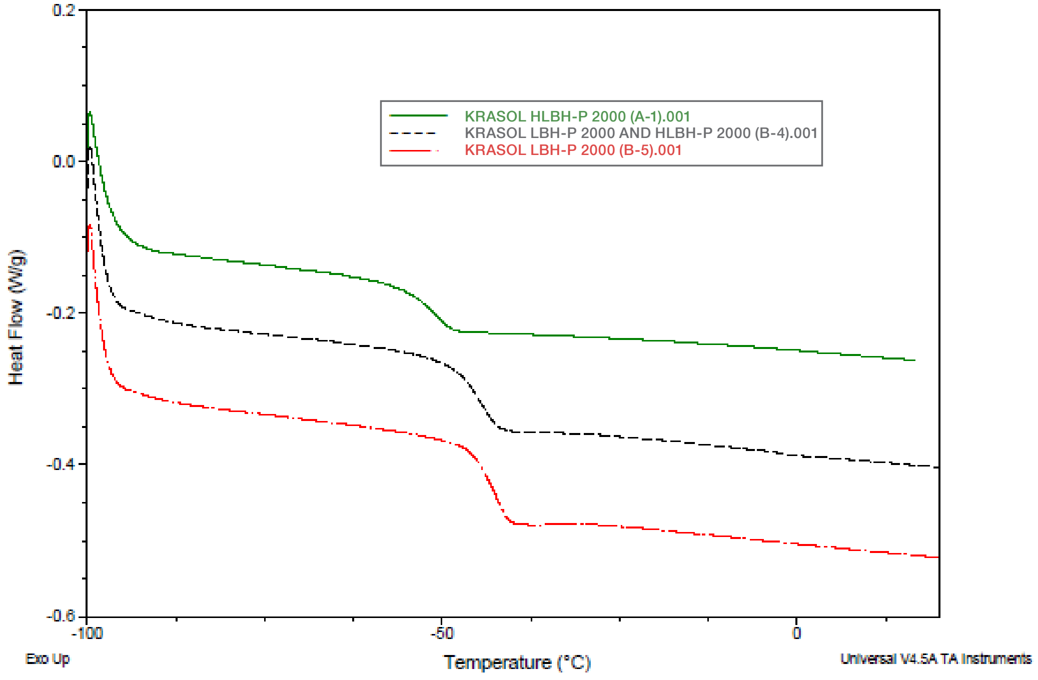

Figure 4: DSC of polyol blends.

Table 4: Glass transition temperatures of polyol blends and polyurethanes made therefrom.

Series B	1	2	3	4	5
Krasol LBH 2000	0	25	50	75	100
Krasol HLBH-P 2000	100	75	50	25	0

Tg, °C of polyol blends	-50.5	-50.3	-50.1	-44.3	-42.5
Tg, °C of cured PU	-42.8	-40.6	-38.4	-35.4	-32.0

The glass transition of polyurethanes derived from the homogeneous polyol mixture is rather sharp. No phase separation is observed by TEM analysis (Figure 5) of sample B-3.

TGA analysis (Figure 6) of samples B-1, B-3 and B-5 shows that the polyurethane containing only Krasol resin takes in slightly less oxygen at an elevated temperature than those containing Poly bd resin in sample A-1 (Figure 3). This behavior can be explained by considering the microstructure of the resin. Krasol resin has fewer allylic protons than Poly bd resin. Further, sample B-3, having 50% Krasol HLBH polyol, absorbs less oxygen as expected than sample B-1 at about the same temperature. The results suggest that blending hydrogenated Krasol polyol may slightly improve the thermal aging effect compared to using only standard Krasol resin.

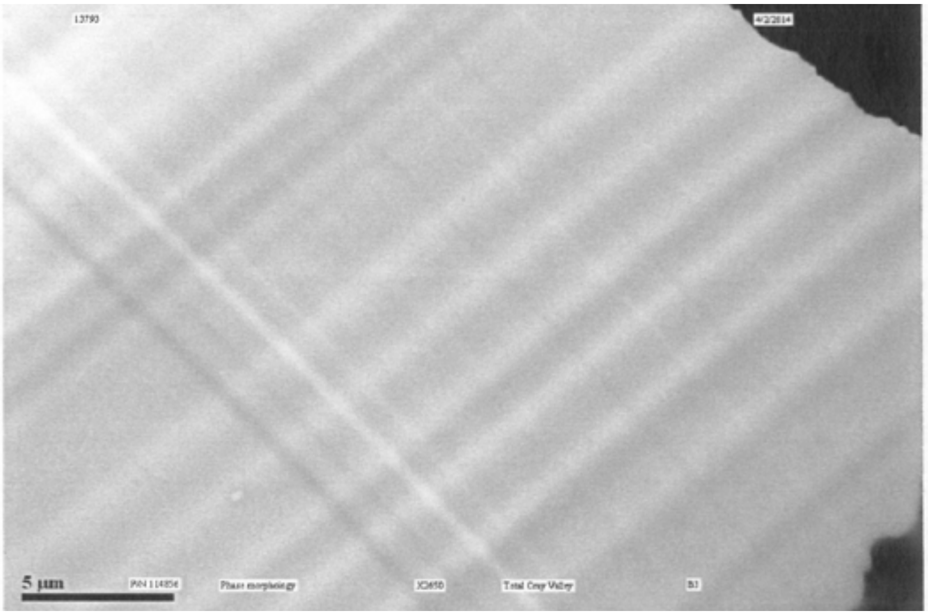

Figure 5: TEM image of the polyurethane derived from Krasol LBH-P 2000/HLBH-P 2000 50/50 blend.

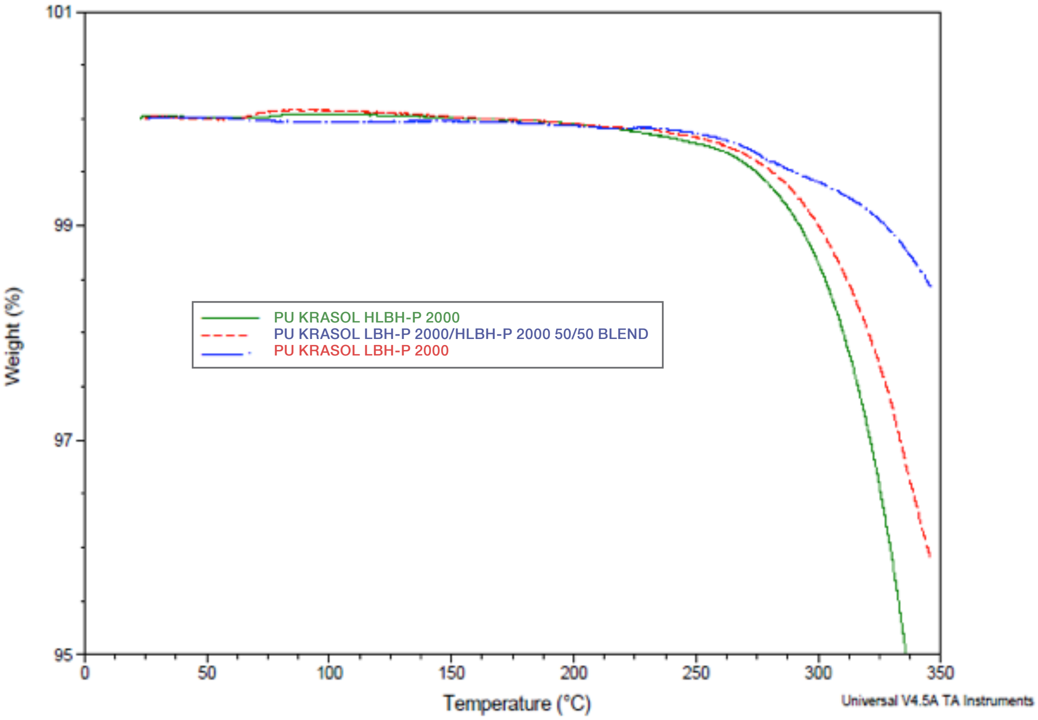

Figure 6: TGA of the polyurethanes from Krasol LBH-P2000,
Krasol LBH-P 2000/HLBH-P 2000 50/50 blend, and Krasol HLBH-P 2000 resins.

Summary

Thermal stability of polyurethanes derived solely from standard unsaturated hydroxyl-terminated polybutadienes (HTPB) can be improved by adding hydrogenated Krasol resin as a starting polyol. Depending on the microstructure of HTPBs, the polyols mixture may not be homogeneous. Naturally, the resulting polyurethane may have only one phase or contain a dispersed phase. Based on TGA analysis, both systems absorb less oxygen than the polyurethanes derived from only neat HTPBs. Further, the inhomogenous blends may have extra advantage of delaying the initiation of oxygen intake to a higher temperature.

About Total Cray Valley

Cray Valley USA, LLC, is the premier global supplier of specialty chemical additives, hydrocarbon specialty chemicals, and liquid and powder tackifying resins used as ingredients in adhesives, rubbers, polymers, coatings and other materials. Cray Valley has pioneered the development of these advanced technologies, introducing hundreds of products that enhance the performance of products in energy, printing, packaging, construction, tire manufacture, electronics and other demanding applications.