Compatibility Between Poly bd® R45HTLO and Polyether or Polyester Polyols

Introduction

Poly bd® resin polyols are liquid, hydroxy-terminated homopolymers of butadiene. Through the use of an isocyanate cure reaction they can produce novel urethane products which are castable, general-purpose elastomers. These elastomers can be reinforced with a variety of low cost processing oils and fillers and find use as caulks, sealants, membranes, sponges, foams, adhesives, coatings, propellant binders, potting and encapsulating compounds, as well as other rubber-fabricated materials.

The unique structure of the Poly bd® resins provides properties which surpass those of conventional polyether and polyester urethane systems as well as conventional, general-purpose rubbers. Due to the hydrocarbon nature of the Poly bd® backbone, the polyurethanes derived from it usually have a superior combination of properties, including:

- Low water absorption
- High hydrolytic stability
- Low moisture permeability
- High resistance to aqueous mineral acids and bases
- Excellent low temperature flexibility
- Good adhesion toward a wide variety of substrates
- Low Glass transition temperature (Tg)

By comparison, polyether and polyester polyols have been widely used in polyurethane formulations because of their low cost and their availability as a myriad of commercial product structures. These polyols give rise to generally poorer water adsorption and low temperature flexibility properties compared to Poly bd® Resins. However, the polyether and polyester polyols can provide outstanding performance in areas such as mechanical properties and weatherability, respectively, to the polyurethanes derived from them.

Therefore, on many occasions users would like to prepare polyurethanes which exhibit a balance of the attractive properties inherent to Poly bd® and polyester or polyether polyol formulations. The most straightforward approach to this goal involves blending polyester or polyether polyols with a Poly bd® Resin before curing with isocyanate. When compatible polyol blends are employed, the polyurethane products would be expected to have tailored properties intermediate between those products of the two different polyol components. However, the miscibility between different polyols is expected to be an issue due to the different structures represented by each class of polyols. If a blend of polyols is immiscible, or not compatible, the resulting urethane product would be expected to be heterogeneous, and would exhibit poor physical properties. The bulletin describes the compatibility between a widely used grade of Poly bd® Resin, R45HTLO, and a variety of different polyether and polyester polyols.

Compatibility Results of Polyether or Polyester Polyols With Poly bd® R45HTLO

Compatibility between Poly bd® R45HTLO and other polyols was evaluated by measuring the turbidity of their blends. A truly compatible blend would be clear, while the more incompatible the polyols, the more turbid their blends would become.

The experimental procedure consisted of mixing different ratios of a polyether or polyester polyol and Poly bd® R45HTLO at high sheer. Resulting solutions were poured into glass bottles and allowed to settle for 20 hours to eliminate air bubbles, which could interfere with the measurement. Turbidity readings were then measured using a turbiditimeter DRT 100B (HF Instrument). Results are shown in Table 1.

Table 1. Summary Of Compatibility Between Poly bd® R45HTLO And Other Polyols

	Difunctional			Trifunctional		
Polyol Type	**Name**	**Mw**	**Maximum Solubility (wt. %)**	**Name**	**Mw**	**Maximum Solubility (wt. %)**
Polypropylene Glycol	Arcol PPG 2000	2000	55	Pluracol TP 4040	4100	50
	Arcol PPG 425	425	35	Arcol LG 56	3000	50
	Tripropylene Glycol	192	15	Voranol 230-112	1500	40
				Arcol LG 650	260	5
Polytetra-Methylene Glycol	Polymeg 1000	1000	25			
	Polymeg 650	650	15			
Polyether/ Polyester polyol				Sovermol 750	525	35
Aromatic	Voranol 220-530	209	15			
	Bisphenol A Propoxylate	344	5			
Amine				Jeffamine T-403	403	70

Summary

All of the polyester or polyether polyols tested are compatible with Poly bd® R45HTLO in low concentrations, ranging from 10 to 50% of the total weight of the blend. Compatibility of those polyols with Poly bd® resin is affected by polyol type, functionality and molecular weight. Polypropylene glycols are in general more compatible with Poly bd® resin than are either polytetramethylene glycols or polyols which contain aromatic groups. Among polypropylene glycols, it appears that diols are more compatible than triols of the same molecular weight. For a given polyol structure, the solubility in Poly bd® resin increases with the molecular weight of the polyol.

Application Uses Of Polyol Blends

1.) One-Part Moisture-Cured Formulations

Since Poly bd® R45HTLO has good compatibility with polypropylene glycol (PPG), a series of MDI-based prepolymers starting from various ratios of Poly bd® R45HTLO to PPG 2000 were made (Table 2). Those prepolymers were then moisture-cured to form elastomeric products. The effect of different polyol ratios on the prepolymer curing rates and the mechanical properties of the final products are summarized in Figures 1 and 2.

Table 2. Prepolymer Compositions (in Parts By Weight, PBW)

	Formulation Number						
Ingredient	**1**	**2**	**3**	**4**	**5**	**6**	**7**
R-45HTLO	100	90	80	50	20	10	0
PPG	0	10	20	50	80	90	100
DOP*	92	92	92	92	92	92	92
M143** with NCO/OH=	2.8	2.8	2.8	2.8	2.8	2.8	2.8

* DOP : dioctyl phthalate ** M143: MDI derivative

All the prepolymers were prepared by first mixing the R-45HTLO, PPG, and DOP before M143 was added to give the final polyurethane formation. The prepolymers were transparent initially but became hazy during moisture-curing. The viscosities of the prepolymers were stable during storage under an inert atmosphere, and they were significantly lower for polyol blends which contained a larger portion of PPG 2000 (Figure 1). Also, the moisture-cured prepolymers exhibited higher water uptake with higher PPG 2000 content. Formulations **5** and **6** contain a concentration of PPG which is outside the compatibility range (Table 2) and therefore the water uptake of their cured prepolymers are even higher than formulation **7** derived from pure PPG 2000.

The mechanical properties of the moisture-cured prepolymers, except elongation at break, do not show significant variation over the range of polyol blend compositions (Figure 2). When the ratio of PPG 2000 to Poly bd® R45HTLO reaches 80/20 or higher elongation improves but the ratios are not compatible. Therefore, phase distribution and domain sizes in the final cured materials are expected to have a strong effect on the mechanical properties.

Figure 1. Viscosity of prepolymers derived from polyol blends and water uptake (Wup) at room temperature (RT) and 100°C of the moisture-cured prepolymers.

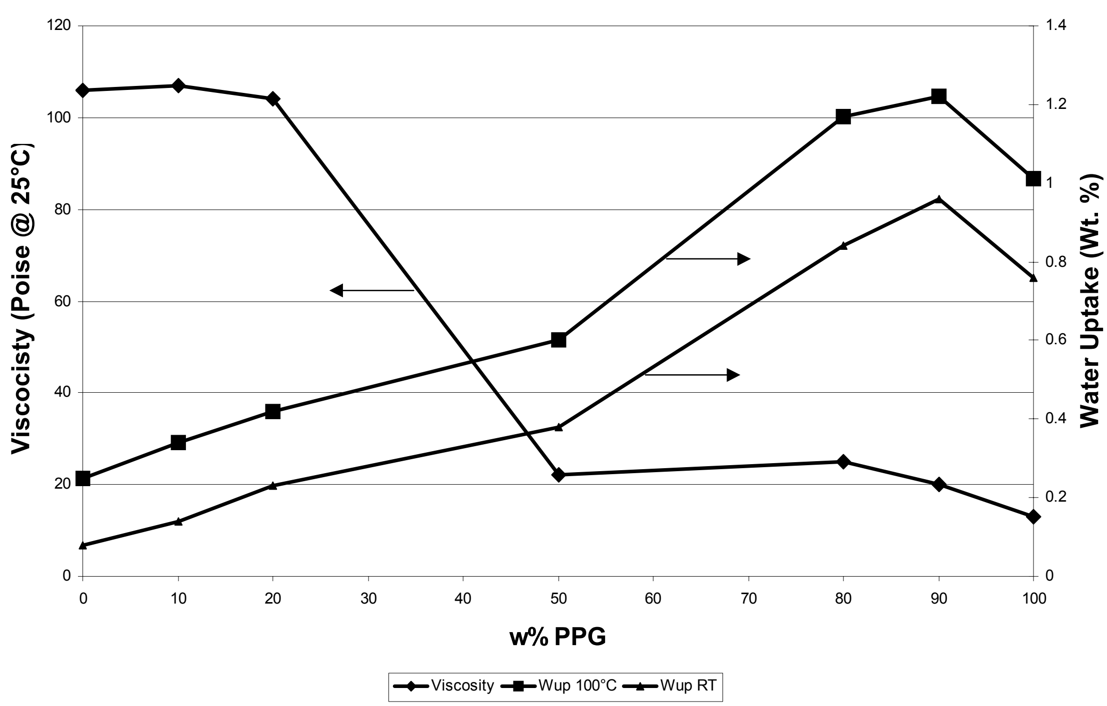


Figure 2. Mechanical properties, such as elongation, hardness, tensile strength, and tear strength of the moisture-cured prepolymers.

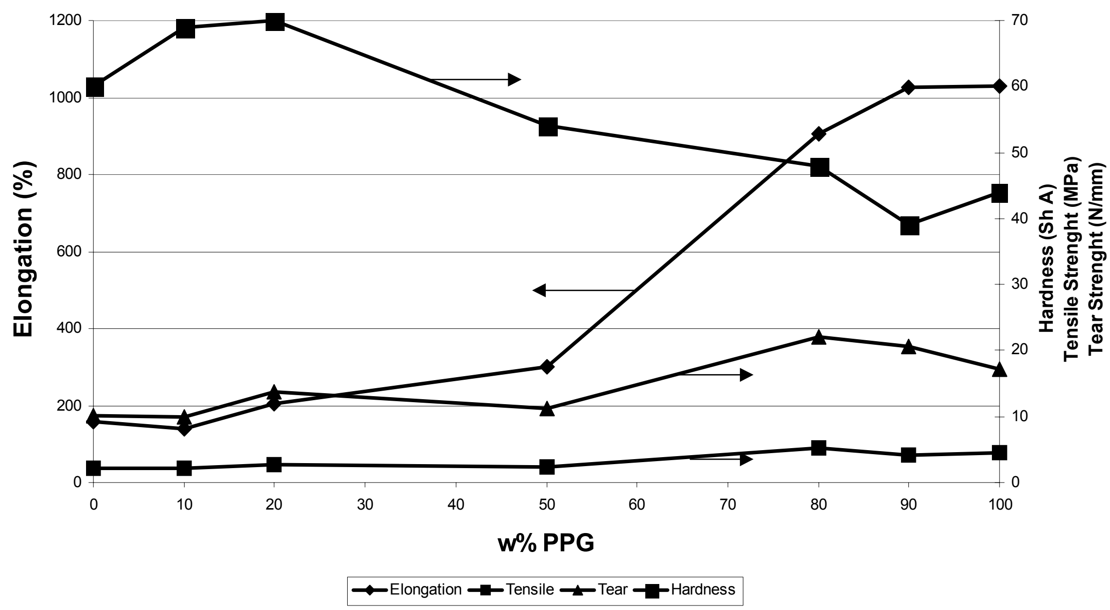
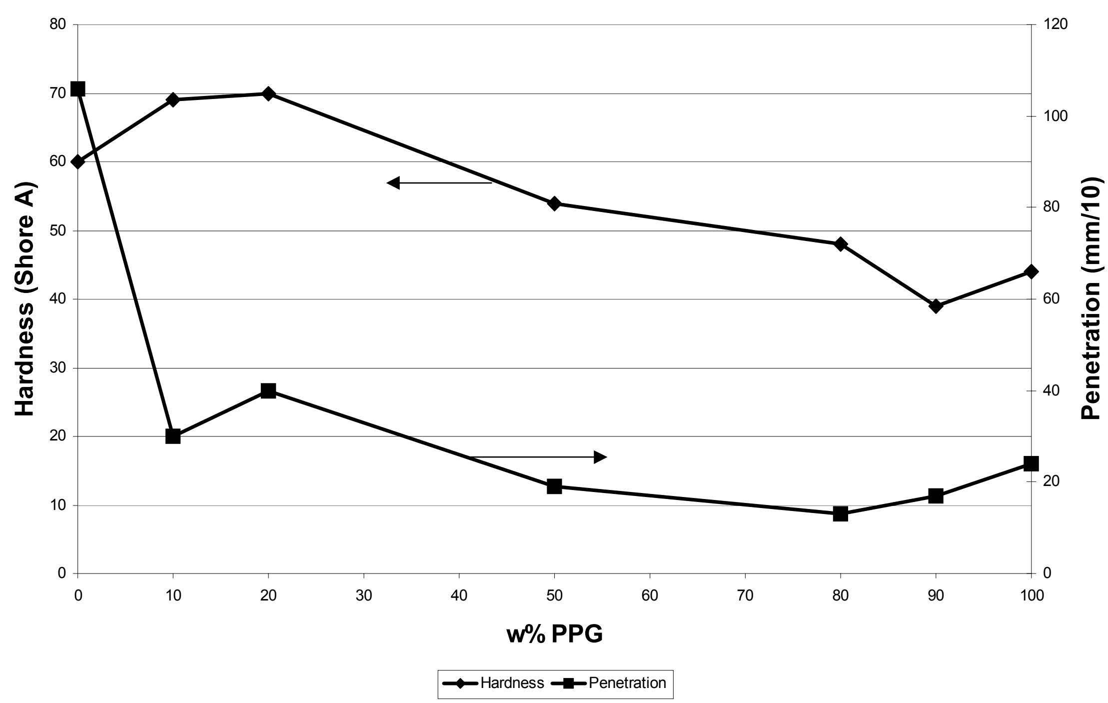


Figure 3. Hardness and penetration of 4 cm thick moisture-cured prepolymers after 7 days.



The depth of penetration of a moisture-cured prepolymer is inversely related to the extent of curing. Therefore, the results show in Figure 3 suggest that the rate of moisture-curing accelerates when the prepolymer contains as low as 10% of PPG 2000. The hydrophilic nature of PPG 2000 increases the rate of water permeation into the prepolymer, with the result that the curing of prepolymers which contain PPG 2000 advance at a faster rate than Poly bd® R45HTLO prepolymers.

In summary, the viscosity of the prepolymer is reduced significantly by adding PPG 2000 to Poly bd® R45HTLO. The elongation at break is increased in the final moisture-cured prepolymers which contain more PPG 2000 in the polyol blends. With a higher concentration of hydroscopic PPG 2000 in the polyol blend, the moisture-curing rate of prepolymers is increased to a more practical level. When one wants to reduce water-uptake in polyurethanes derived from PPG 2000, it is recommended that sufficient Poly bd® R45HTLO is added to give a compatible polyol blend (>45 wt. % Poly bd®).

2.) Integral-Skin Foam Formulations Based on Blends of Poly bd® With Other Polyols

Table 3. Base Formulation and Materials Used in Preparation of Integral-Skin Foams Based on Poly bd® Resins

Ingredients	pbw
Polyol	100
Forane 141b[1]	15
Ethylene glycol	8
1,4-Butane diol	3
Dabco 33LV[2]	0.9
Tegostab B4113[3]	0.5
Water	0.05

[1] 1,1-dichloro-1-fluoroethane, Atofina Chemical Co.
[2] 33% by wt. 1,4-diazabicyclo-[2,2,2]-octane in dipropylene glycol, Air Products and Chemicals
[3] Silicone-based surfactant, Goldschmidt France

Introduction of Poly bd® resins into integral-skin foam formulations based on Multranol 3900, a Bayer product, leads to a substantial improvement in hydrolytic resistance properties, as measured by minimized change in physical properties of humid-aged foams. These improvements are found regardless of the nature of the poyisocyanate and the curing index used (Table 4).

Table 4. Change in Compression Load Deflection (CLD) and Tensile Strength (TS) after Humid Aging of Foams Made with Multranol 3900 and Poly bd® R45HTLO Blends

		Change in CLD (%)		Change in TS (%)	
Isocyanate[4]	Index	Pure Multranol	50/50 Blend	Pure Multranol	50/50 Blend
Suprasec VM 2025	85	-17	-8	-	-
Suprasec VM 2030	85	-48	-5	-24	16
Suprasec VM 2025	105	-54	-35	-24	-9
Suprasec VM 2030	105	-81	-23	-2	-10

[4] Suprasec VM2025, a modified polymeric MDI with % NCO = 24.3%
Suprasec VM2030, a modified polymeric MDI with % NCO = 28.6%
Both are from Huntsman (Europe).

Increasing the foaming agent content gives a steady decrease in overall and core density, allowing a 20% (overall) and 27% (core) weight reduction for the final product. When blending Poly bd® resin with multranol the mechanical properties of the foam can be maintained despite the increase in foaming agent.

Table 5. Influence of Blowing Agent Level on Physical Properties of Integral-Skin Foams (ISF)

Ingredient		
Multranol 3900	100 parts	50 parts
Poly bd® R45HTLO	-	50 parts
Forane 141b	15 parts	20 parts
Suprasec VM 2025 (index)	105	105
Physical properties		
Overall density, kg/m^3	195	162
Core density, kg/m^3	118	106
CLD with skin at 50%, kPa	29	30.4
Core CLD at 50%, kPa	16.7	23.5
Tensile strength, kPa	225	285
Elongation at break, %	104	95
Compression set at 70%, %	16	15
Hardness, Shore A	45	48
Core CLD/Core density	0.14	0.22

The integral skin formulations using polyol blend of Poly bd® R45HTLO and Multranol 3900 have been evaluated with production versions of arm-rest molds. All the formulations had good moldability, regardless of the complexity of the shape of the mold. The formulations had good demolding times, showing good potential for high productivity. Moreover, the foams had good surface characteristics.