CRAY VALLEY
Resins par excellence

APPLICATION BULLETIN

Poly bd® Resins in Construction Applications

Introduction

Poly bd® resins are liquid, hydroxyl terminated homopolymers of butadiene. The reaction of Poly bd® resins with curing agents, such as conventional di- and polyisocyanates, provides an economical route for the preparation of general-purpose elastomers, such as polyurethanes.

The unique structure of the Poly bd® resin allows formulators to produce polyurethanes with properties surpassing those of polyurethanes produced from conventional polyether or polyester polyols, as well as those of general-purpose rubbers. Moreover, the excellent compatibility of Poly bd® resin with asphalt allows formulators to make a variety of polymer-modified asphalt systems.

Uses In Construction Applications

Poly bd® resins have been used to prepare castable elastomers, caulks, sealants, membranes, foams, adhesives, coatings, propellant binders, potting, and encapsulation compounds.

In the construction area, some specific application uses are listed below:

- Penetration joints and adhesives on EPDM or asphalt roofing membranes (pitch pan)
- Adhesives and sealants for crack filling or expansion joints for roofs, roads, bridges, and airport runways, providing excellent resilience, rut resistance, and adhesion to various substrates
- Waterproof membranes, coatings or geomembranes for :
  - parking decks, roof decks, terraces
  - waste water, potable water (NSF 61 approved for direct contact), paper mills, sewage pipes
  - below grade waterproofing
- Self adhering systems (e.g., pressure sensitive adhesives with or without asphalt), providing improved low temperature tack and minimum sagging at high temperatures
- Tank and pipe sprayable coatings
- Self-leveling waterproofing and sound damping adhesives for use between floors in building and for basement joints
- Foamable (intumescent or swellable) formulations
- Vibration absorption membranes, gels, and foams for railroad tracks

Properties Provided By Poly bd® Resins

Due to the molecular structure of the Poly bd® resins, the resulting polyurethane products exhibit some unique characteristics that are especially valued in the construction uses. These characteristics are discussed individually.

Hydrolytic Stability

The hydrophobic backbone of Poly bd® resin imparts excellent hydrolytic stability to the finished product, surpassing properties of any other type of polyurethane. Poly bd®-based urethanes exhibit a low water absorption rate, even in boiling water. The Moisture Vapor Transmission Rate (MVTR) is lower than conventional products derived from polyether or polyester polyols. Some systems can even cure underwater with no change in the product's final characteristics.

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For example, a simple 2-component polyurethane formulation based on Poly bd® R45HTLO resin and a polymeric MDI shows less than 0.01% weight uptake after being immersed in water for a day at room temperature, and less than 0.20% weight gain when immersed in boiling water for 2 hours.

Table 1 describes two starting formulations and the MVTR values of the cured products according to the standard ASTM E96 (38 °C / 90% RH) method.

Table 1

Formulation (parts by wt.)	Non-filled	Asphalt-extended
Poly bd® R45HT resin	100	100
Chain extender (2-Ethyl-1,3-Hexanediol)	10	10
Asphalt (pen. 180/220)		200
Isonate 143L (NCO index=1.05)	33.6	36.2*
MVTR (g. 2mm/m^2.24hr) at 2mm thickness of the samples	5.16	2.14

* The quantity includes the isocyanate equivalency of the asphalt.

Low Temperature Flexibility/High Temperature Resistance

Polyurethane elastomers based on Poly bd® resins exhibit outstanding low temperature properties which are attributed to the "rubbery" polybutadiene backbone. The brittle point of Poly bd® resins is -75 °C (-100 °F), so incorporation of Poly bd® into a formulation usually results in a low brittle point for the finished product. For example, the brittle point of formulations highly filled with asphalt and process oils can typically be -40 °C (-40 °F). In such formulations, only one brittle point is observed, showing that Poly bd® resin is fully compatible with the asphalt and processing oils. Good low temperature flexibility is especially critical for the joint sealants or crack-bridging applications. At low temperatures, the gap between joints or cracks becomes wider as a result of the substrate shrinkage. Thus, a product with excellent elongation at low temperature is ideal for those applications. In addition, since Poly bd® formulations also retain their elastic properties at high temperature, the materials produced with Poly bd® resins maintain outstanding elasticity and elastic return when subjected to temperature cycling.

Chemical Resistance

Polyurethane elastomers based on Poly bd® resins exhibit excellent resistance to aqueous inorganic acids and bases. This characteristic is mainly due to the sturdy carbon-carbon bonds in the polybutadiene backbone. This property is important in applications requiring long-term exposure to acidic and alkaline water, such as sealants, coatings and membranes for landfills, tanks and pipes. Moreover, Poly bd® resin-based polyurethane elastomers have outstanding resistance to brine.

The Poly bd®-based urethanes will swell to a certain extent when exposed to solvents. However, unlike asphalt or even thermoplastic-modified asphalts, which dissolve readily in solvents, the crosslinked polyurethane will maintain its integrity. This characteristic allows the Poly bd®-based polyurethanes to be used as a sealant in airport pavements, where they be exposed to aviation fuel spills or deicing fluids.

Adhesion

Since Poly bd® resins have a low surface tension, they readily wet most common substrates such as concrete, wood, metallic surfaces, glass, plastics and cement. This property provides the necessary condition for establishing good adhesion.

Poly bd® resins can be formulated as two-component adhesives and sealants or as moisture curable prepolymers.

Compatibility With Asphalt and Process Oils

Poly bd® resins are compatible with many hydrocarbon oils, chlorinated oils, asphalts and other related, low-cost materials. Such mixtures can be cured with conventional di-isocyanates to produce oil- or asphalt-extended elastomers. The cure time of preparing asphalt-extended polyurethane with Poly bd® resin can also be controlled with catalysts.

Process oils, such as soybean oil, are generally used as plasticizers to reduce the viscosity, hardness, and cost of elastomeric systems. Process oils can provide improved physical properties, such as increasing the elongation at break of the cured material.

Asphalts such as AC20 or AC5 are fully compatible with Poly bd® R45HTLO resin, but are not as compatible with Poly bd® R20LM resin, which is of lower molecular weight and has a higher concentration of polar hydroxyl groups. Polyurethane formulations based on Poly bd® resins accept large quantities of asphalt. However, the asphalt used needs to have a low moisture content to reduce the side reaction between water and isocyanates during the curing reaction. This can be achieved by addition of molecular sieves into the formulation, where they act as a water scavenger.

In joint sealing or crack filling applications, asphalt-modified Poly bd® urethanes have several advantages compared to SBS-modified systems. First, the preparation of asphalt-modified urethanes based on Poly bd® resins is possible at room temperature, whereas SBS resins are often melted at elevated temperatures prior to formulation. Furthermore, Poly bd® pourable systems (joint sealants) can be formulated without solvents. Not only is this attractive for the environment, but this also can lead to improved final properties, since there is no shrinkage and embrittlement of the final material caused by the evaporation of solvents. The asphalt-modified Poly bd® urethanes produce a thermoset network which has good sag resistance at high temperature and which maintains high elongation at break and elastic return over a wide range of temperatures. In addition, the rut and solvent resistance properties of Poly bd®-modified asphalt are superior to those of SBS-modified asphalt as a result of this thermoset structure.

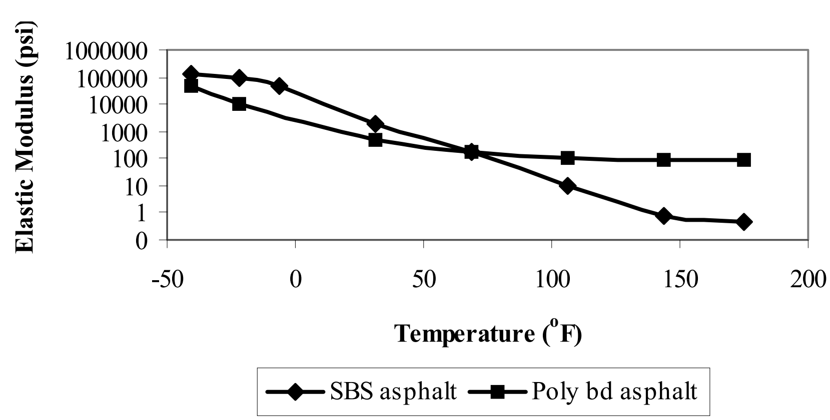
The elastic modulus versus the temperature of an SBS-modified asphalt system and an asphalt-extended polyurethane formulation based on Poly bd® are shown in Figure 1 below. The elastic modulus is measured by DMA (Dynamic Mechanical Analysis).

Figure 1 shows that even though the modulus is the same (145 psi) for both systems at room temperature, the modulus of SBS-modified asphalt becomes10 times lower than that of the Poly bd® resin-modified system at 100 °F. This suggests that the SBS-modified asphalt system softens significantly at elevated temperatures. At -20 °F the Poly bd® urethane-modified asphalt is still elastomeric, having a modulus 10 times lower than that of the SBS-modified product.

Compatibility With High Loadings Of Fillers

Poly bd® resins are known for their ability to accept large amounts of fillers without adverse changes in the properties of the final product. Common fillers such as calcium carbonate, silica, clay, aluminum trihydrate, carbon black and titanium dioxide are dispersed easily in Poly bd® resins. The optimum amount of filler is determined based on the balance of properties, such as viscosity, hardness, elongation at break, modulus and cost of the final products.

Figure 1 Modified Asphalt - SBS vs Poly bd



Other Properties Of Poly bd® Based Formulations

Like many other polyurethane systems, Poly bd® resin-based formulations generally have good abrasion resistance. Furthermore, the curing reactions of Poly bd® resins occur with very low or even no exotherm, and with no or a very low shrinkage.

Starting Point Formulations

Cold-Applied, Two-Component System For An Expansion Joint Sealant Or A Crack-Filling Compound

The information in Table 2 is meant to serve as a starting formulation, and the process parameters and mechanical properties of the cured product can be adjusted to meet specific application needs. For example, a variety of types of asphalt, filler, and isocyanate can be substituted in this formulation. Furthermore, a portion of the asphalt can also be mixed with the isocyanate in Part B. This can facilitate the mixing of the isocyanate and the polyol blend by matching more closely the viscosities of the Parts A and B.

Self-Adhesive Formulations

Poly bd® resin-based polyurethanes can be formulated to make self-adhesive systems. Such systems may contain tackifying resins or asphalt. The key to prepare such a product is to cure the system using a NCO index of less than 1 (preferably between 0.65 and 0.8). This can lead to a very good self-adhesive product. Further, since the glass transition temperature of the Poly bd® resin is very low, the tack is maintained at low temperatures, allowing contractors to work under winter-like weather conditions. Since this is a thermoset system, it also maintains its integrity at high temperature with excellent sag and chemical resistance.

Several starting formulations for self-adhesive applications are listed below; the specific properties depend upon the asphalt, the type of MDI derivatives and the ratios of NCO to OH in the formulations. Based on Formulations 1A&B and 2A-D (see Table 3 and 4), there appears to be no significant difference in performance of adhesives based upon either Isonate 143L or Mondure MRS 2. Further, the tackiness can be increased moderately by reducing the NCO index from 0.7 to 0.65 (Formulations 2A-D).

Different Curing Methods For Poly bd® Resin Formulations

Two-Components Systems

Most of the formulations that use Poly bd® resins in construction applications are two-component urethane systems, with or without asphalt. As previously described, a typical coating formulation can be: Poly bd® R45HTLO resin (100 parts), chain extender, asphalt (100 - 200 parts), filler (100 - 200 parts), plasticizer additives (DUP, process oil, naphtenic or paraffinic oil) in one part, and MDI or an aliphatic isocyanate, or a prepolymer in the other part.

Although the preparation requires a mixing step (usually accomplished with a mixer connected to a drill), there is usually no need to heat the products before use.

An alternative way to cure Poly bd® resins at room temperature without using a polyisocyanate is to use maleinized butadiene resins, such as Ricon® products supplied by Cray Valley Company, Inc. The resulting product is a polyester with improved high- and low-temperatures properties and good elastomeric behavior.

Table 2. Cold Applied, Two-Component System For
A) Expansion Joint Sealant or
B) Crack-Filling Compound

Part A : Resin Ingredients	**Quantity**	**Notes**
Poly bd® R45HTLO	100	Polyol
2-Ethyl-1,3-hexanediol	15	Short polyol (chain extender) used to improve mechanical properties and the mixing ratio
Asphalt (120-150 pen.)	150	Soft grade used in road construction. AC20 or AC5 types of asphalt are the most commonly used
$CaCO_3$	150	Calcium carbonate (alternatively, clay, silica, or other fillers can be used)
Molecular sieve	10	Absorbs the moisture: e.g., Siliporite SA1720 from Atofina (www.siliporite.com)
Dibutyltin dilaurate	0.1	Catalyst to adjust the pot life and the cure time
Process oil	100	Naphthenic or phthalate based to reduce viscosity
Part B: Hardener		
Polymeric MDI(mixing ratio)	100 parts A/ 7.3 parts B	Isocyanate. The curing agent for the polyols
Properties Of Part A Formulation		
Viscosity (Part A formulation) @85 °C @70 °C @50 °C	 18500 cPs 44500 cPs 200000 cPs	Viscosity depends on temperature and can be lowered by adding plasticizer (e.g., 20 pbw Santicizer 160 reduces viscosity by a factor of 2 or more)
Properties Of Final Product		
Hardness (15 sec.) @72 °F @14 °F	 28 shore A 45 shore A	According to ISO 86B (European standard)
Elongation at break @73 °F @14 °F @-22 °F	 345% 307% 232%	Elongation at break remains high. The elastic return is almost 100% as well. Elongation can be higher with more plasticizer. SBS-asphalt systems usually have 2% elongation at break @-22 °F
100% Modulus @73 °F @14 °F @-22 °F	 122 psi 461 psi 1,040 psi	The mechanical properties are measured according to ISO 527 (1993 1BA), at 50 mm/min (or 2 inch/min)
Tensile strength @73 °F @14 °F @-22 °F	 300 psi 810 psi 1190 psi	ISO 527 (1993 1BA), at 50 mm/min (or 2 inch/min)
Tear strength @73 °F @14 °F @-22 °F	 60 pli 160 pli 280 pli	According to ISO 34 method B

Table 3
Formulations 2A-D

Ingredients	Quantity (pbw)	
	A	B
Poly bd® R45HTLO	27.27	27.27
Asphalt AA4909 (407	54.55	54.55
Renoil	18.18	18.18
T-12	0.006	0.006
Isonate 143L	2.16	-
Mondur MRS 2	-	1.98
NCO/OH Ratio	.65	.65

Table 4
Formulations 1A & B:

Ingredients	Quantity (pbw)			
	A	B	C	D
Poly bd® R45HTLO	27.27	27.27	27.27	27.27
Asphalt AA5501 (77 pen.)	54.55	54.55	54.55	54.55
Renoil	18.18	18.18	18.18	18.18
T-12	0.006	0.006	0.006	0.006
Mondur MRS 2	2.13	1.98	-	-
Isonate 143 L	-	-	2.33	2.16
Index	0.7	0.65	0.7	0.65

Moisture Cure Systems

Poly bdò resins can be formulated to make a prepolymer, which, in turn, moisture cures to a polyurea. Cray Valley Company has developed starting formulations to make prepolymers based on Poly bdò resins and MDI. However, since pre-polymers based solely on Poly bdò resin are very hydrophobic, moisture cannot penetrate easily into the deep sections of an article made from the prepolymer to initiate curing. Therefore, other more hydrophilic polyols are usually incorporated into the formulation to enhance the moisture penetration. For example, Poly bdò resin and poly (propylene glycol) (PPG) polyether polyols form compatible blends, and prepolymers made from these blends are good candidates for the moisture cure system. For more information about blending of Poly bdò resins with other polyols, please consult the Cray Valley Technical Bulletin "Compatibility Between Poly bdò R45HTLO and Polyether/Polyester Polyols."

Cray Valley also offers new low functionality Poly bdò Resins which generate prepolymers with lower viscosity. For more information on these resins, please consult the Cray Valley bulletin entitled *Poly bdò Resins in Adhesive Applications*.

Aqueous Dispersions Based On Poly Bdò Resins

Cray Valley Company has developed a waterborne polyurethane dispersion (PUD) based on Poly bdò R45HTLO resin (patent number WO 9948941). A separate brochure is now available to provide more information about this technology.

Reactive Hot Melt

A reactive hot melt based on Poly bdò resin can be handled exactly like a regular non-reactive hot melt with the exception that the fully formulated product has to be stored away from moisture. It can be processed at a relatively mild temperature and cured by moisture after being applied. The crosslinked product has a good elastic return and exhibits improved properties at low and high temperatures.