CRAY VALLEY
Hydrocarbon Specialty Chemicals

# Poly bd® Hydroxyl-Terminated Polybutadiene-Based Polyurethanes for High-Quality Sustainable Insulated Glass Units

## Benefits

- High adhesion to glass
- Excellent UV and temperature resistance
- Very low moisture vapor transmission rates
- Low gas permeation

## Target Markets/Applications

- Polyurethane secondary sealants
- Polyurethane adhesives

## Additional Information

**MSDS/TDS:** Poly bd R45HTLO ( Americas, EU), Poly bd 45V (EU/Asia)

## Description

Cost and energy savings, along with long-lasting performance, are the most important aspects to consider in the selection of materials for construction programs today. Whether for new high-rise construction or for residential renovations, quality windows strongly impact energy consumption. The overall quality of the insulating glass units (IGU) will have a determinantal impact on the windows' appearance and energy consumption over the building lifetime. Such quality is directly linked with the quality of the seal of the IGU.

This paper aims to present the different sealing technology options for IGU and why Poly bd® polyurethanes are the right choice to balance the requirements for process, cost and product efficiency.

### Insulated Glass Sealants (IGS) Application

Insulated glass units generally are comprised of a pair of glass sheets maintained and separated by a spacer with a sealing system around the periphery of the glass sheets as shown in Figure 1. Typically, the spacer assembly is a hollow form that extends around the periphery of the glass sheets. It is filled with a water-absorbent material, such as a molecular sieve or other dehydration compound, to keep the enclosed air space dry. This spacer is applied on the glass sheets via a hot melt adhesive (also called primary sealant). In order to provide IGU mechanical strength and prevent moisture or gas from penetrating into the IGU, a secondary sealant is applied behind the spacer. This secondary sealant is one of the key elements of the quality of an IGU.

The interior primary sealant is typically a thermoplastic hot melt butyl (polyisobutylene or PIB). Its main functions are to seal out moisture and to prevent the exchange of gases. The exterior sealant, also called secondary sealant, is a reactive thermosetting sealant generally based on polyurethane (PU), polysulfide (PS) or silicone (Si) chemistry. On top of its sealing function, the secondary sealant provides structural integrity to the unit by absorbing the mechanical strains between the glass sheets due to continuous fluctuation of temperatures and UV exposure.

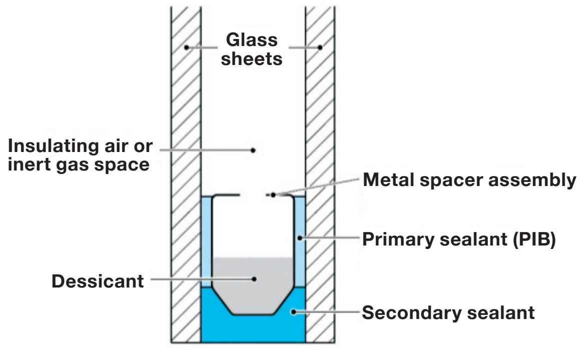


**Figure 1:** Schema of an insulated glass unit (IGU).

Because of product lifetime and weather exposure, insulated glass sealants must meet the highest standards of performance for moisture resistance, UV resistance, gas-proofing, mechanical properties at multiple temperatures, and of course adhesion to the glass and the spacer. Rheology and cure kinetics, just like economic criteria, are also key parameters in the choice of the IGS technology.

## Polyurethane (PU) Technology for Secondary Sealant

Historically, polysulfide (PS) technology was used as secondary sealant, but over the last 20 years, PU technology has gained wider acceptance and increased market share against PS. Today PU accounts for the vast majority of sealant used in Europe and has become the industry reference.

Among the key advantages of PU technology are application, cost and performance benefits.

### Application Benefits

All PU-based sealants employ a polyol (such as hydroxyl-terminated polybutadiene, e.g. Poly bd) to react with isocyanates (NCO) to form a polyurethane, as shown in Figure 2.

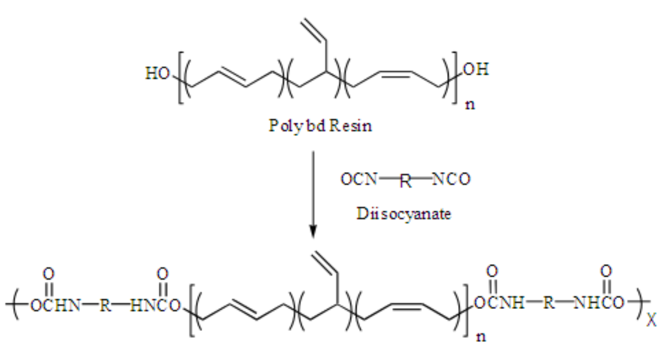


**Figure 2:** Poly bd-based polyurethane.

Compared to the PS technology, the low viscosity of this two-component PU system imparts excellent flow and better wetting properties to glass and spacer. The good rheology prevents sagging. The pot life is long enough to allow for proper application[1] with subsequent high reactivity and network building[2]. Conventional mixing equipment can be used to apply a 2K PU sealant.

### Cost Benefits

Thanks to their lower density, PU sealants are 10% lighter than PS sealants. For the same volume of sealant, the PU technology requires about 50% less polymer in formulation than the PS. Since less material is necessary to fill a given volume, this significantly reduces the applied cost that can be obtained from utilizing PU technology.

### Performance Benefits

PU-based secondary sealants have been shown to demonstrate high adhesion to glass, high UV and temperature resistance, high waterproofing, and low gas permeation compared to other technologies such as PS or Si secondary sealants.

Results from the literature study compare the permeation to moisture vapor (Figure 3), oxygen and argon (Figure 4) of IGU using various secondary sealant technologies like polyisobutyl (PIB), polysulfide (PS), polyurethane (PU) and silicone (Si).

A good-quality IGU must demonstrate low permeation to moisture vapor, oxygen and argon. The results from this study highlight the superiority of the PU system.

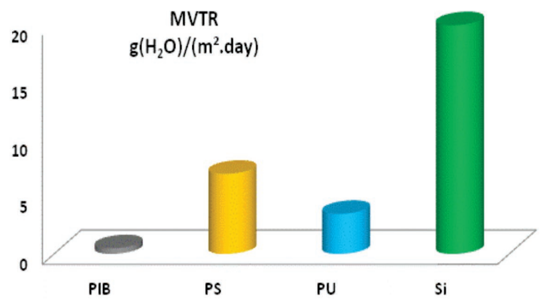


**Figure 3:** Moisture vapor transmission rates for polyisobutyl (PIB), polysulfide (PS), polyurethane (PU) and silicone (Si) sealants.

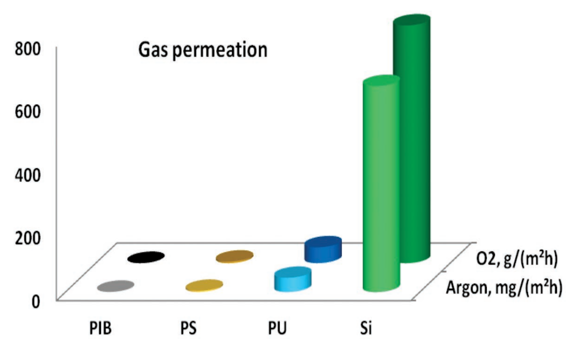


**Figure 4:** Gas permeation rates for polyisobutyl (PIB), polysulfide (PS), polyurethane (PU) and silicone (Si) sealants.

[1] Typical pot life is about 20 minutes for a system based on 80 phr NCO and 0.8 phr mercury-based catalyst. This pot life can be tuned by playing on polyol/NCO ratio and on catalyst nature and content.

[2] Tack-free time on the order of 4 hours, depending on the polyol/NCO ratio and catalyst nature and content.

## Poly bd Resin as Base Polyol for PU IGS

In PU-based sealants, the polyol to be reacted with isocyanate is very often a hydroxyl-terminated polybutadiene resin like Poly bd. The unique flexible, rubbery and hydrophobic structure of the Poly bd resin provides properties that surpass both polyether and polyester urethane systems, especially for long-term properties. For IGU applications, Poly bd-based PUs easily overcome a 10-year lifetime.

Poly bd resin is a liquid hydroxyl-terminated polymer of butadiene. Its primary allylic alcohol groups exhibit high reactivity towards isocyanates.

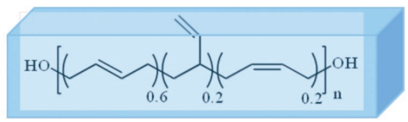


**Figure 5:** Poly bd resin structure – hydroxyl-terminated polybutadiene.

Poly bd-based PU formulations are capable of providing excellence in key properties thanks to the unique advantages inherent to the rubbery, low-vinyl backbone of Poly bd resin as shown in Table 1.

**Table 1:** Key properties of Poly bd-based PU formulations.

| | | |
|---|---|---|
| Low Tg (-70 °C) | ⇨ | High low T flexibility, no crystallization |
| Low viscosity (4,5 Pa.s at 25°C) | ⇨ | Good wetting properties |
| Hydrophobic backbone | ⇨ | Water resistance, very low MVTR |
| Low-density polymer | ⇨ | Cost effectiveness |
| Branched polymer | ⇨ | 3D PU network, mechanical strength |
| Compatible with various fillers | ⇨ | Versatility |
| Acceptance of high loads of fillers | ⇨ | Cost effectiveness |
| Primary –OH group, highly reactive | ⇨ | Productivity |

### Starting Point Formulation

A starting point formulation using Poly bd R45V as the base resin for a PU insulated glass sealant is shown in Table 2. The usual mixing mass ratio A/B is about 100/8.

**Table 2:** Starting point formula for Poly bd R45V-based PU.

**PART A**

| *Product* | *Parts, g* | *%* |
|---|---|---|
| **Polyol = Poly bd R45V** | **100** | **12** |
| **Catalyst = Hg-/Tn-based** | **0.8** | **0.1** |
| Plasticizer | 125 | 15 |
| Chain Extender | 3.3 | 0.4 |
| Antioxidant | 3.3 | 0.4 |
| Molecular Sieve | 8.3 | 1 |
| Calcium Carbonate | 583 | 70 |
| Silica | 8.3 | 1 |
| Titanium Dioxide | 8.3 | 1 |

**PART B**

| *Product* | *Parts, g* | *%* |
|---|---|---|
| **Isocyanate = MDI** | **100** | **29** |
| Plasticizer | 138 | 40 |
| Adhesion Promoter | 48 | 14 |
| Molecular Sieve | 21 | 6 |
| Carbon Black | 38 | 11 |

### Comparison of PU Performances: Poly bd-Based vs. Poly bd-Free PU

Four studies of PU IGS using Poly bd and other polyester polyols compared stability of mechanical properites after hot moisture and UV exposure. The results are presented in Figure 6.

A high-quality IGS must demonstrate good stability of mechanical properties over time and after hot moisture and/or UV exposure.

The results from these studies clearly demonstrate the advantages for the Poly bd-based formulations in terms of aging and hydrolysis resistance. The mechanical properties of a Poly bd-free PU decrease dramatically during aging.

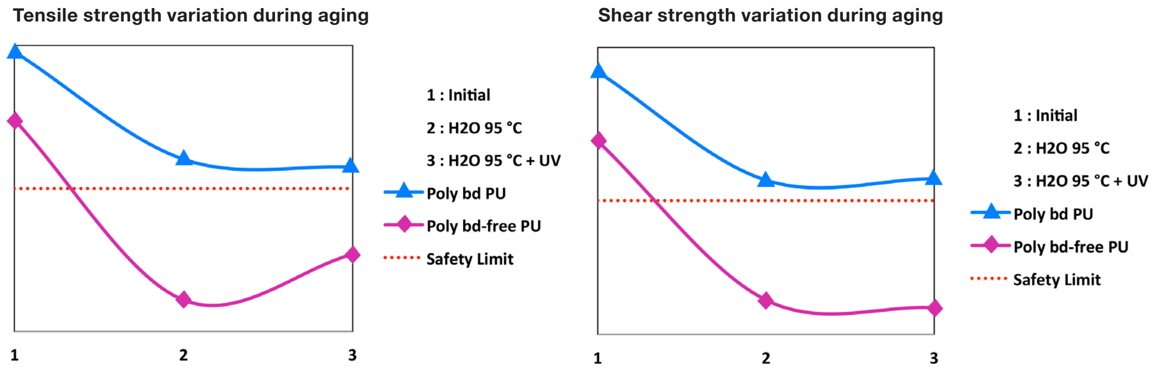


**Figure 6:** Comparison of PU properties: Poly bd-based vs. Poly bd-free PU.
A Poly bd-based PU sealant will retain tensile and shear strength after aging.

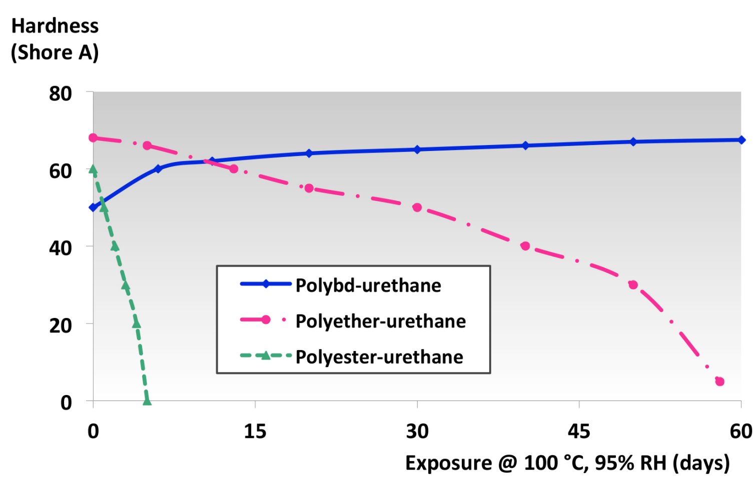


**Figure 7:** Comparative hydrolytic stability of polyurethanes based on various polyols.[3]
A Poly bd-based PU sealant will retain original properties over time.

[3] Gahimer, F.H., and Nieska, “Navy Investigates Reversion Phenomena of Two Elastomers,” Insulation, August (1968), pp. 39-44.

Figure 8 shows the PU sealant adhesion to glass after UV exposure and highlights adhesive failure for PU based on polyether or polyester polyol (the sealant no longer adheres to the glass), while it demonstrates a cohesive failure for PU based on Poly bd (the sealant remains on the glass). The use of Poly bd resin promotes both adhesion to glass and UV resistance.

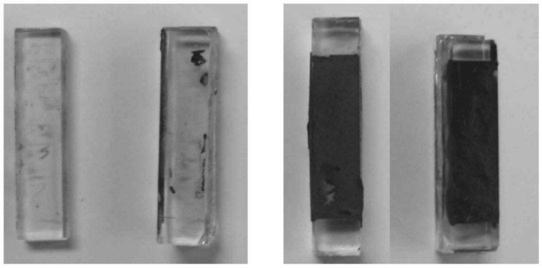

**Figure 8:** Comparative adhesion to glass after UV exposure of Poly bd-free (left) and Poly bd-based (right) PUs. Only the Poly bd-based PUs maintain good adhesion to glass after UV aging.

## Conclusions

Urethane sealants can provide performance and price benefits over polysulfide or silicone alternatives. In IGU applications, Poly bd HTPB-based PUs are capable of providing excellence in adhesion, hydrophobicity, UV exposure resistance, and physical properties over a wide temperature range, making them the appropriate choice for high-quality, sustainable IGUs. These key properties explain why Poly bd polyol has become the reference material for all key producers of insulating glass sealants.

Please find a summary of technologies comparison in Table 3.

**Table 3:** Summary of technologies comparison.

| Property | Poly bd-based Polyurethane | Polysulfide | Silicone |
|---|---|---|---|
| MVTR | + + + | + + | - - |
| Low T flexibility | + + + | + + | + + + |
| Gas retention | + + + | + + + | - - |
| Mechanical | + + | + + | + + |
| UV stability | + + | + + | + + + |
| Cost | + | - | - - |

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***Poly bd Regulatory Notice***

*Cray Valley HSC has extended its Poly bd production capacity in Italy, increasing polyols supply and reinforcing our commitment to the global sealant market. Poly bd R45V from Italy allows exportations to China.*

*N.B.: Another Poly bd grade, Poly bd R-45HTLO from USA, is regulated by the United States Department of Commerce and cannot be exported to China.*

For more information, please contact **TechSupport@CrayValleyUS.com** or visit **www.crayvalley.com**.

## About Cray Valley HSC Division

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.

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TOTAL