

Poly BD[®] Resins In Adhesive Applications

Introduction

Poly BD[®] Resins are hydroxyl-terminated poly-butadiene homopolymers. They are low molecular weight reactive liquids that offer broad formulating opportunities to the adhesives manufacturer. Several key attributes are responsible for the formulating advantages provided by Poly BD[®] Resins:

1. Hydroxyl Functionality

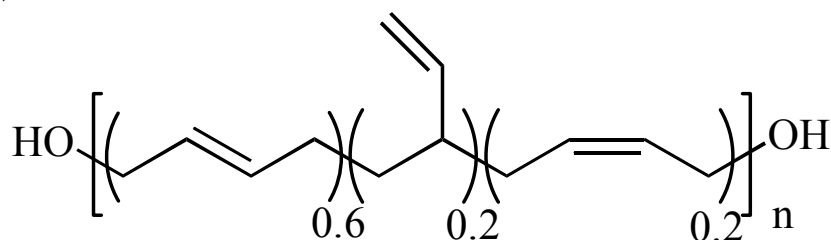
Poly BD[®] Resin endgroups are predominantly primary allylic hydroxyl groups (Figure 1). These groups have high reactivity with a variety of isocyanates to yield polyurethane adhesives and sealants. The hydroxyl functionalities of the two

widely used grades, Poly bd[®] R45 HTLO and Poly bd[®] R-20LM, are typically 2.4-2.6 per polymer chain.

2. Hydrolytic Stability

Poly BD[®] Resins have a hydrophobic, nonpolar hydrocarbon backbone which imparts hydrolytic stability to products prepared from it. The stability properties surpass those of polyurethanes prepared from other polyols that have ester or ether linkages which are more hydrophilic and easier to hydrolyze. Poly BD[®] Resin-based systems can far exceed the 28 day requirement of the Naval Avionics test.¹ For example, measuring hardness versus time at 100°C and 95% relative humidity, it has been shown (Figure 2) that typical Poly BD[®]-based urethanes are essentially unaffected, whereas urethanes prepared from other polyols actually liquefy (revert) under the test conditions.¹

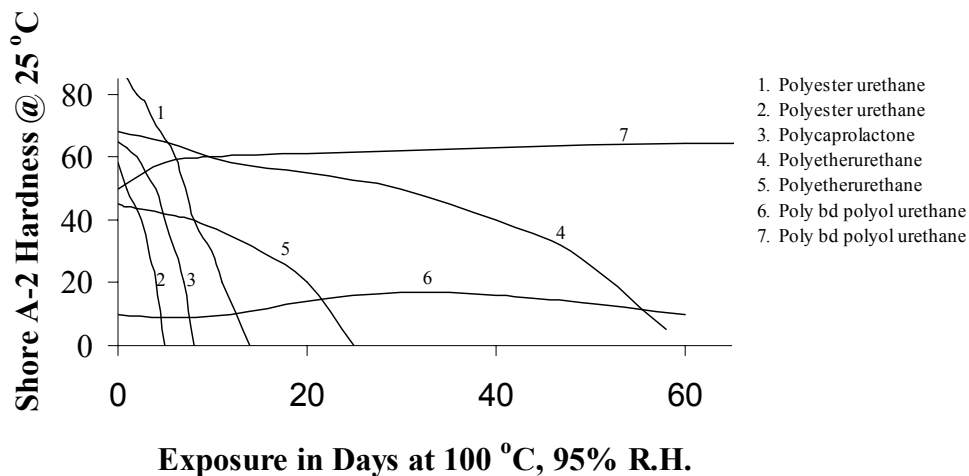
Figure 1. Chemical structures of Poly bd[®] resins



n = 50 for Poly DF[®] R45HTLO

n = 25 for Poly DF[®] R20LMC

Figure 2. Comparative hydrolytic stability of conventional versus Poly BD[®] polyol urethanes



¹ Gahimer, F. H. , and Nieske, "Navy Investigates Reversion Phenomena of Two Elastomers," Insulation, August (1968), p. 39-44.

The addition of even moderate amounts of Poly BD[®] Resin to polyether polyol-based polyurethanes markedly improves the hydrolytic stability of the cured polyurethane. Figures 3, 4, and 5 show test

results from two comparable polyurethane systems. One contains a 24.4 wt. percent Poly BD[®] Resin / 75.6 wt. percent polyether polyol mixture, whereas the other is based only on the polyether polyols.

Figure 3. Change (%) in tensile strength after water immersion at 75°C

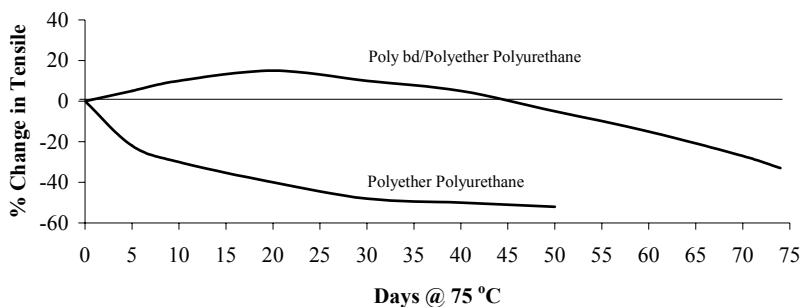


Figure 4. Change (%) in hardness after water immersion at 75°C

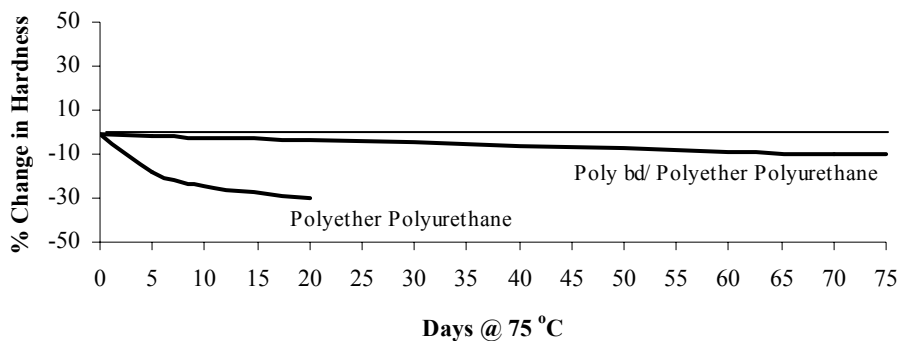
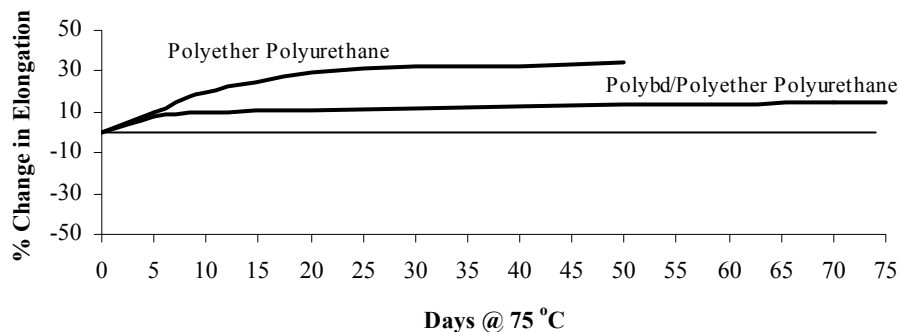


Figure 5. Change (%) in elongation after water immersion at 75°C



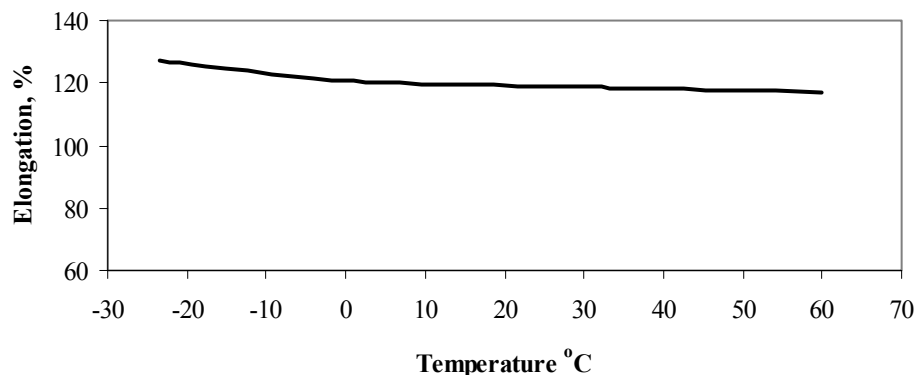
Test specimens were immersed in water at 75°C for the times shown. Elastomers containing Poly BD® Resin had excellent retention of all physical properties even after 75 days. Especially noteworthy is that hardness and tensile strength were virtually unchanged after 50 days immersion. By comparison, the properties of the polyurethane based solely on the polyether polyol deteriorated significantly within 10 days.

3. Low Temperature Flexibility

Another attribute of polyurethane systems based on Poly BD® Resins is their outstanding low temperature properties. This characteristic is attributable to the rubbery polybutadiene backbone.

Many polyurethane elastomers derived from Poly BD® Resins have brittle points as low as -70°C. This characteristic of the Poly BD® Resin-containing formulations also contributes to excellent thermal cycling properties. To illustrate this characteristic, the physical properties of a polyurethane prepared from a 15% free NCO Poly bd® R45 HTLO/isocyanate prepolymer and then further chain-extended with equal equivalents of an amine diol and a propoxylated polyether, were tested over a temperature range from -25°C to +60°C. Figure 6 shows the elongation to be essentially constant over this temperature range. An elongation of 130% at -25°C demonstrates that the Poly BD®-based polyurethane is not brittle and indeed still maintains its performance at this low temperature.

Figure 6. Elongation (%) of a representative urethane derived from Poly BD[®] resin, measure over a wide temperature range



Starting Point Formulations

1. Two-Part Polyurethanes

1.1. Basic Formulation

The basic, two-part adhesive formula used in this study is shown in Table 1. Part A consists of polyols and filler. The two polyols in Part A are Poly BD[®] R45 HTLO resin and a short chain reinforcing diol.

The equivalent ratio of reinforcing diol to Poly BD[®] Resin is 2:1. Clay filler is used to reduce cost of the formulation and to modify the viscosity. An adhesion promoter was incorporated, as well as an agent to reduce foaming during mixing and application of the adhesive. The viscosity of Part A is approximately 50,000 centipoise. The isocyanate used in Part B is a liquid-modified MDI. Initial viscosity after mixing of parts A and B is approximately 30,000 centipoise.

Table 1. Model Formulation Adhesive

Ingredients	Parts
Part A	
Poly BD [®] R45 HTLO resin	100
Voranol 220-530 (chain extender)	17.15
Dixie clay (kaolin, filler)	100
A187 (3-glycidoxypropyl)trimethoxysilane (epoxy silane adhesion promoter)	1.086
Antifoam agent	0.1
Part B	
Isonate 143L	37.2 (1.05)
Polyfunctional liquid MDI (NCO index)	

Many factors influence the adhesive and cohesive strength properties of a formulation. The performance characteristics of the final adhesive can be customized by the incorporation of adhesion promoters, reinforcing diols, fillers or diluents, and by modifying the NCO to OH ratio in the urethanes. The system developed and tested for this paper is a basic adhesive formulation which was not optimized, but can serve as a formulation example to illustrate, in general, the beneficial properties that can be obtained using Poly BD® R45 HTLO resin.

1.1.1. Preparation

As with all urethane formulations, all components should be dry to avoid the undesirable side reactions of water with isocyanate. Drying agents can be incorporated into the formula to control moisture and maximize storage stability. Packaging under dry nitrogen helps to ensure stability. The clay filler for this study was pre-dried in an oven for 16 hours at approximately 135 °C.

The ingredients of parts A and B were hand-mixed,

degassed for 10-15 minutes, and hand-applied to both surfaces of metal lap shear specimens. Working time for lab, scale batches is approximately 20-30 minutes. Lap shear specimens were 1 inch by 4 inches with a 1 inch overlap. Samples were cured at ambient temperatures for 16 hours, and then at 85 °C for 16 hours. Bond thickness was approximately 10 mils.

1.1.2. The Substrates

The steel and aluminum substrates had phosphate-treated surfaces. The oily surface in each case was prepared by wiping a thin film of petroleum distillate oil on the test metal coupon.

Galvanized Steel: ACT HDG G60 2 side extra 01x04x030 B952 P60DIW unpolished

Aluminum ACT: Aluminum 2036T4 01x12x040 B952 P60DIW unpolished

The physical properties of the adhesive film are shown in Table 2. The film thickness was approximately 1/16 inch.

1.1.3. Testing Procedures

Physical Property

Tensile (psi)
Elongation (%)
Tear (pli)
Lap Shear (psi)

Test Protocol

ASTM D638
ASTM D638
ASTM DI 004 - Die C
ASTM D 1002

Exposure Testing

Water Boil
Heat-Aged
Water Immersion
Water Immersion
Humid Aging
Cold Temperature Adhesion
Cold Temperature Adhesion

Test Protocol

2 Hours
2 Weeks @ 90°C, test at ambient
28 days @ 25°C Salt
28 days @ 25°C
28 days @ 38°C, 98% relative humidity
Freeze and test @ 0°C
Freeze and test @ -20°C

Table 2. Physical Properties of Adhesive Film

Tensile (ASTM D638)	1460 psi
Elongation (ASTM D638)	400%
Tear (ASTM D1004-Die C)	190

As can be seen from the data on Table 3, the adhesive properties of the Poly BD[®] R45 HTLO-based polyurethane on galvanized steel remain essentially unaffected by boiling water, heat aging, humid aging, water and salt water immersion. As

expected, cold temperature testing yields slightly higher lap shear values. Similarly, as seen in Table 4, the adhesion properties of Poly BD[®]-based polyurethane on aluminum are nearly constant after exposure to the same challenging environments.

Table 3. Adhesion to Oil-Free Galvanized Steel

Conditions	Lap Shear, psi (ASTM D1002)
Initial	1330 (c) *
Water boil - 2 hr soak	1400 (c)
Heat aged-2 weeks @ 90°C (test at ambient)	1470 (c)
Water immersion - 28 days @ 25°C	1300 (c)
Salt water immersion -28 days @ 25°C	1300 (c)
Humid aging - 28 days @ 38°C, 98% RH	1280 (c)
Cold temperature adhesion - Test @ 0°C	1660 (c)
Cold temperature adhesion - Test @ -20°C	1780 (c)
Lap shear on oily galvanized steel, initial	1520 (c)

*(c) : cohesive failure

Table 4. Adhesion to Oil-Free Aluminum

Conditions	Lap Shear, psi (ASTM D1002)
Initial	1330 (c) *
Water boil - 2 hr soak	1400 (c)
Heat aged - 2 weeks @ 90°C (test at ambient)	1340 (c)
Water immersion - 28 days @ 25°C	1387 (c)
Salt water immersion -28 days @ 25°C	1350 (c)
Humid aging - 28 days @ 38°C, 98% RH	1450 (c)
Cold temperature adhesion -Test @ 0°C	1620 (c)

*(c) : cohesive failure

Table 5. Adhesion to Oily Aluminum

Conditions	Lap Shear, psi (ASTM D1002)
Initial	1183 (c) *
Water boil - 2 hr soak	1374 (c)
Heat aged - 2 weeks @ 90°C (test at ambient)	1355 (c)
Water immersion - 28 days @ 25°C	1350 (c)
Salt water immersion -28 days @ 25°C	1290 (c)
Humid aging - 28 days @ 38°C, 98% RH	1367 (c)
Cold temperature adhesion - Test @ 0°C	1660 (c)

*(c) : cohesive failure

Table 5 exhibits data for oily-surfaced aluminum. The results indicate that Poly BD® R45 HTLO-based urethane adhesives perform equally well on both oily and oil-free metal surfaces.

Failure in each case was 100% cohesive, with the exception of the cold temperature test performed at -20°C where failure was approximately 65% cohesive.

1.2. Other Components In Adhesive Formulations

Poly BD® resins bring superior performance to a broad spectrum of adhesive applications because of the excellent water resistance and low temperature flexibility properties inherent to urethanes prepared from them. Furthermore, Poly BD® resins can be readily extended to reduce formulation costs and fine-tune properties.

Many factors influence the adhesive and cohesive strength of a formulation. Variation of NCO to OH ratio, use of reinforcing polyols and adhesion promoters and the selection of fillers or diluents all need consideration. The following charts and tables show the effects of these variable on a simple polyurethane prepared from Poly BD® R45 HTLO resin and the aromatic isocyanate Isonate 143L from the Dow Chemical Company.

The formulation variable considerations are:

1. Type of adhesion promoter
2. Type of reinforcing polyol
3. The effect of filler type on cohesive strength
4. Recommended antioxidant additives
5. The effect of NCO/OH ratio on peel adhesion to a variety of plastics
6. The effects of a specific adhesion promoter, filler and reinforcing polyol on the peel adhesion to a variety of plastic substrates

1.2.1 Useful Adhesion Promoters

1-3 phr is a typical concentration

Adhesion Promoter	Structure	Substrate
Zonarez 7055 ¹	Polyterpene resin	Rubber
Hercolyn D ²	Hydrogenated rosin methyl ester	Polyester, steel
Pentalyn H ³	Hydrogenated rosin pentaerythritol ester	Rubber
Silquest A 1100 ⁴	γ -Aminopropyltriethoxysilane	Polyester, steel, brass
Santicizer 8 ⁵	Toluene sulfonamide	Polyester, steel, brass, tile
Silquest A 187 ⁶	γ -glycidoxypropyltrimethoxy-silane	Steel, glass, aluminum, polycarbonate, zinc
SynFac 8027 ⁷	Propoxylated bis-phenol A	Steel, ABS, polycarbonate, acrylic

¹ Arizona Chemical Co.; ² Hercules, Inc.; ³ Hercules, Inc.; ⁴ Witco-OSi.; ⁵ Ferro Corp.; ⁶ Witco-Osi.; ⁷ Milliken Chemical Co. ⁸ Cray Valley

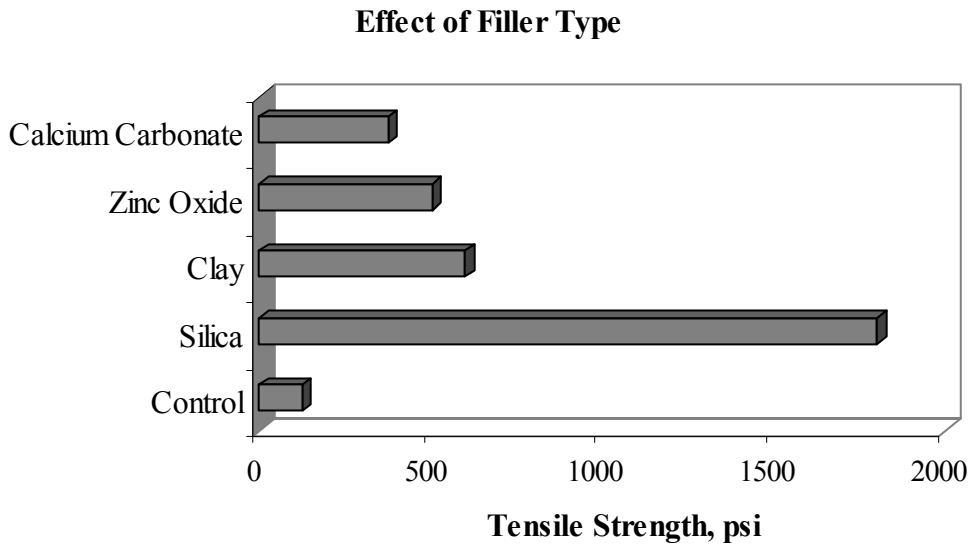
1.2.2. Frequently Used Reinforcing Additives For Polyurethane Formulations

Reinforcing additives	Comments
2-Ethyl-1,3-hexanediol	Highly soluble, reduces viscosity
Voranol 220-530 ¹	Makes stable blends
Castor oil	Highly soluble
Propoxylated bisphenol A ²	Enhances adhesion and strength
Oxazolidines ³	Increases hardness of coatings
Propoxylated polyethers	Reduces viscosity

¹ The Dow Chemical Company.; ² Synfac 8027, Milliken Chemical Company.; ³ QM 1007, Rohm and Haas

1.2.3. Effect Of Filler Type

Filler at 100 parts per 100 parts Poly BD[®] R45 HTLO weight are typical

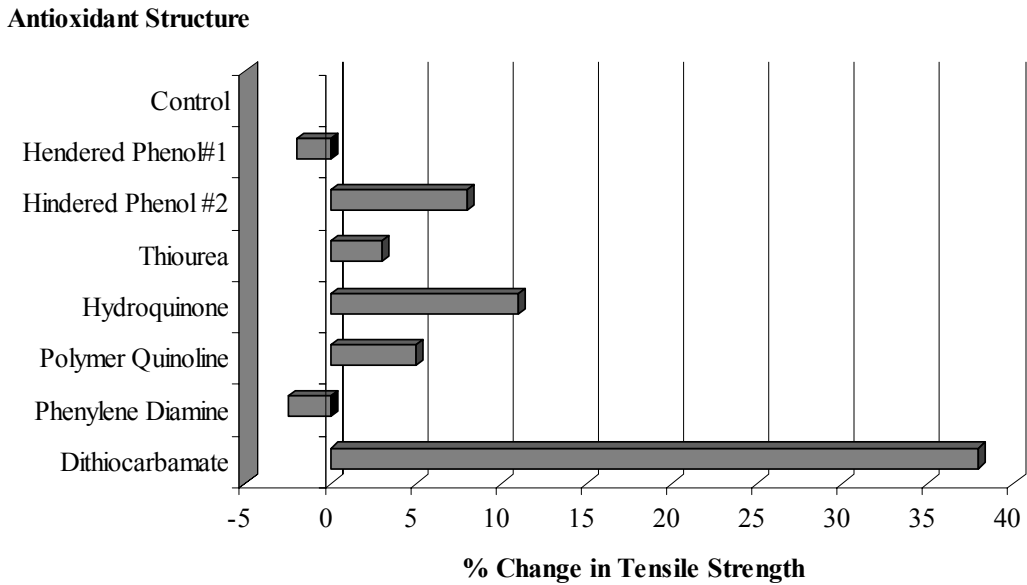


1.2.4. Effect Of Antioxidant Structure On Urethane Tensile Strength

Oxygen bomb aging, ASTM 572

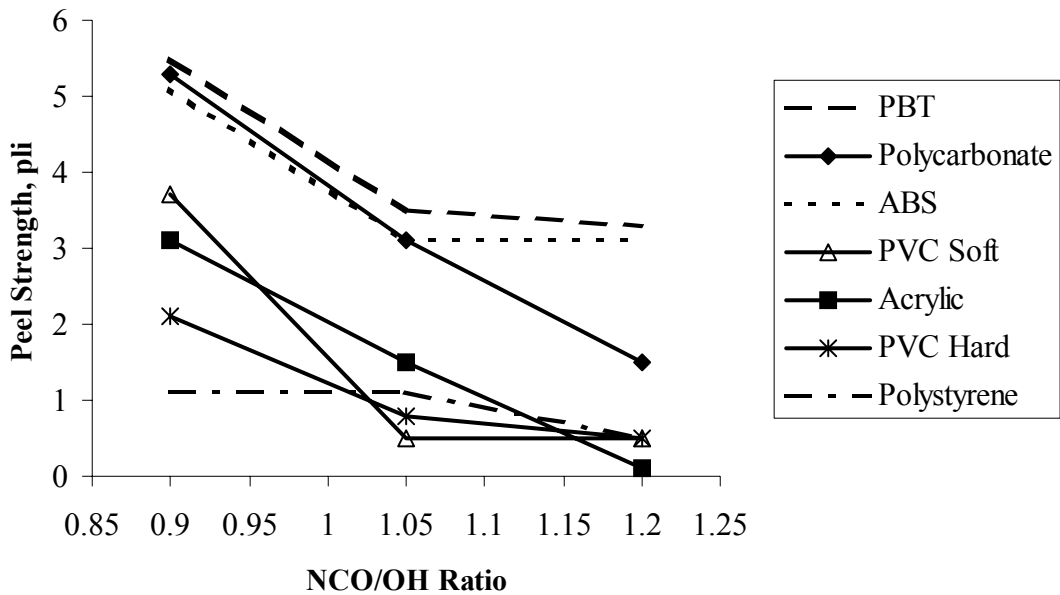
96 hrs at 160°F

Two-part polyurethane with aromatic isocyanate



Antioxidant	Trade name	Supplier
Hindered phenol #1	Cyanox 2246	Cytec
Hindered phenol #2	Santowhite crystals	Flexsys
Thiourea	Santowhite TBTU	Flexsys
Hydroquinone	Santovar A	Flexsys
Polymer quinoline	Flectol H	Flexsys
Phenylene diamine	Santoflex 134	Flexsys
Dithiocarbamate	Ethasan	Flexsys

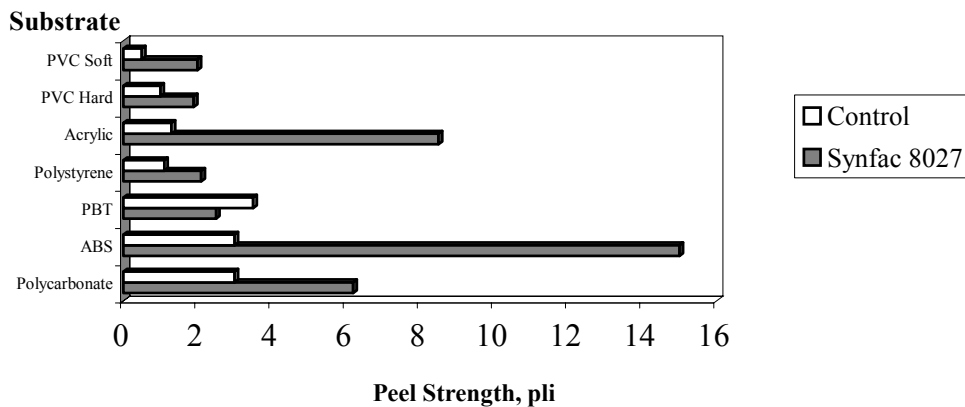
1.2.5. Effect Of NCO/OH Ratio On Peel Adhesion To Plastics



1.2.6. Effect Of A Specific Adhesion Promoter, Filler And Reinforcing Polyol On The Peel Adhesion To A Variety Of Plastic Substrates

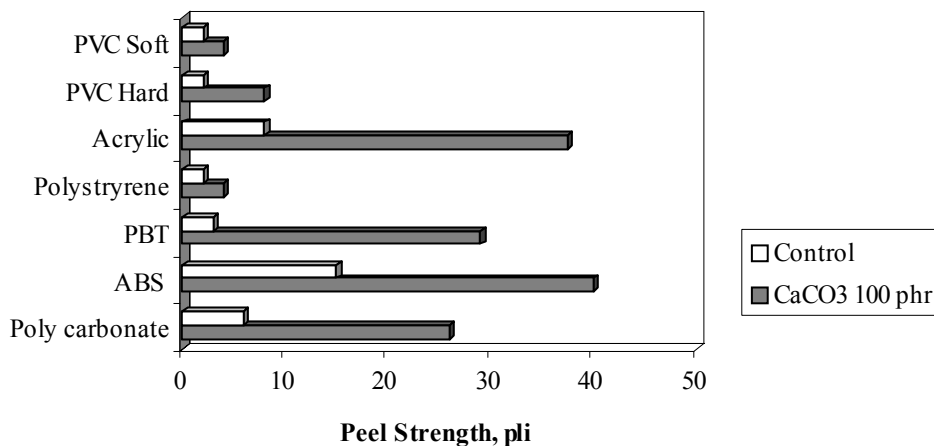
1.2.6.1 Effect of adhesion promoter on peel strength

Formulated with 15.7 phr Synfac 8027, 1.05 NCO/OH ratio

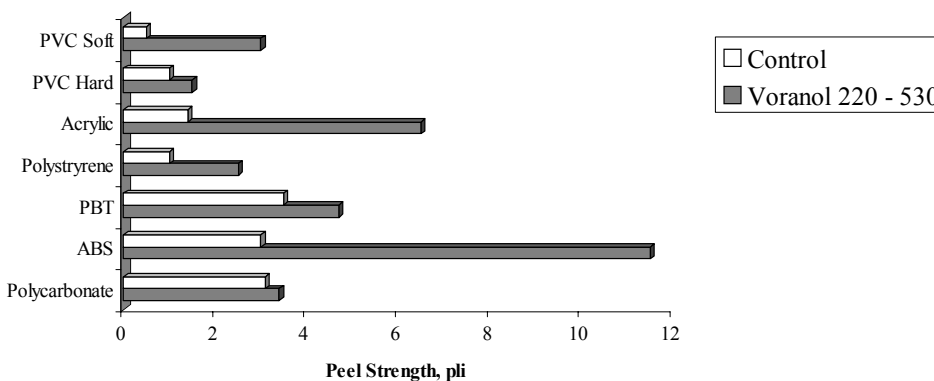


1.2.6.2. Effect Of CaCO₃ Filler On Peel Strength

Formulated with 15.7 phr Synfac 8027; Stearic acid treated CaCO₃; 1.05 NCO/OH ratio



1.2.6.3. Effect Of Reinforcing Polyol On Peel Strength



2. One Part Formulations

2.1. Prepolymer Preparation With Poly bd[®] R45HTLO Of 2.4-2.6 Functionality

Making a prepolymer based on Poly BD[®] R45 HTLO resin can be a challenge because Poly BD[®] Resin has an average functionality of 2.5. This structure results in a prepolymer with very high viscosity especially when a prepolymer is prepared with a low final NCO content.

Prepolymers based on Poly BD[®] Resin are commercially available in Europe (from BAULE SA, for example with a % NCO= 5.5%).

2.1.1. Prepolymer Synthesis

Two starting formulations for making a prepolymer based on Poly BD[®] R45 HTLO resin are listed in Table 6. One (MC50) has a final %NCO = 5 to 5.5% and a viscosity close to that of Poly BD[®] R45 HTLO resin, and the other (MC25) has a final % NCO = 2.5%, but with a higher viscosity. To reduce the viscosity of the final product, those prepolymers contain DOP, a plasticizer. DOP can be replaced with other types of plasticizers such as soybean oil, other phthalate based materials (DINP, DUP) or an aromatic process oil. A chain extender, Voranol 220-530, is used in these formulations in order to improve the final mechanical properties

of the product. In the formulation with a low final %NCO (MC 25), a mono isocyanate is added at

the end of the reaction to improve the stability of the prepolymer.

Table 6. Prepolymer Formulations Based On Poly BD® R45HTLO

Formulation (pbw)	MC 25	MC 50
Poly BD® R45 HTLO	100	100
Voranol 220-530 (Dow Chemical)	8.2	8.2
DOP (dioctylphthalate)	92	92
Irganox 1520 (Ciba)	0.2	0.2
Additif TI (monoisocyanate, Bayer)	2	0
Isonate 125 (MDI, Dow Chemical) (NCO/OH)	37.9 (1.9)	58.4 (2.8)
% NCO	2.5	5.5
Viscosity (Brookfield, RV7, 30°C)	35,000 cps	5,000 cps

2.1.2. Process To Prepare Prepolymer

The reactor was preheated under nitrogen at 80°C. To the reactor were added Poly BD® R45HT, Voranol 220-530 (preheated to 60°C), and DOP. The reaction was then degassed at 80°C under vacuum (2 mbar) with stirring for one hour. The mixture was cooled to 50°C before Isonate 125 (preheated to 60°C) was added with stirring under nitrogen. A mild exotherm can be expected when the isocyanate is added. The mixture was further heated to 80°C under vacuum (2 mbar) with stirring for 3 hours. After 3 hours at 80°C, samples of the prepolymer were taken to measure the free NCO content. If it is correct, Irganox 1520 and Additif TI were added at 80°C under vacuum with stirring for 30 minutes. The final prepolymer was cooled to 60°C and poured into a nitrogen-purged flask. The prepolymer is characterized by viscosity and % free NCO.

2.1.3. Prepolymer Manufacturing And Storage Tips

Some recommendations for storing prepolymers to minimize viscosity increases include:

- Heat the initial mixture (Poly bd® Resin + polyols + plasticizer) at a temperature around

80°C under vacuum to degas and dehydrate the reactants. This is one of the most critical steps in making a stable prepolymer.

- Use pure MDI instead of Isonate 143L. While the functionality of a modified liquid MDI (such as Isonate 143L) is low, it is still higher than 2. Hence, more crosslinking is expected when it is used to make a prepolymer. The viscosity of the prepolymer will be lower when it is made with pure MDI, having a functionality of exactly 2.0. Note that pure MDI is highly viscous at room temperature, and has to be slightly heated before adding to the reaction mixture.
- Add the catalyst (DBTDL or others) at the end of the reaction at the lowest temperature possible (preferably room temperature).
- Add a small amount of an acidic additive at the end of the reaction (such as benzoyl chloride) to prevent viscosity increase during storage
- Add a monoisocyanate at the end of the reaction to improve the prepolymer stability during the prepolymer preparation.
- Use a slightly higher NCO/OH ratio (more than 2.5), if possible, to reduce the viscosity of the prepolymer.

2.3. One-Part Moisture Cure Formulations Since Poly BD[®] Resin is very hydrophobic, a moisture-cured prepolymer formulation will first form a cured skin, which can prevent the resin in deep sections from being exposed to water and curing. Therefore, curing thick layers of a Poly bd[®] Resin-based prepolymer can take a long time. However, the final cured product will exhibit outstanding hydrophobicity, a significant advantage over other moisture-cured systems.

To address the issue of cure speed, refer to the Resin Solutions Technical Bulletin “Compatibility Between Poly BD[®] R45 HTLO and Polyether/Polyester Polyols” which describes hybrid prepolymers based on mixtures of Poly BD[®] Resin and more hydrophilic polyols, such as polyether and polyester polyols. These hybrid formulations can exhibit excellent properties and performance without sacrificing curing speed.

2.4. Reactive Hot Melt Adhesive Formulations

2.4.1. Starting Point Formulations

A moisture-cure hot melt formulation based on EVA- HEA (hydroxyl containing EVA resin) and Poly bd[®] is described below. This hot melt reactive adhesive possesses a relatively low melt viscosity compared with a non-reactive hot-melt adhesive. Furthermore, the Poly bd[®] –based adhesive can be applied at 130°C, offering a significant energy saving for the applicator which usually operates at 180°C. Finally, properties such as resistance to peel on cotton (porous substrate concentration) and SAFT on Kraft are superior to those of classic hot-melt adhesives.

Materials	Wt. (Parts) and Ratios
Polyol (Poly BD [®] R45 HTLO)	30
Terpolymer ¹ (EVA-HEA)	70
Tackyfier ²	100
[NCO*/OH] ₁	7.5
[NCO*/OH] ₂	5
Dodecanol/whole formulation	1.5-2.8%
Synthesis Protocols	One step

¹ Terpolymer: Orevac 9402 (Atofina)

² Tackyfier: Kristalea F-85 (Hercules) [Cray Valley also provides similar product: Norsolene W80 (softening point 75-85°C) and W90 (softening point 85-95°C)]

* Isocyanate (Isonate 125 M)

The [NCO*/OH]₁ is the original ratio of NCO to OH before adding monoalcohol, namely, dodecanol to the formulation. The [NCO*/OH]₂ is the final ratio of NCO to OH, after the addition. In this particular formulation, a one-pot synthesis is recommended since there is no advantage in preparing the prepolymer in two steps.

When a large excess of diisocyanate is required in the formulation, a one-hour gap between the addition of the isocyanate and the monoalcohol (two-step process) does not have a noticeable effect. On the other hand, when the isocyanate excess is low, the one-step process (incorporating isocyanate and monoalcohol at the same time) limits chain extension and the resulting viscosity increase.

2.4.1.1. Terpolymer/Polyol Ratio

A 70/30 mixture of terpolymer/Poly BD[®] Resin gives an adhesive with optimal properties. The Poly BD[®] Resin reduces the viscosity and temperature of solidification of reactive hot melt formulations with a constant NCO/OH ratio. Further, the presence of Poly BD[®] decreases the haze point of the adhesives, as a result of improved compatibility. The cross-linking rate is slightly faster when the concentration of Poly BD[®] is increased based on SAFT results. Apparently, at the 70/30 ratio the hydrophobicity of Poly BD[®] Resin does not significantly retard the curing rate. However, as the polyol ratio decreases from 70/30, the adhesive loses its hot-melt characteristics, namely, it does not solidify before curing. Finally, it should be noted that a decrease in the elongation at break occurs when the concentration of polyol increases.

2.4.1.2. [NCO/OH]₁ Ratio And [NCO/OH]₂ Ratio

For 70/30 terpolymer/Poly %□[®] Resin formulations, [NCO/OH]₁ ratios between 5 and 10 gave best results.

The presence of low concentrations of monoalcohol seems to be beneficial. Its most prominent effect is to decrease the viscosity of the adhesive. The formulation that achieves the best balance of properties has an [NCO/OH]₂ ratio of approximately 5 and an [NCO/OH]₁ of approximately 7.5.

2.4.1.3. " Monoalcohol

The monoalcohol is used to limit the need for using a large excess of diisocyanate, and 1-dodecanol is the preferred one.

2.4.1.4. Wax And Tackifying Resin

Although wax decreases the viscosity and set time as anticipated, it also reduces peel performance, as the adhesive is weakened with inferior mechanical properties. Further, adhesives can be made with satisfactory set time without wax. Thus, wax is excluded from the recommended formulation. On the other hand, the tackifying resin demonstrates a strong compatibilizing effect in the formulations.

The curing of adhesives was carefully monitored for each test. There is possible variability due to variations in thickness of glue joints (100µm for the SAFT and the peel, 1.5 mm for the traction and the viscoelastic behavior) as well as the nature of the tests (the peel test proves to be much more demanding than SAFT). Thus, the time needed to reach the maximal values depends on the test:

- SAFT: 48 hours
- T peel on cotton: 10 to 20 days
- Mechanical properties: 20 to 30 days

2.4.2. Adhesive Properties

- Brookfield viscosity: 8000 mPa/s at 130°C
- Stability of the viscosity to heating: +7% per hour at 130°C
- Storage stability (by viscosity): +20% in 4 months
- Resistance to T peel on cotton at 23°C: 18N/cm
- Resistance to T peel on cotton at 60°C: 8.5N/cm
- Maximal constraint in traction: 8.4Mpa
- Elongation before breaking: 450%
- Set time: 10 seconds
- SAFT: 180°C in 48 hours.

Conclusions

When Poly %□[®] R45 HTLO Resin is cured with an isocyanate to produce a polyurethane adhesive, it imparts excellent adhesive properties, even on oily-coated surfaces. These outstanding properties are maintained after exposure to harsh conditions, such as boiling water, heat aging, water immersion, salt water immersion, humid aging, and cold temperatures. Properties exhibited by polyurethanes prepared from Poly bd[®] Resins include excellent hydrolytic stability, low water absorption, excellent low temperature flexibility and high compatibility with fillers and extenders.

Poly %□[®] Resin is demonstrated to provide broad formulating flexibility for the adhesive manufacturers, finding use in two-part, one-part moisture cure, and one-part reactive hot melt formulations.