CRAY VALLEY
Resins par excellence

Hydroxyl-Terminated Poly bd® Resins In Electric Applications

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HYDROXYL-TERMINATED POLY BD® RESINS IN ELECTRIC APPLICATIONS

Introduction

Poly bd® Resins are used in electrical encapsulation and potting formulations to provide excellent hydrophobicity, low temperature ductility, retention of properties during thermal cycling and low embedment stress properties. Through a combination of ease of handling, superior electrical insulating properties, minimal curing exotherm, excellent low temperature ductility and stability in hot, humid environments, Poly bd® Resin systems outperform other materials.

Poly bd® Resins from Cray Valley Company offer unique formulating opportunities to manufacturers of potting and encapsulation materials. Superior performance properties can be achieved in products based upon these materials. Poly bd® Resin formulations provide excellent thermal cycling capabilities and maintain consistent properties over a range of temperatures from -40 °C to 125 °C. The resin's low glass transition temperature of approximately -70 °C is particularly beneficial in low temperature potting applications.

Two key structural features are responsible for the formulating advantages which Poly bd® Resins offer. First, primary, allylic hydroxyl endgroups allow for room temperature reactions with a variety of isocyanates to yield elastomers. Second, the hydrophobic, nonpolar hydrocarbon backbone reduces water absorption in the formulated product. Consequently, these formulations excel where water resistance or prevention of moisture vapor permeation is critical.

Another attribute of Poly bd® Resin based materials is the minimal embedment stress exhibited at low temperatures. While alternative resin formulations afford protection to encapsulated electrical components, many are unsatisfactory at low temperatures where strong localized stresses on potted electrical components cause premature failure. The low glass transition temperature inherent in Poly bd® Resin- based systems reduces these localized stresses.

This bulletin highlights the superior properties obtained with Poly bd® Resins and demonstrates the value of these resins in the formulation of electrical potting and encapsulation systems.

FORMULATIONS

1. General Benefits

Hydrolytic Stability

Formulations based on hydroxyl-terminated Poly bd® Resin are known for their excellent hydrolytic stability and low moisture permeability. Measuring moisture vapor transmission rates (MVTR) is one method of determining the permeability of a material. Figure 1 shows the MVTR of a variety of Poly bd® Resin-based systems in comparison to other typical electrical potting and encapsulation compounds. The MVTR of Poly bd® Resin-based formulations are competitive, if not superior to the MVTR exhibited by other commonly used electrical potting and encapsulation materials.

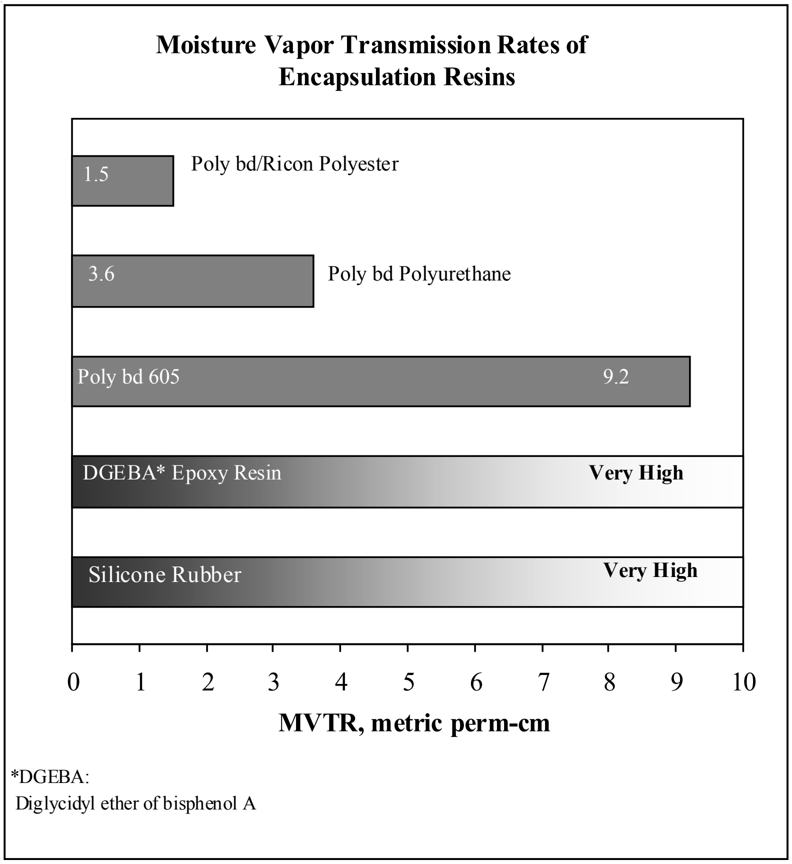
Thermal Shock/Embedment Stress

Poly bd® Resin based elastomers maintain essentially constant elongation and low embedment stress over a wide range of temperatures. This feature allows encapsulation of fragile electrical components in a relatively stress free environment, even at low temperatures. Poly bd® Resins can be formulated into systems exhibiting excellent thermal cycling properties in potting or encapsulation applications. Even at –38 °C, embedment stress is significantly lower than that of most competitive materials.

Low Exotherm/Ambient Temperature Cure

A variety of Poly bd® Resin based systems cure at ambient temperature with minimal exotherm. Poly bd® Resins react with isocyanates at ambient temperature. Pot life and cure time can be adjusted using standard urethane catalysts. Poly bd® Resins also react with anhydrides such as Ricon® MA resins to produce esters. Tertiary amine catalysts can be used to achieve ambient temperature cures.

Figure 1



Minimal Shrinkage

Poly bd® resin systems exhibit minimal shrinkage after curing.

Low Toxicity

In general, the toxicity of Poly bd® homopolymers is very low. For typical applications, polymeric isocyanates with low vapor pressures are recommended. Toxicity and proper handling information for these components of the formulation can be obtained from the respective manufacturers. Material Safety Data Sheets from each manufacturer should be consulted for pertinent safety and handling information.

FORMULATING FLEXIBILITY

The formulating flexibility of Poly bd® Resins permits the production of products which meet specific requirements. Physical properties can be varied using reactive reinforcing materials for harder, stiffer compositions or by using plasticizers or extending oils to produce softer, more flexible products. Thixotropes can modify rheology for non-sag applications.

2. Starting Formulations And Properties

a) Formulations derived from non-radical curing

Poly bd® resins can be used in formulating a variety of materials including polyurethanes, polyesters, and epoxies. Table 1 lists the three Poly bd® Resin systems discussed in this bulletin, along with their respective physical and electrical properties.

Poly bd® R-45HTLO resin, hydroxyl-terminated polybutadiene, can be used in conjunction with isocyanate 143L, a polycarbodiimide-modified liquid MDl, to form a polyurethane. For those who prefer a non-urethane cure, Poly bd® R-45HTLO resin can be used with Ricon®131MA10, maleic anhydride-grafted polybutadiene, to create a polyester system. Poly bd® 605 resin is an internally epoxidized derivative of hydroxyl-terminated polybutadiene and can be used as the sole resin in an epoxy formulation. The systems shown in Table 1 can be modified in a variety of ways to meet the requirements of the formulator.

It is expected that the polyester non-urethane formulation yields the product with the lowest dielectric constant among the three classes of materials examined. This polyester formulation is based solely on ingredients with hydrocarbon backbones, it also has excellent MVTR and low temperature flexibility. Further, its thermal stability is far better than polyurethanes based on thermogravimetric analysis because the ester-acid linkage is less prone to thermal decomposition at a high temperature than the urethane moiety.

Additives

Additives can be used to lower formulation cost or to achieve specific properties in a finished product. Poly bd® systems are capable of accommodating high filler levels, generally with little or no effect on electrical properties. Table 2 provides filler recommendations for changing specific properties in Poly bd® Resin-based systems.

Table 1. Poly bd® Resin Systems

FORMULATION (pbw)			
	Polyurethane	Polyester	Epoxy
Polybd R45HTLO Resin	88.0	54.9	
Poy bd 605 Resin			95.0
Ricon 131MA10		44.8	
Isonate 143L	11.2		
AC-30[1]		0.3	
Leecure B-1550[2]			5.0
PROPERTIES			
Hardness, Shore A	49	37	79
Tensile Strength, psi MPa	110 0.75	80 0.55	200 1.37
Elongation, %	49	48	25
Dielectric Constant, 25 °C, 1kHz	4.49	2.05	2.65
Dielectric Constant, 25 °C, 1000 kHz	4.01	1.84	2.41
Volume Resistivity, 25 °C, ohm-cm	$6x10^{16}$	$1x10^{15}$	$3x10^{11}$
Surface Resistivity, 25 °C, ohm	$1x10^{16}$	$7x10^{16}$	$7x10^{12}$
Glass Transition Temp, (Tg), °C	–71.7	–74.0	–60
MVTR, 10^{-3} metric perm-cm	3.6	1.5	9.2

[1] AC-30: tertiary amine
[2] Leecure B-1550: boron trifluoride complex

Table 2. Modification Of Poly bd® Resin Systems

ATTRIBUTE	**FILLER RECOMMENDATIONS**
Cost Reduction	Calcium Carbonate, Clay, Silica, Talc
Reinforcement	Talc, Mica, Carbon Black, Fumed Silica
Electric Resistance	Mica
Improved UV Stability	Carbon Black, Triazoles, Hindered Amines
Improved Oxidative Stability	Carbon Black, Hindered Phenols
Thixotropy	Carbon Black, Fumed Silica, Bentone Clays
Higher Density	Barium Sulfate
Lower Density Products	Hollow Glass Microspheres
Thermal Conductivity	Tabular Alumina Filler
Electric Conductivity	Carbon Black, Silver Filler
Fire Retardance	Alumina Trihydrate, Antimony Oxide, Halogenated Esters

Extenders

Extenders such as electrical grade hydrocarbon oils or ester plasticizers can be added to the formulation. These materials are generally used to reduce viscosity and/or cost. Increasing levels of oil or plasticizer will increase elongation and reduce tensile and tear strengths. Very high levels of oil or plasticizer (up to 80 parts per 20 parts by weight of resin) will provide a gel-like, cured material in a urethane formulation that will retain electrical insulation characteristics. The addition of extenders can alter pot life and/or cure time. Selection of the extender oil or plasticizer will depend on compatibility and desired viscosity. Typically, oils with at least 40% aromatic content are highly compatible and can be used at relatively high levels. A variety of low viscosity ester plasticizers are also effective as extenders for Poly bd® Resin.

Specific Formulation Guidelines:

- Short Chain Reinforcing Diol-e.g., Voranol® 220-530 or 2-ethyl-1,3-hexanediol
- Increases strength and hardness

- Electrical Grade Oil Extender-e.g., polybutene
- Decreases mix viscosity
- Reduces hardness
- Reduces formulation cost

- Filler-e.g., Burgess KE Clay
- Increases mix viscosity
- Reduces formulation cost

- Plasticizer-e. g., diundecyl phthlate (DUP)
- Reduces mix viscosity
- Typically produces transparent formulations
- DUP can be added to either Part A or Part B of a two-part formulation to obtain even mix ratios
- Tends to lower electrical properties as concentration is increased

- Antioxidant-e.g., Cyanox® 2246 or Irganox® 1010
- Minimizes embrittlement

- UV Stabilizer-e.g., Tinuvin®P
- Minimizes discoloration

More Formulations And Electrical Properties, Demonstrating The Effect Of Additives

Formulation	**1** 1:1 Reinforcing diol/ R45HTLO	**2** 2:1 Reinforcing diol/ R45HTLO	**3** Added Electrical Grade Oil	**4** Added Oil and Filler	**5** Added Plasticizer	**6** Added Oil and Plasticizer
Part A – Resin						
Poly bd® R-45HTLO Resin	100	100	100	100	100	100
Voranol® 220-530	8.58	17.15	8.58	17.15	8.58	8.58
Cyanox® 2246	1	0.1	1	1	1	1
Foamkill® 8D	0.05		0.05			
Dibutyl Tin Dilaurate	0.05	0.05	0.07	0.2	0.07	0.07
Polybutene			52.7	80		26.35
Burgess KE Clay				80		
Diundecyl Phthalate					52.70	26.35
Total	109.68	117.30	161.40	278.35	162.35	162.35
Part B – Isocyanate						
PAPI® 901	19.3					
Isonate® 143		37.19		37.19		
Mondur® MR			22.97		22.97	22.97

Formulation	1	2	3	4	5	6
Cured Physical Properties						
Tensile Strength, psi (MPa)	370 (2.53)	1770 (12.11)	270 (1.85)	910 (6.23)	190 (1.30)	200 (1.37)
Elongation, %	170	207	125	207	95	110
100% Modulus, psi (MPa)	255 (1.74)	868 (5.94)	206 (1.41)	538 (3.68)	185 (1.27)	177 (1.21)
Tear Strength, Die "C", pli	63	149	24	76	19	25
Hardness, Shore A	50	81	42	65	42	42
Electrical Properties						
Volume Resistivity, ohm-cm (ASTM D-257)	7×10^{15}	1×10^{16}	9×10^{15}	1×10^{15}	2×10^{14}	1×10^{15}
Surface Resistivity, ohm (ASTM D-257)	$>2x10^{17}$	1×10^{17}	$>1x10^{17}$	$>1x10^{17}$	$>1x10^{17}$	$>1x10^{17}$
Dielectric Strength, volts/mil @ 25°C (ASTM D-149)	305	622	609	641	548	558
Dielectric Constant @ 25°C (ASTM D-150)	3.1	2.9	2.8	2.9	3.7	3.2
Dissipation Factor, l kHz @ 25°C (ASTM D-150)	0.0268	0.0170	0.0156	0.0128	0.0202	0.00178
Hardness, Shore A –after 28 days @ 100°C, 95% RH	48	81	43	68	42	43
Embedment Stress @ -38°C, psi	360	360	0	0	0	0
Handling Properties						
NCO/OH Equivalent Ratio	1.05	1.05	1.05	10.5	1.05	1.05
Mix Ratio by Weight (A/B)	5.6	3.2	7.1	7.5	7.1	7.1
Mix Viscosity (A+B), mPa•s	4700	7000	2800	13750	1800	1900
Pot Life, mins. To 10^4 mPa•s	45	20	73	32	83	78

Suppliers

Chemicals	Suppliers
Polybutene	BP Chemicals
AC-30	Lonza Group
Diundecyl Phthalate	BASF Corporation
Burgess KE Clay	Burgess Pigment Company
Tinuvin® P	Ciba Specialty Chemicals
Irganox®1010	Ciba Specialty Chemicals
Cyanox® 2246	Cytec Industries Inc.
2-Ethyl-1,3-Hexanediol	Kyowa Hakko USA Inc.
Dibutyltin Dilaurate	Atofina Chemicals, Inc.
Isonate® 143L	The Dow Chemical Company
Foamkill® 8D	Crucible Chemical Company
Mondure® MR	Bayer Corporation
PAPI® 901	The Dow Chemical Company

a) Formulations derived from radical curing

Poly bd® resins are used in electric motors and in high-voltage transformers as insulators with high-temperature resistance. In motors, insulation is rated as Class F (continuous operation at 150 °C). In high-voltage transformers, Poly bd® Resin systems meet a Class H+ rating when used with an aluminum conductor (continuous operation at 220 °C). When a copper conductor is used a Class H (continuous operation at 180 °C) rating is achieved.

The Poly bd® Resin formulations used in these applications are non-urethane systems where Poly bd® Resin is heat-cured via a free radical mechanism. The major components in the formulation are Poly bd® Resin, vinyl monomer, cross-linking agent and catalyst. A typical formulation could contain Poly bd resin, vinyl toluene, trimethylolpropane trimethacrylate (TMPTMA) and dicumyl peroxide.

The same basic formulation is used in two different applications, electrical varnish and dielectric binder. In all cases, the systems are cured at or above the expected temperature of operation.

The relative concentrations of ingredients can be varied to give a range of product hardness, from hard (high Shore D) to soft (low Shore A). For a varnish application, a vacuum impregnation technique is used. In this method, the part is evacuated and the Poly bd® formulation coats the components and replaces the air voids. Removal of air pockets is important, since entrapped air is a source of corona discharge at high voltage. In applications where this is not a problem, for example in environmental coatings, a dip tank can be used in place of vacuum impregnation. In some electrical applications, sand is vibrated to fill areas, and then the part is vacuum impregnated and cured. Sand can be replaced by a dielectric filler slurried in a Poly bd® Resin formulation.

Poly bd® non-urethane resin systems offer the following features in electrical applications:

- Superior insulating characteristics
- Complete bonding of conductors
- Excellent moisture and corrosion resistance
- Low viscosity at 100% solids
- Ease of handling
- Long term storage stability

Starting point formulations are as follows:

	HARD (pbw)	SOFT (pbw)
Poly bd R45HTLO	40	80
Vinyl toluene	60	20
TMPTMA	3	4
Dicumyl Peroxide	2	4

Specific guidelines for formulations

1. Higher concentrations of Poly bd® produce softer materials
2. For high temperature, more TMPTMA should be used, concentration can vary from 3-8 pbw.
3. Hydroquinone (HQ) is a stabilizer for formulations that are heated. HQ needs air to function.
4. When HQ is used, excess peroxide is necessary. Use levels of peroxide vary from 2-6 pbw.

Suppliers

Chemicals	**Suppliers**
Vinyl Toluene	Dow Chemical Co.
TMPTMA /SR350	Cray Valley Company
Dicumyl Peroxide	Atofina Chemicals Inc.