CRAY VALLEY
Resins par excellence

APPLICATION BULLETIN

Polyester Sealant and Potting Formulations From Poly bd® and Ricon® MA Resins

Introduction

Poly bd® resins are hydroxyl-terminated polybutadiene materials which impart excellent hydrophobicity, thermal cycling properties, low glass transition temperature and embedment stress properties to sealants and electrical encapsulation and potting formulations.

Ricon® MA resins are polybutadienes which are grafted with maleic anhydride. The different Ricon® MA grades have a range of molecular weights and anhydride concentrations and can have different ratios of 1,4- and 1,2- vinyl microstructure.

Poly bd® and Ricon® MA resins react to give cured, polyester products. Since both resins are liquids, they can be mixed and used immediately, or they can be formulated as a stable two-part system. With a combination of ease of handling, superior electrical insulating capabilities, minimal curing exotherm, excellent low temperature properties, and stability in hot, humid environments, the re-enterable Poly bd®/Ricon® MA systems outperform other materials in targeted applications.

The crosslinking esterification reaction between the hydroxyl groups of Poly bd® resin and the anhydride groups of Ricon® MA resin can occur at an elevated temperature without any catalyst. However, catalysts can accelerate the reaction to improve production cycle, especially when the polymer content is diluted with processing oils and plasticizers for property improvement and cost reduction.

This bulletin describes several basic formulations and their properties. It also describes results from a catalyst study, where the effect of catalyst type and concentration and reaction temperature on gel times were determined. With this information, one can select a suitable starting formulation for one's intended application.

Formulation Properties

Ingredients

The formulations described are based upon mixtures of Poly bd® R45HTLO and Ricon® 131MA10. Poly bd® R45HTLO, a liquid hydroxyl-terminated polybutadiene material, has a molecular weight of 2800 and hydroxyl functionality of 2.4-2.5 per chain. Ricon® 131MA10 has a molecular weight of 4700 and about 6 anhydride groups grafted per polymer chain. Both resins are available from Cray Valley Company, Inc.

Hardness

Ricon® 131MA10 resin reacts with Poly bd® R45HTLO within one-week at room temperature to produce a material with 25-35 Shore A hardness when no plasticizers or fillers are used. When this reaction is carried out at elevated temperature (cure at 140°C for 16 hours) a product with 50 Shore A hardness is produced. Using a lower molecular weight hydroxyl terminated Poly bd® Resin, such as Poly bd® R20LM, or a Ricon® MA resin with a higher anhydride content is expected to give a more highly cross-linked product which would have increased hardness.

A variety of plasticizers have been used to produce soft polyester gel products. The compatibilities of the Poly bd®/Ricon® MA resin mixtures with oils and phthalate esters are similar to those of Poly bd® resins. Soybean oil exhibits excellent plasticizing properties, as it gives a soft gel which is very stable and which does not exude at elevated temperatures.

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TOTAL

Thermal And Hydrolytic Stability

The ester-acid linkage (half-ester) generated by reacting an anhydride group with a hydroxyl group is known to be thermally irreversible when a high molecular weight alcohol is used. This thermal stability is an advantage when compared to polyurethane gel products, which are thermally reversible at elevated temperatures (see table below).

Product	Hours at specified temperature	Wt. Change, % at 150°C	Wt. Change, % at 175°C
Poly bd®-Derived Polyurethane	500 1000	-1.8 -2.7	-3.4 -4.6
Poly bd®-Ricon® MA Polyester	500 1000	-0.8 -0.8	-1.3 -1.6

Although the ester-acid (half-ester) link is embedded in an extremely hydrophobic gel environment, it is considered to be hydrolytically labile. Moisture is expected to hydrolyze the half-ester bond much faster than a regular ester owing to assistance from the neighboring carboxylic acid group. As a result, the mechanical properties are expected to deteriorate after long-term exposure to wet conditions, even though significant weight loss might not be observed. For such environment, a polyurethane gel derived from Poly bd® R45HTLO would be preferred.

Dielectric Constant

The dielectric constant, or insulating capacity, of the Poly bd®/Ricon® MA polyester product at 1000Hz is superior to that of a Poly bd®-derived polyurethane (see table below), both initially and after aging.

Product	Hours at specified temperature	Dielectric constant (1000 Hz) at 150°C	Dielectric constant (1000 Hz) at 175°C
Poly bd®-Derived Polyurethane	initial 500 1000	5.86 5.30 5.01	5.86 4.93 4.81
Poly bd®-Ricon® MA Polyester	initial 500 1000	3.53 3.77 4.18	3.53 3.96 3.38

Starting 2-Part Formulation

Handling Of Ricon® MA

To insure best performance, store Ricon® MA resin material at room temperature or below. Avoid contact with moist atmosphere since this can cause a skin to develop on the material. Do not heat Ricon® MA with band heaters, since hot spots may cause the material to crosslink and auto-accelerate.

Formulation

Ingredient	Part A	Part B	Manufacturer
Ricon®131 MA10	67.5		Sartomer Company
Drakeol 9	32.4	18.9	Penreco
Poly bd® R45HTLO		74.2	Sartomer Company
Irganox 1010	0.09		Ciba Specialty Chemicals
Tinuvin 770	0.01		Ciba Specialty Chemicals
Sovermol VP650NS		3.95	Cognis Corporation
DAMA 1010		2.95	Albermarle

Mixing Instructions

Part A: Charge materials into mixing vessel; mix at 25-40°C for 2 hours

Part B: Charge materials into mixing vessel; warm to 60°C, stir for 1 hour.

Reaction Ratio: Part A/Part B are mixed in a ratio of 1/1 wt./wt.

Typical properties

Property	Values	Units
Hardness Shore A	24	
Tensile Strength	68	psi
Tg	-90	°C
Water absorption at 25°C for 96 h	0.1	Wt. %
Dielectric Constant	2.6	
Dissipation Factor	0.01	
Volume Resistivity	6.9×10^{11}	Ohms
Surface Resistivity	1.4×10^{14}	Ohms

Catalyst Study

The esterification reaction between the hydroxyl group of Poly bd® resin and the anhydride group of Ricon® MA resin proceeds with moderate speed at an elevated temperature without any catalyst. However, catalysts are able to accelerate the reaction to improve production cycle, especially when the polymer content is diluted with processing oils and plasticizers for property improvement and cost reduction. Tertiary amines have been commonly recommended for this purpose. Furthermore, N,N-dimethylamino-pyridine (DMAP) and its derivatives are a commonly used class of extremely effective catalysts for accelerating similar reactions. To determine the efficiency of these different catalysts, a gel time was carried out.

Formulation I (Total wt. % of Ricon® 131MA10 and Poly bd® R45HTLO = 39%)

Part A				
Ricon® 131MA10	35.0			
Soybean Oil		55.0		
Renoil 100*		10.0		
Part B		**1**	**2**	**3**
Poly bd® R45HTLO		43.0	43.0	43.0
Soybean Oil		10.0	10.0	10.0
Renoil 100		41.0	44.0	46.0
Catalyst		6.0	3.0	1.0

*Renoil 100 is a product of Renkert Oil

Formulation II (Total wt. % of Ricon® 131MA10 and Poly bd® R45HTLO = 19.5%)

Part A				
Ricon® 131MA10	17.5			
Soybean Oil		70.0		
Renoil 100		12.5		
Part B		**1**	**2**	**3**
Poly bd® R45HTLO		21.5	21.5	21.5
Soybean Oil		13.5	13.5	13.5
Renoil 100		59.0	62.0	64.0
Catalyst		6.0	3.0	1.0

Solubility of different catalysts in Part B (Part B is a mixture of Poly bd® R45 HTLO, Renoil 100 process oil, catalyst and soybean Oil)

Component	Solubility in Part B	Appearance	Source
DAMA® 1010 (Didecylmethylamine)	good	liquid	Albemarle
4-(dimethylamino) pyridine	not soluble	solid	Aldrich
4-Pyrrolidinopyridine	good	Waxy solid	Aldrich
Polycat® 41 catalyst	good	liquid	Air Products
4-(Methylpiperidino) Pyridine	good	liquid	Reilly Industries
Ancamine® K54 curing agent	good	liquid	Air Products
Ancamine® 1110 curing agent	partly soluble *	liquid	Air Products

* Increase of turbidity in Part B mixture was observed when catalyst content was increased above 0.5 wt. %. Cured samples had phenol odor as the catalyst Ancamine® 1110 contains < 20% phenol.

Gel Test Procedure

1. Components in Part A and B were weighed and mixed well at room temperature.

2. Gel time was determined by gel time meter 22A (Sunshine Instruments Company) in accordance with ASTM D3056-85. A silicone oil bath with a digital temperature controller was used to control the reaction temperature.

3. Part A and B were mixed for 1.5 minutes at room temperature in a 1:1 weight ratio (equivalent ratio of anhydride from Ricon® 131MA10 to hydroxyl from Polybd® R45HTLO = 1:1). The blend (10g) was then poured into a test tube. Gel time (in seconds) was recorded by the gel time meter at a specific temperature.

Relative Catalytic Activity Of Different Catalysts For Reaction Between Ricon® 131 MA10 and Poly bd® R45HTLO At Different Temperatures

Catalyst	Catalyst content (wt. %)	Gel time (minutes)					
		Formula I (39.0% polymers)			Formula II (19.5% polymers)		
		50°C	60°C	70°C	50°C	60°C	70°C
DAMA® 1010	3.0	19.00	14.33	10.87	49.43	41.77	35.68
	1.5	26.00	19.10	14.30	80.07	60.12	56.45
	0.5	67.48	55.53	41.42	194.52	154.15	127.78
Ancamine® K54	3.0	3.42	3.05	2.17	10.28	9.10	8.23
	1.5	3.63	2.92	2.40	15.03	12.53	10.02
	0.5	9.97	8.33	5.78	25.72	22.52	19.03
Ancamine® 1110	3.0	8.62	7.20	6.67	32.00	23.98	20.83
	1.5	15.22	12.08	10.05	51.90	44.33	35.92
	0.5	46.75	34.40	25.90	184.03	137.72	110.38
4-pyrrolidino-pyridine	3.0	0.15	NA	NA	3.03	2.85	2.60
	1.5	0.83	0.50	0.40	4.30	4.22	3.63
	0.5	4.70	3.48	2.78	11.82	11.22	8.72
Polycat® 41 catalyst	3.0	1.52	1.17	1.05	7.30	5.68	4.70
	1.5	1.90	1.65	1.38	7.70	6.20	5.18
	0.5	2.95	2.63	1.92	9.27	7.77	6.45
4-(Methylpiperidino) pyridine	3.0	2.23	1.83	1.65	9.05	8.02	6.80
	1.5	3.28	2.93	2.23	13.07	11.27	9.45
	0.5	9.38	6.37	5.75	28.73	23.95	21.95

Conclusions

Using the gel meter, we have completed a rate study of several selected catalysts to improve the understanding for the reaction between Poly bd® R45HTLO and Ricon® 131MA10. The results (see table above) indicate that either Polycat 41 or 4-N-pyrrolidinopyridine has outstanding performance, but Polycat 41 is preferred owing to its low cost and commercial availability. Both are more effective catalysts than 2,4,6-tris(dimethyl-aminomethyl)phenol (Ancamine K54). Others, such as dimethylaminomethylphenol (ANCAMINE 1110) or didecylmethylamine (DAMA® 1010) recommended in some of Ricon® resin bulletins, are more suitable for applications requiring longer pot life. Although N,N-dimethylaminopyridine (DMAP) is known to be an excellent catalyst for acylation reactions, it was not examined owing to its poor solubility in the hydrophobic Poly bd®/Ricon® MA mixture.