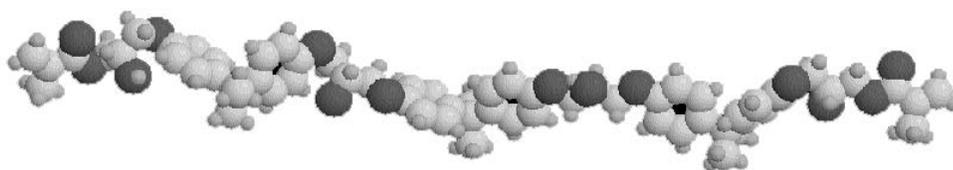


# *Technical Research*



CoREZYN<sup>®</sup> Premium Vinyl Ester Molecule

## High Heat Distortion Vinyl Ester Resins in FRP Tooling and Mold Manufacturing

INTERPLASTIC CORPORATION  
Thermoset Resins Division



## ABSTRACT

Epoxy-based vinyl ester resins are known for their durability, corrosion resistance, strength, resilience and high heat distortion temperatures. Interplastic Corporation has used these properties to develop vinyl ester gel coats and laminating resins for fiberglass reinforced plastic (FRP) tooling and mold-making applications. The inherent properties of vinyl ester resins enable them to withstand the stresses, heat cycling and abuse that fiberglass molds are subjected to. Using these resins instead of standard polyester resins in FRP mold manufacturing should prolong the mold's life, decrease repairs and retain the mold's surface quality longer.

Due to the vinyl ester resin's higher heat distortion temperature characteristic, molds made with vinyl esters also can be used in applications that were typically dominated by epoxy molds. These elevated temperature applications include vacuum-form molding (VFM), resin injection molding (RIM) and resin transfer molding (RTM).

In this work, we compare the high heat distortion property of tooling vinyl ester resins to the rigid orthophthalic and isophthalic laminating resins. We also compared vinyl ester gel coats to those typically used for tooling applications. We examine the tooling vinyl ester's better mechanical properties, excellent low profile capability, increased thermal and dimensional stability, premium corrosion resistance, and exceptional toughness and fatigue resistance. We also explain the economics of using the resin and how that is related to the cost of the finished mold.

## INTRODUCTION

Non-foaming catalyst/promoter systems for vinyl ester resins aid in the production of FRP molds. In thin laminates, composites catalyzed with a non-foaming catalyst/promoter system have faster and better cure development than those cured with methyl ethyl ketone peroxide (MEKP).

The non-foaming catalyst/promoter system has also been incorporated into high heat distortion vinyl ester gel coats. The time between applications of the gel coat and the subsequent laminates decreases because of faster cure development in vinyl esters. This system should also give a more thermally-stable mold because the degree of cure is higher than those made with the standard MEKP system.

## EXPERIMENTAL

We analyzed gel coats and back-up resins for their suitability in mold construction. Our testing focused on highlighting the durability advantages of a vinyl ester composite over conventionally made tools.

The following resins were evaluated: CoREZYN® COR63-AA-017 orthophthalic; COR75-AQ-001 isophthalic, COR61-AA-064 DCPD (dicyclopentadiene); MVR8021 isophthalic/vinyl ester blend; VE8121 thixotropic vinyl ester; and the VE8153 high heat distortion, thixotropic, vinyl ester.

Three gel coats were evaluated for their long-term use capabilities. CoREZYN B-168VE-TUA black vinyl ester gel coat was compared side-by-side with a commercially available orange isophthalic tooling gel coat and the CoREZYN B-816-TCN black orthophthalic tooling gel coat. The liquid and mechanical characteristics of the gel coats are compiled in Table 1.

One-eighth-inch-thick (3.2 mm) clear castings were poured between glass plates, gelled and cured at ambient temperatures using 1% by weight Akzo® Chemie Trigonox 21-OP-50 catalyst. Four days later they were post-cured in a programmable oven. The post-cure heating cycle was ramped from 77°F (25°C) to 250°F (121°C) over five hours and then held at 250°F (121°C) for two additional hours.

The castings' static physical properties were measured (ASTM D790 flexural modulus, ASTM D638 tensile strength) on an Instron Model 4505 tester.

Thermal capability (ASTM D638) was evaluated using a Tinius Olsen heat distortion deflection/temperature profile

Wear resistance was measured by a Teledyne Tabor 503 Standard Abrasion Tester (weight loss with a 1,000 gram load and CS-17 wheel).

Gel coat impact resistance was run on a Dynotup 8200 Drop Weight Impact Tester (ASTM D3763 impact).

Six generic types of back-up resins were also evaluated as clear resin castings. The results are in Table 2. The thermal expansion and contraction coefficients of the tooling materials are compiled in Table 3. Glass reinforced fatigue (ASTM D671) was determined for several of the back-up resins in Table 4.

## RESULTS

The standard mechanical characteristics of the tooling gel coats and tooling resins are contained in Tables 1 and 2 respectively. We investigated three generic, polyester-based resins to use in tooling gel coats and considered a wide variety of laminating resins for the back-up matrix.

Vinyl ester resins help the mold resist deterioration due to impact and abrasion during normal use. The vinyl ester gel coat casting physical data contained in Table 1 shows exceptional tensile strength/modulus/elongation and high heat distortion temperature compared to conventional tooling gel coats.

The data in Table 2 illustrates the inherent strength capabilities of vinyl esters.

The properties that should provide the best composite mold are high heat capability and resilience. CoREZYN VE8151 resin and CoREZYN B-168VE-TUA vinyl ester gel coat have these properties. The vinyl ester gel coats are recommended for tooling applications. Tools should not be stored or used outside due to poor UV stability of the gel coat.

The ability of laminates constructed with CoREZYN VE8151 resins to achieve and retain a low profile surface while being thermally cycled has been previously established. Test panels were cycled every 24 hours to mimic the heat cycling that molds are subjected to during use.

The initial step of the cycle consisted of exposing the panels to heat lights for 12 hours. This raised the panel's surface temperature to 160°F (70°C) in less than one hour. The temperature was maintained for the remainder of 12-hour period. The lights were turned off for the final 12 hours of the cycle and the panels were cooled to 75°F (24°C). The panels had a cumulative heat exposure of 100 hours.

The panel constructed with a 60-mil-thick (1.5 mm) skin coat of VE8151 and and COR63-AA-017 laminating resin, and the panel made with 100% VE8151 distorted less than the DCPD panels after the cycling.

The heat distortion temperatures of the tooling vinyl ester resin and gel coat are higher than the tooling resins. Figure 1 shows the deflection plotted against temperature for vinyl esters versus orthophthalic and isophthalic resins run according to ASTM D648. The high crosslink density tooling vinyl ester starts to deflect at approximately 230°F (110°C). This is 50°F (10°C) below the heat distortion temperature of the resin. The polyesters started distorting at temperatures significantly below the 230°F (110°C) point. The data

illustrates the superior dimensional stability of vinyl ester resin while being thermal stressed further proving that molds constructed of vinyl esters can be used in higher temperature applications than conventional polyester resins.

Vinyl ester resins expand the end uses of molds. Molds made with vinyl ester can be used in resin transfer molding (RTM), resin injection molding (RIM) and vacuum form molding (VFM) where epoxy molds have previously dominated. These vinyl ester resins have several advantages over the epoxies typically used in the production of molds. Typical polyester spray-up and hand lay-up equipment and techniques can be used to make molds with these vinyl ester resins. They are lower in viscosity relative to typical epoxies and are significantly easier to handle because they are thixotropic.

The mold can be made and cured at room temperatures and if made properly, it will not need the post-cure that epoxies require to reach their ultimate properties unless they are going to be exposed to temperature within 50°F/28°C of the heat distortion temperature. The gel and cure are initiated by adding small amounts of peroxides, not the large amounts of curing agent, like amine and anhydrides, typically used for epoxies. Overall, the handling characteristics and workability of vinyl esters are better than the standard epoxy systems.

The corrosion resistance of vinyl esters has been documented to be superior to isophthalic polyesters. The corrosion resistance of the base resin used for this family of tooling resins was tested according to ASTM C581. The ability of this type of resin to resist 100% styrene and 78% hydrogen peroxide at ambient conditions are shown in Figures 4 and 5. These chemicals were chosen because they simulate different environments experienced by the gel coat and they affect hardness and weight changes in the laminate that would influence the performance of the mold surface. The appearance of the parts made from the mold as well as the performance of the mold would be adversely affected as the gel coat softens and swells due to the absorption and attack of these chemicals.

The exposure to styrene simulates the period after the resin or gel coat is applied to the mold surface until it is sufficiently cured to a very low residual styrene level.

Hydrogen peroxide exposure is representative of MEKP dripping from the spray gun onto the mold during the production of the part. Actual exposures would be more rigorous than those experienced in the ambient tests due to the elevated temperatures caused by the exothermic reaction of the laminate. However, the exposure time would be much less and the concentration of chemicals would be lower in

actual use compared to the test conditions.

Figures 4 and 5 are a graphic display of the six-month corrosion data generated on this high heat distortion vinyl ester resin. The hardness was measured by a Barber-Colman GYZJ 934-1 Barcol Impressor gauge. The hardness in the styrene exposure decreased from 45 to 30 in seven weeks and then it leveled off. The weight increased over a six month period by 1.1%. The hardness after the hydrogen peroxide exposure was 25 after seven weeks and 17 after six months at which time the weight gain was 1.4%. As a point of reference, the hardness of a corrosion resistant isophthalic polyester typically decreases to ten or less with a weight gain of 7 to 30% in the same timeframe.

The ability of this vinyl ester to stand up to harsh conditions allows us to conclude that molds made with vinyl ester tooling gel coats will be less susceptible than isophthalic gel coats to attack by these chemicals. The superior corrosion resistance creates a more durable mold surface than those manufactured with standard tooling gel coats made with isophthalic and orthophthalic unsaturated polyester resins.

Molds are thermally and physically cycled due to the exothermic reaction of the resins in the FRP composites. The heating and cooling of the composite cause it to expand and contract. Thermal cycling of the mold creates stresses in the laminate. The stresses are caused by differential expansion and contraction of the resin and reinforcement. The coefficients of thermal expansion and contraction for various resins and reinforcements are compiled in Table 3.

These stresses can cause the bond between the fiberglass reinforcement and the cured resin to break. These delaminated areas will reduce the strength and rigidity of the composites. Vinyl ester resins are able to absorb these stresses better than their polyester counterparts. Illustrations of their ability to absorb mechanical stress are the flexural and tensile curves shown in Figures 2 and 3. The areas under the curves are related to the amount of energy the samples can absorb before breaking and the vinyl ester resins have significantly more area.

The resiliency of CoREZYN VE8150 series resins is a property that should also be advantageous when incorporated into FRP molds. Laminates made with this family of thixotropic vinyl ester resins produce a composite superior to those built with the standard tooling unsaturated polyester resins.

Thermal expansion and contraction are only one type of stress FRP composites are subjected to in their lifetime. The mold is also stressed when it is transported to the production facility, moved around the production areas, and as parts are demolded, just to name a few. The resulting strain causes cracks or fatigue in the

laminate. The fatigue resistance of vinyl ester, isophthalic, orthophthalic, DCPD and blends of these resins in Table 4 show the vinyl esters to be far superior. The accumulated fatigue can cause and propagate cracks in the laminate behind the gel coat. The cracks then are translated into the gel coat layer. Vinyl ester resins are superior to other high heat distortion polyesters such as isophthalic or DCPD resins in flexural fatigue resistance.

Many boat manufacturers have built boat molds with isophthalic polyester tooling gel coat reinforced and the structural composite containing CoREZYN VE8151. These molds were compared to similar molds made with the same type of gel coat but an isophthalic tooling resin was used in the structural composite. After 15 months in service, the mold with the vinyl ester has already required less repair.

An acrylic spa manufacturer, constructed two test molds with vinyl ester tooling gel coat and vinyl ester tooling resin. Their standard molds have severe cracking after 1,000 parts are pulled. The typical number of parts pulled from these molds during their lifespan is only 1,000 to 2,000 parts. The vinyl ester molds had over 2,000 parts pulled without any cracking and have already decreased repairs and extended the useful life of these molds compared to the polyester molds they currently use. They looked as good as new.

The prices listed in Table 5 show that the vinyl ester resins are more expensive than isophthalics. This will slightly increase the initial cost of the mold, however the savings in repairs of vinyl ester molds should offset this.

Table 6 contains a breakdown on the costs involved in making a tank mold 8 ft (2.44 m) in diameter by 12 ft (3.7 m) tall 402 ft<sup>2</sup> (37m<sup>2</sup>) of surface area, as well as a whirlpool mold with 125 ft<sup>2</sup> (12 m<sup>2</sup>) of surface area. The cost of making the tank mold out of vinyl ester gel coat and vinyl ester laminating resin increases the cost by approximately 9% over a similar construction using isophthalic tooling resins. The whirlpool mold cost increased by approximately 10%.

Figure 6 shows a percentage breakdown of the overall costs related to the manufacturing of these vinyl ester molds. The raw material cost for the production of molds are not insignificant but the labor costs are a much higher percentage of the final cost. The figure also illustrates the fact that the smaller the mold the higher percent of the cost is labor. A reduction in overall costs should be realized in less maintenance and longer service life.

## CONCLUSION

The high heat distortion vinyl ester tooling resin and gel coat have chemical resistance combined with toughness and superior thermal stability. These characteristics translate into fewer repairs and a longer mold life. The vinyl ester tooling gel coat and/or vinyl ester tooling laminating resin provide the designer with the means to improve mold performance, economy, and part making productivity. The high heat distortion temperature of the vinyl ester laminating resin and vinyl ester tooling gel coat opens up new markets to unsaturated resins like vacuum form molding, thermoform molding, resin injection molding, and resin transfer molding applications that were typically dominated by molds made from epoxies.

## REFERENCE

This work is based on the original technical paper "High Heat Distortion Vinyl Ester Resins in Fiberglass Reinforced Plastic Tooling and Mold Manufacturing Applications," published in 1990 by Interplastic Corporation for the 45th Annual SPI Conference and Expo. It is available from the American Composites Manufacturing Association (ACMA).

# DATA

**Table 1: Tooling Gel Coat Liquid/Mechanical/Performance Characteristics**

<b>Gel Coat Description:</b>	High Heat Distortion Vinyl Ester	Isophthalic	Orthophthalic
<b>Product Number:</b>	B-168VE-T	Commercially Available	B-816-T
<b>Liquid Properties:</b>			
Color	Black	Orange	Black
Viscosity, cps	13,500	18,000	14,000
Weight per gallon, lb	8.8	9.2	9.1
Specific Gravity <sup>1</sup>	1.06	1.11	1.11
<b>Cured Physical Properties<sup>2</sup>: 1/8 in. (3.2 mm) Casting</b>			
Flexural Strength, psi/MPa (ASTM D790)	14,200/97.9	18,400/127	9,100/62.8
Flexural Modulus, psi/MPa	514,000/3,550	516,000/3,560	600,000/4,140
Tensile Strength, psi/MPa (ASTM D638)	8,600/59.2	6,200/42.8	4,000/27.6
Tensile Modulus, psi/MPa	525,000/3,620	539,000/3,720	589,000/4,060
Percent Elongation	2.1	1.3	0.7
Heat Distortion, °F/°C (ASTM D648)	249/121	209/98	214/101
Barcol Hardness, 934-1 (ASTM D2583)	42	50	50
Specific Gravity (ASTM D792)	1.136	1.232	1.214
Apparent Density <sup>3</sup> , (lb/ft <sup>3</sup> )	70.7	76.7	75.6
<b>Performance Testing:</b>			
Corrosion Resistance	Excellent	Good	Poor
Impact Resistance, ft/lb (ASTM D3763)	1.43	0.99	0.69
Impact Resistance, joules (ASTM D3763)	1.85	1.28	0.89
Abrasion Resistance (gm loss @ 2000 cycles)	0.12	0.58	0.20

1. As compared to H<sub>2</sub>O @ 77°F, 8.31 lb/gal (25°C, 0.997 kg/l).
2. Gel coats were catalyzed with 1% Trigonox® 21-OP-50 and post-cured.
3. As compared to H<sub>2</sub>O @ 77°F, 62.24 lb/ft<sup>3</sup> (25°C, 997 kg/m<sup>3</sup>).

# DATA

**Table 2: Back-up Laminating Resin Liquid/Mechanical Characteristics**

<b>CoREZYN Product:</b>	COR63-AA-017	COR61-AA-164	COR75-AQ-001	MVR8021	VE8121	VE8153
<b>Generic Formula Type:</b>	All-PG* Orthophthalic	All-MA** DCPD	All-PG Isophthalic	Isophthalic/ VE Blend	Bisphenol-A Epoxy	High Heat Distortion
<b>Typical Application:</b>	General Purpose	Low Profile	Polyester Laminating	Modified Vinyl Ester	Thixotropic Vinyl Ester	Thixotropic Vinyl Ester
<b>Liquid Properties:</b>						
Viscosity, cps	436	500	400	650	450	460
Thixotropic Index	3.21	2.20	2.38	2.80	2.67	2.72
Percent Non-Volatile	52	58	56	53	52	57
Weight per gallon, lb	8.99	9.02	9.00	8.94	8.60	8.95
Specific Gravity <sup>1</sup>	1.082	1.086	1.083	1.076	1.035	1.077
<b>Cured Physical Properties<sup>2</sup>: 1/8 in. (3.2 mm) Casting</b>						
Flexural Strength, psi/MPa (ASTM D790)	16,300/112	8,400/57.9	18,500/128	18,000/124	19,000/131	16,600/114
Flexural Modulus, (psi/MPa)	545,000/3,760	427,000/2,940	518,000/3,570	460,000/3,170	470,000/3,240	467,000/3,220
Tensile Strength, psi/MPa (ASTM D638)	8,600/59.3	4,300/29.7	10,300/71.0	9,400/64.8	11,800/81.4	12,600/86.9
Tensile Modulus, psi/MPa	532,000/3,689	536,000/3,880	565,000/3,900	500,000/3,450	500,000/3,450	429,000/2,960
Percent Elongation	1.5	0.8	2.0	4.5	4.5	4.2
Heat Distortion, °F/ °C (ASTM D648)	163/73	221/105	189/87	210/99	210/99	284/140
Barcol Hardness, 934-1 (ASTM D2583)	39	47	46	35	35	43
Apparent Density <sup>3</sup> , (lb/ft <sup>3</sup> )	74.4	72.2	74.0	72.2	69.7	73.9
Specific Gravity (ASTM D792)	1.195	1.160	1.189	1.160	1.120	1.188
Percent Volumetric Shrink <sup>4</sup>	9.5	6.4	8.9	7.2	7.6	9.4

\* PG: Propylene Glycol

\*\* MA: Maleic Anhydride

1. As compared to H<sub>2</sub>O @ 77°F, 8.31 lb/gal (25°C, 0.997 kg/liter).

2. Resins were catalyzed with 1% MEKP and post-cured.

3. As compared to H<sub>2</sub>O @ 77°F, 62.24 lb/ft<sup>3</sup> (25°C, 997 kg/m<sup>3</sup>).

4. Percent Shrink = [(SG<sub>S</sub> - SG<sub>I</sub>) / SG<sub>I</sub>] x 100.

# DATA

**Table 3: Coefficient of Thermal Contraction of Tooling Materials**

Mold Building Material Type:	Contraction Coefficient		Temperature T (range in °F/°C)
	K (%/°F x 10 <sup>-5</sup> )	K (%/°C x 10 <sup>-5</sup> )	
<b>Literature Values:</b>			
96% Silica Glass	0.044 / 0.080		77 - 572 / 25 - 300
Rigid Styrene Polyester	3.90 - 5.60 / 7.09 - 10.2		77 - 300 / 25 - 149
Glass Fiber Polyester Laminate	1.20 - 4.00 / 2.18 - 7.27		-----
<b>Back-up Resin Casting:</b>			
Low Reactivity Orthophthalic	8.50/15.5		70 - 300 / 21 - 149
Medium Reactivity Orthophthalic	8.50/15.5		70 - 300 / 21 - 149
Medium Reactivity Isophthalic	5.30/9.64		77 - 250 / 25 - 121
Standard Vinyl Ester	5.60/10.2		70 - 300 / 21 - 149
High Heat Distortion Vinyl Ester	4.30/7.82		77 - 250 / 25 - 121
High Reactivity DCPD	6.30/11.5		70 - 300 / 21 - 149
<b>Reinforced Composites:</b>			
Isophthalic 35% Glass Laminate	1.30		-----
Orthophthalic 35% Glass Laminate	1.30		-----
<b>Gel Coat Castings:</b>			
Isophthalic	3.50/6.36		77 - 250 / 25 - 121
High Heat Distortion Vinyl Ester	3.30/6.00		77 - 250 / 25 - 121

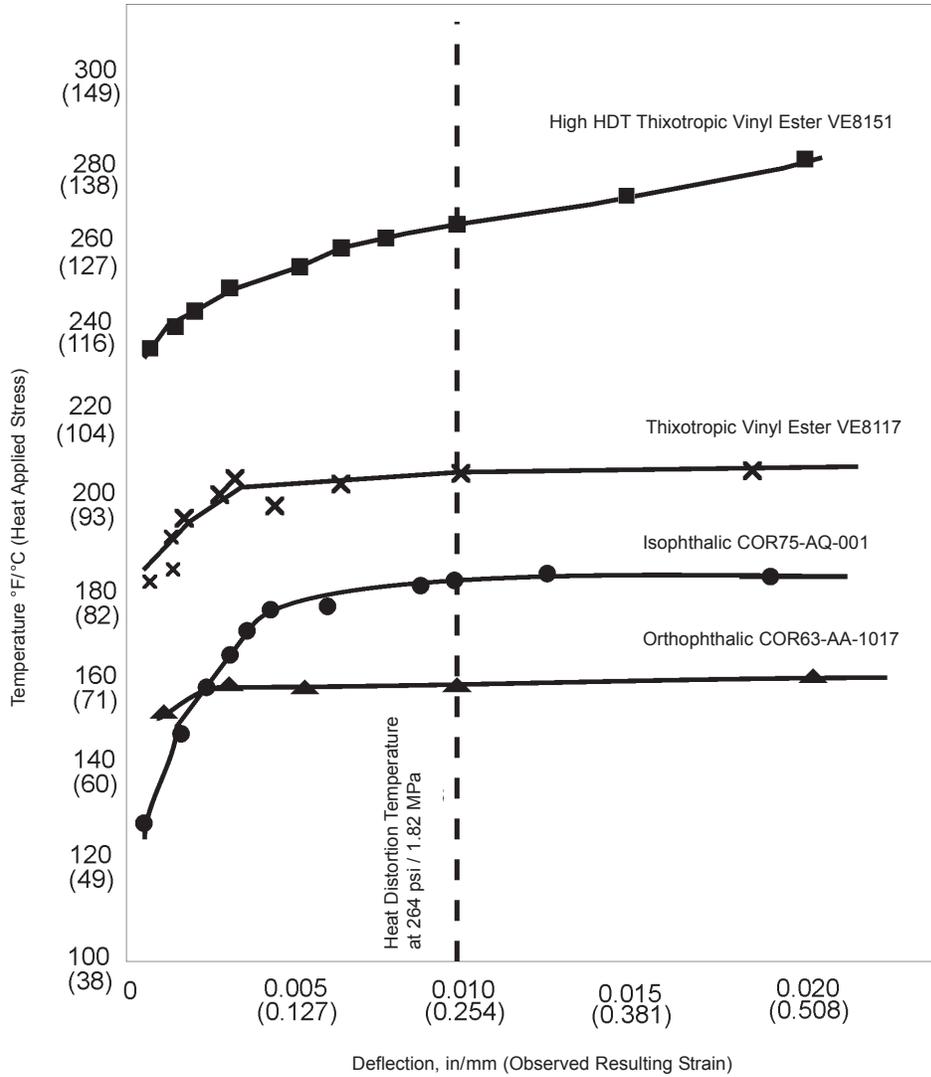
**Table 4: Influence of Resin Type on Composite Flexural Fatigue (ASTM D671)**

Resins in Laminate	Strength, psi/MPa for 1 Cycle	Cycles at 8,500 psi/ 58.6 MPa	Cycles at 10,000 psi/ 70.0 MPa	Cycles at 11,500 psi/ 79.3 MPa	Cycles at 13,000 psi/ 89.7 MPa
Orthophthalic	14,436/99.56	2,517,450	60,738	1,465	35
Isophthalic	16,117/111.2	1,744,815	103,939	6,083	358
DCPD Blend	17,579/121.2	230,973	30,022	3,902	507
DCPD	22,571/155.7	71,351	21,677	6,586	2,001
Iso Modified VE	14,252/98.29	322,410	11,800	432	16
Standard Vinyl Ester	21,218/146.3	5,448,341	874,487	140,360	22,528
Thixotropic Vinyl Ester	22,390/154.4	4,934,871	934,257	934,257	176,871

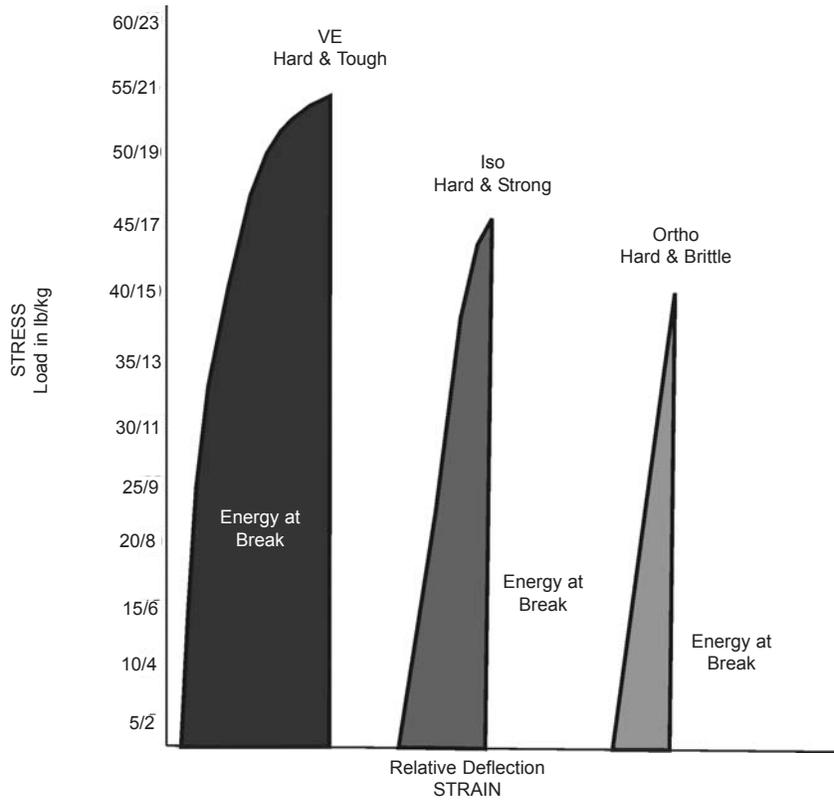
The laminate construction was alternating layers of 3/4-ounce mat (230 gram/meter<sup>2</sup>) with 24-ounce (0.814 g/m<sup>2</sup>) woven roving, beginning and ending with the 3/4-ounce mat (230 gram/m<sup>2</sup>). The resin-to-glass ratio was 75:25. Cyclic lifetimes are computed from the curve fit equation to the data.

# DATA

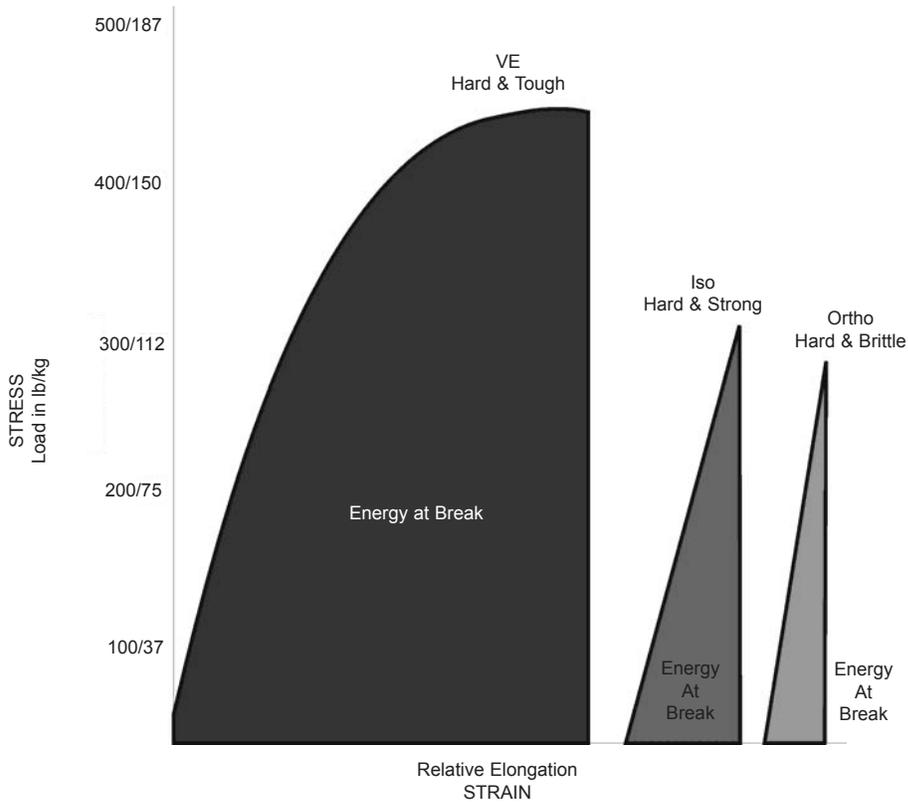
**Figure 1: Thermal Stress-Strain Deflection of Back-Up Polymers by ASTM D648**



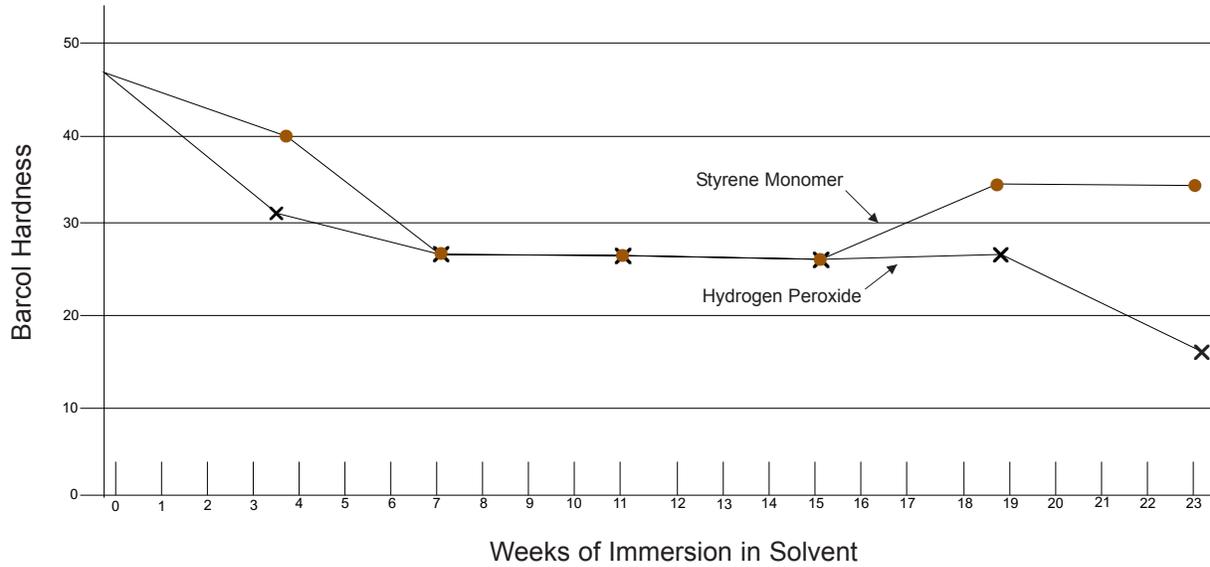
**Figure 2: Stress/Strain Curve in Flexural Test**



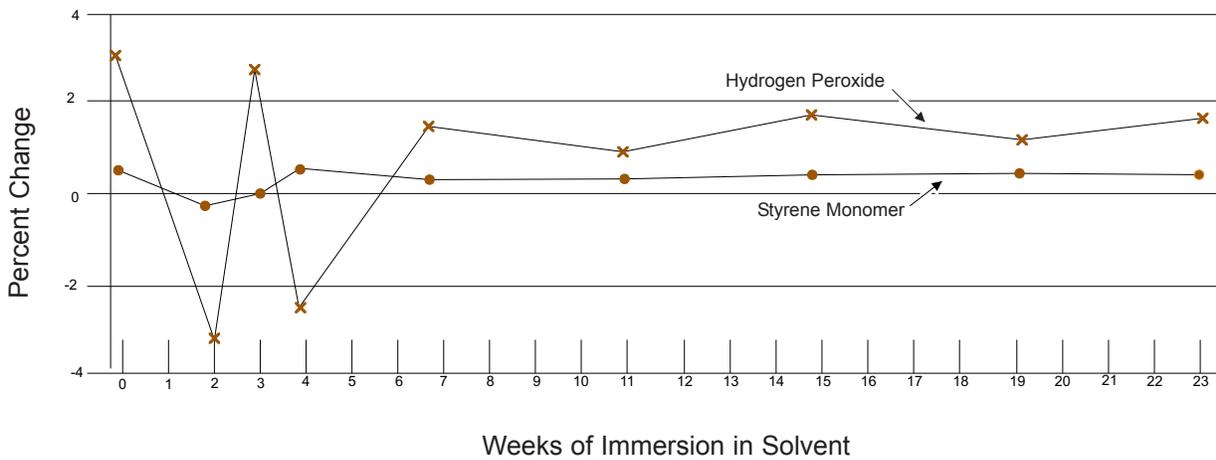
**Figure 3: Stress/Strain Curve in Tensile Test**



**Figure 4: Profile of Hardness Retention  
Tooling Vinyl Ester Base ASTM C581 Exposure**



**Figure 5: Profile of Weight Change  
Tooling Vinyl Ester Base ASTM C581 Exposure**



# DATA

**Table 5: Prices of Materials and Labor**

Vinyl ester tooling gel coat	\$ 3.25
Vinyl ester tooling laminating resin	\$ 2.45
Isophthalic tooling gel coat	\$ 3.00
Isophthalic tooling resin	\$ 1.80
Gun roving	\$ 1.00
Woven roving - 18 oz.	\$ 1.65
Labor	\$45.00

All prices are U.S. dollars as of January 2006. Materials prices are cost per pound.  
Labor is based on wages and benefits per hour.

**Table 6: Cost Comparison**

### Tank Mold

8 x 12 ft (402 ft<sup>2</sup>)

2.44 x 3.7 m (37 m<sup>2</sup>)

Materials	Quantity	Cost of Iso	Cost of VE
Gel Coat	180 lb	\$ 540.00	\$ 585.00
Resin	1350 lb	\$ 2,430.00	\$ 3,307.50
Gun Roving	500 lb	\$ 500.00	\$ 500.00
Woven Roving	670 lb	\$ 1,005.50	\$ 1,005.50
Labor	180 hours	\$ 8,100.00	\$ 8,100.00
<b>Total</b>		<b>\$12,675.50</b>	<b>\$13,498.00</b>

All prices are U.S. dollars as of January 2006.

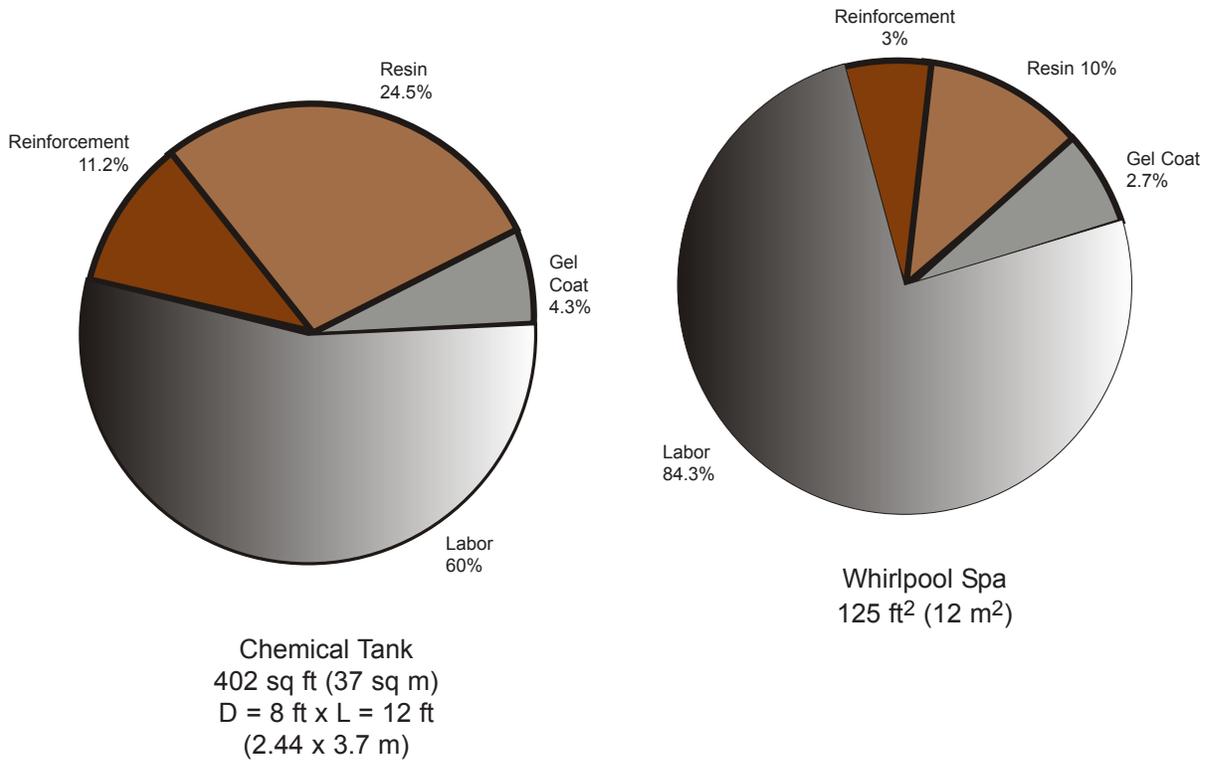
### Spa Mold

125 ft<sup>2</sup> (12 m<sup>2</sup>)

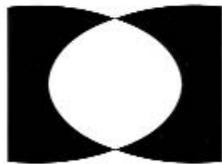
Materials	Quantity	Cost of Iso	Cost of VE
Gel Coat	28 lb	\$ 84.00	\$ 91.00
Resin	132 lb	\$ 237.60	\$ 323.40
Gun Roving	60 lb	\$ 60.00	\$ 60.00
Woven Roving	15 lb	\$ 24.75	\$ 24.75
Labor	60 hours	\$2,700.00	\$2,700.00
<b>Total</b>		<b>\$3,106.35</b>	<b>\$3,199.15</b>

All prices are U.S. dollars as of January 2006.

**Figure 6: Economics of Vinyl Ester Molds  
Cost Analysis of Tool Construction**







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