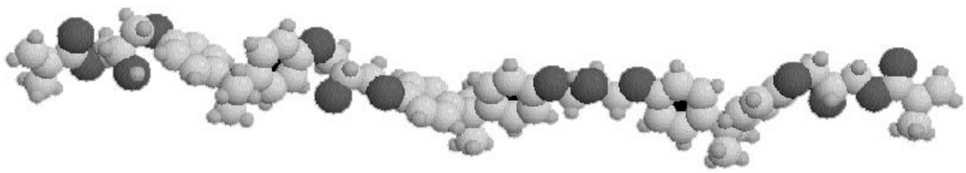
Technical Research



CoREZYN Premium Vinyl Ester Molecule

Cycle Test Evaluation of Polyester Resins and a Mathematical Model for Projecting Flexural Fatigue Endurance

INTERPLASTIC CORPORATION
Thermoset Resins Division

Introduction

We analyzed unsaturated polyester laminating resins by chemical type, static physical properties and dynamic physical properties to learn how useful they may be to marine composites engineers. An analysis of the static physical properties of a general purpose orthophthalic, corrosion resistant isophthalic, or premium grade vinyl ester resin does not immediately reveal why a particular resin type should be chosen for marine laminate construction.

Relative economics and "over-building" tend to persuade most laminate designers to determine the relative capabilities of a series of different polymer types. A boat hull flexes millions of times over its life. Laminates that are more capable of resistance to fatigue will provide superior aging capability; they are more durable. The superior resin, due to its physical properties, may allow for reduced thickness and weight in the finished composite.

Conversely, the marine laminate that is less capable of flexural fatigue will always "age" or deteriorate faster and have to be more massive (heavier) initially to be as capable.

We demonstrate the comparative superiority of a CoREZYN® vinyl ester resin in these flexural fatigue tests to determine clearly, their suitability in boat design and building. Further, a mathematical model is shown fitting the fatigue data to a curve. The resins we tested are illustrated in Figure 1.

Comparisons of standard physical testing results (Fig. 2) reveals there are adequate strengths in each system. Graphic presentations of static testing is depicted in Figures 3a and b. This pictorial example of "toughness" (integral of area under the stress-strain curve) shows the marine laminate designer the polymer type is relevant to desired structural properties.

Industry trends toward lower weight composites that achieve design and fuel economies require us to consider cyclic testing for fatigue durability. In conjunction with the United States Testing Company, Inc., we evaluated a series of laminates in "flexural fatigue endurance limit" tests. The samples were evaluated in accordance with the procedures outlined in ASTM Test Method D671, "Constant Stress Fatigue Testing." Type A specimens were used in this evaluation (Fig. 4). Constant amplitude of force was applied to the specimen in a fixed cantilever-type testing machine and the number of cycles-to-failure was observed. We attempt to allow comparisons of fatigue resistance in similar laminates changing over the resin type.

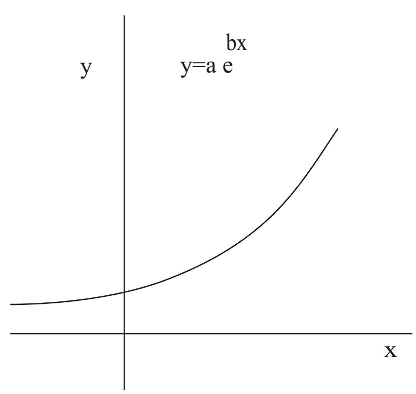
Preparation of Composites

The laminates were designed as presented in Figure 5. The orthophthalic laminating resin, CoREZYN 1097-121S; the isophthalic laminating resin, CoREZYN 9503; and the Bisphenol A-epichlorohydrin epoxy based vinyl ester, CoREZYN VE8300 are all commercially available resin systems being used in marine composites. We also compared the pre-promoted and thixotropic vinyl ester CoREZYN VE8121 to a "standard" vinyl ester - CoREZYN VE8300. The ASTM D671 was accomplished as in Figure 6 using Type A flexural test coupons and described in Fig. 4 (contrasting to flexural test coupons used in ASTM D790). The laminate construction sequence was alternating layers of 0.75-oz/ft^2 (230 g/m^2) mat with 24-oz/yd^2 (841 g/m^2) woven roving, beginning and ending with the 0.75-oz. (23 gm) mat. The resin-to-glass ration was held at 75:25.

Test Results by ASTM D671

A graphic representation of the months of continuous testing at U.S. Testing, Inc., is depicted at Figures 7a, b, and c. This summarized data is reported in U.S. Testing Report 88110-2. To be useful, this data has to be further analyzed to allow comparisons for strength at one cycle (static testing of this laminate design); and results in psi/MPa at specific numbers of cycles. We will show psi/MPa at 8,500/58.6, 10,000/69.0, 11,500/79.3 and 13,500/93.1 cycles.

The data we derived was applied in the standard formula for exponential curve fit:



$$b = \frac{\Sigma x_i \ln y - \frac{1}{n}(\Sigma x_i)(\Sigma \ln y_i)}{\Sigma x_i^2 - \frac{1}{n}(\Sigma x_i)^2}$$

$$a = \exp\left[\frac{\Sigma \ln y_i}{n} - b\,\frac{\Sigma x_i}{n}\right]$$

$$r^2 = \frac{\left[\Sigma x_i \ln y_i - \frac{1}{n}\,\Sigma x_i \Sigma \ln y_i\right]^2}{\left[\Sigma x_i - \frac{(\Sigma x_i)^2}{n}\right]\ \Sigma(\ln y_i)^2 - \left[\frac{(\Sigma \ln y_i)^2}{n}\right]}$$

An obvious use of the results would be to graph the projected cycles-to-failure using the applied stress in psi/MPa as the other variable (Fig. 8). An example of this graphic representation at 8,500 psi/58.6 MPa shows the results becoming increasingly obvious and useful to the marine laminate designer. As the change is made from orthophthalic to isophthalic to vinyl ester, so increases the projected cycles-to-failure in comparison to applied stress.

A Model for Data Projection

The ASTM D671 flexural fatigue test results provide us with useful information on the relative ability of these four resins to resist the development of cracks or general mechanical deterioration due to repeated stress and strain. Rather than fit a curve by eye on semi-logarithmic graph paper, an exponential curve fit can be calculated where:

$$y = ae^{bx} \text{ ; or } x = \frac{\ln\left(\frac{y}{a}\right)}{b}$$

where:

x = psi of the applied stress level
y = number of cycles to failure
r^2 = coefficient of determination (0 is poor and 1.00 is a good fit of the data of the curve.)

Then the following could occur:

Laminate	Regression Coefficients a	b x 10^{-3}	r^2
Orthophthalic CoREZYN 1097-121S	3.68796×10^{15}	-2.4830	0.99
Isopthalic CoREZYN COR75-AQ-001	1.61084×10^{13}	-1.8868	0.96
Vinyl Ester - Standard CoREZYN VE8300	1.73179×10^{11}	-1.2196	0.91
Vinyl Ester - Thixotropic CoREZYN VE8121	6.15452×10^{10}	- 1.1096	0.96

From further calculation, we can derive the projected failure due to cyclic flexural testing:

	Orthophthalic CoREZYN 1097-121S	Isophthalic CoREZYN 9503	Vinyl Ester Standard VE8300	Vinyl Ester Thixotropic VE8119
Strength, psi/MPa 1 cycle	14,436/99.6	16,117/111	21,218/146	22,390/154
Cycles at 8,500/58.6 psi/MPa	2,517,450	1,744,815	5,448,341	4,934,871
Cycles at 10,000/69.0 psi/MPa	60,738	102,939	874,487	934,257
Cycles at 11,500/79.3 psi/MPa	1,465	6,083	140,360	176,871
Cycles at 13,000/93.1 psi/MPa	35	358	22,528	33,485

Other Possibilities for Consideration

Interplastic Corporation tests and customer laboratory data suggest a direct correlation between resin type and the percentage of water absorption; and a direct correlation between resin type and the onset of gel coat blistering at elevated temperatures.

Conclusion

Cyclic flexural testing of specific polyester resin types resulted in predictable data that oriented them by polymer description, i.e., orthophthalic was exceeded by isophthalic and both of these were exceeded by vinyl ester type resins. Little difference was observed between the standard vinyl ester and the pre-promoted, thixotropic vinyl ester.

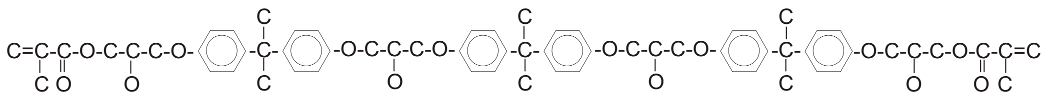
A mathematical model is useful to compare cycle test results at an exact loading. The regression analysis used was above the 95% confidence limit in three cases and above 90% confidence in the fourth. Results such as these should allow the marine engineer to design higher strength, lower weight laminates. Another advantage may be the reduction or elimination of gel coat blisters in the properly designed FRP boat hull.

Bibliography

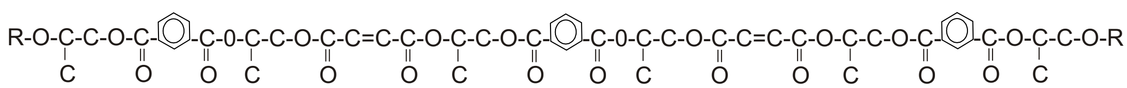
This work is based on the original technical paper of the same title, published in 1986, by P. Burrell, T. McCabe, and R. de la Rosa on behalf of Interplastic Corporation. The original document is available through the American Composites Manufacturing Association (ACMA).

Data

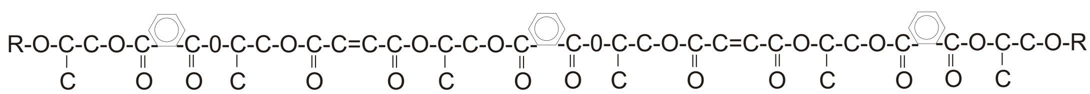
Figure 1: Polymer Structures



Vinyl Ester CoREZYN VE8300, Bisphenol-A Epichlorohydrin Epoxy Based



Isophthalic CoREZYN COR75-AQ-001 (1.1 Propylene Glycol/0.5 Isophthalic Acid/ 0.5 Maleic Anhydride)



Orthophthalic CoREZYN COR60-AA-121S (1.1 Propylene Glycol/0.5 Orthophthalic Acid/ 0.5 Maleic Anhydride)

Figure 2: 1/8-in./3.2 mm Cured Casting Physical Properties

Polymer Description	**Orthophthalic COR60-AA-1213**	**Isophthalic COR75-AQ-001**	**Standard Vinyl Ester VE8300**	**Thixotrophic Vinyl Ester VE8119**
Flexural Strength, psi/MPa ASTM D790	17,500/121	18,500/128	19,000/131	19,000/131
Flexural Modulus, psi/MPa	5.21/3,540	5.40/3,720	4.50/3,100	4.70/3,240
Tensile Strength, psi/MPa ASTM D638	9,000/62.1	9,500/65.5	11,500/79.3	11,800/81.4
Tensile Modulus, psi/MPa	5.91/4,080	5.20/3,590	5.00/3,450	4.50/3,100
Elongation, %	2.0	1.4	5.0	4.0
Heat Distortion, °F/°C ASTM D648	158/70	216/102	210/99	212/100
Barcol Hardness, 934-1 ASTM D2583	40	45	38	36
Specific Gravity ASTM D792	1.19	1.18	1.12	1.11

Figure 3a: Stress/Strain Curve in Flexural Test

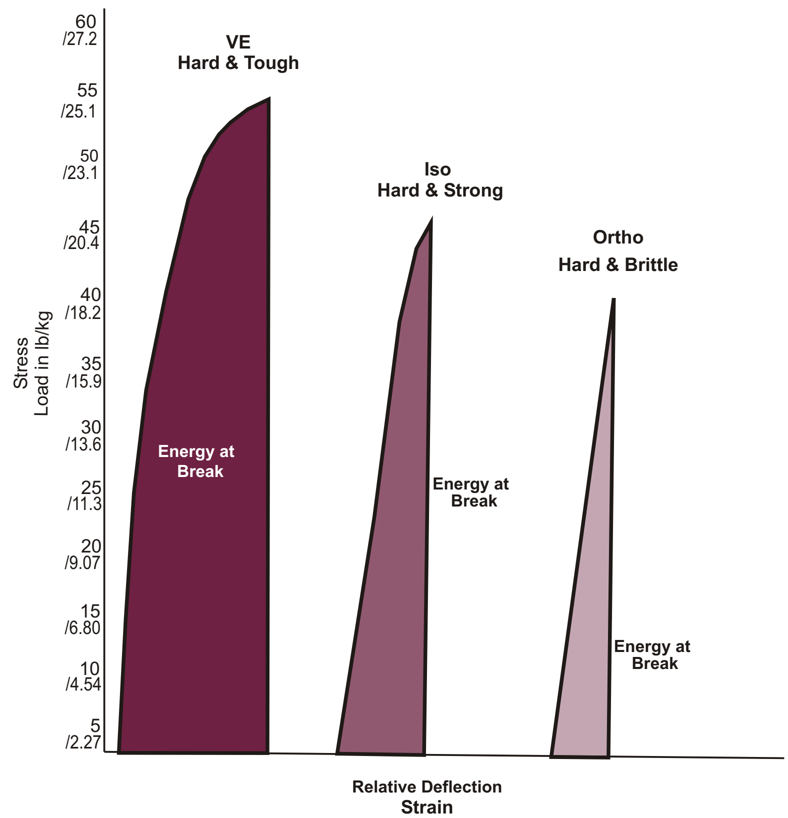


Figure 3b: Stress/Strain Curve in Tensile Test

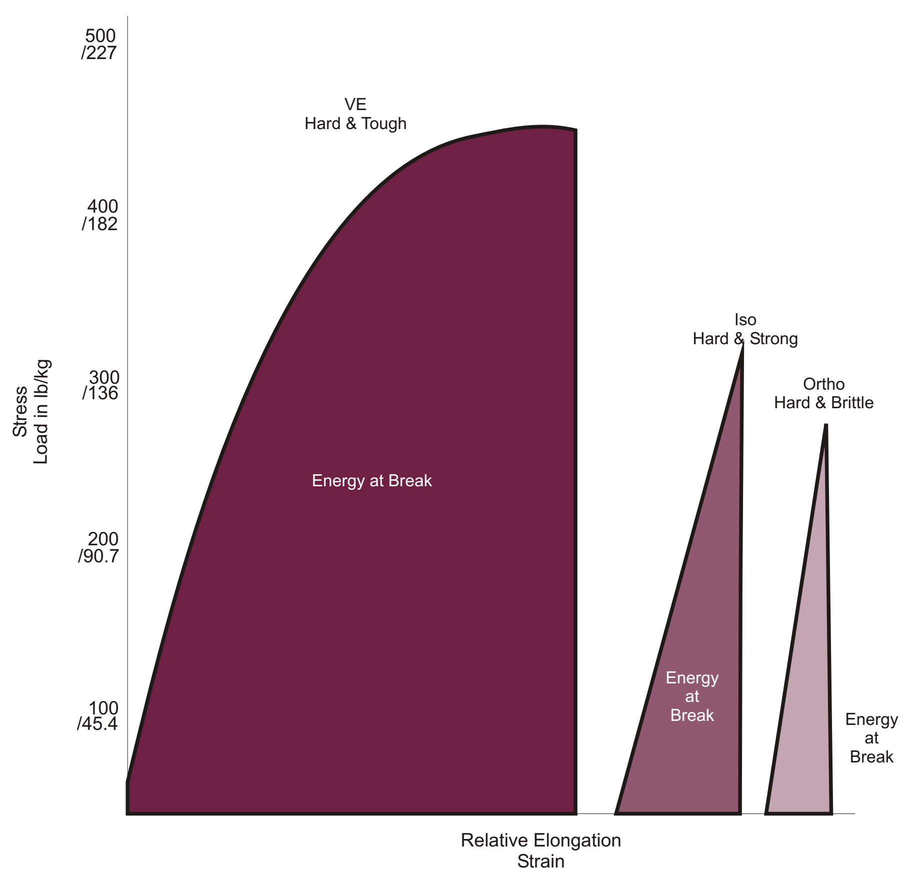
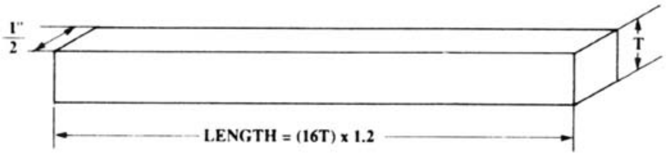
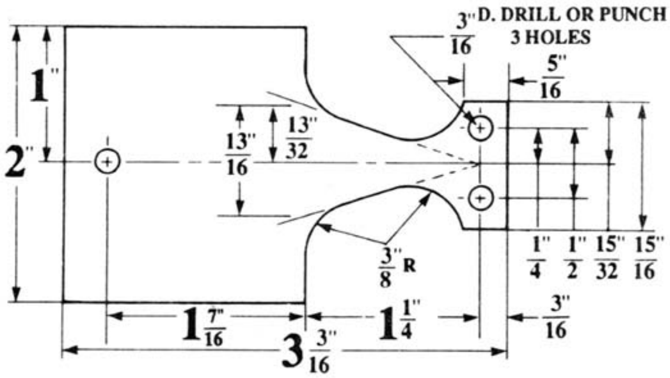


Figure 4: Specimen Dimensions



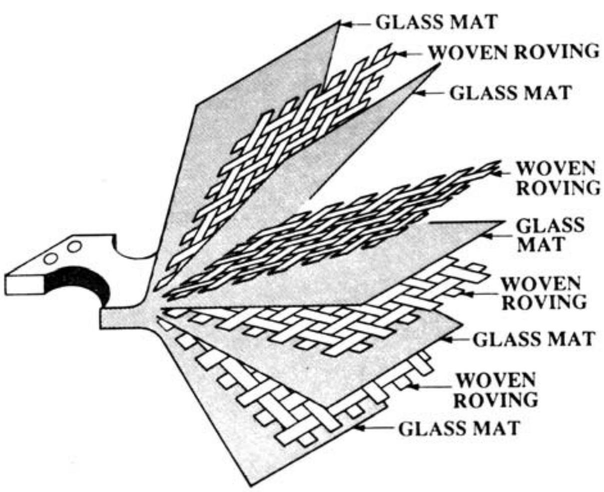
FLEXURAL TESTING ASTM D790

TYPE A



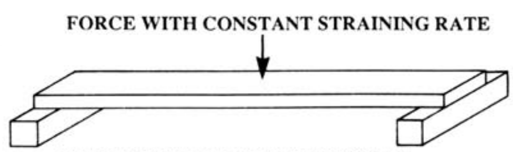
FLEXURAL FATIGUE TESTING ASTM D671

Figure 5: Flexural Fatigue Specimen Composition

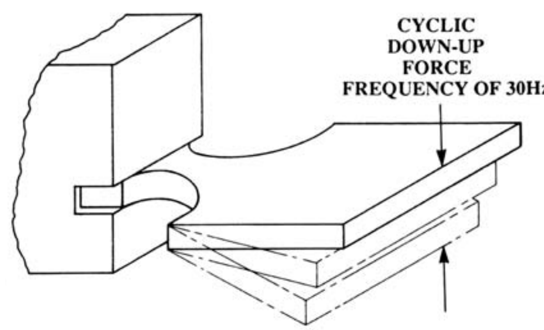


ASTM D671 TYPE A

Figure 6: ASTM Flexural Testing Types



SIMPLE BEAM FLEXURAL TESTING
ASTM D-790
(STATIC)



CONSTANT FORCE CANTILEVER TYPE
FLEXURAL FATIGUE TESTING
ASTM D671 (DYNAMIC)

Figure 7a: Curve Fit of ASTM D671 Data for Various Types of Unsaturated Polyester Resins

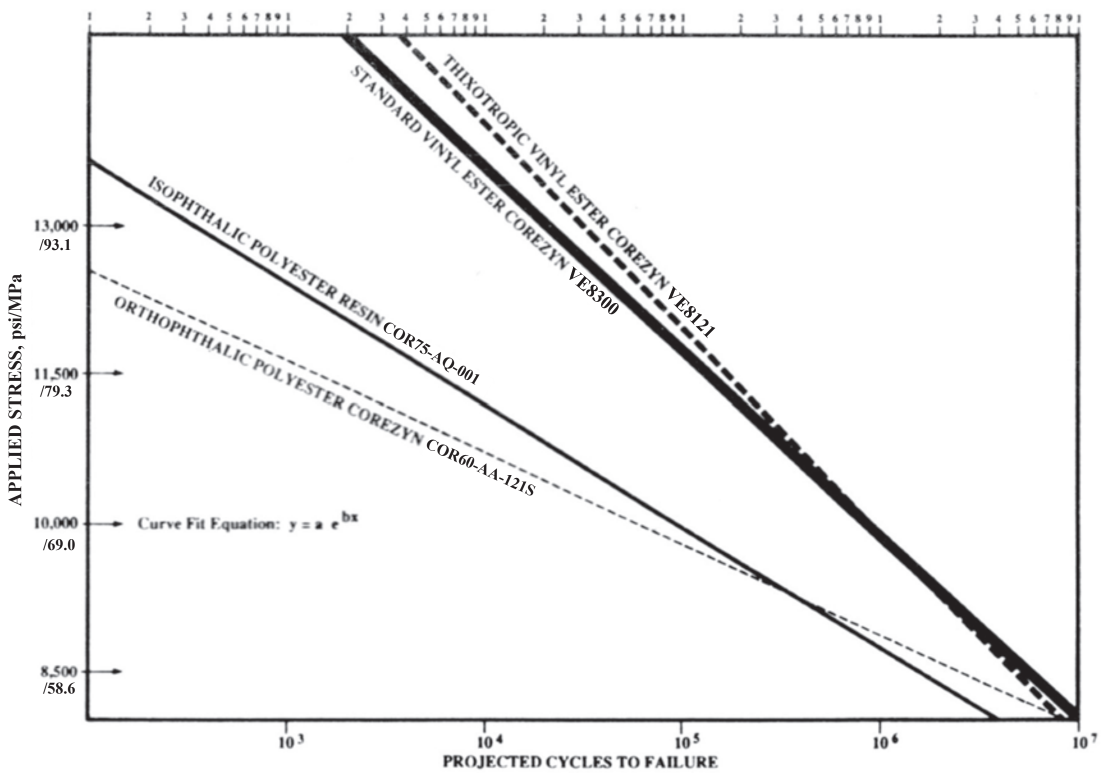


Figure 7b: ASTM D671 Flexural Fatigue Data vs. Curve Fit for Isophthalic Resin and Standard Vinyl Ester Resin

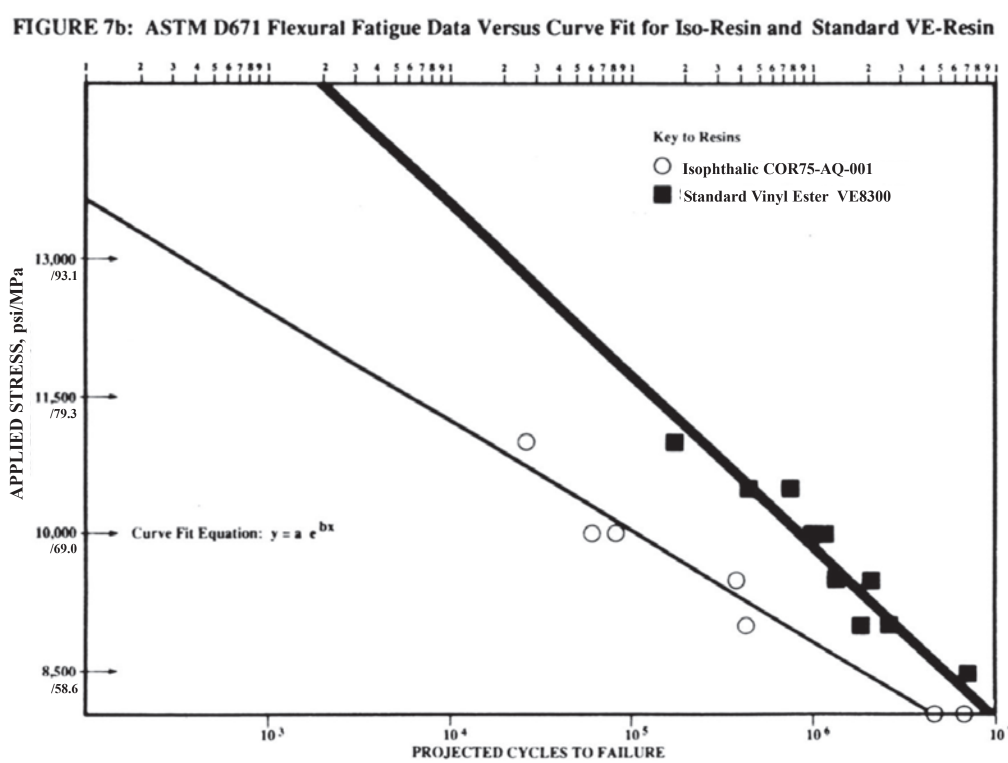


Figure 7c: ASTM D671 Flexural Data vs. Curve Fit
for Orthophthalic Resin and Thixotropic Vinyl Ester Resin

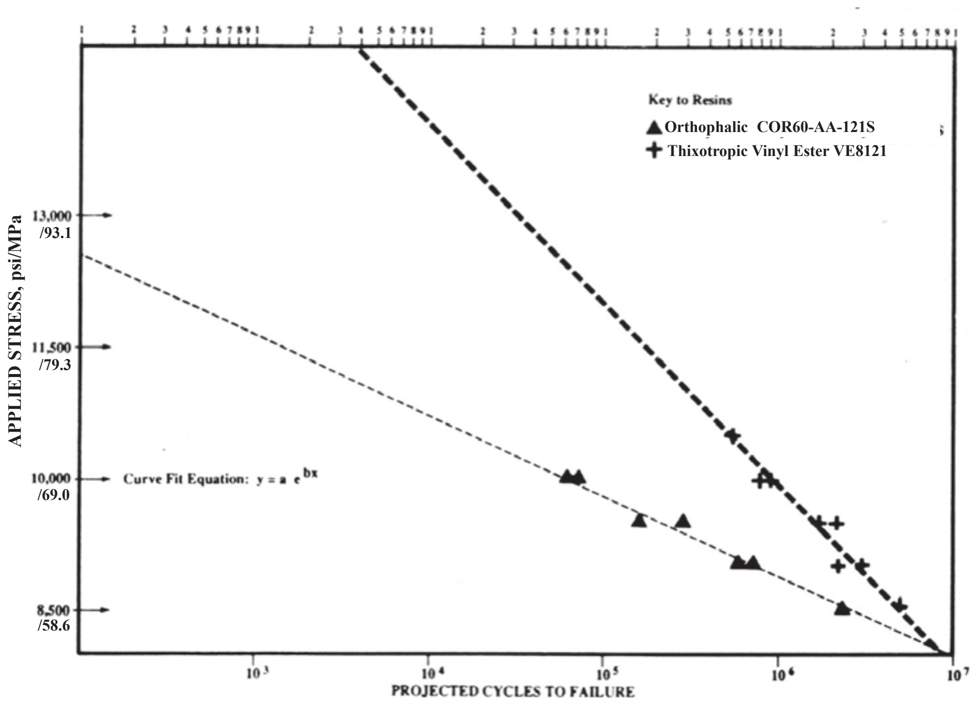
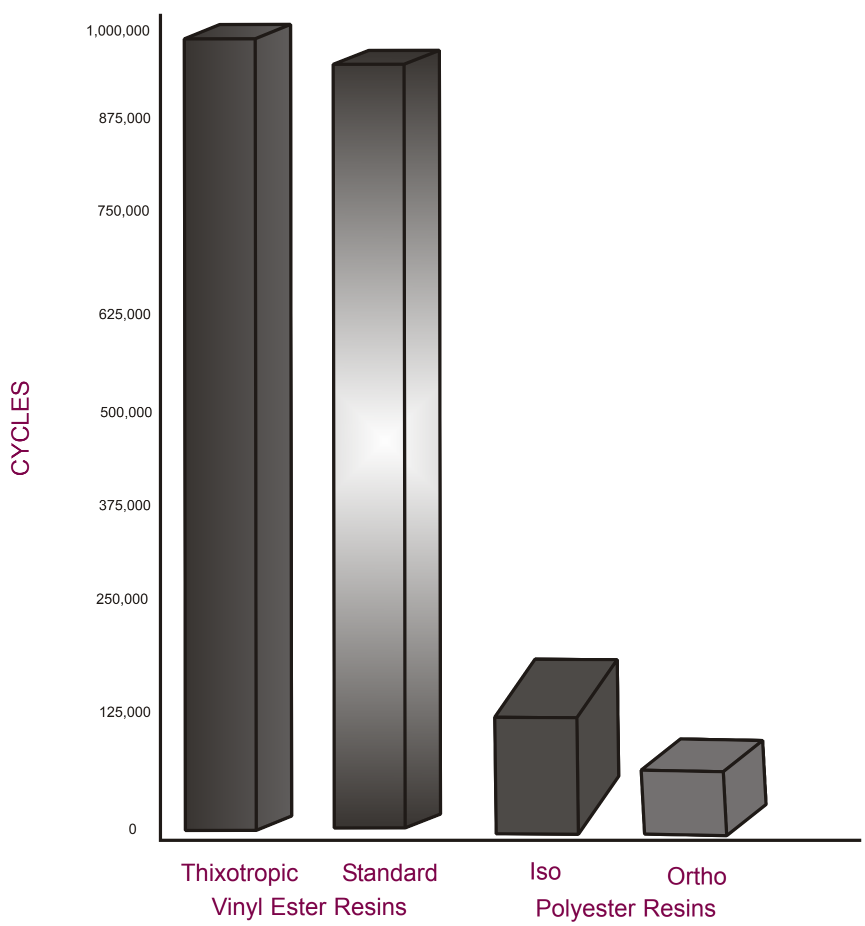


Figure 8: Resin Type vs. Relative Projected Flexural Fatigue at 10,000 psi/69.0 MPa Loading



INTERPLASTIC CORPORATION
Thermoset Resins Division

1225 Willow Lake Blvd., St. Paul MN 55110-5145 Telephone (651) 481-6860 Fax (651) 481-9836
www.interplastic.com