Technical Research

CoREZYN Premium Vinyl Ester Molecule

Physical Properties Evaluation of FRP Composites After 15-Year Immersion in Water

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ABSTRACT

Reinforced composites made from unsaturated polyester and vinyl ester resins are used in the construction of tanks, boats, swimming pools, baffles, pipes, and other reinforced composites. Many of these composites are designed on a strength safety factor of 5 to 10. Long-term studies span one to three years and are projected out 10 to 50 years. Field use of the designed composites can range from 10 to 50 years.

This paper presents data on the retention of a variety of physical properties after 10 and 15 years of constant water immersion. The panels were tested to evaluate the changes in properties on the composites during this long-term exposure and determine if the cross-linked polymers were being degraded. The discussions include the flexural strength, flexural modulus, and Izod impact strength.

INTRODUCTION

This paper is a continuation of the 2002 paper entitled "The Effective Use of Permeation Barriers in Marine Composites to Prevent Blistering". The initial paper explored the relationship between blistering in the gel coat surface and water absorption data. It also compared water absorption and the time lapse to the first formation of blisters at ambient temperature and at two elevated temperatures.

Past studies have been done over six months to two years on composites and that data was projected out 10 to 50 years. However, there has not been actual long-term data to support those projections. Tanks, pipes and other composites used in corrosive environments have been removed from service after 10 to 25 years and evaluated to show little to no degradation of the inner, resin-rich surface.

This research looks at the testing done by resin manufacturers to standards such as ASTM C581, ASTM F5813, ASTM F1743 and ASTM F1216. It creates a link between the previous one- to two-year-long studies and the long-term service being sought by the users of composites.

Exposure to aqueous environments in applications such as brine tanks, wastewater treatment plants, livestock water tanks, septic tanks, etcetera, are growing. This data could be used to project the long-term performance of composites in these and other aqueous exposures.

EXPERIMENTAL

Three resins were used in the study. The CoREZYN® CORVE8117 thixotropic vinyl ester resin, (hereafter referred to as the vinyl ester), the isophthalic resin used is a two-stage isophthalic resin designed for corrosion applications; and the orthophthalic resin is a type of polyester commonly on the marine market at the time the panels were made. Their physical properties are listed in Table 1.

GEL-COATED PANEL CONSTRUCTION

The test panels were gel-coated on both sides. A premium, neopentyl glycol-isophthalic gel coat was catalyzed with 2% of 9% active oxygen MEKP. Then it was drawn down at 20 mils (0.51 mm) thick by 8 in. (203.2 mm) wide, on two plates of glass. It was cured for two hours at ambient temperature.

Next the laminates were made with fiberglass and resin at a 1:2 ratio. Each of the resins was catalyzed with 1.5% of 9% active oxygen MEKP containing a high dimer content. Each gel-coated plate was laminated with four plies of 0.75-oz (230 g/m^2) chopped strand fiberglass mat. The panels were pressed together before they gelled, taking care to eliminate entrapped air.

SKIN-COATED LAMINATE CONSTRUCTION

The set of panels constructed with a vinyl ester skin coat had an additional step. The glass plates were first gel-coated and then cured for two hours. To construct the laminate, the vinyl ester was catalyzed with 1.75% by weight of 9% active oxygen MEKP containing a high dimer content. Then, two plies of 0.75 oz (230 g/m^2) strand fiberglass mat and the vinyl ester resin, at a 1:2 ratio, approximately 30 mils thick (0.76 mm) were put down. The vinyl ester laminate was allowed to cure until it reached a measured hardness of 5-20 using a Barber Coleman 934-1 impressor gauge.

The center reinforcing laminate was built of orthophthalic resin catalyzed with 1% of 9% active oxygen MEKP. This was followed by two plies of 0.75 oz (230 g/m^2) strand fiberglass mat and orthophthalic resin at a 1:2 ratio. It was laid up on the vinyl ester skin coat and then the two panels were pressed together before they gelled, taking care to minimize entrapped air.

FINISHING TECHNIQUES

All of these panels were allowed to cure for 16 hours at ambient temperatures. Then they were cut into 5.5 in^2 (14 cm^2) panels. Their edges were coated with a thin layer of vinyl ester to seal them and prevent the possibility of water wicking into the laminate while immersed. These edge-coated panels were allowed to cure for 16 hours and then post-cured at 250°F (121°C) for two hours.

Test Conditions

All the panels were totally immersed in a container filled with tap water. The panels were spaced to allow the water to circulate between their surfaces.

The ambient temperature immersion test was as “real world” as possible with the test temperatures ranging as high as 90°F (32°C) in the summer months, to 50°F (10°C) during the winter. The typical temperature range for a majority of the 15-year test was 65°F to 80°F (18°C to 27°C).

When the coupons were removed from the water at inspection times, they were patted dry with an absorbent cloth and allowed to adjust to room temperature. Once they reached ambient conditions, each specimen was weighed and then re-immersed in its appropriate container. After 10 and 15 years, one of the coupons from each set was removed and tested for a variety of properties such as wet physical properties, weight loss after totally drying and dry physical properties.

Results and Discussion

The long term testing reflects only three different times for each composite: an initial point, 10 years and 15 years. This is not enough data to plot and extrapolate long-term projections, but it can be analyzed to yield general trends and comparisons of the performance of the four composites.

Weight Gain

All of the panels gained weight during the immersion and the data are compiled in Table 2. The vinyl ester had a fast weight gain in the initial 150 days at which time it had comparable results with the other three composites. The rate of weight gain for the vinyl ester was slowing at that time and it was surpassed by the other three composites between 150 and 300 days. The vinyl ester panel reached a steady state between 12 and 15 months when the weight gain leveled off while the other panels continued to gain weight.

The isophthalic composite continued to gain weight but the rate of uptake slowed after 400 days compared to the orthophthalic, at which time it only showed a gain of 0.1% over the next 14 years. The orthophthalic and vinyl ester/orthophthalic composites continued to gain weight over the whole test period. The orthophthalic gained more weight than the vinyl ester/orthophthalic composite. A simple model, based on the amount of each material in the composite and the weight gain of those individual materials, reliably predicts the weight gain of the vinyl ester/orthophthalic composite. See Figure 1 for a plot of the data.

Weight Loss of Dry Panels

The panels were dried to a consistent weight in a heating cycle and then their weight loss was determined and shown in Table 3.

The vinyl ester lost < 0.10% of its weight over 15 years, the least amount of the four composite constructions and appeared to have reached equilibrium.

The other three resins had fairly consistent weight loss of 0.20% to 0.25% after 10 years.

The vinyl ester/orthophthalic composite appeared to reach an equilibriated state of 0.19% to 0.20% weight losses at 10 and 15 years respectively. This weight loss is about 2.5 times more than the amount of weight lost in the 100% vinyl ester composite.

The isophthalic and orthophthalic panels continued to lose weight with an additional 0.02% and 0.05% changes respectively between 10 and 15 years.

All this data is plotted in Figure 2.

Flexural Strength of Wet Panels

The vinyl ester had very little loss of properties after 15 years of immersion in ambient water.

The isophthalic and orthophthalic resins’ properties both dropped off similarly, appeared to continue to lose strength and lost approximately 50% of their original strength over the 15-year period.

The panel made with the vinyl ester skin coat and orthophthalic interior had little loss of properties after 15 years, similar to the retention of properties of the 100% vinyl ester panel.

The flexural strength of the wet panels data is compiled in Table 4 and graphed in Figure 3.

Flexural Strength of Dried Panels

After the panels were dried and their weight loss was recorded, they were tested to see how their physical properties changed over the 15-year period.

The vinyl ester and vinyl ester skin/orthophthalic panels showed very little loss over the 15-year period. The isophthalic and orthophthalic panels lost 25%

to 30% of their original strengths.

The data is presented in Table 5 and graphed in Figure 4.

FLEXURAL MODULUS OF WET PANELS

The orthophthalic and isophthalic panels had 10% to 20% loss after 15 years while the vinyl ester and vinyl ester/orthophthalic panels statistically had no change after 15 years.

This data is compiled in Table 6 and graphed in Figure 5.

FLEXURAL MODULUS OF DRIED PANELS

All four panels statistically had no change in modulus over the 15-year test.

This data is presented in Table 7.

IZOD IMPACT STRENGTH OF WET PANELS

The vinyl ester/orthophthalic panel had the best performance and retained 78% to 90%. The vinyl ester was the next best at 65% to 82%. The isophthalic and orthophthalic both retained 35% to 45% in 10 to 15 years.

This data is compiled in Table 8 and graphed in Figure 6.

IZOD IMPACT STRENGTH OF DRIED PANELS

The vinyl ester, vinyl ester/orthophthalic and orthophthalic panels had comparable retention of Izod impact strength at 77% to 97%. The isophthalic had the poorest performance retaining 48% to 55% in 10 to 15 years.

This data is compiled in Table 9 and graphed in Figure 7.

Overall, the vinyl ester resin was rated the best in performance in the wet and dry environments. This was expected due to the polymer’s corrosion resistance and excellent performance in the marine market for the past 17 years.

The second best performance was the vinyl ester/orthophthalic panel, followed by the isophthalic, and finally the orthophthalic panels.

The vinyl ester/orthophthalic composite performed almost as well as the 100% vinyl ester composite in the retention of properties. Viewing the composite as sandwich construction, the layer of vinyl ester/fiberglass on each of the surfaces acts as the skin of the sandwich composite and the skins give the sandwich its strength. Once the integrity of the surface is disrupted, the panel fails. The vinyl ester on the surfaces of the panels performed well and retained its properties, similar to what was seen in the performance of the 100% vinyl ester composite.

The other attribute of a sandwich composite is that the thickness in the inside portion contributes to the overall stiffness, as measured by the flexural modulus. As the composite is made thicker, the panel becomes stiffer. A simple illustration of this is a 0.25-in. (6.35 mm) thick piece of wood compared to a 1-in. (25.4 mm) thick piece. The thicker piece of wood is stiffer (harder to bend).

The isophthalic and orthophthalic composites did not have a high retention of initial flexural strength and showed a continual drop to lower than 55% over the 15-year test period. After drying, the recovery to 75% of their original properties is an indication that the polymer was not being degraded as much as the blister formation seen in the panels lead us to believe. The blisters may have been caused by a disruption at the fiberglass-resin interface.

Overall, the vinyl ester showed the best retention as a wet and a dry composite. This resin is very corrosion-resistant and does not degrade like other polymers.

Future work should include additional analysis of the composite to determine the mechanism that is causing the loss of properties.

REFERENCE

This work is based on the original technical paper entitled *Evaluation of Marine Composites' Physical Properties After 15-Year Immersion in Water,* published in 2004, by David J. Herzog and Paul P. Burrell, on behalf of Interplastic Corporation. It is available from the American Composites Manufacturing Association (ACMA).

Data

Table 1: Clear Casting Physical Properties

Property	ASTM	Units	Orthophthalic	Isophthalic	Vinyl Ester
Flexural Strength	D790	psi (MPa)	16,300 (112)	18,500 (128)	16,900 (117)
Flexural Modulus	D790	ksi (GPa)	545 (3.76)	518 (3.57)	438 (3.02)
Tensile Strength	D638	psi (MPa)	8,600 (59.3)	10,300 (71.0)	11,500 (79.3)
Tensile Modulus	D638	ksi (GPa)	632 (4.36)	565 (3.90)	446 (3.08)
Tensile Elongation	D638	%	1.5	2.0	6.0
Heat Distortion	D648	°F/°C	163 (73)	188 (87)	222 (106)
Barcol Hardness	D2565	934-1 Gauge	39	46	36
Glass Transition	*	°F/°C	145 (63)	201 (94)	232 (111)

*Tested according to Interplastic test method CRSTP 92, which is similar to ASTM E1640-99.

Figure 1: Weight Gain

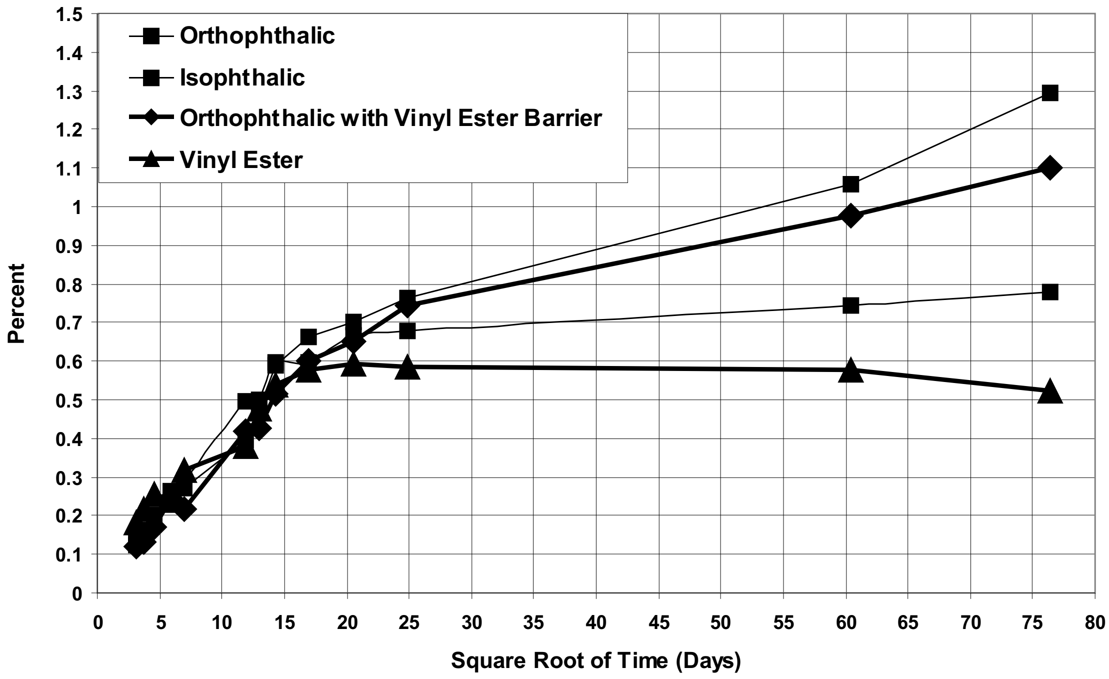

Table 2: Percent Weight Gain

DAYS	ORTHOPHTHALIC	ISOPHTHALIC	ORTHOPHTHALIC WITH VINYL ESTER BARRIER	VINYL ESTER
10	0.123	0.138	0.119	0.812
14	0.156	0.162	0.133	0.517
21	0.203	0.201	0.172	0.257
35	0.242	0.262	0.243	0.241
49	0.272	0.291	0.218	0.317
140	0.395	0.495	0.418	0.381
168	0.476	0.499	0.428	0.475
203	0.590	0.596	0.517	0.537
287	0.661	0.596	0.601	0.577
420	0.702	0.666	0.650	0.593
616	0.765	0.679	0.744	0.584
3650	1.057	0.745	0.976	0.577
5840	1.293	0.778	1.101	0.524

Figure 2: Weight Loss

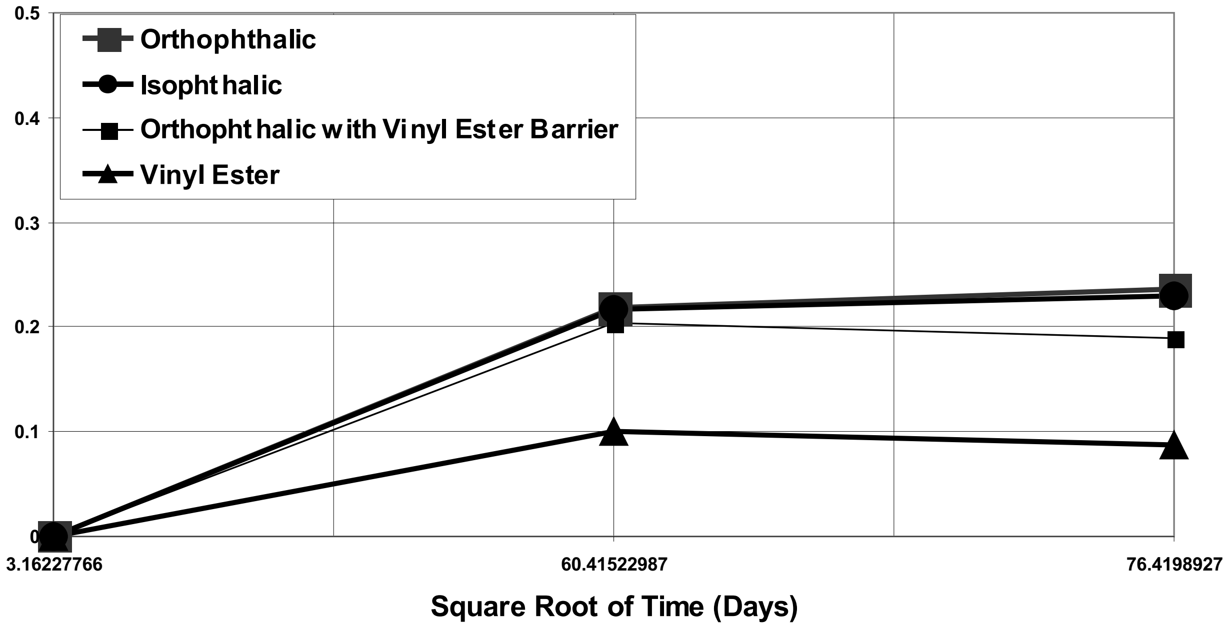

Table 3: Percent Weight Loss

Years	Orthophthalic	Isophthalic	Orthophthalic with Vinyl Ester Barrier	Vinyl Ester
10	0.219	0.217	0.204	0.100
15	0.236	0.231	0.189	0.088

Figure 3: Flexural Strength of Wet Coupons

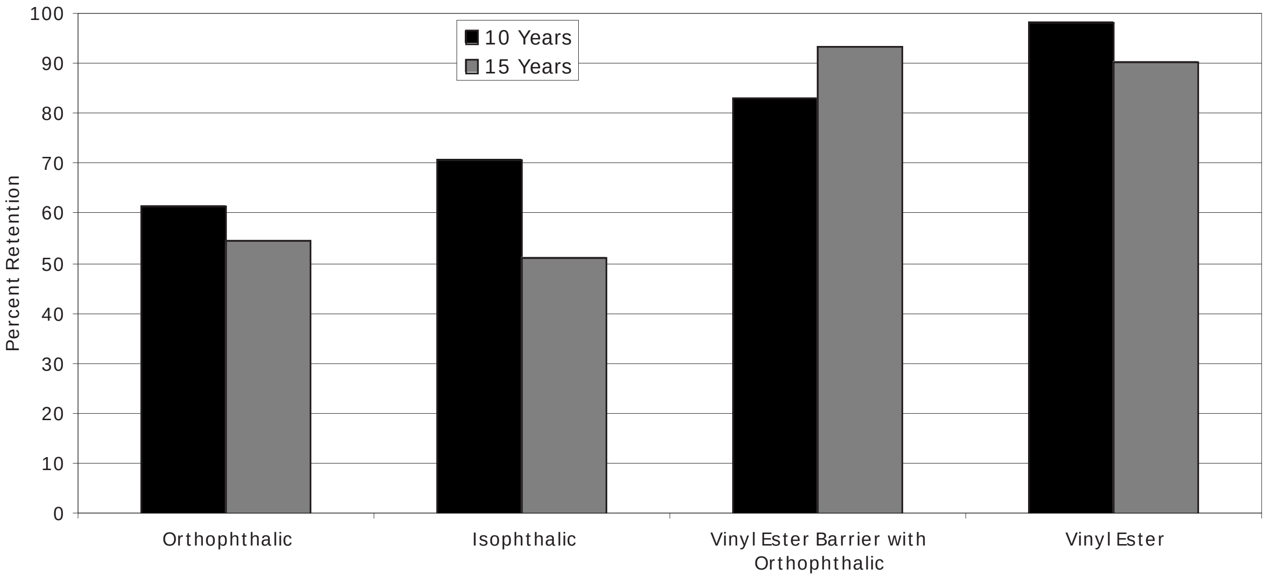

Table 4: Flexural Strength of Wet Coupons, psi (MPa)

Years	Orthophthalic	Isophthalic	Orthophthalic with Vinyl Ester Barrier	Vinyl Ester
Initial	26,000 (179)	27,500 (190)	23,400 (161)	26,900 (186)
10	18,200 (126)	19,500 (134)	19,500 (134)	26,400 (182)
15	14,800 (102)	14,100 (97.2)	21,900 (151)	24,300 (168)

Figure 4: Flexural Strength of Dry Coupons

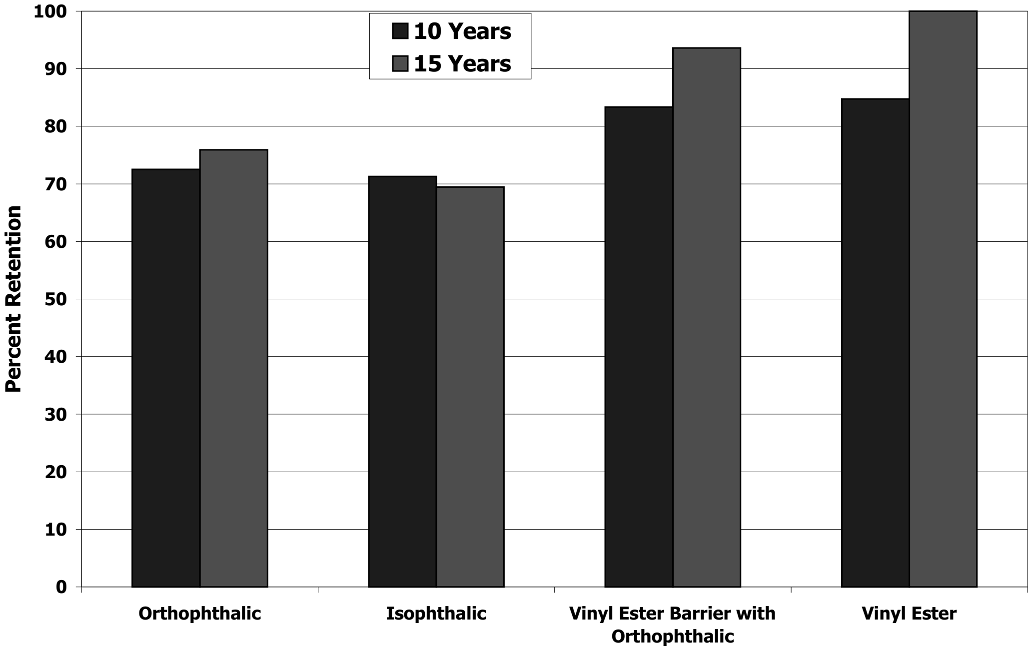

Table 5: Flexural Strength of Dried Coupons, psi (MPa)

Years	Orthophthalic	Isophthalic	Orthophthalic with Vinyl Ester Barrier	Vinyl Ester
Initial	26,000 (179)	27,500 (190)	23,400 (161)	26,900 (186)
10	23,300 (161)	19,600 (135)	19,500 (134)	22,800 (157)
15	22,300 (154)	19,100 (132)	21,900 (151)	26,900 (186)

Figure 5: Flexural Modulus of Wet Coupons

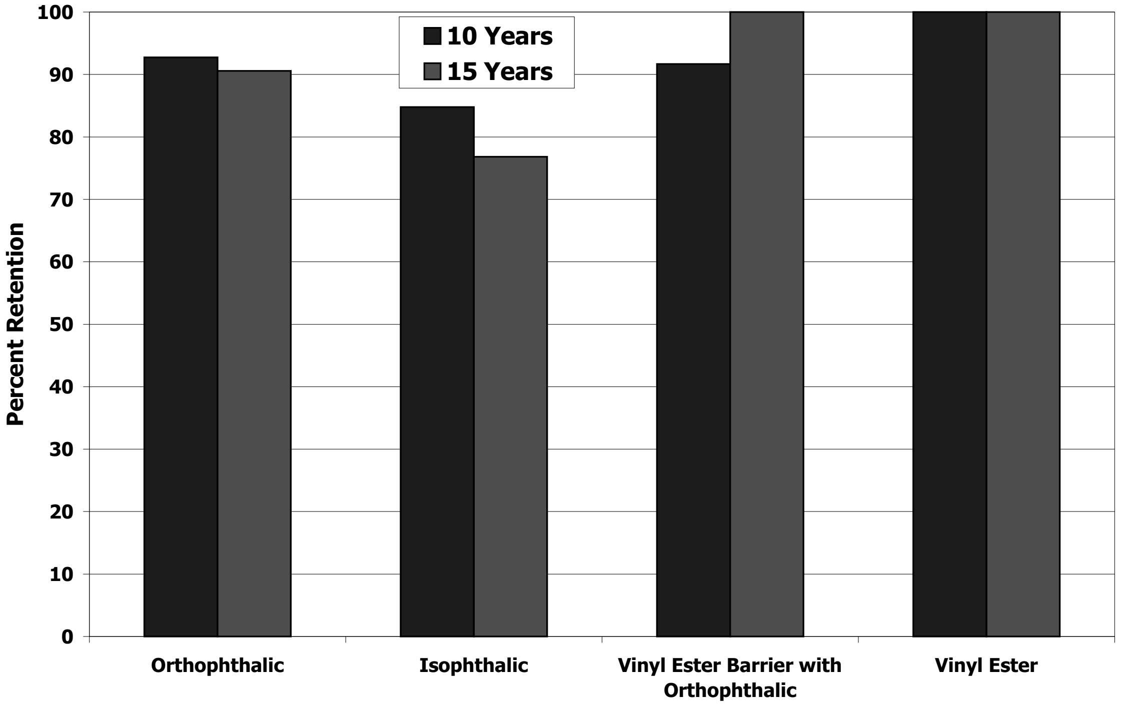

Table 6: Flexural Modulus of Wet Coupons, ksi (GPa)

Years	Orthophthalic	Isophthalic	Orthophthalic with Vinyl Ester Barrier	Vinyl Ester
Initial	1,380 (9.52)	1,320 (9.10)	1,300 (8.97)	1,260 (8.69)
10	1,190 (8.21)	1,280 (8.83)	1,210 (8.34)	1,290 (8.90)
15	1,050 (7.24)	1,160 (8.00)	1,320 (9.10)	1,410 (9.72)

Figure 6: Impact Strength of Wet Coupons

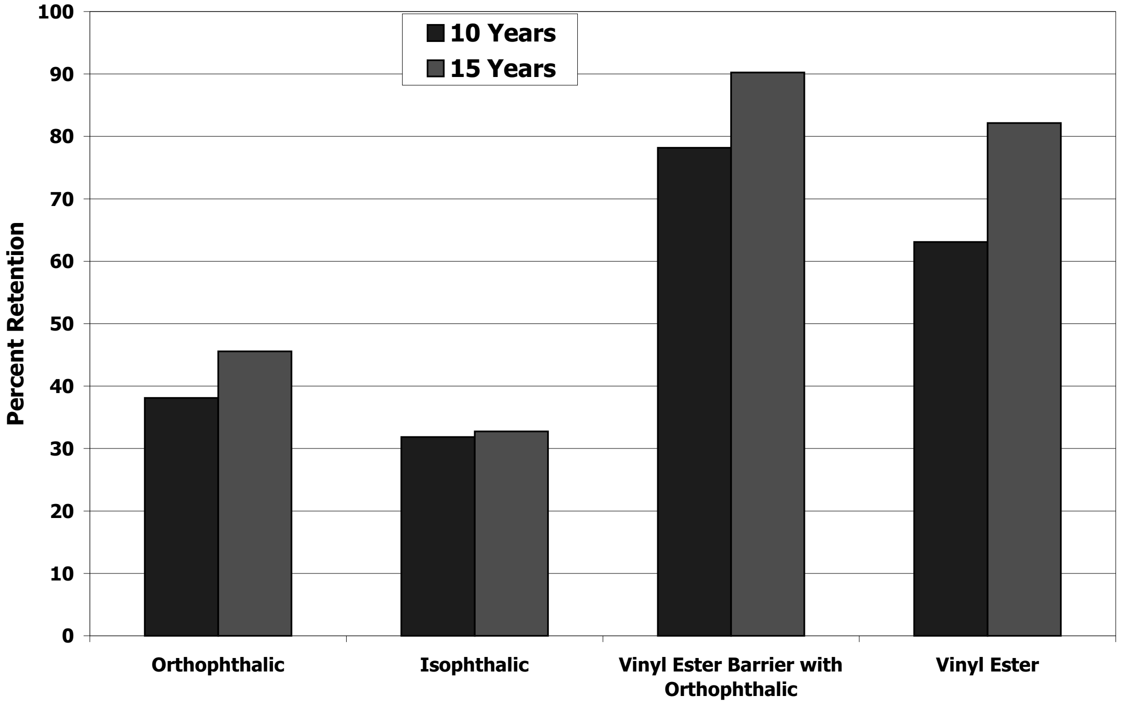

Table 7: Flexural Modulus of Dried Coupons, ksi (GPa)

Years	Orthophthalic	Isophthalic	Orthophthalic with Vinyl Ester Barrier	Vinyl Ester
Initial	1,380 (9.52)	1,320 (9.10)	1,300 (8.97)	1,260 (8.69)
10	1,290 (8.90)	1,310 (9.03)	1,210 (8.34)	1,250 (8.62)
15	1,470 (10.3)	1,310 (9.03)	1,320 (9.10)	1,290 (8.90)

Figure 7: Impact Strength of Dry Coupons

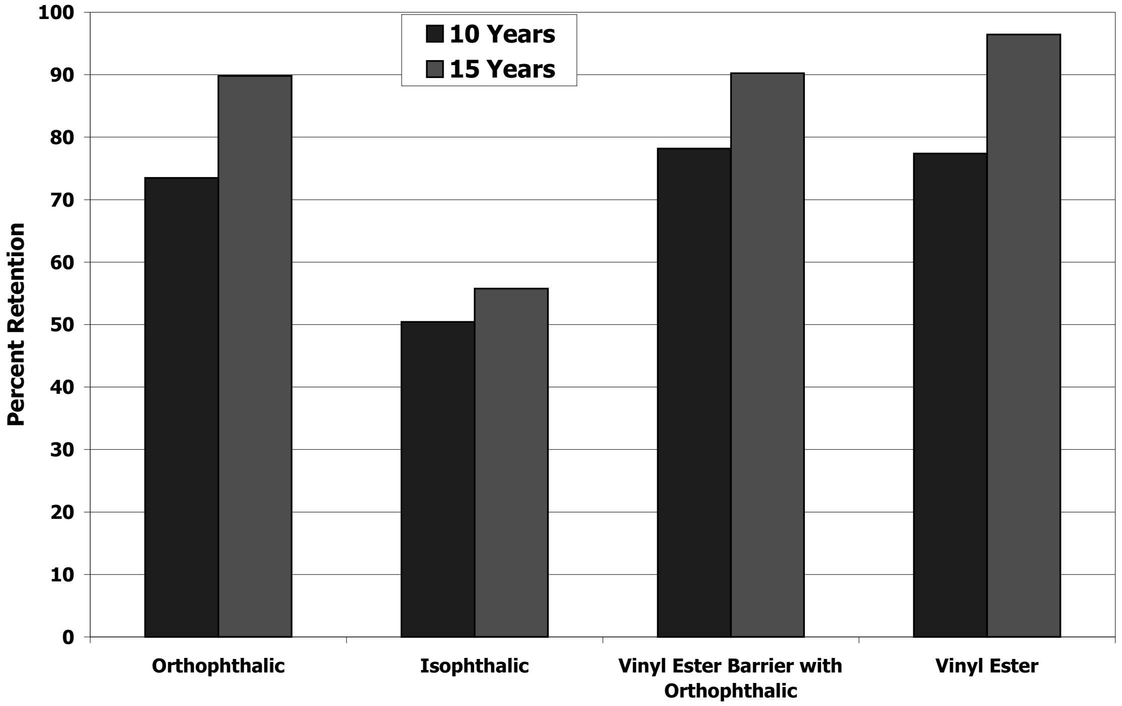

Table 8: Noticed Izod Impact Strength of Wet Coupons, ft lb/in. (cm N/cm)

Years	Orthophthalic	Isophthalic	Orthophthalic with Vinyl Ester Barrier	Vinyl Ester
Initial	11.5 (615)	11.3 (604)	13.3 (711)	8.40 (449)
10	5.30 (283)	3.60 (193)	10.4 (556)	5.30 (283)
15	5.60 (299)	3.70 (199)	12.0 (642)	6.00 (321)

Table 9: Notched Izod Impact Strength of Dried Coupons, ft lb/in. (cm N/cm)

Years	Orthophthalic	Isophthalic	Orthophthalic with Vinyl Ester Barrier	Vinyl Ester
Initial	11.5 (615)	11.3 (604)	13.3 (711)	8.40 (449)
10	12.9 (690)	5.70 (305)	10.4 (556)	6.50 (348)
15	12.0 (642)	6.30 (337)	12.0 (642)	8.10 (433)

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