

Statistical Comparison of
Eastman CHDA, Eastman PIA, and HHPA
in High-Performance Gel Coats Based on
Eastman NPG Glycol



Photo courtesy of Maxum Boats

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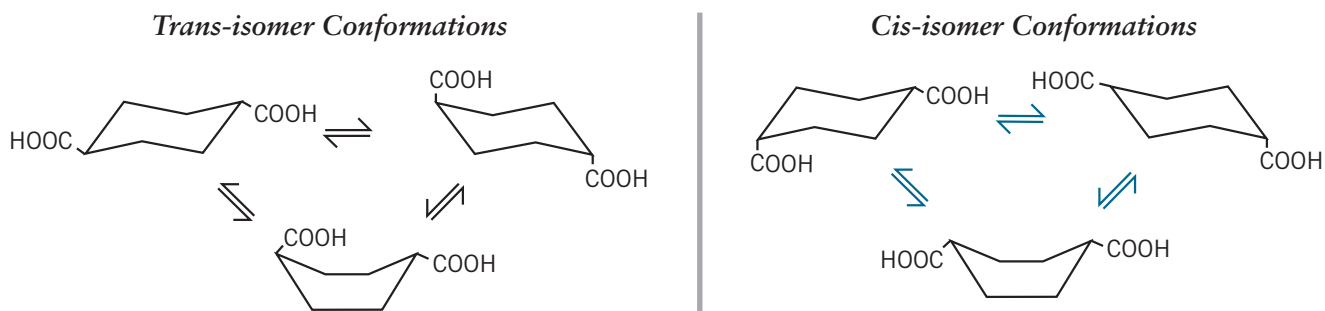
Introduction

Eastman offers the polyester resins industry a selection of diacid and glycol products that allow resin producers to meet ever increasing consumer demands. *Eastman* Isophthalic Acid (PIA) and *Eastman* 1,4-cyclohexanedicarboxylic acid (CHDA), in combination with a high-performance glycol such as *Eastman* NPG glycol, are used to prepare premium quality unsaturated polyester resins

for use in gel coat applications in the composites industry. Since the mid 1960's, NPG/ISO gel coat resins have been and still are the gold standard by which other gel coat formulations are judged. The purpose of this literature is to compare the performance of PIA, CHDA, and hexahydrophthalic anhydride (HHPA) in NPG/PG based unsaturated polyester resins for use in gel coats.

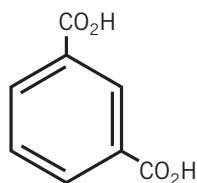
Cycloaliphatic Structure of *Eastman* CHDA (1,4-Cyclohexanedicarboxylic Acid)

Movement between the boat and chair conformations equals flexibility.



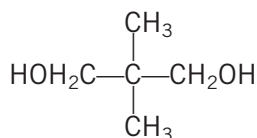
Aromatic Structure of *Eastman* PIA (Purified Isophthalic Acid)

Rigid aromatic cyclic structure equals excellent hardness.



Neo-Structure of *Eastman* NPG Glycol (Neopentyl Glycol)

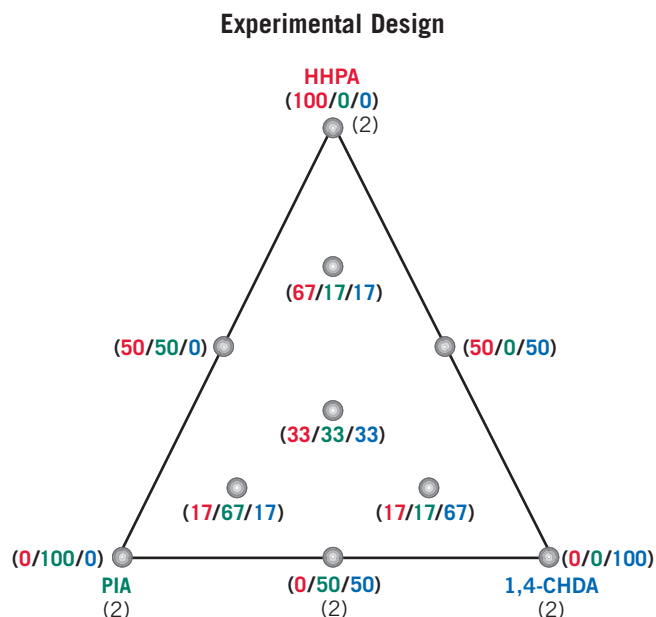
Neo-structure equals excellent weatherability, hydrolytic stability, and stain resistance.



Experimental Design

The experiment was a statistically designed mixture study generated by Stat-Ease, Inc. *Design Expert* Version 6.0.7 software. Each data point identifies a prepared resin with varied HHPA/PIA/CHDA molar ratios. The total moles of diacid components were held constant at 3.57. Those resin compositions with a 2 in parentheses were duplicated to determine statistical integrity of the design and subsequent responses modeled from the data.

Each resin was used to prepare two sets of composite panels for evaluation. One set involved applying the fiberglass/laminate resin directly onto the gel coat. The other set incorporated a vinyl ester resin barrier coat between the fiberglass/laminate resin and gel coat. Differences in gel coat performance were evaluated with and without a vinyl ester barrier coat.



Resin Composition

The base resin composition (Table 1) contained neopentyl glycol (NPG), propylene glycol (PG), and maleic anhydride (MAN). Resins were prepared as two-stage cooks with MAN added in the second stage. Each resin was diluted initially with styrene to 70 wt% solids for storage then further to 55 wt% solids just prior to use. Refrigeration was used to minimize gel time drift and ensure fresh resins for gel coat preparation.

Table 1

Resin Parameters and Composition

Resin Parameters	
NPG/PG molar ratio	85:15
Diacid:MAN molar ratio	1:1
Maleic anhydride level	20.4–21.2 Wt% ^a
Acid number	10–15
Target Mn	2500
Resin Molar Composition	
NPG/PG/Diacid/MAN	6.34/1.12/3.57/3.57
Molar Ratio of Diacids	
PIA } CHDA } HHPA }	Varies

^aWt% MAN varies slightly between formulations due to molecular weight differences of the diacids.

Casting and Laminate Preparation

Resin castings (1/8") for mechanical testing were prepared by catalyzing (Table 2) a 55% resin in styrene solution and transferring to a mold. Castings were post cured at 120°C for two hours.

Table 2

Cure Package for Castings

Ingredients	Weight, g
Resin (55 wt% in styrene)	200.00
<i>Nuodex</i> octoate cobalt 6% catalyst ^a	0.80
<i>Eastman</i> DMAA copromoter ^b	0.60
<i>Eastman</i> hydroquinone inhibitor ^b	0.02
<i>Norox</i> MEKP-925 initiator ^c	2.00
Total	203.42

^a*Huls America*

^b*Eastman Chemical Company*

^c*Norac, Inc.*

Gel Coat Resin Preparation

The gel coats (Table 3) were prepared from a pigment grind using a Cowles disperser followed by let down with additional resin.

Table 3

Gel Coat Resin Preparation

	Weight, g
Grind	
Resin (55 wt% in styrene)	53.28
<i>Ti-Pure</i> R-902 TiO ₂ pigment ^a	79.92
Let Down	
Resin (55 wt% in styrene)	260.80
<i>Cab-O-Sil</i> M-5 fumed silica ^b	6.00
Total	400.00
Gel Coat Formulation	
Gel coat resin (35.3 wt% styrene)	110.00
<i>Nuodex</i> octoate cobalt 6% catalyst ^c	0.44
BYK-A 500 air release additive ^d	0.28
<i>Eastman</i> DMAA copromoter ^e	0.33
<i>Eastman</i> hydroquinone inhibitor ^e	0.01
<i>Norox</i> MEKP-925 initiator ^f	1.10
Gel coat	112.16
Final pigment concentration: 20 wt%	
W% styrene: 35.3	
Thix Index: 5.0–5.5	

^a*Du Pont*

^b*Cabot Corporation*

^c*Huls America*

^d*BYK Chemie*

^e*Eastman Chemical Company*

^f*Norac, Inc.*

Gel Coat Laminate Preparation

Gel coat laminate was prepared by making 35-mil wet draw downs of catalyzed gel coat onto a polished, mold-release treated glass plate. The laminating resin (Table 4) was a commercial DCPD product targeted for general-purpose marine applications.

Table 4

Gel Coat Laminate Composition

Laminating Resin Formulation	Weight, g
<i>Aropol Q 63304 T 35</i> ^a	375.00
<i>Norox MEKP-925 initiator</i> ^b	5.63
Total	380.63

Laminate Parameters

Xtend 804 Release^c
Fiberglas M-723 1.5 oz chopped strand mat^d
DCPD resin/fiberglass ratio: 70:30
Allowed to cure at room temperature overnight
Post Cure: 2 hrs @ 66°C

^aAshland Composite Polymers Division

^bNorac, Inc.

^cAxel Mold Release

^dOwens-Corning

Gel Coat Laminate With Vinyl Ester Barrier Coat Preparation

The materials and basic preparation used for gel coat laminates were used to prepare vinyl ester barrier coat laminates. The vinyl ester was supplied fully formulated (Table 5) requiring addition of cumeme hydroperoxide catalyst only. Application of the vinyl ester resin was between the gel coat and DCPD resin/fiberglass laminate. A vinyl ester film thickness of 15–20 mils was targeted for the study. The same lamination schedule was used for these panels.

Table 5

Vinyl Ester Formulation

	Weight, g
<i>Hydrex 100 HF (33375-30)</i> ^a	100.00
<i>Norox CHP</i> ^b	1.50
Total	101.50

^aReichhold

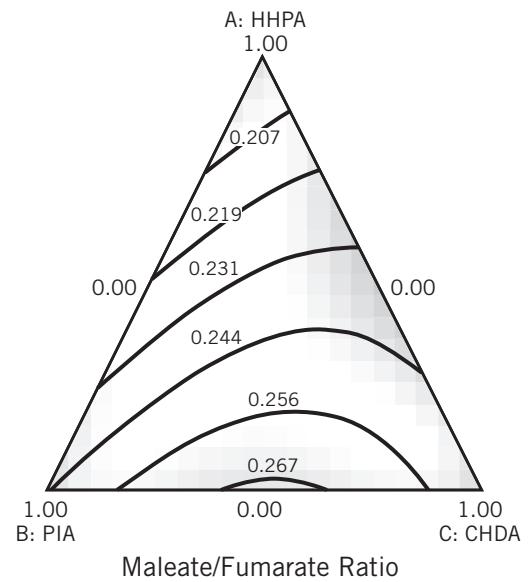
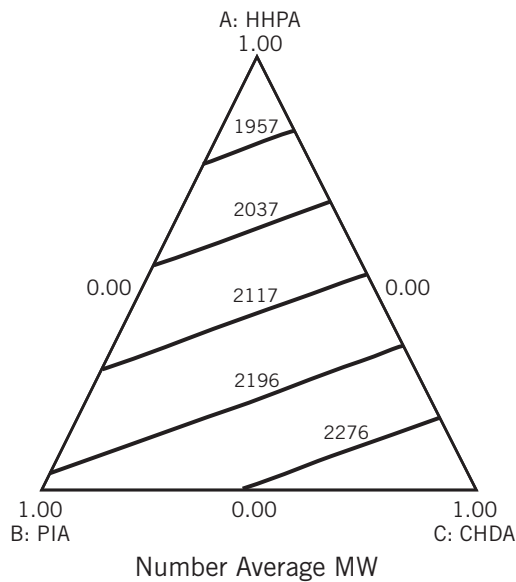
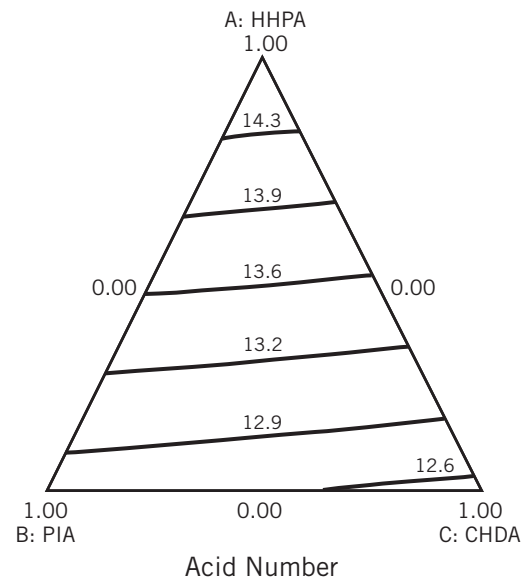
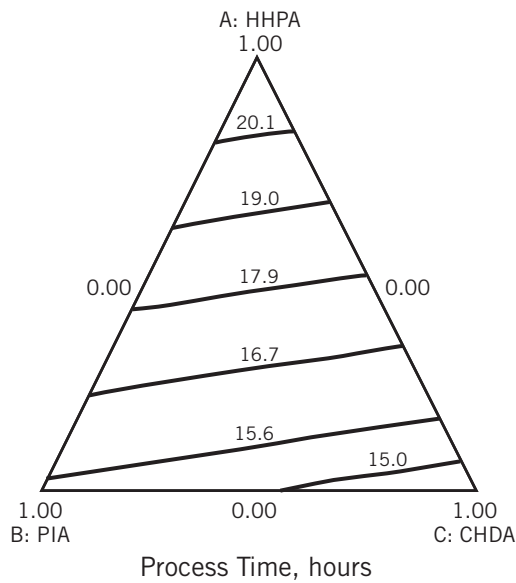
^bNorac, Inc.

Results

Performance trends are presented in 2D contour plots using regression analysis. Gray areas within the plots indicate less confidence level with this area.

Resin Processability

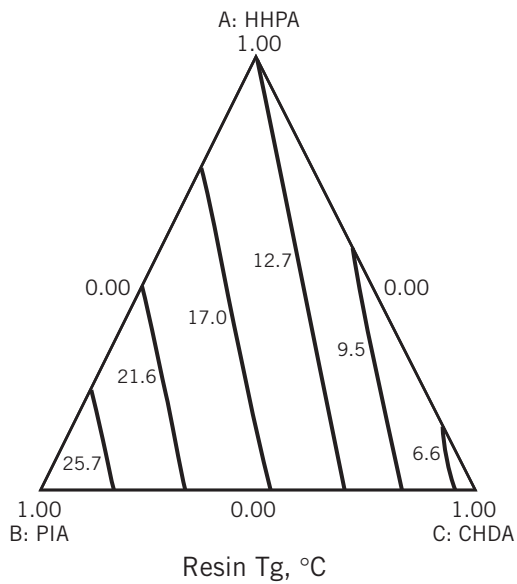
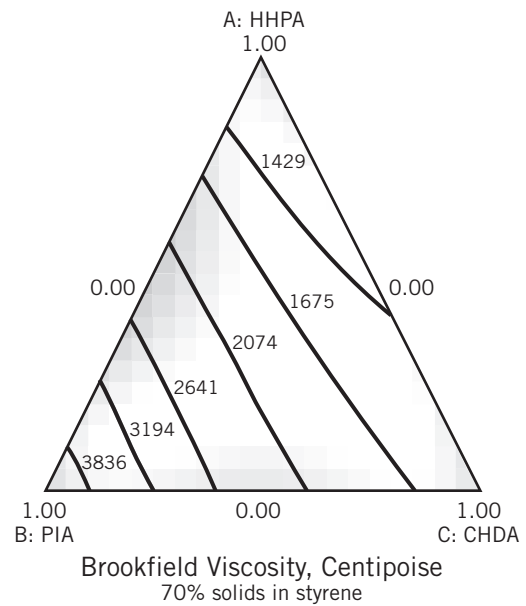
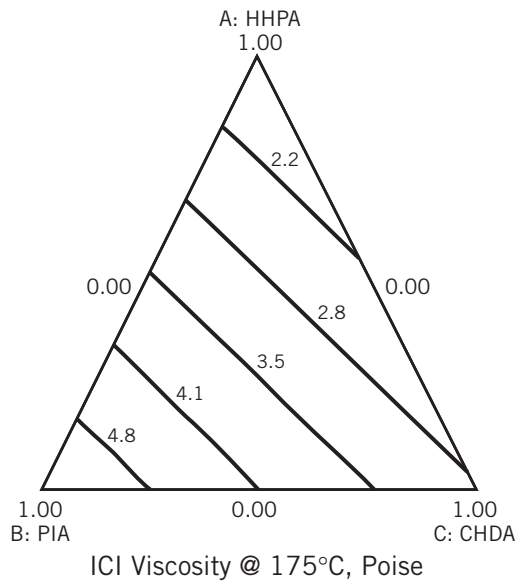
- Order of reactivity: CHDA > PIA >> HHPA
- CHDA achieved the target acid number and highest molecular weight in the shortest reaction time.
- HHPA required > 30% longer reaction time with lower molecular weight and higher acid number.
- PIA behaves more like CHDA than HHPA in processing parameters.
- HHPA gives higher maleate to fumarate isomerization due to longer reaction times.



Number average molecular weight determined via Gel Permeation Chromatography based on polystyrene equivalents.

Resin Properties

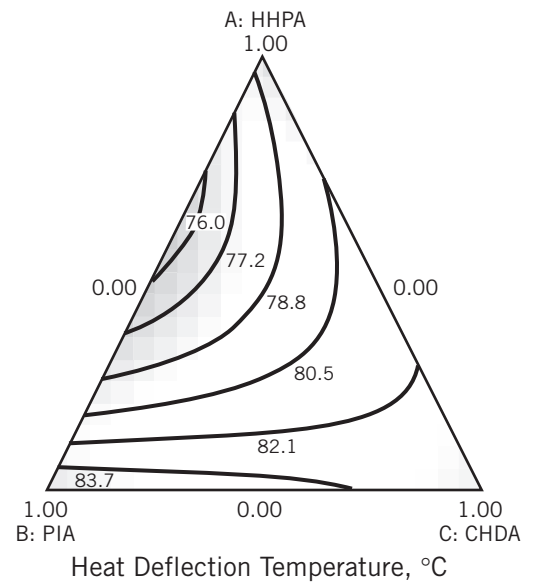
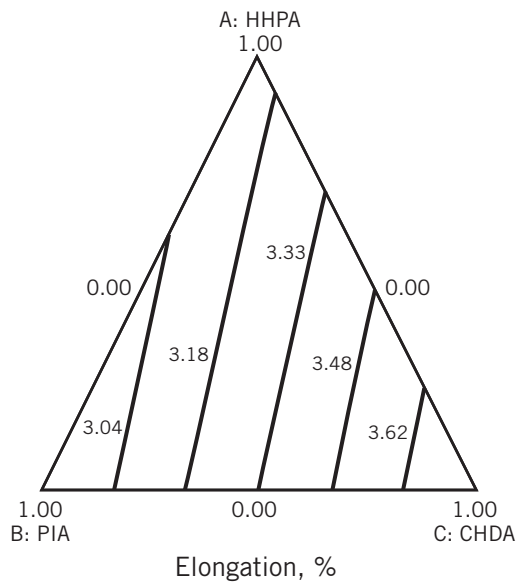
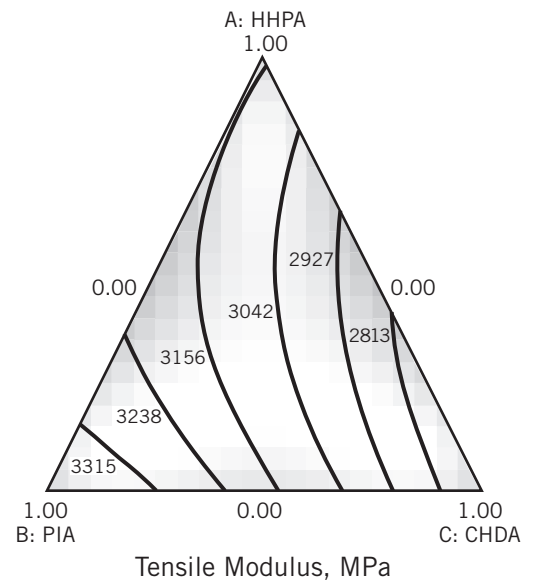
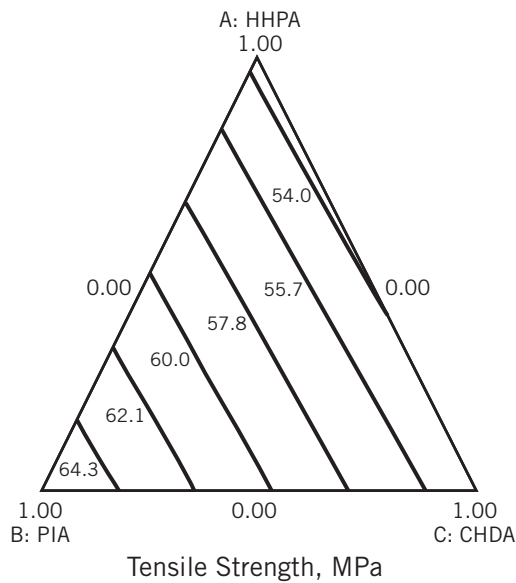
- PIA increases ICI viscosity, resin Tg, and solution viscosity.
- CHDA and HHPA reduce ICI viscosity, resin Tg, and solution viscosity compared to PIA.
- CHDA gave the lowest resin Tg with moderate ICI viscosity.
- CHDA solution viscosity behaved more like HHPA.
- CHDA solution viscosity was similar to HHPA even though the CHDA resins were higher molecular weight than HHPA.



Tensile Properties

- Tensile strength: PIA > CHDA = HHPA
- CHDA gave lowest tensile modulus and provided the greatest percent elongation.

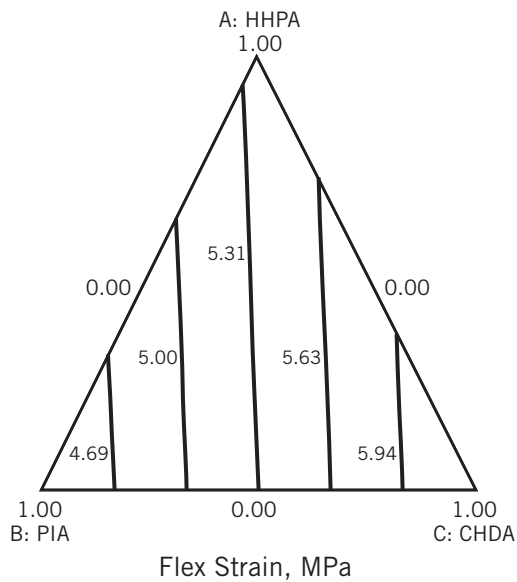
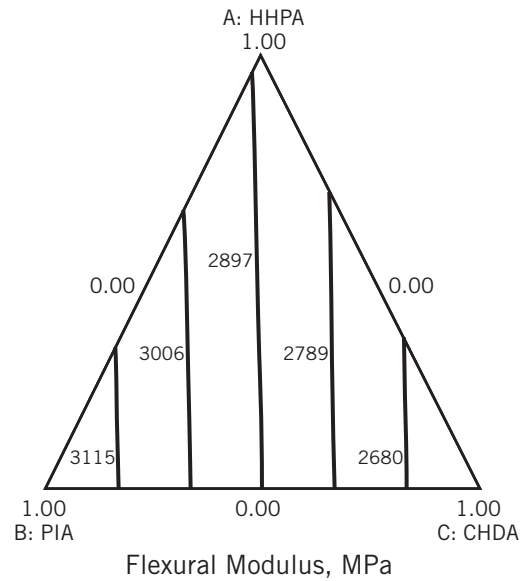
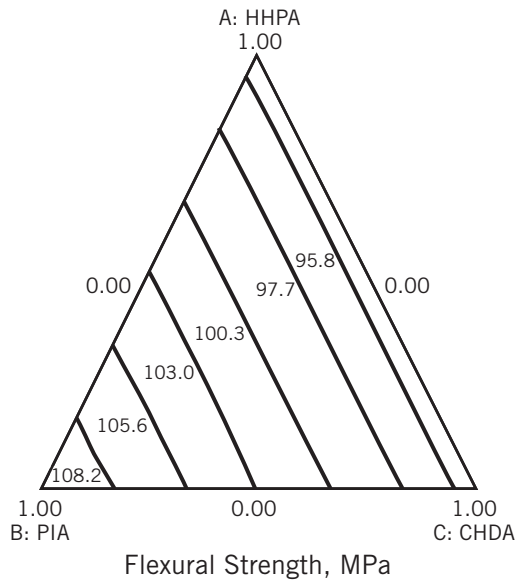
- PIA enhanced heat deflection temperatures (HDT).
- PIA/HHPA blends exhibited lowest HDT compared to PIA/CHDA blends.



Tensile properties determined via ASTM D638.
HDT determined via ASTM D648.

Flexural Properties

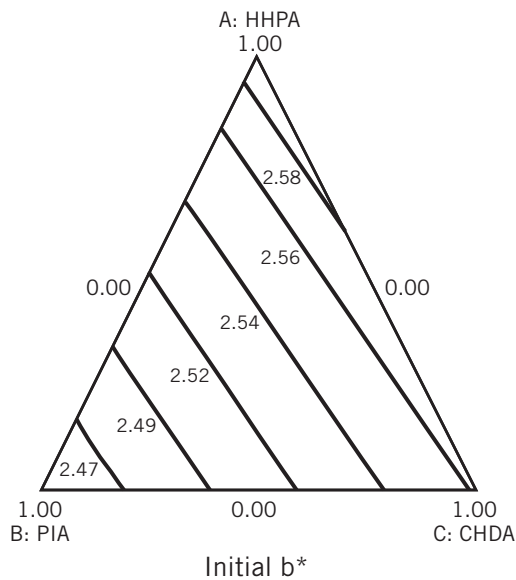
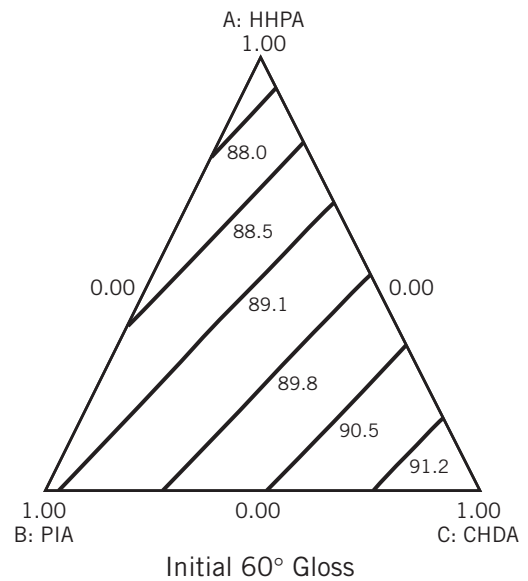
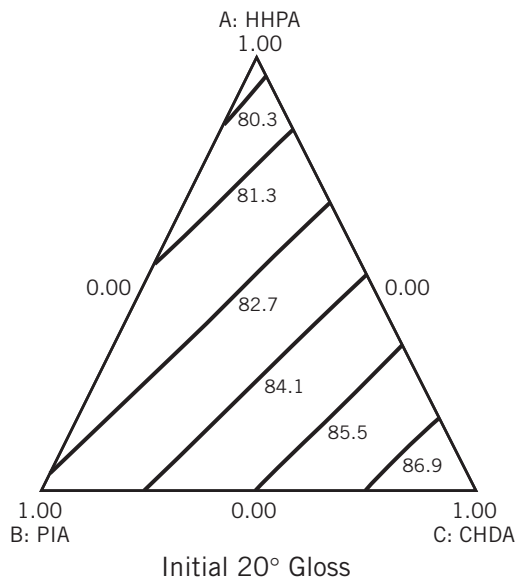
- Flexural strength: PIA > CHDA = HHPA
- Increasing CHDA levels provides resins with lowest flexural modulus but increased flexural strain.
- A 50:50 PIA: CHDA blend provides similar flexural modulus and strain as 95:5 HHPA: PIA.



Flexural properties determined via ASTM D790.

Initial Gloss and b* Color

- Initial gloss: CHDA > PIA > HHPA
- HHPA gave the lowest initial gloss of the resins evaluated.
- Initial b* color was the same for the gel coat formulations evaluated but still presented as a reference for subsequent weathering test.
- Subsequent color values for exposed panels are reported as Delta E.
- Delta E¹ values were driven by Δb* via yellowing of the gel coat resin. Values for ΔL* and Δa* changed very little, thus changes in Delta E essentially represent changes in Δb*.

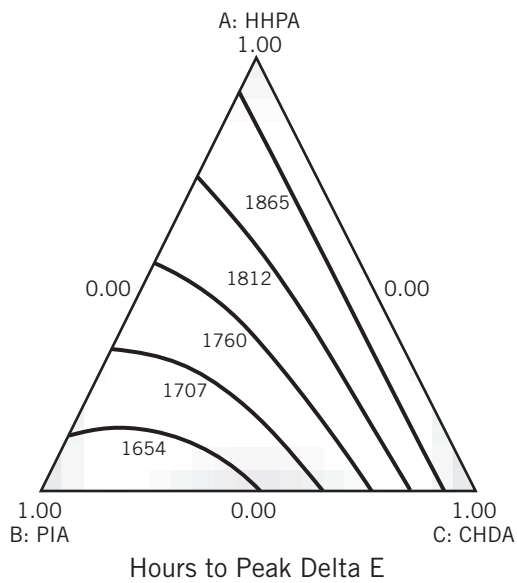
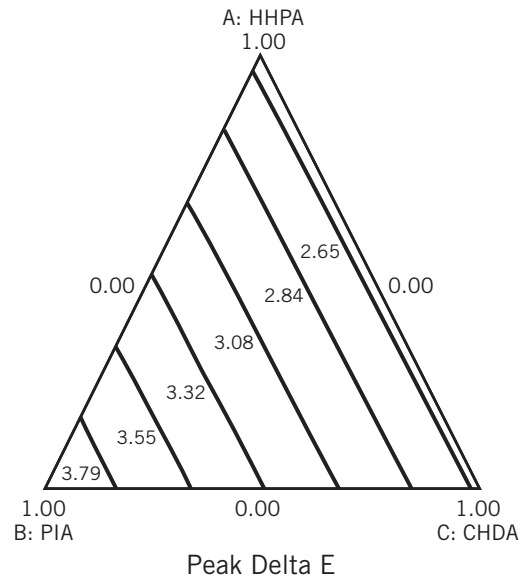
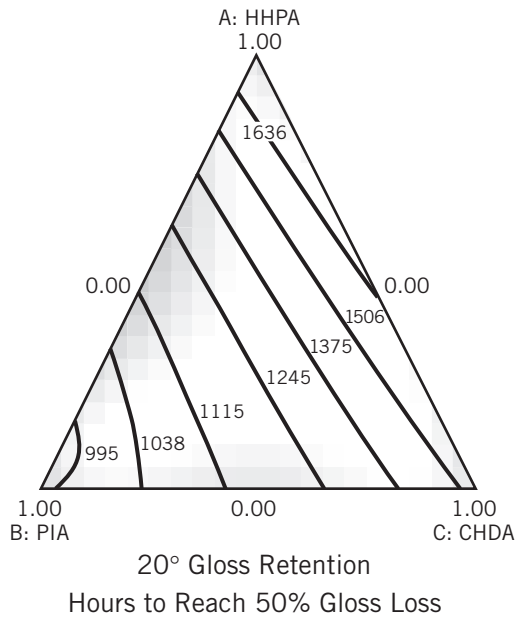


¹Delta E encompasses the parameters of the L,a,b color solid per the following equation:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

Weathering—Xenon Arc Exposure

- Increasing levels of aromatic diacid, PIA, results in poorest gloss retention and greatest color development.
- 60° gloss exhibited similar trends thus not presented.
- CHDA and HHPA have similar Peak Delta E.
- Hours required to reach Peak Delta E similar for CHDA and HHPA.

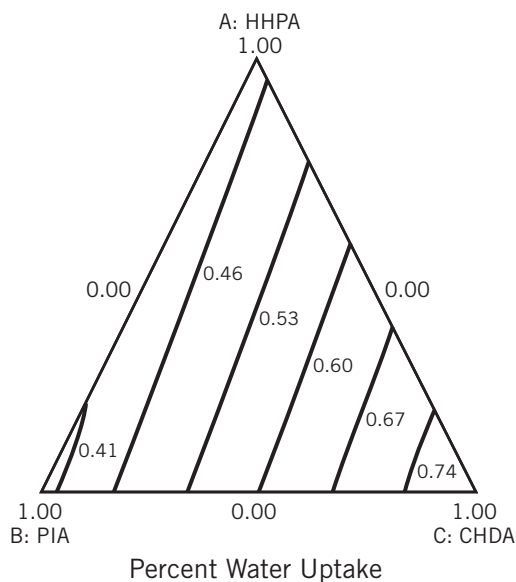
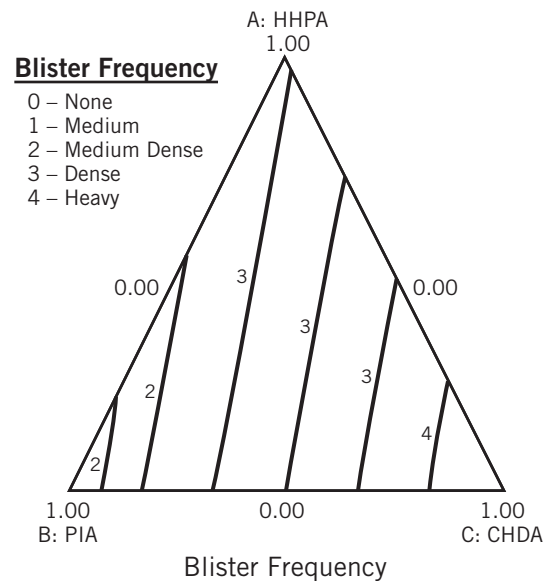
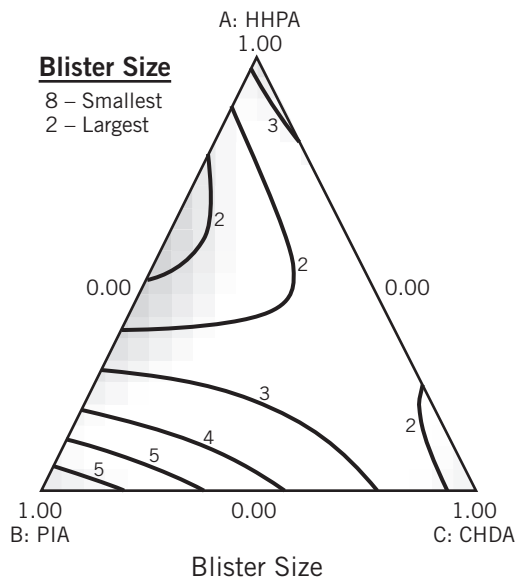


Weathering—Hot Water Resistance¹

- PIA provides gel coats with excellent blister resistance.
- CHDA and HHPA performed similarly with respect to blister resistance.
- Percent water uptake for HHPA is similar to PIA but visual evaluations were similar to CHDA.
- Gel coat flexibility imparted by CHDA results in blisters that did not rupture as frequently as those

with increasing HHPA levels. Thus, CHDA gel coats held more water resulting in greater % water uptake.

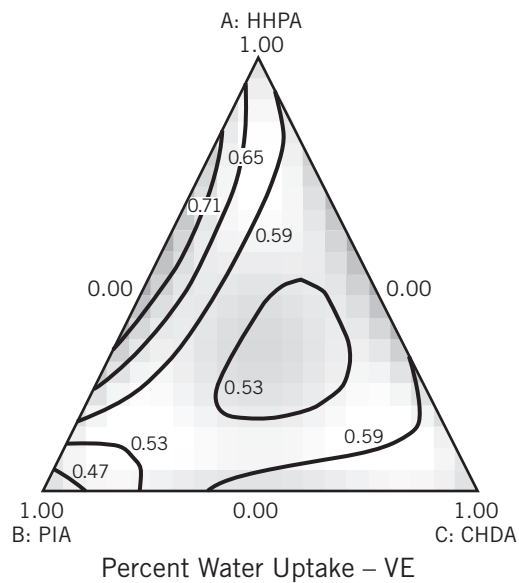
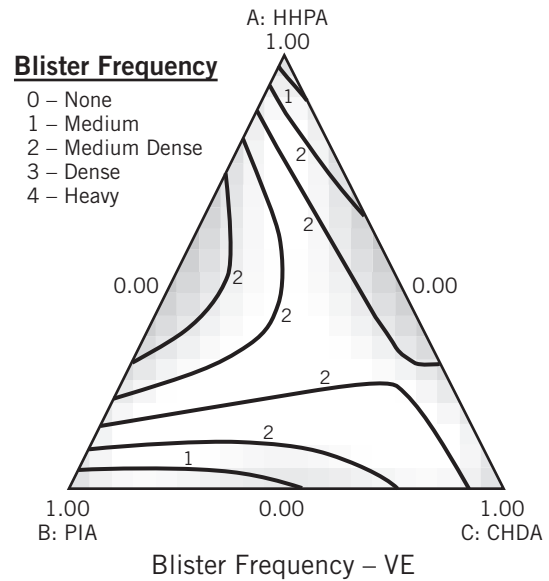
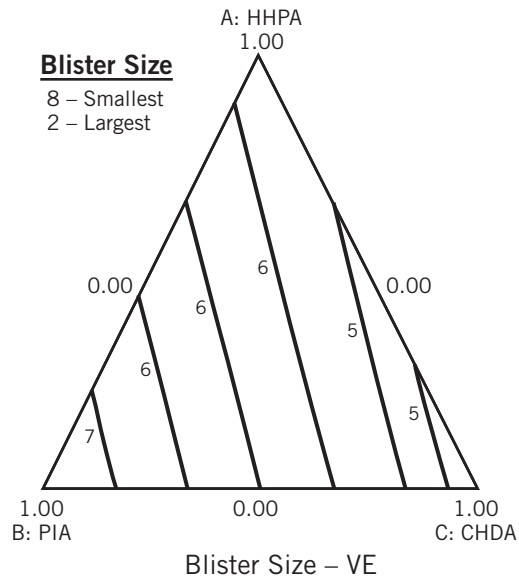
- PIA/CHDA blends perform better than PIA/HHPA blends with respect to blister size.
- Compared to PIA, both CHDA and HHPA are more susceptible to hot water blistering.



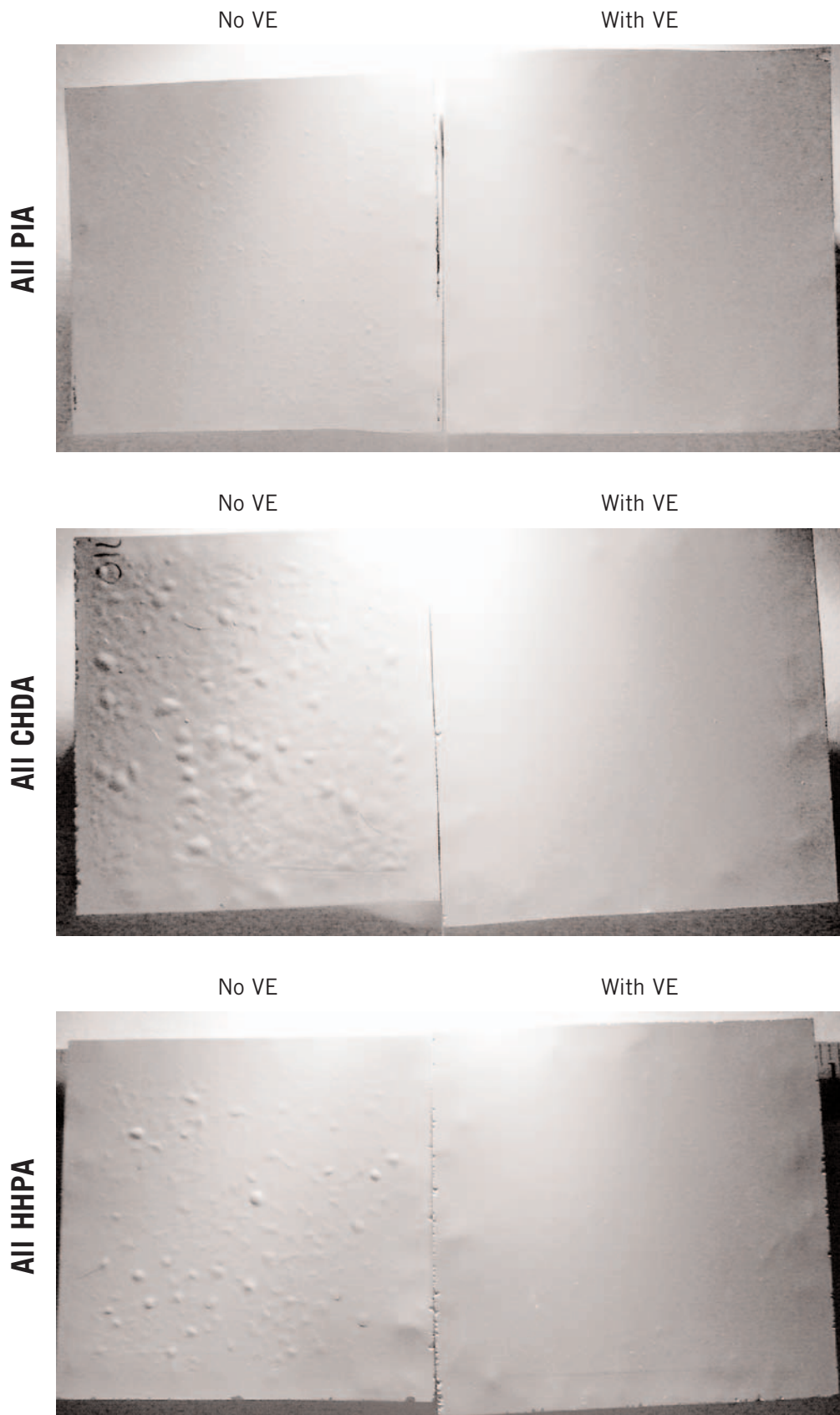
¹Test was carried out at 150°F using demineralized water for 1,500 hours with panel evaluations every 100 hours. Test simulates approximately 22 years continuous water exposure. ASTM D714 Evaluating Degree of Blistering of Paints was used as a guide to determine blistering size and frequency.

Effect of Vinyl Ester Barrier Coat on Blister Resistance

- Addition of the vinyl ester barrier coat between the gel coat and DCPD laminate layer significantly improved blister resistance.
- Improvement was greatest with cycloaliphatic monomers than with aromatic monomers.

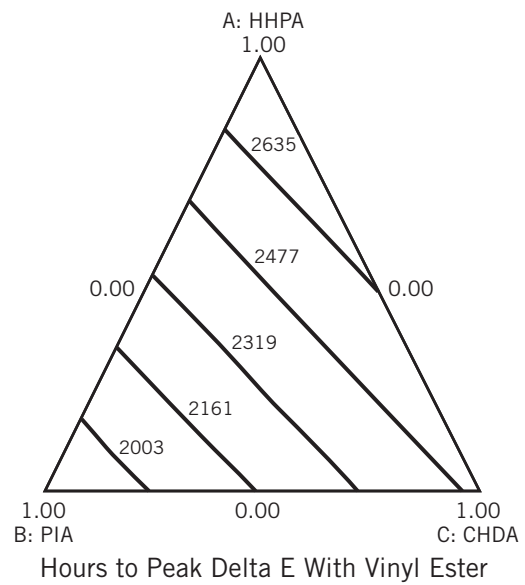
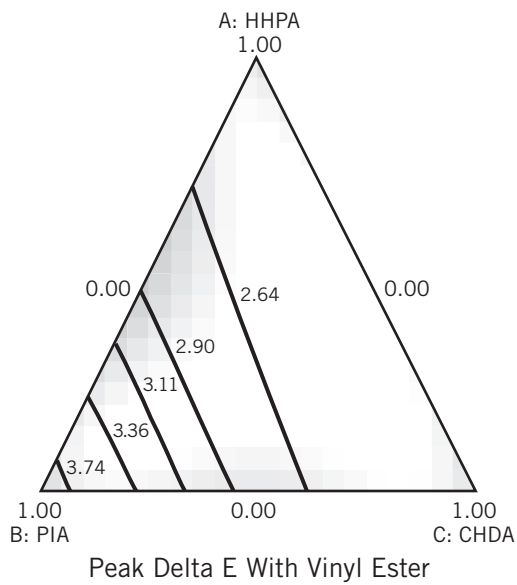
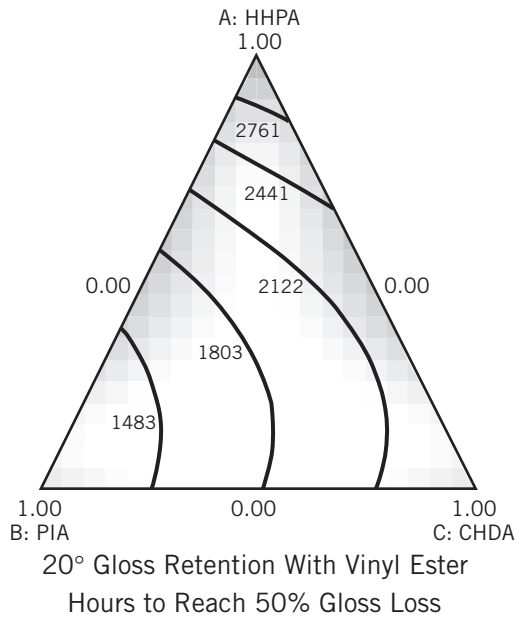


Pictorial Comparison of Vinyl Ester Barrier Coat on Blister Resistance



Effect of Vinyl Ester Barrier Coat on Xenon Arc Weathering

- Use of VE improved gloss retention and minimized Delta E color development.
- Increasing PIA concentrations resulted in more color development and lower gloss retention than those with increasing levels of cycloaliphatic monomer even with a VE barrier coat.



Property Summary—Resin Synthesis and Mechanical Properties

Resin Synthesis Properties

Property	Trend
Process Time	HHPA >> PIA > CHDA
MW Build	CHDA > PIA > HHPA
M/F Ratio	HHPA > PIA > CHDA
Resin Tg	PIA > HHPA > CHDA
ICI Viscosity	PIA > CHDA > HHPA
Brookfield Viscosity	PIA >> CHDA > HHPA

Mechanical Properties

Property	Trend
Tensile Strength	PIA > HHPA = CHDA
Tensile Modulus	PIA > HHPA > CHDA
Flexural Strength	PIA > CHDA = HHPA
Flexural Modulus	PIA > HHPA > CHDA
Elongation	CHDA > HHPA > PIA
Flex Strain	CHDA > HHPA > PIA
Heat Deflection Temperature	PIA > CHDA > HHPA

Property Summary—Weathering Without and With Barrier Coat

Weathering Properties No Vinyl Ester Barrier

Property	Trend
Initial Gloss	CHDA > PIA > HHPA
Initial b* Color	CHDA = PIA = HHPA
20° Gloss Retention	HHPA > CHDA > PIA
Delta E Color	PIA > HHPA > CHDA
Blister Resistance	PIA >> HHPA > CHDA

Weathering Properties Vinyl Ester Barrier

Property	Trend
20° Gloss Retention	HHPA > CHDA > PIA
Delta E Color	PIA > HHPA > CHDA
Blister Resistance	PIA > HHPA = CHDA

Conclusions

- CHDA esterifies quickly compared to HHPA and PIA.
- Synthesis time for all HHPA was 42% longer than with all CHDA.
- CHDA offers a balanced set of resin properties: fast reacting, quick MW build, and reduced solution viscosity.
- CHDA offers excellent flexural properties and elongation yet with HDT similar to PIA highlighting the flexibility/hardness balance of CHDA.
- PIA provided resins with the greatest physical properties. Physical properties of CHDA resin could possibly be enhanced by using fumaric acid.
- CHDA weathering was excellent with high initial gloss, excellent gloss retention, and color retention.
- Vinyl ester barrier coat significantly improves blister resistance of cycloaliphatic structures.

Performance Benefits

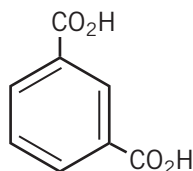
PIA

Gel Coat Performance

- Hardness
- Toughness
- Stiffness
- Chemical Resistance
- Excellent Blister Resistance
- Good Heat Deflection Temperature

Resin Processing

- Moderate Glycol Solubility
- Low Resin Color
- Excellent Thermal Stability



CAS: 121-91-5

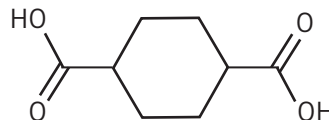
CHDA

Gel Coat Performance

- Hardness/Flexibility Balance
- Exceptional Gloss Retention
- Excellent Anti-Yellowing
- Good Heat Deflection Temperature
- Higher Elongation @ Break

Resin Processing

- Excellent Solubility in Glycols
- Rapid Esterification
- Low Resin Color
- Excellent Thermal Stability



CAS: 1076-97-7

PIA has long been the diacid of choice for high-quality gel coats. It offers good reactivity, excellent physical properties, and good blister resistance.

Eastman CHDA offers manufacturers of gel coat resins a diacid monomer for high-performance differentiated products consumers continue to demand. CHDA gives resin producers the ability to produce unsaturated polyesters based on all aliphatic components. This minimizes UV absorbance and subsequently reduces polyester degradation within the gel coat resin commonly experienced with aromatic diacids. The result is improved gloss retention and color stability. CHDA based gel coats benefit significantly from the use of a barrier coat layer in between the gel coat and

laminar matrix. The greatest improvement is in blister resistance but gloss retention and resistance to yellowing also improve with use of a barrier coat.

Contact *Eastman* Technical Service for additional information on how to use PIA and CHDA in your company's high-performance gel coats. *Eastman* Technical Service can also provide information on other high quality *Eastman* products used in the composites industry such as *Eastman* NPG glycol, *Eastman* TMPD glycol, *Eastman* DMAA copromoter, and a broad line of hydroquinone based inhibitors. *Eastman* publication GN-417 contains a list of products and general properties of each used in the unsaturated polyester industry.

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