



New liquid low emission resin systems for anti-corrosion – properties and application examples

TÜV Unlimited Munich, 6th – 7th of February 2018 Stefanie Römhild, Livio Bollani



Outline of the presentation

■ Background – why low styrene and styrene free systems
☐ Styrene free and low styrene resin technology and properties
☐ Chemical resistance properties
☐ Application properties
☐ Case studies

POLYNT AND REICHHOLD COMPLETE MERGER TO CREATE A GLOBAL SPECIALTY CHEMICALS GROUP

May 19, 2017 – Polynt and Reichhold are pleased to announce the closing of the combination announced last year, after having received all regulatory approvals. The new Polynt-Reichhold (or "the Group") is a global company in the Intermediates, Coating and Composite Resins, Thermoset Compounds, Gel-coats and niche Specialties with over €2 billion in revenues. Investindustrial and Black Diamond Capital Management, L.L.C. ("Black Diamond") are equal investors in the new group.

This combination enhances the Group's leading position as a global vertically integrated specialty chemicals player, with significant global presence in Europe, North America and Asia, a strategy initiated by Polynt with the successful integration of PCCR and CCP in the last five years and now further reinforced by Reichhold's global scale, extensive product portfolio and R&D competencies. The Group's excellence in serving customers around the world will be further strengthened by the merger of best in class innovation and a customer oriented approach.





Why low styrene or styrene free?

- ☐ New regulations with respect to allowable styrene emission at workshops come/have come into place. E.g. France
- □ Need for low odor and odor control.
- ☐ In the chemical processing and piping industry there is a need for open mold processes, many in confined space with limited or no ventilation; including e.g. repair work, new installations on site, etc. Some sites may apply the same maximum styrene emission rules as in workshop.
- ☐ Low emission and chemical resistance required.
- ☐ Examples are storage tank linings and internal composite floating roofs, pipe fitting/ joining and rehabilitation.

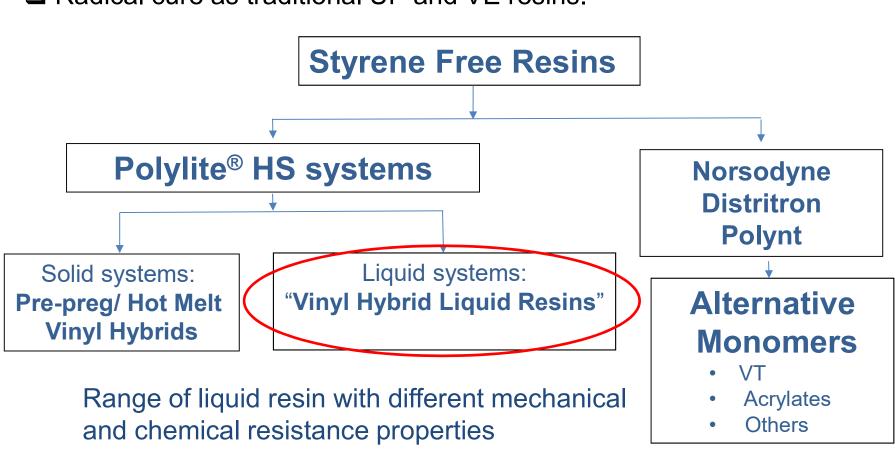






Polylite® HS technology

- □ Polylite® HS resins are based on reactive diluent free vinyl hybrid resin technology
- ☐ Base resins do not include styrene, very low emissions.
- ☐ Radical cure as traditional UP and VE resins.





Resin platforms

Targets for a new resin system:

- Significantly reducing styrene emissions and/or odor
- Matching the anti-corrosion styrenated resin systems' chemical resistance
- Similar application properties with respect to e.g. compatibility with available reinforcement, cure, etc.

Polylite[®] HS 35060

Vinyl Hybrid resin with high cross-linking density

High chemical resistance

Tanks relining, internal tank installations, etc.

Polylite® HS VH-1233

Urethane modified Vinyl Hybrid resin with medium cross-linking density

Medium corrosion resistance

Pipe fitting & rehabilitation





Polylite HS Anti-corrosion resins

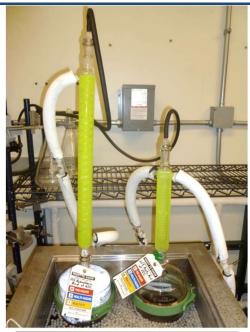
- □Polylite® HS 35060 (VH)
- □ Pre-accelerated Polylite HS® 35060 modification for open-mold hand and machine lamination containing 5% styrene (VH MOD)
- □Standard styrenated resins of type novolac epoxy vinyl ester resin, Dion[®] Impact 9400 (NOV)

	Unit	VH	VH MOD	NOV
Viscosity Cone and plate at 23°C	mPas	800-1500	750-950	350-550
Tensile strength	MPa	47	72	72
Elongation at break	%	1.5	2.6	2.5-3
Tensile modulus	MPa	3500	3450	3700
Flexural strength	MPa	97	115	130
Flexural modulus	MPa	3700	3550	3600
HDT	°C	150	130	135
Barcol hardness	-	43	45	45



Corrosion resistance

- □ASTM C581, immersion testing
- □Standard corrosion testing coupons based on laminates made with chopped strand mat reinforcement and a C-glass surface veil or double synthetic veil.
- □Post-cured for 4 h at 100°C if not specified other.
- ☐ Testing environments selected based on typical environments in the field, to reflect different chemistries:
 - **Different types of solvents**: Methanol, ethanol, toluene, hexane @ 35°C/40°C and Fuel type C (toluene: iso-octane 1:1) + 10% ethanol @ 25°C
 - Chlorinated aromatic solvent: Chlorobenzene @ 25°C
 - Alkaline environment: Sodium hydroxide @ 40 and 60°C, sodium silicate @ 40°C
 - Organic amine: Diethanol amine @ 40°C
 - Alkaline oxidizing environment: 15% sodium hypochlorite @ 40°C
 - Strong acids: 36% hydrochloric acid, 35% nitric acid, 75% sulfuric acid at 25°C

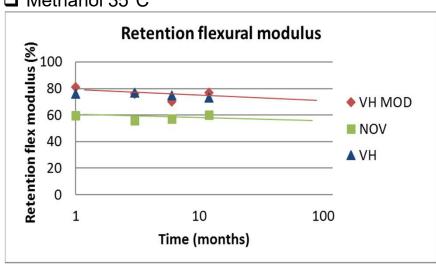


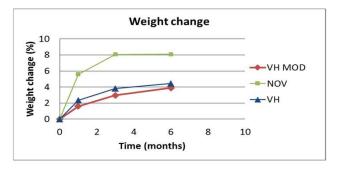


Solvents



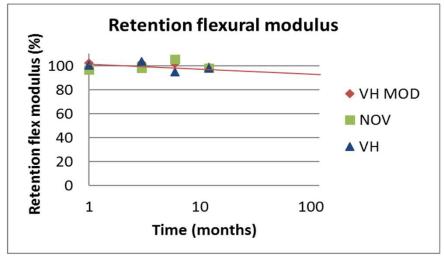
■ Methanol 35°C

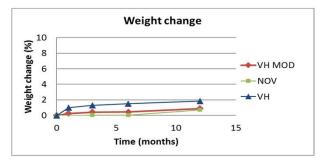




☐ In alcohols such as methanol and ethanol, VH and VH MOD perform significantly better and show lower absorption.

☐ Toluene 35°C

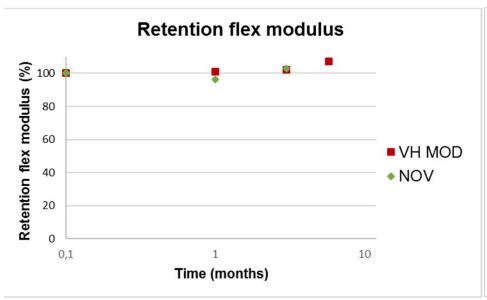


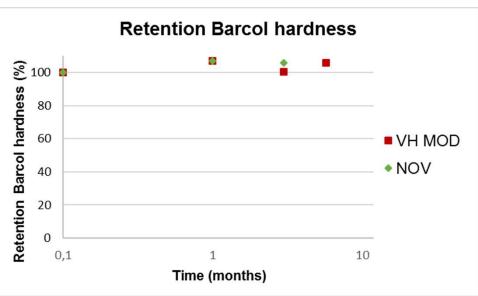


- ☐ Mechanical properties are hardly affected. VH and VH mod in line with NOV.
- ☐ Results propose higher usage temperature possible. 40°C resistance confirmed (6 months testing time)

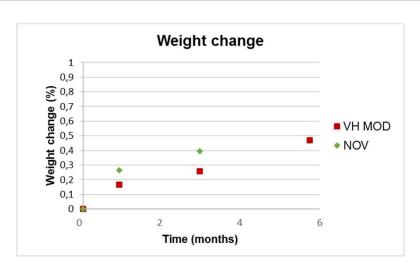


Chlorinated aromatic solvent





- ☐ Chlorobenzene @ 25°C
- ☐ VH MOD performs in line with NOV with respect to mechanical retention values, absorption levels and visual appearance properties.

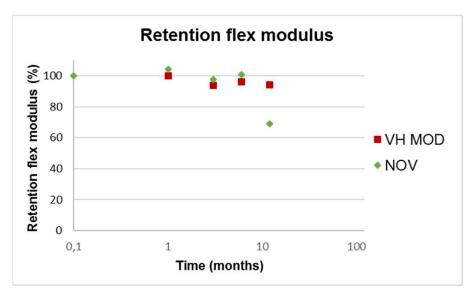


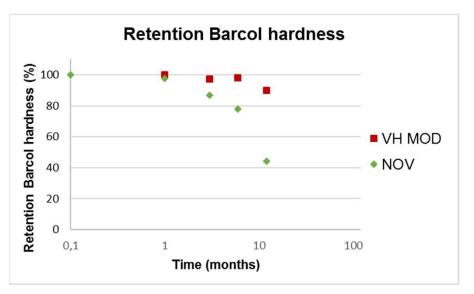




Inorganic alkaline environments

- ☐ VH MOD compared to NOV exposed to 20% sodium hydroxide @ 40°C
- ☐ VH MOD performs at least as good as NOV. Visual and microscopic investigation indicate better performance of VH MOD.
- ☐ Tests at 60°C in 5 and 50% sodium hydroxide solution (6 months) confirm better corrosion resistance than NOV. 12-months-testing data for final evaluation needed.





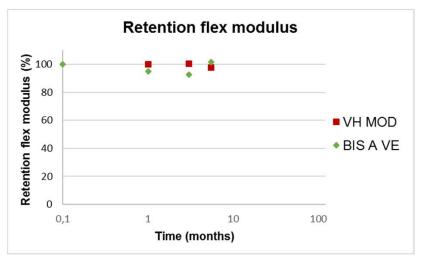
20% NaOH @ 40°C

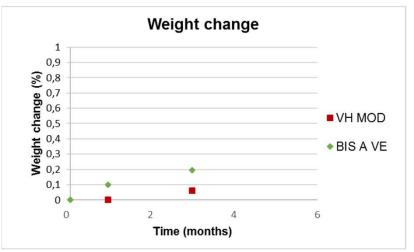


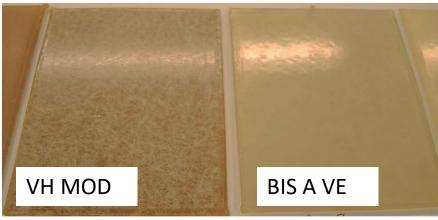


Alkaline oxidising environment

- ☐ 15% sodium hypochlorite solution @ 40°C, pH > 11
- □ VE MOD compared to standard bisphenol A vinylester (BIS A VE)
- □ VE MOD performs close to the BIS A VE showing promising results which indicate that the resin can be suitable for adjusted temperature and concentration ranges.





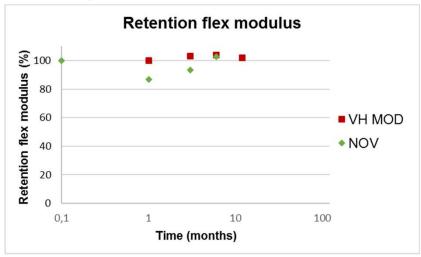


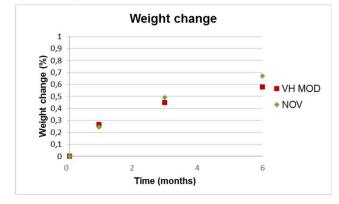




Strong acidic environments

- □75% sulfuric acid, 36% hydrochloric acid, 35% nitric acid @ 25°C, 5,5 months data
- ☐ In all environments, VE MOD shows
 - Retention values at 100% level
 - Weight change comparable to that of the NOV resin
 - Visually unaffected laminate except for color change in hydrochloric acid





36% hydrochloric acid



Nitric acid 5,5 months



Sulfuric acid 5,5 months

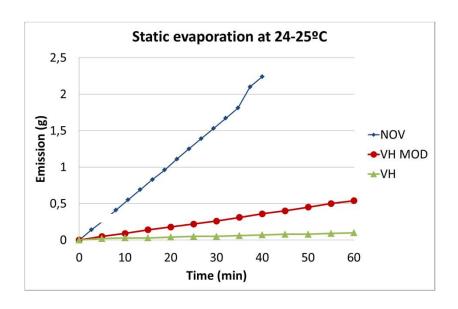


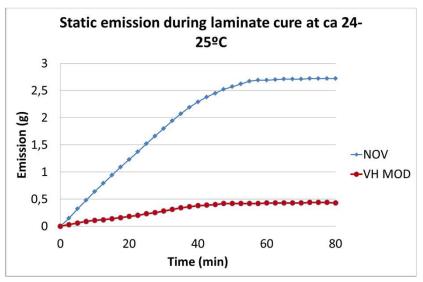
Hydrochloric acid 5,5 months

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Emission reduction

- ☐ Static emission measurement at 24-25°C (recording weight change over time is recorded either for pure resin or a typical laminate during cure)
- ☐ Emissions in the 5% styrenated resin and the styrene free resin are significantly reduced.









Laminating properties VH MOD

□Surface cure

- The surface cure is different. Acceptable surface cure can be obtained after 2-3 h.
- For a completely tack free surface a plastic film can be applied.

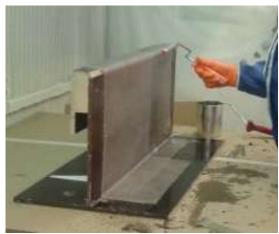
□Impregnation and wetting of reinforcement:

- Good wetting and impregnation of traditional fabric can be achieved.
- Traditional CSM works well for flat laminations.
 For complex geometries binder-free CSM types can be successfully used (e.g. Ilium and OCV).

□Secondary bonding

 Cohesive failure observed after 1-5 days overlamination time.

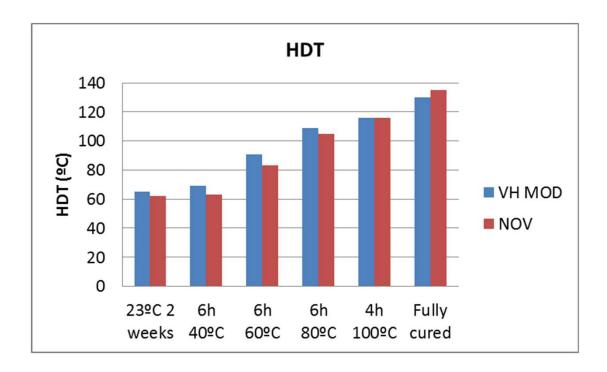






Post-curing

- ☐ Already at relatively low post-curing temperatures of 60°C good conversion and postcuring can be acheived for the VH MOD.
- ☐ For the VH resin this difference in post-curing at lower temperatures can be even more pronounced.





Post-curing

- ☐ Effect on corrosion resistance
 - Example Fuel type C + 10 % ethanol at 25°C
 - VH MOD

	Non-	post-c	ured	6 h at 60°C			4 h at 100°C		
Exp. time (months)	Ret flexural modulus	Ret Barcol hardness	Weight change (%)	Ret flexural modulus	Ret Barcol hardness	Weight change (%)	Ret flexural modulus	Ret Barcol hardness	Weight change (%)
0	100	100	0.0	100	100	0.0	100	100	0.0
1	105	90	0.8	97	93	0.4	97	108	0.1
3	84	83	1.1	91	92	0.6	97	100	0.2
6	90	70	1.4	90	80	0.9	97	93	0.4

Retention of flexural modulus Absorption – weight change



Case studies

- ☐ Composite structures inside storage tanks for different types of fuels and refinery products and by-products.
- ☐ The work has to be performed inside the tank in confined space
 - Styrene emissions are critical.
 - Ventilation is difficult and expensive.
 - If allowable styrene emissions are exceeded the work has to be stopped.
- ☐ The VH MOD resin shows excellent resistance to solvents in line with epoxy novolac or similar resins used today.
- ☐ Styrene emissions were significantly reduced giving better work environment and shorter total installation time.
- ☐ The resins showed good application properties.





"The styrene concentrations as measured in the breathing zone of six workers during top lamination with lowemission resin are well below the 8-h TWA exposure limit of 85 mg/m3 (maximum of 13,5 mg/m3 or 16% of the OEL). "

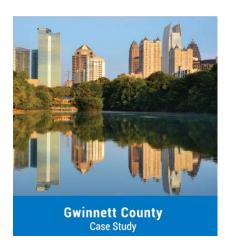
CIPP



- ☐ VH resin as CIPP resin
- ☐ Vinyl hybrid resin especially formulated for Cured-In-Place Pipe
 - Similar liquid properties to styrenated
 - Similar wet-out and cure characteristics compared to styrenated
 - Meet chemical resistance criteria in ASTM F1216
 - Similar flexural creep profile (D2990)
 - Provide a more environmentally and organism friendly alternative, perceived as odorless



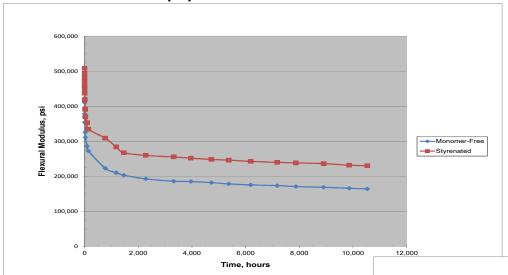
Resin	Units	Monomer-Free	Styrenated
Туре		Neat	Neat
Non-Volatiles	%	>96.0	58.0
Viscosity	cps	4,250	4,300
Thix Index		4.5	4.5
Specific Gravity		1.1	1.1
Gel Time @ 140°F	min	20 – 30	20 - 30
Time to Peak Exotherm @ 60°C	min	25 – 35	25 – 35
Peak Exotherm @ 60°C	°C	250 - 300	360 – 410



CIPP (2)

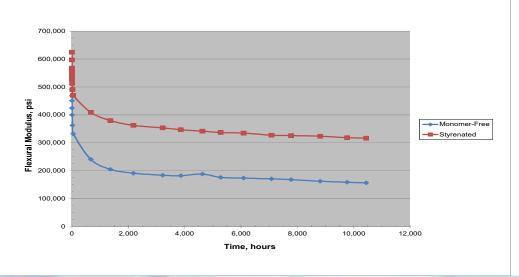


☐ Flexural creep profile



ASTM D2990 Comparison of Monomer-Free and Conventional Styrenated Resin Creep Modulus - Neat

ASTM D2990 Comparison of Monomer-Free and Conventional Styrenated Resin Creep Modulus - Filled



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Concluding remarks

- ☐ Polylite® HS technology enables a **significant emission reduction**.
- ☐ The VH and the pre-accelerated modification thereof, VH MOD, have shown very good corrosion resistance in the tested environments. Minimum 6-months-testing proposes good resistance to
 - Solvents including alcohols, aromatics and chlorinated aromatics
 - Alkaline environments such as sodium hydroxide
 - Organic amines as diethanol amine
 - Strong inorganic acids
 - Relatively good resistance to sodium hypochlorite
- ☐ The application properties have been assessed as good including impregnation and wetting of fabrics and CSM reinforcement and hand-lamination process.





Thank you!

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