derakane™ signia™ resins

low styrene emission

introduction

Introduced in 1965 to combat corrosion in hot, wet chlorine environments, Derakane™ epoxy vinyl ester resins have become the industry standard for corrosion-resistant fiber reinforced polymer (FRP) equipment. High performing derivatives have been introduced over the years to allow vinyl ester solutions for expanded chemical environments, high temperature performance and areas requiring improved toughness. With the introduction of Derakane™ Signia™, Ashland has leveraged new production capabilities to modernize resin features including enhanced environmental performance, better workability, improved workplace conditions and worker satisfaction.

features

Derakane™ Signia™ resins provide significant advantages for fabricators, designing engineers and owner/end users of corrosion-resistant FRP equipment.

in the shop

- low styrene emission
- improved shop efficiency
- longer shelf life

in the field

- unchanged polymer backbone
- identifiable resin system

In this paper we will review Derakane™ Signia™ resin low styrene emission technology. Derakane™ Signia™ 411 bisphenol-A epoxy vinyl ester resin was evaluated in both laboratory studies and shop trials to demonstrate how this valuable new technology provides a cleaner, more efficient shop environment, while simultaneously meeting regional styrene emission requirements.

Today many fabricators are challenged with finding and retaining qualified, experienced operators to meet current demands. Anticipating these needs, Derakane™ Signia™ resins were designed to deliver improved processing characteristics driving faster laminate consolidation, lower foaming, and greatly reduced sanding for application of secondary laminations. These benefits, combined with reduced styrene emissions and less odor in finished parts, lead to greatly improved shop efficiency and cleanliness, ultimately resulting in a more desirable workplace.

vapor suppression effectiveness

Reduction of styrene emission has gained importance to the composites industry over the past several years with the introduction of MACT and many regulations around the globe regarding human exposure to styrene. Derakane™ Signia™ resins contain a unique vapor suppression technology that greatly reduces styrene emissions upon curing. Because the suppression technology requires air to pass over the laminate surface in order to promote formation of the vapor suppressant film, the FRP fabrication method used governs its efficacy. Once formed, this film creates a barrier to block the evaporation of volatile compounds like styrene. For laminate production by hand layup the suppression film begins to form once consolidation and rollout has stopped. In non-atomized spray-up applications, the suppression film forms once resin spray-up stops. Styrene emission occurs when the resin surface is disturbed for processing, but the suppression film quickly re-forms. In filament winding the rotating mandrel provides good air flow at the laminate surface and promotes rapid formation of the vapor suppression film.

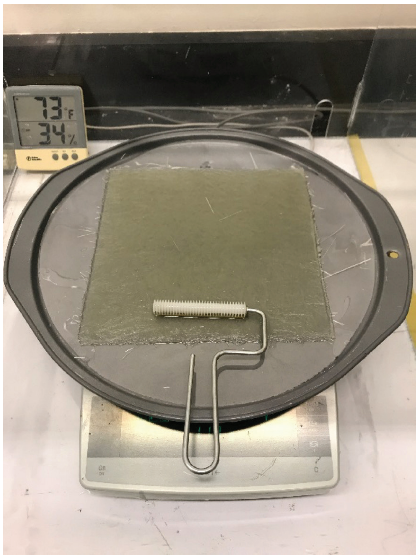


Figure 1: Derakane™ Signia™ 411 vapor supression effectiveness test specimen

All vapor suppression testing was performed and results calculated according to rules promulgated by U.S. EPA regulations establishing the RPC MACT (Subpart WWWW). Test methods used are defined on page 46, Appendix A to Subpart WWWW – Test Methods Vapor Suppressant Effectiveness Test Protocol[1]. A Signia™ 411 test specimen is pictured in Figure 1.

The calculated Vapor Suppression Effectiveness (VSE) factor for Derakane™ Signia™ 411 and Equivalent Non-Vapor Suppressed (also known as non-LSE) Styrene Content are reported in Table 1. The actual styrene content in Derakane™ Signia™ 411 is 44%, but its vapor suppression technology allows it to perform the same as resins with far less styrene content. This is seen in the second row of Table 1 – the percent of styrene shown here is what a typical resin would contain to achieve the same emissions as the EPA calculates for manual layup, non-atomized spray-up or by filament winding. Reinforcement content also affects the rate of styrene emission.

resin application method	manual	non-atomized mechanical	filament winding
derakane™ signia™ 411 resin emissions (lbs/ton)	104	78	118
equivalent non-vapor suppressed styrene content (%)	37	35.7	32.4
40 C.F.R. Part 63 Subpart WWWW Emission Calculation Factor (VSE Factor): 0.55[1]			

Table 1: Derakane™ Signia™ 411 Resin Emissions Calculations.

lower styrene odor

In trials at various fabrication shops, workers noted far less styrene odor during fabrication. Finished, cured laminates also had considerably less styrene odor as compared to non-Signia™ resins. When samples were transported in closed containers, a lack of styrene odor was noted upon opening as compared to traditional epoxy vinyl ester (EVER) and unsaturated polyester (UPR) resins based composites. At the Ashland Corrosion Science Center the amount of styrene emitted by neat castings of cured resin was measured using headspace gas chromatography (HSGC)[2] with a mass spectrum detector (MSD). A typical sample within a 25 mL headspace vial is represented in Figure 2. Resin samples were tested 2 and 24 hours after cure. This interval was chosen since this time is representative of how long a fabricator would be working on an FRP part in a typical shop. Test samples were prepared by adding a drop of promoted and initiated resin with a 15 minute cure to a 25 mL headspace vial. The vial then was sealed and measured at 25 °C (75 °F) by headspace GC using a fused silica HP-624 capillary column attached to a MSD operating in single ion mode (m/z 57 and 91).

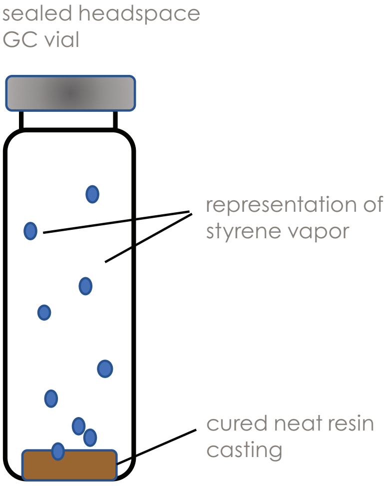


Figure 2: Sealed headspace gas chromatography vial with cured resin casting.

Looking at Figure 3, we see the amount of styrene emitted by Derakane™ Momentum™ 411-350 is dramatically higher than that of Derakane™ Signia™ 411. In fact, the Momentum™ resin casting overloaded the detector when measured 2 hours after cure. If the detector had been able to measure the amount of styrene emitted from the Momentum™ casting 2 hours after cure, it would have been several orders of magnitude higher than what is seen for the Signia™ sample, Figure 3, top graph. This dramatic difference in measured styrene emission after cure demonstrates why customers experienced substantially reduced styrene odor in finished laminates for Signia™ 411 compared to other epoxy vinyl ester resins during shop trials.

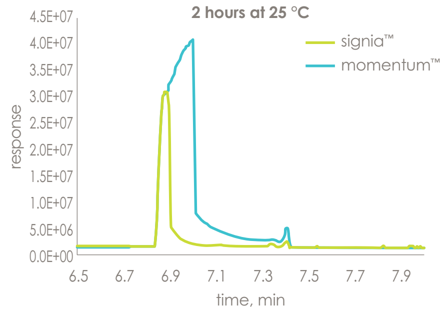
less material loss

As Derakane™ Signia™ 411 cures, its low styrene emission technology significantly reduces the loss of styrene compared to non-LSE resin systems. This means that more of the styrene present in Signia™ resin is converted to cured laminate. Derakane™ Momentum™ 411-350 and Derakane™ Signia™ 411 serve nicely to demonstrate this effect by comparing the amount of weight lost after cure for both resins. Data presented in Figure 4 was collected using the same test apparatus (Figure 1) and method employed to derive the VSE values described earlier in this paper. Looking at Figure 4, Derakane™ Signia™ 411 retains 3% more weight than Momentum™ 411-350. For a cured laminate this means 3% less liquid Signia™ 411 resin is needed to obtain the same resin to reinforcement ratio as Momentum™ 411-350. It's important to note the savings is specific to the laminate construction used to establish the VSE factor. A different laminate construction might lead to a different styrene loss fraction. We also compared the performance of Derakane™ Signia™ 411 to other commercially available LSE technologies and found its performance to be comparable or slightly better, Figure 4.

summary

The chemistry of epoxy vinyl ester resins makes them highly reactive. When first invented they were unstable and difficult to use. Introduction of better production capabilities improved their stability and allowed them to become a material of choice for corrosion applications where alloys cannot perform. In Derakane™ Signia™ resins, Ashland has combined the best technological features of the Derakane™ and Hetron™ lineage with additional new learnings to introduce a leap forward in stability and usability compared to previous generations of epoxy vinyl ester resins.

For shop owners, styrene emission is an important consideration for environmental permitting requirements as well as for the quality of the working environment for their employees. This paper demonstrates how the low styrene emission technology built into Derakane™ Signia™ resins addresses these needs by reducing styrene emissions during fabrication of FRP equipment. In Signia™ resin trials shop workers routinely commented and acknowledged lower styrene odor in their work area. This, combined with Derakane™ Signia™ 411's improved processing characteristics, lead fabricators to prefer working with Derakane™ Signia™ resins.



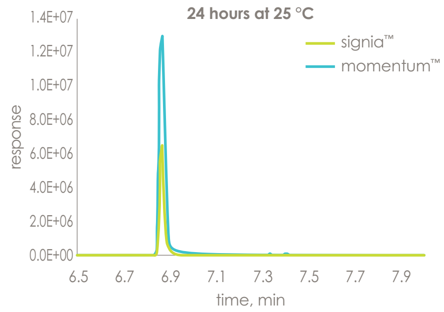


Figure 3: Styrene emission from resin castings 2 hours after and 24 hours after cure.

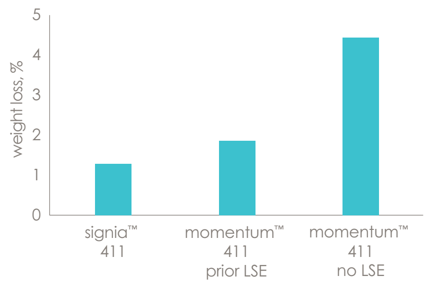


Figure 4: Percent weight loss after cure of low styrene emission and non-low styrene emission test specimens.

[1] *40 C.F.R. Part 63, Subpart WWWW, Table 1*

[2] *https://en.wikipedia.org/wiki/Headspace_gas_chromatography_for_dissolved_gas_measurement*

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