derakane™ signia™ resins

improved shop efficiency

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 improved environmental performance, better workability, improved workplace conditions and worker satisfaction.

features

Derakane™ Signia™ resins provide significant advantages for fabricators, design 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 expand on how Derakane™ Signia™ resins improve shop efficiency. Numerous shop trials performed with Derakane™ Signia™ 411 bisphenol-A epoxy vinyl ester resin demonstrate how Signia™ technology provides a cleaner, more efficient shop environment.

Today many fabricators are challenged with finding qualified and experienced operators to meet current order 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. Additional benefits include reduced styrene emissions and odor with innovative cure packages that can eliminate production steps when making thick parts. All of these characteristics lead to greatly improved shop efficiency and cleanliness resulting in a much more desirable workplace.

improved laminating

reduced foaming

Reduced foaming in Derakane™ Signia™ resins leads to fewer entrapped gas bubbles and faster consolidation of reinforcement layers. In Figure 1, the foaming of Derakane™ Signia™ 411 (left) and Derakane™ Momentum™ 411-350 resins (right) is compared 90 seconds after adding Norox®[1] 925H MEKP. The lower foaming observed in the Derakane™ Signia™ sample leads to easier rollout resulting in laminates with fewer voids. In this study, Derakane™ Signia™ 411 was promoted with 0.2 parts per hundred (pph) Cobalt Naphthenate 6% and 0.05 pph Dimethylaniline (DMA) and Derakane™ Momentum™ 411-350 was promoted with 0.2 pph Cobalt Naphthenate 6%. Both were initiated with 1 phr of high dimer Norox® 925H MEKP for a 15 minute gel time.

Figure 1: Comparison of foaming in promoted and initiated Derakane™ Signia™ 411 (left) and Derakane™ Momentum™ 411 (right) resin 90 seconds after initiation.

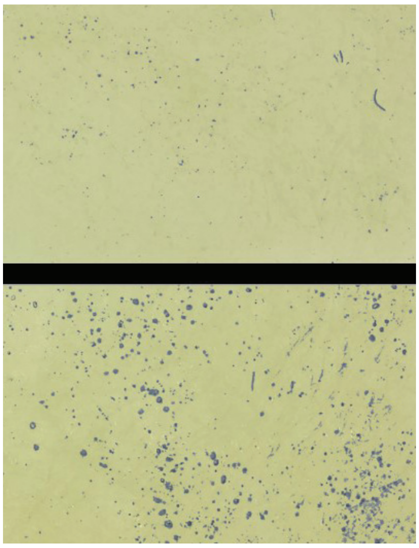

Figure 2: Backlit images of Derakane™ Signia™ 411 (top) and Derakane™ Momentum™ 411 (bottom) laminates used in image analysis for void content analysis.

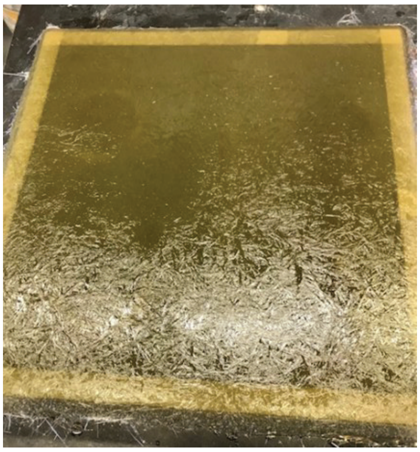

Figure 3. Picture of a completed secondary bonding test laminate with border tape separating the edge of the first and secondary layers.

fewer entrapped voids

In shop trials with Derakane™ Signia™ 411 resin, operators consistently noted that wet-out and air release improved significantly when compared to Derakane™ Momentum™ 411-350 and Hetron™ 922. To demonstrate this improvement, experiments were conducted on laminates made with 2 plies of 450 g/m² (1.5 oz/ft²) chopped strand glass mat with 10 passes of a serrated roller to consolidate the plies and eliminate air bubbles. The resin to glass ratio for these experiments was controlled at 65% resin to 35% glass. Figure 2 shows typical images of laminates from this experiment. Note the appearance of fewer voids in the Signia™ resin laminate (top) compared to the Momentum™ laminate (bottom). An in-house imaging tool was used to quantify the number of voids in each laminate. Derakane™ Signia™ laminates had 0.008 to 0.01 percent voids compared to 0.04 to 0.06 percent voids in the Derakane™ Momentum™ laminates.

easy surface preparation

Reducing fabrication steps is one of the best paths to improve shop efficiency. Reducing the amount of preparation needed to apply secondary lay-ups of FRP is a key benefit of Derakane™ Signia™ resins. Two methods were used to confirm good secondary bonding with Signia™ 411 – qualitative analysis through fiber tear evaluation and quantitative shear strength values through ASME RTP-1-2017 Appendix M5 bonding test standard[2].

secondary bonding test laminate preparation – fiber tear evaluation

Fiberglass-reinforced laminates were prepared for fiber tear evaluation using standard hand lay-up preparation methods. The laminates were prepared in the Ashland Corrosion Science Center (Dublin, Ohio) and at various customer locations. Several resin cure schedules based on MEKP, Cobalt Naphthenate, and Dimethylaniline were used. To understand the effect of reactive mass on cure and secondary bonding fiber tear, thick and thin laminates were prepared. Primary laminates were fabricated, aged, and subjected to surface preparation by sanding/grinding or no surface preparation at all. A secondary lamination was then applied to the primary laminate. The final laminate constructions were split at the interface between the primary and secondary layers using a wedge. The degree of fiber tear due to the failure of the secondary bond was evaluated according to an established scale.

thick laminate preparation

Primary laminates were constructed using 7 plies of 450 g/m² (1.5 oz/ft²) chopped strand mat and a promoted and initiated epoxy vinyl ester resin. The primary laminates were cured at ambient conditions for 24 hours. In some cases, primary laminates were post-cured for 4 hours at 82 °C (180 °F) to simulate extended aging. A secondary lay-up of 7 plies of 450 g/m² (1.5 oz/ft²) chopped strand mat and a promoted and initiated epoxy vinyl ester resin was applied on top of the primary laminate. For ease of driving the wedge between the primary and secondary layers, a one-inch border of tape was applied to the primary laminate before application of the secondary layer (see Figure 3). The laminates were cured at ambient conditions, 17 °C to 26 °C (63 °F to 79 °F), for a minimum of 72 hours, followed by separation of the primary and secondary layers to evaluate bond peel resistance and fiber tear. A completed secondary bonding laminate is shown in Figure 3.

thin laminate preparation

Thin laminates were prepared as described above in the Thick Laminate Preparation section, but using 3 plies of 450 g/m^2 (1.5 oz/ft^2) chopped strand mat instead of 7 plies.

secondary bonding fiber tear

The measurement of secondary bonding using the wedge or peel test is difficult due to the subjective nature of the test. Therefore, a wedge test standard was developed by Ashland Technical Service. Figure 4 shows the relative level of fiber tear at 20, 60 and 100%.

The general set-up of the wedge test is shown in the first picture of Figure 5, with the wedge placed between the primary and secondary laminate layers. Figure 5 also shows fiber tear results from Derakane™ Signia™ laminates without a post cure and with a post cure of 4 hours at 82 °C (180 °F). The tested laminates exhibited excellent fiber tear and are representative of the typical fiber tear observed in Derakane™ Signia™ shop trials and Ashland lab trials.

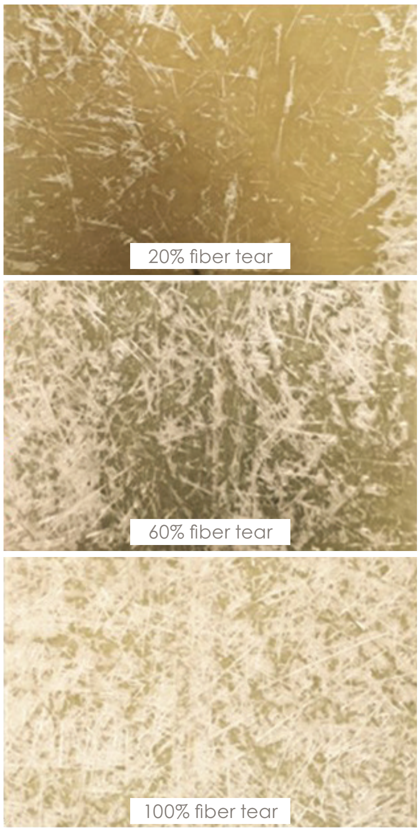

Figure 4. Secondary Bonding Wedge Test example scale.

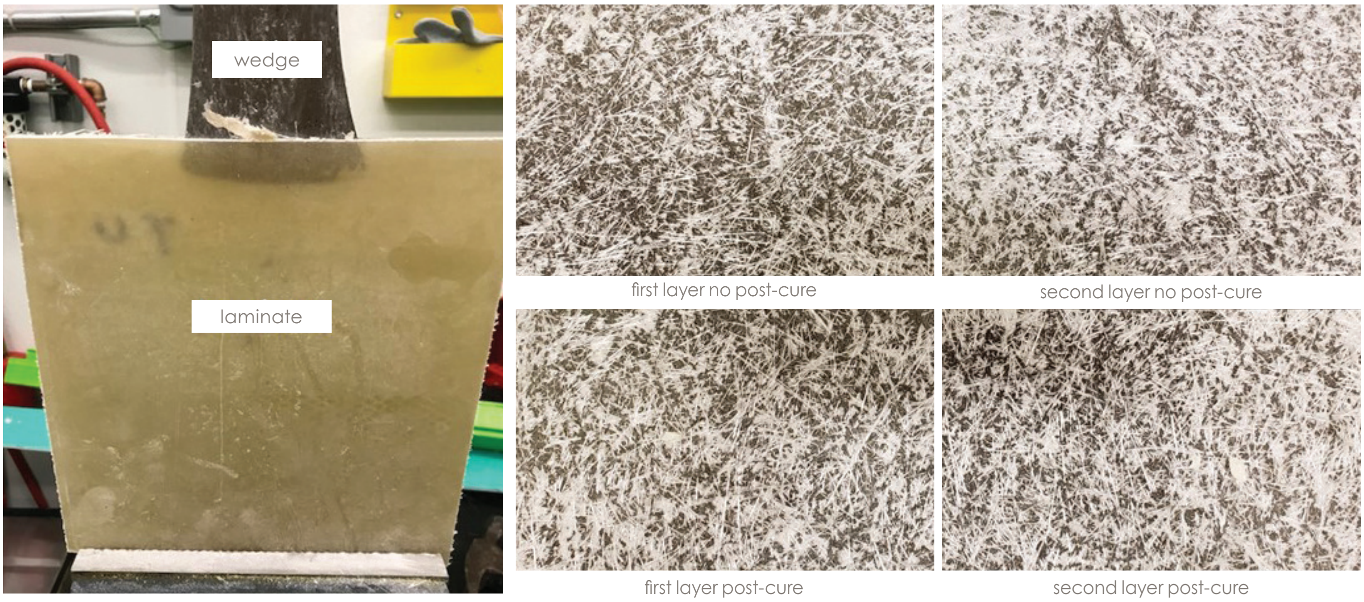

Figure 5. Secondary bonding wedge test setup (top) and tested secondary bonding laminates with no surface preparation by sanding of the primary layer (bottom).

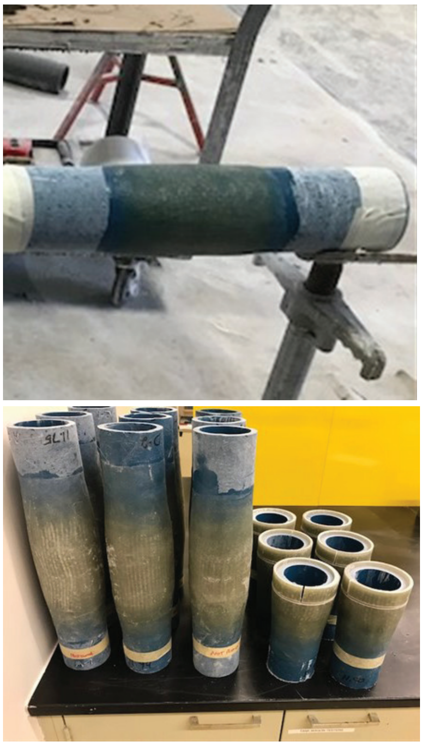

Figure 6. Preparation of M5 test specimens in a customer's shop (top) and precut and machined M5 test specimens (bottom).

In tests conducted on laminates where the corrosion barrier was the interface with the secondary layer, poor secondary bonding was typically observed. Upon evaluation, it was found dis-bonding occurred due to a lack of reinforcement at the interface. Because the corrosion barrier is resin-rich, the bond is only as strong as the resin. When trying to bond to the surfaces that had cured against the mold, we found residual mold release also caused clean dis-bonding with no fiber tear. Another impediment to secondary bonding was found with filament wound laminates where there was no chopped strand glass or intimate contact of glass between the primary and secondary layers. Based on these observations, when there is a continuous resin rich layer, some type of surface prep or application of chopped strand glass should be applied to prevent dis-bonding.

When fabricating equipment to a manufacturing standard such as RTP-1 or an end user specific specification where sanding is mandated between secondary layers, these procedures should be followed and surface preparation should be performed as directed by the standard or specification. In cases where sanding was done, fabricators commented that Derakane™ Signia™ resin did not gum up the sanding disks as much as current resins. This benefit is attributed to the improved surface cure driven by the kinetics of the Signia™ cure and the styrene suppression film that prevents air inhibited cure at the resin surface. In secondary bonding studies and in full scale equipment fabrication trials, Derakane™ Signia™ resins typically developed a higher Barcol in a shorter period of time – typically, greater than 30 in 1.5 hours. Further studies on this capability are being conducted and will be presented in the near future.

ASME RTP-1-2017 appendix M5 secondary bond test specimen construction and testing

The ability to quantify secondary bonding in a way that is meaningful to fabricators was done using the ASME RTP-1-2017 Appendix M5 Secondary Bonding test standard. Following the procedures defined in Appendix M5, an FRP pipe section was fabricated using Derakane™ Signia™ 411 resin. A 15 minute gel time was used for the pipe and secondary lay-up of the M5 test specimens. The pipe was allowed to cure for a minimum of 72 hours between 21 °C (70 °F) and 27 °C (80 °F) before the secondary laminate was applied. The secondary lay-up on prefabricated pipe is shown in the top picture of Figure 6. The pipe is pigmented blue so the pipe laminate can be distinguished from the secondary laminate for test specimen machining. Machined specimens are shown in the bottom picture of Figure 6. ASME RTP-1-2017 Section 4-320 and Appendix M5 specify that the pipe surface should be sanded before application of the secondary laminate. The goal of this testing was to evaluate the ability of Derakane™ Signia™ 411 resin to bond to prepared and unprepared surfaces; therefore, some samples were made with surface preparation while others were made with no surface preparation.

Machining and testing of specimens were conducted by Fiberglass Engineering Mechanics (FEMech) Testing Lab, in Harrison, AR, as well as the Ashland Physical Testing Lab (APTL) in Dublin, OH. The top picture in Figure 7 shows a close-up view of the M5 test specimen after machining. The bottom picture shows a close-up view of the M5 test specimen in the Instron™ compression fixture.

Using the ASME RTP-1-2017 Appendix M5 test standard, a shear strength value is calculated to evaluate how well a secondary bond is made by a fabricator. To pass, the specimen must reach a minimum shear strength value of 13.79 MPa (2000 psi). Test samples were prepared in two RTP-1 certified shops by Appendix M5 certified fabricators. Sanded and un-sanded pipe samples were sent to Ashland's Physical Testing Lab (an ISO9001 independently certified lab) and to FEMech Testing Lab.

Test results are summarized in Figure 8. This data clearly shows that shear strength values for sanded (Prep) and non-sanded (No-Prep) pipe are similar and, in all cases, bonding exceeded the minimum M5 shear strength requirement of 13.79 MPa.

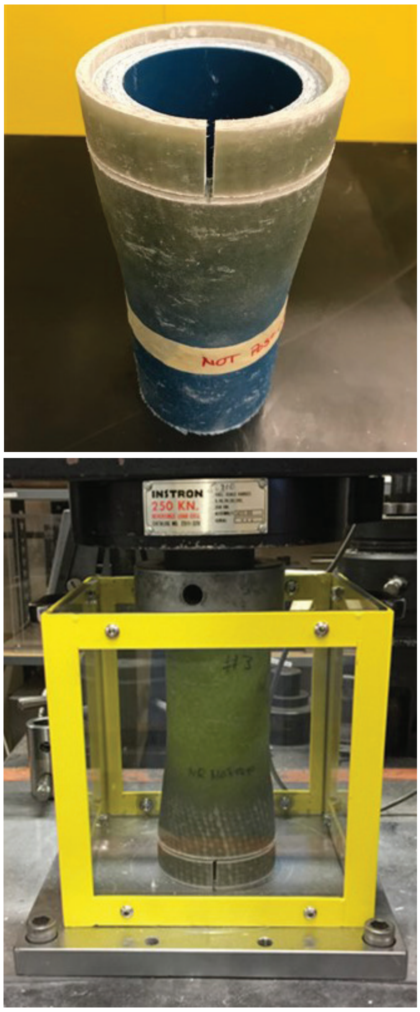

Figure 7. Machined M5 test specimen after machining (top) and M5 test specimen mounted in the Instron compression fixture (bottom).

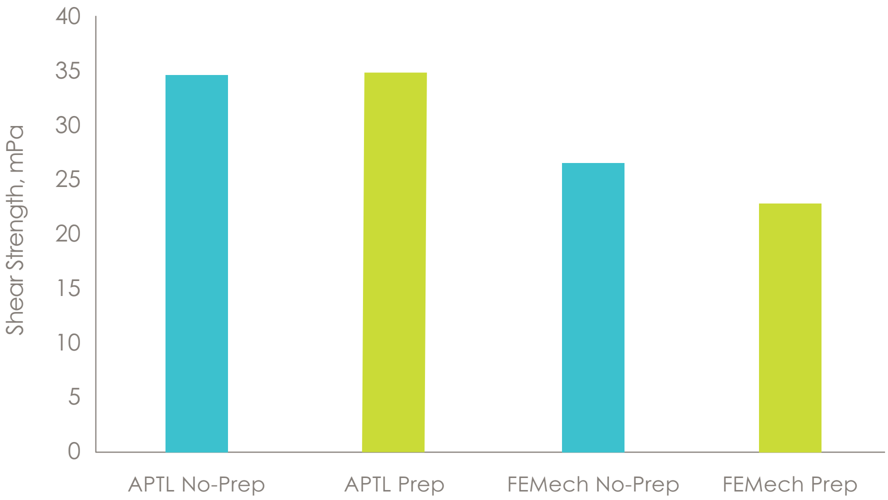

Figure 8. ASME RTP-1 Appendix M5 secondary bonding shear strength values for sanded (Prep) and un-sanded (No-Prep) test specimens.

Figure 9: Measurement of thick filament wound tank section made in a single continuous step with Derakane™ Signia™ 411 resin.

faster fabrication

The curing and processing characteristics of Derakane™ Signia™ 411 resin make it possible to reduce the number of steps required to make thick parts, such as a hand lay-up flange on a filament wound vessel. Derakane™ Signia™ is not sensitive to air inhibition which leads to excellent Barcol development and surface cure, allowing fabricators to begin secondary lay-ups sooner than with other resin systems. This is useful in flange attachment lay-ups and application of repad for construction of headers, columns and tanks. Derakane™ Signia™ resin technology allows the fabrication of thick parts without warping and scorching related to heat generated during exotherm. In several customer trials, very thick parts were made successfully without any issues related to heat development.

filament winding of thick tank sections

The vessel wall pictured in Figure 9 is 27 mm (2 in.) thick with a high glass content (~65%). It was produced in one continuous winding process using a common MEKP / Cobalt Naphthenate cure. When fabricating vessels by filament winding, the fabricator can build the corrosion barrier by hand lay-up and spray-up and then take advantage of Derakane™ Signia™ 411 resin's excellent secondary bonding by not having to sand the surface before starting the winding process. It's important to note that the best practice is to apply a layer of resin and chopped strand glass between the cured corrosion barrier and the filament winding layer. This practice is common when laying up on a sanded surface.

hand lay-up of thick laminates

When building large manway flanges, it commonly takes a fabricator three to four steps to lay up the complete corrosion barrier and structural layer. It is common for there to be 26 to 36 layers of alternating 450 g/m^2 (1.5 oz/ft^2) chopped strand mat and 680 g (24 oz) woven roving. Typically, MEKP/CHP initiator blends are required to achieve the necessary working time and minimize heat development during exotherm. With Derakane™ Signia™ 411 resin, Copper Naphthenate (CuNap) has been successfully used to reduce the peak exotherm and extend the gel-to-peak exotherm with minimal effect on gel time. This gives fabricators the time needed to lay up the full reinforcement sequence for the flange, while preventing high heat development that can scorch the upper layers of resin and reinforcement. In Table 1, the effect of CuNap can be seen in standard 100 gram cup gel time studies. According to this data, high hydrogen peroxide (H_2O_2) containing MEKP initiators like Luperox®[3] DDM-9 are more effective at reducing the peak exotherm temperature when used in conjunction with CuNap. The exotherm reduction is not as large with high dimer MEKP initiators like Norox® 925H.

resin temperature, °F	75	75	75	75
derakane™ signia™ 411 resin, pph	100	100	100	100
6% cobalt, pph	0.15	0.15	0.15	0.15
10% cunap 8%, pph	0	0.25	0	0.25
high dimer MEKP, pph	1	1	—	—
high H_2O_2 MEKP, pph	—	—	1	1
GT, min	28	28	27	33
G-PE, min	20	41	23	54
PE °F	325	275	310	110

Table 1: Effect of Copper Naphthenate in parts per hundred (pph) on and MEKP choice on gel time (GT), gel-to-peak exotherm (G-PE) and peak exotherm (PE) in 100 gram T-Cam cup gels.

In a recent trial, a fabricator made a manway with an inside diameter of 91 cm (36 in.) and a 20 mm (¾ in.) thick flange in one layup, significantly reducing the amount of time needed to make the part. The amount of drawback or "curl" of the final part is also critical in determining the acceptability of the part. Figure 10 illustrates the minimal drawback on the finished flange made with the continuous lay-up process. This amount of drawback is consistent with flanges made using the current multi-step process. Using Derakane™ Signia™ 411 resin with CuNap allowed the customer to reduce fabrication time from a multi-step production process that took 2–3 days from start to demold to a 6 hour process from start to demold.

Figure 10: Derakane™ Signia™ 411 with CuNap manway on mold (top) and measure of flange drawback or curl after cure (bottom).

summary

The chemistry of epoxy vinyl ester resins makes them highly reactive and, when first invented, they were unstable and difficult to use. The introduction of better production capabilities improved their stability and allowed them to become a material of choice for corrosion applications where alloy could not 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.

The experiments described in this paper demonstrate Derakane™ Signia™ resin technology is capable of improving shop efficiency through less surface preparation, faster Barcol development, less waiting time between the application of additional laminates, and the ability to make thicker parts. This results in improved labor efficiency through a reduction or removal of entire fabrication steps, improved shop cleanliness and overall faster processing of high quality FRP parts. Since Ashland's introduction of Derakane™ Signia™ resin technology, it has been widely embraced by shop fabricators and owners for the landmark improvements and value it brings.

[1] *Norox® is a registered trademark of United Initiators.*

[2] *ASME Standard RTP-1-2017, Appendix M5, Qualification of Laminators and Secondary Bonders, The American Society of Mechanical Engineers, Two Park Avenue, New York, NY 10016-5990, 2017.*

[3] *Luperox® is a registered trademark of Arkema Inc.*

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