Low Emission Epoxy Vinyl Ester Resin in Pultrusion

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By

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Introduction

The Clean Air Act is now being enforced. Since styrene is considered a Hazardous Air Pollutant (HAP), it has effects on the Pultrusion Industry in the US. The final ruling\(^1\), published April 21, 2003, has reviewed the best available data in the industry and established a maximum achievable control technology (MACT). This establishes a minimum level of control that local authorities are responsible for enforcing. In reviewing the best available data, the Federal EPA determined certain technologies were ineffective, and others quite effective at reducing styrene emissions. In particular, lowering the styrene in a resin was established to have an insignificant effect on emissions. While the MACT has been set for the Federal concerns, local authorities often wish to have tougher regulations. This seems to be turning into a demand for lower styrene resins for pultrusion operations. This demand is present for both unsaturated polyester resins and vinyl ester resins. While there are acceptable low styrene solutions in epoxy vinyl ester resins, there does not seem to be any evidence it will reduce on emissions.

PIC/SPI\(^2\) studies

**PHASE 1**

In the early 1990’s the Pultrusion Industry Council (PIC), in coordination with the SPI set up a study to determine styrene emissions in a pultrusion operation. The first phase of the study had two main goals. The first was to establish a process to measure emissions and prove that it was an accurate measurement. The second goal was to identify factors that had a significant effect on styrene emissions. After developing and validating the test procedure, the potential control factors they examined were:

1. Resin mixture bath and reservoir surface area
2. Covering
3. Resin mixture temperature
4. Resin % styrene
5. Line speed
6. Part surface area
7. Blower speed

This study showed that the percent styrene in the resin did not have a significant effect on the styrene emissions. Although a surprise to everyone, it is tough to deny the results.

**PHASE 2**

With the results of Phase 1 showing that air movement over the resin (referred to as ‘wet areas’) as the only significant variable in determining emissions, Phase 2 focused on different methods to control air flow over the resin. The goal was to quantify the effect of several process adaptations on the emissions. The study evaluated covering the wet areas – both at the maximum level, and at 66% of the maximum level. This was done with and without an exhaust. Other process controls evaluated were direct die injection and preform injection. The final variable was to reduce the air flow in the wet areas to 15 ft/sec.

Like the Phase 1 study, the entire pultrusion operation was inside a totally enclosed tent. Air flow out of the enclosure was constant, as were temperature, humidity, air flow over wet area (100 ft/sec except on the experiments with low air flow over the wet area), styrene content of resin, pull rate, and part design. Sampling started after emission became steady (+/- 10%).

The following conclusions were reached by this study:

1. Covering the resin bath had no significant effect on emissions.
2. Use of 66% wet area enclosure (WAE) gave 21% reduction in emissions.
3. Exhausting the 66% WAE captured 65% of the emissions, but had no effect on total emissions.
4. Use of maximum WAE gave 58% reduction in emissions.
5. Exhausting the max WAE captured 91% of the emissions, but increased the total emissions by a factor of 1.74.
6. Exhausting the resin bath to the max WAE slightly increased total emissions.
7. Use of proprietary die injection resulted in 99% reduction in emissions.
8. Use of proprietary preform injection gave a 91% decrease in emissions.
9. Reducing plant flow at the wet area from 100 ft/sec to 15 ft/sec gave a 46% reduction in emissions.

\(^1\) The MACT for Composites is listed in the Federal Register, Vol. 68, No. 76, Monday, 4/21/93.
\(^2\) The PIC/SPI studies are owned by those organizations, and available to their members. The Phase 2 study can be found on the ACMA website - http://www.acmanet.org/.
**NESHAP: Reinforced Plastic Composites as it applies to the Pultrusion process.**

The Maximum Achievable Control Technology (MACT) target for pultrusion is to reduce the total HAP emissions by 60%. Pultrusion operations making parts with a 1,000 or more reinforcements and a cross sectional area of 60 square inches or more were given an exemption to this MACT. Several work practices to manage air flow were cited as the appropriate MACT for such operations.

The EPA recognized five ways to reduce HAP emissions. In a very basic form, they were – capture and destroy, use of WAEs, direct die injection, preform injection and any combination of these four. Specific instruction as to what qualifies for each are detailed in the Federal Register. They allow that proper use of WAEs will give a 60% reduction. Proper use of either direct die or perform injection are credited with a 90% reduction. When employing capture and destroy technology, you would need to establish what percentage is captured and destroyed.

The conclusions reached by the EPA are very similar to those shown in the SPI/PIC studies. The styrene percentage in the resin is not believed to lower styrene emissions at all. This is unfortunate, because if it were effective, it is a simple, and available answer. Our concern is that there seems to be a fair amount of pressure from local authorities to use lower styrene resins in pultrusion operations. While we are always hesitant to address regulatory concerns with unproven technology, this seems to be one step beyond that. This technology is unproven, the best available research indicates it is ineffective.

**Solutions to HAP emissions from applications outside of pultrusion.**

As we look at how HAP emissions from vinyl esters have been addressed in other applications, there are four basic routes. The first is process conditions, which is what the EPA recommends for pultrusion. The second is use of lower styrene resins. The third is to add a vapor suppressant. For vinyl esters, this traditionally needs to be added at the fabricator, as the vapor suppressants effective in vinyl esters can separate out on storage. The fourth solution has been to replace some portion of the HAP, with a non HAP monomer. Since local authorities regulate VOCs, and the federal government does not recognize a relationship between styrene percentage and emissions, this approach would seem to have limited value to pultruders.

**Vapor Suppressed vinyl ester resins**

Although not currently commercialized in vinyl esters sold into the pultrusion market, we do have the technology to formulate epoxy vinyl ester resins with effective and storage stable vapor suppressants. When high styrene vinyl ester resins are formulated in this manner, they perform extremely well in the EPA’s vapor suppressant test. This test is basically to make a hand lay up panel, in triplicate with and without the vapor suppressant in the resin. Use of the vapor suppressant reduces the loss of styrene by 79%. Unfortunately, no simple tests have been developed to evaluate the performance of a suppressed resin in a pultrusion operation. One would have to set up a pultrusion operation in a total enclosure and collect all the emissions to prove performance. This is expensive, and we really have no way to carry this out. One could imagine since air flow is the major variable for styrene emissions in a pultrusion operation, a vapor suppressant may be an effective solution. Vapor suppressants are activated by styrene evaporation, and deactivated by mixing. We did carry out a very simple test. We placed a 3.75 inch Petri dish on a scale, in a relatively protected area. We filled it with 75 grams of resin, and simply measured how much styrene was lost. The results are in the table below.

<table>
<thead>
<tr>
<th></th>
<th>45% EVER</th>
<th>45% LSE EVER</th>
<th>33% EVER</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>75g</td>
<td>75g</td>
<td>75g</td>
</tr>
<tr>
<td>30 min</td>
<td>74.47g</td>
<td>74.73g</td>
<td>74.50g</td>
</tr>
<tr>
<td>1 hour</td>
<td>74.05g</td>
<td>74.70g</td>
<td>74.04g</td>
</tr>
<tr>
<td>2 hour</td>
<td>73.27g</td>
<td>74.67g</td>
<td>73.15g</td>
</tr>
<tr>
<td>3 hour</td>
<td>72.49g</td>
<td>74.63g</td>
<td>72.25g</td>
</tr>
<tr>
<td>4 hour</td>
<td>71.77g</td>
<td>74.61g</td>
<td>71.44g</td>
</tr>
</tbody>
</table>

While this is a simple test, one can see that without atomization, a lower styrene resin does not seem to have a large effect on styrene emissions. It also shows that a styrene suppressed version may have a positive effect on emissions. We really can not prove one way or the other.

**Low styrene EVERs:**

For the purpose of this study we will be looking at three polymer backbones A ‘standard,’ BPA extended EVER thinned to 45% styrene. A lower molecular weight BPA extended EVER thinned to 33% styrene. Both of these polymers are currently sold into the pultrusion market. The formulations (inhibitor package, styrene level) may differ slightly, but for our purpose they can be considered identical to current commercial products. The third product will be a novel BPA EVER. Its molecular weight was chosen to match the styrene level of the lower molecular weight. Increasing that molecular weight generates a product with equal HDT, higher elongation and higher tensile modulus. It would also require a higher styrene level to give the same viscosity. The following is a table of the liquid properties of these resins, as prepared in our labs:
Therefore, with the same inhibitor package, the novel EVER is slightly more reactive than the low styrene EVER, which is distinctly more reactive than the standard BPA EVER. Lab results have shown that making the novel EVER higher molecular weight forms a more reactive resin (judged by SPI interval). We need to appreciate that the gel times are easily modified to shorter lengths by adjusting the inhibitor packages. As we move on, and look at the physical properties of these three products an interesting data point comes out.

<table>
<thead>
<tr>
<th></th>
<th>Standard BPA EVER</th>
<th>Low Sty BPA EVER</th>
<th>Novel BPA EVER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Visc (cps)</td>
<td>350</td>
<td>430</td>
<td>680</td>
</tr>
<tr>
<td>% styrene</td>
<td>45</td>
<td>33</td>
<td>29</td>
</tr>
<tr>
<td>SPIG (min)</td>
<td>13</td>
<td>12</td>
<td>10.6</td>
</tr>
<tr>
<td>SPI int (min)</td>
<td>3</td>
<td>2</td>
<td>1.8</td>
</tr>
<tr>
<td>Peak exo (°C)</td>
<td>190</td>
<td>191</td>
<td>184</td>
</tr>
</tbody>
</table>

The novel EVER, as formulated, measures close to 20% higher in flexural modulus. Other properties are very similar to the low styrene BPA EVER.

Conclusion:
There are currently no proven ‘resin solutions’ to lower styrene emissions in a pultrusion operation. Studies indicate lowering the % styrene has very little effect on emissions. No work has been done on suppressants and they are not a proven practice. There are non-commercial novel EVERs which deliver improved properties. The need for low styrene EVERs needs to be substantiated prior to bringing these novel EVERs to market.