Non-Styrene Options For Cured In Place Pipe

ABSTRACT
Styrene based polyester and vinyl ester resins are the preferred choice for Cured-In-Place-Pipe (CIPP) applications. However, there are situations where a styrene based resin is not appropriate, or not allowed by the customer specifications. This paper will discuss the non-styrene options for CIPP applications, including the advantages and limitations of each alternative. A recent CIPP application where a non-styrene, VOC free resin was used will also be covered. For this installation, a non-styrene, VOC free CIPP liner was used to rehabilitate storm water lines running through a golf course and draining into a river in Toronto, Ontario, Canada.

INTRODUCTION
Unsaturated polyester resins were first prepared in the 1800s, but the process saw significant advancement through the work of Wallace Carothers in the 1920s. The original work was done on unsaturated polyesters that contained no monomers and the materials reacted sluggishly and were solid or very high viscosity, relatively immobile liquids. The breakthrough that led to the polyester resins as we know them today was the discovery by Carlton Ellis that the addition of liquid unsaturated monomers such as styrene resulted in resins which would copolymerize at rates twenty to thirty times faster and were significantly lower in viscosity making them much easier to process.

Styrene proved to be the optimal monomeric diluent for unsaturated polyesters but initially it was expensive. The economics shifted when during World War II it was discovered that styrenated polyester resins reinforced with fiberglass yielded high strength low weight structures that also had relatively high transparency to radar beams. In addition large styrene plants were being built with assistance from the government to provide the styrene necessary for the production of styrene-butadiene synthetic rubber. Today styrene is a high volume commodity chemical with over fifty billion pounds produced annually world wide.

Insituform developed the cured in place pipe process and installed the first CIPP liners using styrene based unsaturated polyester resins in 1971. Today tens of thousands of feet of CIPP liner are installed every day with the vast majority using styrene based polyester or vinyl ester resins. Testing has shown that using styrene based resins in the CIPP process does not pose a significant heat effect for workers or the public. The exposure levels of styrene for CIPP workers and the public are well below the threshold values established by the Occupational Safety & Health Administration.

There are some CIPP applications for which styrene based resins are not recommended or their use is not permitted based on the client’s specifications. Two of the main reasons for client specifications not allowing styrene based resins are potential odor issues in homes or business connected to the line being rehabilitated, and discharge limits of styrene or other volatile organic compounds (VOCs) or hazardous air pollutants (HAPs). Styrene based CIPP resins are also not recommended for the rehabilitation of potable water lines. This paper will discuss some of the alternatives to styrene based CIPP resins for these applications and the advantages and limitations of each solution.

ALTERNATIVES TO STYRENE BASED CIPP RESINS
There are two common alternatives to styrene based CIPP resins. The first alternative is to replace the styrene in the unsaturated polyester or vinyl ester resin with an alternative reactive monomer. The second alternative is the use of an epoxy resin rather than a styrene based polyester or vinyl ester resin. There are advantages and disadvantages to each of these choices and the final solution will usually be determined by a number of factors.

There is a wide variety of potential reactive monomers that can be used as a replacement for styrene in unsaturated polyester and vinyl ester resins. The selec-
tion of the reactive monomer used to replace styrene will be influenced by the requirements of a particular application or the basis for which a CIPP specification does not allow the use of styrene. Some of the “Fitness For Use” factors affecting the selection of the replacement reactive monomer or other alternative resins for use in CIPP applications are as follows:

- **Adequate Mechanical Properties** – The choice of reactive monomer will impact the mechanical properties of the unsaturated polyester or vinyl ester resin composite. Properties in the presence of water will also need to be considered when used in CIPP applications. Adequate Mechanical Properties – The choice of reactive monomer will impact the mechanical properties of the unsaturated polyester or vinyl ester resin composite. Properties in the presence of water will also need to be considered when used in CIPP applications.

- **Adequate Corrosion Properties** – Any resin used in CIPP applications must meet the corrosion requirements as outlined in the various ASTM standards, or in some cases requirements as outlined by various specifications or those established by individual or groups of municipalities.

- **Adequate Cure and Stability Properties** – Some reactive monomers or combinations of reactive monomers cure sluggishly which can be a potential problem with CIPP applications. Reactive monomers can also have different stability characteristics affecting their fitness for use in some CIPP applications.

- **Reduced Odor Issues** – The choice of reactive monomer will have an influence on the potential for odor issues in homes or businesses in CIPP applications.

- **Need For VOC or HAP Free Resin** – Not all replacement reactive monomers will meet the requirement of VOC free or non-HAP.

- **Meeting NSF/ANSI 61 Potable Water Requirements** – Not all replacement reactive monomers will have the potential to meet the requirements of the ANSI/NSF 61 Potable Water standard in CIPP applications.

- **Cost** – The price of potential replacement reactive monomers can vary significantly but all will be higher in cost than styrene.

Epoxy resins can also be used as a replacement for styrene based vinyl ester and polyester resins. Commercial production and wide spread use of epoxy resins started in the late 1940s and they have been used in CIPP applications for 25 years. Epoxy resins form a thermoset polymer either through catalytic homopolymerization or by forming a heteropolymer by coreacting through their functional epoxide groups with different curatives called curing agents. With a heteropolymer epoxy reaction the multifunctional curing agent becomes chemically bound in the final three-dimensional structure which can strongly influence the properties of the final product. Much like the wide variety of reactive monomer alternatives there are numerous combinations of epoxy resins and curing agents. The same resin combined with different curing agents can have dramatically different properties and handling characteristics. It is also important to have the proper stoichiometric relationship between the curing agents and the resin when using multifunctional coreactants.

For the purposes of this paper we will limit the discussion to epoxy resin and hardener combinations that have been used in CIPP applications. The selection of an epoxy resin for CIPP applications requires many of the same Fitness For Use considerations pointed out when discussing the selection of the alternative reactive monomers for styrene.

**FITNESS FOR USE IN CIPP APPLICATIONS**

Determining if a non-styrene resin meets the Fitness For Use requirements of a CIPP application can vary based on the reason for requiring a non-styrene solution. Requirements will remain the same regardless of the reason for specifying a non-styrene resin while other requirements are more specific and may not allow for some solutions which may otherwise be suitable for CIPP applications. The Fitness For Use factors will be evaluated individually as each may require or allow different solutions.

Mechanical Properties - CIPP liners are designed and the required thickness determined based on their flexural strength, flexural modulus, and tensile strength. Flexural modulus is typically the controlling
factor for circular pipe, flexural strength the controlling factor in flat wall pipe, and tensile strength for internal pressure applications. Minimum design values for gravity and pressure pipes are outlined in ASTM standards F1216 and F1743. Because flexural modulus is typically the controlling factor in gravity pipeline design, resin enhancers are often used to increase the flexural modulus of resins allowing for thinner liner designs which improve flow capacity and reduce material costs. Mechanical properties of some non-styrene and epoxy CIPP resins are shown in Table 1.

The resins shown in Table 1 meet the mechanical property requirements of the ASTM standards. The mechanical properties in PET felt will show lower flexural strength and tensile strength values, similar modulus values and significantly lower tensile elongation values when compared to the neat resin cast properties. The low HDT and high elongation of CIPP Epoxy Resin I results in a product that will have a lower maximum service temperature and a lower creep retention value.

**Corrosion Properties** – The ASTM F1216 and F1743 standards contain a one month corrosion test that includes water, gasoline, vegetable oil, three different acid solutions, a soap solution, and a detergent solution. ASTM D5813 includes a one year corrosion test which includes six chemical solutions which are the same as the one month tests but with lower concentrations of the acid solutions and excludes water and phosphoric acid. In addition to the corrosion tests some municipalities have their own corrosion requirements and some specifications include different corrosion tests which may simply be variations on those found in the ASTM standards.

The corrosion properties of resins made with alternative reactive monomers can vary significantly. The choice of epoxy resin and hardener combination can also result in significantly different corrosion properties. Any resin selected must meet the corrosion requirements outlined in the CIPP specifications for any particular job.

**Table 1. Neat Resin Cast Mechanical Properties of Non-Styrene Resins.**

<table>
<thead>
<tr>
<th></th>
<th>Filled ISO Resin with Vinyl Toluene</th>
<th>Filled VOC Free VE Resin</th>
<th>Neat VOC Free VE Resin</th>
<th>CIPP Epoxy Resin I</th>
<th>CIPP Epoxy Resin II</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Flexural Strength</strong></td>
<td>10,840 psi 74.8 MPa</td>
<td>12,580 psi 86.8 MPa</td>
<td>15,250 psi 105.2 MPa</td>
<td>12,600 psi 86.9 MPa</td>
<td>15,600 psi 107.6 MPa</td>
</tr>
<tr>
<td><strong>Flexural Modulus</strong></td>
<td>660,000 psi 4,552 MPa</td>
<td>710,000 psi 4,897 MPa</td>
<td>510,000 psi 3,517 MPa</td>
<td>435,000 psi 3,000 MPa</td>
<td>442,000 psi 3,048 MPa</td>
</tr>
<tr>
<td><strong>Tensile Strength</strong></td>
<td>8,700 psi 60 MPa</td>
<td>7,440 psi 51.3 MPa</td>
<td>8,790 psi 60.6 MPa</td>
<td>7,500 psi 51.7 MPa</td>
<td>10,100 psi 69.7 MPa</td>
</tr>
<tr>
<td><strong>Tensile Modulus</strong></td>
<td>670,000 psi 4,621 MPa</td>
<td>670,000 psi 4,612 MPa</td>
<td>470,000 psi 3,241 MPa</td>
<td>386,000 psi 2,662 MPa</td>
<td>456,000 psi 3,145 MPa</td>
</tr>
<tr>
<td><strong>Tensile Elongation</strong></td>
<td>1.70% 1.90%</td>
<td>2.50%</td>
<td>11.50%</td>
<td>3.90%</td>
<td></td>
</tr>
<tr>
<td><strong>HDT</strong></td>
<td>113°C 117°C</td>
<td>105°C</td>
<td>50°C</td>
<td>77°C</td>
<td></td>
</tr>
</tbody>
</table>
Cure and Stability Properties – CIPP liners are generally cured using hot water, steam, or ultraviolet light. Some applications are also cured at ambient temperatures but the size of these liners is limited by the working time of the ambient cure system which typically limits them to spot repair liners or lateral connections or lines. For hot water and steam cure systems the stability is a function of temperature. For liners that require hours to wet out and install the resin requires sufficient stability to saturate the liner prior to putting it into a refrigerated truck for transport to the job site. Cooling the liner extends the stability of the resin for transportation to the job site and installation of the liner. The CIPP liner is cured by applying heat to the inside of the pipe and it is important that the resin system can cure effectively through the thickness of the laminate and on the outside of the liner that is exposed to the host pipe.

The copolymerization of styrene with polyester or vinyl ester resins is very efficient. When alternative reactive monomers are used to replace styrene it is important to ensure that the monomer or monomer combination reacts effectively and in a manner that forms a quality composite. Reactive monomers have different reactivity ratios which can be used to select monomers that will react efficiently with the polyester or vinyl ester resin or with other reactive monomers that may be part of the formulation. The choice of reactive monomer can also impact the storage stability of the resin and also the cure of the resin at the temperatures obtainable by the CIPP process. Some of the options for replacement monomers also show poor performance in the presence of water which can be a significant issue in CIPP applications.

The cure and stability properties of epoxy resins are dependent on the choice of hardener. It is also important that the proper stoichiometric balance between resin and hardener is achieved. A “gram/equivalent” value for a hardener is determined by dividing the molecular weight of the hardener by the number of reactive hydrogen atoms available. This will be the theoretical level required to react with one equivalent weight of the epoxy resin. Epoxy resin suppliers provide the proper mix ratios for the epoxy resin and hardener and it is important that the processor maintain these ratios. The final properties of epoxy resins can be also be affected by the cure cycle and cure time and temperature guidelines from the manufacture should be followed.

Epoxy resins have lower polymerization shrinkage than polyester and vinyl ester resins during cure. The choice of reactive monomer will affect the polymerization shrinkage of polyester or vinyl ester resins and the use of fillers can reduce the amount of shrinkage. A general guideline for polymerization shrinkage is three percent for epoxy resins and six to seven percent for polyester and vinyl ester resins.

Epoxy resins typically have significantly shorter catalyzed stability than polyester and vinyl ester resins. Epoxy resins can have a catalyzed stability of seven hours or even shorter and are generally less than twenty four hours even in a small mass. The catalyzed stability of most polyester and vinyl ester resins used in CIPP applications is closer to forty eight hours or even longer. The exotherm of an epoxy resin is propagated during cure prior to gelation rather than after gelation occurs as is the case for polyester and vinyl ester resins. The exotherm prior to gelation makes the catalyzed stability of epoxy resins very mass sensitive. A large mass of epoxy resin can not dissipate the heat from the exotherm efficiently and the temperature of the resin rises further reducing the stability. The mass sensitivity of epoxy resins can limit the size or length of CIPP liner that can be wet out and installed without significant risk of premature gelation and loss of the liner. The storage time of an epoxy CIPP liner is also limited by the short stability and the wet out and installation is often done onsite to minimize the risks.

Reduced Odor – One of the potential issues with styrene based polyester and vinyl ester resins is the styrene odor that can be released into the atmosphere during installation and cure. Styrene has an extremely low odor threshold and for most humans it can be detected at less than 0.5 parts per million. There have been cases where small levels of styrene, well below any hazardous level, have entered homes or businesses connected to a sewer or drain line being rehabilitated with the CIPP process. For this reason there are some CIPP specifications that do not allow styrene based resins to be used. To meet these specification limits CIPP installers can use epoxy resins, or polyester or vinyl ester resins that use alternative reactive monomers as a replacement for styrene.
Epoxy resins typically have very low odor levels and should not cause any odor issues in CIPP applications. When using alternative reactive monomers to replace styrene, the choice of the reactive monomer will impact the chance of odors being given off during the installation and cure of a CIPP liner. The potential for a reactive monomer to give off detectable odors will be related to its vapor pressure, boiling point, and odor threshold. The lower the odor threshold for a substance the lower the concentration of that substance required in the air to allow for human detection. The lower the vapor pressure and higher the boiling point of a substance the lower the potential for that substance to be released into the atmosphere. The vapor pressure of a liquid is the equilibrium pressure of a vapor above its liquid in a closed container. The boiling point of a liquid is the temperature at which the vapor pressure is equal to atmospheric pressure. Low vapor pressure liquids and subsequently high boiling point liquids are not readily released as vapor into the atmosphere.

**VOC or HAP Free** - Volatile Organic Compounds or VOCs are defined differently by some government bodies. The EPA defines VOCs as “any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions, except those designated by EPA as having negligible photochemical reactivity”. Environmental Canada defines VOCs as “any VOC that participates in atmospheric photochemical reactions” with a list of excluded compounds. The European Union generally defines VOCs as any organic compound having an initial boiling point less than or equal to 250ºC measured at standard atmospheric pressure of 101.3 kPa.

<table>
<thead>
<tr>
<th>Reactive Monomer</th>
<th>Odor Threshold (ppm)</th>
<th>Vapor Pressure (mm of Hg)</th>
<th>Boiling Point (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>0.32</td>
<td>5*</td>
<td>145</td>
</tr>
<tr>
<td>Vinyl Toluene</td>
<td>10 – 60</td>
<td>1.1*</td>
<td>168</td>
</tr>
<tr>
<td>Tertiary Butyl Styrene</td>
<td>NA</td>
<td>0.18*</td>
<td>219</td>
</tr>
<tr>
<td>Diallyl Phthalate</td>
<td>NA</td>
<td>0.0002**</td>
<td>329</td>
</tr>
<tr>
<td>Trimethololpropane Triacrylate</td>
<td>NA</td>
<td>0.000005**</td>
<td>381</td>
</tr>
</tbody>
</table>

* Measured at 20ºC.  
** Measured at 25ºC.  
NA = Not Available.
Based on the boiling point definition of VOC, of the chemicals listed in Table 2, styrene, vinyl toluene, and tertiary butyl styrene are VOCs and diallyl phthalate and trimethylolpropane triacrylate are not VOCs. The Clean Air Act Amendments of 1990 listed 187 chemicals as Hazardous Air Pollutants or HAPs, which included “those pollutants that cause or may cause cancer or other serious health effects such as reproductive effects or birth defects, or adverse environmental and ecological effects”. Of the chemicals listed in Table 2 only styrene is on the list of HAPs.

Epoxy resins used for CIPP applications do not fall under the categories of VOCs or HAPs. CIPP specifications which prohibit the use of HAPs would not allow for the use of styrene based resins but would allow for the use of epoxy resins or polyester or vinyl ester resins that use an alternative reactive monomer to replace styrene. Specifications that prohibit the use of both VOCs and HAPs would limit CIPP installers to epoxy resins or a polyester or vinyl ester resin that uses reactive monomers that have a boiling point above 250ºC (using the temperature based definition of VOC).

NSF/ANSI 61 Potable Water Approval – NSF/ANSI 61 is the standard which “establishes minimum health effects requirements for the chemical contaminants and impurities that are indirectly imparted to drinking water from products, components, and materials used in drinking water systems”. All drinking water components, including CIPP products used to rehabilitate drinking water lines must be tested against this standard and approved by NSF or other certified testing agencies.

Styrene based resins have been used in applications and products that meet the requirements of NSF/ANSI 61. The drinking water regulatory level of styrene is 0.1 ppm. To meet the 0.1 ppm extractable styrene limit the resins must be one hundred percent cured and post curing of pipes will typically be required to meet this requirement. For CIPP applications the heat is applied to the liner from the inside of the pipe only making it very difficult to cure a styrene to a level of one hundred percent in order to meet the NSF/ANSI 61 drinking water requirements.

Epoxy resins have been used in CIPP applications which are able to meet the requirements of NSF/ANSI 61. Some vinyl ester resins using alternative reactive monomers have also been able to meet the requirements of NSF/ANSI 61 in a CIPP application. It is important that the epoxy or alternative monomer based resins contain no free materials which can be extracted from the cured laminate and that the CIPP liner is thoroughly cured.

**Cost** - Styrene is the by far the dominant reactive monomer used in unsaturated polyester and vinyl ester resins providing the best combination of mechanical properties and processing characteristics. With over fifty billion pounds produced annually styrene is also the most economical of the reactive monomer choices for unsaturated polyester and vinyl ester resin production.

Vinyl toluene is the reactive monomer which is the closest to styrene in terms of performance and cost. The volume of vinyl toluene produced is a small fraction of the amount of styrene produced and the cost of vinyl toluene is significantly higher than styrene. A vinyl toluene based polyester or vinyl ester resin can be fifty percent or more above the cost of a comparable styrene based resin. Other options for alternative reactive monomers are generally even more expensive than vinyl toluene. Some alternative reactive monomers require the use of a vinyl ester resin rather than a lower cost polyester resin in order to meet the mechanical property requirements necessary for CIPP applications. Resins made with alternative reactive monomers other then vinyl toluene can easily cost three or four times more then a standard styrene based polyester CIPP resin.

**STYRENE FREE CIPP CASE STUDY**

The City of Toronto needed to rehabilitate approximately two hundred meters of storm water lines and culverts that carried water through a golf course and ultimately draining into the Don River which drains into Lake Ontario. The pipes needing to be repaired ranged in size from 750 to 1200 millimeters in diameter. A pipe failure in the 750 millimeter section led to the flooding of an apartment building and golf course. A CCTV inspection revealed that all pipe sections were showing sighs of rust and decay that caused leaking and threatened the integrity of the pipe.
Capital Sewer Services, INC., of Hamilton, Ontario was contracted to rehabilitate the pipes using the CIPP process. Because the storm lines emptied into a river the resin approved by the City of Toronto was a VOC free, non-styrene vinyl ester resin. The installation became part of a pilot program with the City of Toronto to reduce VOC emissions. A photo of the job site is shown in Figure 1.

The felt liners were supplied by National Liner LLC and were impregnated at Capitol Sewer’s facility and transported to the job site in refrigerated trucks. The liners were installed using water or air pressure and cured using hot water or steam. The result was a new, seam-less, liner with excellent durability and corrosion resistance and with zero VOC emissions during the wet out or installation and cure. A photo of the terminating culvert is shown in Figure 2.

CONCLUSIONS
Most CIPP installations use a styrene based unsaturated polyester or vinyl ester resin. These styrene based resins have proven to be safe and reliable and ideally suited for CIPP applications. There are situations or customer driven specifications that preclude the use of styrene based resins and for these applications an alternative product must be used. The basis for prohibiting the use of a styrene based unsaturated polyester or vinyl ester resin should be considered when determining the most suitable alternative resin system.

Vinyl toluene based unsaturated polyester or vinyl ester resins are the most economical alternative to styrene based CIPP resins and they also offer the closest match in terms of properties and performance. The higher odor threshold, higher boiling point and lower vapor pressure make them less likely than styrene based resin to cause odor issues.

Vinyl toluene is not a HAP but it is a VOC compound and like styrene it would probably not be suitable for potable water CIPP applications.

There are alternative reactive monomers that can be used to replace styrene that are not HAP or VOC compounds and which should not cause any odor issues in CIPP applications. Some of these reactive monomers have also been shown to successfully meet the NSF/ANSI 61 potable water requirements for CIPP applications. The choice of replacement reactive monomer and resin combination must meet the mechanical property and corrosion requirements of CIPP applications.

The choice of replacement reactive monomer and resin combination must meet the mechanical property and corrosion requirements of CIPP applications. The alternative reactive monomer and resin combination must process and cure properly in CIPP applications and should not perform poorly in the presence of water. Alternative reactive monomers are significantly more expensive than styrene and the resulting CIPP resins will be much more costly than a standard styrene based unsaturated polyester or vinyl ester CIPP resin system.
Epoxy resins can also be used as a replacement for styrene based polyester or vinyl ester resins. Epoxy resins have less odor issues than styrene based resins and the epoxy resins used for CIPP are not HAP or VOC compounds. Some epoxy resins have been used to meet the NSF/ANSI 61 potable water requirements. The use of epoxy resins in CIPP applications can be limited by the shorter stability and mass sensitivity of these resin systems. Epoxy resins are also significantly more expensive than styrene based polyester and vinyl ester resins.

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