Vinyl esters lead the corrosion challenge

50 years of in-service experience means composites are no longer considered ‘the last resort’ for corrosion resistant applications. Amanda Jacob reports on how the latest developments in vinyl ester resins are helping to advance composites into even more applications. Amanda Jacob reports.

Corrosion resistance is one of the key selling points of fibre reinforced plastics (FRP) over other materials. Composites don’t corrode like metals and they are capable of surviving in high temperature, severely corrosive environments. The corrosion resistance (CR) market for composites covers a wide range of applications and industries, from equipment for dealing with highly corrosive chemicals, through pharmaceuticals and food processing, to wastewater treatment. Products include tanks and storage vessels, pipes and ducting, pipe lining systems, fume extraction systems and gas cleaning units.

A brief history
Composites first found applications in the corrosion market in the early 1950s, according to Ike Shank, director of specialty resins for Ashland Specialty Chemicals Composite Polymers business. The first applications of composites in chlor-alkali facilities (where chlorine-based products are produced via electrolytic processes) utilized chlorendic polyester chemistries. Due to an inherent resistance to chlorine attack and long service life, composites of bisphenol-A chemistries were subsequently adopted by the pulp and paper industry as a stainless steel replacement. Over the years composites have become widely accepted in this industry and are now the material of choice, says Shank.

In the early 1960s another application area emerged – metal treatment and metal refining. Here the electrowinning processes and large process tanks required lend themselves to composites. There are also a myriad of applications in the wastewater treatment industry, such as sewer pipes and sewer pipe rehabilitation (a growing application), and (particularly in North America in the 1990s) odour abatement systems.

Another major application area is semiconductor fabrication facilities, where fire retardant fume systems and scrubbers are required to treat the gases coming off the process.

In terms of resin chemistry, the 1970s saw the emergence of vinyl ester resin as material of choice, mainly because of its
Award-winning projects

These FRP nozzles were made by SUSEWIND Kunststofftechnik GmbH of Winterberg, Germany, for Aluminium Bahrain BSC of Manama, Bahrain. The nozzles need to work in temperatures up to 220°C and were fabricated via hand lay-up using Dow's Derakane 470HT epoxy vinyl ester. This resin was originally designed to withstand the high temperatures associated with flue gas and this is the first known use in this particular application.

This project won one of Dow's European Fabricator Excellence Awards for Derakane and Derakane Momentum resins, which were presented during the IEC Composites Show in Paris this April. The other two awards went to Ameron International BV's Fiberglass Composite Pipe Group of Geldern, the Netherlands, for the fabrication of a high-pressure glass reinforced epoxy piping system for customers in the Middle East and South America, and Forca-Onuk JV of Istanbul, Turkey, for fabricating a family of Multi Role Tactical Platform (MRTP) boats of 9.75 m in length.

Derakane resins were introduced to the CR market in 1966, and next generation Derakane Momentum products in 2000.

better mechanical properties, says Shank. Vinyl ester has displaced bisphenol-A polyester in most areas, although chloroaluminate polyester is still used in some specific applications (such as the chloroalkali process), he says.

Flame retardant ...

Developments in vinyl ester chemistry continue, with the aim of moving composites into new areas of application. Research and development activities are concentrating on improving the performance of the resins, making processing easier for fabricators, and meeting new standards.

"Most recently Ashland has been focusing on improving the heat distortion temperature (HDT) and maximum operating temperature of its vinyl ester product line," Shank told Reinforced Plastics.

Flame retardant grades are another area of recent development. One of the traditional methods of forming flame retardant vinyl esters is to add antimony trioxide, but Ashland’s HETRON® FR 992 SR vinyl ester eliminates the need to handle and mix antimony trioxide powder, offering 'Class 1 performance right out of the drum,’ says Shank. This means that laminates made using this resin exhibit a flame spread of 25 or less in the ASTM E84 fire spread test. A value below 25 is classified as a Class 1 product, the highest rating in the test.

The resin also leads to other benefits, notes Shank. Since fabricators do not have to mix the antimony trioxide into the resin they get better uniformity of the final product, and the new resin produces translucent laminates (as opposed to the opaque laminates produced when antimony trioxide is added separately).

AOC has also been active in corrosion resistant applications for decades and continues to expand its product offerings for specialty corrosion and fire retardant applications. Its fire retardant grades include VIPER® K022-CN, a bisphenol-A epoxy vinyl ester, which contains an antimony synergist so that fabricators do not need to add one. The product contains less than 10% styrene. Laminates made with K022-CN have met a flame spread rating of 10 in the ASTM E84 fire test. Applications for the product include pipes and tanks.

For oxidizing environments typical of pulp and paper mills AOC has developed Vipel K095, a fire retardant, epoxy novolac vinyl ester containing less than 35% styrene. This product meets ASTM E84 Class I with the addition of 3% antimony trioxide - without this it meets ASTM E84 Class II. For milder chemical environments such as hoods and ducts, there is Vipel K733, a fire retardant, isophthalic polyester that contains under 40% styrene. The K733-A series has an ASTM E84 Class I flame spread rating and the K733-B series has a Class I rating following the addition of 1.5% antimony trioxide.

Dow Composite Resins' latest products include DERAKANE 510C-350 FR, a Class 1 fire retardant epoxy vinyl ester resin, with added antimony, Derakane Poolmax for use in swimming pool and spa applications (a market previously untapped by Dow), and Derakane 470HT-400, designed for gaseous desulphurisation applications and with the ability to withstand 180°C.

... with lower styrene

Lowering the styrene content of corrosion resistant resins, in line with the latest legislation, is also a priority.

AOC's latest products include Vipel F010, a bisphenol-A epoxy vinyl ester that typically contains 5% less styrene than comparable vinyl esters, according to Bruce Curry, AOC's Product Leader - Corrosion. This will help fabricators to meet the USA's new lower Maximum Achievable Control Technology (MACT) standards on styrene emissions that will be imposed on the composites industry in 2004. This resin has also just met all the requirements of the Los Angeles, California, 'Green Book' corrosion test for cured-in-place pipe. This test is designed to ensure that the cured-in-place pipe can handle periodic injections of sodium
hydroxide into the sewer. Sewer rehabilitation is one of the strongest segments for corrosion-resistant resins, says Curry.

Ashland’s vinyl ester line is available with 35% styrene to meet MACT regulations. Hetron FR 998/35 is a flame retardant product, containing less than 35% styrene. Laminates made with this resin exhibit a flame spread of 25 or less in the ASTM E84 test without additional antimony trioxide.

**Process specific**

The most widely used processes for fabricating corrosion resistant parts are hand lay-up, which is ideal for one-off and low-volume products and very large structures, and filament winding, for cylindrical items such as pipes and tanks.

One of DSM Composite Resins’ recent developments is an epoxy vinyl ester resin designed to meet the needs of filament winders, Atac E-Nova FW 1045. Flowtite Norway evaluated this product in its search for an improved vinyl ester that could come close to equalling the pipe production speeds of a standard unsaturated polyester resin. The resin also needed good mechanical properties and high levels of chemical resistance. Vinyl ester resins are also inherently low in styrene content which makes them preferable to unsaturated polyester in open moulding processes such as filament winding, notes DSM.

Flowtite tested several vinyl esters from leading producers in the filament winding of a small-diameter pipe. The best results it had previously been able to

achieve with a vinyl ester were 75% of the unsaturated polyester winding speed. With Atac E-Nova FW 1045, Flowtite was able to raise that efficiency level to 90%. Tests on the cured pipe confirmed that the faster processing speed had not compromised the high mechanical strength and stiffness properties needed.

Because Atac E-Nova FW 1045 performed so well in the trial, Flowtite used the resin for a 1 m diameter pipe project with a wall thickness of 20 mm. The production results mirrored the findings of the trial.

For infrastructure applications such as floor gratings, stairs and handrails, pultruded profiles are often used. Dow Composite Resins’ global business manager for composites Mark Siebert told **Reinforced Plastics** that the company is currently commercialising a new pultrusion product, which it will probably launch at the Composites Fabricators Association trade show in California in October. Siebert says Dow has also recently gained access to a proprietary pultrusion software program. This means that instead of making a die and testing it, the process can be modelled. Dow has introduced the software to a few customers and has received promising feedback. It wants to make the software more broadly available but has not decided on the commercial basis for this yet. Siebert says the program is unique to Dow and it is not restricted to epoxy resins.

**Business slow**

According to Siebert, the CR business is tough at present. Dow is receiving enquiries about projects up to 12 months down the line but current business is poor. The heavy corrosion market is strongly tied to industrial spending he notes, and no money is going into capital investment at present. Dow has not seen the pick-up in the second half of this year that it expected. The SARS virus is affecting business in Asia, and Europe and North America are not showing sustained recovery in demand either. The corrosion market is always very cyclical.

Siebert says Dow is not going to meet volume projections for this year and the pick-up in business is now expected to be in the fourth quarter or into 2004. He admits Dow may have been hit harder than other companies with more diverse product lines, such as polyester resins.

AOC’s Emilio Ormas, Business Manager: Corrosion & Distribution, agrees that the chemical processing sector has been hit by the weak global economy and poor earnings throughout the chemical industry resulting from overcapacity and high feedstock costs. Plant capital expenditures have been curtailed, delayed or even cancelled, which offers no new opportunities in the short term for composites. Ormas says it’s difficult to predict when the chemical industry will rebound.

The pulp and paper market is also depressed, Ormas notes. New facilities are badly needed but no construction is anticipated until recovery is well established. Until then business will come from repair and maintenance work.

The semiconductor sector is also slow as a result of contraction in the global electronics market and the overall weak economies. Some rationalization of players has occurred, with ensuing changes in capacity, and the remaining key players are discussing requirements for new facilities when recovery occurs. New facilities are anticipated, particularly in the Far East.

But it’s not all bad news, Ormas says the wastewater treatment and odour control segments is growing. Factors driving this growth include the revamping of existing infrastructure and expansion of existing systems. This involves composite cured-in-place-pipe, and repair of older, elliptical-shaped pipe, plus ductwork and scrubbers. Many projects are driven by US Environmental Protection Agency (EPA) regulations.

Demand for composites in the power market also continues to grow. Composites use in plant infrastructure is steady, with growth areas for composites including flue gas desulphurization, natural gas transmission and transportation,
Online corrosion guides

A Corrosion Guide is available at the Composite Polymers Division section on Ashland Specialty Chemical Co's website www.ashchem.com. The Guide link takes you to a table listing chemical environment, concentration of chemical (%) and maximum temperature for Ashland HETRON® epoxy vinyl ester resins and AROPCL™ unsaturated polyester resins. Click on the chemical name to show the recommendations in a separate table. There's also a search function allowing you to look for a particular chemical or a mixture of two or more. AOC has set up a separate corrosion section at www.corrosionresins.com (also accessible from www.aoc-resins.com/us) for its VIFEL® and FIREFEL® epoxy vinyl ester and polyester resins. The Resin Selector allows you to search for recommended resins in three ways - by market segment, corrosion environment, or competitive product. In the market section you choose from a list of nine industries and a list of suitable AOC products is presented. The corrosion environment section allows you to choose by chemical, concentration and temperature. The competitive product section allows you to choose a product from Ashland, Dow, Interplastics or Reichhold and find a list of comparable AOC products. On the product lists, click on the product name to go straight to a pdf file of the product data sheet.

Dow Chemical's website for DERAKANE and DERAKANE MOMENTUM epoxy vinyl ester resins at www.derakane.com includes a Fabricator Centre. Frequently Asked Questions (FAQ) section, Product and Case History Finders. The Case History Finder allows you to search for finished projects by chemical type/temperature. A Chemical Resistance Guide is available as a pdf file.

DSM Composite Resins' Chemical Resistance Guide can be accessed from www.dsm.com. You can enter the name of the chemical and its concentration, and a list of suitable DSM resins is given together with an indication of their maximum service temperature.

Interplastics' Resin Wizard at www.interplastic.com makes recommendations for its CoREZYN® vinyl ester, modified vinyl ester and isophthalic corrosion resistant resins. You input the chemical environment, maximum concentration by weight (%) and maximum temperature of exposure and a list of suitable products is presented.

and wind power generation. New uses for composite-wrapped steel pipe for gas transmission lines is showing great promise due to the lower weight, easier installation, corrosion resistant abilities and safety attributes of the composite-wrapped pipe. Compressed natural gas transportation modules are among the newest concepts in the power generation segment, as natural gas exploration companies need to transport liquid gas from fields off the continental shelf of North America.

Progress

As well as technical advances in resin chemistry, other factors are helping to increase composites' penetration of the corrosion market.

Service history is one. FRP has now been used in the corrosion market for decades and resin companies have significant case histories documenting successful projects. "It's extremely helpful to be able to provide case histories," says Ashland's Ike Shank. "Generally end-users have less knowledge about the capabilities of composites than they do of alloys when they leave universities."

Another area which Shank believes has advanced over the years is design capability with composites, and understanding that composites have non-isotropic properties and are not homogeneous like steel. Improved design software is helping to increase end-user confidence, but Shank admits that he must still spend a significant amount of time educating end-users about the capabilities of composites.

Last, but by no means least, the resin suppliers emphasise that strong technical support is essential to continue the progress of composites in this market.

Shank, who has spent 38 years in the corrosion industry, concludes that in the early days composites were either thought of as 'the last resort' for severe corrosion problems or used only as experimental projects. Reinforced plastics are now thankfully past that stage and are considered a truly viable corrosion resistant material.