Bondable Fluoropolymer Resins Can Expand Your Horizons

Many benefits can be gained by substituting fluoropolymer resins for the stainless steel and exotic alloys commonly specified for fluid contact components

‘The bond is not destroyed by immersion in petrol-based fluid &#151 not even after six months at high temperatures.’ By Anthony Bonnet and Richard Perrinaud

Today’s chemical process equipment is designed to resist the destructive forces of corrosion and abrasion and to maintain the high purity of water and chemicals needed by the pharmaceutical, medical, biotech and other process industries. It also meets the strict clean air and water requirements of the EPA, as well as the demanding safety requirements of OSHA, related to handling hazardous and toxic fluids. It’s impressive how much equipment features non-metallic materials of construction to accomplish these objectives, while simultaneously increasing productivity and reducing maintenance costs. Of particular interest is the substitution of fluoropolymer resins for the stainless steel and exotic alloys commonly specified for fluid contact components such as piping, process vessels, pumps, valves and other equipment for the handling of aggressive chemicals. The recent development of a technology that enables the production of a reactive polyvinylidene fluoride (PVDF) material is significant. Research in this area has resulted in a family of PVDF materials that offers physical, thermal, corrosion and abrasion resistance, high purity properties and unique bonding. Since the reactive chemical group is added into &#151 and chemically bonded to &#151 the backbone of the PVDF, it cannot be removed or released from the material.

What does this mean for chemical engineers and plant managers? Consider seven possible applications for such bondable resins. 1. New fluoropolymers can be bonded to other lower cost resins, such as polyethylene, polypropylene or engineered plastics, including thermoplastic polyurethanes and polyamides. 2. Reactive groups of modified PVDF offer outstanding adhesion onto metals, in some cases without the use of a primer. Because of this unique capability, they can be applied as powder coatings to steel or aluminum products requiring corrosion or chemical resistance superior to stainless alloys. 3. Bondable fluoropolymers can be used for the multilayer pipe needed for the transport of corrosive and highly permeable or high purity fluids required by the chemical, pharmaceutical and other process industries. 4. Such multilayer pipe can be used by the oil and gas industries. Bondable fluoropolymer also can be used as a protective layer in down-

hole and offshore multilayer pipe or as a barrier for fuel lines. 5. Due to its high strength and permeability resistance, bondable fluoropolymers can be specified by the food and beverage industries for multilayer pipe for the transport of drinking water and beverages. 6. The capabilities of bondable fluoropolymers allow them to be co-extruded with other lower cost and high-performance engineered plastics to fine-tune and improve their mechanical, chemical and barrier properties to specific application requirements. 7. Reactive resins have rheology that is adaptable to most processes used for the transformation of thermoplastic resins into pipe, tubing, injected parts, blown film, cast film and extrusion coatings. Reactive PVDF categories include both solvent processable grades and extrudable grades.

Now consider three innovative uses already adopted for reactive PVDF material. 1. Reactive PVDF material is being used as a liner for a two-inch, five-layer pipe that handles petrol-based fluids. A thick layer of polyethylene is sandwiched between two outer layers of reactive PVDF. There is high bond strength between the layers, and the bond is not destroyed by immersion in petrol-based fluid &#151 not even after six months at high temperatures. This same structure can be used for pipes, tubing and containers used to handle aggressive chemicals. 2. Reactive PVDF material is also being used to improve the barrier properties to alcohol of the polyamide layer in offshore flexible piping. The polyamide used in the offshore industry is recognized for its excellent aging behavior at high temperatures as well as its very good mechanical properties. In order to improve its barrier properties to fluids, such as methanol, a layer of reactive PVDF is co-extruded with the polyamide layer. The two-layer pipe offers good interlayer adhesion as well as toughness at low temperature while effectively enhancing barrier properties. 3. In a third application, reactive PVDF material is being applied as a thin protective coating on metal parts. Primers are not needed because direct adhesion is obtained on the metal parts with very good aging behavior. A variety of metals, such as aluminum, steel and copper, have been tested successfully. Salt spray tests demonstrate excellent adhesion retention of reactive PVDF/aluminum sandwiches after 10,000 hours of aging. Both chemical and corrosion resistance have been dramatically improved. Gloss and transparency of these bondable reactive fluoropolymers remain constant over extended periods of time. In addition, powder coating and solvent-based processes can be used to apply these reactive fluoropolymers. Saying there\rquote s only four major railroads doesn\rquote t paint the whole picture. The situation is even more concentrated than it seems, notes Tom Schick, senior director of distribution for the American Chemistry Council (ACC). In many cases, there\rquote s only one railroad that services a chemical plant. So for that plant, it doesn\rquote t matter if other major railroads exist, there is only one for them. No other railroad can or will take traffic to or from that plant. We surveyed our members and 63 percent of the chemical-producing plants that use rail service said they had only one railroad with access to the plant, meaning 63 percent of our industry is held captive by a monopolistic carrier. However, Raymond Atkins, associate general counsel for the Surface Transportation Board (STB), disagrees that this much of the chemical industry is captive. There is a test created by Congress that says if people\rquote s rates are below 180 percent of their variable cost, then it is presumed that they have competition and there\rquote s no market dominance. Right now at least 60 percent of chemical rail traffic falls beneath that

threshold and is deemed competitive by Congress, says Atkins. However, chemical industry spokespeople maintain there are plenty of captive plants that are being abused. When there is only one railroad available to a plant, as is the case for 63 percent of the chemical industry, it becomes a monopoly provider and the service isn\rquote t particularly good, says Schick. When there is no alternative railroad, the one that has you captive knows it is going to get your business no matter how bad the service so there is no incentive for them to improve. The chemical industry believes this situation creates an environment that not only permits poor service but also fosters higher rates. When the railroad operates on a virtual monopoly, they can charge whatever they want and the shipper must take that quote, whatever it is, says Borne. It\rquote s really a case of take it or leave it, meaning if the chemical plant doesn\rquote t take the quote, the railroad will leave the cargo. In addition, the railroad will not, according to chemical industry representatives, provide rate quotes to interchanges &#151 areas where one rail service provider\rquote s line meets with another &#151 where a plant\rquote s cargo could be shipped and then transferred to another railroad to be carried to the final destination. Obviously, pricing from this point would become more competitive. When this happens, we are not able to get competitive rates from the origin to the termination of our shipments even though part of the route might be competitive, says Borne. However, the American Association of Railroads (AAR) disputes allegations of high prices and monopolies that don\rquote t allow competition. The argument that these groups are making is, to put it politely, horse manure, says Tom White, spokesperson for the AAR. In fact, our rates have gone down ever since railroads were partially deregulated in the 1980s. I think a 25-year record of rate reductions speaks very strongly of the fact that there is not a rail monopoly. What has happened over that period of time is that railroads have made a lot of productivity improvements and almost all of those improvements have gone to their customers in the form of lower rates. As a matter of fact, White continues, the average rail rates for chemicals went up four-tenths of one percent over the last 10-year period ending in 2004. You can make numbers sing any tune you want, argues Borne. The fact of the matter is the railroads are making money hand over fist. They are bragging about it and saying they are doing so without raising rates on the average. Maybe this is true according to \lquote the average,\rquote but ask any of the captive chemical shippers if their rates have been raised and they\rquote ll tell you some stories. It seems Borne has a point. Barbara Little, vice president of government relations at Albemarle\rquote s Magnolia, Arkansas, plant, tells a dramatic one. There is only one railroad that can service our Magnolia plant and over the past few years they started to raise rates. The situation came to a head this fall when the railroad representative informed us that our contract was cancelled and they would discontinue our service if we didn\rquote t sign a new one, she says. According to Little, when contract negotiations were fruitless, the railroad implemented drastic rate hikes. Following a 20,000 percent increase in storage fees and a 350 percent increase in switching fees, Albemarle\rquote s rail rates increased from $250,000 to more than $20 million annually. When they kept adding more charges and threatening to stop service, we went to court and got a restraining order against them so they had to keep servicing our plant. But since the court has no jurisdiction over rates, we had to take the case to the STB and that\rquote s where we are now, she says. The good news is we are currently paying our previous contract rates until the case is settled. The bad news is filing

the complaint costs a lot of money, and, if we lose, we will have to pay the railroad retroactive fees at the rates they wanted to charge before the restraining order. However, filing the complaint is our only hope. *Anthony Bonnet, Ph.D. is Arkema's development manager for Kynar films and Kynar ADX PVDF resin in Europe. Bonnet has a degree in material science from the Textile and Chemical Institute of Lyon and a doctorate in the research of intractable polymer processing from the Applied Science National Institute of Lyon. Richard Perrinaud, Ph.D. is Arkema's market manager for Kynar industrial applications and has more than a dozen years in polymer research in the U.S. and France as well as a doctorate in polymer physics. Arkema Inc., 2000 Market St., Philadelphia, PA 19103, is a diversified chemicals manufacturer. Questions about this article can be addressed to Perrinaud at 215-419-7000. Additional information is available at www.arkema-inc.com.*