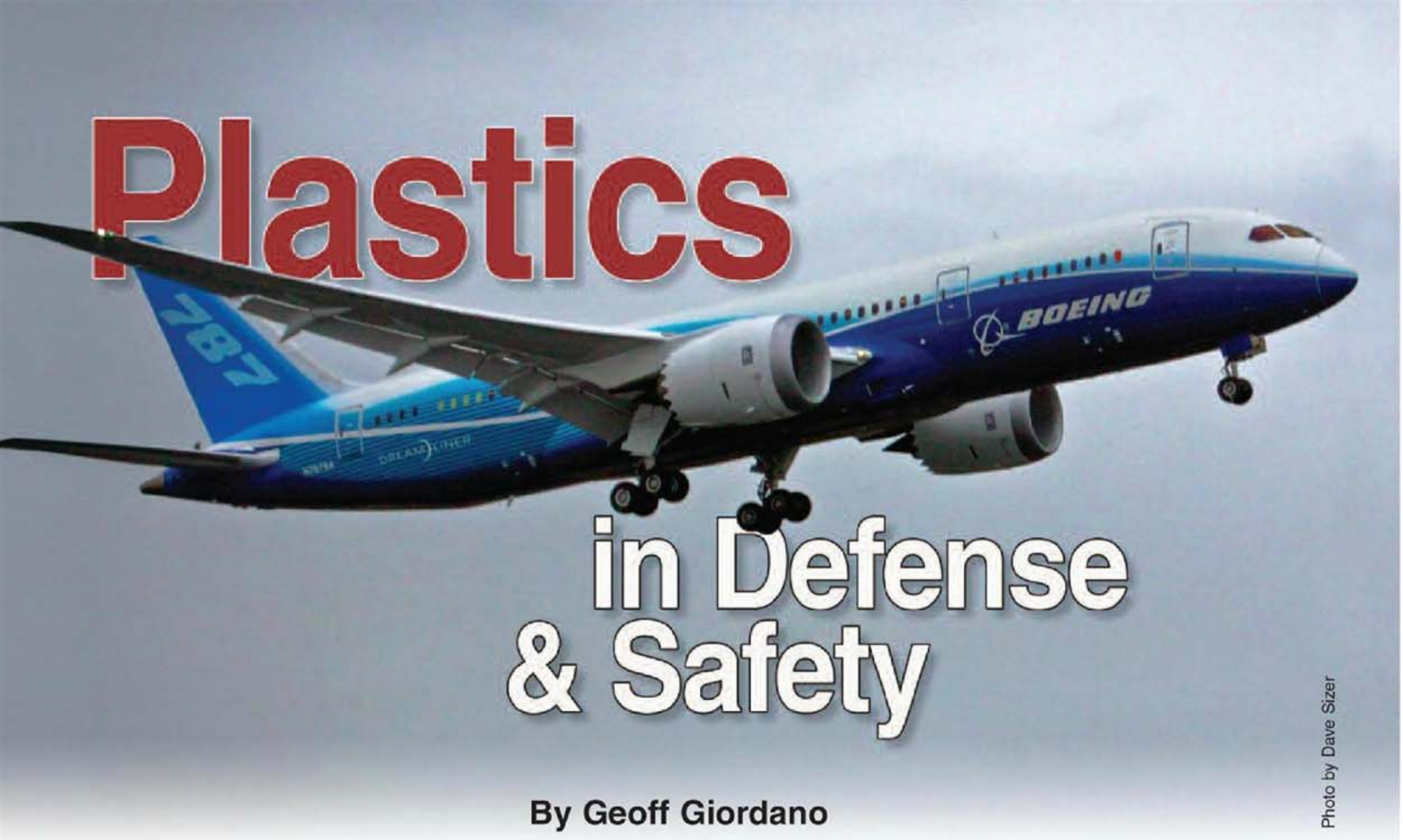

Photo by Dave Sizer

Plastics in Defense & Safety

By Geoff Giordano

The first official delivery of a Boeing 787 Dreamliner in September dramatically brought the innovative uses of plastics squarely into the public eye. Featuring a fuselage and wings made of high-strength composite plastic, the airliner is the latest innovation in a range of next-generation explorations of the benefits plastics can provide in the areas of public safety and defense.

More durable and impact-resistant plastics have been the primary success story, with increasing research interest focused on self-healing polymer technologies. In the case of the Dreamliner, the intricate production method required for the carbon fiber–based components is a little of both, in a sense. The final baking process of the composite parts produces a super-strong shell; the carbon fiber at the heart of the composites is impregnated with an epoxy that can prevent any cracks that might be inflicted upon the surface from spreading. Because of the composite material's durability advantage over traditional aluminum, the traditional six-year wear inspection can be extended to 12 years, meaning more service time between such structural tests. And a plastic skin means 80% fewer fasteners vs. what an aluminum skin requires, Boeing says. Fewer parts equal fewer chances for mechanical failure.

Plastics critical to public safety have evolved into uses down to the level of the durable all-plastic spindle nuts used in the electronic adjustment assemblies of automotive steering columns. Vestakeep Peek polymers by Evonik Industries won approval by BMW this year for use in this vital component because the nuts will not break in an accident and disrupt the function of other critical parts, like airbags. Additionally, plastic-based parts are being substituted for their metal-based and glass-based counterparts in the manufacture of pharmaceutical products, as discussed by Dennis Jenke in his 2009 book *Compatibility of Pharmaceutical Solutions and Contact Materials: Safety Assessments of Extractables and Leachables for Pharmaceutical Products*, published by John Wiley & Sons. On a larger scale, thin coatings that resist damage are increasingly being considered as protective material for components essential to public safety.

In terms of bodily safety—on the battlefield and in civilian life—improvements continue to be made in terms of protective armor that resists high impact and flame. PBI Performance Products of Charlotte, N.C., has produced polybenzimidazole fiber and Celazole PBI polymer for nearly three decades to protect soldiers, fire and rescue personnel, and petrochemical workers.

Of course, novel projects like the U.S. Defense Advanced Research Project Agency's plastic-like "black polymer ice"—a synthetic slippery coating unveiled in a 2007 proposal that could used to reduce an enemy's traction in hot climes (like those in Afghanistan and Iraq)—will continue to draw mainstream media interest. Less widely discussed but vital are intensive studies such as supersonic rain erosion tests being prepared by the U.S. Air Force Research Laboratory (AFRL) that will subject plastics-based components to precipitation at speeds up to Mach 2 to examine durability.

Responding to Need

PBI fiber provides a classic study in how a newly discovered technology can suddenly find a use in safeguarding human lives. PBI was synthesized by Dr. Carl Marvel in the late 1950s and refined in 1961 to exploit the polymer's thermal stability. The deaths of astronauts Virgil Grissom, Edward White, and Roger Chaffee in a flash fire during a launch-pad test on Jan. 27, 1967, made clear the need for more flame-retardant material in the command module and astronaut flight suits.

"If you find a polymer that doesn't melt, much less burn, it's commercially very unfeasible because you can't mold it into any shapes or extrude it into any forms," says Walter Lehmann, senior vice president of sales and marketing for PBI and a veteran of more than 20 years as an engineer of resins. "But that NASA incident did inspire both the engineers at NASA and the Celanese polymer scientists to look at some way to possibly convert this polymer into something functional, and indeed did figure out how to spin it into a fiber (in research conducted throughout the 1970s)."

With the majority of PBI's fibers being used in firefighting gear, the company is seeing a rapid growth in demand from police units around the world and gearing up to meet that demand. "In many countries, police and military are one and the same," Lehmann notes. As the August riots in London demonstrated, police crews "need not only something that's comfortable but something that's flame-resistant."

PBI's flexibility is likely to offer safety options down the road, adds PBI's Mike Gruender, whose markets are primarily compression-molded billets from which machine parts are made for industrial applications.

"We've delved into [larger applications for thin coatings]. We do have a very high-temperature material, and there are a number of chemical process industries—oil and gas in particular—where they're looking for higher-temperature coating materials to line pipes with. It's still a little early; getting good adhesion and sufficient thickness for the lifecycle expectations of the product are challenging. Their applications are fairly limited right now but can offer electrical insulation, thermal insulation, chemical protection for steel, copper, and aluminum. We're developing wire coatings with the material right now, but we don't have any commercial applications (yet)."

The Science of Safety

"There's been more in terms of application in terms of making polymers intrinsically tougher than there has been in making polymers that can heal themselves, but there has been a lot of work in the latter in the laboratory," notes Michael R. Kessler, PhD, with the Department of Materials Science and Engineering at Iowa State University in Ames, Iowa, USA. "There have been a lot of research papers, but not a lot of self-healing materials have transitioned from the lab scale to actual application."

In terms of making materials tougher, "that's continually happening," he says. "One area is in the block copolymers—polymers that have multiple polymers attached together and phase separate to create a morphology that has a lot of energy-absorbing capabilities."

Composites—using conventional and nanoscale reinforcement—are also an area of significant develop-

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ment of tougher plastics and polymers.

"We had a paper published about two years ago where we added carbon nanotubes that were functionalized into a polydicyclopentadiene matrix that showed a 900% increase in the tensile toughness by adding less than a few percent of modified carbon nanotubes," Kessler notes.

Michael R. Kessler

Polymer synthesis has facilitated the creation of heretofore hard-to-produce composites, thanks to the recently developed ruthenium catalyst that polymerizes that polymer, he adds.

Polydicyclopentadiene "is a material polymerized by a ring-opening metathesis polymerization that only really was done in the late '90s when the Grubbs catalyst was developed," Kessler explains. "That polymer is really tough. It's a crosslinked thermoset polymer. You can shoot a bullet, and it may just get lodged into a thick block of that thermoset. It's also got good toughness at lower temperatures, so it's used in snowmobile cowlings and hoods or parts of machinery that used to be made out of maybe a fiberglass composite, but now it's just made out of a pure polymer because the polymer's tough enough and they can make it without needing the fiber reinforcement."

Meantime, the U.S. Army is doing a lot of work in composite armor, Kessler notes. "These are very complex composite systems that include ceramic tiles and polymer composites and adhesives between the tiles to have function where they can absorb huge amounts of energy from a ballistic impact but be light enough to be a deployable force, (for example) a tank that can be flown in an airplane."

With self-healing polymers, "in terms of applications there's been more in the area of coatings that heal from a scratch," he says.

One of Kessler's priorities is civil infrastructure, primarily repairing some of the thousands of miles of aging pipeline crisscrossing the U.S. "The traditional way to repair a pipeline is to take that pipe offline," Kessler notes. "The damaged section is cut out, and a new section is welded into the spot. What we've developed are external composite wraps. You can restore the structural integrity and strength of the pipeline."

Some of the same technology is applied to bridges and docks, he points out, with crews retrofitting deteriorating infrastructure.

Supersonic Strength

The U.S. Department of Defense (DoD) has assembled so-called erosion working groups and indicated the need for a test facility for supersonic rain erosion testing. Before this year, the only means of such testing had been the "rocket sled" at Holloman Air Force Base in New Mexico, says Mike Spicer, program manager for the AFRL's coatings lab.

"That's a very expensive test," Spicer says. "They needed a less-expensive test facility that can weed out some of the poor polymer performers prior to going to the rocket sled."

Using a Small Business Innovative Research program, the AFRL developed a one-of-a-kind prototype for testing materials against raindrops at twice the speed of sound. Such testing is primarily intended to evaluate the durability of the leading edges of aircraft, "whether it's fixed-wing aircraft, missiles, or rockets," Spicer notes. "It's just about anything that could see rain droplets at supersonic speeds."

The AFRL soon will develop a test procedure and evaluate a number of materials. "The main thing we test is coatings: organic coatings or inorganic coatings," he says. "Some of the substrates are polymers such as canopies, windshields, and things of that nature."

Prior to venturing into supersonic testing, the AFRL had engaged in plenty of subsonic testing—up to about 650 mph—"that simulates a one-inch rainfall, and there are some military specifications written around that method."

Heal Thyself

In the early to mid-2000s, Arkema began exploring the idea of elastomers that featured strong but reversible chemical bonds. The final result, Reverlink self-healing elastomers, is a triumph of supramolecular chemistry.

"Reverlink technology began as a joint research program [with chemistry professor Ludwik Leibler of the Paris-based École supérieure de physique et de chimie industrielles de la Ville de Paris]," says Dr. Michael E. Smith, technical development manager for Arkema. "It was part of our corporate initiative for novel materials, ideally biobased materials. Most of what is in a Reverlink self-healing rubber is biosourced: 70% to 80%, depending on the grade."

While many researchers have pursued the concept of assembling large molecular structures from smaller building blocks—without necessarily having them be permanent — [Leibler] "came up with the idea of trying to simulate plastic and rubber structures where you have a controlled number of reversible connections," Smith says.

Based on hydrogen bonds that are similar to the link between the base pairs of amino acids in DNA strands, Arkema's Reverlink technology was created with the idea that a linker structure could allow the attachment of complementary hydrogen bonds to plastics and rubbery materials.

The results, Smith says, are promising: "You can imagine you have seals, where you've got some sort of gasket or connection, and if some event occurs (and) you can design it properly so the pieces stay in place—even if there's cracking—as long as they are in contact with each other, they will reform their bonds. [Other technologies] are valuable for things like coatings, where you have wear and tear and chipping and such; you bring it in to the base and you can very quickly reseal or recure the coating."

Photos courtesy of PBI Performance Products.

In comparing self-healing technologies, Smith notes that unlike those that require an activator, Reverlink technology "does not require heating (or) any sort of (UV) light or anything else. You just need to bring the cut surfaces back into contact within about an hour, and the actual chemistry will allow the connections to form."

Prospects for the adoption of Reverlink materials are in the early stages. "At the moment, the quantity that can be generated is large enough to do hundreds of pounds, thousands of pounds," Smith says. "You can make real trials in real-world applications; it's not a lab material where you can only get a one-pound jar." Arkema and its partners are working on potential applications in the military/defense and commercial sectors.

The Future

The trend toward exploring nonpetroleum, biobased polymers (derived from vegetable oils or chemical feedstock that comes from biomass) like polylactic acid will present continuing challenges for material toughness, Iowa State's Kessler predicts.

"Some of the vegetable oil–based thermosets that have been developed in the past several years could have application (in the repair of significant infrastructure)"—competing with unsaturated polyesters and epoxy resins, he says.

Meantime, the AFRL's Spicer says, commercial polymer development is the primary focus of research stemming from the supersonic rain erosion studies as well as the AFRL's other test capabilities. "We have developed a CRADA (Cooperative Research and Development Agreement), and that allows third-party polymer developers to use this facility to evaluate their polymers such that they can then claim the performance and then come back and sell it to DoD or the commercial world," he says. "With our subsonic rain erosion—and we do have a dust and particle erosion test capability—we do a lot of work for commercial companies that develop materials for both DoD and (commercial uses), and they come through the CRADA and get the testing done."

Noting that not even NASA has the test capability of the AFRL, Spicer says: "We have some customers waiting in the queue. They are probably going to come in here [soon] to test materials to develop parameters for test methods that we'll put into a material specification. We will eventually be developing better polymers because we've got some applications (in which) polymers aren't performing as we would have hoped."