Fantastic Plastic

By IVAN AMATO

t's tougher than weather, clear as crystal, flexible as paper, and can even transform baby breaths or speeding stardust into tiny electrical signals that you can keep an eye on." That's what engineer Victor Chatigny of Pennwalt Corp. in Valley Forge, Pa., might say if he made a television ad for a seemingly does-it-all plastic that his company sells as Kynar Piezo Film.

Pennwalt designs the high-tech superpolymer into components that industrial buyers use for making singing balloons, paper-thin microphones and television screens, particle sensors on satellites, blood flow sensors, pressure sensors in underground nuclear test sites — even a so-called "smart" skin to damp vibrations on the proposed space station and perhaps one day for use in platforms that convert the mechanical energy in ocean waves into electrical power.

Kynar, known generically as polyvinylidene difluoride (PVDF), starts out as a tougher version of Saran plastic, or polyvinylidene dichloride. Both polymers consist of twisted chain-like molecules with carbon atoms at the heart of each link. The carbon atoms in the Saran plastic molecules hook not only to each other but alternately to a pair of hydrogen or chlorine atoms. Substitute fluorine for chlorine atoms and you get PVDF. Since the sun's ultraviolet radiation, which degrades most polymers, passes harmlessly through PVDF, the material makes for a lasting protective plastic.

In the late 1960s, a Japanese scientist figured out how to process the tough PVDF into a far more versatile form that has the curious ability to respond to physical deformations by generating electrical signals, a phenomenon called piezoelectricity. But it was not until the past few years that the cost of making the material came down enough — and researchers became expert enough with it — to make feasible the menagerie of devices and applications now on the market or under development. "Now it's really beginning to take off," Chatigny says.

According to the trade newspaper Plastics News, a 40,000-pound truckload of raw PVDF sells for about \$250,000, or about \$6.50 per pound. Processing the raw plastic into piezoelectric films and components raises the price. Five years ago, a pound of Pennwalt's Piezo Film went for about \$20,000, or about \$100 for each square foot of paper-thin film. Now the same square foot sells for under \$10, and the per-pound price has dropped to roughly \$2,000. Most of the world's supply

It talks, listens and knows if you're there

of piezoelectric PVDF comes from Pennwalt, but other chemical companies such as Solvay of Belgium and Kureha of Japan also make it.

oating something with PVDF is like putting Saran plastic around it to protect it from the weather and other environmental onslaughts. Exposed metal parts of the famous Liberty Place skyscraper in Philadelphia and some buildings in Houston are coated with it. The Whitford Corp. in Frazer, Pa., sells PVDF-based coatings for lining chemical vats and tanks. The "unleaded gasoline only" stickers by your car's gas tank are made of it.

The great appeal of the piezoelectric material lies in its versatility. A few processing steps turn the protective form of PVDF into a material suitable for a variety of applications even in the unwelcoming environments of outer space and underground bomb-testing wells.

Getting the polymer into its piezoelectric form takes some doing. First take some PVDF resin and stretch it after it pushes through a sheet-shaping extruder. This causes otherwise randomly arranged carbon chains in the sheet to align like a stack of zigzagging pipes. Next, press electrodes against each face of the film and place the metal-PVDF-metal sandwich within a strong electric field. This step causes pairs of alternately arranged fluorine and hydrogen atoms to swivel to opposite sides of the polymer's backbone.

The result: a form of PVDF that displays the intriguing property of piezoelectricity (from the Greek word "piezein," meaning to press), first reported in crystals such as quartz and sodium chloride in the early 1880s by Pierre Curie and his brother Jacques. Pennwalt first started making piezoelectric PVDF in small, experimental quantities about 20 years ago when researchers were discovering that many organic materials, including artificial polymers and even human skin, are piezoelectric. Like inorganic piezoelectric materials, which are mostly ceramic or crystalline and used in sonar and other pressure sensors, PVDF generates an electrical voltage when bent or otherwise stressed; conversely, it changes shape when a voltage is applied to it. Engineers can form the polymer into intricate, flexible shapes, a virtually impossible option

with brittle, inorganic materials.

Piezoelectric PVDF works like an electric sponge. Push down on a saturated kitchen sponge and water comes out. Push a little or a lot, fast or slow, and different amounts of water come out at different rates. Release the pressure on the sponge and it draws water back in. With the polymer, electrical current is what moves in and out. And because electricity can easily be shunted through wires and then to nearby or remote circuitry, the new plastic forms the heart of increasingly more sensors, switches and other devices.

cientists around the world use the piezopolymer for a huge and growing list of applications, ranging from robotic tactile sensors to sleepapnea monitors to help prevent sudden infant death syndrome. With the aid of electronic circuitry for processing the raw electrical signals coming from the piezoelectric films, researchers can detect and interpret mechanical deformations that take place over a period as long as 100 seconds or as fleeting as a hundred-millionths of a second. Striking a keyboard key or pressing an elevator button generates 10 volts or more of easily processed electrical signal in film fitted to the key or button. The U.S. Olympic karate team uses piezoelectric sensors to measure the force of team members' kicks and punches. Some football coaches use similar sensors to measure the force of their linemen's hits. Some high-speed impact printers have a strip of the film behind the target area to monitor whether an impact has occurred. Where security rates top priority, entire rooms and vaults have been lined with the film to detect any penetration into the enclosure.

The film can also serve as a microphone. Talking into a postage-stamp-sized piece of the polymer creates a sequence of electrical signals clear enough for recording on tape or sending through an amplifier and speaker. "You can cut a ribbon of it a quarter of an inch wide, place it down the length of a hallway and listen to all the conversations along the way," Chatigny says. He will neither confirm nor deny that the federal government is interested in the material for this purpose.

"We are making sheets of piezofilm that

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will cover entire structures and be able to detect the presence or absence of flaws," Chatigny says. One specific application might be for the increasingly important job of inspecting the structural integrity of the nation's aging jet fleet. By "wallpapering" a plane with such a film and using it to monitor ultrasonic pulses sent through the plane's "skin," inspectors could detect flaws without having to remove and reassemble large sections of the craft. The pulses' echoes generally come from the signals bouncing off the back surface of a plane's skin. Cracks or peeling in the skin cause the echoes to return sooner than they would from flawless skin. Moreover, since jolting the piezoplastic with electric pulses of differing frequencies drives it like a speaker, the same film can serve as both sender and receiver of sound and ultrasound.

Engineers George W. Taylor and Joseph R. Burns – co-founders of Ocean Power Technologies, Inc., in Princeton, N.J. envision power-generating applications of piezoelectric polymers. "The combination of the virtually unlimited amounts of mechanical energy available in ocean waves with piezoelectric polymers offers the possibility of the large-scale, direct conversion of ocean wave power into

The PVDF that forms the heart of this piezoelectric switch responds to bending with an electrical signal.



electricity," they suggest. They hold several patents for a new power-generating technology called hydropiezoelectricity, which in the most promising designs would use tons of piezoelectric polymer to convert some of the ocean's vast and powerful motions into electrical power.

They envision building ocean-based platforms that hold piezoelectric plastic slabs, which ocean waves would indefatigably deform to produce a continuous current of electricity. Laboratory tests indicate that each pound of the material could generate more than 2 watts of electricity; a 1-megawatt facility would require about 220 tons of the material.

hough piezoelectric materials respond electrically to mechanical pressures, they also respond mechanically to electrical pressures. Apply a voltage across the film and the film gets longer or shorter. Send a pattern of changing voltages across a piece of film and you get a speaker. Store a song electronically on a chip, connect the chip to a piece of piezoelectric film glued inside a helium-filled balloon, and you get a floating globe that appears to produce music of its own accord.

By gluing together two 11/2-inch-long strips of the film so that their respective fluorine and hydrogen atoms point in opposite directions, engineers have made what might be thought of as plastic muscles. Putting a voltage across the glued strips makes the short assembly curl in on itself. Strahl Technologies, Inc., in Vancouver, British Columbia, offers giant, color-television-like screens made with millions of fiber-optic elements, each with its own, individually controllable, piezoelectric flap serving as a shutter. The Houston Astrodome will get two of these high-resolution systems next year, says Strahl President J. Rodney

Gage. "And the material is everything but bullet-proof," he adds. The company also markets robotic tactile sensors, which

Gage calls "artificial skin."

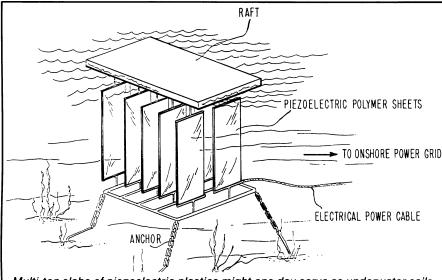
An extremely sensitive version of the film has made an extraterrestrial appearance on a Soviet satellite. Vega II, a spacecraft with instruments and detectors from several nations, carried a square foot of 1-millimeter-thick piezoelectric film to count high-speed dust particles as it approached the tail of Halley's comet in 1986. According to University of Chicago scientists who analyzed the resulting data, the dust detector at times sensed thousands of particles per second, some with a mass of onetenth of a trillionth of a gram and some traveling at roughly 170,000 mph.

Highlighting the huge range in mechanical stresses the film can detect, researchers at the federally funded Sandia National Laboratories in Albuquerque, N.M., use a piezofilm-based sensor, designed by a French scientist, for monitoring seismic and pressure waves generated during underground nuclear tests and other explosions. The sensors can measure pressures equivalent to what 400,000 stacked Earth atmospheres would produce, according to Sandia research scientist Robert A. Graham. He says other piezoelectric materials, such as quartz, cannot measure pressures that high and are far less versatile than the flexible, tough film. "It's clearly revolutionary," Graham says.

In addition to having prodigious piezo-electric ability, PVDF is in the major leagues of pyroelectric materials, which respond to heat by establishing a voltage across their surfaces. "God was good to us," Chatigny says, "because the film absorbs infrared of exactly the wavelengths [5 to 15 microns] at which the human body emits infrared." With suitable infrared-focusing optics, a piece of the film can detect a person walking 50 to 100 feet in front of it. "It then can set off an alarm for an intrusion detection system," Chatigny says. In another design, the pyroelectric film senses overheating in train brakes.

Taylor and Burns of Ocean Power Technologies and other researchers are now investigating polymers related to PVDF in a search for piezoelectric polymers even better suited for applications such as ocean power. By adding a couple of fluorine atoms to the molecular units of polymers and controlling the shapes of the polymer molecules, scientists could create materials that pack yet bigger piezoelectric and pyroelectric punches, Taylor suggests. He says these would make hydropiezoelectric power even more promising for tapping ocean energy.

And beyond the world's oceans, some researchers envision the more sensitive piezopolymers one day tracking even gentler baby breaths and finer stardust than those monitored today.



Multi-ton slabs of piezoelectric plastics might one day serve as underwater sails to transform the vast and ever-present mechanical power of ocean waves into electrical power.

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