Flexible PVF$_2$ Film: An Exceptional Polymer for Transducers

The thin, clear sheets of poly(vinylidene fluoride), viewed for the first time, appear to be plastic wrap for leftover food. But this exceptional polymer material, also known as PVF$_2$, combines so well the mechanical properties of flexible films with the electrical properties of existing ceramic transducers that it is finding its way into a diverse array of applications. Possible uses range from an underwater hydrophone for detecting enemy submarines to a blood flow sensor that works just by wrapping the film around a finger or a toe. Remarkably, polymer scientists, after nearly a decade of intensive study, still do not know precisely why PVF$_2$ works as well as it does, although experiments of the last year or so seem to be narrowing the options.

A transducer is a device for converting energy from one form to another, electrical to mechanical, thermal to electrical, and so forth. Materials with the ability to convert mechanical to electrical energy (and vice versa) are said to exhibit piezoelectric activity; materials that interconvert thermal and electrical energy have pyroelectric activity. PVF$_2$ can do both, and the various uses, present and projected, to which it is being put depend on one or another of these properties.

The Pioneer Electronics Corporation, Tokyo, for example, has taken advantage of the piezoelectric property of PVF$_2$ in some of its stereo speakers and headphones. A voltage applied to a piezoelectric material causes it to change its dimensions slightly. In the case of PVF$_2$, a voltage applied perpendicular to the plane of the film causes the film to expand or shrink (depending on the sign of the voltage). If the film has two opposite edges fixed in place, then an alternating elongation and contraction becomes transformed into a pulsating motion, which is the action of the sound-producing element in a speaker.

The pyroelectric activity has been used by at least three companies in designing an intrusion detector. The body of an intruder radiates heat, which is sensed by a PVF$_2$ element in the detector and converted into an electrical voltage. Since the object is to determine whether unauthorized individuals are moving in the monitored area, the detector is designed with two PVF$_2$ elements oriented so that they produce equal and opposite voltages that cancel each other when picking up heat from a stationary source. Moving intruders produce unequal voltages from the two elements, and the resulting net signal triggers an alarm.

PVF$_2$ is actually an old and venerable material; only recently have its electrical properties become of interest. According to Richard Ferren of the Pennwalt Corporation, King of Prussia, Pennsylvania, PVF$_2$ has been exploited as a coating for the protection of metal surfaces because, like other fluorocarbons such as Teflon, it is chemically inert and electrically insulating. Exterior coatings of all kinds of buildings have been a major application. One is tempted to joke, for example, that the Watergate burglars wish they had covered their escape as well as PVF$_2$ covers—and protects—the Watergate building complex.

Interest in the electrical properties of PVF$_2$ picked up after 1969 when Heiji Kawai of the Kobayashi Institute of Physical Research, Tokyo, reported that the material exhibited an extraordinarily large piezoelectric activity for a polymer. Soon afterward, J. G. Bergman, J. H. McFee, and G. R. Crane of Bell Laboratories reported on the pyroelectric behavior of PVF$_2$. These and other early results were encouraging enough to stimulate worldwide interest in PVF$_2$, although the country that has made the largest contribution is probably Japan. Although the rise of the Japanese microelectronics industry is better known, observers say that the Japanese are increasingly at the cutting edge of new polymer materials development. The Kureha Chemical Industry Company, Tokyo, for example, is the only commercial source of piezo- and pyroelectrically active PVF$_2$.

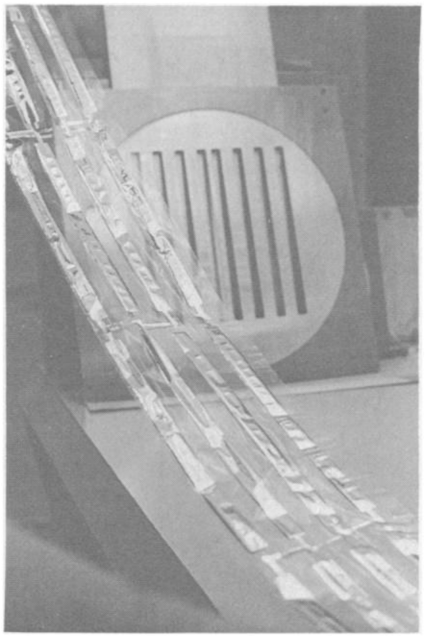

Fig. 1. Poly(vinylidene fluoride) film with evaporated metal electrodes designed for use as a pressure monitor for printing presses. Pressure applied perpendicular to the film generates by way of the piezoelectric effect a voltage between the electrodes on the top and bottom of the film. [Source: G. T. Davis, National Bureau of Standards]

As befits a material with an unusual combination of properties, making PVF$_2$ films with the desired characteristics is as much art as science. To start, the vinylidene fluoride monomer is made into PVF$_2$ by various polymerization processes. The monomer, however, is not the only ingredient in the starting material, and the role of the numerous resulting impurities is still a topic of debate. To illustrate the range of impurities that may be encountered, a solution of dissolved PVF$_2$ may be red or yellow depending on where it was made and by whom. Next, the polymer resins are pressed into sheet form (Fig. 1). This can be accomplished by melting the resins between the plates of a press and cooling under pressure.

Two additional steps are needed to obtain electrically active films. First, the pressed films are "oriented" by stretching them. The stretching operation, which may involve drawing ratios of 5:1 or more, may be either uniaxial or biaxial—that is, stretching may be either in only one direction in the plane of the film or in two perpendicular directions. Which orientation is preferable depends on the geometry of the device. In the case of piezoelectricity, for example, a voltage applied perpendicular to the film causes it to expand or contract in the direction of stretching. Stretched films have thicknesses ranging from 6 to 50 micrometers. The second step, called poling, is required because PVF$_2$ is not inherently electrically active but must be primed for the task. In poling, films are usually, but not always, heated and then are subjected to a large electric field, as large as a few million volts per centimeter applied perpendicular to the plane of the film. Then the films are cooled, sometimes while still under the electric field. Poling induces a large permanent electrical polarization across the thickness of the film, which is necessary before piezo- or pyroelectric activity of a

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useful magnitude can be obtained. It is changes in this polarization, which are induced by a mechanical strain or by a temperature change, that constitute the piezo- or pyroelectric signal.

PVF_2 films made in this way have piezo- and pyroelectric properties that are, in some cases, comparable to those of existing materials that perform similar functions and, in other cases, not quite as good. It is the combination of mechanical and electrical properties that makes PVF_2 so interesting. A commonly used piezoelectric material, for example, is polycrystalline lead zirconate titanate (PZT), which has a large piezoelectric coefficient but is brittle and not readily obtainable in the form of a thin film. Because the active ceramic element must be mounted in a fixture of some sort, whereas PVF_2 sheets together with electrical leads can by themselves constitute the active device, the geometries of ceramic devices are also more restricted.

A number of applications of PVF_2 that take advantage of its unique combination of properties are under study. Seymour Edelman and his colleagues at the National Bureau of Standards (NBS), Gaithersburg, Maryland, are working with the Bureau of Engraving to design a pressure sensor for the presses that print our currency. Apparently one of the tricks of the trade is to operate the presses at much higher pressures than used in most printing processes and, in particular, at pressures higher than counterfeiters can reach. The high pressure, however, brings with it the possibility of damage to the presses, and it is necessary to closely monitor the operation. The NBS researchers have built a thin sheet pressure sensor that can be embedded in the soft surfaces of the presses. Test devices have performed as expected. Making a practical sensor is next.

The Naval Underwater Systems Center at New London, Connecticut, is testing underwater hydrophones with PVF_2 as the sensing element. Hydrophones today are made with ceramic piezoelectric sensors. Carried by or towed behind ships or mounted at certain fixed sites, hydrophones are used to detect submarine activity. The hydrophones are the inverse of the stereo speaker application in that acoustic pressure waves generated in the water by the submarine are picked up and converted into an electrical signal. The underwater environment is not exactly benign nor, for that matter, is that aboard ship, and current hydrophones are susceptible to breakage. According to Charles LeBlanc of the underwater systems center, the fact that flexible PVF_2 sheets are impact resistant, lightweight, and compact and have a piezoelectric performance comparable to that of ceramic elements makes PVF_2 of great interest. So far, experimental hydrophones of PVF_2 perform electrically about as well as those made from ceramics.

The flexibility of PVF_2 is also being exploited by Bolt Beranek & Newman Incorporated (BBN) in their development of a blood flow monitor. Tony Clemente of BBN emphasizes that what the device detects is not blood pressure but a measure of the mechanical output of the heart. The monitor is thus complementary, in a way, to an electrocardiograph, which measures the electrical output. A clinical comparison of the BBN device and the electrocardiograph to determine the degree to which the two kinds of devices provide similar information is slated to begin later this year.

The monitoring action is obtained simply by wrapping a PVF_2 film around a part of the body, usually an extremity. Because the film is flexible, it does not constrict blood flow in any way. An electronics package computes and drives a digital meter that displays the pulse rate and arrythmia counts. If desired, the pulse waveform can be shown on an oscilloscope.

Ultrasonic Imaging

Another virtue of PVF_2 is its low mechanical or acoustic impedance. In alternating-current electrical circuits, the impedance is a measure of the resistance to current flow. In applications where power must be transferred from one circuit to another, such as in a transformer, the transfer occurs most efficiently if the impedances of the two circuits match. The same situation holds for acoustic circuits. In particular, the acoustic impedance of PVF_2 is quite close to that of water (this is one more reason why the hydrophone application works so well) and is nearly the same as that of the human body, which therefore means that PVF_2 can be effectively used to monitor mechanical waves originating within a person.

Coupled with the low acoustic impedance of PVF_2 is an extremely wide bandwidth—that is, the range of frequencies to which a device is sensitive. Also, the frequency response of PVF_2 is uniform throughout the bandwidth; there are no sharp spectral features. These characteristics make PVF_2 a good candidate for use as ultrasonic receivers (transducers) for imaging of the human body or for nondestructive testing of metallic or ceramic structures. Jerry Harris of the Bureau of Radiological Health, Rockville, Maryland, for example, is collaborating with the NBS researchers to develop miniature ultrasonic sensors that will be used to determine whether medical ultrasonic imaging is really as safe as it is generally presumed to be. It is not known, for example, whether there are highly localized spots where ultrasonic energy may temporarily concentrate and thus raise the dose at that location by a factor of up to a thousand. The large transducers currently in use do not have the spatial resolution to indicate whether such concentration occurs.

One reason the sensors can be small is that the PVF_2 sheet can be cut to any desired size. Another is that the active area of the sheet, which is defined during the poling process, can be made as small as desired. Small active areas are achieved by making the poling electrodes, which are applied simply by evaporating metal through a mask in a vacuum bell jar, very tiny. An illustration of how small the active PVF_2 elements can be is provided by the work of Jim Plummer and R. G. Schwartz of Stanford University. These investigators fabricated an array of ultrasonic transducers which was physically bonded to a microelectronic circuit that contained an array of multiplexers and amplifiers. Each element of the array, consisting of one transducer and one multiplexer-amplifier, filled a square about 3.5 millimeters on a side. More densely packed arrays are under development for use in an ultrasonic imaging system also being built at Stanford.

Still another important characteristic needed for ultrasonic imaging is impulse response because the signal that is detected is usually the reflection from an object of a pulse sent out by a generating device, as in radar. A good impulse response is obtained when the shape of the electrical pulse put out by the transducer is a near-replica of the detected mechanical pulse. Since a pulse can be conceived as a superposition of several waves of differing frequencies, impulse response is closely related to bandwidth. H. John Shaw and his associates at Stanford are interested in PVF_2 as an ultrasonic transducer for nondestructive testing because of the large bandwidth (and impulse response) and because its flexibility allows transducers to be applied directly to test objects of varying geometry without the need for a coupling medium, such as a water bath.

Shaw and his colleagues are trying to build the ultrasonic equivalent of a phased-array radar system. By electronically controlling the phase of the pulses emitted by each element in the array, a phased-array radar achieves the scanning action normally accomplished by physically moving the radar dish. The Stanford researchers want to improve on this capability by adding a focusing function to the array. In this way, they hope to scan the volume of test objects with a finely focused beam in a search for structural defects, such as cracks in ceramic turbine blades, as small as the wavelength of the ultrasonic wave (a fraction of a millimeter). To date, experiments have been limited to single transducers, but computer modeling of the entire array indicates that it will perform much better with PVF_2 than with ceramic transducers. For example, a ten-times-wider scanning angle is achievable with PVF_2. In addition, the PVF_2 array can be put on a single sheet of polymer, but each element in a ceramic array must be discrete.

Despite the many pending applications, researchers still do not fully understand the origin of the electrical properties of PVF_2. Years of experiments seem to indicate that more than one mechanism is at work. Even studies from the same laboratory yield contradictory conclusions. Evidence accumulated over the last year, however, is being increasingly accepted as supporting the "dipole orientation" model as the primary source of the piezo- and pyroelectric activity of PVF_2. The main competitor is called the "trapped charge" model; but there are many ways that charge can be trapped in PVF_2, and thus there are many such models. According to J. Charles Hicks of the Naval Ocean Systems Center, San Diego, California, probably only about 20 percent of polymer researchers still believe that trapped charge plays an important role. The Navy scientist adds that, in his opinion, experimental results that seem to support the trapped-charge theory can actually be analyzed in terms of dipole orientation. Other researchers are more circumspect in their judgments, however.

The dipole orientation model can be understood in terms of the structure of PVF_2. Several years ago, x-ray diffraction studies by Jerome Lando and W. W. Doll of Case Western Reserve University, and by others in Japan and the U.S.S.R., showed that PVF_2 is a semicrystalline polymer that exhibits several structures. Semicrystalline means that the solid polymer is partially crystalline, with the ordered regions being separated by amorphous, glasslike areas. Depending on the method of preparation, PVF_2 can be up to 90 percent crystalline, but 50 percent is more typical. Within the crystalline regions, the polymer chains are arrayed in lamellar structures, with the direction of the chain perpendicular to the plane of the lamellae. The different structures assumed by PVF_2 are determined by the details of the chain configurations within the lamellae.

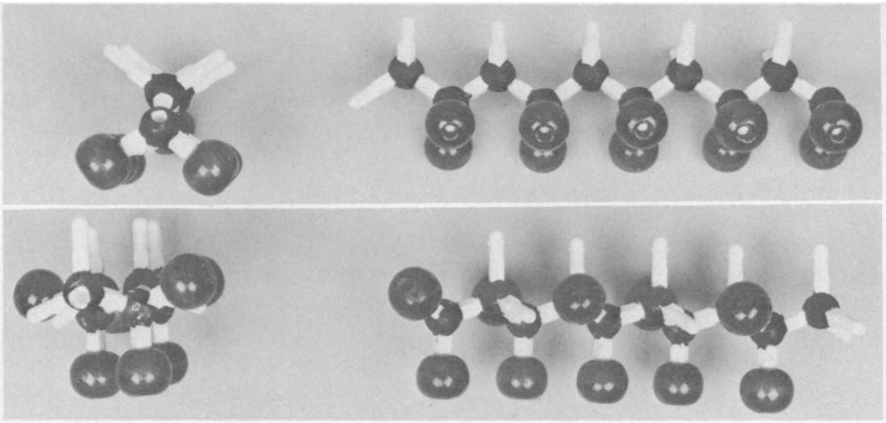

Fig. 2. Models of the alpha (bottom) and beta (top) structures of poly(vinylidene fluoride). The small black spheres are carbon atoms; the large spheres are fluorine atoms; hydrogen atoms sit at the end of the sticks (bonds) where there are no spheres. For a given number of carbon atoms, the alpha structure chain is shorter than the beta chain. Thus, it is plausible that the stretching procedure applied to PVF_2 should cause the naturally occurring alpha form to transform to the beta. [Source: M. G. Broadhurst, National Bureau of Standards]

In the dipole orientation model, the electric polarization (induced by poling) that gives rise to the piezo- and pyroelectric activity of PVF_2 is postulated to derive from an intrinsic dipole moment within each $-CH_2-CF_2-$ unit of the polymer. The dipole moment, in turn, is produced by the exceptionally high electronegativity of the fluorine atoms as compared to the carbon and hydrogen atoms. In a randomly oriented polymer chain, the dipole moments would cancel. But the crystalline character of PVF_2 imparts some constraints on the allowed chain configurations. The high electric field present during poling further tends to align dipoles.

The most common form of PVF_2 is called the alpha phase. In the alpha phase, there is a rotation of 120° at every other carbon-carbon bond (in polymer parlance, a *trans-gauche-trans-gauche'* configuration) (Fig. 2). There is still a net dipole moment for a given chain, but the chains are packed in the lamellae in such a way that the overall moment is zero. The electrically active form of PVF_2 is called the beta phase. There is no rotation at the carbon-carbon bonds, and the net dipole moment of a chain is even larger than in the alpha phase (Fig. 2). More importantly, the chains are all aligned the same way in the lamellae, and the overall moment is quite large.

Research by numerous groups has shown that, first, the inactive alpha phase is the form normally obtained in pressed polymer films and, second, that stretching the pressed films partially transforms the alpha regions into the beta structure. The high electric field present during poling, according to x-ray and infrared evidence, further aids the phase transformation to the beta form. This alone would not be enough, however, and the main point of the dipole model is that, given the beta phase structure, the field interacts with the dipoles to ensure that all are aligned. For example, even if each lamella had a large net moment, randomly oriented lamellae would cancel each other's electrical activity.

Recently, Martin Broadhurst, G. Thomas Davis, and their associates at NBS have constructed a classical electrical model of a dielectric material (insulator) containing dipoles of this type. Incorporating most conceivable interactions between the dipoles and an applied field, temperature, and mechanical strain in their model, they attempt to calculate the piezo- and pyroelectric response of PVF_2 from a given magnitude of the polarization. The results of the model agree well with measured piezo- and pyroelectric responses, an indication that the important features of the effects are understood. At present, the investigators calculate that the maximum obtainable polarization is about twice that typically achieved in well-polarized samples.

An indication of the knottiness of the dipole-trapped charge issue, however, is illustrated by seemingly contradictory results from the IBM Research Laboratory, San Jose, California. Do Yoon and Dieter Naegele (Naegele is now at the University of Mainz in West Germany) have evidence from infrared absorption data that seems to show that dipoles do change their orientation under the influence of the poling field. The experimenters prepared PVF_2 films with transparent electrodes and observed the change in the magnitude of certain infrared absorption lines as the field strength and direction was varied. The observed changes indicated that the orientation of the dipoles (which are in the molecular group responsible for the absorption) was following the field. Moreover, the observed variation in dipole orientation with applied field was similar to the behavior of the polarization induced by a variable poling field, as obtained by other researchers, including, most recently, R. Glen Kepler of Sandia Laboratories, Albuquerque, New Mexico, and Hicks and his associates at the Naval Ocean Systems Center.

The difficulty is that Heinrich Sussner of the Max Planck Institute, Stüttgart, and Yoon, working in the IBM laboratory, found similarly conclusive evidence for the transfer of electrical charge between PVF_2 and metal electrodes. Their results back up those obtained earlier by Gus Pfister and his associates of the Xerox Webster Research Center, Webster, New York, by Naohiro Murayama and his colleagues at Kureha Chemical Industry Company, and by others.

Yoon and Sussner found that the size of the pyroelectric response of PVF_2 varied strongly when different metals were used as the electrodes during poling. In particular, using two metals with different work functions (a measure of the energy needed to eject an electron from the metal), they found that the largest response came when the metal with the higher work function was the positive electrode during poling. Similar effects are well known to physicists studying metal-insulator interfaces and are interpreted as indicating that electrical charge from the electrode is being transferred into the PVF_2.

One way to reconcile the two results, according to Yoon and others, is to assume that the electrical charge injected from the electrodes acts in conjunction with the applied poling field to produce an effective "local" electric field that then acts to orient the molecular dipoles. In this scheme, the induced polarization is directly due to dipole orientation and only indirectly to the injected charge.

Making PVF_2 Even Better

If a precise explanation of the origin of piezo- and pyroelectric activity of PVF_2 has so far evaded polymer scientists, efforts to improve the performance of the material are proceeding undeterred by the lack of information. According to Ken Wynn of the Office of Naval Research, Arlington, Virginia, much of the action in the next few years will be concentrated on finding out how well PVF_2 holds up over long periods of time and at temperatures well above ambient. A microphone under development for the Army must function at temperatures up to 70°C, for example. Some activity is also directed toward increasing the magnitude of the piezo- and pyroelectric coefficients of PVF_2.

To this end, some investigators are looking at copolymers of PVF_2. A copolymer is a polymer in which two different monomers are chemically bonded to one another. Mortimer Labes, Robert Salomon, and their colleagues at Temple University, for example, have been studying a copolymer of 90 percent PVF_2 and 10 percent Teflon. According to Labes, the addition of Teflon causes pressed polymer films to assume a predominantly beta phase structure, even without the stretching operation. (Other researchers have reported the same observation.) Moreover, says Labes, the electrically inactive Teflon portion of the copolymer affects the structure of PVF_2 in such a way that dipoles become more easily aligned, and lower poling fields are needed to obtain the maximum electrical activity. (Recently, however, several investigators have found ways to apply very high fields to PVF_2 without causing electrical breakdown. Thus the need for high poling fields is not a problem.)

Copolymerization has disadvantages, as well as benefits. Richard Shuford of the Army Materials and Mechanics Research Center, Watertown, Massachusetts, points out that the presence of Teflon has a mixed effect on the high-temperature performance of PVF_2. Shuford and his colleagues have tested PVF_2 that was maintained continuously at temperatures up to 100°C, which is near the temperature at which poling of pure PVF_2 is done, for over $1^1/_2$ years. The scientists observed an initial decrease in electrical activity of 20 to 40 percent, followed by a period of constant performance, in films without Teflon. The presence of Teflon helps protect against degradation with time at high temperatures, says Shuford, but the maximum operating temperature is reduced.

Another approach, labeled highly speculative by some observers, is being tried by Lando, Morton Litt, and their co-workers at Case Western. These investigators are trying to grow oriented films of PVF_2 on a substrate (epitaxial growth). Such growth, if achieved, will eliminate the need for the stretching operation, which is only partially effective, and the need for poling. Among other advantages, obtaining electrical activity without poling would eliminate once and for all the controversy of the role of electrical charge injected by electrodes. And the use of ultrapure starting material, another stratagem being tried at Case Western, would greatly reduce the possibility of trapped charge being introduced by impurities in the PVF_2.

Other Polymers Studied

A third direction is to start from scratch with altogether new materials. There are other polymers, poly(acrylonitrile) for one, that have larger dipole moments than does PVF_2. But, as ONR's Wynn observes, there are so many conditions that must be met simultaneously that it will be hard to find a better performer than PVF_2. Among other virtues, a prospective material must have a large dipole moment per unit volume and a structure that permits alignment of the dipoles during poling and at the same time keeps them aligned afterward.

Steven Carr of Northwestern University, for example, began studying poly(acrylonitrile) some years ago because of its large dipole moment in hopes of finding a high-performance piezoelectric material. For a number of reasons including the fact that poly(acrylonitrile) is entirely amorphous, thus providing no means for retaining the alignment of dipoles oriented during poling, the material has never had a high electrical activity.

Litt and his colleagues at Case are studying the possibility of using so-called odd nylons. (Odd refers to an odd number of carbon atoms between connecting groups of the polymer.) Some of the odd nylons, based on their dipole moments and crystal structures, could be up to 100 percent more active than PVF_2, according to Litt. So far, however, it has not been possible to obtain polarized films of most odd nylons. Either a way to make polarized nylon films must be found or a strategy such as epitaxial growth of oriented films adopted before the usefulness of odd nylons can be ascertained.

Still facing polymer researchers is the problem of understanding the mechanisms operating in PVF_2 well enough to devise effective strategies for improving the material. For example, if the NBS calculations are correct, only a factor of 2 increase in the performance of PVF_2 could be expected under optimum conditions. Other evidence exists that a factor of 5 or more improvement is possible if all dipoles would remain as aligned as they seem to be during poling (an unverified rumor has it that Japanese scientists have recently found a way to accomplish this). Even without such advances, however, it seems likely that PVF_2 will become one more example of how polymer materials are creeping into more and more corners of our lives.

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