Sensors and Their Applications

Cambridge University Press
978-1-107-40889-0 - Materials Research Society Symposium Proceedings: Volume 889: Electroresponsive Polymers and their Applications
Editors: Vivek Bharti, Yoseph Bar-Cohen, Zhong-Yang Cheng, Qiming Zhang and John Madden
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Mater. Res. Soc. Symp. Proc. Vol. 889 © 2006 Materials Research Society 0889-W01-01

Lesser-known piezoelectric and pyroelectric applications of electroactive polymers

Sidney B. Lang[1] and Supasarote Muensit[2]
[1]Dept. of Chemical Engineering, Ben-Gurion University of the Negev, Beer Sheva, Israel
[2]Dept. of Physics, Prince of Songkla University, Hatyai, Thailand

ABSTRACT

The piezoelectric effect was first observed in polyvinylidene fluoride polymer (PVDF) in 1969 and the pyroelectric effect was found several years later. A number of additional ferroelectric polymers have been discovered since that time including the copolymer PVDF with trifluoroethylene (P(VDF-TrFE)), and the odd-numbered nylons. A large number of applications of piezoelectricity and pyroelectricity have been developed. The magnitudes of the effects in polymers are much lower than those of ferroelectric ceramics (an exception is the piezoelectric effect in porous polymers). However, other factors make these very desirable materials for applications. The polymers have low permittivities, low acoustic impedances and low thermal conductivities. They are available in large area sheets and they are flexible and relatively low in cost. Major applications include microphones and loudspeakers, ultrasonic devices, SAW transducers, actuators, infrared detectors and many others. This review will describe some of the lesser-known applications of these materials in the fields of tactile devices, energy conversion, porous polymers, property measurement, pyroelectric infrared sensors, shock sensors and space science.

INTRODUCTION

Pyroelectricity was first observed more than 2400 years ago by the Greek philosopher Theophrastus [1, 2] and piezoelectricity was discovered by Jacques and Pierre Curie in 1980 [3]. Piezoelectricity was first found in a polymer, polyvinylide fluoride (PVDF), by Kawai in 1969 [4]. The pyroelectric effect in PVDF was found two years later by Bergman *et al.* [5] and by Nakamura and Wada [6]. These effects have been observed in a number of additional polymers including polyvinylidene fluoride-trifluoroethylene copolymer (P(VDF-TrFE)), vinylidene cyanide, odd-numbered nylons and polyurea. However, only PVDF and P(VDF-TrFE) have been used significantly in applications. The physical properties of these two polymers are compared with that of the ferroelectric ceramic PZT-4 (lead-zirconate-titanate) in table I. Both the piezoelectric strain constants (d coefficients) and the pyroelectric coefficients of the polymers are very low in comparison to those of PZT-4. However, the low permittivities of the polymers lead to high values of the piezoelectric voltage constants ($d/\varepsilon\varepsilon_0$) and pyroelectric voltage figure-of-merit (proportional to p/ε). The acoustic impedances of the polymers are much lower than those of ceramic materials and much closer to those of water and air. The polymers can be prepared in large area, very thin sheets and they are relatively inexpensive. Consequently, they are used in a large number of applications. The pie chart of figure 1 shows the approximate distribution of papers published during the five-year period from 1999 through 2004 on various applications. The five most frequently described applications were actuators, vibration control,

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Table I. Physical properties of polymers and a ferroelectric ceramic.

Property	Units	PVDF	P(VDF/TrFE) (75/25)	PZT-4
Piezoelectric coefficient (d_{31})	pC N^{-1}	16.5	7	-123
Piezoelectric coefficient (d_{33})	pC N^{-1}	-33	-38	289
Piezoelectric coefficient (d_{15})	pC N^{-1}	-15.7	-31	-496
Elastic coefficient (c_{33})	GPa	10	11	115
Relative permittivity (ε_3)	Dimensionless	9	7	1300
Pyroelectric coefficient (p_3)	μC m^{-2} K^{-1}	25	31	289
Acoustic impedance (Z_3)	Pa s m^{-1}	4.2 x 10^6	4.4 x 10^6	3.0 x 10^7

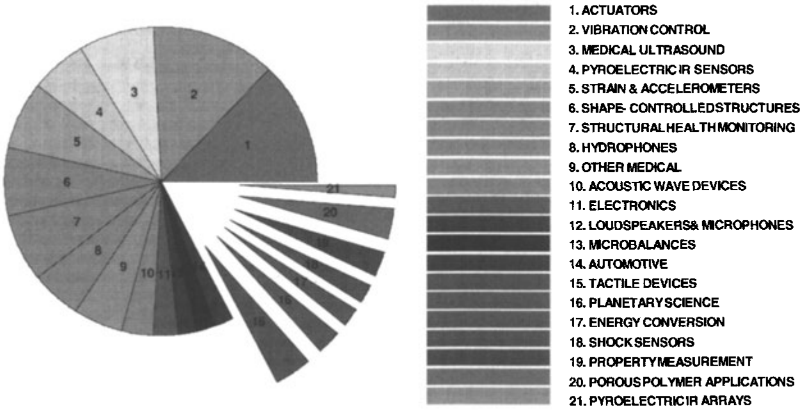

Figure 1. Piezoelectric and pyroelectric applications of electroactive polymers during the years from 1999 to 2004.

medical ultrasound, pyroelectric infrared sensors, and strain and acceleration measurement devices. However, this paper will describe some of the seven lesser-known applications shown in the exploded portion of the pie chart.

TACTILE SENSORS

PVDF has number of attractive properties as a touch or tactile sensor. This is due to its low weight, formability into thin sheets between 5 μm and 2 mm in thickness, and good mechanical properties. A thin layer of metallization is applied to both sides of the sheet to collect the charge and serve as electrical connections. This section describes several applications of PVDF to tactile sensing.

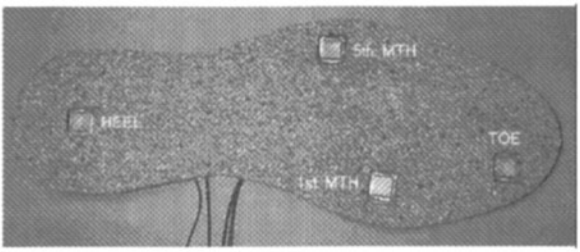

Figure 2. Insole with four embedded triaxial force measurement transducers. (From Ref. [7]).

There is increasing awareness of the necessity to measure forces between the plantar surface of the foot and the shoe for the diagnosis and treatment of various foot disorders. In particular, the simultaneous measurement of both shear and vertical forces is required. Razian and Pepper [7] developed a tri-axial pressure transducer with 10 x 10 mm and 500-µm thick elements of PVDF-TrFE. They were sandwiched between three 0.7-mm thick double-sided PCB transducer boards. An ultralow-noise tricoax-cable was imbedded in a central groove in the lower PCBs. The four layers were bonded together with an epoxy resin to make a transducer element that was 13- x 13- x 2.7-mm in thickness and weighed about 2 g. The transducers were calibrated in a special jig and the average sensitivity for vertical normal forces was 20 pC N^{-1} and for horizontal shear forces, 2.2 pC N^{-1}. Linearity and hysteresis were measured for applied load ranges of 0 to 700 N for vertical and 0 to 400 N for the horizontal axes. The linearity was better than 1% and the hysteresis was less than 2% in all cases. The authors were very concerned about crosstalk between the axes. The average crosstalk between the vertical and the shear axes was about 2% and between the two shear axes, about 1%. The combination of errors due to a pyroelectric effect and temperature dependence of the piezoelectric coefficients in a worst case scenario was less than 2%. Four transducers were embedded in a thin insole inside a shoe in locations as shown in figure 2. Force-time measurements were taken for three steps taken during a duration of four seconds by a normal individual. The authors believe that this device will be very beneficial in obtaining a better understanding of all of the forces acting on the plantar surface of the foot.

Tactile sensors for monitoring skin conditions were developed by several groups in Japan. Jiang *et al.* [8] made a soft tribo-sensor that simulated a human finger. It consisted of an aluminum pipe covered with concentric layers of sponge rubber, a 28-µm thick film of PVDF and a protective layer of cellophane tape. The device was tested on three types of paper with different roughness: superfine paper, newspaper and toilet paper. The sensor was scanned over the papers at velocities from 0.1 to 0.5 m s^{-1}. The raw data signals were very complex and difficult to analyze. Three data analysis techniques were devised and a wavelet transform method was found to be the most satisfactory. Tanaka *et al.* [9, 10] developed a "haptic finger" consisting of a copper plate with a layer of vulcanized rubber on top of which was an electroded PVDF film with a protective surface layer. The device was translated across various fabrics and also human skin from persons with various skin disorders. A strain gauge was used to measure the force applied to the haptic finger and the signals from the PVDF foil were recorded with a digital oscilloscope. Wavelet analysis was used to obtain an index of surface roughness, and dispersion of the power spectrum density in the frequency domain was used to characterize hardness. Good agreement was obtained between the results measured on skin with the haptic finger and an analysis by a clinician. Minimally invasive surgery is a recent technique in which surgical procedures on internal organs are performed using very small incisions. Surgical mechanisms and an endoscope are inserted for manipulation and viewing the surgical site. It is desired that the surgeon should be able to feel the tissue during the procedure. A tactile sensor is required that is able to determine the magnitude of the applied force between the sensor and the tissue. Dargahi [11, 12] developed an endoscopic grasper with a tooth-like structure formed of silicon. It contained a 25-μm PVDF film with four electrodes that was sandwiched between the silicon and a Plexiglass substrate. In use, the magnitude of the applied force could be found from the magnitude of the output of the PVDF and the position of application of the load was found from the slope of the output.

ENERGY CONVERSION

Taylor *et al.* [13] developed a device using piezoelectric polymers for converting the mechanical flow energy available in oceans and rivers, to electrical power. The structure was called an Energy Harvesting Eel. It used the trail of traveling vortices behind a bluff body to strain the piezoelectric elements. The undulation of the polymer resembled that of a natural eel swimming. Figure 3 is an illustration of the device. A PVDF prototype with eight independent electrode pairs was tested in a flow tank. It had a length of 24 cm in the direction of the flow, width of 7.5 cm and a thickness of 150 μm. It was placed in a flow tank and tested at flow rates of 0.35, 0.5 and 0.67 m s^{-1}. Data were acquired on all segments at a 50-Hz sample rate. A Fast Fourier Transform was used to calculate the frequency spectrum of data collected by the head and tail segments during a 20 s period with a flow rate of 0.5 m s^{-1}. The fundamental frequency measured in the head segment was 1 Hz. In addition to this frequency, the tail segment contained the third harmonic at 3 Hz but it was down 13 db from the fundamental. The tail generated less power and with more harmonics, possibly due to a whipping action at the free boundary. The phase relationship of the peak power point for each segment varied linearly along the length of the polymer sheet. It was found that the maximum power transfer occurred when the flapping frequency matched the vortex shedding frequency. Computer modeling showed that the elastic strain and, consequently, the power obtained could be increased by constructing an Eel with two piezoelectric layers enclosing a central inactive layer. However, an Eel that is too thick will not move. Consequently there is an optimal central layer thickness to maximize the power. Operation of the Eel at electrical resonance frequencies was not practical because of the low frequency of the motion (1-2 Hz). A special switching circuit was developed to maximize the useful power. The concept will be scaled up in a multi-element system with five Eels, each 130 x 15 cm and capable of producing 1 W in a nominal 1-m s^{-1} flow in real ocean environments.

Ikura [14, 15] noted that vast amounts of industrial heat are emitted to the environment because of the unfavorable economics of recovering waste heat or converting it to more useful forms of energy. They studied a system for direct conversion of low-grade waste heat to electricity using pyroelectric conversion. The technique was based upon the Olsen cycle [16]. Figure 4 illustrates a low temperature ferroelectric hysteresis loop superimposed on a high

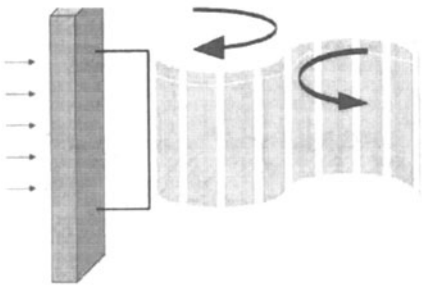

Figure 3. Eel movement behind bluff body. (From Ref. [13]).

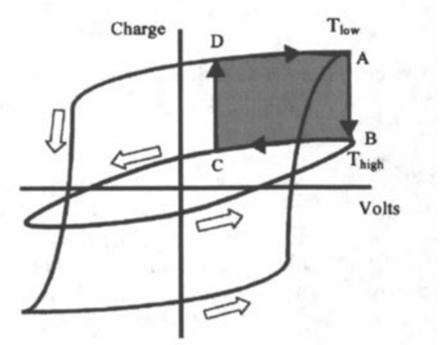

Figure 4. Copolymer hysteresis curves and Olsen cycle. (From Ref. [14]).

temperature loop. The loop ABCD is traversed in a counter-clockwise direction. When the temperature of a pyroelectric film is decreased at low voltage, charge accumulates on the film along C-D. This occurs because the crystal structure within the pyroelectric film begins to transform from the paraelectric to the ferroelectric phase. As the voltage is raised from low to high at the low film temperature, the charge increases along D-A. If the temperature of the film is increased at high voltage, the charge is released along A-B. This results because the ability of the film to store the charge decreases as the crystal structure is transformed from the ferroelectric to the paraelectric phase. Finally, the external voltage is lowered from high to low and a further discharge occurs along B-C, thus completing a heat-to-electric conversion cycle. The authors mounted 40-µm thick films of 60/40 P(VDF-TrFE) between brass sheets and inserted the assembly in a plate-type heat exchanger. A number of temperature and applied voltage ranges were tested. It was found that the two most significant parameters affecting the net power output were proper synchronization of voltage control with temperature cycling and minimization of the internal leakage current. The leakage current could be minimized by switching the voltage from high to low as soon as the pyroelectric output decreased to a negligible level. Especially good operation was found with temperature and voltage ranges of 40-70°C and 400-800 V, respectively. They believe that it is possible to reach a net power output of 250 J per liter of

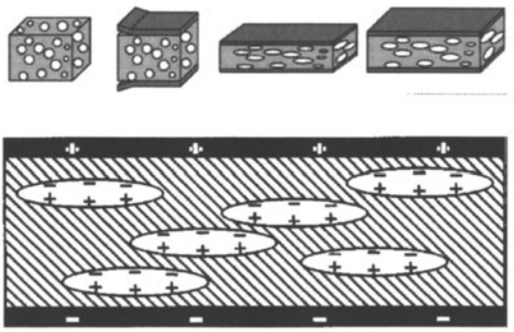

Figure 5. Upper: Steps in processing porous polymer films (from Ref. [17]. Lower: Schematic diagram showing charge deposition (from Ref. [18]).

material. A preliminary cost estimation indicated that a 1 MW pyroelectric production facility could be constructed for a cost of about $1000 per kW and the production cost would be less than 2 cents per kWh.

POROUS POLYMERS

A soft piezoelectric transducer material made from cellular polymers has been developed recently [17, 19]. The material contains microscopic voids on the internal surfaces of which are positive and negative charges. They are strongly piezoelectric and have found a large number of applications. The method of preparation and some of the applications are described in the sections below.

Preparation

The steps in the preparation are shown in figure 5 (upper). A polypropylene polymer film is filled with inorganic particles. This film is coextruded between two thin unvoided films. During biaxial stretching, the particles serve as stress concentrators for microcracks which develop into lenslike voids. The size of the voids can be varied by an inflation process using gases such as nitrogen or carbon dioxide at a typical pressure of 5 MPa. A thermal treatment at temperatures between 100 and 160°C is used to increase the crystallinity of the polymer matrix and to stiffen and stabilize the foam structure. Cellular polypropylene can be charged by a corona discharge without a grid at a high corona-point voltage around or above 20 kV.The resulting surface-charge layers lead to very high electric fields across the thickness of cellular foam layers and thus to internal breakdown in the disk-shaped voids. After breakdown, a void is charged to top and bottom polarities that are opposite to the respective surface-charge and electrode polarities of the cellular film (figure 5 (lower)). These microplasma discharges are not destructive. If ac voltages above the threshold for breakdown of the gas in the voids are applied to cellular polymers, breakdown events occur during each half cycle of the applied voltage. In each half cycle, the direction of the "macroscopic" dipole formed by the charged void is

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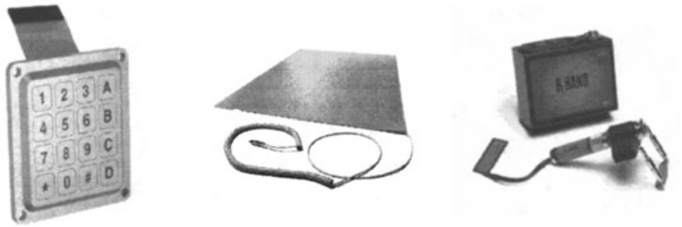

Figure 6. Applications of porous ferroelectrets: keypad, safety doormat, and musical pickup. URLs cited in Ref. [17].

Figure 7. Cellular polypropylene sensor element for detecting forces acting upon dog limbs [20].

switched. This process can be seen as analogous to the switching between thermally stable polarization states in ferroelectric materials, the threshold for breakdown being the analogue of the coercive voltage in ferroelectrics. The sign of polarity of the films can be reversed by changing the charging polarity and hysteresis-like behavior can be induced by cycling the polarity. These materials are called ferroelectrets because of the similarity to hysteresis in ferroelectrics. Large values of up to several hundred pC N^{-1} are commonly achieved for d_{33}, more than an order of magnitude greater than in conventional ferroelectric polymers and comparable to the values found in ferroelectric ceramics. Consequently, a wide range of applications has now been found.

Applications

Push buttons for keyboards, keypads and control panels with small areas have been made with cellular polymer films. Their high sensitivity allows the implementation of sensors behind protective layers of different materials so as to achieve vandal-proof control panels usable, for example, for cash dispensers or ticket machines (figure 6 (left)). Because the films are soft and flexible, curved keyboards can also be constructed. Several devices useful in nursing homes or hospitals have been made. Figure 6 (center) illustrates a pad placed in front of a door that will signal an alarm if a person exits through the door. This can be used to track persons with dementia. It can also be used as a fall sensor. Similar devices can be used to determine if an ill person leaves her/his bed or chair, again to warn of the possibility of falls. Various types of

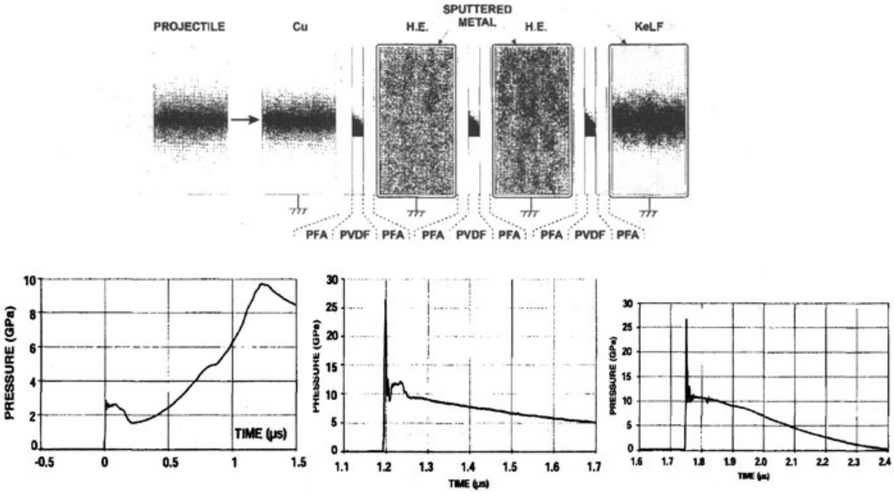

Figure 8. Upper: Experimental arrangement for high-explosive pressure measurements. Lower: Responses of the three PVDF gauges. (From Ref. [21]).

microphones and musical pickups can be constructed from the polymers. Figure 6 (right) shows a pickup with a frequency response from 50 Hz to 33 kHz that can be attached to a violin. A sensor that can be used to detect forces acting upon dog limbs was developed by Heikkinen *et al.* [20] (figure 7). It was sufficiently light in weight that it did not have a significant adverse effect on the biomechanics of the limbs. Other applications include orthopedic diagnostics, sports studies, respiration monitoring, loudspeakers, hydrophones, pressure distributions between vocal chords, etc.

SHOCK SENSORS

Piezoelectric materials are widely used as active elements in stress gauges uscd to provide nanosecond, time-resolved stress measurements of rapid impulsive stress pulses produced by impact, explosion, or rapid deposition of radiation. Piezoelectric PVDF devices are the sensors of choice for a wide range of measurement applications because of their unique characteristics, i.e., rapid responses (ns), large stress range (kPa to Gpa), large signal to noise ratio and high sensitivity (4µC cm^{-2} for 10GPa). In addition, the sensors are very thin (less than 25 µm), self powered, and adaptable to complex contours. Their direct stress-derivative or stress-rate signals of a few nanoseconds duration, and higher operating stress limits, provide capabilities not available with any other technique. Bauer [21] devised a cyclic poling process so that reproducible remanent polarizations as large as 9 µC cm^{-2} could be achieved routinely. The behavior of PVDF was studied over a wide range of pressures using high pressure shock loading yielding well-behaved, reproducible data up to 25 GPa in inert materials. Grounded thin metallic layers were sputtered on both the projectile and the sample, effectively eliminating the capacitive coupling of the sensor to the environment. Shock pressure profiles were measured in porous high explosives in a detonation regime. The experimental arrangement is shown in figure 8 (upper). The shock pressure profiles of the three PVDF gauges are shown in