



Application of poly (3,4-ethylenedioxythiophene)-poly(styrene sulfonate) to poly(vinylidene fluoride) as a replacement for traditional electrodes
by Jill Irene Lorenz-Hallenberg

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering
Montana State University
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Abstract:

Piezoelectric devices can be made more efficient by replacing the metal electrodes with polymer electrodes. Different conducting polymers were investigated to replace the metal electrodes currently used to actuate PVDF. After two years of working with the conducting polymer poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate), PEDOT-PSS, it was successfully deposited on the piezoelectric polymer poly(vinylidene fluoride), PVDF in 5-10 micron thick layers.

The biggest challenge presented was polymer on polymer adhesion. The fluorine in PVDF gives it the same “non-stick” properties as Teflon®. Similar to applying metal electrodes, PVDF must be surface treated before the polymer will adhere. Unlike metal electrodes, a special primer must be applied before a layer of PEDOT-PSS can be applied. The primer used in this study is a modified recipe originating from a formulation developed by the Bayer/Starck Corp. This primer adheres the PEDOT-PSS to the PVDF using a polyurethane polymer mixed with PEDOT-PSS and a solvent.

The primer and the PEDOT-PSS mixture are applied using an artist’s airbrush to lightly spray each thin layer. Each layer is then dried using cool, forced air. This procedure is repeated until a layer approximately 10 microns thick has been achieved. Once the last layer is dry, the conductivity can be measured. Using two brass blocks to measure the resistance, the conductivity of the PEDOT-PSS layer is obtained. It has been found that the sprayed layer of PEDOT-PSS has a conductivity of ~0.05 S/cm; this is 2.5% of the published conductivity of ~2 S/cm. This level of conductivity is high enough to operate PVDF within the frequency range of 20 Hz to 300 Hz.

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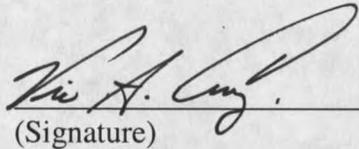
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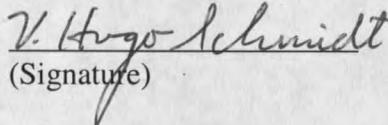
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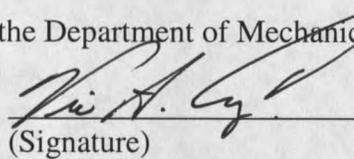
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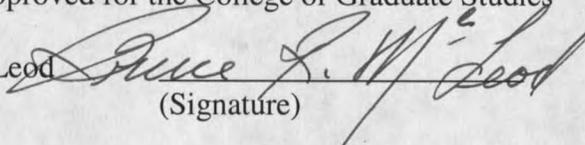
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ABSTRACT

Piezoelectric devices can be made more efficient by replacing the metal electrodes with polymer electrodes. Different conducting polymers were investigated to replace the metal electrodes currently used to actuate PVDF. After two years of working with the conducting polymer poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate), PEDOT-PSS, it was successfully deposited on the piezoelectric polymer poly(vinylidene fluoride), PVDF, in 5-10 micron thick layers.

The biggest challenge presented was polymer on polymer adhesion. The fluorine in PVDF gives it the same "non-stick" properties as Teflon[®]. Similar to applying metal electrodes, PVDF must be surface treated before the polymer will adhere. Unlike metal electrodes, a special primer must be applied before a layer of PEDOT-PSS can be applied. The primer used in this study is a modified recipe originating from a formulation developed by the Bayer/Starck Corp. This primer adheres the PEDOT-PSS to the PVDF using a polyurethane polymer mixed with PEDOT-PSS and a solvent.

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CHAPTER 1

Introduction

Today, smart materials can be found in just about everything from credit cards to computer screens to windshield wipers on the Mars Rover. Some dielectric materials are a prime example of smart materials found commercially as well as in experimental research labs. Dielectric materials can be further broken down into subgroups: piezoelectric, pyroelectric, and ferroelectric. Figure 1-1 below shows that a material that is ferroelectric, is also pyro- and piezoelectric, however, if a material is piezoelectric, it is not necessarily pyro- or ferroelectric.

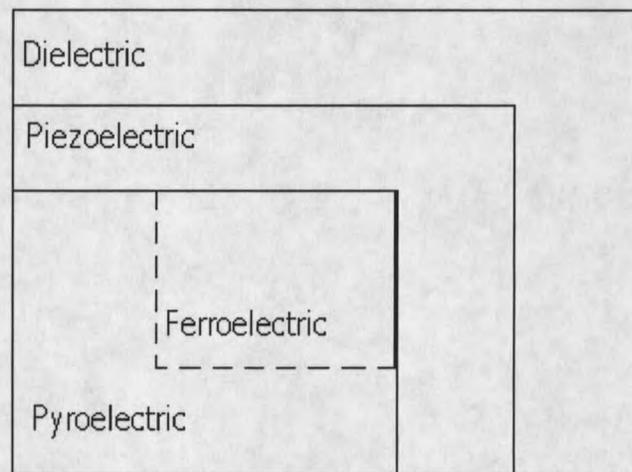


Figure 1-1: The family of dielectric materials.

Looking specifically at piezoelectric materials, there are three main types: single crystal, ceramic, and semi-crystalline, or piezo-polymers. Piezoelectric materials are

characterized by their use of relatively high voltage and low current draw, and can be found in sensors, actuators, and power sources. Even more specifically, the semi-crystalline piezopolymers are highly flexible, and can provide large displacements in typical actuator designs. One of these polymers, poly(vinylidene fluoride), known as PVDF and discussed in detail below, is commercially available, used in multiple commercial applications, and is a popular material in a number of research applications. When used for its dielectric or piezoelectric properties, a thin metal electrode must be applied to both faces of a PVDF sheet in order to induce an electric field. These metal electrodes impede the mechanical performance of the PVDF film by limiting the amount of strain that can be induced. It was hypothesized that a conducting polymer can replace the metal electrodes to create a more efficient all-polymer electro-active actuator. A program is under way to implement this hypothesis. Major steps in this program are:

1. Replace silver electrode with conducting polymer electrode on PVDF
2. Get good adhesion between conducting polymer and PVDF
3. Develop a repeatable and efficient application process
4. Measure the mechanical properties of the conducting polymer
5. Measure the conductivity of the conducting polymer
6. Measure the dielectric properties of the all-polymer film
7. Measure the piezoelectric response of an all-polymer-film bimorph
8. Reproduce MSU actuator (described in Chap. 2) and measure its performance

This thesis presents the procedures and success in carrying out the first five steps in the above program.

Many different conducting polymers are in the experimental stage; however, there is one that is commercially available and can be found keeping computer screens, TV screens, and various optical equipment dust free. This material was developed by the Bayer/Starck corporation, and is known as Baytron P[®], or poly(3,4-ethylenedioxythiophene) –poly(styrene sulfonate) or PEDOT-PSS. This material is discussed in further detail later.

Using two commercially available polymers, one conductive, and one piezoelectric, the challenge lies in applying the PEDOT-PSS to the PVDF as an electrode. Unfortunately this is not an easy task, for very little sticks to PVDF. The following will discuss a brief history of each polymer, list some commercial applications, explain experimental methods used in applying PEDOT-PSS to PVDF, discuss results of dielectric and other measurements, and provide recommendations for future analysis.

Poly(vinylidene fluoride)

In 1880, the Curies [1] discovered crystals in which mechanical energy is converted with high efficiency into electrical energy. Today, these crystals are known as piezoelectric crystals. These crystals are characterized as piezoelectric because of their ability to convert mechanical energy into electrical energy and vice versa.

Almost 90 years later, in 1969, H. Kawai [1] discovered strong piezoelectric effects could be induced in a polymer film called poly(vinylidene fluoride), hereafter referred to as PVDF. Its chemical formula is $(\text{CH}_2\text{CF}_2)_n$. Kawai found that by stretching PVDF several times the original length, applying a static electric field of about 300

kV/cm along the thickness, raising the temperature gradually from room temperature to 90° C, and then slowly cooling, the polymer chains in the crystalline portions align themselves in a *trans* configuration (see Figure 1-2, p. 6) to form orthorhombic piezoelectric crystallites.

F. Swarts, a Belgian chemist, [1] first synthesized the vinylidene fluoride (VDF) monomer in 1901. The VDF monomer is a gas at standard temperature and pressure, has a boiling point of -85 C, is relatively stable, and does not require an inhibitor to prevent spontaneous polymerization. Commercial synthesis of the vinylidene fluoride monomer involves gaseous pyrolysis reactions. A number of starting materials are used; pyrolysis products include VDF and small amounts of other compounds including saturated and unsaturated halogenated compounds.

Laboratory and historical syntheses of VDF involve the generation of gaseous VDF from liquid phase reactions. The first preparation by Swarts [1] was the reaction of 1,1 difluoro-2bromoethane with potassium hydroxide in a solution of ethanol. The polymer PVDF is prepared by an addition reaction; that is, the polymer is formed by sequential addition of monomer units. A substance that forms a free radical initiates the polymerization, allowing monomers to add to this free radical to form a growing free radical chain terminated only after high molecular weight is obtained.

The other type of polymerization, condensation, occurs with the formation of some other product in addition to the polymer. Usually this product is a small molecule such as water or an alcohol. It is often difficult to obtain the long chain lengths needed to produce high molecular weight polymers. Consequently, when it is possible to form a

particular polymer structure by either an addition or a condensation reaction, the addition reaction is usually the reaction of choice. PVDF is the only commercially available piezopolymer film, and when poled, has the highest piezo and pyroelectric activity of any polymeric material so far investigated. [1]

Poly(vinylidene fluoride) is a polymer with various useful material characteristics. As an untreated polymer, PVDF is known and used for its high electrical resistance, good flame resistance, and its resistance to damage by various chemicals and ultraviolet light. When treated properly, PVDF becomes a piezoelectric polymer, which also has pyroelectric and ferroelectric properties. A piezoelectric material is one that will change shape when it is placed in an electric field, or will create an electric field when mechanical force is applied.

The polymer, PVDF, is transformed into a piezoelectric material first by stretching the polymer sheet so that its crystallites transform from the alpha phase into the polar beta phase. Rolls of piezo film are produced in a clean room environment. The process begins with the melt extrusion of PVDF pellets into a sheet form, followed by the stretching step. The material is stretched to one-fifth of its extruded thickness before it is annealed and polarized. This polarization is accomplished by annealing the polymer in an electric field. Once PVDF is properly annealed, it will maintain fairly constant piezoelectric properties as the temperature varies over the operating range of about -20° to 100° C.

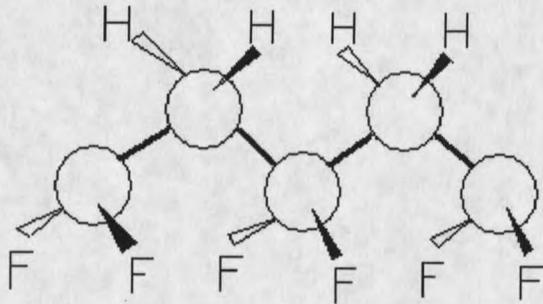


Figure 1-2: PVDF polarized chain

Observing PVDF on the microscopic level, one can explain why it has piezoelectric characteristics. A segment of a vinylidene fluoride (CH_2CF_2) chain that is part of the unit cell of the non-centrosymmetric space group $\text{Cm}2\text{m}$, or $\text{mm}2$ is shown in Figure 1-2. [2] The crystalline unit cell structure itself is orthorhombic consisting of two VDF monomers. Part of the dipole moment exists because the fluorine is so much more electronegative than the carbon. The fluorine atoms attract the electrons away from the carbon atoms making the CF_2 in the chain very polar. The same effect occurs in the CH_2 except the carbon is more electronegative than the hydrogen, creating another dipole in the same direction.

The last step in making the piezo-polymer useful is applying an electrode layer. PVDF is closely related to Teflon[®], hence it is difficult to adhere electrode materials. Accordingly, the polymer is subject to an intense surface treatment to promote adhesion.

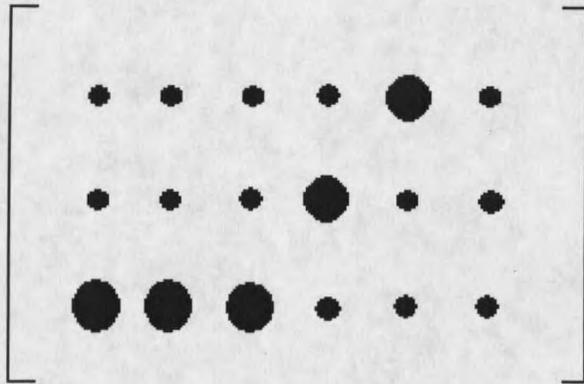


Figure 1-3: Piezoelectric matrix for $mm2$ point group [2]

The tensor matrix shown in Figure 1-3 indicates the circumstances in which a crystal space group will respond to electrical, thermal, or mechanical stimuli. The piezoelectric matrix for point group $mm2$ shows how PVDF will respond piezoelectrically. For example, a thick dot in the d_{31} space indicates that when an electric field is applied in the 3 direction, the sample will expand or contract in the 1 direction. Published values for the dielectric constants are also used in calculations for a bimorph used in vibration suppression and other applications. Tensor matrices and measured values also exist for pyroelectric, dielectric, and mechanical properties, but will not be discussed here.

In other areas, extensive research is being conducted on a copolymer, P(VDF-TrFE). In this copolymer, a percentage of the trifluoroethylene monomer, CHF-CH_2 , is inserted along the PVDF chain. The copolymer presents many advantages over PVDF in that it has the advantage of crystallizing directly into the beta phase, and the degree of

material crystallization is elevated from 55% in PVDF, up to 90% in P(VDF-TrFE). The major disadvantage of the copolymer is the higher cost.[3]

There are many commercial applications for PVDF in the nonpolar state as well as the polar form. Not only is PVDF an excellent thermal and electrical insulator, but it is also chemically inert. These properties make the nonpolar PVDF an excellent insulator for electrical wires in aircraft and computers. The semi-crystalline, piezoelectric PVDF can be found in sensors, actuators, and power sources.

Poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate)

Wanting to produce a plastic material that would enable the flow of electrons, Hideki Shirakawa [4] undertook the first experiments in the direction of conducting polymers. Shirakawa chose to work with polyacetylene and was unsuccessful until an accident in the lab led to an amazing discovery. When his graduate student mistakenly added 1000 times the otherwise normal amount of catalyst to a reaction, a silvery, glossy plastic film was produced which had properties somewhat like those of the semiconductor silicon. Further experimentation showed that the electrical conductivity was drastically improved when iodine was added to the mix. It was eventually discovered that when using specially prepared catalysts, adding iodine, and mechanically stretching the polymer, almost one-fifth of the conductivity of copper could be achieved. Shirikawa shared this discovery with Dr.'s Alan MacDiarmid and Alan Heeger, who performed further tests on the material and in 1976, and conducting polymers were born.

The scientists found that they were able to control electrical conductivity of polymers over the full range from insulator to metal by chemical or electrochemical doping.

“Conductivity results from the existence of charge carriers (through doping) and from the ability of those charge carriers to move along the pi-bonded ‘highway’. Consequently, doped conjugated polymers are good conductors for two reasons:

1. Doping introduces carriers into the electronic structure. Since every repeat unit is a potential redox site, conjugated polymers can be doped to a relatively high density of charge carriers
2. The attraction of an electron in one repeat unit to the nuclei in the neighboring units leads to carrier delocalization along the polymer chain and to charge carrier mobility, which is extended into three dimensions through interchain electron transfer

Disorder, however, limits the carrier mobility and, in the metallic state, limits the electrical conductivity. Indeed, research directed toward conjugated polymers with improved structural order and hence high mobility is a focus of current activity in the field.” [4]

Twenty years later, in 1993, scientists in the Bayer lab discovered a particularly long-term stable, electrically conducting, plastic material: PEDOT. [5] Research scientists Friedrich Jonas, Gerhard Heywang, and W. Schmidtberg found that the compound of PEDOT and PSS (poly(styrene sulfonate)) proved especially useful in practical situations, such as anti-static coatings. Applications of PEDOT-PSS in the fields of circuit boards, capacitors, and antistatic films have improved industrial products and methods of production. For example, by applying a thin, transparent layer of PEDOT-PSS to photographic films, the so-called “flashes” produced when unwinding the film can be eliminated. These flashes occur because when film is wound or rewound it becomes electrostatically charged, causing sparks that leave specks on developed

pictures. Another application can be found in printed circuit boards; lining drilled holes with PEDOT-PSS and electroplating copper over the polymer can achieve positive contact between the surfaces. PEDOT-PSS can also be found replacing manganese dioxide cathodes of capacitors which are used in mobile phones, laptops, and camcorders [5], and has also been used in some fuel cell research. There are many different conducting polymers. Shown in Figure 1-4 are the molecular structures of some conjugated polymers prior to doping.

