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 PVDR. 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.
APPLICATION OF POLY(3,4-ETHYLENEDIOXYTHIOPHENE)-POLY(STYRENE SULFONATE) TO POLY(VINYLDENE FLUORIDE) AS A REPLACEMENT FOR TRADITIONAL ELECTRODES

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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.

![Dielectric Materials Diagram]

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 (CH₂CF₂)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$_2$CF$_2$) chain that is part of the unit cell of the non-centrosymmetric space group Cm2m, or mm2 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.

\textit{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.
Figure 1-4: Molecular structure of various polymers [4]
The Concept of Doping

Before a conjugated organic polymer is doped, it is either an electrical insulator or semiconductor. Those polymers that can have their conductivity increased by several orders of magnitude can be referred to as electronic polymers, or conductive polymers. Below in Figure 1-5, it is illustrated how doping can increase the conductivity of a conjugated polymer, such as polyaniline. So what is doping, and how does it change a conjugated polymer into a conducting polymer? According to Dr. MacDiarmid:

![Conductivity chart](image_url)

Figure 1-5: Conductivity chart [6]

"Redox doping involves either the partial addition (reduction) or removal (oxidation) of electrons to or from the pi system of the polymer backbone. During the doping process, an organic polymer, either an insulator or a semiconductor having a small conductivity is converted to a polymer which is in the "metallic" conducting regime. The controlled addition of known, usually small nonstoichiometric quantities of chemical species results in dramatic changes in the electronic, electrical, magnetic, optical, and structural properties of the
polymer. Doping is reversible to produce the original polymer with little or no degradation of the polymer backbone.” [6]
CHAPTER 2

Motivation and Technical Challenges

In hopes of improving the performance of a piezoelectric actuator being developed by Dr. Hugo Schmidt, Professor of Physics at Montana State University, it became obvious that elimination of the metal electrodes would be adventurous. Piezoelectric polymer mechanical performance is greatly reduced in a mechanical sense by the metal electrodes required to create an electric field. By developing a conductive polymer to replace these metal electrodes, the goal is to enhance the mechanical properties of piezoelectric polymer actuators. This piezoelectric actuator is discussed in detail below.

Piezoelectric Actuator

A lightweight, low power consumption piezoelectric actuator is currently being developed to control noise and vibration in micro-gravity environments. The manufacturing process of this actuator has proved to be the most important step to success. If the material is damaged during the manufacturing process, arcing will occur when high voltage is applied. Stiffness and the spring constant of the actuator are also important factors that are affected by the manufacturing process. Between each bimorph is an epoxy layer; the thickness of this epoxy layer has a large effect on the stiffness of the resulting bimorph and the thicker the epoxy layer, the higher the elastic modulus of the bimorph. Our goal is to have high flexibility,
thus a low modulus of elasticity. The final assembly of a successful actuator includes special mounts that attach it to the experiment box to be free floated and the space shuttle’s wall.

Properly stretched and polarized PVDF is obtained from Measurement Specialties. This company, through a silk-screen process, also applies the silver electrode pattern shown below in Figure 2-1.

![Figure 2-1: Actuator electrode pattern, inside, and outside](image)

Copper tabs are used for signal routing from one bimorph to the other. Using a special conductive tape, the electrodes are attached to the silver paint on the PVDF. Once the sheet has all the proper electrical connections, epoxy is applied and another sheet of PVDF is placed on top to make a bimorph.

The two main requirements for the actuators are to reduce the epoxy layer thickness and to make the actuators more uniform. Several methods of applying the epoxy were developed, tested, and compared. It was found that each method gave
desirable results in different areas. The steps that gave desirable results from each method tested were combined into a new process which produced the most uniform epoxy layer averaging about 10 microns thick (actual thickness ranged from 5 to 12 microns, Figure 2-2). This method was adopted and rigorously followed to achieve consistent results. The new bimorphs showed a 66% glue layer reduction from previous bimorphs.

Figure 2-2: The plot on the left show a surface plot of the epoxy layer thickness (microns) and the plot on the right shows the surface contour plot of the epoxy layer thickness (microns).

In order to determine if the epoxy layer thickness affected the performance of the actuator, a voltage vs. displacement test and a force vs. displacement test were performed to determine the electrical and mechanical stiffness of each actuator. The results in Figure 2-3 show a displacement ranging from 0.0133 μm/volt to 0.0136 μm/volt on the right and 5.4 N/m to 7.7 N/m on the left. The experimental results were used to calculate
a more accurate modulus of elasticity which was then compared to theoretical results.
The experimental results were almost identical to the theoretical results. [7]

Figure 2-3: Force vs. Displacement and Voltage vs. Displacement graphs

The next step in building the actuator is gluing the edges of the bimorphs together
to create a bellows actuator, (Figure 2-4). Two single bellows actuators are then glued
together to create a double bellows actuator stack, (Figure 2-5).

Figure 2-4: Bellows actuator, edge view. Expansion/contraction direction shown by the
double-ended arrow.
Notice that the actuators in the double bellows stack are perpendicular to each other. Since the actuator is made of a thin film, it is unable to withstand shear stresses. This bellows design allows the actuator to maneuver freely in the 1 and 2 directions, but the 3 direction is primarily immobile and the actuator will tear if any mechanical load is applied. To eliminate this problem, the actuators were stacked perpendicular to each other to allow maneuverability in three directions. Mounting arms were placed on each side to eliminate the remaining shear stresses that the perpendicular stack was not able to eliminate. The mounting arm was designed not only to absorb shear stress, but also to maintain very small angles between the inner box plane and outer box plane.
The actuator mount is a simple device. Looking at the diagram in Figure 2-6, one can see that the actuator is attached to the inner and outer walls by a flexible wire acting as a hinge. This hinge is used to eliminate small angles created by the movement of the free-floating box. This design also creates more room for the free-floating box to follow the frame without impacting the walls.

The actuator stack has two primary functions: first is to isolate vibration, and the second to relay signals from the outer box to the inner box. Figure 2-1 on page 15, shows two extra electrode paths at the bottom of the PVDF sheet. These paths can carry a signal up to ±15 V with no measurable displacement effect.[8] By using these extra signal paths, the need for an extra umbilical from the outer box to the inner box was eliminated without the use of infrared technology.
The next technical challenge for improving the actuator performance is elimination of the silver electrodes in hopes of achieving a higher displacement per volt. The data above have made it clear that the performance of the actuator is highly affected by the electrodes and manufacturing process. The true challenge lies in not only applying the conductive polymer, but also applying a uniform layer that is thick enough to create the appropriate electric field, and thin enough to avoid high spring stiffness.

Measurement of electromechanical constitutive properties

The most important measurement for this research is to be able to measure the conductivity of the conducting polymer. In order to replace metal electrodes with polymer electrodes, the conductivity must be high enough to create an appropriate electric field across the piezoelectric polymer when an ac voltage is applied. This field is also dependent on the thickness of the electrode; a thicker electrode eases the flow of current through the polymer. This introduces the question of how thick is too thick? If the polymer electrode is too thick, it will adversely affect the mechanical properties of the all-polymer actuator. The conducting polymer must also be stable enough in a thick film to remain intact.

The first measurements will be taken from a single film with electrodes. By attaching a tab and applying a constant voltage and a varying frequency from 20 Hz to 300 kHz, the impedance and phase angle can be measured and used to calculate the real and imaginary permittivity of the material, otherwise known as a Cole-Cole plot.
comparing the data from the silver electrodes to the data from the conducting polymer electrodes, it can be determined if PEDOT-PSS really can replace metal as an electrode. Calculations used to create the impedance spectroscopy plot and Cole-Cole plot can be found on p. 34. After measuring the single film, a bimorph will be made and leads will be attached to the all-polymer bimorph, and the dielectric properties will be measured and compared to existing data taken with silver electrodes. This bimorph will then be used to produce an actuator for force vs. displacement and volt vs. displacement testing.

**Printing electrode patterns of PEDOT-PSS**

There are many different methods for printing electrodes onto materials, one of the most popular being screen-printing. This method is used commercially to print detailed silver electrode patterns onto various substrates. Considering its success with silver, the question is why not use it to print PEDOT-PSS? The screen-printing process in general is very uncomplicated; basically the electrode paste is forced through a screen by a squeegee onto the substrate. A picture of the screen-printing apparatus located at NASA Langley Research Center is shown in Figure 2-7.
The "trick" to screen-printing is obtaining the right viscosity and solvent solution for the material being forced through the screen, hereafter referred to as the paste. The paste must be thick enough to not flow freely through the screen, but it must also be thin enough to be forced through the screen in a uniform distribution (Figure 2-8).

Figure 2-7: Picture of screen-printer

Figure 2-8: Diagram of Screen-Printing process
This posed a problem with PEDOT-PSS because it is a suspended solution in water; hence a dilute solution has nearly the viscosity of water. Fortunately, PEDOT-PSS can be evaporated to create a more viscous solution. This poses the question of how much water should be evaporated to get the appropriate viscosity, and what solvents, if any, should be added to avoid sticking to the screen. The final challenge is printing the paste onto a PVDF substrate. It was discovered early on that PEDOT-PSS and untreated PVDF do not adhere to each other, so the PVDF was replaced with treated Mylar to find the proper paste solution.

Airbrushing is another less accurate method to apply a thin layer of PEDOT-PSS requiring some artistic ability. Using an artist's airbrush, a thinned solution of PEDOT-PSS can be sprayed onto PVDF one thin layer at a time. By controlling the spray, a uniform layer can be sprayed onto a substrate with relative ease; however a pattern cannot be painted without a template.

Both screen-printing and airbrushing techniques will be discussed in further detail in Chapter 3, Experimental Methods.
CHAPTER 3

Experimental Methods

Many problems were encountered in attaching the new electrode layer, the first being the need for appropriate printing formulations of PEDOT-PSS. Upon contacting the Bayer/Starck Corporation, many different formulations for printing PEDOT-PSS were supplied and can be found in Appendix A. Many of the following formulations were for transparent antistatic coatings:

1. CPUD2 - Baytron conductive polyurethane dispersion II. All purpose coating formulation for a variety of substrates.

2. CPP 103T - For antistatic coatings with good adhesion properties on many plastic surfaces.

3. CPP 105T - For antistatic coatings with higher conductivity, good adhesion properties on plastic and glass surfaces, and resistance to both aliphatic and aromatic hydrocarbon solvents.

4. CPP 116.6 - For antistatic coating with good adhesion properties on polycarbonate or PVC plastic surfaces.

5. CPP 134.18 - For highly transparent static dissipative coatings with good adhesion properties on polycarbonate or PVC plastic surfaces. Good for dip-coating applications.

6. CPP-135 - For alcohol-resistant transparent dissipative coatings with good adhesion properties on polycarbonate or PVC plastic surfaces.

7. CPP 4531 I – For thermoformable coatings with good adhesion properties on many plastic surfaces.
8. CPP 4532 E3D – For conductive coatings on plastic surfaces as pretreatment for electrostatic coating. Also especially suited for coatings on corona-treated polyethylene and/or polypropylene.

9. CPG 130.6 – For scratch-resistant antistatic coatings with good adhesion properties on glass surfaces.

After testing the selected formulations that boasted good adhesion on plastics, it was discovered that the conductivity of these formulations was not high enough. The addition of polyurethane and other additives increased the resistivity of the PEDOT-PSS which defeats the purpose of using PEDOT-PSS for its conductive properties.

Abandoning these formulations for two more conductive formulations provided by Jill Simpson of the Bayer Co., (Baytron S and CPP 141D), experimentation recommenced. The Baytron S and CPP 141D proved to be more conductive than the above antistatic coatings, but not conductive enough. Upon visiting with Dr. Nick Pinto and Dr. Alan MacDiarmid, at the University of Pennsylvania, it was discovered that PEDOT-PSS does not need to be mixed with anything to be used as an electrode; however, adhesion may present a problem.

It was discovered that PEDOT-PSS will not adhere to untreated PVDF, in fact it beads similar to water on Teflon®. This type of reaction is not unexpected, because PVDF is a cousin to Teflon®. To counteract this “beading” effect, the PVDF surface needs to be roughened. There are many different methods for roughening a surface ranging from mechanical to chemical. For the sake of simplicity, a piece of steel wool was used to scratch the PVDF surface. Unfortunately, this treatment is very harsh on the PVDF surface; and water beading was still a problem. Next a chemical etch using a light
base was attempted, but this also failed. An ion beam was used next to bombard the PVDF surface, and finally an oxygenated plasma cleaning treatment was employed, which was successful when combined with a slightly modified “primer”, developed by the Bayer/Starck Co.

The exact ingredients of the “primer” are as follows:

11 g PEDOT-PSS (2.8 %)
3 g Bayhydrol 140
10 g n-methyl 2-pyrrolidinone
3 g 2-ethoxyethanol
0.03 g Silquest 187A
0.05 g Bayowet FT215

This primer is mixed on a stir plate at room temperature. It must be mixed in the order that the chemicals are listed. Constant stirring is essential to proper mixing.

Film casting

Before a film of PEDOT-PSS can be cast, the polymer dispersion must be properly prepared. Similar to screen-printing preparation, the viscosity must be lowered significantly. However, since the polymer is not being forced through a screen, large particles in the dispersion must be removed. This is accomplished by stirring the evaporated solution for about two days, keeping in mind that no evaporation should take place during the stirring. This slow stirring process also helps to eliminate tiny air bubbles that will cause pinholes during drying.
The substrate used must also be prepared prior to casting a film. Traditionally a glass plate is used as the substrate. This glass plate is cleaned using the following procedure:

1. Clean with glass cleaner
2. Run razor across surface until smooth clean surface is achieved
3. Clean with glass cleaner
4. Clean with acetone; this helps dissolve the glass cleaner and other impurities
5. Clean with isopropanol; this eliminate moisture from surface
6. Dry with heat gun, do not want isopropanol on surface
7. Put in low humidity chamber for 15-20 minutes before casting film

The drying conditions vary from using a dry chamber at room temperature to heating under vacuum. These drying conditions are dependent on the polymer being cast; some have to be cured in an oven with a specific atmosphere, i.e. nitrogen or argon; others can be dried slowly in a dry chamber, or quickly in a vacuum. PEDOT-PSS cannot be dried slowly, and cannot be baked. To date the best films have been created under vacuum at room temperature. However, if the vacuum is applied too long the material becomes too dry and is very brittle. Shown in Figures 3-1 and 3-2 is the film casting process. In Figure 3-1, the front of the casting blade is shown with a puddle of PEDOT-PSS. The casting blade is drawn over the puddle to create the uniform wet film shown in Figure 3-2. This wet film is then dried to achieve a film of PEDOT-PSS.
Figure 3-1: casting wet PEDOT-PSS

Figure 3-2: wet PEDOT-PSS films
**Airbrushing**

Applying PEDOT-PSS to PVDF using an airbrush requires the following equipment:

1. Artist’s airbrush kit
2. Template
3. Forced air gun

Using an airbrush for material application is an art and each individual must develop the proper technique. The following guidelines have been developed to help achieve good results:

1. Mounting the PVDF:

   When mounting the PVDF to the template, it must be flat. It must not have wrinkles present during spraying. Wrinkles cause pooling of the wet PEDOT-PSS. Masking tape can be used to attach the PVDF film to the template. This masking tape can later be used as a film label after spraying is complete. A PVDF film mounted in a square template as shown in Figure 3-3. This template assists in controlling the shape and pattern of the PEDOT-PSS electrode, as well as protecting and restraining the PVDF during spraying.
2. Layer order:

After mounting the PVDF in the template, one layer of the primer developed for applying PEDOT-PSS to PVDF must be sprayed on using the technique described next. The primer from p. 26, must be allowed to dry for at least 30 minutes to allow proper etching of the PVDF without forced air. Without this chemical etch, the PEDOT-PSS layer will not adhere to the PVDF. After the primer layer is dry, successive very thin layers of PEDOT-PSS mix are applied, following the spraying technique described below.

3. Spraying technique:

It is important to hold the spray gun perpendicular to the substrate. The spray nozzle should be about 8 to 10 inches from the substrate to achieve an even coat. Smooth continuous passes without change of spray direction are required while crossing the
substrate. After the pass is complete, one can change direction for the next pass. This prevents pooling and over-spraying of the edges. Each layer should look like a matt finish while wet, similar to the matt finish on a photograph. One can allow each layer to dry flat under cool forced air; even though this is not required, it speeds up the drying process. The air supply should be far enough away to not disturb the wet layer, yet close enough to dry the layer in a reasonable amount of time. The dry layer will be shiny, similar to a glossy finish photograph. This process must be repeated until the desired thickness is reached. About 20 such layers are required to obtain a 3 to 4 micron film. As shown in Figure 3-4, the substrate should be held in a vertical position with the spray gun perpendicular to the surface. It is apparent in Figure 3-4, that each PEDOT-PSS layer applied is very thin and transparent.
4. Equipment Maintenance:

Cleaning the airbrush at the end of each spraying session prevents flocculent build-up (usually after 2-3 hours of non-use) in the nozzle. If the floccules are not removed from the nozzle, they will work loose during the spraying process and embed in the layer being sprayed. The airbrush can be easily disassembled for cleaning. Then each part should be sonically cleaned in a non-specific soap solution to completely remove any caked-on PEDOT-PSS. The parts must be rinsed and dried completely before reassembly.

Screen-Printing

Prior to screen-printing, the PEDOT-PSS must be evaporated to increase its viscosity. By evaporating a 1.2% solid weight solution of PEDOT-PSS provided by the Bayer/Starck Corp., a thicker 2.7% solid weight solution can be produced. This more viscous solution was mixed with a solvent, 2-ethoxyethanol, in a 4:1 mix. The solvent used was selected after discussing screen-printing techniques with Nancy Brown, a technical service specialist from Creative Materials Inc; Ms. Brown suggested using a glycol-ether as a solvent. Using her advice, two different glycol-ethers were tried: 2-methoxyether, and 2-ethoxyethanol. After printing multiple samples made with each solvent, it was found that the 2-ethoxyethanol gave the best results.

Through trial and error, it was found that PEDOT-PSS can be screen-printed. Using a 110-mesh 45° vinyl screen, and multiple passes, detailed patterns of PEDOT-PSS were successfully printed onto plasma-treated Mylar.
Printing of PEDOT-PSS onto PVDF has not yet been accomplished. Since the screen-printing apparatus is located at NASA LaRC, NASA scientists will perform any further experimentation in this area.

Electromechanical Constitutive Properties

According to Alan MacDiarmid [6] of the University of Pennsylvania, PEDOT-PSS has a conductivity of ~2 S/cm. This conductivity has been shown to be high enough to operate PVDF devices for practical electrode thicknesses over a useful frequency range. There are many different methods for measuring conductivity of materials. When making measurements on a resistive material such as PEDOT-PSS, a possible problem is leakage of current between the input terminals of the ohmmeter via routes other than the intended through the specimen. Surfaces often provide a low resistance path through the accumulation of dirt and moisture.[9] There are different ways of avoiding this surface problem, such as guard rings when measuring resistance across a layer, and varying layer thickness when measuring resistance along a layer. Another problem when measuring resistance along a layer is “spreading resistance” if the electrode configuration is incorrect. Upon discussing this problem with Dr. Hugo Schmidt of Montana State University, it was decided that accurate measurements could be obtained using a large “length to distance” ratio. If the length of the electrode transverse to current flow is several times larger than the distance between the electrodes, this spreading resistance effect is negligible. Using two brass blocks 17.23 mm in length set at a constant 3.22 mm
apart, the resistance of PEDOT-PSS films could be determined. Using the thickness of
the film at the point of measurement, the conductivity, $\sigma$, can be calculated:

$$\sigma = \frac{d}{Rht}$$  \hspace{1cm} (3-1)

d=distance between the electrodes (m)
R=measured resistance (ohms)
h=length of the brass electrode (m)
t=thickness of the PEDOT-PSS layer (m)

Determining the conductivity alone does not answer the question of the efficacy
of actuating PVDF with ac voltages using polymer electrodes. More experimental data
are required to answer this question. The experimental approach, impedance
spectroscopy, is useful to determine the apparent permittivity in the form of a Cole-Cole
plot. This apparent permittivity of the PVDF layer can be calculated over a frequency
range from measurements of the impedance magnitude and phase angle. Permittivity, $\varepsilon$, is defined as:

$$\varepsilon = \frac{1}{j\omega Z C_c}$$  \hspace{1cm} (3-2)

$$C_c = \frac{A \varepsilon_0}{d}$$  \hspace{1cm} (3-3)

$C_c$=geometric capacitance (empty cell capacitance) (F)
$Z=Z_re^{jZ_im}$=Impedance (ohms) (the impedance is split into real and imaginary
parts)
A = area of electrode (m²)

\( d \) = thickness of PVDF (m)

\( \varepsilon_0 = 8.85 \times 10^{-12} \text{ (F/m)} \) (SI unit conversion factor)

\( \omega = 2\pi \times \text{freq} \) (Hz)

Substituting the complex impedance into equation 3-2 and expanding the equation:

\[
\varepsilon = \frac{1}{j\omega (Z_{re} + jZ_{im})C_c} = \frac{1}{j\omega C_c \cdot Z_{re} - \omega C_c \cdot Z_{im}}.
\]

(3-4)

Multiplying the right side of equation 3-4 by its complex conjugate:

\[
\frac{-\omega C_c \cdot Z_{im} - j\omega C_c \cdot Z_{re}}{-\omega C_c \cdot Z_{im} - j\omega C_c \cdot Z_{re} \cdot j\omega C_c \cdot Z_{re} - \omega C_c \cdot Z_{im}} \cdot \frac{1}{\omega C_c \cdot Z_{im} - j\omega C_c \cdot Z_{re}} = \frac{-\omega C_c \cdot Z_{im} - j\omega C_c \cdot Z_{re}}{(\omega C_c \cdot Z_{im})^2 + (\omega C_c \cdot Z_{re})^2}.
\]

(3-5)

Finally, separating into real and imaginary parts of the permittivity:

\[
\varepsilon_{re} = \frac{-Z_{im}}{\omega \left(Z_{im}^2 + Z_{re}^2\right) C_c}.
\]

(3-6)

\[
\varepsilon_{im} = \frac{-Z_{re}}{\omega \left(Z_{im}^2 + Z_{re}^2\right) C_c}.
\]

(3-7)

Here, the \( Z_{re} \) is positive but \( Z_{im} \) is negative. The Cole-Cole plot is obtained by graphing the real vs. imaginary permittivity obtained over a frequency range.

To measure the impedance and phase angle of PVDF, two aluminum semi-circular tabs with a radius of 0.95 cm was attached to the silver electrode painted on the
PVDF. Using the Wayne-Kerr Precision Component Analyzer 6425, 1 volt (ac) was applied to the electrodes and the impedance and phase angle were measured over the frequency range of 20 Hz to 300 kHz. An example of the semi-circular tabs on the film can be seen in Figure 3-5.

This same method was initially used for the PEDOT-PSS electrode, but it was discovered that there was not complete contact between the aluminum and the PEDOT-PSS. To overcome this problem, it was decided to use a wet pool of PEDOT-PSS, with wires dipped into the pool leading to the Wayne-Kerr. A special jig was designed to hold a semi-circular pool of wet PEDOT-PSS on each side of the PVDF. This experimental setup can be seen in Figure 3-6.
This new jig and electrode design proved to eliminate the previous problem of poor contact to the polymer electrodes. Evidence of this problem and its solution is discussed in further detail in Chapter 4, Results and Evaluation.
Results and Evaluation

The following chapter discusses the results of different methods used to cast films of PEDOT-PSS, and the two selected methods of applying an electrode layer to PVDF. The first section, film casting, gives a detailed account each film casting, how it was prepared, how it was dried, and the resulting film. The next section talks about airbrushing and how the technique was developed. The last section discusses the results from the conductivity measurements and the dielectric measurements. In this final section, graphs of actual data collected are analyzed, and theoretical approximations are compared to measured numerical data.

Film Casting

In attempts to cast a free-standing film of PEDOT-PSS usable for mechanical testing, failures have outnumbered the successes, and successes have been more by accident and have not been repeatable. In an attempt to measure the mechanical properties of PEDOT-PSS, many attempts at casting a workable film were made. Below is a list of film casting trials with a brief description of how the PEDOT-PSS was prepared and how the film was cured.
Film #1: A solution of Baytron S was prepared for casting and dried slowly in a low humidity chamber. The resulting film stuck to the plate, and broke into very fragile, tissue paper like pieces when removed from the substrate.

Film #2: A thicker solution of Baytron S was prepared and cast. It was cured at 130 degrees C for 15 minutes. It resulted in “spider web” type film.

Film #3: The same Baytron S solution was cast and cured at 60 degrees C for 30 minutes producing the same results.

Film #4: The same Baytron S solution was cast and cured at 60 degrees C for 15 minutes producing the same results. The Baytron S formula was abandoned.

Film #5: Some PEDOT-PSS was evaporated from 1.2% weight to a more viscous 3.6% weight and homogenized 20 minutes. Five grams of 2-methoxyethyether was added to 14.36 g of PEDOT-PSS (3.6%), and homogenized for 5 minutes. The solution was put in a shaker for 2 hours to degas the solution.

Film #6: Some PEDOT-PSS was evaporated from 1.2% weight to a more viscous 3.6% weight and homogenized 20 minutes. Five grams of 2-ethoxyethanol was added to 14.93 g of PEDOT-PSS (3.6%), and homogenized for 5 minutes. The solution was put in a shaker for 2 hours to degas the solution.

Cast films #5, #6 cured at 60 deg C in 17” vacuum 15 min.

Film #5 chunky when wet.

Film #6 smooth when wet.

Both films were still wet after 15 minutes, so a full vacuum was pulled for 10 minutes. The films dried nicely, however there were many air bubbles present (#5 worse than #6).

Film #7: A sample of pure PEDOT-PSS, evaporated to a 3.6% weight viscous fluid, was cast and dried under full vacuum, and no heat (cast films of #5, #6 solution as well). The resulting films all had air bubbles present.

Added 4.5 g 2-methoxyether to film #7’s solution. Put it on the shaker for 2 hours. It dried under vacuum, resulting in a film with “chunks” present and again, the air bubbles.

Film #8: Used a mixture of 15.33g PEDOT-PSS (3.6%) and 5 g 2-ethoxyethanol. It was put on the shaker for 2 hours, and dried under vacuum, resulting in a film with “chunks” present and again, air bubbles.
Film #9: Used the same solution for #8, but homogenized the solution. During the homogenization, the vial was held in hand and moved around to get maximum mixing for about 10 minutes. The solution was very watery, and not as many bubbles were present when wet. A cast film was dried at 51 degrees C under a 15” vacuum, then the temperature was turned off and a full vacuum applied. The film bubbled like a melting gremlin in sunshine.

Recast film solutions #7, #9, and allowed them to cure overnight in a low humidity chamber. Film #9 still looked good, and film #7 started to shrink when checked the next morning, but both films were still wet. Made mistake of baking the films; they dried very brittle and were destroyed.

Conclusion: Baking PEDOT-PSS is not advisable. Films should not be cured under continuous vacuum. Since a usable film of PEDOT-PSS has not been obtained in a reasonable time, the mechanical measurements cannot be made at this time.

Airbrushing

The most effective method for applying PEDOT-PSS onto PVDF film is definitely a layer-by-layer spray method using an airbrush. When sprayed properly, an even, uniform film of PEDOT-PSS can be applied. Using an airbrush, however, is more of an art than a science. It takes time, practice, technique, and an understanding of chemistry and patience.

Early on, it was observed that PEDOT-PSS would bead on PVDF. In hopes of filling in the “gaps” left by the dried beaded layer, another layer would be sprayed. This second layer, theoretically, would fill in the gaps and a uniform layer would occur. This did not occur. The second applied layer beaded and bonded nicely to the previously sprayed PEDOT-PSS, leaving the same gaps.
Analysis and discussion of this problem resulted in the need to surface treat the PVDF. Mechanical scratching, chemical acid etching, ion beam etching, and plasma cleaning were attempted. Mechanical scratching with a piece of steel wool did not solve the problem. The PEDOT-PSS still beaded, and what didn’t bead, did not adhere.

Next, multiple samples were treated with the ion beam gun. At first the PEDOT-PSS seemed to be spreading evenly, with no beading, passing the “tape” test. This tape test involves using a piece of Scotch® tape, placing it over the electrode, adhering it to the electrode, and pulling the tape up. If the electrode pulls up with the tape, adhesion has not been achieved. Unfortunately, the early success did not last using this method of surface treatment. As the number of applied layers increased, they started to peel, removing the previously applied layers.

The next option was chemical etching. A mixture of sodium hydroxide diluted in water was used to etch three different samples of PVDF that had been ion beam treated. Sample one was etched for five minutes and rinsed with water and ethanol. Sample two was etched and rinsed with water, and sample three was etched and not rinsed. None of these samples resulted in successful adhesion.

The last option was plasma cleaning, but questions persisted: how long does the film need to be treated, and what power setting should be used? While testing different settings on the plasma cleaner, it was also decided to add a type of surfactant to the PEDOT-PSS. A co-worker at NASA, Lana Hicks-Olsen, suggested mixing egg whites with the PEDOT-PSS. It was theorized that since egg whites were mixed with the paint used to create the Mona Lisa, and other famous Renaissance paintings, it should work for
PEDOT-PSS application. The mixture was made, and sprayed onto the plasma-cleaned samples in a uniform film. Adhesion was good, uniformity was good, but the electrical resistance was also very high. Apparently, egg whites are a perfect insulator, which would not be a problem if achieving a good insulating layer was the primary goal. It was later found that the PEDOT-PSS layers became dry and brittle, and cracked into small pieces that fell off the PVDF after two days. The egg white technique was abandoned.

On August 7, 2002, while looking through the Baytron Coating Guide Formulations manual, the solution to the beading problem was found. Formula CPP 4532 E3D, refer to page 25, presented a promising solution. It was decided to use this formula as a primer coat prior to spraying pure PEDOT-PSS. The original formulation for CPP 4532 E3D can be found in Appendix A on page 87, as well as other formulations from the Baytron Coating Guide. The modified formula can be found on page 26.

Successful spraying of PEDOT-PSS on PVDF had finally commenced. Now the problem of spraying a uniform, layer with a repeatable process was the challenge. Spraying too thick a layer caused pooling, and patchy drying. The trick is to spray a thin, even layer and allow it to dry, and then add more layers. Impatience during the spraying process usually resulted in a patchy layer, as shown in Figure 4-1. The picture clearly shows how the PEDOT-PSS pooled and dried in an irregular, non-uniform pattern. This was the result of impatience during the spraying process.
Figure 4-1: Example of poorly sprayed layer of PEDOT-PSS on PVDF. The layer was too thick prior to drying.

Patience, practice, and following good technique resulted in a good sample that would provide good measurements. Figure 4-2 below shows what was thought to be a properly sprayed layer of PEDOT-PSS on PVDF. The film is uniform across the surface area, and there is no pooling or pinholes. However, closer inspection of the sample shows flaking of the PEDOT-PSS layer at the edges of the film. Conductivity measurement can be made, but the robustness of the film is not good. Flaking and peeling of the PEDOT-PSS layer were still problems, as well as adhesion.
On June 11, 2003, e-mail correspondence with Nancy Holloway at NASA LaRC solved the adhesion problem. Upon discussing spraying techniques with Ms. Holloway, it was found that replacing the isopropanol as the main solvent in the primer with n-methyl 2-pyrrolidinone, NMP, adhesion could be achieved.

“I get great coatings when I use your primer. The coatings pass the tape test over and over again!! Nothing sticks without the primer. The PEDOT-PSS just will not wet that surface even with a long plasma etch! Since the primer you left here was very viscous...I thinned it down with NMP...

In your original batch of primer, you had NMP - right? Did the films coated with the original batch of primer (the one with I am assuming less NMP) not pass the tape test? I got to thinking about that NMP and I wonder if it is slightly dissolving the film and helping the primer to stick? ...” ~Nancy Holloway
Ironically, similar to the discovery of conducting polymers, the accidental mixing of the wrong solvent in a pre-formulated primer solved the adhesion problem. It was found that getting repetitive results was not only in the technique, but in the PEDOT-PSS solution itself. Prior to this e-mail message, a small amount of cross-linking agent was added to the PEDOT-PSS before spraying had also solved the flaking problem. It was discovered that when the cross-linking agent called Silquest 187A was added to the PEDOT-PSS solution, smooth uniform films were sprayed. These films did not crack when dry and the edges of the electrode did not fray as they did in previous samples.

The spraying process is an important factor in achieving a good PEDOT-PSS layer, but just as important is the drying process. How to dry each layer was just as puzzling as how to spray each layer. The first method of drying, being the most obvious, was open air drying. This method took too much time and introduced the possibility of layer contamination. To speed up the process, and reduce the risk of contamination, each layer was dried under a full vacuum. This process worked, but proved to be a problem as the PEDOT-PSS layer got thicker. Cracks started to appear from over-drying of the PEDOT-PSS. After abandoning the vacuum drying process, recollection of how Dr. Nick Pinto, (University of Pennsylvania) dried his films, provided a solution. Instead of forcing the moisture out of the PEDOT-PSS using a vacuum, the layer could be gently dried by forcing cool air across the layer. This speeds up the drying process, doesn’t over-dry the PEDOT-PSS, and reduces contamination as well. Figure 4-3 shows the drying set-up used at Montana State University.
Figure 4-3: Using a heat gun to force cool air across a wet layer of PEDOT-PSS.

Through two years of trial and error and experimentation, it has been concluded that in order to get a successful layer of PEDOT-PSS on PVDF, the guidelines outlined in chapter 3 on page 29 must be followed.

1. Proper mounting of the PVDF
2. Layer order
3. Spraying technique
4. Equipment maintenance

Shown in Figure 4-4, is a PVDF film with PEDOT-PSS applied to both sides. The films are uniform on both sides and of comparable thickness. The process is
repeatable, and can easily be automated producing a more equivalent thickness with a higher tolerance on both sides of the PVDF.

Figure 4-4: Successful double-sided application of PEDOT-PSS on PVDF.

This process as well as the new primer helped the PEDOT-PSS electrode pass the "tape" test, described earlier, as well as what is called a "crease" test. The "crease" test involves folding the all-polymer film and literally creasing it. If the electrode cracks, then the material did not pass the test. Fortunately, the new primer promoted adhesion so well, that the PEDOT-PSS electrode neither cracked nor delaminated in this test.
Electromechanical measurements

According to Ikeda's Fundamentals of Piezoelectricity[2], the important features of a linear interaction process can be stated as follows:

1. “In order to determine a principal constant (e.g. a stiffness) of one of the two systems mutually coupled, it is necessary to specify the situation of the other system as a condition…
2. A principal constant cannot be larger than an intrinsic constant when there is no coupling. In other words, no interaction process stiffens the medium.
3. A principal constant of one system for the condition of the constant extensive variable (of the other system) is related to that for the constant intensive variable, in terms of $1-k^2$ through use of the coupling coefficients.”

These features above are important to note when taking electromechanical measurements of a piezoelectric material. Similar to the constitutive equation for a mechanical system, there exists a series of constitutive equations for dielectric materials taking into account these coupled systems. There are three main factors to consider when measuring or calculating these coupling coefficients: dielectric response, mechanical response, and thermal response. As stated in feature 1 above, it is necessary to specify the condition of the systems. For example, to measure the dielectric constant, the temperature in the room, and the stress applied to the material must be specified. Recall the definition of a piezoelectric material: "piezoelectricity" is an interaction between mechanical and electrical systems. Ikeda [2] also states "Piezoelectricity' is a fundamental process of electromechanical interaction and is representative of linear coupling in energy conversion.”
Having stated the above facts, one can now conclude that an in-depth analysis of the piezoelectric effects of using PEDOT-PSS as an electrode on PVDF will not be a factor in this research because the mechanical properties of PEDOT-PSS have not yet been determined. However, the question: “Can PVDF devices be operated with a PEDOT-PSS electrode?” must still be addressed.

Measurements of the conductivity of the sprayed on PEDOT-PSS layers conducted at Montana State University have ranged from 0.01 S/cm to 0.1 S/cm in 4 to 6 micron thick layers. The published conductivity of PEDOT-PSS is 2 S/cm, much higher than the measured values obtained in this work. The lower conductivity could be the result of many different factors including the cross-linking agent used to spray the polymer, or the spraying process itself. Again, the question of PVDF operation arises. Is 0.01 S/cm enough to operate a PVDF device over a useful frequency range for thin (not too stiff) electrode layers? According to the Cole-Cole charts and the dielectric constant calculations, there is enough conductivity. The following calculations were used to determine the experimental dielectric constant (permittivity) for the PEDOT-PSS/PVDF sample. Given the equation for capacitance C, impedance Z, area A of the electrode, frequency f, and the thickness d of the PVDF,

\[ C = \frac{A \varepsilon \varepsilon_0}{d} \]  \hspace{1cm} (4-1)

\[ Z = \frac{1}{2\pi f C} \]  \hspace{1cm} (4-2)
Substituting equation 4-1 into equation 4-2 and solving for the permittivity,

\[ \varepsilon = \frac{d}{2\pi f\epsilon_0 A Z} \]  

(4-3)

Taking the average impedance of the three measured samples gives a permittivity of \( \varepsilon = 13.42 \), which is comparable to the actual permittivity of PVDF, \( \varepsilon = 11 \).

In November 2000, Gary Bohannan presented an idealized permittivity representation known as the Debye model. His representation of typical results for this model is shown in Figure 4-5. The Debye model was developed by P. Debye, [10] in connection with his theory of dielectric relaxation of polar molecules in a viscous medium. In his model, Debye shows how the real and imaginary parts of the permittivity can be predicted.[10]

![Figure 4-5](image)

**Figure 4-5**: Debye Model, characterized by a single exponential relaxation time associated with the loss peak [10]
From the Debye prediction, a schematic representation of the real vs. imaginary permittivity can be determined (Figure 4-6).

Figure 4-6: Debye model predicts a semi-circular arc when plotting the real vs. imaginary permittivity [10]

However, in dielectric solids, the assumption of non-interacting dipoles no longer applies, and the Debye model is no longer adequate. S. Cole and R. Cole found that, “at least for a range of frequencies around the loss peak, the permittivity data for non-dilute materials looked more like that shown in Figure 4-7.” [11] Unlike the Debye model, the low frequency dispersion in the Cole-Cole model is not constant, it is a slightly decaying function which is evident in Figure 4-7.
In the Cole-Cole plot, the circular arc depicted by the Debye model is shifted so the center of the arc actually lies below the real axis as shown in Figure 4-8. A more in depth discussion on the differences between the Debye model and the Cole-Cole model appears in Dr. Gary Bohannan’s doctoral thesis, reference [12] pp. 11-15.
In Figure 4-9, the all-polymer permittivity data is plotted against the frequency as depicted above in Figures 4-5 (p. 50) and 4-7 (p. 52). Three all-polymer films were made, two using the developed methods; and the third, film 428-70, was made using a "sloppier" and "impatient" method producing poor electrode layers. It can be clearly seen that the third all-polymer film responded in the same manner as the other two films. However, the dielectric constant is significantly lower. This data shows that the method of applying the conducting polymer electrode greatly affects the performance of the all-polymer film.
Figure 4-9: Cole-Cole model using data measured from PEDOT-PSS/PVDF sample. (See Appendix B for full size graphs)

The measured impedance spectroscopy data mentioned above can be used to calculate material properties, including the PVDF dielectric constant and the PEDOT-PSS resistivity. As described in chapter 3 on page 34, impedance spectroscopy data were gathered and plotted. In Figure 4-10, the plot of the first set of impedance and phase angle data taken with the all polymer actuator is shown. Basically, these data are not useable.
Figure 4-10: Impedance spectroscopy data from all polymer piezo-film.

The test was repeated for technique confirmation. After obtaining similar results, it was discovered that the contact between the aluminum and PEDOT-PSS electrodes was faulty. This problem was also evident when the film did not "sing" within the 2 kHz to 20 kHz range, or the range of human hearing. As described in Chapter 3 on page 36, this problem was solved and the data resulted in the plot of Figure 4-11. This new data shows a linear response with a positive slope. The actual numerical data show that the phase angle changes significantly with the change in frequency. As the frequency is increased, the phase angle becomes more resistive until about the 2 kHz region where it starts to become more capacitive, and then switches again in the high frequency ranges. This behavior is depicted in the changes in slope in the impedance spectroscopy.
From the impedance spectroscopy data, a Cole-Cole plot similar to that in Figure 4-8 (p. 53) was made and appears in Figure 4-12. Included in this plot are data taken from a film with silver electrodes for comparison. By comparing the silver data to the PEDOT-PSS data, it can be concluded that the entire capacitive aspect of the material is being represented.
It must be emphasized that the “permittivity” shown in Figures 4-9 (p. 54) and 4-12 is based on a composite sample consisting not only of the PVDF layer, but also of the PEDOT-PSS or silver electrodes. The following interpretation of the Cole-Cole plots in Figures 4-9 and 4-12 shows that the results are consistent with what is expected from the dc conductivity measurements of PEDOT-PSS, the permittivity of PVDF, and the test specimen dimensions. Each test specimen for the successful tests was a 0.047 by 0.047 m² square of PVDF, 28 microns thick. With assumed permittivity of 11, its capacitance is $C_2 = 7.68 \text{nF}$. The PVDF sheet is electroded on each side with a layer of PEDOT-PSS of thickness 5 microns and resistivity 0.05 ohm-m as determined by dc measurements described previously. Contact to these conducting layers is made by semicircular tabs of
radius $r_1=0.0127$ m composed of considerably thicker PEDOT-PSS (refer to Figure 3-4, p. 31). At the upper end of the experimental frequency range (300 kHz), little charge has time to flow through the conducting polymer past these tabs, so the sample acts as a capacitor based only on the PVDF area under the tabs, with capacitance $C_1=0.88$ nF. Thus the ratio of high-f to low-f capacitance should be $C_2/C_1=7.68/0.88=8.7$, quite close to the high-f to low-f permittivity ratio from Figure 4-12 which is $14/2=7$. Added confidence in the experimental results comes from the fact that measured permittivities of 12, 14, and 14, at low frequency for which the electrodes have little effect, are not much different from the accepted range of $11\pm 1$.

Figure 4-13: R-C Model used in theoretical approximations

Now that it has been shown that the low-f and high-f behaviors are consistent with what is expected, the next step is to examine the intermediate-f behavior. At low
frequency the resistance of the PEDOT-PSS layers is negligible, and at high frequencies it can be approximated as infinite, but at intermediate frequencies an accurate treatment must be based on distributed R and C. Shown in Figure 4-13 is a diagram of the R-C model used. A physics graduate student, Laura Lediaev, is carrying out such a calculation, which will appear elsewhere. The present calculation is approximate, based on considering the two PEDOT-PSS layers as a single resistor R in series with a capacitor $C = C_2 - C_1 = 6.80 \text{ nF}$ corresponding to the PVDF area not under the tabs. Thus the equivalent circuit for the sample is R and C in series, with this series string in parallel with $C_1$. Comparing Figures 4-6 (p. 51) and 4-12 can determine the accuracy of this approach immediately. The half-circle in Figure 4-6 is exactly the shape expected for such an equivalent circuit; that is, the height of the curve is exactly half the difference between $\varepsilon_s$ and $\varepsilon_\infty$. The experiment result has a difference 14-2=12, half of which is 6, whereas the height of the curve is only 4.5. This difference can be attributed to the inaccuracy of treating distributed R and C as lumped parameters. Accordingly, this lumped-parameter approach is qualitatively correct but quantitatively inaccurate.
The remaining task in interpreting the Cole-Cole plot of Fig. 4-12 is to determine whether the peak of the curve occurs at the expected frequency. The distance $r_3$ that the current must flow from the tab to the center of the capacitor $C$ is taken as 0.02 m (Figure 4-14), about half the distance from the tab to the far end of the sample. The cross-sectional area through which the current must flow varies with radius from the tab center, but can be approximated by the conducting layer thickness of 5 microns multiplied by $(\pi/2)$ and by an average radius 0.0181 m. These dimensions, together with the resistivity 0.05 ohm-m, give a combined resistance $R$ of 14,000 ohms for the two electrodes. The peak of $\varepsilon''$ thus should occur at $f=1/2\pi RC=1,672$ Hz, whereas experimentally it occurs at 1,500 Hz. This excellent agreement provides additional confidence that the above interpretation of the experimental results is basically correct.

The behavior of the silver-electrode test specimen at 300 kHz is similar to that of the polymer-electrode test specimen at 150 Hz, so it seems likely that the resistance per square of the silver electrode is about 2,000 times lower than that of the polymer electrode.

What is the practicality of using PEDOT-PSS electrodes? Their thickness in these tests is about half that of the silver electrodes, so they will be much less stiff, and substantial improvement in electromechanical performance can be expected. It seems likely that automated methods of applying these electrodes can be developed, to keep their cost from being prohibitive. From Fig. 4-12, the apparent permittivity starts falling off substantially near 300 Hz, so applications will be restricted to lower frequencies or else the electrode thickness and/or the polymer conductivity must be increased. Another
concern is the power required to drive the actuator, and the corresponding heat that must be dissipated. These can be calculated fairly accurately from the above lumped-parameter RC model by standard ac circuit analysis techniques. Determination of the temperature rise depends on device configuration and any cooling that is provided, and is likely to require a complicated heat transfer calculation.

Based on discussions with Dr. Gary Bohannan, the measured data clearly show that the actual PVDF permittivity (the values measured at the lowest frequencies) is affected by the electrode layer. This is made apparent by comparing the PEDOT-PSS data with the silver electrode data. The silver electrode gives a lower permittivity than the PEDOT-PSS, perhaps because its higher stiffness inhibits the dielectric response of the PVDF. The question of which aspects of a permittivity diagram are due to bulk and which to electrode/electrolyte boundary or the electrode itself is a very active one. The only real test is to use a wide variety of electrode layers. These conducting electrode layer data provide some insight, but do not completely answer the question.

An important test for future work is to find whether the piezoelectric coefficients also increase when the PEDOT-PSS electrode replaces the silver electrode. Since the silver is substantially less compliant than the polymer electrode, the PVDF is under a more constrained mechanical condition when covered in silver. The resulting measured difference in the dielectric response agrees with the theory discussed at the beginning of this section. The mechanical and electrical responses are coupled via the piezoelectric constant, so it is hoped that the piezoelectric coefficients will increase also when using polymer electrodes. Unfortunately, neither set-up has ideal constant boundary
conditions, but the argument still holds. An encouraging observation is that with the polymer electrodes there is a considerable increase in the purity of the tone heard when frequency within the audible range (2 kHz-20 kHz) is applied.
CHAPTER 5

Conclusion

The primary goal of this research was to create an all-polymer piezoelectric film. This film has been successfully developed.

The following were the secondary goals to be achieved during this research:

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 conductivity of the conducting polymer

5. Measure the dielectric properties of the all-polymer film

6. Measure the piezoelectric response of an all-polymer-film bimorph

7. Measure the mechanical properties of the conducting polymer

8. Reproduce MSU actuator and measure its performance

Goals 1-5 were achieved.

The silver electrode layer was replaced with a conducting polymer layer, PEDOT-PSS. An all-polymer film was produced. Good adhesion between the conducting polymer and the piezoelectric polymer was achieved. The chemical etching combined with a plasma cleaning made adhesion possible. The process developed for applying PEDOT-PSS is repeatable and can be automated for better efficiency.

The conductivity measurements taken from the sprayed layer of PEDOT-PSS are high enough to provide an electric field to the PVDF film. The dielectric response of the
all-polymer film shows a promising future. Further testing of this new composite is required before accurate results can be published.
CHAPTER 6

Recommendations for Future Work

Screen Printing

It is highly recommended that the continuation of screen-printing PEDOT-PSS onto PVDF. This process is used commercially and is economically feasible. A suitable formulation for PEDOT-PSS has been found as well as the appropriate screen for printing. The hard part has already been accomplished. It is believed that by following the same guidelines outlined for preparing PVDF for spraying, and the application of the primer layer, screen-printing of PEDOT-PSS is possible. With the advantage of screen-printing, the printing of intricate electrode patterns will become a reality. Methods currently used, such as rolling, and spraying can be replaced with a more efficient and controlled method.

Reproducing the ‘MSU’ Actuator

Now that a method for applying PEDOT-PSS to PVDF has been secured, the next step is building an actuator. The “MSU” actuator was invented by Dr. Hugo Schmidt and has been improved upon in many different ways over the past decade. This actuator was discussed in detail in chapter 1. The most recent improvement proposed was replacing the silver electrode with PEDOT-PSS in hopes of getting a more compliant and more efficient actuator. In the past, many tests have been conducted in micro-gravity conditions as well as standard conditions. Some of the more simple tests involve
displacement vs. voltage, and force vs. voltage. These tests can be easily repeated and compared. Another test would involve using the all-polymer actuator as a vibration damper in the 1-D pendulum test apparatus, and comparing results with those from previous actuators.

Some problems foreseen in producing these actuators is in the glue layer. It is possible that the epoxy used may not adhere to the PEDOT-PSS. It is also possible that the chemical make-up of the epoxy may cause the PEDOT-PSS to delaminate, but that is highly doubtful. The biggest problem would most likely be in transferring the voltage from the input to the actuator itself. The original actuator used small copper tabs, but impedance spectroscopy tests showed that care must be taken to insure good current transfer from the metal electrode to the PEDOT-PSS.

Curing Characteristics of a PEDOT-PSS Film

The curing of PEDOT-PSS plays a major role in how the film turns out. If the film is baked, it becomes brittle, sometimes charred. If it is left in vacuum too long, it becomes brittle. Slow curing in a low humidity chamber does not give good results. Why is it important to cast a dry film of PEDOT-PSS? The film can be used to find its material properties such as the glass transition temperature, the elastic modulus, the yield stress, dielectric effects if they exist, conductivity, and other properties.

Obviously the material properties are affected by the curing characteristics. Drying time, temperature, and pressure all play a major role in the resulting film. This topic alone could be another thesis project.
Impedance Spectroscopy

Analysis of the impedance spectroscopy is definitely the job for a physics doctoral candidate. The data have been obtained, and more data is obtainable, but what is it really telling us? Studies in the area have been conducted with the silver electroded PVDF. These same studies can be repeated with the all-polymer film, and comparisons made. Is the all-polymer model more efficient, more compliant, better than the metal electrode? Deep analysis of the impedance spectroscopy and Cole-Cole plots will hopefully answer these questions.

Apply PEDOT-PSS to Other Polymers/Polyimides

NASA LaRC is currently developing piezoelectric and electrostrictive polymers and polyimides. Similar to PVDF, these materials require a metal electrode to actuate. Can PEDOT-PSS be applied to these other materials? Can proper adhesion be achieved? Is PEDOT-PSS conductive enough for these materials? Can PEDOT-PSS withstand the harsh environment of space?
REFERENCES CITED


APPENDICES
Chemical Designation
Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) or PEDT/PSS
CAS number 155090-83-8

Characteristic properties and physical data of Baytron P

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<td>Form</td>
<td>liquid</td>
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<tr>
<td>Odor</td>
<td>odorless</td>
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<tr>
<td>Color</td>
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<td>Boiling point</td>
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<tr>
<td>Density</td>
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<td>at 20 °C</td>
<td></td>
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<tr>
<td>Vapor pressure</td>
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<tr>
<td>pH value</td>
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<tr>
<td>PEDT content</td>
<td>approximately 0.5% by weight</td>
</tr>
<tr>
<td>PSS content</td>
<td>approximately 0.8% by weight</td>
</tr>
<tr>
<td>PEDT band gap</td>
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</tr>
<tr>
<td>Refractive index, n</td>
<td>1.5228 at 589 nm</td>
</tr>
</tbody>
</table>
Notes on Using Baytron P

Baytron P is an aqueous dispersion of the intrinsically conductive polymer PEDT/PSS [poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate)]

Baytron P can be used to coat glass and plastics. For more information see the Guide Formulations.

The coatings are intrinsically conductive, transparent, and virtually colorless (pale blue).

Properties of Baytron P

PEDT/PSS displays markedly better properties than other organic conductors such as polypyrrole and polyaniline.

- Higher transmission in the visible spectrum with comparable conductivity = transparent, colorless to bluish coatings
- Minimum surface resistivity of approximately 150 ohms/square can be achieved, depending on the manufacturing conditions.
- Better resistance to hydrolysis
- Good photostability and good thermal stability
- Virtually 100% absorption in the range of 900 to 2000 nm.
- No absorption maximum in the visible spectrum up to 800 nm.

Baytron P must be protected from direct sunlight.

According to experience to date, Baytron P is stable for at least 6 months when stored at 20 °C in sealed, dark containers.

Once the container is opened, care must be taken to ensure that the dispersion does not dry on the walls, as the product can no longer be dispersed in water if dry and the optical properties of the PEDT coating could be impaired.

For more information, please observe the Material Safety Data Sheet for Baytron P.
3. Antistatic Coating of Plastics

Static charge on plastic surfaces leads to numerous problems. Coating with BAYTRON® permits plastic surfaces to be given an antistatic finish.

Virtually all plastics can be coated with PEDT, including polycarbonate, polyethylene, polyethylene terephthalate, polyamide, and polypropylene. A surface activation like Corona treatment should be performed prior to coating in the case of PET and polyolefins to enhance adhesion to the substrate.

Typical applications for BAYTRON®-based antistatic and static dissipative coatings on plastic surfaces:
- Electronic packaging (carrier tapes, bags, boxes)
- Plastic electronic component housings and windows
- Clean-room packaging

Thermoformable coatings can be obtained by using "soft" binders e.g. contained in CPP 4531 type guide formulations (see section 6). Such coatings can be stretched by more than 200% during deep drawing. By this the initial surface resistance is increased by one or two orders of magnitude only.

4. Coating of Glass

It is also possible to produce transparent, conductive coatings on glass using BAYTRON®.

Typical applications for BAYTRON®-based coating on glass:
- Monitors and TV screens (antistatic effect, shielding)
- Glass apparatus in explosion-hazard areas

By combining BAYTRON® with silanes, e.g. tetraethoxysilane, high hardness, scratch resistance, and surface resistance can be obtained. For achieving optimum hardness curing temperatures of about 180°C are required.

**Scratch-resistant antistatic coating**

Guide formulation CPG 130.6 allows the application of antistatic coatings with good scratch resistance.

Surface resistance: < 10^10 Ohm

Pencil hardness: 9 H

Quantity of BAYTRON® P used per m²: approx. 2g (spray application)
Highly conductive coatings
Higher conductivity can be achieved by using guide formulation CPP 105D. The hardness of the coating is, however, lower than when using guide formulation CPG 130.6.
Surface resistance: < 10Ω Ohm/cm/
Quantity of BAYTRON® P used per m²: approx 6 g
The BAYTRON® coatings can be either applied by spraying or the spin-coating method.

5. Electrostatic Coatings
As a rule, plastic components cannot be coated electrostatically as their surfaces are not electrically conductive. Coating with BAYTRON® generates the necessary surface conductivity.
Possible coating methods:
• Powder coating
• Electrostatic spray coating (wet)
Suitable formulations based on our recommendations permit good adhesion and conductivity of the primer coats on many plastic substrates (e.g. polyurethane, polypropylene).
Advantages over carbon black-filles primers and plastics:
• The necessary surface conductivity can be attained with very thin films.
2
• The transparency of BAYTRON® allows the use of light brilliant coatings.
• There are no negative effects on the mechanical properties of the plastic.
We recommend guide formulation CPP 4531 E3D for the conductive coating of plastics as pretreatment for electrostatic coating.
Wet film thickness: 2-4 μm
Surface resistance: < 10Ω Ohm/cm/
Quantity of BAYTRON® P coating per m²: approx. 0.75 to 1.5 g
Other BAYTRON® coating formulations may also be used as electrostatic primer coatings.
For more information, see below.

6. BAYTRON Coating Guide Formulations
To assist customers in their formulation work with BAYTRON® conductive polymers, we have developed several coating formulations
that contain BAYTRON® P. These coating formulations have been optimized for individual substrates, such as PVC, polycarbonate, glass, etc. at different wet film thicknesses and surface resistivities and are mainly used for dissipation of static surface charges on various substrates. The coatings may be applied by conventional coating methods such as brushing, spin-coating, printing processes, spraying, dipping, and roller-coating techniques. BAYTRON® Guide Formulations include:

**CPP 103D**: For antistatic coatings with good adhesion properties on many plastic surfaces.
**CPP 105D**: For antistatic coatings with higher conductivity, good adhesion properties on plastic and glass surfaces, and resistance to both aliphatic and aromatic hydrocarbon solvents.
**CPP 116.6D**: For antistatic coatings with good adhesion properties on polycarbonate or PVC plastic surfaces.
**CPP 134.18D**: For highly transparent static dissipative coatings with good adhesion properties on polycarbonate or PVC plastic surfaces. Good for dip-coating applications.
**CPP 135D**: For alcohol-resistant transparent dissipative coatings with good adhesion properties on polycarbonate or PVC plastic surfaces.
**CPP 141D**: For the application of clear, hard, alcohol-resistant, antistatic coatings with good adhesion properties on aluminum, polycarbonate, and PVC surfaces.
**CPP 4532I**: For thermoformable coatings with good adhesion properties on many plastic surfaces.
**CPP 4532E3D**: For conductive coatings on plastic surfaces as pretreatment for electrostatic coating. Also especially suited for coatings on corona-treated polyethylene and/or polypropylene.
**CPG 130.6**: For scratch-resistant antistatic coatings with good adhesion properties on glass surfaces.
BAYTRON® Coating Guide Formulation CPP 103D

For the application of clear antistatic coatings with good adhesion properties on plastic surfaces.

Wet film thickness: 6 µm
Quantity of BAYTRON® P used per m²: 1.5 g
Surface resistivity: 10⁷-10⁸ Ohm/m²

Properties of the dispersion:
Solid content: 12 %
Viscosity: 60 mPa.s
pH value: 8
Density: 0.979 g/cm³

Above values are approximate

BAYTRON® P 25.86
Dimethylaminoethanol, 50% in water 0.12
A B U710 38.79
N-Methyl-2-pyrrolidinone 9.05
Silquest® A 187™ 0.26
Isopropanol 25.62
Dynol™ 604 0.30
Total 100.00

Notes
All components must be mixed in the above order under constant agitation.
The coating can be applied by conventional coating methods such as brushing, spin-coating, printing, spraying, and roller-coating.
Corona treatment should be performed prior to coating polypropylene or polyethylene substrates.
Coating should be cured at approximately 80-120°C for a minimum of three to five minutes.
Surface resistivity measurements made according to IEC Standard 93 (VDE 0303, Part 30) or ASTM D 257.

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BAYTRON® Coating Guide Formulation CPP 105D

*For the application of antistatic coatings with higher conductivity, good adhesion properties on plastic and glass surfaces, and resistance to both aliphatic and aromatic hydrocarbon solvents.*

on plastic on glass

- Wet film thickness: 6 µm - 12 µm
- Surface resistivity: < 10⁴ Ohm/m² < 10⁵ Ohm/m²
- Quantity of BAYTRON® P: 2.6 g - 5.2 g used per m²

**Properties of the dispersion:**

- Solid content: 1.2 %
- Viscosity: 30 mPa.s
- pH value: 2.8
- Density: 0.900 g/cm³

Above values are approximate.

BAYTRON® P 42.92
N-Methyl-2-pyrrolidinone 2.58
Silquest® A 187™ 0.86
Isopropanol 53.34
Dynol™ 604 0.30
Total 100.00

**Notes**

- All components must be mixed in the above order under constant agitation.
- The coating can be applied by conventional coating methods such as brushing, spin-coating, printing, spraying, and roller-coating.
- Corona treatment should be performed prior to coating polypropylene or polyethylene substrates.
- Coating should be cured at approximately 80-120°C for a minimum of three to five minutes.
- Surface resistivity measurements made according to IEC Standard 93 (VDE 0303, Part 30) or ASTM D 257.

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BAYTRON® Coating Guide Formulation CPP 116.6D

For the application of antistatic coatings with good adhesion properties on polycarbonate or PVC plastic surfaces.

Wet film thickness 6 μm 12 μm 18 μm
Surface resistivity 5 x 10⁵ Ohm/“ 2 x 10⁵ Ohm/“ 5 x 10⁴ Ohm/“
Quantity of BAYTRON® P used per m² 1.4 g 2.8 g 4.3 g
Above values are approximate.

BAYTRON® P 23.90
Dimethylamino ethanol, 50% in water 0.18
Sancure® 825 17.90
Silquest® A 187™ 0.24
Deionized water 19.89
Isopropanol 29.90
n-Butanol 7.89
Dynol™ 604 0.10
Total 100.00

Notes
All components must be mixed in the above order under constant agitation. The coating can be applied by conventional coating methods such as printing, pourcoating, or dip-coating.

The coated film/sheet should be dried at approximately 80-120 °C for at least 3 to 5 minutes.

Surface resistivity measurements made according to IEC Standard 93 (VDE 0303, Part 30) or ASTM D 257.

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100-025008.00
BAYTRON® Coating Guide Formulation CPP 134.18D

For the application of highly transparent static dissipative coatings with good adhesion properties on polycarbonate or PVC plastic surfaces. This formulation has been used to dip coat irregularly shaped plastic articles.

Wet film thickness 20 µm
Surface resistivity 1 x 10^9 Ohm/m
Quantity of BAYTRON® P used per m² 1.7 g

Properties of the dispersion:
- Solid content: 2.2 %
- Viscosity: 10 mPa.s
- pH value: 8
- Density: 0.926 g/cm³

Above values are approximate.

BAYTRON® P 8.62
Dimethylaminoethanol, 50% in water 0.02
Deionized water 41.67
Isopropanol 41.58
Sancure® 825 6.47
n-Butanol 1.50
Silquest® A 187™ 0.04
Dynol™ 604 0.10
Total 100.00

Notes
- All components must be mixed in the above order under constant agitation.
- The coating can be applied by conventional coating methods such as printing, pour-coating, or dip-coating.
- The coated film/sheet or plastic article should be dried at approximately 80 - 120°C for at least 3 to 5 minutes.
- Surface resistivity measurements made according to IEC Standard 93 (VDE 0303, Part 30) or ASTM D 257.

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any patent. In case of order please refer to issue number of the respective product data sheet. All deliveries are based on the
latest issue of the product data sheet and the latest version of our General Conditions of Sale and Delivery.
BAYTRON® Coating Guide Formulation CPP 135D

For the application of alcohol-resistant transparent static dissipative coatings with good adhesion properties on polycarbonate or PVC plastic surfaces.

Wet film thickness 6 μm 18 μm
Surface resistivity 5 x 10^5 Ohm/" 5 x 10^4 Ohm/"
Quantity of BAYTRON® P used per m² 1.5 g 4.5 g

Properties of the dispersion:
- Solid content: 8%
- Viscosity: 25 mPa.s
- pH value: 8
- Density: 0.959 g/cm³

Above values are approximate.

BAYTRON® P 24.20
Dimethylaminoethanol, 50% in water 0.11
NeoRez® R986 20.20
Silquest® A 187™ 0.25
Deionized water 20.90
Isopropanol 30.30
N-Methyl-2-pyrrolidinone 3.93
Dynol™ 604 0.11
Total 100.00

Notes
- All components must be mixed in the above order under constant agitation.
- The coating mixture should be filtered through a 3 or 5 micron filter twice before using: once directly after mixing and again six hours later.
- The coating can be applied by conventional coating methods such as printing, pour-coating, or dip-coating. Spray coating has not yet been tested.
- The coated film/sheet should be dried at approximately 80-120 °C for at least 3 to 5 minutes.
- Surface resistivity measurements made according to IEC Standard 93 (VDE 0303, Part 30) or ASTM D 257.

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BAYTRON® Coating Guide Formulation CPP 141D

For the application of clear, hard, alcohol-resistant, antistatic coatings with good adhesion properties on aluminum, polycarbonate, and PVC surfaces.

Wet film thickness 4 to 6 μm
Surface Resistivity $10^6$ Ohm/"*
Transmission at 550 nm > 95% [for 4 to 12 μm wet film thicknesses]
Quantity of BAYTRON® P used per m² 2.1 to 3.2 g

Properties of the dispersion:
Solid content: 18%
Viscosity: 25 mPa.s
pH value: 8

Above values are approximate.

BAYTRON® P 52.6
Dimethyldimethyloctanol, 50% in water 0.3
NeoRez® R986 31.4
Eastek® 1200-02-30% 10.5
Isopropanol 2.0
N-Methyl-2-pyrrolidinone 3.1
Dynol™ 604 0.1
Total 100.00

Notes
All components must be mixed in the above order under constant agitation. The coating can be applied by conventional coating methods such as printing, pour-coating, dip-coating, and spray coating.

The coated film/sheet should be dried at approximately 80-120°C for at least 3 to 5 minutes.

Surface resistivity measurements made according to IEC Standard 93 (VDE 0303, Part 30) or ASTM D 257.

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BAYTRON® Coating Guide Formulation CPP 4532I
For the application of thermoformable coatings with good adhesion properties on plastic surfaces. Even after thermoforming, the PEDT coating is still conductive enough to guarantee an antistatic effect.
Wet film thickness: 4 µm 6 µm 24 µm
Surface resistivity: < 10⁵ Ohm/" 3.0 x 10⁴ Ohm/" 9.0 x 10³ Ohm/
Quantity of BAYTRON® P used in coating: 2.3 g/m² 3.45 g/m² 13.8 g/m²

Properties of the dispersion:
Solid content: 8 %
Viscosity: 70 mPa.s
pH value: 2
Above values are approximate.

BAYTRON® P 57.65
Bayhydrol® 140AQ 15.63
N-Methyl-2-pyrrolidinone 3.48
Isopropanol 23.24
Total 100.00

Notes
All components must be mixed in the above order under constant agitation. The coating can be applied by conventional coating methods such as brushing, spincoating, printing, spraying, and roller-coating.
Corona treatment should be performed prior to coating polypropylene or polyethylene substrates.
Coating should be cured at approximately 80-120°C for a minimum of three to five minutes.
Surface resistivity measurements made according to IEC Standard 93 (VDE 0303, Part 30) or ASTM D 257.
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BAYTRON® Coating Guide Formulation CPP 4532 E3D

For the application of conductive coatings on plastic surfaces as pretreatment for electrostatic coating.
For the application of conductive coatings with good adhesion to corona-treated polyethylene surfaces.

Wet film thickness 2 μm 4 μm 6 μm 24 μm
Surface resistivity < 10⁷ Ohm/“ < 10⁷ Ohm/“ 5.0 x 10⁴ Ohm/“ 1.4 x 10⁴ Ohm/“
Quantity of BAYTRON® P used in coating 0.8 g/m² 1.7 g/m² 2.5 g/m² 10.2 g/m²

Properties of the dispersion:
- Solid content: 4.5 %
- Viscosity: 50 mPa.s
- pH value: 2.4
- Density 0.911 g/cm³

Above values are approximate.

BAYTRON® P 38.36
Bayhydrol® 140AQ 10.40
N-Methyl-2-pyrrolidinone 2.32
Isopropanol 48.58
Dynol™ 604 0.20
Silquest® A 187™ 0.14
Total 100.00

Notes
All components must be mixed in the above order under constant agitation and filtered through a 10 micron filter prior to using or storing.
The coating can be applied by conventional coating methods such as brushing, spin-coating, printing, spraying, and roller-coating.
Organic binders such as polyurethane dispersions or polyvinyl acetate can be added to the BAYTRON® P polymer dispersion to improve the adhesive properties.
Coating should be cured at approximately 80-120°C for a minimum of three to five minutes.
Surface resistivity measurements made according to IEC Standard 93 (VDE 0303, Part 30) or ASTM D 257.

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100-02006.00
BAYTRON® Coating Guide Formulation CPG 130.6

*For the application of scratch-resistant antistatic coatings with good adhesion properties on glass surfaces.*

Surface Resistivity < 10⁶ Ohm/m²
Pencil Hardness 9 H
Quantity of BAYTRON® P used per m²: 2 g (spray application)
Above values are approximate.

BAYTRON® P 31.70
Isopropanol 39.70
Ethylene glycol 15.90
Tetraethoxysilane 11.90
Acetic acid (100%) 0.80
Total 100.00

**Notes**

All components must be mixed in the above order under constant agitation.
The coating can be applied by conventional spray-coating or spin-coating methods.
Coated substrates should preferably be dried for 10 minutes at 50°C.
Evaporation of the solvent is followed by post-curing for 30 minutes at 180°C.
Surface resistivity measurements made according to IEC Standard 93 (VDE 0303, Part 30) or ASTM D 257.
Refractive index of coating CPG 130.6 on glass was found to be \( n_D = 1.4565 \) at 589.3 nm.

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A Bayer Company
# BaytronÆ® Technical Information

## Conductive Polymers

### List of Suppliers—Complete

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>CHEMICAL DESIGNATION</th>
<th>SUPPLIER</th>
<th>FUNCTION</th>
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</thead>
<tbody>
<tr>
<td>AB U 710</td>
<td>Aliphatic polyester polyurethane</td>
<td>Alberdingk Boley, Inc</td>
<td>Organic resin/binder</td>
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<tr>
<td></td>
<td></td>
<td>8605 Cliff Cameron Drive Suite 150</td>
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<tr>
<td></td>
<td></td>
<td>Charlotte, NC 28269-9785</td>
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<tr>
<td></td>
<td></td>
<td>Ph: (704) 503-6137</td>
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<tr>
<td></td>
<td></td>
<td>Fax: (704) 503-6118</td>
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<tr>
<td></td>
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<td><a href="mailto:Info@alberdingkusa.com">Info@alberdingkusa.com</a></td>
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<tr>
<td></td>
<td></td>
<td>Cust. Service: (866) 220-4750</td>
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<td><a href="http://www.alberdingk.com">www.alberdingk.com</a></td>
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</tbody>
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**Bayderm® Finish 85 UD**

Anionic aqueous polyurethane dispersion of proprietary composition, NJTSRN (931765300002)-5824P

Bayer Polymers Coatings and Colorants Division

100 Bayer Road

Pittsburgh, PA 15205

Tel: (412) 777-2000

Organic resin/binder

**BAYHYDROL 140**

AQ CAN BE USED IN PLACE OF BAYDERM FINISH 85 UD!
Bayhydrol® 121
Anionic aqueous polyurethane
dispersion of proprietary
composition, NJTSRN
(31765300002)-5229P
Bayer Polymers
Coatings and Colorants Division
100 Bayer Road
Pittsburgh, PA 15205
Tel: (412) 777-2000
For samples, call CMC:
(888) 888-7553
www.bayerus.com
www.coatingsandcolorants.com
Organic resin/binder

Bayhydrol® 140AQ
Anionic aqueous aliphatic
polyurethane dispersion of
proprietary composition,
NJTSRN (31765300002)-
5158P
Bayer Polymers
Coatings and Colorants Division
100 Bayer Road
Pittsburgh, PA 15205
Tel: (412) 777-2000
For samples, call CMC:
(888) 888-7553
www.bayerus.com
www.coatingsandcolorants.com
Organic resin/binder

Baytron® P
Poly(3,4-
ethylenedioxythiophene)/
poly(styrenesulfonate) as an
aqueous dispersion
H. C. Starck, Inc.
Electronic Chemicals Group
100 Bayer Road
Pittsburgh, PA 15205
(412) 777-3892
www.bayer-echmicals.com
www.hcstarck.com
Conductive polymer
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and processing of our products and the products manufactured by you on the bases of our technical advice are beyond
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therefore, entirely your own responsibility. Our products are sold in accordance with our General Conditions of Sale and Delivery.

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DMEA 50%
\text{\textit{N,N-\text{Dimethylethanolamine,}}} \\
\text{\textit{2-(dimethylamino)ethanol,}}} \\
\text{\textit{50\% \text{wt in water}}} \\
\text{Aldrich} \\
(800) 558-9160 \\
www.sigmaaldrich.com \\
pH adjustment [6-8 recommended]

\text{\textit{Dynol\textsuperscript{TM} 604 Ultra-low VOC nonionic surfactant}} \\
\text{Air Product's & Chemicals, Inc.} \\
\text{Performance Chemicals Division} \\
7201 Hamilton Boulevard \\
Allentown, PA 18195-1501 \\
(800) 345-3148 \\
www.airproducts.com/surfynol \\
Wetting agent

\text{\textit{Eastek\textsuperscript{®} 1200-02-}}} \\
\text{\textit{30\% Aqueous sulfopolyester}} \\
\text{Eastman Chemical Company} \\
100 North Eastman Road \\
PO Box 511 \\
Kingsport, TN 37662-5075 \\
(423) 229-2000 \\
www.eastman.com \\
Organic resin/binder

\text{\textit{Ethylene glycol Ethylene glycol}} \\
\text{Aldrich} \\
(800) 558-9160 \\
www.sigmaaldrich.com \\
Solvent
Isopropanol 2-Propanol
Aldrich
(800) 558-9160
www.sigmaaldrich.com
Solvent for quickdrying, wetting agent

NeoRez® R9603 Aliphatic polyurethane
NeoResins
(a subsidiary of Avecia)
730 Main Street
Wilmington, MA 01887
(978) 658-6600
Or call NeoResins in:
Indiana: (765) 659-4721
www.NeoResins.com
Organic resin/binder
(for increased hardness in coatings using NeoRez
R9603, add 0.36% CX-100 crosslinker
just prior to coating)

N-Methyl-2-
pyrrolidinone
1-Methyl-2-pyrrolidinone, 1-Methyl-2-pyrrolidone, NMP
Aldrich
(800) 558-9160
www.sigmaaldrich.com
Solvent, wetting agent

Sancure® 825 Aqueous polyurethane
Noveon, Inc.
Industrial Specialties Division
9911 Brecksville Road
Cleveland, OH 44141-3247
(800) 331-1144
or (216) 447-5000
www.noveonsolutions.com
Organic resin/binder
Silquest® A 187™ 3-glycidoxypropyltrimethoxysilane
Crompton Corporation
Customer Service
OSi Specialties, Silanes
318-24 Fourth Avenue, Plaza IV
South Charleston, WV 25303-3802
(800) 523-5862
osina@cromptoncorp.com
www.cromptoncorp.com
Crosslinking agent
for PSS,
Adhesive agent

Tetraethoxysilane Tetraethyl orthosilicate
Aldrich
(800) 558-9160
www.sigmaaldrich.com
Silane for
improvement of
scratch resistance
on glass
COPY OF EMAIL FOR PERMISSION TO USE BAYER GUIDE

From: “Jill Simpson” jil.simpson.b@bayer.com
Subject: Re: Baytron P
To: “Jil Hallenberg” jil_hallenberg@yahoo.com
CC: “Ron Lubianez” ron.lubianex.b@bayer.com
Date: Fri, 18 Jul 2003 11:26:20 -0400

Dear Jil,

Sure. Attached is an updated version if that helps.
(See attached file: Baytorn_Coating_Guide_VersionUSA.pdf)

Good luck with your defense!

--Jill

From: “Jil Hallenberg” <jil_hallenberg>
To: “Jill Simpson” jill.simpson.b@bayer.com
Cc: 
Subject: Bayton P
Date: 07/17/03 05:52 PM

Dear Jill,

I am currently finishing my thesis (due Monday) and I was wondering if it was ok if I included part of the Bayer Formulations Guide as an appendix to my thesis? I mainly wanted to list the anti-static formulations.

Thank you,

~jil
APPENDIX B

GRAPHS
Impedance Spectroscopy Film 428-66 Silver

![Graph showing impedance spectroscopy results for film 428-66 silver. The graph plots imaginary part of impedance (Im Z) against real part of impedance (Re Z) in kilohms.]
Cole-Cole Plot film 428-66 Silver electrode
Impedance Spectroscopy Film 428-67 Silver electrode

![Graph showing impedance spectroscopy data for Film 428-67 Silver electrode.](image)
Impedance Spectroscopy Film 428-63 PEDOT w/ contacts
Cole-Cole plot film 428-63

```
Cole-Cole plot film 428-63
```

![Cole-Cole plot](image)
Impedance Spectroscopy film 428-69 PEDOT-PSS

![Graph showing impedance spectroscopy data for PEDOT-PSS film 428-69. The graph plots ReZ (kOhms) on the x-axis and ImZ (kOhms) on the y-axis.]
Impedance film 428-70 PEDOT-PSS electrode
Debye Model 428-70

Frequency (log scale)

Permittivity (linear scale)

- Real
- Imaginary
Cole-Cole Plot PEDOT vs Silver
Cole-Cole model PEDOT-PSS samples