

All-Polymer Electromechanical Systems Consisting of Electrostrictive Poly(vinylidene fluoride-trifluoroethylene) and Conductive Polyaniline

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ABSTRACT: The low elastic modulus and the ability to withstand high strain without failure make the conducting polymer attractive for a wide range of acoustic applications based on high-strain electroactive polymers. In this article, we examine the electric and electromechanical performance of all-polymer electromechanical systems, fabricated by painting conductive polyaniline (PANI) doped with camphor sulfonic acid (HCSA) on both sides of electrostrictive Poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) copolymer films, and compare them with those from the same copolymers with gold electrodes. The all-polymer composite films are flexible, with strong coherent interfaces between the electrostrictive polymer layer and the conductive polymer layer. The electric performance such as dielectric properties and polarization hysteresis loops from P(VDF-TrFE)/PANI film is nearly identical to those of P(VDF-TrFE)/gold films in a wide temperature (from -50 to 120°C), and frequency range (from 1 Hz to 1 MHz). The all-polymer systems also show a similar or even larger electric field induced strain response than that of films with electrodes under identical measurement conditions. The results demonstrate that the polyaniline/HCSA is good candidate material as the electrodes for electroactive polymers. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 945–951, 2000

Key words: electrostrictive polymer; conducting polymer; poly(vinylidene fluoride-trifluoroethylene) copolymer; polyaniline; all-polymer systems

INTRODUCTION

Polymers that exhibit a large strain response induced by electric fields have attracted a great deal of attention in recent years. These polymers include Polyvinylidene fluoride (PVDF) and its copolymer with trifluoroethylene, polyurethane, odd-numbered nylons, etc. Recently, we reported that electron-irradiated P(VDF-TrFE) copolymers exhibit an exceptionally high electrostrictive

response,¹ which will have a great impact in transducer, sensor, and actuator technologies.² However, increased interest in using high strain electroactive polymeric materials for electroacoustic and electromechanical applications also raises the issue of new electrode materials to meet new requirements and to provide better performance. For instance, to achieve high acoustic transparency, very small acoustic impedance mismatching between the electrode and electrostrictive polymers is required. Because of a high elastic modulus compared with electrostrictive polymers, the commonly used metal electrodes, such as Au and Al, may impose mechanical clamping on the polymer, which can reduce the electric field induced strain level and the efficiency of the elec-

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tromechanical transduction. In addition, in the newly developed electrostrictive P(VDF-TrFE) copolymer, a large transverse strain, more than 3%, can be achieved.³ In general, at such a high strain level, thin metal electrodes will crack and cause failure in the devices. Hence, a new electrode material that can lower the clamping effect and withstand high strain is highly desirable. It is believed that a conducting polymer electrode will meet these requirements.^{4,5} Due to the flexibility, low acoustic impedance, and elastic modulus of conductive polymer electrodes, such all-polymer electrostrictive systems may improve the performance of electromechanical polymer materials in acoustic and electromechanical applications.

For electroacoustic and electromechanical applications, in addition to the mechanical properties of the electrodes, the possible effect of conductive polymers on the electric and also electromechanical responses of the polymer systems should also be examined. For example, in many applications, a high electric power and high electric field will be delivered through polymer electrodes in electromechanical devices, and hence, the current density under high voltage of the conductive polymer electrode is of great concern. Furthermore, these polymer electrodes should be able to operate in a relatively wide temperature and frequency range.

As one of the most promising conductive polymers, Polyaniline (PANI) has been studied extensively in the past decade because of its many attractive features: the monomer is relatively inexpensive, the polymerization method is simple with high yield; and more importantly, PANI exhibits higher stability in air than other conducting polymers. After doping with functional protonic acid, such as camphor sulfonic acid (HCSA) and dodecylbenesulfonic acid (DBSA), the conductivity of polyaniline film can reach as high as 300 S/cm.^{6,7} Moreover, functionally doped PANI can be dissolved in common solvents and processed in the conducting form directly, and therefore, requires no postprocessing chemical treatment. This is quite convenient for applications in electromechanical and microelectronic devices, especially in multilayer polymer devices. In addition, it has been shown that PANI doped with HCSA can carry a relatively high current density without failure.⁸

In this article, an all-polymer system, consisting of electrostrictive poly(vinylidene fluoride-trifluoroethylene) copolymer and polyaniline doped with HCSA and casting from *m*-cresol, was fabri-

cated. In this system, a thin layer of about 1- μ m thick soft conducting PANI/HCSA was coated onto opposing surfaces of P(VDF-TrFE) films to form a sandwich structure. The dielectric properties of this all-polymer system were characterized over a wide temperature and frequency range. The polarization and electric field induced strain were also evaluated. These results are compared with those of gold electroded films. The results demonstrate that the all-polymer films exhibit comparable dielectric properties to gold-electroded P(VDF-TrFE) films in a wide temperature (from -50 to 120°C) and frequency range (from 1 Hz to 1 MHz). In addition, the all-polymer films seem to show similar or even larger electric field induced strain responses than those from films with gold electrodes under identical measurement conditions.

EXPERIMENTAL

Sample Preparation

The P(VDF-TrFE) copolymer with different vinylidene content was from Solvay and Cie of Bruxelles, Belgium. In the present work, the content of vinylidene are 50 and 65% (mol percent), denoted as P(VDF-TrFE) 50/50 and P(VDF-TrFE) 65/35, respectively. The films were prepared by melt-pressing powder at 225°C and then slowly cooling it to room temperature. The final film thickness was about 30 μm . Two types of films were prepared for the investigation of irradiated films: unstretched and stretched films. For unstretched films, they were annealed at 140°C under vacuum for 24 h and then cooled down slowly to room temperature before the irradiation. For stretched films, films were uniaxially stretched at a temperature between 25 – 50°C with a stretching ratio of five times. The films were then annealed at 140°C under vacuum for 24 h and afterwards cooled down slowly to room temperature. The irradiation was carried out at either 95 or 120°C under nitrogen atmosphere by electrons at 3 MeV energy with different doses.

Polyaniline in salt form was prepared by chemical oxidation of aniline with ammonium persulfates oxidant in 1.5M HCl solution at about 0°C according to the ref. 9. An emeraldine base form (EB) of PANI was obtained by treating the salt form with 3% NH_4OH for 2 h. The EB powder was mixed with HCSA in the molar ratio of 0.5 HCSA per repeat unit of PANI. The mixture was ground

under a nitrogen atmosphere to a fine powder and then dissolve in *m*-cresol. The solution was treated in an ultrasonic bath and subsequently centrifuged. Minor insoluble solids were removed by decanting.

To prepare conductive polymer electrodes, the solution of PANI/HCSA was coated on both sides of the P(VDF-TrFE) film by either printing or stamping with a mask. The composite films were dried with an infrared lamp in the hood for 10 min to remove the solvent. The temperature was controlled below 50°C. The thickness of conductive polymer layer can be adjusted by varying the concentration of PANI/HCSA solution and coating times. The temperature must be controlled to below 50°C when the composite films are dried; otherwise, there will be some dissolving of P(VDF-TrFE) in the interface between the PANI layer and the P(VDF-TrFE) layer though the solvent, i.e., *m*-cresol, evaporates easily in the hood at a higher temperature. However, after irradiation at appropriate conditions, P(VDF-TrFE) copolymers become highly crosslinked, and will not be dissolved in any solvent. The composite films are soft and flexible.

Gold electroded P(VDF-TrFE) films were also prepared by sputting Au on opposing faces of the films. The thickness of the gold layer is about 500 Å. For conductivity measurement, freestanding PANI/HCSA films were obtained by casting the above-mentioned solution on a glass slide and dried on a hot plate at 50°C.

Measurement of Relevant Properties

The polarization hysteresis loops of these films were measured by a Sawyer Tower circuit¹⁰ at the frequency of 1 and 10 Hz under different electric fields.

Dielectric properties of the P(VDF-TrFE) films with conductive polymer electrodes were characterized and compared with those of the P(VDF-TrFE) films with gold electrodes. The temperature dependence of dielectric properties was measured on DEA 2870 Dielectric Analyzer (TA Instruments Co., 30 Hz–100 kHz) in the temperature range from –50 to 130°C. The heating rate employed was 2°C/min. The frequency dependence of dielectric properties was measured using an HP 4192A Impedance Analyzer in the frequency range between 100 Hz and 13 MHz.

The electric field induced strain was characterized with bimorph-based strain sensors designed specially for polymer film strain measurement in

our lab,¹¹ which consists of a piezoelectric bimorph-based cantilever dilatometer, a lock-in amplifier (Stanford Research System SR830 DSP), and a high voltage source (KEPCO-BOP 1000M).

RESULTS AND DISCUSSION

The so-prepared all-polymer systems have a sandwich structure of (PANI/HCSA)|P(VDF-TrFE)|(PANI/HCSA). The electrostrictive P(VDF-TrFE) copolymer acts as the functional layer and the green, semitransparent PANI/HCSA layer as electrodes. Different shapes of electrodes for different measurements can be prepared by coating conductive polymer with different masks.

The electrical conductivity was measured by the standard four-probe method on free-standing films casting from above-mentioned PANI/HCSA solution. The conductivity is about 250 S/cm. The current density was also measured on free-standing PANI/HCSA films, the limiting value is about 1500 A/cm². As will be shown in the following, the conductivity and current density of PANI/HCSA are appropriate for its intended use in the present research.

Polarization Hysteresis Loops and Field-Induced Strain Responses

The polarization hysteresis loop is one of the most important characteristics of ferroelectric materials, which reflects directly the microstructure of materials. The typical hysteresis loops for P(VDF-TrFE)/PANI and P(VDF-TrFE)/gold films are shown in Figure 1(a)–(b). Figure 1(a) is for P(VDF-TrFE) 65/35 unstretched films before any irradiation treatment, and the films have not been annealed at high temperature (hence, the polarization level is not very high). Figure 1(b) is for stretched 65/35 films irradiated at 120°C with 60 Mrad doses. The polarization loops measured from the conducting polymer electrode and gold electrode show a quite similar polarization loop. The coercive fields and the remnant polarization of P(VDF-TrFE) films with two different electrode systems measured at different electric fields also exhibit closed values. The similar results were observed for the polarization hysteresis loops measured at 10 Hz. The results indicate that electrically, the conductive polymer can sustain an electric field more than 120 MV/m (the voltage limit of the polarization measurement setup) with a similar performance as that of the gold elec-

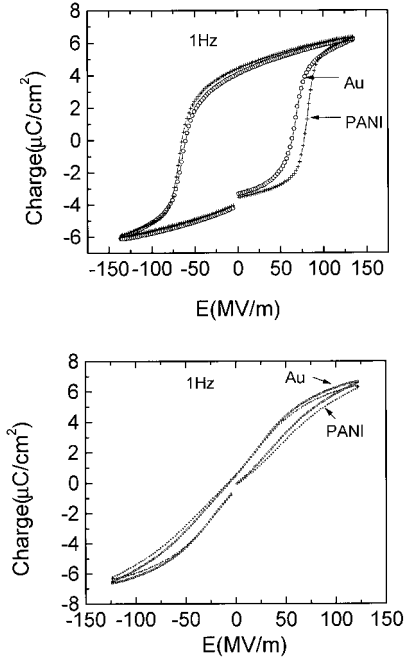


Figure 1 The polarization hysteresis loops of P(VDF-TrFE) 65/35 copolymer (a) unirradiated and unstretched films, (b) films of stretched and irradiated with 60 Mrad at 95°C.

trode. It is concluded that the all-polymer films show similar polarization properties as the gold electroded films under identical measurement condition.

The electrostrictive strains of the irradiated unstretched P(VDF-TrFE) 65/35 copolymers were measured and Figure 2 compares the longitudinal strain induced by external electric fields in the P(VDF-TrFE) films with conductive polymer electrodes and with gold electrodes, respectively. The data is presented as the amplitude of the induced strain vs. the amplitude of the applied field. Clearly, the two yield nearly identical results for applied electric fields up to 140 MV/m. Figure 2(b) shows the slim strain hysteresis loops measured from the two systems, which are also very similar to each other. It should be pointed out that although the data in Figure 2 shows that the longitudinal strains for the unstretched 65/35 films are nearly identical for films with different electrode materials; in some cases studied, the films with conducting polymer electrodes exhibit slightly higher strains than those from gold electroded films.

For electromechanical applications, in addition to the longitudinal response, the transverse strain response is also of great importance.

Transverse strain responses are utilized in many areas, and because the applied electric field is perpendicular to the strain direction, it offers a convenient means in generating large actuation over large distances without the need to raise the driving voltage. Interestingly, for unstretched films, the transverse strains are quite small compared with longitudinal strains, and hence, they were not investigated here further. On the other hand, for stretched films, it was found that a large transverse strain can be achieved along the stretching direction. Figure 3 illustrates the electric field induced transverse strains of stretched (PVDF-TrFE) 65/35 films measured along the stretching direction and the comparison between the films with PANI and with gold electrodes. These films were irradiated with 60 and 70 Mrad doses at 95°C. The transverse strain measured from PANI electroded films is higher than that from gold electroded films. Part of the reasons for this difference could be due to the reduced mechanical clamping from the electrodes. In addition, due to the match of the acoustic impedance

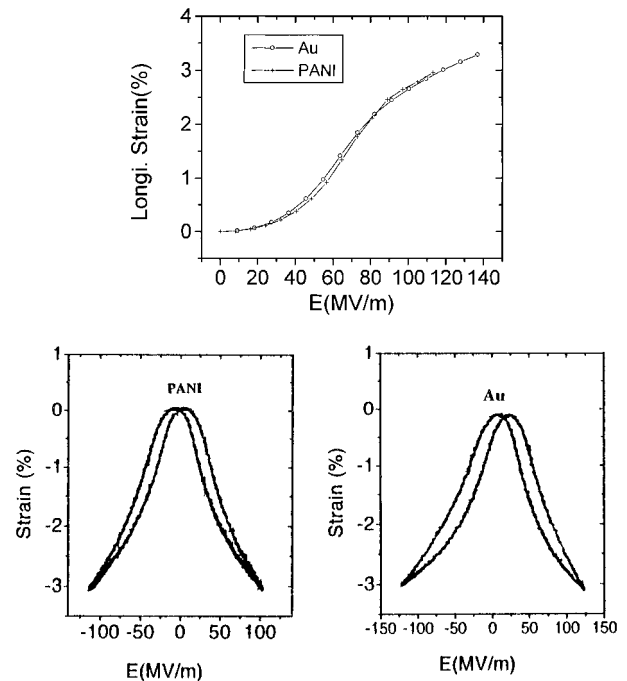


Figure 2 Comparison of the longitudinal electric field induced response of P(VDF-TrFE) films (65/35, unstretched and irradiated at 60 Mrad, 120°C) with a conductive polymer electrode and a gold electrode. (a) The amplitude of longitudinal strain as a function of the amplitude of applied electric field; (b) strain hysteresis loops.

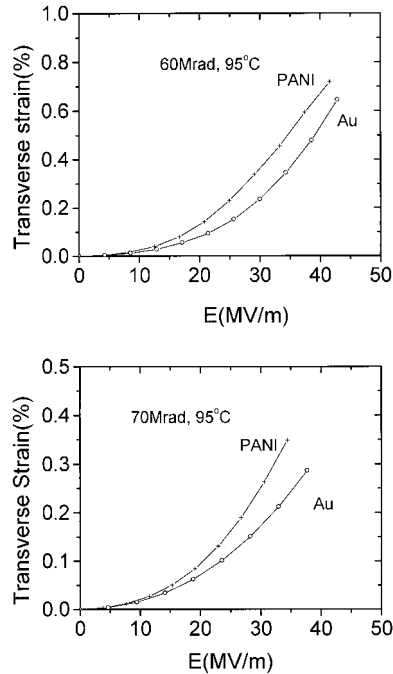


Figure 3 Transverse strain responses induced by electric fields of stretched irradiated P(VDF-TrFE) 65/35 films with a conductive polymer electrode and a gold electrode: (a) irradiated with 60 Mrad at 95°C, and (b) 70 Mrad at 95°C.

of the conductive polymer electrode with that of the electrostrictive polymers, all-polymer systems may improve the performance of electrostrictive polymer systems in acoustic and ultrasonic applications.

For the polymer films investigated, the transverse strain responses are smaller than longitudinal strain responses.

Dielectric Properties

The results presented show that the conductive polymer studied here is suitable for the electrodes on electroactive polymers. To probe the properties further, it is necessary to carry out a study over a broad temperature and frequency range. For example, in our early study of conductive polypyrrole electrode-polyurethane system, it was found that at temperatures above 40°C there is a large increase in the measured dielectric loss from the system due to the dehydration phenomena in the conductive polypyrrole.¹² Thus, the dielectric properties of the polymer systems are characterized in a broad temperature and frequency range.

Temperature dependence of the dielectric constant and dielectric loss measured at 100 kHz for

the electron irradiated P(VDF-TrFE) 50/50 copolymer films (unstretched and irradiated with 30 Mrad at 120°C) with conductive polymer electrodes are shown in Figure 4, which are nearly the same as the dielectric properties of the same copolymer with gold electrodes shown in the same figure. This demonstrates that the polymer electrode developed here works well in the temperature range at least from -50 to +120°C, which is more than enough for most applications using the P(VDF-TrFE) copolymers. Although Figure 4 presents the data measured at 100 kHz, the data obtained at other frequencies also show the similar results (from 30 Hz to 100 kHz). The drop of the dielectric constant of gold electroded films at high temperatures ($\sim 125^\circ\text{C}$) is due to the melt of the sample. It is interesting to note that after the high-temperature dielectric measurement, the gold electroded films deformed while the films with conductive polymer electrodes were intact, which could be caused by a large difference in thermal expansion between the gold electrodes and P(VDF-TrFE) films.

The temperature range investigated covers the main transitions of irradiated P(VDF-TrFE) copolymers, i.e., the glass transition (at about -25°C) in the amorphous and the melting process (about 120°C) in the crystal phase. This indicates that the conductive PANI/HCSA electrodes function well, and do not have the problem as encountered in the conductive polypyrrole electrode.¹¹ In addition, the method of preparing polymer electrodes in the present work is simple and takes a little time.

The frequency dependence of the dielectric constant and loss of P(VDF-TrFE) 50/50 copolymer films with different electrodes and measured at room temperature is shown in Figure 5. It is

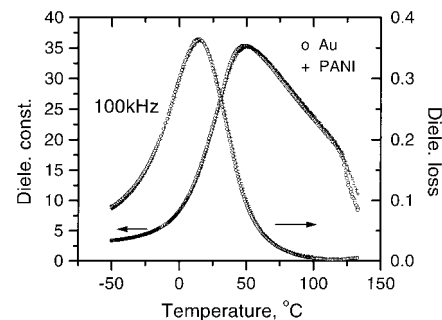


Figure 4 Temperature dependence of the dielectric constant and dielectric loss of PANI electroded and gold electroded irradiated P(VDF-TrFE) 50/50 copolymer unstretched film irradiated with 30 Mrad at 120°C.

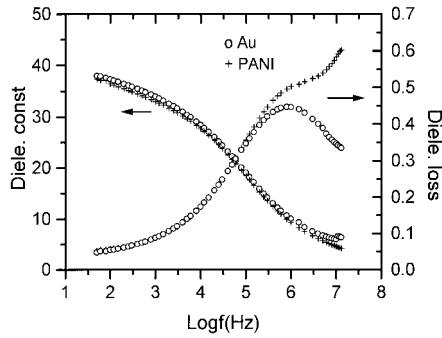


Figure 5 Comparison of frequency dependence of the dielectric constant and dielectric loss of conductive polymer electrode and gold electrode P(VDF-TrFE) 650/35 copolymer film (stretched and irradiated with 60 Mrad at 95°C).

observed that the two systems show very similar dielectric properties over a wide frequency range. The dielectric loss is nearly identical in frequencies from 100 Hz to 300 kHz, and the dielectric constant exhibits nearly the same value in frequencies from 100 Hz to 2 MHz. When the frequency is higher than 300 kHz, the dielectric loss of P(VDF-TrFE) film with conductive polymer electrodes starts increasing and becomes higher than that measured from the film with gold electrodes. The dielectric constant of PANI electrode film is lower than that of gold electrode film above 2 MHz.

The increase of the dielectric loss at high frequencies is due to the higher resistivity of the conductive polymer electrodes compared with gold electrodes. Using a model of a resistor in series with a P(VDF-TrFE) capacitor that has the complex dielectric constant as those from the P(VDF-TrFE)/gold electrode system, the loss data of the P(VDF-TrFE)/PANI system can be reproduced very well, as shown in Figure 6. Here, the resistor in the model has a frequency independent resistance of 1 k Ω , indicating that at weak fields, the resistivity of the conductive polymer used here is not frequency dependent in the frequency range examined (up to 10 MHz). In addition, the resistance value of 1 k Ω is very close to what is expected from that determined using the conductivity and dimensions of the conductive polymer electrodes. The consistency between the measured and model results indicate that the dielectric behaviors of P(VDF-TrFE) film itself with the conductive PANI electrode are the same as those with the gold electrode. That is, the conductive polymer electrode does not change the P(VDF-

TrFE) films. Thus, there is no fundamental limitation in using the conductive polymer electrodes for P(VDF-TrFE) copolymers for electromechanical and electroacoustic applications. The main issue to be addressed is how to reduce the resistance of the conductive polymer electrodes, which may be solved by increasing the conductivity or the thickness of the conductive polymer electrode.

CONCLUSIONS

All-polymer electromechanical systems were fabricated with electrostrictive poly(vinylidene fluoride-trifluoroethylene) copolymer and conductive polyaniline doped with camphor sulfonic acid. The P(VDF-TrFE)/PANI composite films are soft and flexible with strong coherent interfaces between an electrostrictive polymer layer and a conductive polymer layer. These all-polymer systems exhibit similar dielectric properties as those from P(VDF-TrFE) films with the gold electrode in a wide temperature (from -50 to 120°) and frequency range (from 100 Hz to 1 MHz). The P(VDF-TrFE)/PANI and P(VDF-TrFE)/gold also exhibit similar polarization hysteresis loops. Moreover, in many cases, the all-polymer systems show a larger electric field-induced strain response than that of films with gold electrodes under identical measurement conditions. The experimental results suggest that as far as the P(VDF-TrFE) film itself is concerned, the conductive PANI electrodes function in a very similar manner as that of the gold electrodes. Most of the

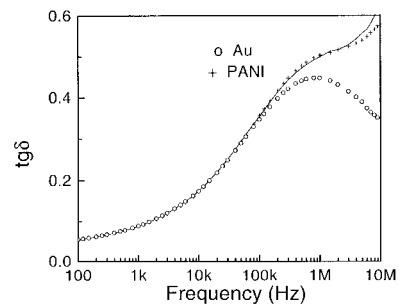


Figure 6 Simulation of frequency dependence of dielectric loss for the data from the film with a conductive polymer electrode. The solid curve is from the simulation and the pluses are the experimental data from the film with conductive polymer electrode. There is close agreement between the simulation and the data. The open circles are the data from the gold electrode film.

observed differences between the two systems can be accounted for by the difference in the electric resistance and elastic modulus between the two different electrodes.

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