

4.1 Introduction

This chapter covers the main features and material examples of the electric field activated electroactive polymers. This class of electroactive polymers (EAPs) is very attractive in performing the energy conversion between the electric and mechanical form and hence can be utilized as both solid-state electromechanical actuators and motion sensors. As will be discussed in the chapter, the electromechanical response in this class of polymers can be linear such as in typical piezoelectric polymers or electrets, or nonlinear such as the electrostrictive polymers and Maxwell stress effect induced response.

Most of the piezoelectric polymers under investigation and in commercial use are based on poled ferroelectric polymers including PVDF-based and nylon-based ferroelectric polymers. This chapter will discuss in detail the properties of these ferroelectric polymers. In comparison with the electromechanical responses in inorganic materials, the electromechanical activity in these polymers is relatively low. In order to significantly improve the electromechanical properties in electric field activated EAPs, new avenues or approaches have to be explored. From the basic material consideration, these approaches include the strain change accompanied with the molecular conformation change, due to the polar vector reorientation, and from the Maxwell stress effect in soft polymer elastomers. This chapter will discuss the recent results based on those approaches, which have produced remarkable improvements in terms of the electric-field-induced strain level, elastic energy density, and electromechanical conversion efficiency in the electric field activated EAPs.

4.2 General Terminology of Electromechanical Effects in Electric EAP

4.2.1 Piezoelectric and Electrostriction Effects

The piezoelectric effect is a linear electromechanical effect where the mechanical strain (S) and stress (T) are coupled to the electric field (E) and displacement (or charge density D) linearly, i.e.,

$$S = d E, \quad (1a)$$

$$D = d T. \quad (1b)$$

In the literature, the effect in Eq. (1a) is often known as the converse piezoelectric effect and in Eq. (1b) as the direct piezoelectric effect. The variable d in Eq. (1) is the piezoelectric coefficient. Adding the linear elastic (Hook's law) and dielectric relations to Eq. (1) and writing it out in the full tensor form, we will have the piezoelectric constitutive equations [Nye, 1987; *IEEE Standard on Piezoelectricity*, 1988]:

$$S_{ij} = d_{kij} E_k + s_{ijkl}^E T_{kl} \quad (2a)$$

$$D_i = \epsilon_{ik}^T E_k + d_{ikl} T_{kl} \quad (2b)$$

where s_{ijkl}^E is the elastic compliance, ϵ_{ik}^T is the dielectric permittivity, and $i, j, k, l = 1-3$. In the equation, the convention in which repeated indices are summed is used. The superscripts E and T refer to the condition under which these quantities are measured. That is, compliance is measured under a constant electric field (short circuit condition) and dielectric constant under a constant stress. Due to the electromechanical coupling in a piezoelectric material, the elastic compliance under a constant electric field can be very different from that under constant charge. In order to write the elastic and piezoelectric tensors in the form of a matrix array, a compressed matrix notation is introduced. In the matrix notation, ij or kl is replaced by p or q according to [Nye, 1987; *IEEE Standard on Piezoelectricity*, 1988], so

$$11 \rightarrow 1, \quad 22 \rightarrow 2, \quad 33 \rightarrow 3, \quad 23 \text{ or } 32 \rightarrow 4, \quad 31 \text{ or } 13 \rightarrow 5, \quad \text{and } 12 \text{ or } 21 \rightarrow 6.$$

Equation (2) is the complete constitutive equation for a piezoelectric material. For a given piezoelectric material, the number of independent parameters can be reduced using symmetry relations in the material. For instance, for an unstretched and poled P(VDF-TrFE) copolymer which has a point group ∞m , the piezoelectric coefficient, the dielectric permittivity ($\epsilon_{ij} = K_{ij} \epsilon_0$, where K_{ij} is the relative permittivity and ϵ_0 is the vacuum permittivity), and elastic compliance matrices are

$$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix}, \begin{pmatrix} K_{11} & 0 & 0 \\ 0 & K_{11} & 0 \\ 0 & 0 & K_{33} \end{pmatrix},$$

$$\begin{pmatrix} s_{11} & s_{12} & s_{13} & 0 & 0 & 0 \\ s_{12} & s_{11} & s_{13} & 0 & 0 & 0 \\ s_{13} & s_{13} & s_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & s_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & s_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & s_{66} [= 2(s_{11} - s_{12})] \end{pmatrix},$$

where the 3-direction is the polymer poling direction.

In addition to Eq. (2) where the stress T and electric field E are the independent variables, the piezoelectric constitutive equations have three other forms [Nye, 1987; *IEEE Standard on Piezoelectricity*, 1988]:

5.10 Recent Progress

As yet, there is no working, electrically driven gel muscle in practical use. This section reviews recent progress to improve upon the various drawbacks of gel systems and take them closer to a practical artificial muscle. Progress is needed on speed, strength, processability and force developed.

5.10.1 Strength

As was mentioned in Sec. 5.7 above, gel strength is not well understood but most gels fail by crack propagation like a brittle plastic. Natural gels, such as cartilage or the bodies of soft marine animals, tend to be composites with reinforcing fibers. Since there are many actual or potential medical applications for gels, including contact lenses and soft tissue prostheses, there is considerable interest in improving their properties. Most of this work involves preparation of composites, but also explores promising combinations of materials rather than the detailed design of a system.

If we want a gel that delivers a maximum stress, similar to muscle, of about 300 kPa, we would hope for a gel with a breaking strength of 500 kPa or more. An N-isopropylacrylamide gel responding to electrical heating has been reported to have a strength of 10 kPa [Kato et al., 1998]. A cross-linked copolymer gel of hydrophilic and hydrophobic segments was reported to have a strength of 200–500 kPa [Isayeva et al., 2002]. The strength is very dependent on water content and many modifications will increase strength by reducing swelling. For example, contact lenses have water contents of 30–50% and strengths of 2–4 MPa [Willis et al., 2001]. There have been many recent studies of composite gels made by irradiation of mixed solutions of polymers and increases in strength have been reported when compared to single polymer gels (Relleve et al., 1999). One would expect that the properties of these disordered systems would primarily follow the water content.

Likewise freeze-thaw modified polyvinylalcohol gels with water contents of around 80% were found to fail in compression at a few MPa [Stammen et al., 2001]. As was found by earlier workers [Suzuki, 1991], this freeze-thaw process produces a two-phase composite structure that is stronger and has recently been studied in more detail [Matsumura et al., 1998; Shapiro, 1999]. Composite gels with polyvinylalcohol reinforcing water-soluble polymers have also been studied [Nho and Park, 2002].

A number of studies have considered reinforcement of gels with inorganic fibers or plates both added before gelation and grown *in situ* in the gel and a significant increase in modulus is certainly seen [Gao et al., 1999; Xia et al., 2003; Yamaguchi et al., 2003]. One very attractive approach, based on the analogy to collagen-reinforced biological gels, is to reinforce gels with fibrils of rigid-rod polymers [Philippova et al., 1998]. This particular system does show a significant increase in modulus but from low values and a lack of strength, data is given. Thus the full potential of composites of this type has yet to be explored. A

simple version of this approach is to reinforce a gel with a textile, such as nonwoven polypropylene [Wu et al., 1999; Lopergolo et al., 2002].

5.10.2 Speed

Unlike piezoelectric or dielectric polymers, gel muscles change volume by a local uptake or loss of water. Since this is a diffusional process, the response time will increase roughly with the square of the diameter of the muscle fiber. There will be additional dependencies on the rate of generation of ions electrically, on the relationship between gel charge and equilibrium swelling and on the chemical kinetics of ionization of the gel. The complex inter-relationship of these factors means that a complete muscle system must be modeled in order to predict a response rate. Such a model has been presented for polyacrylic acid-polyvinylalcohol gels [Marra et al., 2002].

In general porous composites will respond more rapidly than monolithic gels (Kato et al., 1998; Chen and Park 2000; Gemeinhart et al., 2000) and fibers (Schreyer et al., 2000) Recently, 30- μm contractile bodies have been found in plants [Knoblauch et al., 2003]. These “forisomes” contract in response to calcium ions in about 50 msec and develop a force of 11 kPa.

5.10.3 Processability

Many of the electro-active polymers are unable to be processed by conventional polymer methods, such as extrusion and molding. A successful artificial gel muscle is likely to be an assembly of fine fibers or films and metal electrodes. Cross-linked gels may be formed by irradiation of existing shapes or by casting and polymerization of monomer solutions. Liu and Calvert (2000) did apply free-form fabrication methods to making more complex shapes, but there is a need for new gel chemistries that might be more readily processed. In particular, the free-radical polymerization used to make polyacrylic acid is very air and impurity sensitive, so that fine-scale structures cannot be made without elaborate precautions.

With this in mind, Liu and Calvert explored gels based on epoxy chemistry, which is relatively robust and reproducible. A range of gels was made based on water-soluble di-epoxides of glycerol and glycols coupled with aminated polyethers [Yoshioka and Calvert, 2002]. These materials could be readily formed by extruding toothpaste-like physical gels and warming them to drive the cross-linking reaction. The gels were highly swollen in acid and contracted in base. Small cylinders, about 100 μm in diameter, responded to pH change or electrical stimulus in about 5 minutes.

Extrudable blends of colloidal conducting polymer and hydrogels have been described [Kim et al., 2000]. Photo cross-linkable gels have been developed based on a nitrocinamate photosensitive group attached to peg [Micic et al., 2003]. Self-assembly methods have been discussed for artificial muscles and other responsive polymers (Zhang, 2002). A method has been described for

8.7.3 Actuation in Aligned MWNT Arrays

To date it has been difficult to study the actuation in MWNTs due to the difficulty in producing macroscopic sheets with adequate mechanical properties. However, the synthesis method giving “forests” of MWNTs and the methods developed to transfer such arrays to other substrates [Huang et al., 1999; Yang et al., 1999; Dai and Mau, 2000; Huang et al., 2000; Li et al., 2000; Qidao and Dai, 2000] have enabled the demonstration of MWNT actuation. MWNT arrays were prepared on a flexible gold foil and immersed in 1 M NaNO₃ electrolyte. Application of a potential of +1 V or -1 V vs. SCE produced bending of the unimorph structure in opposite directions. Higher voltages (+/- 2 V produced larger deformations (Fig. 13). Proper patterning of the aligned nanotube array surface with appropriate non-conducting polymers can lead to controllable actuation paths [Soundarrajan 2003], suggesting that the aligned MWNT actuators eventually might be useful for MEMS applications.

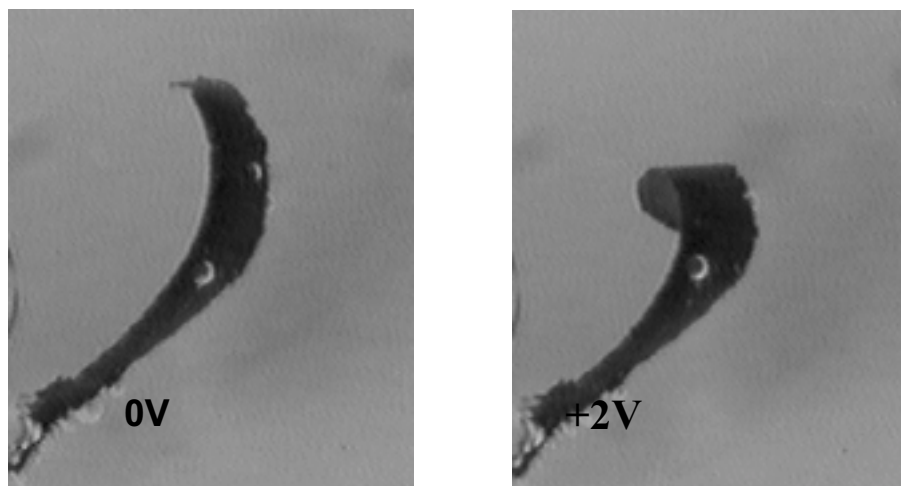


Figure 13: Bending of aligned MWNT arrays on a gold foil by application of +2 V or -2 V (vs. SCE).

The gravimetric capacitance for the forests of MWNTs is about 30 F/g, which is similar to that for the SWNT bucky paper. However, the above cantilever-based actuator response for the forests of SWNTs is believed to be electrostatic. Electrostatic repulsion between different tubes in the nanotube forest would cause repulsion between these tubes. Since the nanotubes are firmly anchored to the substrate, the effect of this repulsion is a bending of the sheet, so that the separation between unanchored nanotube ends is increased. While scientifically interesting, this inter-tube electrostatic actuator mechanism is much less promising for applications than actuation mechanisms that seem to principally involve the direct effect of charge injection on nanotube dimensions.

Moreover, possible pneumatic actuation cannot be ruled out for cantilevered forests of nanotubes, as bubble generation was observed throughout the actuation process.

8.8 Conclusions and Future Developments

The demonstration of carbon nanotube actuation driven by a non-Faradaic charging may eventually lead to game-changing actuator devices. However, major improvements in the structure and mechanical properties of nanotube assemblies (fibers or sheets) are required before applications can be realized. While the observed actuator strains are quite large, the primitively prepared SWNT mats have a Young's modulus (up to 5 GPa) that is well below that determined for individual NT bundles (~600 GPa). Significant improvements in strength and stiffness have been achieved by obtaining indefinitely long nanotube fibers that comprise highly aligned SWNTs in a polymer matrix. The modulus of these assemblies now approaches 100 GPa and the strength reaches about 2 GPa. However, the polymer "glue" that holds the nanotube fibers together in these composite fibers interferes with the charge injection needed for actuation if this polymer is not a good ionic conductor. Alternatively, conversion of the host polymers in the nanotube fibers to ionic conductors (for example, by incorporating phosphoric acid in a polyvinyl alcohol host) degrades the mechanical properties of the fiber. Hence, there is a need for ionic conductor that effectively couples the nanotubes together without interfering with electrochemical charge injection. Recent developments in the covalent attachment of organic groups [Boul et al., 1999] and polymers [Curran et al., 1999] to NTs provide one direction for improving inter-tube bonding in NT mats and fibers. As the understanding of NT synthesis, characterization, and processing further develops, other approaches for improving the bulk mechanical properties of macroscopic NT assemblies are expected.

Nanoscale actuators based on single nanotubes do not have these problems. The challenge here is to develop methods for measuring actuation at the nanoscale, and then to manipulate single nanotubes in the fabrication of practical devices. Recent publications provide some guidance. The AFM techniques, used by Salvetat et al., [1999] and Walters et al., [1999], have enabled mechanical properties measurements (modulus and yield strain) on small-diameter NT bundles. Similar techniques may well demonstrate the true potential of NT actuators in terms of actuator strain, strain rates, cycle life, and stress generation.

8.9 References

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16.1.1 Motivation for a New Actuator Technology

To understand the issues involved with the application of dielectric elastomer actuators, one must first understand the motivation for developing a new actuation technology. Table 1 summarizes parameters that are commonly used to select actuators. EAPs in general and dielectric elastomers in particular do not offer the best performance all performance metrics. However, considering the full parameter space of actuator specifications, EAPs can offer performance and characteristics that cannot be reproduced by other technologies. For example, their combination of large strains, high energy density, fast speed of response, and good efficiency is unique. Table 2 compares dielectric elastomer EAPs with other actuator technologies. It should be noted that the values in Table 2 have been collected from several different sources and are not based on uniform measurement standards. In some cases, the reported values are projections of performance, rather than actual measurements. Efficiency, in particular, is seldom measured directly. Thus, Table 2 should be considered a preliminary comparison. Another comparison of EAPs with other actuator technologies is given by Wax and Sands [1999]. Topic 5 discusses performance measurements of EAPs in more detail. In the case of dielectric elastomers, the values in Table 2 are the maximum performance achieved in dielectric elastomer materials. Practical dielectric elastomer actuators will likely have lower performance.

Other desirable features of actuators are not easily expressed by metrics such as those in Table 1. These features include ruggedness, the ability to be mass-produced on a single substrate, and compatibility with electronic circuit manufacturing techniques and materials. Again, EAPs may excel in these areas.

Although usually disregarded by many researchers, cost can often drive the selection of actuators for a given application. Fortunately, the materials and manufacturing cost of EAP materials and devices is expected to be low in contrast to that of more exotic materials such as magnetostrictive ceramics, single-crystal piezoelectrics, or even shape memory alloys.

Figure 1 graphically illustrates application areas where EAPs can address the shortcomings of traditional actuators and open up a range of new applications. Many new application opportunities may involve the mere replacement of traditional actuators with EAP actuators so as to improve the performance or lower the cost of a device. Table 3 shows several applications where EAP actuators can effectively replace traditional electric actuator technologies. Several of these applications, as well as more exotic actuators with applications related to other application areas shown in Fig. 1, are discussed in Sec. 16.5 below.

Table 1: Common actuator specifications.

Parameter	Scale-Invariant Version	Comments
Energy and Power		
Energy output	Specific energy	Over full cycle
Power output	Specific power	Average or instantaneous
Energy conversion efficiency	Same	Energy out over a full cycle / energy in over a full cycle (excluding recovered energy)
Response time	Same (response time is not generally scale invariant)	For one direction or full cycle
State Variables		
Displacement	Strain	Instantaneous or maximum over a cycle
Force	Stress, pressure	Instantaneous or maximum during a cycle
Velocity	Strain rate	Instantaneous or maximum
Impedance and Controllability		
Stiffness	Elastic modulus	Usually nonlinear (not a constant)
Damping	Specific damping, loss factor, loss tangent	Usually nonlinear (not a constant)
Accuracy (displacement or force) (%)	Percentage of strain or stress	Usually percentage of maximums
Repeatability (%)	Same	Usually percentage of maximums
Linearity or sensitivity (%)	Same	Deviation from linear input-output relationship
Operational Characteristics		
Environmental tolerance	Same	Recommended ranges of temperature, humidity, etc., or effect of variations on temperature, humidity, etc., on the above parameters
Durability, reliability	Same	Number of cycles before degradation threshold or total failure, degradation per cycle or time
Input impedance (power supply requirements)	Specific impedance	Voltage and current requirements or pressure and flow, depending on power mode

18.1.2 Recent EAP Advances

For many years so-called “artificial muscles” have been reported in various forums and news media. Even though these materials showed promise, they have fallen short for use in themed entertainment. Recent years’ progress, as reported in Chapter 1 and Topic 3, has added exciting new options to the palette of EAP materials [Bar-Cohen, 1999 and 2000]. These include dielectric-elastomers at SRI International, the Relaxor Ferroelectric P(VDF-TrFE) at Penn State University, the carbon nanotubes at Honeywell and University of Texas at Dallas, and the conductive polymers at JPL, MIT, San Sebastian University (Spain), Pisa University (Italy), Risoe National Laboratory (Denmark), and SFST (Santa Fe, New Mexico).

Of these EAP materials, two stand out as appearing to be closest to implementation in terms of technological readiness for character animation. First, ion exchange polymer/metal composite (IPMC) actuators have shown large strains and significant robustness in experiments at JPL, EAMEX, Japan, University of New Mexico, and University of Washington. These actuators have been demonstrated in spring 2003 in what may be the first EAP-actuated entertainment product. Developed by Eamex, Japan, and manufactured by Daiichi Kogei, Japan, this animated fish swims about an aquarium (see Fig. 1, Chapter 1) propelled by IPMC actuators energized using electromagnetic induction from coils located above and below the aquarium. Specifically an entertainment product, the fish robot confirms the idea that entertainment is a “low-hanging branch” for practical application of EAP actuators. The requirements for these fish are far different than those for a humanoid robot, so much work remains. Nevertheless, these robotic fish are an extremely promising step in the evolution of EAP-powered entertainment robots.

Second, the dielectric EAP actuators developed at SRI International [Chapter 16; Pelrine et al., 2000] have shown strain, response speed, and stored mechanical energy density in the range of biological muscles [Chapter 3; Full and Meijer, 1999]. However, the challenges to these actuators are severe; they require up to 5000 V to operate, they expand when stimulated (especially tough for facial-expression animation), and they appear delicate in construction. SRI’s recent tubular actuators expand the options of these dielectric actuators, operating as gimbals that may be controlled to bend in any direction.

Many other EAP actuator technologies may pull ahead to satisfy the needs of entertainment robots. Although not fully mature, the relaxor ferroelectric [Chapter 4; Zhang et al., 1998] shows high strain, fast response, and relatively high stored mechanical energy density, likely comparable to biological muscle. This EAP material also requires lower voltages, but is difficult to mass produce. Carbon nanotubes [Chapter 8; Baughman et al., 2000] offer immensely high power density and astonishing strength at low voltages, but they induce low strain at the level of 1% and they are a long way from practicable application. On the other hand, conductive polymers [Chapter 7; Olazábal et al., 2001] offer a relatively high actuation force of several hundred times the ratio of carrying force

to their own weight, and require single-digit voltage. However, they are sensitive to fatigue and cannot be strained for extensive cycles due to the material's strength constraints. The above new materials may lead to the first generation of effective EAP actuators for entertainment applications, if their shortcomings can be addressed.

In addition to synthetic polymers, biologically derived electro-active polymers may be useful as actuators. The most promising class of such biopolymers would be cytoskeletal motor proteins such as myosins, kinesins, and dyneins. These protein polymers, being the motors of most cellular and subcellular biosystems) are inherently biologically compatible, and bioextracted muscle tissues have actually been used via electroactivation to drive swimming robots [Dennis et al., 1999]. Proteomics, the science of proteins and their dynamical systems, has been exploding with advancements recently, largely thanks to improving imaging technology and supercomputing simulations. Preliminary successes in engineering these proteins as nanoactuators are encouraging, though they do not indicate any near-term applicability [Wada, et al, 2003; Kull and Endow, 2002]. Beyond the engineering breakthroughs required to implement protein actuators on a nanoscopic scale, these mechanisms will further need to be assembled into large macro-arrays in order to be capable of effecting motion in an entertainment robot.

Although EAP as artificial muscles for motor-actuation is the topic here, other electroactive polymer capabilities may be useful to entertainment and so also merit mention. Recently, substantial progress has been made in flexible polymer display screens, such as Universal Display Corporation's OLED displays, and light-emitting polymers (LEPs) are finding active use in industry at the present. One can imagine that, in time, a character's skin could light up and display text or images as desired. Perhaps more exciting still is electroactive polymer computation, which has shown rapid progress in recent years [Higgins et al., 2003]. While not as inherently fast as silicon computation, computing polymers are materially flexible have other useful characteristics, such as the low cost of mass production. Additionally, electroactive-polymer-sensing arrays have recently been successfully tested in humanlike simulated skin materials at the University of Illinois at Urbana-Champaign [Engel et al., 2003].

Many such useful capabilities of EAP can be achieved within one single polymer material, a multiplicity of functions that potentially decreases the requirements of space, material use, and cost. One exemplary multifunction material would be carbon nanotubes, which promise to simultaneously serve as mechanical structure, transistorized computer, light emitter, and actuator.

While EAP materials are progressing in their capabilities, robotics research may complementarily facilitate the use of EAP actuators in entertainment, particularly by reducing the force required to actuate entertainment automatons. This idea motivated research conducted by the author in the spring of 2002, wherein a novel class of polymers dubbed "F'rubber" (a contraction of "face" and "rubber") was invented that requires less than one-tenth the force required by