State-of-the-Art Developments in the Field of Electroactive Polymers

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ABSTRACT
The paper presents a brief review in the field of electroactive polymers. It outlines the main classes of electroactive polymers, their properties and applications. Current efforts to synthesize electroactive polymers with novel or improved characteristics along with the challenges, opportunities and future research directions in the subject area are discussed.

INTRODUCTION
In the past decades, rapid advances in synthetic polymer science have led to an explosive growth in the development of polymers with novel characteristics. Electroactive polymers occupy a special place as smart materials due to their ability to detect changes in the loading or environmental conditions, decide rationally on a set of the respective actions, and carry out these actions in a controlled manner. Responses of this type are often compared with biological reactions that, by nature, transform the sensed information into a certain response.

The properties of electroactive polymers can be tailored to achieve the desired outcome. Essentially, refinement or modifications in chemistry or processing of electroactive polymers produce new material morphology, yielding novel performance outcomes. In general, the ability of electroactive polymers to perform designated functions is determined by their coupled mechanical, chemical and physical properties. However, the structure-property-response interrelations of electroactive polymers are complex, often lack clear understanding and, consequently, present serious challenges. Yet, applications of electroactive polymer systems tend to expand at unprecedented rates. It is clear that continuing progress in this field cannot be sustained without intensified interdisciplinary research efforts.

GENERAL CHARACTERISTICS OF ELECTROACTIVE POLYMERS
The group of electroactive polymers (EAP) [Bar-Cohen, 2004] comprises a wide array of different materials, including piezoelectric, electrostrictive, ionic and conductive polymers, elastomers, polymeric blends, electroactive foams and electrorheological fluids. Each of these material types is characterized by its unique material properties and functional abilities.

The response of piezoelectric polymers is observed either in the form of an electric charge or voltage produced by applied mechanical forces or, conversely, in the form of mechanical deformation induced by an applied electric field. These piezoelectric effects have been defined, respectively, as “direct” and “converse.”

Electrostriction, which is a property of all dielectrics, is similar to piezoelectricity. The distinct characteristic of electrostrictive polymers is that they undergo mechanical deformations proportional to the square of the electric field, whereas in piezoelectric materials

this functional relation is linear. Respectively, electrostriction is always observed in the form of material elongation irrespective of the electric field direction while the deformation is reversed in piezoelectric polymers under the same conditions.

Strong piezoelectric effects have been observed in a group of commercial synthetic polymers polyvinylidene fluoride (PVDF or PVF_2) and PVDF co-polymers. Polyvinylidene fluoride is a semi-crystalline polymer with typical crystallinity of, approximately, 50%. The amorphous phase of the polymer has the properties of a supercooled liquid with the glass transition temperature of about -50°C. Permanent dipole polarization of PVDF is obtained through a technological process that involves stretching and polling of extruded thin sheets of the polymer. In general, polarization in PVDF depends on such factors as poling temperature, poling time, poling process, and electrode conditions [Hilczer and Malecki, 1986]. Typically, PVDF is produced in the form of thin films with thicknesses ranging from 9 to 800 μm (10^{-6} m). A thin layer of nickel, silver or copper is deposited on both material surfaces to provide electrical conductivity when an electric field is applied, or to allow measurements of the charge induced by mechanical deformations. The general properties of PVDF and PVDF copolymers include stable response characteristics in a wide frequency range of up to 10^9 Hz, low acoustic impedance, high degree of resistance to impact, resistance to moisture absorption, and insensitivity to intense ultraviolet and nuclear radiation [Gandhi and Thompson, 1992; Vinogradov, 2002] .

Ionic polymers form a separate group of EAP. Their electroactive response is based on the mobility or diffusion of ions controlled by an electrically stimulated chemical reaction such that the cathode side of the sample is alkaline and the anode side is acidic. As a result, the polymer undergoes mechanical deformation. The main advantage of ionic EAP as compared with other electroactive polymers is their ability to produce large actuation strains in response to electrical stimuli. Whereas electronic EAP require a high activation fields above 100 MV/m, i.e., close to their breakdown level, ionic polymers can be activated by driving voltages as low as 1-2 Volts. Other useful properties of ionic EAP include a large range of motion with high precision and speed, high strain energy density, low voltage/power requirements, low weight, tailorability of properties, high resilience, and damage tolerance. However, to function properly, ionic polymers must continuously maintain their wetness. Besides, DC induced displacements are difficult to sustain, and a multilayered ionic gel structures is relatively slow to react to an applied electric field [Calvert, 2001].

Another EAP group comprises conductive electroactive polymers including polypyrroles, polyanillines, and polythiophenes. The functional response of these polymers is determined by couplings of their chemical, electrical and mechanical properties. Specific practical advantages of CEP include the tailorabilty of their response at the molecular level, and the abilities to facilitate transport of electrical information and perform actuation functions. The functional control of these materials can be achieved electronically hence, their behavior can be manipulated in situ, using appropriate electronic signals [Wallace et al, 1997].

Electro-rheological fluids (ERF) belong to a class of materials that respond to electric stimuli by changing their viscocity. They effectively represent a colloidal system in which one kind of particulate material is dispersed in a nonconductive liquid base. Typically, electro-rheological fluids consist of a base fluid and dielectric particles of 0.1–100 μm in size with a volume fraction between 20% and 60%. An ERF can be synthesized using a variety of components. As an example, an electro-rheological fluid, known as LID 3354, consists of fluorosilicone base oil and 35% by volume of polymer particles. The typical physical

properties of this ERF material are as follows: density of 1.46 x 103 kg/m3; viscocity of 125 MPa.sec at 30°C; boiling temperature above 200oC; and freezing temperature below – 20°C. When an electric field of several kilovolts per millimeter is applied, ER fluids reversibly change from a liquid state to a solid crystallized state. However, the mechanism behind this transition is not clearly understood [Hao, 2002].

Relatively recently, attention of several research groups has been attracted to piezoelectric properties of soft polymeric foams with cellular microstructure. The development of cellular polymers began in 1990 in Finland, and since that time, interest in these materials has expanded due to their useful properties such as light weight, low acoustic impedance and easy integration in structural design [Bauer et al, 2004].

BIOMIMETICS AND THE ROLE OF EAP MATERIALS

Humans throughout history have always sought to mimic the appearance, mobility, functionality, intelligent operation, and thinking process of biological creatures. This field of imitating biology is know as biomimetics [Bar-Cohen, 2005]. Some of the technologies that have evolved include artificial muscles, artificial intelligence, and artificial vision to which significant advancements in materials science, mechanics, electronics, and computing science have contributed greatly. for Electroactive polymers as artificial muscles are an important part of this field offering capabilities that can be critical to making devices with mobility, manipulation and articulation functions. To take advantage of these materials, efforts are made worldwide to establish a strong infrastructure ranging from analytical modeling and comprehensive understanding of their response mechanism to effective processing and characterization techniques [Bar-Cohen, 2004]. The field is still in its emerging state and robust materials are still not readily available however in recent years significant progress has been made and commercial products have already started to appear.

APPLICATIONS

In general, electroactive polymers have been used as active elements capable of sensing and responding intelligently to external stimuli. On this basis, a new generation of so-called “smart structures” or “smart material systems” has emerged that can detect changes in the loading or environmental conditions, decide rationally on a set of the respective actions, and carry out these actions in a controlled manner.

Material selection in the design of smart systems involves considerations of such factors as the maximum achievable strain, stiffness, spatial resolution, frequency bandwidth, and temperature sensitivity, to name a few. The key factor that defines the application range of piezoelectric polymers is their use in the design of transducers, sensors, and actuators. An impressive array of applications of piezoelectric polymers in transducers includes loudspeakers; flexure mode transducers such as optical scanners, light deflectors, variable aperture diaphragms, modulators for fiber optics, pyroelectric detectors, and capacitors. Polymer based piezoelectric transducers are particularly effective in high frequency applications such as acoustics, ultrasonics and nondestructive material evaluation. Examples of such applications include medical diagnostics, marine fouling prevention, and acoustic microscopy [Rao and Sunar, 1994].

Piezoelectric sensors have been typically used for strain measurements through the readings of voltage, rates of voltage change, or the frequency spectra of the signal generated by the sensor. Various commercial applications of piezoelectric film sensors include contact switches, musical instruments, and vibration sensing devices. By reacting to temperature

changes, PVDF based motion sensors are widely used in energy management systems to control room lights, appliance displays, and HVAC equipment. Piezoelectric polymers have been recently employed in more advanced sensing technologies, for example, tactile sensors capable of recognizing objects with high degree of precision, and temperature and pressure sensors that can replicate the functions of human skin. At present, nondestructive evaluation technologies are in the state of fundamental transition from conventional ultrasonics methods to a new paradigm of structural health monitoring using an array of piezoelectric sensors capable of identifying the presence of defects and incipient damage [Giurgiutiu, 2003].

A number of polymer based piezoelectric actuators have been developed for different modes of operation. Traditionally, bending mode actuators have been designed in the form of bimorph beams consisting of two piezoelectric layers of opposite polarity bonded together. When an electric field is applied, one of the layers tends to expand while another contracts, producing bending deformation. Piezoelectric bimorph actuators in the form of cantilever beams can generate considerable tip displacements, although they tend to produce low forces. Thicker films and multi-layer designs can expand the range of produced forces, but tend to reduce the respective displacements [Vinogradov, 2002; Rao and Sunar, 1994].

Piezoelectric polymers represent a group of primary candidate materials for shape and position control of flexible structures in weight sensitive applications. Examples of such applications are smart skin for airborne structures and highly compliant smart material systems for space applications [Jenkins et al, 1998]. The latter comprise a diverse range of ultra-lightweight structures such as solar sails, deployable membrane mirrors, atmospheric balloons, antennae, and reflectors. By incorporating the capabilities of piezoelectric polymers in structural design, it is possible to enhance the performance of such structures through active control of their shape and stability.

Technologies based on the use of electroactive ionic and conductive polymers, and electrorheological fluids can be characterized as being still in their embryonic state. In particular, ionic polymers typically serve as actuators in miniature devices and robotic components with primary applications in biomedical fields [Calvert, 2001]. Conductive polymers have been recently considered as candidate materials for replacing traditional metal electrodes in electroactive polymer systems. By eliminating the deformation constraints imposed by relatively stiff metallic surface layers, conductive polymers have the potential to increase the strain range of piezoelectric and electrostrictive systems. The application range of electrorheological fluids is currently limited to such damping devices as clutches, fluid brakes and shock absorbers, hydraulic systems, and circuits [Filisko, 2002]. Regarding the practical use of piezoelectric foams it is envisioned that these materials will replace the traditional piezoelectric polymers in a variety of transducer applications, microphones, headphones and loudspeakers [Bauer et al, 2004].

ENHANCEMENT OF ELECTROMECHANICAL RESPONSE

The search for new electroactive polymers has produced materials with enhanced performance characteristics. Major accomplishments in this area can be summarized as follows.

Strong electrostrictive response of polyvinylidene fluoride-trifluoroethylene (PVDF-TrFE) has been obtained as a result of material irradiation [Zhang and Bharti, 2002], and by chemically increasing the degree of polymer cross-linking [Casalini, and Roland, 2002]. Certain changes in manufacturing processes have provided significant improvements in the electrostrictive response of PVDF-HFP co-polymer [Jayasuriya et al, 2001]. An elecrostrictive

graft-elastomer (G-elastomer), showing a significant increase in electromechanical output power density, has been developed by a special thermal annealing treatment [Su et al, 1998].

Enhanced electroactive responses of composite polymer systems have been achieved by combining the properties of two or several different materials. Some of such systems provide dual sensing-actuating functionality. In particular, electroactive composite systems have been synthesized using high dielectric organic compounds and electroactive polymers. These organic polymer blends are characterized by high dielectric constants. A promising composite material of this type represents a system of CuPc powders used as a filler and the electrostrictive polymer P(VDF-TrFE) serving as a matrix. The resulting blend is characterized by high elastic modulus, high elastic energy density, and large strains [Zhang et al, 2002b]. Similarly to the described polymer blend, an all-polymer composite material has been synthesized using the conductive polymer polyaniline (PANI) as the dielectric-enhancement component and the terpolymer P(VDF-TrFE-CTFE) as the matrix. This system requires a relatively low concentration of the filler to raise considerably the dielectric coefficient which, in general, depends on the relative proportion between the constituents. This electroactive composite is characterized by large, up to 2.6% electromechanical strains induced by an electric field of less than 16 V/μm, high elastic modulus, and elastic energy density of about 0.18 J/cm^3 [Huang, 2003]. A combination of an electrostrictive graft elastomer (G-elastomer) described above and a piezoelectric poly(vinylidene fluoride-trifluoroethylene) copolymer have together produced several types of ferroelectric-electrostrictive molecular composite systems with dual functionality involving two types of responses, piezoelectric and electrostrictive. Such materials can form a basis for various multifunctional smart systems with the advantage of using a single film for both sensor and actuator functions [Su et al, 2000].

OPPORTUNITIES AND CHALLENGES

An overview of technological developments involving electroactive polymers clearly indicates that the field expands at unprecedented rates. The guiding principles behind this progress are efficiency, functionality, and precision of these materials.

However, effective implementation of electroactive polymers directly depends on the degree of understanding of their behavior and properties. In this regard, challenges arise due to the sensitivity of the polymers to variations in their fabrication, time and temperature dependent effects, and nonlinearity of their coupled mechanical, physical and chemical properties.

A problem of immediate significance stems from the fact that electroactive polymers are often used as damping elements for vibration, noise and position control. In fact, these materials are considered as primary candidates for distributed control of compliant structures. The inherent damping properties of polymers combined with their control functions tend to produce new unexplored effects that must be fully understood. It is also of importance that electroactive polymers perform their functions in dynamic environments over a wide range of temperatures and frequencies. Such conditions tend to accelerate their degradation and, consequently, alter their functional response through electromechanical couplings.

Besides the experimental investigations required to address the outlined problem areas, there is a need to advance computational material science of electroactive polymers. It is important in this regard that modeling and simulation are treated as an integral part of design and manufacturing processes.

In the immediate future, continuing progress in the field of smart polymers will depend on the intensity of research efforts directed towards the development of electroactive polymer

systems with enhanced adaptive capabilities. Concurrently, it is critical to develop innovative testing methodologies, consistent material characterization, and formulation of advanced theoretical models. On this basis, the unprecedented opportunities offered by the new generation of electroactive polymers will continue to stimulate further technological progress.

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