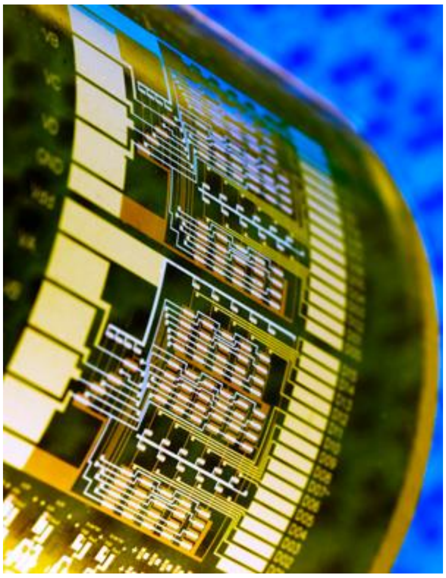
White Paper:
EletroActive Polymers and Flexible Electronics



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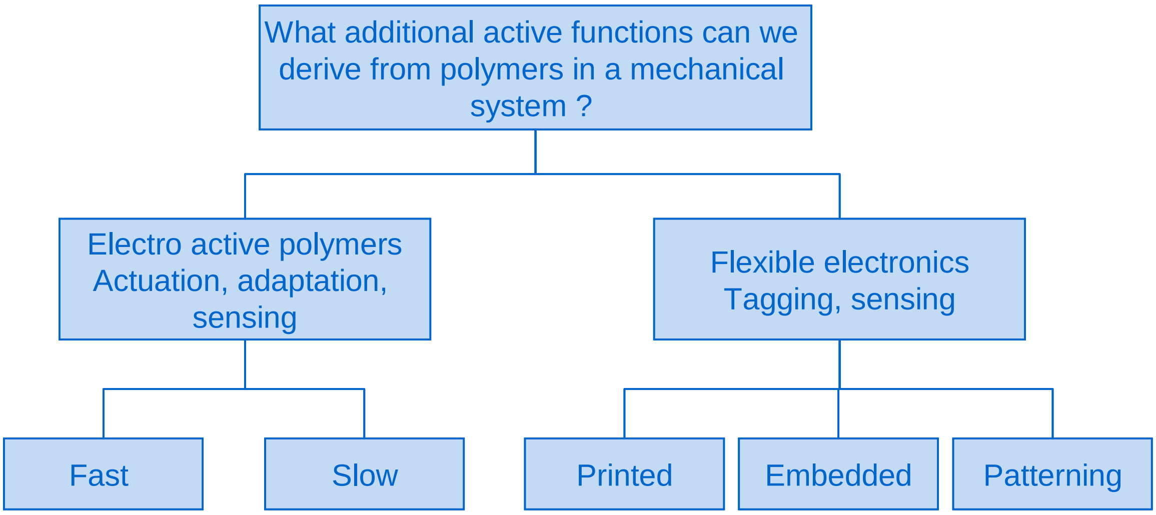
Abstract The paper reviews the current state of technology and potential implications of the development of ElectroActive Polymers (EAP) and Flexible Electronics (FE). Polymers are highly attractive for their inherent properties of mechanical flexibility, light weight and easy processing. This white paper focus on two approaches to add functionalities to polymers: electroactive actuators and sensors and flexible/organic electronics. There are many types of known polymers that respond electromechanically and they can be grouped into field-activated and ionic EAP. Organic electronics is a platform technology that is based on organic conducting, semi-conducting and other functional materials. The printing (roll-to-roll) processing allows for flexibility in design for putting electronics/intelligence where conventional silicon is not suitable.

Structure of the paper

The paper is structured around the following framework:



In order to convey a general overview on the subject, the sequence of topics will be the following:

a) Introduction

b) Description of the technology

c) Who is active in the field.

d) Potential fit of this technology within **the electro-mechanical industry.**

e) Conclusions and recommendations.

What is not included in this white paper

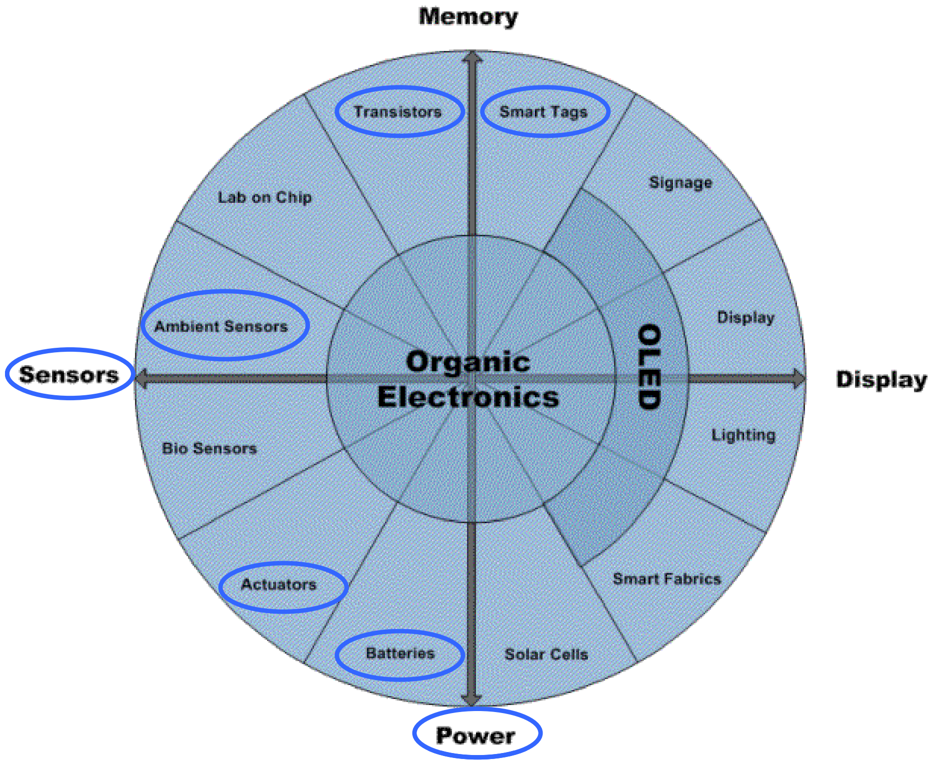
The area of ElectroActive polymers and flexible electronics is very vast and covers a wide variety of applications. Some of them are expected to be massive but are not judged as relevant to the field of expertise and potential areas of expansion of the electro-mechanical industry. This white paper does not, therefore, include the developments in the areas of:

a) Photovoltaic

b) OLED and displays

c) Transparent conductors.

The paper therefore covers the circle topics in the next figure:



This essay does not include the embedding of conventional (silicon) electronics in rubber or in polymers. Several activities have been developed and are actively brought forward to conceived smart/intelligent tires or robotic wheels but they are not based on flexible electronics or electroactive polymer. Their focus is on the integration of small conventional electronics within the tire and the peripheral structure around it. The criterion to be included in this paper is have some highly bendable electronics and not just a flexible interface with a rigid circuit.

1. Introduction

The basis of organic electronics and electroActive polymers is based on the ability of a class of or functional organic molecules to actively transport charge, emit light or absorb light under appropriate conditions. ElectroActive polymers (EAP) are materials that respond mechanically to electrical stimulation. Their electro-mechanical response, exhibiting large strain when stimulated makes them the human-made actuators that most closely emulate natural muscles.

The worldwide market for polymer electronic products has been estimated to be worth up to 15 billion euros by 2015 and the opportunity of new markets could be as high as 125 billion euros by 2025. The rapid development of organic based electronics has revealed the possibility for transforming the electronics market by offering lighter, flexible and more cost-effective alternatives to conventional materials and products. With applications ranging from printed, flexible conductors & novel semiconductors components, actuators, sensors to intelligent labels, large area displays and solar panels, products that were previously unimaginable are beginning to be commercialized.

The potential to print at high throughput and high resolution from formulated inks offers the greatest commercial opportunity, driving solutions-processable material development. Interest and development are especially intense in the fields where cost is a strong market driver. The polymer base of EAP and flexible electronics materials allows many attractive properties and characteristics including low weight, fracture tolerance, pliability. Further, they can be configured into almost any shape and their properties can be tailored to suit a brad range or requirements. For instance, the electromechanical properties of some EAP materials allow them to serve as both actuator and sensors. When they are stimulated to respond with shape or dimensional changes, they can be sued an actuator, while if they exhibit the inverse effect, the can be used as sensors or even power generators.

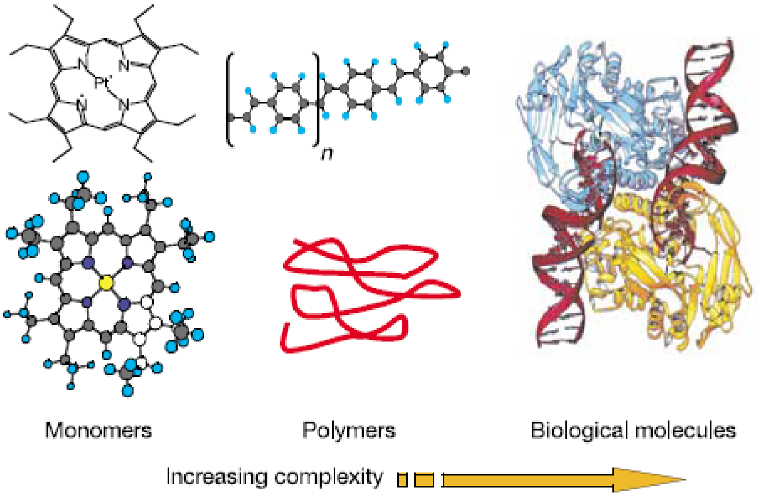


Figure 1: Several types of organic electronics materials

In figure 1, various types of organic electronic materials, are ranged in order of increasing complexity from left (simplest) to right (most complex). Monomeric compounds (left), are single compact molecular units with a well-defined molecular weight that are generally, although not always, deposited in vacuum. Dendrimers are larger variants of small-molecular weight compounds. Next in complexity are polymers (centre), forming chains of repeating monomeric units. The chains are not of a well-defined length, and thus their molecular weight varies over a considerable range. Polymers are generally, although not always, deposited from liquid solution. Finally, the most complex materials are of biological origin (right), consisting of proteins and strands of DNA. Currently, there are no clear demonstrations of the utility of these complex structures for use in electronic applications.

Although the cost of the organic materials used in most thin-film devices is low, in electronics the materials cost rarely determines that of the end product; where fabrication and packaging costs typically dominate. Hence, the successful application of this interesting materials platform will depend on capturing its low-cost potential through the innovative fabrication of devices on inexpensive, large-area substrates. This suggests that conventional semiconductor device fabrication technologies need to be adapted to handle the large-area substrates spanned by organic macroelectronic circuits, and to be compatible with the physical and chemical properties of these fascinating compounds. Also, solids based on organic compounds are typically bonded by weak van der Waals forces that decrease as $1/R^6$, where R is the intermolecular spacing. This is in contrast to inorganic semiconductors that are covalently bonded, whose strength falls off as $1/R^2$. Hence, organic electronic materials are soft and fragile, whereas inorganic semiconductors are hard, brittle, and relatively robust when exposed to adverse environmental agents such as moisture and the corrosive reagents and plasmas commonly used in device fabrication. This has also opened the door to a suite of innovative fabrication methods that are simpler to implement on a large scale than has been thought possible in the world of inorganic semiconductors. Many processes involve direct printing through use of contact with stamps, or alternatively via ink-jets and other solution-based methods.

Flexible electronics and silicon electronics are not exactly similar. As shown in figure 2, printed electronics (one of the dominant process for flexible electronics) have longer switching times and reduced levels of integration but show the

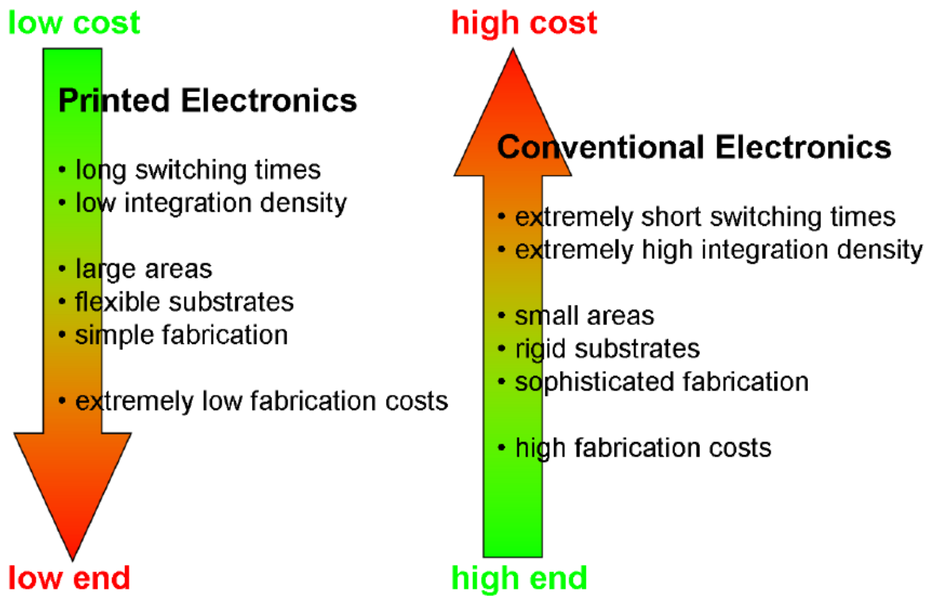


Figure 2: Printed electronics vs. Conventional electronics

possibility of simple fabrication methods for large areas devices and very low manufacturing costs. Many of the developments are aiming at plastic foil, thin metal, textile substrates with very strong focus for robustness/flexibility, body compatibility and low cost. Schematically, the areas of main development are indicated in figure 3. Only those of relevance for the electro-mechanical industry. will be cover in the present white paper. There are different technologies which match application needs. The opportunities will drive these different technologies forward at different speeds, and all technologies will be present for some time. Alignment of effort is required

Polymers that can be activated to change shape or size have been available for many years. The activation mechanisms include chemical, thermal, pneumatic, optical, and magnetic. The convenience and practicality of electrical stimulation, and technology progress led to a growing interest in EAP materials. The largest progress in EAP materials development has been reported in the last fifteen years where materials that can create linear strains that can reach up to 380% have been developed. EAP materials are attractive as actuators, particularly for their resilience, damage tolerance, and ability to induce large actuation strains (stretching, contracting, or bending). The application of these materials as actuators to drive various manipulation, mobility, and robotic devices involves multi-disciplines including materials, chemistry, electromechanics, computers, and electronics. Even though the actuation force of existing EAP materials and their reliability require further improvement, there has already been a series of reported successes in developing EAP-actuated mechanisms.

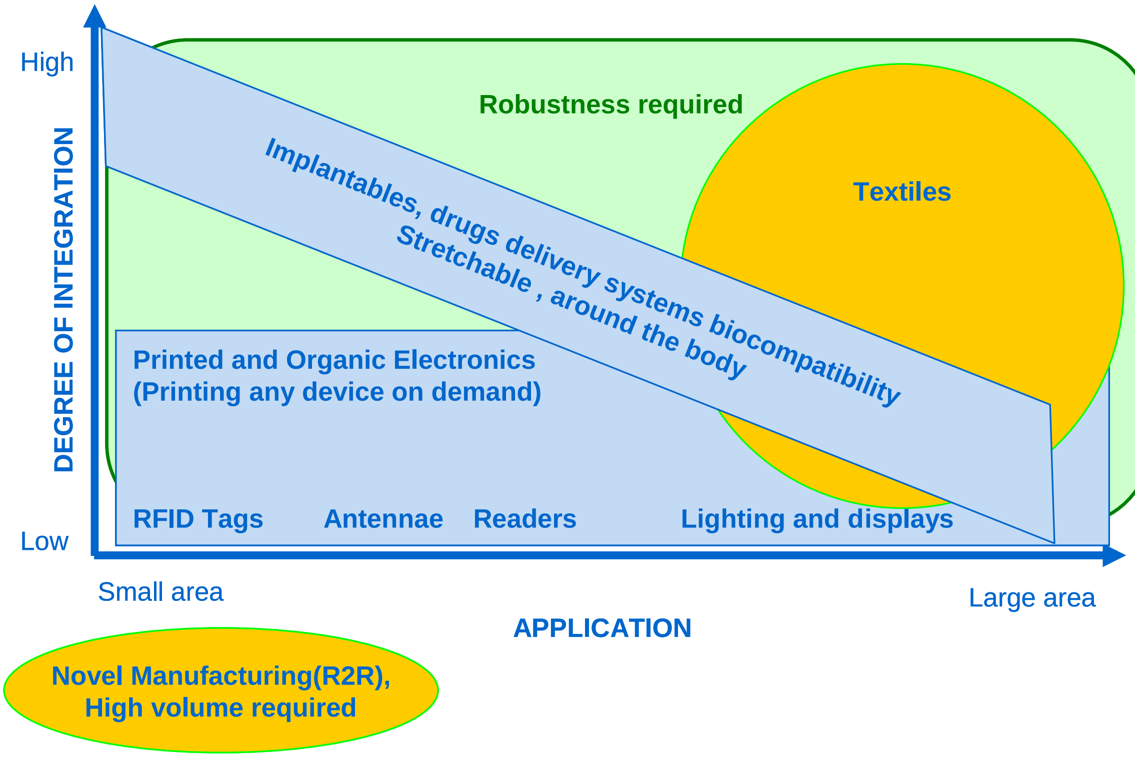


Figure 3: flexible electronics landscape and main focus areas

The processes of synthesizing, fabricating, electroding, shaping and handling are being refined to maximize the EAP materials actuation capability and robustness. Methods of reliably characterizing the response of these materials are required to establish database with documented material properties in order to support design engineers considering use of these materials and towards making EAP as actuators of choice. Various configurations of EAP actuators and sensors need to be studied and modelled to produce an arsenal of effective smart EAP driven system. The development of the infrastructure is a multidisciplinary task involving materials science, chemistry, electro-mechanics, computers, electronics, and others.

2. Description of the technology

2.1. ElectroActive Polymers (EAP)

Polymers are highly attractive for their inherent properties of mechanical flexibility, light weight, and easy processing. Additionally, some polymers exhibit large property changes in response to electrical stimulation, much beyond what is achievable by inorganic materials. This adds significant benefits to their potential applications.

Electroactive Polymers (EAP) is materials that respond mechanically to electrical stimulation. Their electromechanical response, exhibiting large strain when subjected to electrical stimulation, makes them the human-made actuators that most closely emulate natural muscles. There are many polymers that are considered to be EAP, and there are several different mechanisms that deter their response to electrical stimulation.

Impressive advances in improving the actuation strain capability of EAPs are attracting the attention of engineers and scientists from different disciplines. The electromechanical properties of some EAP materials enable them to serve as both actuators and sensors. When they are stimulated to respond with shape or dimensional changes, they can be used as actuators; if they exhibit the inverse effect, they can be used as sensors or even power generators.

The key EAP material types known today are divided into two major groups: field-activated and ionic EAPs.
Field-activated EAPs are driven by the Coulomb interaction (electrostatic force) produced by the electric field created between the coating electrodes in films or by a charge on the local scale. The strain manifests from molecular, microscopic or macroscopic phenomena in response to an applied electric field (see annexed tables). The field may induce a molecular conformation change as the dipoles are aligned with the field.

Examples include piezo-electric strain concomitants with a ferro-electric response during the crystalline phase, and a bulk elastic strain from local field changes at non-uniform material features and trapped spaces charges. Since the actuation does not involve the diffusion of charge species, they respond quite fast ($\leq 10^{-3}$ s). This type of EAP can hold the induced displacement while activated under a DC voltage without consuming electrical energy, making these EAPs highly efficient for robotic (mechatronics) applications. These materials have a high mechanical energy density. However, generating a large deformation requires a high activation field of 100 V/m or more, which may be close to the electric breakdown level. From a basic energy-conservation point of view, the required high activation field is the result of the low dielectric constant in the polymer, which is typically less than 10. Substantially raising the dielectric constant of the activated polymer while maintaining a high electric breakdown strength is a challenge and a worthy research area to further advance field activated EAPs. The performances of these EAPs may also be improved by employing multilayer structures with film thickness of less than a micron, to generate a high field with a low voltage.
In contrast to the field-activated EAP materials, ionic EAPs are materials that involve the drifting or diffusion of ions. They consist of an electrolyte between two electrodes. Examples of ionic EAP materials include ionic polymer-metal composites (IPMC), conductive polymers and gels. Because of the actuation mechanism (ionic motion) and their mechanical properties, carbon nanotube actuators are also classified as ionic EAP materials.

Conductive polymers exhibit volume constriction as water and anions leave an oxidized polymer during reduction. Ionic polymer-metal composites with stationary have some directional volume expansion as hydrated cations move towards one electrode. Gels show volume expansion as water forms at the anode and flows toward the cathode in a cell. Sheets of carbon nanotubes bend as carbon-carbon bond length change and cation surface charges interact with the applied field. One unique advantage is that the activation of the ionic EAP can be done at levels as low as 1-2 V. On the other hand, high current density is required in order to make up for the electrical energy input in actuation. The macroscopic motion of charged species, responsible for the actuation, results in low actuation speed (in the order of seconds). Other disadvantages include their need to maintain wetness (electrolytes) and their low efficiencies (around 1%).
An emerging field in EAP is that of *molecular motors* - organic molecules displaying a large shape under electric excitation. Recent advances in the field of EAP have led to strains of 40-60 % and energy densities (at the molecular level) of around 50 J/cm^3. Having such energy density values makes these motors potentially able to perform significant manipulation tasks at the micron scales.

Despite the enormous progress that has been made in recent years, EAP materials are still far from being considered the actuator material of first choice by engineers and designers. Some of the current limitations of EAP materials include their low durability and performance reproducibility, as well as the lack of established databases and standard products. To reach the required level of maturity, there is a need for establishing scientific and engineering foundations. Improving understanding of the basic principles that drive the various EAP materials types, designing effective computational chemistry models and electromechanical analytical tools, developing comprehensive knowledge of the related material science and enhancing materials processing techniques are required.

Table 1. Summary of the leading Ionic and Field-activated EAP materials type

EAP material	Principle	Reported materials
	Field-activated EAP	
Ferromagnetic polymers	These polymers exhibit spontaneous polarization that can be switched by external electric fields. They can exhibit piezoelectric response when poled and electrostriction in non-polar phase. Recent introduction of defects in PVDF-TiFE copolymer crystalline structure by electron irradiation or copolymerizing with a third bulky monomer dramatically increases the induced strain	- Electron-radiated poly (vinylidene-fluoride trifluoroethylene) - PVDF-TrFE-based terpolymers
Dielectric EAP or electrostatically stricted polymers	Coulomb forces between the electrodes squeeze the material causing it to expand in the plane of the electrodes. When the stillness is low, a thin film can be shown to stretch more than 100%	- Silicone - Polyurethane - Modified copolymer-PVDF-TrFE
Electrostrictive graft elastomores	Electric field causes molecular alignment of the pendant group made of graft crystalline elastomers attached to the backbone	- Modified copolymer-PVDF-TrFE
	Ionic EAP	
Ionic gels	Application of voltage causes movement of hydrogen ions in or out of the get. The effect is a simulation of the chemical analogue of reaction with acid and alkaline	- Poly(vinylalcohol gel with dimethyl sulfoxide - Poly(acrylonitrile) with conductive fibres
Ionomeric polymer-metal composites (IPMC)	The base ionomers provide channels for cations to move in a fixed network of negative ions on interconnected clusters. Mobile cations from the anode are responsible for the bending actuation	Base ionomers: - Nafion® (perfluorosulfonate) DuPont - Flemion® (perfluoro-carboxylate) Asahi Glass (Japan) Cations: - Tetra-n-butylammonium - Li^+ - Na^+ Metal: Pt and gold
Conductive Polymers (CP)	Materials that swell in response to an applied voltage as a result oxidation or reduction, depending on the polarity, causing insertion or de-insertion of (possibly solvated) ions	Polypyrrole, Poly(ethylene dioxithiophene) Ply(p-phenylene vinylene)s, Polyanline and polythiophenes.
Carbon Nanotubes (CNT)	The carbon-carbon bond of nanotubes suspended in an electrolyte changes length as a result of charge injection that affects the ionic charge balance between the CN T and the electrolyte	Single or multiwalled carbon nanotubes.

The electronic polymers (electrostrictive, electrostatic, piezoelectric, and ferroelectric) are driven by electric fields and can be made to hold the induced displacement under activation of a dc voltage, allowing them to be considered for robotic applications. Also, these materials have a greater mechanical energy density and they can be operated in air with no major constraints. However, they require a high activation field (>100 MV/meter) close to the breakdown level. In contrast, ionic EAP materials (gels, polymer-metal composites, conductive polymers, and carbon nanotubes.) are driven by diffusion of ions and they require an electrolyte for the actuation mechanism. Their major advantage is the requirement for drive voltages as low as 1 to 2 volts. However, there is a need to maintain their wetness, and except for conductive polymers and carbon nanotubes it is difficult to sustain dc-induced displacements. The induced displacement of both the electronic and ionic EAP can be geometrically designed to bend, stretch, or contract. Any of the existing EAP materials can be made to bend with a significant curving response, offering actuators with an easy to see reaction and an appealing response. However, bending actuators have relatively limited applications due to the low force or torque that can be induced. Table 2 reports a comparative analysis of the two major families of EAP.

Table 2. Summary of advantages and disadvantages of different EAP materials

EAP type	Advantages	Disadvantages
Field activated (also called electronic EAP)	• Exhibit rapid response (milliseconds) • Can hold strain under dc activation • Induces relatively large actuation forces • Exhibits high mechanical energy density • Can operate for a long time in room conditions	• Requires high voltages (~100 MV/meter). Recent development allowed for (~20 MV/meter) in the Ferroelectric EAP • Independent of the voltage polarity, it produces mostly monopolar actuation due to associated electrostriction effect.
Ionic EAP	• Natural bi-directional actuation that depends on the voltage polarity. • Requires low voltage • Some ionic EAP like conducting polymers have a unique capability of bi-stability	• Requires using an electrolyte • Require encapsulation or protective layer in order to operate in open air conditions • Low electromechanical coupling efficiency • Except for CPs and NTs, ionic EAPs do not hold strain under dc voltage • Slow response (fraction of a second) • Bending EAPs induce a relatively low actuation force • Electrolysis occurs in aqueous systems at >1.23 V

2.2. Flexible electronics

A principle advantage of organic electronics (OE) is that large, flexible and low-cost substrates can be used. Polymer films, such as polyester, are the most widely used today, but paper, cardboard, thin glass and stainless steel are also potential candidates. Special surface treatments or barrier layers can be added if necessary. The material best suited for a specific application depends on the process conditions, surface roughness, thermal expansion and barrier properties.

A generic large area electronic structure is composed of 1) a substrate, 2) backplane electronics, 3) a front plane and 4) encapsulation. To make the substrate flexible, all components must comply with bending to some degree without losing their function. Two basic approaches have been employed to make flexible electronics:

a) Transfer and bonding of completed circuits to a flexible substrate and

b) Fabrication of circuits directly on the flexible substrate.

In the transfer-and-bond approach, the whole structure is fabricated by standard methods on a carrier substrate like a Si wafer or a glass plate. Then it is transferred to a flexible substrate. The transfer-and-bond approach has been extended to the bonding of ribbons of Si and GaAs devices to a stretch elastomer, which up relaxation forms a “wavy” semiconductor than can be stretched and relaxed reversibly. The transfer approaches have the advantage of providing high performance devices on flexible substrates. These processes are sophisticated advances over the original flexible wafer-based solar cell arrays. Their drawbacks are small surface area coverage and high cost. Bonded circuit will likely be added to large area electronic surfaces at low density for high speed communication and computation, lasing and similarly demanding applications.

In many applications, the majority of the surface will have covered with electronics fabricated directly on the substrate. There are many approaches to integrating different materials and flexible substrates that are not fully compatible with existing silicon microfabrication processes. Direct fabrication may require

a) Relying on polycrystalline or amorphous semiconductors because these can be grown on foreign substrates,

b) developing new process techniques

c) Introducing new materials and

d) Sticking a compromise between device performance and the low process temperatures tolerated by polymer foil substrates.

Flexibility can man many different properties to manufacturers and users. As a mechanical characteristic, it is conveniently classified in three categories: 1) bendable or rollable, 2) permanently shaped and 3) elastically stretchable. The tools for the microfabrication haven developed for flat substrates. Therefore, at present, all manufacturing is done on a flat workpiece that is shaped only as late as possible in the process. This approach benefits from the tremendous technology based established by the planar integrated circuit and display industries.

Flexible substrates must meet many requirements:

a) Optical properties: transmissive or bottom-emitting displays need optical clear substrates.

b) Surface roughness: the thinner the device films, the more sensitive their electrical function is to surface roughness. Asperities and roughness over short distance must be avoided, but roughness over long distance is acceptable. As-received metal substrates usually are rough on both scales, while plastic substrates may be rough only over long distances.

c) Chemical properties: the substrate should not release contaminants and should be inert against the process chemicals.

d) Thermal and thermomechanical properties: The working temperature of the substrate, for example the glass transition of a polymer (T_g) of a polymer must be compatible with the maximum fabrication process ($T_{ma}x$). The maximum. Thermal mismatch between the substrate and the device film may could cause the film to break. A rule of thumb is to keep the coefficient of thermal expansion coefficient between 0.1 and 0.3 %.

e) Mechanical properties: a high elastic modulus makes the substrate stiff and a hard surface support the device layer under impact.

f) Electrical and magnetic properties: Conductive and substrates may serve as a common node and as an electromagnetic shield. Electrically insulation substrates minimize coupling capacitance. Magnetic substrates can be used for the temporarily mounting of the substrate during fabrication.

Depending on the physical characteristics required by the application, such as operating temperature, frequency or mechanical strength, various types of organic materials including paper impregnated with phenolic resin, woven or non-woven glass cloth, polyimide or polyestercan be used as base material in flexible electronics. Low cost, ease of manufacture and reparability are also among the parameters affecting the choice of material. Polyimide film (Kapton®) is one of the most commonly substrate-used materials in flexible electronics. It has excellent thermal stability, solvent resistance and adhesion. Kapton® is being used to produce laminates with metal such as copper. The major draw backs of polyimide are its high cost and difficult fabrication steps. Phenolic resins are also used as base material in electronics. They exhibit high thermal and chemical resistivity. Phenolic resins have comparatively low cost and ease of processing. The major disadvantages of phenolic resins are poor resistance to bases and oxidizers, and requirement for fillers during molding. Cyanate ester, epoxy/cyanate ester blends and Teflon® are among other substrate materials used in today’s technology.

In order to understand the electronic properties of polymers, it can be considered that every repeating unit is a separate molecule having molecular orbitals in a certain electronic state. Controllable physical and chemical properties of polymers make them favorable in many areas including electronics. The next section discusses the use of electrically insulating polymeric materials used in flexible electronics. Insulating Polymers for Flexible Electronics Polymers have been used in electronics as resists, encapsulants, insulators and intermediate dielectrics for more than forty years. The high electrical resistivity and good mechanical properties of polymers made them useful as a passive material meaning that these materials do not take any active role in the functioning device.

Radiation-sensitive polymers play an important role in the semiconductor industry. These polymers undergo molecular rearrangement when irradiated and either degrade or crosslink following exposure. Such radiation-sensitive polymers can be used to stencil and transfer a two-dimensional circuit pattern to underlying layers. Using this idea, silicon substrates or printed circuit boards can be patterned to fabricate advanced logic and memory chips

Encapsulation of high-power and large integrated circuit devices is another very important application area of polymers in electronics. The basic purpose of the encapsulation of integrated circuits is to enhance the life time of the device by protecting it from harsh environmental conditions such as moisture, radiation and mechanical impact. Every year the dimensions of semiconductor circuit devices are decreasing and consequently the number of the components per chip is increasing enormously. The number of components per chip has been increased over a million times during the last forty years and it is continuing to increase with new advances in molecular electronics. This tremendous increase results in faster operation speed, higher power consumption and therefore more heat dissipation. Hence, encapsulation technology has become more challenging. Encapsulation polymers should have high electrical resistance, good adhesion, resistance to thermal and mechanical shock as well as resistance to moisture and solvents. Both inorganic and organic materials can be used as encapsulants. Silicon dioxide, silicon nitride, diamond and silicon carbide are among the inorganic encapsulants. Organic encapsulants can be divided into three groups;1) thermosetting polymers, 2) thermoplastics and 3) elastomers. Silicone compounds are one of the thermoset polymers most commonly used as encapsulants.

2.3. Electric contacts and electrically conductive polymers.

Fretting is known to be a major cause of contact deterioration and failure; commonly exhibited as the contact resistance increases from a few milliohms, in the case of a new metallic contacts, to in excess of several ohms for exposed contacts. Fretting is generated by external influences on the electrical contact interface, such as vibration and temperature changes, and as such applies to both power and electronic connections. The fretting process leads to complex interactions of physical processes. Two technologies are discussed; firstly, extrinsically conducting polymer (ECP), where highly conductive interconnects are formed using metallized particles embedded within a high temperature polymer compound, and secondly; intrinsically conducting polymers (ICPs). The use of highly conductive interconnects where metallised particles are embedded within a high temperature polymer compound, better known as extrinsically conducting polymer (ECP) proves to be an avenue of interest for automotive research and development due to their low-cost fabrication and compactness.

However, concerns regarding the abrasion (or fretting) at the surface interfaces of the doped metallic particles within the ECPs would vary the resistance of the material and effectively affect the overall system over long periods of operation, especially when operating in an environment where fretting is likely to take place. In order to satisfy such requirements in the connector design, the employment of intrinsically conducting polymers (ICPs) are explored so as to deal with the abrasiveness experienced within ECPs. Being homogeneous and free from metallic additives, ICPs retain the ability to conduct naturally and the influence of external forces would most likely be minimized with adequate levels of polymeric elasticity. ICP has been attracting a large amount of attention and interest due to its ease of synthesis, stability and environmental factors. A key advantage of this technology is the potential ability for the polymer interface to reduce the fretting potential.

2.4. Processing

One of the most important advantages of conducting polymers is the variety of device fabrication methods that may be used to form them into useful devices. It is possible to use traditional vacuum and lithography methods to fabricate organic electronic devices. However, traditional methods include expensive production steps such as chemical or physical vapor deposition and plasma etching, which generally require high temperature and high vacuum. Inkjet printing techniques, have been gaining attention recently because of their unique features, such as simplicity of fabrication, compatibility with different substrates, feasibility of non-contact and no-mask patterning, low temperature processing and low-cost. Generally, inkjet printers can be divided into two groups; continuous and drop-on-demand. In continuous jet printers the ink is pumped through a nozzle and the formed liquid jet is deflected by electrostatic plates to the paper or to a reservoir for recirculation.
Today most inkjet printers are based on the drop formation process, which is called drop on- demand (DOD). The drop-on-demand method provides smaller drops and higher placement accuracy compared to those possible using the continuous inkjet printers. In this method the pulse that creates ink drop can be generated either thermally or piezoelectrically.

Inkjet printing is one of the most frequently used techniques to deposit and pattern solution processable insulators, semiconductors and metals. The most crucial parameter of the inkjet printing process is the ink. Ink chemistry and formulation not only affects the resolution of the inkjetted patterns but also affects the drop ejection characteristics. Generally, the viscosity of the ink should be lower than 20 cP. If the viscosity of the ink is too high, ink droplets are not ejected through the nozzle due to high viscously dissipated kinetic energy. Because of this, polymer inks should be sufficiently dilute, consisting of about 1-2 weight percent solids. Surface tension is another important parameter. Typically, it should be about 30 mN/m. If the surface tension is too low, ink will not be stable on the printing head surface. On the other hand, if it is too high, ink cannot be jetted properly. There is an interest in nanoparticle inks for inkjet printing technology, especially nanoparticle magnetic and metallic inks. Printable metallic nanoparticle inks are favourable due to the need for low cost interconnection and electrodes for electronic devices. Inkjet printed silver, copper, diamond, and gold nanoparticles have been reported.

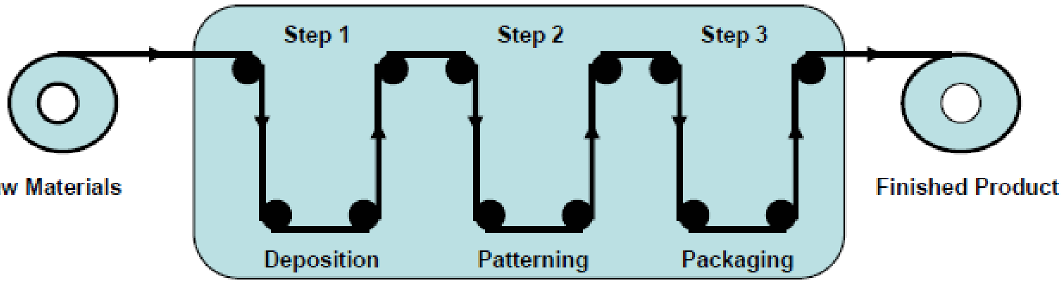
Self assembly is a process of a self-organization of molecules upon dipping a substrate into a solution of molecules. After removing the substrate from the solution and rinsing, a monolayer of molecules will stay on the surface as a result of minimization of the energy
in a stable state. By self assembly both two and three-dimensional arrays and networks of molecules, nanowires or nanotubes can be obtained Self assembled monolayers can be held together by electrostatic forces. This type of self assembly is called electrostatic self assembly (ESA) and relies on the formation of alternating simple polyelectrolyte monolayers

Micro contact printing (μCP), which is a flexible, non-photolithographic method, was introduced by Whitesides and co-workers. A structured, elastomeric stamp is used in this method to transfer an “ink” to the surface of a substrate by contact. After transferring the stamp’s pattern onto the substrate, different self assembled monolayers can be formed on the stamped or unstamped regions.

The three essential steps of R2R manufacturing are deposition, patterning and packaging. Figure 4A shows schematically the process while 4b shows a prototype machines at VTT in Finland. 4c and 4d illustrate the nature of the products that can be obtained from R2R processes.

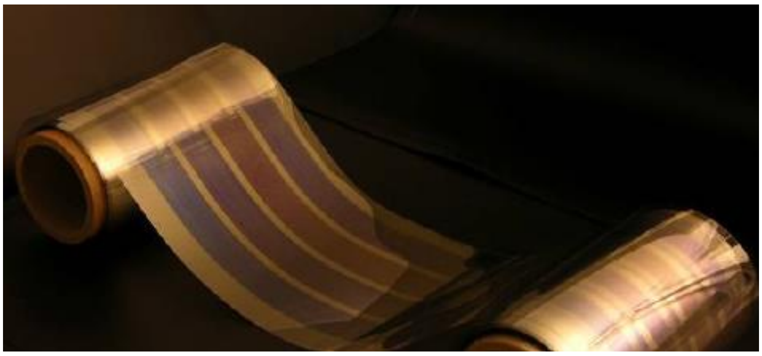
Plastic engineered films are very appealing substrate materials for flexible electronics due to their low cost and toughness, of which Dupont’s Teonex® brand of polyethylene naphthalate (PEN), is a leading candidate. PEN shows a remarkably smooth, defect-free surface quality after pre-treatment with an adhesion layer, but has a Young’s Modulus three times higher than amorphous plastic films due to its semicrystalline, biaxially oriented nature. This stiffness may hinder PEN’s placement into an R2R processing format. Substrates for flexible electronics must be able to withstand temperature cycles required for the deposition of barrier and indium tin oxide coatings. During these heating cycles that can reach temperatures over 250 °C.

A)



B)

C)



D)

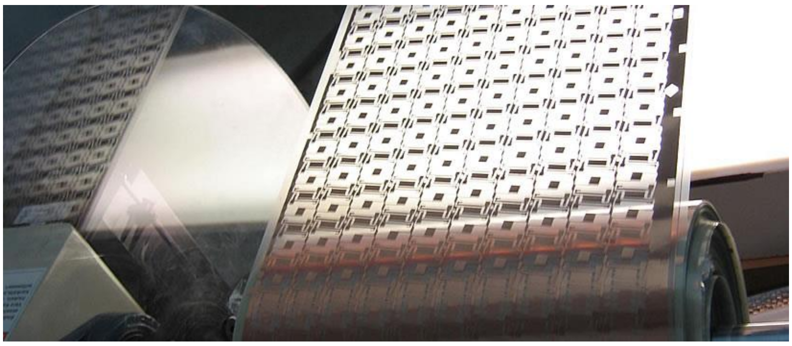


Figure 4: Roll-to-Roll process. A) schematic diagram, B) prototype machine, C&D) printed plastic sheets with circuits.

The goal of R2R fabrication of flexible electronics is stimulating innovations in equipment and process design, process recipes and system integration. Although the field of flexible electronics has made significant advances in technical and process capabilities in recent years, much more work needs to be done before the field is ready to be scaled up for R2R process technology. It is not a given that roll-to-roll processing will ever come to full fruition. If the technology matures within the next decade, new substrate materials and cheap, innovative patterning techniques must be combined with creative product development teams to come up with compelling flexible electronics applications. The combination of novel consumer products and the ability to manufacture them using an ultra low-cost production capability such as roll to roll processing will entice an adventurous company to take the risk and invest in a full scale flexible electronics factory.

Table 3: Potential Materials for Roll-to-Roll processes

Candidate materials for Roll-to-Roll (R2R) processing in flexible electronics			
Property	Stainless steel	Plastics (PEN, PI)	Glass
Thickness (μm)	100	100	100
Density (g/m^2)	800	120	220
Safe bending radius (cm)	4	4	40
R2R processable?	Yes	Likely	Unlikely
Visually transparent	No	Some	Yes
Max process temperature (°C)	1000	180-300	600
Coefficient of thermal expansion (ppm/ °C)	10	16	5
Elastic modulus	200	5	70
Permeable O_2, H_2O	No	Yes	No
Pre-bake required	No	Yes	Maybe
Planarization required	Yes	Maybe	No
Electrical conductivity	High	None	None

2.5. Batteries

There is a $50B battery market worldwide in 2005. Within that market is a place for evolution of next generation devices; of which include thin film Lithium and Lithium Ion batteries. These technologies depend on the further evolution of nanotechnology. There's a quiet revolution taking place in the rechargeable battery industry. It is occurring at the confluence of modern nano-technology and 140-year-old printing technology. The result is a small, high-powered, light-weight rechargeable lithium-based battery with unprecedented flexibility.

Thin film batteries (TFB) are positioned to become the next generation of lithium batteries for portable electronic applications. Research has showed the chemistry of turning the hazardous liquid Lithium ion into a solid, creating the ability to use lithium ion as an ink or particle that in not hazardous.

Results obtained in the laboratory are being translated into commercial products. Thin film solid state batteries are because the lithium ion that is implemented as a liquid electrolyte in traditional batteries is replaced with a solid form of the chemical. Thin film solid-state batteries are constructed by depositing the components of the battery as thin films. This conversion of chemical energy to electrical energy is potentially 100% efficient, whereas the conversion of chemical energy to mechanical energy via a thermal conversion (e.g., internal combustion of gasoline in cars) always results in heat transfer losses limiting the intrinsic efficiency.

The effective surface area of an electrode can be increased without increasing its physical size by making its surface porous and using materials with very fine particle size. This can increase the effective surface area of the electrodes by 1000 to 100,000 times enabling higher current rates to be achieved. In this manner, nanotechnology holds enormous promise for this market. Nanoparticles can be developed that are used to make a surface very porous and increase the effective surface area of the electrodes.

High capacity cells require large volumes of electrolyte that must be accommodated between the electrodes. This has a double effect in reducing the cell power handling capability. The electrodes must be smaller and further apart to make space for the extra electrolyte and hence they can carry less current. Increased volume of the electrolyte means it takes longer for the chemical actions associated with charging and discharging to propagate completely through the electrolyte to complete the chemical conversion process.

Lithium ion polymer batteries, or more commonly lithium polymer batteries (Abbreviated Li-Poly or LiPo)are rechargeable batteries which have technologically evolved from lithium ion batteries. Ultimately, the lithium salt electrolyte is not held in an organic solvent like in the proven lithium ion design, but in a solid polymer composite such as polyacrylonitrile. There are many advantages of this design over the classic lithium ion design, including that the solid polymer electrolyte is not flammable (unlike the organic solvent that the Li-Ion cell uses), thus these batteries are less hazardous if mistreated.

Thin-film batteries typically use solid electrolytes instead of liquid or gel, and their electrodes are typically made of lithium combined with metals such as nickel, cobalt, or manganese. The salt-and-paper battery is an ideal replacement for the lithium ones used in many low-power portable devices, such as wireless sensors, smart cards, medical implants, and RFID tags. For these applications, the thinner and smaller thebattery, the better. Thin-film batteries have other attractive features. They have a long shelf life, retaining their charge after being stored for many years, and they can be charged and discharged tens of thousands of times enabling wireless sensors that can last for decades with an appropriate energy harvester attached.

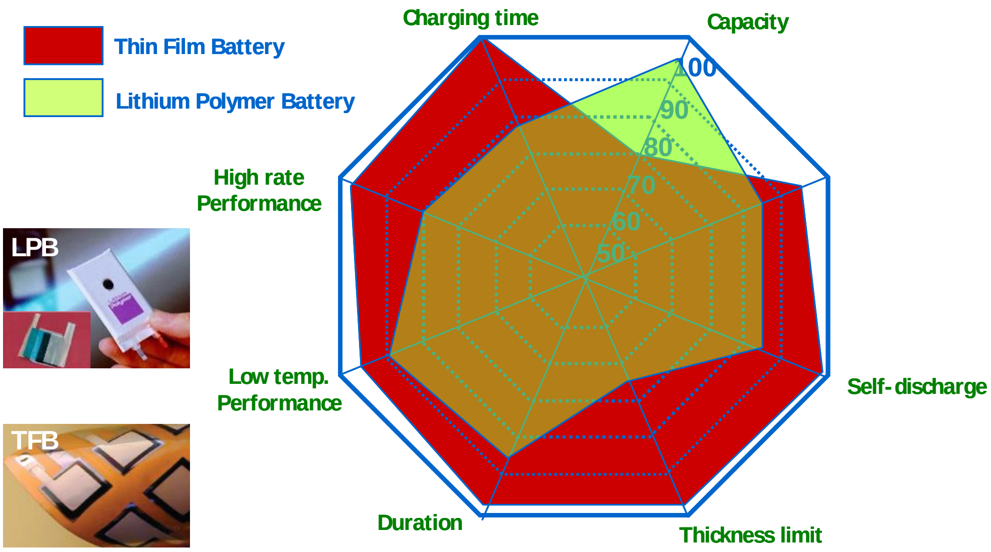


Figure 5: Lithium Polymer batteries vs. Lithium Film batteries

2.6. Sensor

Chemical sensors transform the concentrations of analytes to other detectable physical signals, such as currents, absorbance, mass or acoustic variables. After exposing to the vapor of an analyte, the active sensing material of the sensor interacted with the analyte, which causes the physical property changes of the sensing material. The interactions between the analytes and sensing materials are multiform, according to different analytes and different active materials.

Conducting polymers, such as polypyrrole (PPy), polyaniline (Pani), polythiophene (PTh) and their derivatives, have been used as the active layers of gas sensors since early 1980s . In comparison with most of the commercially available sensors, based usually on metal oxides and operated at high temperatures, the sensors made of conducting polymers have many improved characteristics. They have high sensitivities and short response time; especially, these feathers are ensured at room temperature. Conducting polymers are easy to be synthesized through chemical or electrochemical processes, and their molecular chain structure can be modified conveniently by copolymerization or structural derivations. Furthermore, conducting polymers have good mechanical properties, which allow a facile fabrication of sensors. As a result, more and more attentions have been paid to the sensors fabricated from conducting polymers.

Active layer is the heart of a sensor. Various techniques have been developed to prepare conducting polymer films, in order to adapt to different sensing materials and different types of sensor configurations. Thus, herein we first discuss how to deposit conducting polymer films:

a) Electrochemical deposition
b) Dip-coating.
c) Spin-coating.
d) Layer-by-layer (LBL) self-assembly technique.
e) Thermal evaporation.
f) Vapor deposition polymerization
g) Drop-coating.

Chemiresistors are the most common type of sensors. They can be fabricated through a cheap and convenient process. A chemiresistor is a resistor, whose electric resistance is sensitive to the chemical environment. Chemiresistor consists of one or several pairs of electrodes and a layer of conducting polymer in contacting with the electrodes The electrical resistance change of the sensing material is measured as the output, so a simple ohmmeter is enough to collect the data

The sensitivity of a sensor also strongly depends on the temperature and the ambient humidity. Like other semiconductors, the conductance of conducting polymers increases with the increase of temperature. For a chemiresistors, the initial conductance of conducting polymer is changed as the temperature alters. Water vapor itself is an important analyte, and many sensors are sensitive to humidity. Thus, the signal of other gas in humid atmosphere is a corporate response of the analyte and water. Sometimes change of humidity can produce a similar response as analyte does, which may confuse the results. Generally, competitive adsorption between water and the analyte molecules occurs. Pressure and current are also to be taken into consideration: when pressure changes, a phase transition will occur in PPy, causing alternation of conductivity. When designing a chemiresistor, the influence of current also should not be neglected. Stronger current flow through conducting polymer will produce heat, which can affect the response as described above

2.7. Smart materials combining EAP and flexible electronics.

Electroactive or intrinsically conducting polymers[1] such as polyaniline, polythiophene, or polypyrrole that combine the electrical conductivity of a metal with the mechanical flexibility and processing properties of a polymer, hold great promise as smart materials for flexible plastic and wearable electronics.[2] Unfortunately, degradation issues resulting from their low environmental, thermal, and electronic stability, as well as processing problems, affect their reliability and long-term operational functionality.

To address these issues and improve their overall properties, novel nanoscale concepts aimed at adding functionality at the molecular level have generated significant interest. In this context, combining electroactive polymers with carbon

nanotubes (CNTs) represents an attractive solution. These materials consist of tiny graphene cylinders of nanometer diameter and micrometer length with unique structural, mechanical, thermal, electronic and optical properties.[3] However, simple mixing procedures usually fail to yield homogeneous and stable CNT dispersions, thus hindering effective interactions as well as further material processing.
To overcome these problems, we used an in-situ approach in which the polymerization of the electroactive polymer was carried out in the presence of CNTs (see figure 4)

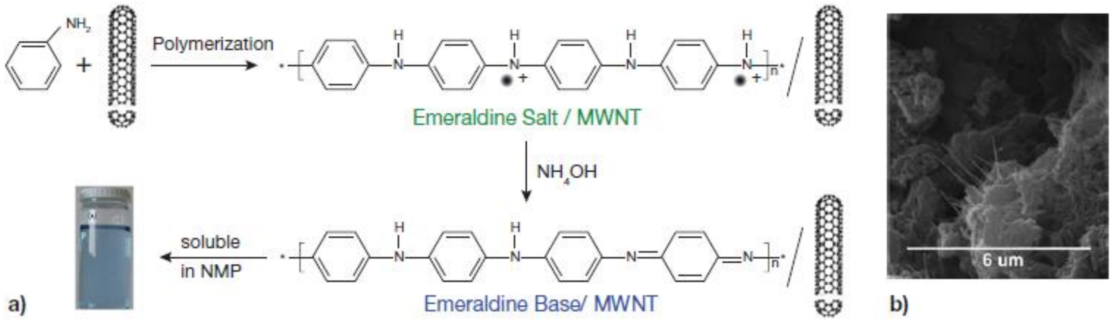


Figure 6: In-situ polymerization of an EAP with multiwall carbon nano tubes (MWCT).
a) fully soluble and b) SEM image of the solid powder.

In-situ polymerization approach allows to obtain highly favourable interactions between the electroactive polymer chains and the CNTs, resulting in a highly functional and completely soluble composite. The material shows enhanced conductivity, as well as improved thermal and deprotonation stability. It is also luminescent, optically active and can be processed from solutions into coatings, films and fibres. Carbon nanotubes combined with intrinsically conducting polymers may contribute to further progress in nanoelectronics and to the development of improved electronic and optoelectronic devices based on the formation of a highly functional and completely soluble polyaniline-multi-wall carbon nanotube composite.

3. Who is active in the field?

Very strong and very wide industry and academia support activities are backing the development of both EAP and OE (and their combinations). From the wearable electronics, medical devices, smart card, & tags, sensing, displaying to end user integrated development, the areas has attracted very wide and enthusiastic development activities across the a very broad industry spectrum. All published roadmaps about the development of EAP and OE agree on the key market of reference that they are approaching:

a) Food (Nestle, Kraft, Sara Lee, Unilever, Kellogg): Flexible sensors and displays
b) Medical equipment (GE, Philips, Solvay, Pfizer, Johnson & Johnson): Flexible lab-on-chip, monitoring devices, sensors.
c) Supply chain RFID: Walmart, Tesco, London transport, Red Cross): Tags, sensors, displays
d) Military devices (Lockheed Martin, US armed forces, Thermo Fischer): Energy scavenging, foldable solar cells, displays, batteries, memories.
e) Consumer electronics (Nokia, Samsung, Apple, Sony): Flexible display, battery, antenna, sensors.

Table 3: Some players in the field of EAP and OE

Non-exhaustive list of players (in fields of close to THE ELECTRO-MECHANICAL INDUSTRY.)				
Class	Name	EAP	OE	Remarks
Private Companies	VTT (Finland)	✔	✔	R2R processes
	IBM (US)	✔	✔	Polymer semiconductors
	E-ink (US)		✔	Electronic paper, Tags
	HP (US)		✔	RFID tags, displays
	NEC (Japan)	✔	✔	Organic radical battery
	Power paper (Israel)		✔	Alcaline paper batteries
	Voltaflex (USA)		✔	Lithium polymer batteries
	Dupont (US)	✔	✔	Specific polymers
	Philips (NL)	✔	✔	Actuators and medical devices. Lighting.
	Hitachi /Cambridge		✔	Thin film transistors physics
	Xerox	✔	✔	
	Santa Fe Science	✔		Polymer MEMS
	BASF	✔	✔	Biomedical sensors and actuators
	GE	✔	✔	Substrates and thin films
	Sarnoff (US)		✔	Flexible displays and circuits
	Konarka (Germany)	✔	✔	Solar cells
	MERK (Germany		✔	Printed electronics
	OCE” (NL)		✔	Printed electronics
	Freudenberg (Germany)	✔	✔	Magnetic polymers within printed sensors.
Universities, Research bodies, Program consortia	Tsinghua (China)	✔	✔	Gas sensors on conducting polymers
	Ecole Polytechnique Montreal (Canada)		✔	RFID business model integration and optimization. (Value chain integration)
	Oak Ridge (US)	✔	✔	Thin film batteries.
	IMEC (Belgium)	✔	✔	Foldable chips, encapsulation
	Holst (NL)	✔	✔	Flexible electronics, R2R, sensors.
	DARPA (US)	✔	✔	future soldier devices
	Cornell (US)	✔	✔	Manufacturing methods for EAP and OE.
	Princeton (US)	✔	✔	Nanopolymers, nanotransfer printing
	Harvard (US)		✔	Microprinting
	Imperial College (UK)	✔	✔	Field effect devices and transistors
	California (SB) (US)		✔	Organic photoelectronics
	Batelle (US)		✔	Encapsulation of OE devices.
	Standford (US)	✔	✔	Piezoelectric organic films
	Cambridge (UK)		✔	Thin film transistors
	Weisman Institute (Israel)	✔	✔	Carbon nanotubes/fullerenes composites
	Hebrew Univeristy (Israel)	✔		EAP testing, robotic arm, EAP driven actuators.
	University of texas	✔		Nano-tech for EAP
	Wollongong (Aust))	✔	✔	Smart materials (EAP+CNT)
	Aachen (Germany)	✔	✔	Micro nano plastic processing
	PARC (US)	✔	✔	Organic electronics and CNT
	Stella consortium (Freudenberg lead)	✔	✔	Large stretchable polymer applications project under European finance
	CEA (France)	✔	✔	Micro-batteries management
	Fraaunhofer (Ger)	✔	✔	Stretchable electronics.
	JPL & Cal-Tech (US)	✔	✔	EAP actuators, robotics

They key focus on the development of EAP and OE is concentrated on solving manufacturing processing to lead to reliable and cheap products in this field. The main market drivers close to the electro-mechanical industry. interest are:

a) Flexible user interfaces: Printed sensor & displays. Advanced paper based Graphic units for small computers, flexible displays.
b) Flexible RFID for internal asset tracking (up to the item level RFID tagging): Higher capacity printed memories, & batteries.
c) Smart packaging integrated with printed displays, sensors antennas to sense quality for tracking along the supply chain.

Not mentioned above but clearly dominant trends are those related to wearable (and washable textile) electronics, implantable electronics (including drug delivery), flexible photovoltaics and light emitting on extended surfaces based on organic LED (OLED).

The main technology drivers could be summarized as:
- Strong industry backing
- Enablers of new application and markets
- High-volume manufacturing and low-cost potential
- Ease of device integration
- Flexibility / stretchability and light weight

The main technology challenges are:
- Manufacturing
- Lifetime issues of organic materials
- Design challenges. Lacking of established knowledge base
- Better encapsulation methods
- Standardized testing.

4. Potential fit of these technologies within Electro-Mechanical Industty

Among flexible electronics applications, the printed RFID tag is more mature than the others. The Radio Frequency Identification (RFID) technique is supported by Wal-Mart and is becoming one of the most popular wireless communication techniques in the world.

Radio frequency identification (RFID) is a method of remotely storing and retrieving data using devices called RFID tags. These tags are small objects, attached into a product, that contain antennae which enable them to receive and respond to radio-frequency queries from an RFID transceiver. Thus, tags can be read from a distance, not requiring direct line of sight like barcodes. RFID tags are divided into two subgroups: passive and active. Passive tags simply use the electromagnetic waves received during the communication to run its process of sending information back to the reader. Active tags don't rely on the signal for power; instead a battery runs the chip's circuitry. Active tags are therefore much larger, more expensive, but able to transmit from further distances. Active tags can get as small as the size of a coin, cost around $1.00, and transmit up to 100 meters, while passive tags can be as small as 0.4 mm x 0.4 mm, cost $0.40, and transmit from 10 mm to 5 meters. Experts estimate that in order for the technology to be worthwhile, passive tags must cost around $0.10. Passive tagging is the more feasible of the two due to its cheaper price and longer lifetime.

Cost isn't the only thing preventing mass acceptance of RFID, however. Standards haven't been fully implemented to govern the use of RFID. Radio frequency ranges have been set up, but the U.S. often operates on a range different from the rest of the world. The ranges are: low frequency tags (between 125 to 134 kilohertz), high frequency tags (13.56 megahertz), ultra-high frequency tags (868 to 956 megahertz), and microwave tags (2.45 gigahertz). Table 4 shows various kinds of typical RFID systems. In general, RFID systems can be classified into three different types by operating methods which are passive, semi-active and active system. There are different operation frequency and standards in different countries. Of all of these standards, the passive 13.56MHz RFID system has been well developed and adopted in worldwide industry

If Company A puts an RFID tag on a product, but it can't be read by Company B unless they both use the same RFID system from the same vendor operating on the same frequency. Some security concerns about RFID have been raised: what would happen if anyone could take a reader to a storage facility and read the tags if they have it on the right frequency? Competitors could easily track what's leaving the shelves at the facility and adjust their own prices and products in order to compete.

Table 4: RFID main features.

	RFID features			
	Near-field RFID		Far-field RFID	
Frequency	30-400 kHz 125-134 kHz	3-30 MHz 13.56 MHz	433 MHz 865-965 MHz	2.45 GHz 5.8 GHz
Reading distance	Short	Higher	Long	Long
Data Rate	Very Low	Low	Higher	Highest
Working mechanism	Inductive coupling	Inductive coupling	Electromagnetic radiation	Electromagnetic radiation
Applications	Animal ID, car access control	-Smart labels, -Contact less cards -Item level tracking	-Logistic tracking -Supply chain	-Moving vehicle toll, -Asset tracking

I can foresee there being a problem with reading tags with an external reader due to the standardization of RFID technology. Steps will have to be taken to counter such problems, and a potential solution is to use a form of encryption. If the tags send their messages in an encrypted format, only the authorized reader will be able to decipher the signal.

Current trends indicate that the RFID market will grow fast in the next 10 years. With 600 million tags being sold in 2007 alone, the value of the market, including hardware, systems and services, is expected to increase by a factor of ten between 2008 and 2018. The number of tags delivered in 2018 will be over 450 times the number delivered in 2008!

Business applications using RFID such as transport and logistics, access control, real time location, supply chain management, manufacturing and processing, agriculture, medicine and pharmaceuticals, are expected to grow strongly

Wireless sensor nodes have come to be an emerging area of study for many groups around the world. The characteristics of networked sensor systems determine its design. These characteristics include size, low power consumption, concurrent operation, software and robustness. The nodes (also called motes since the early work at Berkeley on smartDust) normally have a small battery as a power source and needs to preserve as much power as possible to function as long as it can. As the motes do not have a large amount of memory on them, information must be moved from mote to mote quickly and efficiently so as to use as less power as possible and relay information gathered before more information is found. If one node fails, the network will automatically reconfigure itself. All communications is based on a node-to-node, short range flow. To communicate, the motes use wireless transmission through radio and ad-hoc routing schemes which are necessary as when motes are deployed, there is no organized connectivity before deployment.

Reconfigurable smart sensor nodes enable sensor devices to be self-aware, self-reconfigurable and autonomous. The main benefits of these features are:
a) Support local and system surveillance applications using reconfigurable sensor network nodes that are capable of forming impromptu network assembling themselves without central administration
b) Provide capabilities for sensor networks to adapt dynamically to device failure and degradation and changes in task and network requirements
c) Integrate various application-specific network and system services provided by mixed types of sensor nodes and embedded engineering applications.
Organic electronics provides flexibility to the development and to the deployment of local conformal sensors as well as by providing small thin and cheap batteries to support the deployment of such a wireless self routing sensor networks.
Even if the current developments in the roll-to-roll process technologies are not aiming specifically at any application close to the fields of activity of the electro-mechanical industry. (e.g. seals), the developments are aiming at higher

temperature resistance for the devices making them more and more compatible with vulcanization process or other curing processes.

5. Conclusions and recommendations

Polymer electronics is an emerging technology that focuses on the development of electronic devices incorporating electrically conductive and semiconductive organic materials. It offers the prospect of an advanced electronics platforms using new materials, processes and electronic devices. Polymer conductors and semiconductors open up prospects for microelectronic systems that go beyond the scope of conventional electronics based on silicon as the semiconductor.

The main advantage of polymer electronics compared to with conventional electronics is the simplicity with which the polymer electronic devices can be produced. While conventional electronics demands high-class clean rooms as well as complex vacuum and high temperature processes, the production of processes in polymer electronics are significantly simpler. There are many different ways of producing polymer electronics, including vacuum processes, but the most economical is printing.

On the application side, three developments (close to the electro-mechanical industry fields of application) will be cited: RFID, Sensors and Smart objects. RFID tags based on polymer electronics enable RFID to be used in high-volume, cost-sensitive areas, especially in consumer products. Initial goals of these tags are electronic brand protection, anti-counterfeiting, logistics and automation

Conductive organic materials are often sensitive to factors such as temperature, humidity and pressure but they can also be made sensitive to specific chemicals and parameters. This makes it possible to create large area tin thin and flexible sensors. In a temperature sensor, a printed resistor depends on the temperature and the change in conductivity can be measured by simple electronic means.

Polymer electronics is a new technology platform which will open up new applications where there is a demand for thing, flexible, light weight and low-cost electronics, and where the functionalities of the electronic devices can be limited. It will not replace conventional electronics. Polymer electronics is still a young technology that is not yet fully established on the market. The polymer electronics is based on conductive and semi conductive organic materials. These materials can be of many different classes, including organic molecules and polymers, nanomaterials organic and inorganic (like carbon nanotubes for example).

The materials and processes used in polymer electronics enable different electronic devices to be combined in a way that was not possible with conventional electronics. Devices such as a solar cell or a battery, a logic circuit, a sensor, a memory and a display can be integrated on one flexible substrate in a single production process. Such combinations are just starting to be realized today.

The best way of obtaining the best functionality from OE and EAP is to start thinking at the applications from the unique set of properties (and limitations) that they show. Their potential for growth will make them a reality at affordable conditions that will open engineering possibilities not yet known. The forcing of embedding polymer electronics for tribological applications may not yield the life performance that may be expected. Thinking outside of the box on the comprehensive integration of these new materials is a fundamental requirement to find original ways to capitalize on their business/technology opportunity. The field should be monitored regularly and efforts/partnerships should be aimed at integrating (not developing) them into systems with increased added value. The RFID technology is mature enough to pursue its deployment in the electro-mechanical industry. and could add a new dimension to our logistic competences. It is recommended that a study is carried out focalizing on the business model changes associated with the massive integration of RFID both by us and by end users.