



Design and Development of a new kind of "smart" electro conductive snow melting membrane for lightweight structures

A Master's Thesis submitted for the degree of "Master of Engineering"

Supervised by Dr.-Ing.habil. Rainer Blum

> Slaveyko Slaveykov 1028528

Dimitrovgrad City, Bulgaria 13.09.2013



Affidavit

I, Slaveyko Slaveykov, hereby declare

- that I am the sole author of the present Master's Thesis, "Design and Development of a new kind of "smart" electro conductive snow melting membrane for lightweight structures" 78 pages, bound, and that I have not used any source or tool other than those referenced or any other illicit aid or tool, and
- 2. that I have not prior to this date submitted this Master's Thesis as an examination paper in any form in Austria or abroad.

Vienna, 13.09.2013

Signature

Design and Development of a new kind of "smart" electro conductive snow melting membrane for lightweight structures

COPYRIGHT

Attention is drawn to the fact that the copyright of this thesis rests with the author. This copy of the thesis has been supplied on condition that anyone who consults it is understood to recognize that its copyright rests with the author.

The thesis may be made available within the University Library for the purpose of consultation.

Acknowledgement

I would like to express my thanks to Dr.-Ing.habil. Rainer Blum for his support knowledge and experience. I would also like to thank for the support of Robert Wehdorn-Roithmayr and Dr. Jamshid Avloni.

Table of contents

Abstract		6
Chapter 1 - Ge	eneral Introduction	7
1.1	Motivation	8
Chapter 2 - Li	terature Survey on Conductive Polymers	11
2.1	Conductive Polymers	12
Chapter 3 - Cl	assification of Smart Materials	18
3.1	Passive Smart Textiles	20
3.2	Active Smart Textiles	21
3.3	Ultra Smart Textiles	25
Chapter 4 - Re	esearch Approach	27
4.1	Definition of the research problem	28
4.2	Polymer fibber conductive treatments	30
4.3	Conductive polymers	31
4.4	Synthesis of Polypyrrole	32
4.5	Conductive polymer based coating	34
4.6	Methods of deposition	35
4.7	Conductive polymer properties	39
4.8	Conductive Textile Resistive Heaters	41
4.9	Commercial cond. textile and cond. polymer coating	44
4.10	Resistive electric heating and Electric conductivity	46
Chapter 5 – E	xperimental	58
5.1	Conductive polymer fabric properties	59
5.2	Conductive polymer fabric sample preparation	61
5.3	Experimental stand, materials and equipment used	61
5.4	Experimental data	61
5.5	Experimental data discussion	62
5.6Further worksChapter 6 – Conclusion		72 73

Bibliography

75

Abstract

An application of Smart Polymers and nanotechnologies in membrane structure materials was observed. The objective of research is to explore the opportunities provided by emerged technology of Smart Polymers. The particular object of investigation is conductive polymers and a feasibility study their applications in membrane structures materials design and fabrication. The possibility of creating a new kind of electro conductive fabrics and their performance are explored experimentally. Theory and applications of conductive polymers are surveyed extensively in help of future works on conductive fabrics. The case study application is electrical heating of high conductive fabric and the use that heating for deicing and snowmelt. Since the conductive/resistive material is a part of structural fabric a sustain efficiency improvement is expected. The basic theory of electric heating is provided for understand the principle of operation and limitations of fabric embedded eclectic heaters. The problems of electrically heated deicing and snow melting systems are observed in perspective of its application in tensile structures, air-supported domes and other lightweight structures. The experimental part is modeling snow melding by conductive fabric specimen in realistic conditions. Some problems of practical implementation are listed and addressed such as wiring, secondary power supply (voltage converters), electrical safety etc. Special attention is paid to paneling, optimal power distribution, which is considered to be critical issues in conductive polymer heating application in membrane structures design. A feedback, environment sensing and rely smart operation by means of embedded electronic devices is discussed as way to achieve reactivity, user-friendly operation and power savings.

Key words: smart fabric, smart polymers, smart membrane structure materials, electrically conductive textile, snow melting architectural membrane.

Chapter 1

General Introduction

1.1 Motivation

The enormous progress of membrane structure design, fabrication and building demand a new materials. According to innovative approaches of emerging disciplines such as nanotechnologies, the new materials would be designed with inherent desirable properties. Composite materials used in membrane structures such as coated fabrics show a little progress on conceptual level during last decade. Smart polymers have been suggested as visionary breakthrough in industrial and architectural textile branch.

A permanent problem and serious limitation of tensile and inflatable structures is the snow loads bearing.

General approach is to design the membrane for snow loads as they are recorded in local construction codes. In many cases this is impractical or simply impossible. For example the internal pressure in air-supported domes rarely exceed 500 Pa. This is far from design snow loads for most of Europe, and North America. The only practical solution is a snow control system to be installed.

The other problem at wintertime in moderate climate zones where the most of world population lives is icing. It can cause in-proportional damages by worsening snowing problem, by preventing melting snow water to be drain properly and by specific damages of frizzing water expansion phenomenon.

A special case is retractable structures. Snowing and icing may be an obstacle to its proper operation with catastrophic consequences.[1]

The active measures against snowing use snow melting systems utilizing heating by hot air or by electric heaters. Usual approach to eclectic heating is applying a flexible heater, which incorporate thin metal wires. This method is expensive and may cause local overheating and consequential lost of strength of membrane fabric. A promising solution may be found by applying of smart polymers. More specifically, we suggest further to be used electro conducting polymer coating of standard polyester fabric. After electro conductive treatment the polyester would be coated by one of well-known protective coating systems – PVC /PVDF, silicone polymer etc. The idea is to combine well-established technologies in a new product - composite fabric combining the structural properties of architectural membranes and incorporated electric heater.

Snow loads and icing problems of membrane structures and active measures A constant problem and serious limitation of tensile and inflatable structures is the snow. General approach is to design the membrane for snow loads as it is recorded in local construction codes. In many cased this is impractical or simply impossible. For example, the internal pressure in air-supported domes rarely exceeds 500 Pa, which is far from design snow loads pressure for most of Europe North America and Asia. The only reasonable solution is a snow control system to be installed.

Snow load on roofs partially increases because of snowdrift caused by complicated relief of membrane roofs. The load should be considered as concentrated. Snow eaves are sometimes up to 2 to 3 meters deep. Therefore, it should be considered as a concentrated load with a density of about 4kN/m3. The impact force might be twice the gravity force. Design loads of such magnitude are very unusual for membrane structure.

The other problem at wintertime in moderate climate zones where the most of world population lives is icing. It can cause in-proportional damages by worsening snowing problem, by preventing meting snow water to be drain properly and by specific damages of frizzing water expansion phenomenon.

A spatial case is retractable structures. Snowing and icing may be an obstacle to its proper operation with catastrophic consequences. "A good example is one of most ambitious projects of retractable roof – the Olympic stadium in Montréal."(Fig.1)



Fig.1 "Damaged membrane of the Olympic stadium in Montréal under the snow load".¹

According to some research [2] a melting system that melts all the snow on a roof all the time consumes a lot of energy, and a melting system that only works after some snow has accumulated is inefficient because of snow caving between the snow and the roof. After early trials, a new method was studied. With this method, a thin ice layer is created and then melted, thus inducing snow sliding and consuming little energy. This approach requires the membrane roof to be designed in way to ensure the snow sliding. This method involves controllable heating of membrane. Electric heating is the reliable and versatile technique based on experience in variety areas such as building and infrastructure construction, aviation,

¹ http://news.nationalpost.com/2012/12/13/montreal-olympic-stadium/

Chapter 2

Literature Survey on Conductive Polymers

2.1 Conductive Polymers

Conductive polymers or, more specificly, *intrinsically conducting polymers* (ICPs) are *organic* polymers that conduct electricity. "..*ICP may have metallic conductivity or can be semiconductors*"(Conductive Polymers,

http://www.technologyed.com/courses-2013) i.e. the electric current is transferred by electrons not by ions.

Polymers are generally insulators and they have been increasingly used as substitutes for structural materials, such as metals, wood, and ceramics, because they can be produced from cheap raw materials in addition to being light weight, low temperature processible, and corrosion resistant, and demonstrating high mechanical strength. However, until the last few decades, polymers have been unsuccessful in replacing metals and semiconductors in electrical and electronic applications owing to their insulating properties.

In the 1970s a new class of polymers possessing high electronic conductivity have been discovered, somewhat surprisingly, in the partially oxidized or, in some cases in the reduced state. Three collaborating scientists, Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa, played a major role in this breakthrough. "..*They received the Nobel Prize in Chemistry in 2000 "for the discovery and development of electronically conductive polymers*" (3.Shirakawa H, Louis EJ, MacDiarmid AG, Chiang CK, Heeger AJ (1977) J Chem Soc Chem Commun 579)

The true understanding of conductive polymers application has only taken shape in the resent years despite of fact that general knowledge about that polymers has been available for many years. This is attributable to advancements in materials and processing techniques for example textile conductive coatings. Chemical and textile industry have only begun to explore the design freedom and the economic benefits of specifying conductive polymers and plastics in industrial and consumer products applications.

"...These polymers are a different class of materials than conducting polymers, which are merely a physical mixture of a non-conductive polymer with a conducting material such as metal or carbon powder. Initially these intrinsically conducting polymers were neither processable nor air stable. However, later generations of these polymers were processable into powders, films, and fibers from a wide variety of solvents, and also air stable. Some forms of these intrinsically conducting polymers can be blended into traditional polymers to form electrically conductive blends." (Synthetic Metals^o: A Novel Role for Organic Polymers (Nobel Lecture) Alan G. MacDiarmid 2001, 40, 2590) The electrical conductivities of the intrinsically conducting polymer systems now range of almost 14 orders - from that typical of insulators to that typical of semiconductors to nearly that of a good metal. (<10⁻¹⁰ S/cm to 10⁴ S/cm) [S = Ω^{-1}]). (Compare conductivity for silicon ~10⁻⁵ S/cm and for copper 5.10⁵ S/cm).2,4 Applications of polyanilines particularly, have begun to emerge. The area of applications includes blends and coatings for electrostatic dissipation and electromagnetic interference (EMIshielding), electromagnetic radiation absorbers for RF welding of plastics, conductive layers for light emitting polymer devices, and anticorrosion (electrochemically induced) coatings for iron and steel. [4]

We will focus our scope on Polypyrrole because of its proven characteristics and technological maturity and because of commercially available coatings based on polypyrrole polymer.

Polypyrrole most popular and well-studied representative of a group of organic compounds known as conjugated polymers. Conjugated polymers macromolecule chains consist at least of one backbone chain of alternating double- and single-bonds. The electron conductivity of polymer chains consisted of altering double and single bounds may be adequate explain only by quantum mechanics. Further, a very simplified picture of so-called delocalization of molecular orbits is depicted. Due to the fact that the π -orbitals of the alternating double-and single-bonds mesomerize more or less, i.e. the single and double bonds becomes similar and actually indefinable, double-bonds overlaps also over the single bonds. "*..Furthermore, the* π -electrons can be easier moved from one bond to the other, this way conjugated polymers to be one-dimensional semiconductors." (Conjugated Polymers, University of Vienna, Wichard J. D. Beenken Institute for Theoretical Chemistry and Structural Biology ,2010).Inorganic semiconductors, they can be doped, to increase their conductivity extremely. "*..Alan J. Heeger, Alan G. MacDiarmid, Hideki Shirakawa received the Nobel prize in chemistry 2000 for the* *discovery and development of such polymers*"(*https://uwspace.uwaterloo.ca*) The simplest conjugated polymer is polyacetylene. Actually polyacetylene consist of only of alternating single- and double-bonds in a single chain.



Fig. 2 conjugated chain (polyacethilen)²

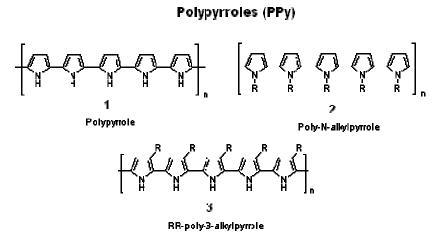


Fig. 3 Polypyrroles [3]

Polypyrrole (Ppy) Fig.3 is one of the most extensively used conducting polymers in design of high conductivity coating of different materials including woven fabrics. Among the conducting polymers known to date, ones based upon PPy have attracted special interest because of their high conductivity, their ease and high flexibility in preparation, their stability and good mechanical properties. Dall'olio et al. (1968) discovered PPy, at the time called pyrrole black. However, it was not until 1977 that Shirakawa and his co-workers wrote their seminal paper showing that halogen doping of polyacetylene dramatically increased its conductivity (to around 10^3 s m⁻¹ in the case of I-doped trans-polyacetylene). The major breakthrough with regard to the routine synthesis of conducting polymers, however, was achieved by Diaz and

co-workers when they reported the formation of a highly conductive, stable and manageable PPy film under controlled electrochemical conditions. [5] [6] Since then, in the context of cell-material studies, PPy has mainly been produced by electrochemical reaction

However, along with chemical synthesis, other polymerization methods have involved photochemistry, metathesis, concentrated emulsion, inclusion, solid-state, plasma, pyrolysis and soluble precursor polymer preparation [7].

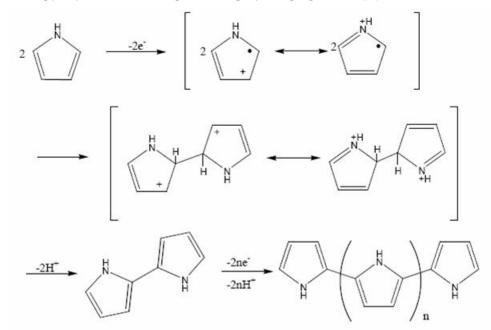


Fig. 4 Chemical polymerization of Polypyrrole [4].

Chemically synthesized conjugated polymers are initially insulators (i.e. in a neutral state) and it is only through oxidation (p-doping) and less frequently reduction (n-doping) by chemical or electrochemical means, that the necessary mobile charge carriers for conductivity are formed." *In the case of PPy for instance, the backbone is neutral in the reduced state and positively charged in the oxidized state. Therefore, to maintain electroneutrality, some counterion is required to diffuse into the polymer during charging and out during neutralization. The oxidation process may also be accompanied by significant change in polymer volume upon ingress of the mobile*

anionic species, a characteristic exploited in actuator applications.. "(8. Otero T.F, Sansinena J.M 1995 Artificial muscles based on conducting polymers. Bioelectroch. Bioener. 38, 411–414.)

Overoxidation of conducting polymers, notably PPy, where the polymer is held above the standard oxidative potential, leads to loss of conductivity and dedoping.[9]

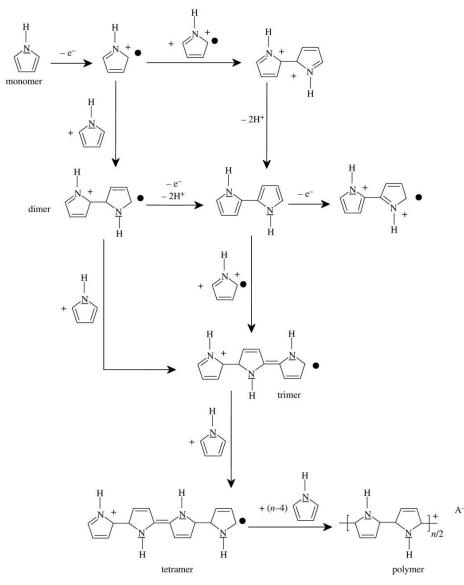


Fig. 5 *Electropolymerizaion mechanism of polypyrrole. Monomer units are adsorbed onto the surface of the working electrode resulting in one-electron oxidation to form a pyrrole cation radical.*(10,11)

Polypyrrole is generally synthesized by chemical or electrochemical means. *Chemical synthesis is used when large quantities of material are required and* involves mixing a strong oxidizing agent (typically FeCl3) with a monomer solution (10,11. Duchet J, Legras R, Demoustier-Champagne S 1998 Chemical synthesis of polypyrrole: structure-properties relationship. Synth. Met. 98, 113–122). Electrochemical synthesis is preferred for research purposes due to the simplicity of the technique, control over material thickness, geometry and location, the facility for doping during synthesis, the wide choice of available dopant ions and the generation of good quality films.[12] [13]. It preferred for research purposes due to the simplicity of the technique. Electrochemically deposited from the bulk solution phase of monomer units poly pyrrole is formed adherent surface conformal deposits i.e. thin solid films. The electrodeposition on the positively polarized working electrode takes place via a condensation reaction between the monomer units (five-membered heterocycle pyrrole on Fig. 5). On the other side, negatively charged counterions must be present in solution in order to maintain charge balance within the polymer since positive charges are developed along the Polypyrrole polymer chains. This process is referred to as doping. The choice of counterion (negatively charged in example above) affects formed polymer properties.

Chapter 3 Classification of Smart Materials

Literature survey on Smart materials

Widely, smart materials, particularly smart textiles are defined as that can sense and react to environmental conditions or stimuli. Stimuli might be from mechanical, thermal, chemical, electrical, magnetic sources.

As it is well known from cybernetics, three components may be present in any reactive system - sensor, actuator and controlling unit. Some of the fabrics act only as sensors and some act as both sensors and actuators. Smart Textiles are able to sense or/and respond to external stimuli in predetermined way.

"...According to functional activity smart textiles can be classified in three categories "(14. Z.X.Ziang, X.M.Tao, "Smart Textiles" Textile Asia June 2001)

- Passive Smart materials: The first generations of smart textiles, which can only sense the environmental conditions or stimuli, are called Passive Smart Textiles. Conductive fabrics (electric blankets for example) and optical fiberembedded fabrics are the good examples of passive smart textiles.
- Active Smart materials: They have both actuators and sensors. The Active Smart materials are considered to be the second generation. The actuators act upon the detected signal either directly by means of embedded properties of material itself or from a auxiliary central control unit. Active Smart textiles foe example are heat evolving fabric and electrically heated suits shape memory chameleonic water-resistant and vapor permeable heat storage, thermo regulated, vapor absorbing.
- Ultra Smart materials: Very smart textiles are depicted as third generation of smart textiles. They can not only sense and react but also adopt themselves to environmental conditions or stimuli. A very smart or intelligent textile must include some kind a control unit. The production of very smart textiles is now a reality thanks to productive collaboration of traditional textiles and clothing technology with other branches of science such as material science, advance processing technology and structural mechanics, from one side and sensor and actuator technology, communication, artificial intelligence, or even biology from the other.

The different kinds of "smartness" cited above can be incorporated in textile.

The smart properties may be incorporated in textile on different stages of textile production technology. Smartness can be developed by incorporating some active material in spinning dope or polymer chips prior to spinning. For example, modified the lyocell fiber by admixture of electrically conductive components during production to make it electrically conductive cellulose fiber. These fibers can be used to make antistatic textiles, in electrically heated textiles or as electromagnetic wave absorbers for EMI reduction of consumer products or radar camouflage of military equipment.

The smartness of a textile can be improved by incorporating the smartness in yarn before weaving and by implanting active materials, sensors and activators during fabric formation.

At finishing stage, smart textiles may be produced by applying some active finishes and in a combination of embedded electronic control units.

3.1 Passive Smart Textiles *Ultraviolet Protective Clothing*: The clothing, which has an ability to reflect or absorb the harmful ultraviolet rays in terms of passive heat retention use of UV absorbing chemicals. Alternatively, absorption may be achived micro-fiber constructions - numerous pores in textile product by means of bulked the fibre. UV protective clothes can improve so called Ultraviolet Protection Factor (UPF) for wearer [15]. UPF for most of synthetic yarn fabrics are unsatisfactory without a special treatment.

Multi-layer composite yarns & textiles give realistic oprtunity to implant predefined behavior in textile preserving in the same time to mechanical properties of basic fiber.

The optical fiber sensors are widly considered as a mean to incorporate smart features in textiles. In military applications for example they are able to sense a various battlefield hazards like chemical, biological and other toxic substances warfare threats. The polyurethane-diacetylene copolymer was used as the photochemical polymer for chemical sensor application in such applications. these sensitive materials replace the passive cladding of the optic fiber and the sensory system was integrated into textile structures. The pH sensitive sensors are developed and woven into the fabric of soldier's clothing as have been reported in [16]. The plastic optical fiber is spirally wounded over the basic yarn during the fabric production process without any discontinuities at the armhole or seams by a novel modification in the weaving process. The plastic optical fiber was incorporated in an X-Y grid. A break in this grid would reveal the location of the damage. A Fabry-Perot interferometer was used for localized sensing of heartbeat in smart cloth medical sensors.

Conductive Fiber and Fabric and its application in membrane structure design is the main objective of this research. Most of the conductive fabrics are made of or include conductive fibers and yarns, e.g. metallic silk organza, stainless steel filament, copper, silver and gold or stainless steel wire-wrapped polymer filament, metal-clad aramid fiber, conductive polymer fiber, special carbon, etc. The other one utilize conductive material coating and fiber /fabric. Electroconductive fabrics have been applied to the manufacture of fabric sensors for different physical properties such as temperature, pressure and so one.

3.2 Active Smart textiles Probably the fist smart material widely utilized in membrane structure industry is Photocatalytic membrane structures which utilize TiO_2 coating technology with inherit self-cleaning properties that's far superior to conventional membranes. It's called the Photocatalytic Decomposition Process, a self-cleaning action that occurs as the TiO_2 causes any organic matter such as stain or pollutant to be decomposed through Photocatalytic oxidation toward simple components such as CO_2 , H_2O , N_2 and simple soluble organic components. The decomposition residue does not adhere to the surface and simply is washed away by rainwater even not fly dissolved.

When PVC coated polyester the most widely used tensile membrane fabric are treated with titanium dioxide (TiO_2) photo-catalyst they inherit self cleaning properties that are adding a new feature to conventional PVC materials. PTFEcoated fiberglass membranes treated with TiO_2 highly improve their self-cleaning ability since actively dissolve pollutants. Photocatalytic membranes also remove significant volumes of nitrogen oxide (NOx) from the atmosphere. In this reaction between atmospheric oxygen and moisture in the air activated by TiO2, both nitrogen and sulphur oxide from vehicle exhaust emission, are decomposed to produce cleaner air.

The photocatalyst may be regarded as composed of two parts of photovoltaic element and catalyst – both are semiconductors stimulated by light energy. When TiO_2 electrons (e⁻) and the holes (h⁺) resulted from the electron layers energy, then the electron deficiency are formed. The reduction reaction caused by electrons and produce superoxide anion radical (•O₂ _) from molecular oxygen content in air. In the same time the holes produced react during a oxidation reaction with water and the moisture in the air and produce •OH radicals. Both radicals are extremely reactive in contact with different organic and contaminants and decompose them. As a result of decomposition of the organic materials their poisonous and dangerous characteristics are removed and the produced materials are less hazardous and less poisonous [17].

$$\begin{split} &\text{TiO}_2 + hv \rightarrow h^+ + e^- \\ &e^- + \text{Ti}^{4+} \rightarrow \text{Ti}^{3+} \\ &\text{Ti}^{3+} + \text{O}_{2(g)} \rightarrow \text{Ti}^{4+} + \text{O}_2^- (ads) \\ &\text{O}_2^- (ads) + h^+ \rightarrow \text{O}_{2(g)} \uparrow \end{split}$$

Fig. 6. *Photocatalytic mechanism of TiO* $_2$ (S. Ganjouhaghighi, Produce and Study the Hydrophilic and Photocatalytic Effect of Au Dopped on TiO2 and SiO2 Films, M.Sc. Thesis, Sharif University (2007).

Self-healing materials. Self-healing materials are materials with inherent ability to react in specific way on the environmental stimuli and which may firmly categorized as Smart materials. This a large group of materials are polymers, metals, ceramics and their composites that when damaged through thermal, mechanical, ballistic or other means have the ability to heal and restore the material. They may recover to its original set of properties or modified itself in a way to continue serve in their application. [18]

Researchers at Stanford University for example have developed a pressure-sensitive synthetic material that can heal itself when torn or cut. This property gives it potential for use in next-generation prostheses or self-healing electronic devices. The final goal is to create a material that combines the self-healing ability of a plastic polymer with the conductivity of a metal. The Stanford team in the lab of chemical engineering Professor Zhenan Bao, explore a polymers made of long chains of molecules joined by hydrogen bonds. These bonds are created by the relatively weak attractions between the positively charged region of one hydrogen atom and the negatively charged region of the next caused by polarization. A special feature of hydrogen bonds is their ability to reorganize themselves in reversible way and reconnected so that the structure of material can be restored after being damaged. The new material is also bendable at room temperature unlike the metal. Researchers added nickel nanoparticles to provide the conductivity required to make the material pressure-sensitive. The rough nanoscale surfaces of the nickel concentrate an electrical field to make it easier for a current to flow from one particle to the next as well as increasing the mechanical strength of the material. The result was a conductive plastic with self-healing properties.

Many electrically active smart fibers contain add ones of electric conductive materials such as *Phase Change Materials (PCM)*, and graphite particles, which can conduct electricity. In this way, the resistance of the fiber is changeable along with the change of fiber volume caused of temperature change. Typically, the polymer expansion rate is higher and during , its explanation they reduces conductivity between graphic particles. These materials used in heaters can automatically regulate the on/off of the electricity and keep the temperature in predefined range. PCM microcapsule was developed many years ago by NASA. PCM is introduced into the textile in the production process of fiber matrix in microcapsule form. These capsules suppress temperature variations by phase change discontinuing temperature increases when the defined temperature is reached. The continuous energy fed from environment or form human body to is stored increased thermal capacity of PCM capules. Inversely PCM materials give up their stored by phase change heat as the environment cool down. Capsulated paraffins melting in particular are used for this function in the textile.

The thermo catch heat developed by Mitsubishi Rayon with acrylic fiber s contains in the fiber core fine ceramic particles, which convert light into heat, and with an antimony / stannic oxide component in the fiber sheath. in The Mobile-Thermo' Snow jacket was used Such bicomponent yarn with an integral heating system inside the garment which guaranteed precise temperature control. Notably, that snow jacket was worn during 1998 Winter Olympics by members of Swiss team and 300 media persons in Nagano Japan. It would be very interesting to explore opportunities of application of similar materials in architectural textiles.

Shape memory materials ".. are materials that are stable at two or more temperature states keeping deferent shapes in said states. In other words, they have the potential to assume different shapes, when their transformation temperatures have been reached" (Hayashi, " Properties and application of Polyurethane-based shape Memory Polymer" US-Japan workshop on Smart Materials and Structures held at University of Washington. Dec.3-4, 1995) Shape memory is a property of many polymers that have hard segments and soft segment e.g. polyurethane, polyester ether, styrene -butadiene copolymer etc. the Shape-memory materials exhibit such behavior in magnitude it could be utilized. Actually, the shape memory may be considered side effect in many plastics some times undesired side effect. But because a novel performances such as sensitivity, actuation, damping and adaptive response to external stimuli such as temperature, lighting, stress and field, which can be utilized in various ways in smart systems. Shape memory polymers were first developed in France and consequently commercialized in Japan in 1984. Since the shape memory was initially found in Ni Ti alloys some smart textile use shape memory alloy in multiplayer fabric systems that change shape within a certain temperature range. This multilayered system can be utilized to change the density between the individual layers. When temperature rises, an additional layer of insulating air is chanced thermal conductivity of the fabric and serve as a thermoregulatory mean [19], [20].

Heat storage textiles: The main object of heat storage or thermal regulatory textiles is wear for extreme conditions. The goal is to maintain the wearer in a state of thermophysiological comfort under the widest possible range of thermal workloads and ambient conditions. Heat storage and thermoregulated textiles are novel comfort textiles that can absorb, redistribute and release heat by phase change in low melting point materials incorporated in textile rather than separate thermoregulated system. "*NASA planned to put the Phase Chancing Materials into gloves to keep pilot's hand warm. NASA also developed textiles that aimed to improve the protection of instruments and astronauts against extreme fluctuations in temperature in space on the basis of heat absorbing and temperature regulating technology based on PCM.*"(20. Potential uses of Shape Memory films in clothing Technical Textile International October 1999, 17)

3.3UltraSmartTextiles

Very smart textile are an effort to make electronic devices a genuine part clothes by embedding entire systems into clothing. This way a new level of permanent and extensive data access is visional to revolutionize the fields of personal communication, information, security, and health care. These concepts might be became possible by a new textile technology that enables fabrics to function as electronic interfaces. So called SOFTswitch was exhibited to public in July 2000. SOFTswitch is now working on development projects with broad spectrum of companies, and will market applications from intelligent industrial fabrics to wearable electronics.

SOFTswitch is among few practical steps toward real "Ultra Smart Textiles" by combining lightweight conductive fabrics with a very thin layer of composite material having unique electronic properties. This composite material is an elastoresistive and is a step to integration of complete electronic system in woven fabric.

Interesting example of smart materials is *Phase Change Materials* (PCM) in the Textiles composite or *Quantum Tunneling Composite* (QTC). This composite in its normal state it is an insulator; however compressing or twisting it reduces the resistance until metal-like connectivity is achieved. Unlike the other pressure sensitive materials the mechanism of conduction in this composite is based on Fieldinduced quantum tunneling i.e. on purely quantum mechanic effects. In the QTC Composites, metallic particles are held in close proximity within a polymer matrix, but never allowed to come into real contact. When the fabrics containing the composite material are compressed or distorted the distance between the metallic particles decreases allowing this way electrons to tunnel between them and current to flow.

So called SOFTswitch fabrics exhibit a very broad change in Ohmic resistance, more than that the resistance change is proportional to the deformation tensor. In this way with a small deformation, the resistance can be reduced from billions of times. Such behavior may have applications where proportional control of electronic devices is required. We cold speculate about a tensile membrane fabric incorporated QTC fibers and reacting on applied stress to initialize some kind of reaction such dangerous stress alert .

Chapter 4 Research Approach

4.1 Definition of the research problem

As have been illustrated in introduction, the snow control is a keen issue in membrane structure design and practice. The snowing and icing by passive means only is not always possible or ill founded economically. The active measures include heating almost always. An economic, flexible, intelligent way of targeted heating of architectural membranes does mot exit at the date.

The common method of applying thermal energy to architectural membranes is warm air blowing widely used in air-supported domes. The warm air is ducted between external skin and insulation liner. The method looks simple but in practice is energy inefficient and poorly compatible with single skin tensile membranes. In airsupported domes the hot air flow is usually derived from HAVC (heating, ventilation, and air conditioning) system which is coupled with air blowing fans pressurizing the dome. In case of intensive snowfall, the power of heating system is insufficient for snow melting over entire membrane surface. On the other hand, the hot air flow is not easy to be redirected toward problem areas.

The other heating method is resistive electric heating usually by applying electric mats or other resistive eclectic heaters on backside of the protected membrane. Indirect heating of the membrane is used because of lack of membrane material witch incorporate means for resistive heating. Indirect heating arise a number of problems as need of additional structure, poor thermal contact between heater and membrane, hot spots and overheating. As consequence, the energy efficiency becomes unacceptable low, the system and power cost rise dramatically. Overheating cause increasing ageing of membrane material and may cause irreversible damages. Since tensile strength of many structural fibers lake a polyester yarn falls significantly above $\sim 80^{\circ}$ C, a safety factor should be increased.

The solution of that technical controversy is possible by eclectic heater integrated within composite membrane. The resistive heater is a very smile device consists of

conductors with predetermined eclectic resistance and current supply wires. By incorporating in textile a eclectic conductivity we have so called Conductive textile. Conductive textiles can be produced by weaving thin metallic or carbon wires, impregnating fiber materials with conducting powders, moralizing material, or by blending filament-sized fibers of stainless steel or carbon fiber. Conducting fibers have also been made from conducting polymers by solution spinning, however, they are typically brittle, expensive to produce and hard to manufacture on a large scale.

Conducting powder (carbon) incorporation is most cost effective, though the high content required to yield percolation reduces the mechanical properties of the fibers. Core/shell strategies, where normal textile fibers are coated with a conducting material, maintain the original mechanical strength. Conducting polymers have been use for this application, and yield conductivities that fall between moralized fabrics and carbon-based blends.

An example of material with incorporated electrical heater is SEFAR® PowerHeat. It is made of PET monofilaments and conductive fibers. Its overall properties are shown in data sheet [21]:

- very quick heating up due to low mass
- no hotspots
- energy efficient: high achievable temperature by given electrical power
- up to 1000W/m2 heating power feasible on air
- also feasible for heating liquids
- homogeneous temperature distribution at surface
- light-weight (<90 g/m2)</p>
- high air permeability (> 8'000 l/m2s, depending on fabric design)
- large heating areas (up to 0.78m width, unlimited length) different temperature profiles possible within the fabric

Even a "homogeneous temperature distribution at surface" is declared in cited datasheet a significant difference of surface temperature may be surveyed on Thermo-Image (Fig. 7)

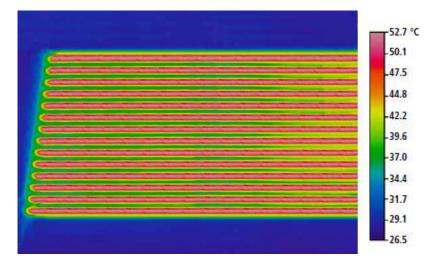


Fig. 7 Thermo-Image of a SEFAR® PowerHeat panel (SEFAR ltd)

The common drawback of all reviewed conductive textiles is their unsatisfactory mechanical properties, unsuitable for structural membranes. That finding motivates us to explore possibilities to obtain conductivity of standard structural textile with no affecting its mechanical properties. Most promising approach was found to be a conductive polymer coating of polyester fabric. Moreover, this method has been developed toward mature, commercially available technology.

4.2 Polymer fibber conductive treatments

Today a variety of synthetic fibers are available that contain a conductive core of carbon black, thereby providing the textile structure with the desired electrical conductance. Fibers with metal coatings were also developed for higher degrees of conductance. Materials such as aluminum, copper, silver, and nickel have been commercially used to produce metal-coated fibers. While vapor deposition is more predominant in the production of metal-coated films, electrodes plating of textiles is probably the preferred way to produce metal-coated fabrics. Other inorganic conductive materials such as tin oxide or copper sulfide have also been successfully developed. Unfortunately, all this treatments is associated with hi additional cost or/and are not compatible with coating technologies of architectural textiles.

4.3 Conductive polymers

Polypyrrole is one of the intrinsic conducting polymers very promising for wide thermoelectric applications because of it several attractive properties, such as easy preparation with low costs. Polypyrrole chemically synthesized on PET fiber (polyethilentereftalat) gives rise to textiles with a high electric conductivity, suitable for several applications from antistatics to electromagnetic interference shielding devices. Last technological achievements in preparing a high conductivity, durable enough electro conductive coatings made possible a composite fabric based heaters with performances not offered till resent times i.e. EeonTex[™] by Eeonyx Corp. Chesterfield, MO, USA. Eeonyx has developed a line of conductive polymer coatings that can be applied to fabrics and other materials over a large range of tunable resistances. [22]. Since the pure conductive polymers has poor mechanical properties it is unpractical to make fibers of them. Instead, a thin layer coating of conducting polymers onto substrates, such as polyester textiles, was overcomes many of the processing problems associated with pure conducting polymers. For instance, the mechanical properties such as strength, flexibility etc. is defined by base fabric and electrical properties by conducting polymer. It is proved the thin coatings do not intact the mechanicals of the base fabrics.

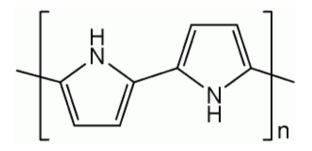


Fig 8 Polypyrrole chain structure

Since the first discovery in 1977 that chemical treatment with iodine converts electrically insulating polyacetylene into a highly conducting material with electrical conductivity above 104 S=cm [23], many electrically conducting polymers have been

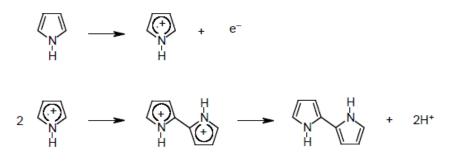
reported. The electrically conducting polymers are able to transfer electrical charges to the same extent as an electrical conductor or a semiconductor. Due to their metallike conductivity and other fascinating properties, conducting polymers have played indispensable roles in specialized industrial applications in spite of their short history. However, the major aspect useful for most applications is not the metal-like electrical property itself, but the combination of electrical conductivity and polymeric properties such as flexibility, low density, and ease of structural modification and excellent compatibility with other polymers. The last property make them very attractive for fabricating of conductive textiles in combination with standard proven in practice polymer fibers like polyester nylon aramid (Kevlar) etc. "... Among the conducting polymers, polypyrrole (PPy) has attracted great attention because of its high electrical conductivity and good environmental stability" (20. S.Nato, Temperature-Sensitive Colouring Materials SWAY, Sen-1 Kikai Gakkaishi (1989) 42 (9) 435-439) PPy has been considered as the key material to specific potential applications such as woven electric heaters. The heteroaromatic and extended π -conjugated backbone structure of PPy provide it with chemical stability and electrical conductivity, respectively. However, the p-conjugated backbone structure is not sufficient to produce appreciable conductivity on its own. Partial charge extraction from PPy chain is also required, which is achieved by a chemical or an electrochemical process referred to as doping. The conductivity of the neutral PPy is remarkably changed from an insulating regime to a metallic one by doping. This is a very worthwhile feature for applications in which the electrical conductivity of a material must be controlled.

4.4 Synthesis of Polypyrrole. PPy may be prepared by either chemical or electrochemical oxidation of pyrrole monomer. The most widely accepted polymerization mechanism of PPy is the coupling between radical cations (Fig. 9) [24] In the initiation step, the oxidation of a pyrrole monomer yields a radical cation. Coupling of the two generated radical cations and deprotonation produces a bipyrrole, as confirmed by Andrieux et al. [25]. The bipyrrole is oxidized again and couples with another oxidized segment. In the propagation step, reoxidation, coupling, and deprotonation continue to form oligomers and finally PPy. The radical coupling between oligomeric pyrrole species is favored since the oxidation potential

32

of oligomeric or polymeric pyrrole species is lower than that of the monomer [26]. Once the chain length of the oligomers exceeds the solubility limit of the solvent, precipitation of PPy occurs. The termination step has not been fully elucidated but is presumed to involve nucleophilic attack on the polymer chain . On the other hand, an alternative mechanism has been proposed, in which a radical cation attacks a neutral pyrrole monomer as in common chain polymerization, but this explanation is not generally accepted [27].

Initiation step



Propagation step

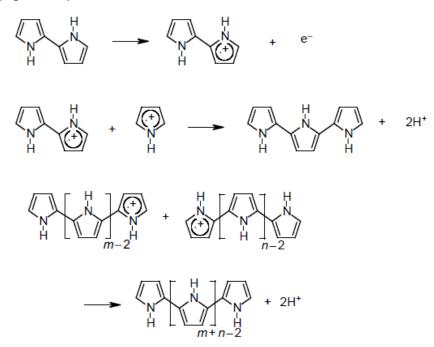


Fig. 9 Polymerization mechanism of pyrrole through the coupling of two radical cations. (20)

Highly transmissive, electroactive, and conductive poly[(3,4-alkylenedioxy)pyrrole-2,5-diyl] thin films were prepared by in situ chemical polymerization [28]. The process possesses a significant advantage as environmentally harmful organic solvents are not required since coatings can be obtained directly on the substrate. Many factors such as temperature, pH, nature of dopant, and oxidant were found to influence the film formation. PXDOPs were also synthesized from flexibly functionalized monomers, and showed highly stable aqueous compatibility and therefore unique potential for biomedical implications [29]. The effect of the substrate surface, where in situ PPy deposition process occurs by chemical oxidative polymerization, has also been investigated [30]. Deposition of continuous granular particles was observed on the hydrophobic surface, while spherical particles were deposited on the hydrophilic surface. The conductivity of the PPy deposited on the hydrophobic substrate was found to be ~10⁴ higher than that of PPy deposited on the hydrophobic surface.

4.5 Conductive polymer based coating

Textiles are among the oldest materials known to humankind. Textiles now play a crucial role in tensile and inflatable structure engineering materials. Most of those materials are coated fabrics. Searching a suitable technology to make a composite fabric electro conductive enough is the main goal of this research. As have been illustrated in previous sections products based on traditional approaches like the incorporation of conductive fillers, (carbon or metal) or coating of textiles with metals is not suitable for this particular application –eclectic hater embedded in structural membrane textile.

Conducting polymers offer an interesting alternative to coated or filled plastics and textiles. However, these materials have several severe processing limitations. Considering these limitations, textiles of various kinds represent a reasonable choice as a substrate for thin coatings of such polymers. Conductive textile composites based on polypyrrole or result in structures showing surface resistances of 10-10³ ohms/square. This falls in between metallized fabrics with a surface resistance that is usually below 1 ohms/square and carbon-based blends with surface resistances

above 10^3 ohms/square. These textile com- posites have a considerable advantage over metal- coated fabrics because of their excellent adhesion noncorrosive character. The remainder of this chapter focuses on the synthesis, properties, and applications of these industrially useful products.

4.6 Methods of deposition.

In situ polymerization

When pyrrole is chemically polymerized, particularly from aqueous solutions, many researchers have observed the formation of films on either the liquid/air or the liquid/solid interface [31]. This spontaneous molecular assembly has been used to polymerize conductive polymers on the surface of numerous materials, and has been successfully applied to textiles [32]. Considering industrial applications, it is fortunate that this in situ adsorption and polymerization proceeds especially well from aqueous solutions. Because of the desirability of aqueous processing, most of the research involving chemical oxidative polymerization on substrates has employed the water-soluble monomers pyrrole as starting materials. It is known that the polymerization of pyrrole proceeds through the formation of radical cations that couple to form oligomers, which are further oxidized to form additional radical cations. These oligomers have been isolated in the electropolymerization of pyrrole [52] The polymerization on the surface of textiles must proceed through one of these oligometric intermediates, as neither the monomer nor the oxidizing agent adsorbs to the fabric and can not used for in situ polymerization on fiber. In addition, the oxidation of the monomer must be sufficiently slow to obtain uniform adsorption. The polymerization rate can be controlled by the monomer and oxidant concentrations, the reaction temperature, or the addition of an Fe(III) complexing agent. Ideal monomer concentrations for such reactions are 1-2 g/L. Under these conditions, the polymerization occurs solely on the surface of the fiber and no polymer is observed in the liquid phase. Industrially, these polymerizations can be performed in textile dyeing equipment. An interesting modification of the in situ process that results in a fabric with low surface resistance is reported in [33]. An aqueous pyrrole solution containing a dopant is combined with a ferric chloride

solution in an agitated vessel. The combined liquor is sprayed on the surface of a textile that is supported by a polyethylene film. The textile fabric and the support are rolled up and stored at a reduced temperature in a cylindrical vessel filled with the reaction mixture. After washing and drying, the procedure can be repeated several times to obtain surface resistances as low as 5 /ohm/sq.

Two-Step Processes. A large body of work describes the polymerization of conducting polymers by a two-step method. While in situ polymerizations are normally conducted in aqueous media, a two-step process can be accomplished using a variety of solvents. The choice of solvent may have a profound influence on the properties of the resulting composite structures. Several variations of the process have been reported; for example, the monomer may be applied from the vapor phase [34], or a porous substrate can be impregnated with a polymerizable monomer followed by exposure to an appropriate oxidizing agent [35] The major advantage of a two-step process is its potential adaptation to a continuous process that is highly desirable for industrial applications. It is, however, more difficult to control and may not produce the ordered structures obtainable by an in situ template polymerization.

Polypyrrole on textiles. It is remarkable that the bulkiness of the literature on conductive textiles concerns the use of polypyrrole. This is widely considered is considered by the its distinctive ability of the polymerizing species to adsorb onto hydrophobic surfaces and also form uniform coherent films. This reaction is naturally favored in the one-bath process but may also occur to some extent in the two-bath processes. At present time at least three groups of researchers are actively pursuing the in situ polymerization of pyrrole on textiles. Achilles Corporation in Tokyo, Japan, Milliken Research Corporation in Spartanburg, South Carolina, and Centre d'Etudes et de Reserches sur les Materiaux (CEREM) in Grenoble, France have active research groups in this field. Some of the early patent literature is summarized in Tables 35.1 and 35.2. The first reference to an in situ polymerization of pyrrole is described by Bjorklund and Lundstrom [35], who polymerized pyrrole from a dilute aqueous solution of ferric chloride to the surface of paper pulp. This resulted in a chloride-doped polypyrrole deposit of relatively low conductance and low stability on the cellulose fibrils. The process was later modified by researchers at

Milliken Research Corporation and applied to textiles [10]. Since then, numerous investigators have used this process successfully on textiles and other substrates [36], [37], [38], [39].

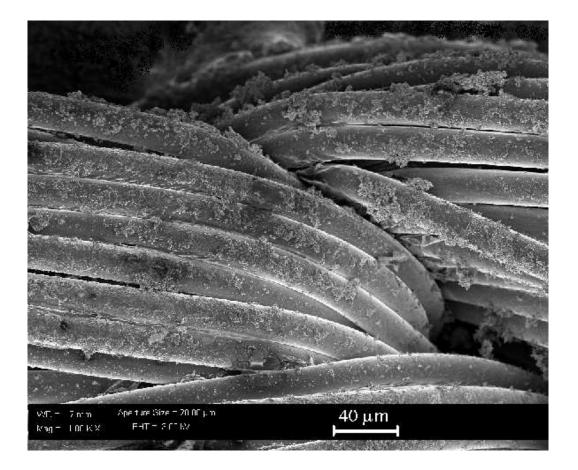


Fig. 10 Scanning electron microscope SEM images of the samples with polypyrrolecoated fibers. The dust is due to polymer particles in solution, deposited on the *net(*.K. Yasubaand M. Matsunaga, Manufacture of electri- cally conductive synthetic fiber textiles by coating with polypyrrole, Jpn. Patent 63,042,972 A2 (1988).

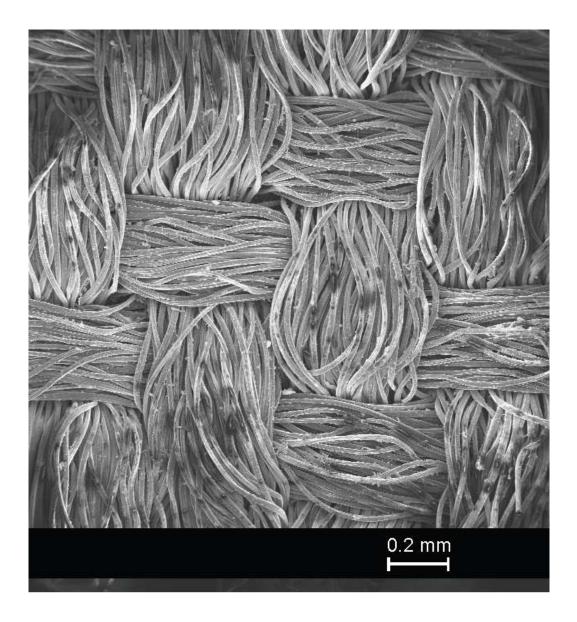


Fig. 11 SEM images of PPy coated fibers.

As can readily be seen in Fig.10, polypyrrole provides a uniform relatively smooth surface even under magnification of 2500 X. These photomicrographs show a relatively featureless, smooth surface that is in striking contrast to the rough surface from chemical or electrochemical polymerizations reported in the current literature. In addition, a cross-section of a treated fiber, shown in Figure 10, clearly shows the very uniform coating of the conducting polymer encasing the entire fiber. For our polypyrrole system, we believe this uniformity is due to our previously described mechanism of polymer growth that may involve a precursor complex of pyrrole and

oxidizing agent, which is followed by the epitaxial growth of the polypyrrole on the surface of the textile fibers.



Fig.12 Cross section of a fiber treated with polypyrrole magnification 960 X .

4.7 Conductive polymer properties.

Mechanical properties. With few exceptions, the mechanical properties of conductive polymers are rather poor. This is a result of the cross-linked nature and aromatic character of the back- bone. As have been remarked upper the use of a textile substrate is a most suitable method of introducing mechanical strength, flexibility, and processibility to conducting polymers for practical applications. Fabrics coated with a thin layer of polypyrrole or polyaniline have essentially the same mechanical properties as the textile substrate, with minor variations depending on processing conditions. Even fibers that are highly susceptible to oxidation or hydrolysis under acidic conditions, such as cotton or nylon, do not deteriorate during the in situ polymerization of pyrrole. The resistance of these fibers to degradation in a reaction

The measured tensile and other physical properties of polypyrrole or polyaniline coated fabrics, on a number of different substrates, are virtually unchanged from untreated fabrics. It is surprising that even fibers that are highly susceptible to hydrolysis under acid conditions, such as nylon or cotton, do not deteriorate process, which is conducted at a pH below one. The quick formation of a thin polymer layer appears to protect the fibers from hydrolysis.(51)

Electrical properties. The electrical properties of conducting textiles depends on the intrinsic volume conductivity of the conducting polymer, the mass of the substrate, the diameter of the textile fibers, the thickness of the adsorbed conductive layer. Volume conductivities for polyaniline-coated textiles as high as 20 S/cm have been reported, whereas polypyrrole coatings have been measured in the 100 S/cm range. surface resistances as low as 5 ohm/sq have been reported using multiple coatings. By adjusting the concentration of the reaction media, the surface resistance can be tailored to any desired value, with a lower limit somewhat dependent on the substrate weight. Investigators at Milliken Research Corporation reproducibly prepared polypyrrole-coated fabrics with surface resistances ranging from 20 to 2000 ohm/sq on textile substrates weighing 50-200 g/m2. The reproducibility within this range has been within 5%. Although textiles with surface resistances of $\sim 10^5$ 5 ohm/sq can be prepared, the reproducibility is somewhat less reliable due to the small amount of polypyrrole deposited. The resistance of conducting textiles can be measured using a four-probe technique as in measurements of conducting films or pressed pellets. Since the coating is much thinner than the substrate material, the resistance is normally expressed as a sheet resistance in ohms per square rather than a volume resistivity or conductivity. To obtain reliable measurements of resistance on the uneven surfaces of woven or knitted textiles, significant pressure must be applied at the electrical contacts. For this reason, it may be preferable to use the established two-probe AATCC test method 76-1987, "Electrical Resistivity of Fabrics." We have found that a pressure of 1500 g for a 2 in. wide gold-coated clamp, 1/16 in. thick, gives accurate and repeatable values for surface resistance on most fabrics. The same instrumentation may be used to measure the resistance per unit length of yarns or fibers. It should be noted that since polypyrrole and polyaniline, like other conducting polymers, are semiconducting materials, their conductance increases with increasing temperature. An increase of 10% in the conductance of polypyrrole-coated polyester fabrics has been observed

Stability of conducting textile. In many applications, the stability of conducting materials is an important concern. Metal-coated fabrics, fabrics coated with inorganic conducting particles, and carbon-filled materials generally demonstrate stabilities that are equivalent to those of the parent conducting materials when monitored in a

noncorrosive environment. Corrosion, or the degradation of the substrate, which causes interruptions in the percolating network, is normally the limiting factor in the ultimate lifetime of these materials. Organic materials, including conducting polymers, are much less stable in air owing to their relatively high reactivity with a variety of atmospheric chemicals, most notably oxygen. The stability of conducting polymers and conducting polymer-coated textiles has been shown to be improved dramatically when the material is isolated from the environment with a protective coating or laminate [40]. Miinstedt [41] found no loss of conductivity in a polypyrrole film after 200 days at 80°C in a nitrogen atmosphere. In some applications, the requirement of highly flexible conducting textiles precludes the use of thick coatings, and the intrinsic resistance of the conducting polymer to oxidation becomes a limiting factor. Investigations into the stability of polypyrrole powders, films, and coatings have been carried out by several groups. The results indicate that the degradation of polypyrrole on textile substrates follows the same rate laws, and presumably the same mechanism, as the degradation of polypyrrole powders and films. In almost all cases, however, the stability of electrochemically grown polypyrrole films is superior to that of chemically synthesized polypyrrole coatings or powders [42]. This can be attributed to two factors: (I) the increased control of oxidation potential in electrochemical polymerizations, and therefore the polymerization rate, leading to films with fewer defects, and (II) the control of the dopant ions by selection of the electrolyte in electrochemical polymerizations. At oxidation potentials achieved during the chemical synthesis of polypyrrole by ferric chloride, overoxidation can occur, leading to nonconjugated moieties and decreased stability within the polymer chain [43]. In addition, significant thermal dedoping has been shown to occur with chloride-doped polypyrrole [44].

4.8 Conductive Textile Resistive Heaters

Their range of resistance makes conducting textiles suitable for resistive heating applications. Conductance can be provided by incorporating graphite into the fabric or coating it with a metal or a conducting polymer. Regardless of the conducting material, textiles are particularly well suited for large-area radiant or contact heating. A conducting textile offers many potential advantages over traditional heaters consisting of rigid resistive wires. Not the least of these is the diffuse nature of the conducting surface, which gives rise to fast, even heating over the entire surface. It also improves reliability, since a tear in any one area will not disrupt the current. By contrast, traditional heaters are usually wired in series, so that a break anywhere along the wire interrupts the current and renders the heater inoperative. The absence of wires also allows for a thin, flexible construction. If tactile properties are important, for instance in a heated seat, the use of conducting fabric necessitates no additional cushioning. Considering these advantages, there are many applications where a conducting fabric could be superior. Items that already contain fabric, such as car seats, mattress pads, blankets, and clothing, could easily be made to provide warmth simply by including a piece of conducting fabric in the construction and providing a power source. Other applications could include rapid heating with radiant panels [53], electric heating in floors and walls, ice-melting on aircraft [54] or ground surfaces, heating chemical drums, or virtually any need now filled by largearea wire heaters. In some instances, the thinness of the fabric offers a weight and space advantage. In others, the simplicity of the heating component makes construction of the final product easier. Current, voltage, and power requirements for a heater made of conducting textiles will vary depending on the application. Devices are best defined in terms of the power demands per unit area of heating surface. Contact heaters such as a heated seat or vest will typically require less than 0.1 W/in.2. Radiant heaters may operate in the neighborhood of 0.1-1.0 W/in². Other applications could demand up to a few watts per square inch. For simplicity, assume a rectangular heating surface on which two electrodes of length w are separated by a distance l. The total resistance of the surface is given by R = rl/w, where r is the surface resistance per unit area (as in ohm/sq). At a given voltage V, the current draw will be:

$$I = Vw/rl,$$

and the power density (per unit area) is given by:

$$P = V^2 / r l^2.$$

Figure 13 relates power density and voltage for various electrode spacing (and hence fabric resistances). The temperature generated by a given power density depends on

the configuration and environment of the device. Figure14 shows the radiant temperature measured 3 and 6 in. from the surface of a large sheet of "Contex" as a function of the power density.

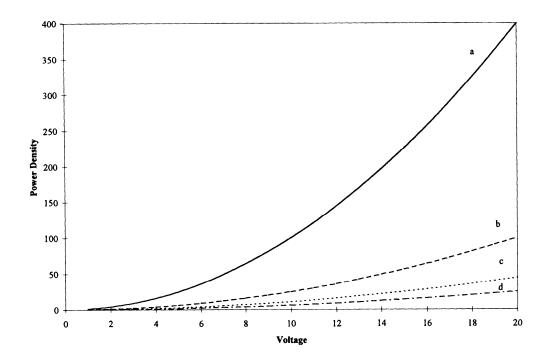


Fig. 13 Theoretical power density versus voltage for resistive heaters based on polypyrrole-coated polyester fabrics with various electrode spacings. (a) $l = l_0$; (b) $l = 2l_0$; (c) $l = 3l_0$; (d) $l = 4l_0$.

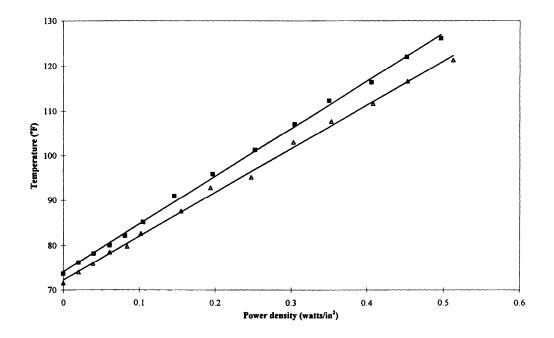


Fig. 12 Temperature versus power density for resistive heaters based on polypyrrolecoated polyester fabrics. Temperature probes were placed at a distance of (\blacksquare) 3 ins. and (\blacktriangle) 6 ins. from the fabric.

4.9 Commercial conductive textile and conductive polymer coating

Eeonyx Corp. has developed a line of conductive polymer coatings that can be applied to fabrics, felts, foams, films, powders, and plastic parts over a large range of tunable resistances.

"...By coating thin layers of conducting polymers onto substrates, such as textiles, one overcomes many of the processing problems associated with pure conducting polymers. For instance, if one coats a fabric with a conducting polymer, one now has a strong, flexible, sometimes stretchy conductive material" (H. Kuhn and D. Child, in Handbook of Conducting Polymers, 2nd edition, T. A. Skotheim, R.L.Elsenbaumer, and J.R. Reynolds, eds., chap. 35, pp. 993-1013, Marcel Dekker, New York (1997).. The thin coatings do not change the mechanicals of the base fabrics.

"...Eeonyx's proprietary processing technology that allows us to make all the products discussed below involves immersion of the base substrates in aqueous solutions. One of the main advantages of the present technology is that the conductive polymer coatings can be applied onto almost any surface in almost any form. The most common materials that have been coated with conducting polymers are textiles of polyester, nylon, glass, and polyurethanes. In addition, quartz, aramids, acrylics, and polyimides are readily coated" (EeonTex (privat communication 2013).. With a surface pretreatment, even low-surface energy materials, such as polyolefins, fluoropolymers [45], and silicones, can be made conductive on the surface with good coating adhesion. "..*Another major advantage* of this coating technology is that it results in uniform, coherent, nonparticulate coatings that afford a very wide range of surface resistivities. Depending on the particular substrate, surface resistivities from about 10 Ohm/sq up to 10 billion Ohm/sq can be obtained" (EeonTex (privat communication 2013).. The basic technology is in-situ deposition of conducting polymers onto fabrics [46].

"...Conducting polymers, such as polypyrrole (PPY), polyaniline (PAni), and polyethylenedioxythiophene (PEDOT) have been deposited onto various textiles in the forms of woven fabrics, knit fabrics, felts, other nonwoven structures, and fibers. For a given amount of coating add-on, it has been found that, of the three ICP's mentioned, PPY tends to produce the most conductive end materials. The coatings usually are applied to full-width, long rolls of fabric or to fabricated items." (EeonTex (privat communication 2013)..

Being able to choose the starting fabric construction for certain properties (e.g., strength, porosity, stretch, thickness, etc.) and subsequently control the end surface resistivity with customized conductive polymer coatings allows one to prepare fabrics that possess a broad range of properties.

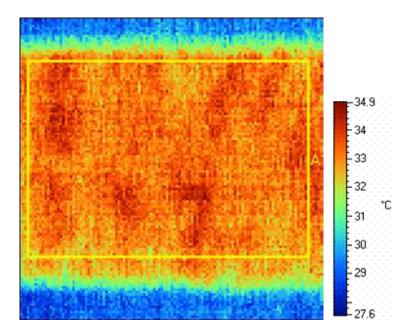


Fig. 14. *Demonstration of uniform, resistive heating of a conductively coated fabric in a flexible, surgical warming blanket. IR- temperature image* (EeonTex^(TM))

4.10 Resistive electric heating and Electric conductivity

When a voltage (electric potential), U (in volts V), is applied between two points on a material an electric field, E, is set up. Depending upon the electrode geometry and other factors the electric field may or may not be uniform. Electrically charged particles in the material will experience an electrostatic force in the direction of the electric field equal to the product of their charge and the electric field. If the charges are free to move, the force causes them to drift through the material. The rate at which the charge is transported is known as electric current, I. This is a system property whose material equivalent is the current density, J (amps per square metre A/m2).

Ohm's law, the result of empirical observations, states that current through a conductor due to drift is proportional to the voltage across it:

$$I = U/R \tag{1}$$

where R (in ohms Ω) is the resistance of the conductor to current flow. Ohm's law can also be expressed in terms of the material properties, field E and current density J as:

$$J = (1/\sigma)E = \sigma E, \qquad (2)$$

where ρ is the resistivity of the material ([Ω m]) and $\sigma = (1/\rho)$ is the conductivity ([Ω m⁻¹]). This implies that the mean velocity of the charged particles in the direction of the field, the so-called drift velocity, is proportional to the applied field. Materials display an extremely wide range of resistivity, possibly wider than any other physical parameter. Superconductors have resistivity $<10^{-25} \Omega$ m, typical metal conductors $\sim 10^{-8} \Omega$ m, semiconductors $10^{-4} \dots 10^{10} \Omega$ m, and insulators $10^{10} \Omega \dots 10^{20} \Omega$ m. Conductors exhibit a linear Ohmic current density dependence upon electric field up to high current densities, even up to the point where they fuse. In semiconductors Ohmic behavior is also observed at low fields. However, above a critical field the drift velocity, and hence the current, reaches a limiting value in semiconductors, resulting in an apparent increase of resistivity with the field and current is no longer proportional against voltage.

The basic unit of resistance measurement is the Ohm, and the basic unit of conductivity measurement is the Siemens. "..*Conductivity is the conductance as measured between opposite faces of a 1 cm cube of a given material. This measurement is in units of Siemens/cm. The corresponding terms for specific resistivity are ohm-cm."* (871CC Contacting Conductivity/Resistivity Sensors and Accessories -1997) The conductivity of a material due to charge carriers is dependent on the electric charge on each carrier, its mobility, and the concentration of charges. Charge carrier species are many, e.g., electrons, holes, protons, and ions, but normally one charge carrier is likely to dominate. Mobility is dependent on the charge carrier is likely to dominate. Mobility is dependent on the charge carrier's size and material structure, as in polymers, insulators, covalent bonding and crystal structures. The concentration of charge carriers may vary from near zero to more than one per atom (<10²⁹ m⁻³).

Conductivity in metals

Early attempts to explain the electronic configurations of the metals with ionized atoms in which the free electrons form a homogeneous free moving sea of negative charge failed. The principal objection to this theory was that the metals should then have higher specific heats than they do. The Pauli exclusion principle states that no two electrons occupying the same space can have exactly the same energy, although two electrons can occupy the same energy level if they have opposite spin. According to the band theory, any given metal atom has only a limited number of valence electrons with which to bond to all of its nearest neighbors. Extensive sharing of electrons among individual atoms is therefore required. This sharing of electrons is accomplished through overlap of equivalent energy atomic orbitals on the metal atoms that are immediately adjacent to one another. This overlap is delocalized throughout the entire metal sample to form extensive orbitals that span the entire solid rather than being part of individual atoms. Each of these orbitals lies at different energies. The orbitals, equal in number to the number of individual atomic orbitals that have been combined, hold two electrons, and are filled in order from the lowest to the highest energy until the number of available electrons has been used up. Groups of electrons are then said to reside in bands, which are collections of orbitals. Each band has a range of energy values that the electrons must possess to be part of that band. The highest energy band in a metal is not filled with electrons because metals characteristically possess too few electrons to fill it. The high thermal electrical conductivities of metals are then explained by the notion that electrons may be promoted by absorption of thermal energy into these unfilled energy levels of the band.

Conductivity in plastics

Typical polymers are a type of molecular crystals, albeit with extremely large molecules, and therefore have very strong intra-molecular bonding but only very weak, van der Waals, inter-molecular binding forces. The relatively simple band theory model must therefore be modified for polymers. The energy bands in perfect crystalline structures, like metals, have infinite periodicity in all directions and the nuclei interact with the three-dimensional electron wave in the same way in any unit cell. On the other hand, the long polymer chains are essentially one-dimensional.

Intrinsically conductive polymers contain long conjugated chains formed by double bonds and heteroatoms. "..*The polymers can be rendered conductive by modifying the p- and p-p-electron systems in their double bonds and heteroatoms. Charge carriers are electrons or holes originated by adding to the polymer certain blending or doping agents, which will serve as electron receptors or electron donors in the polymer*. "(US Patent US5662833 A Hannele Jarvinen, Jukka Laakso, Jan-Erik Osterholm ,1997) Thereby electron holes or extra electrons are formed in the polymer chain, enabling electric current to travel along the conjugated chain. 1 The conductive polymers were based on conjugated electron structures, so-called resonant structures. Typically the conductive polymer materials are semiconductors, say four decades less conductive than metal substances. Their light, moisture, and pH reactions were considered major disadvantages for the materials but, e.g., in sensors the features are more than welcome.[47]

Surface resistivity and surface resistance

Concepts of surface resistance and surface resistivity can be sometimes confusing. "...Dentitions of both terms can be found in many books and standards" (48 ASTM Standard D 257-99. Standard test methods for D-C resistance or conductance of insulating materials, 1999.; Michael B. Heaney. The Measurement, Instrumentation and Sensors Handbook, chapter Electrical Conductivity and Resistivity. CRC Press, 1999).

Surface resistance, Rs, is defined in all of the aforementioned literature sources as the ratio of a DC voltage U to the current, I_s flowing between two electrodes of specified configuration that are in contact with the same side of a material under test

$$I_s = \frac{U}{R_s}$$

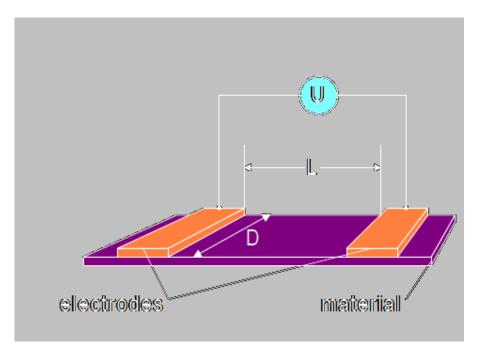


Fig. 15 Surface resistivity definition

Surface resistivity ρ_s , on the other hand, is determined by the ratio of DC voltage U drop per unit length L to the surface current Is per unit width D.

$$\rho_s = \frac{\frac{U}{L}}{\frac{I_s}{D}}$$

Surface resistivity is a property of a material. Theoretically, it should remain constant regardless of the method and configuration of the electrodes used for the surface resistivity measurement. A result of the surface resistance measurement depends on both the material and the geometry of the electrodes used in the measurement. "..*The physical unit of surface resistivity is Ohm* (Ω). *The legitimate unit of the surface resistance resistance also Ohm. Because of that surface resistivity and the surface resistance are often mixed up. In order to differentiate between the two, surface resistivity is often expressed also in Ohm/square* (Ω / sq.) which is not a valid unit from the dimensional analysis point of view.

Because the bulk resistance is multiplied with a dimensionless quantity to obtain sheet resistance, the units of sheet resistance are ohms. An alternate, common unit is "ohms per square" (denoted " Ω /sq"), which is dimensionally equal to an ohm, but is exclusively used for sheet resistance. This is an advantage, because sheet resistance of 1 Ω could be taken out of context and misinterpreted as bulk resistance of 1 ohm, whereas sheet resistance of 1 Ω /sq cannot thusly be misinterpreted. The reason for the name "ohms per square" is that a square sheet with sheet resistance 10 ohm/square has an actual resistance of 10 ohm, regardless of the size of the square" (Surface Resistivity and Surface Resistance Measurements, William A. Maryniak, Toshio Uehara, Maciej A. Noras 2013) (For a square, L=W, so Rs=R.).

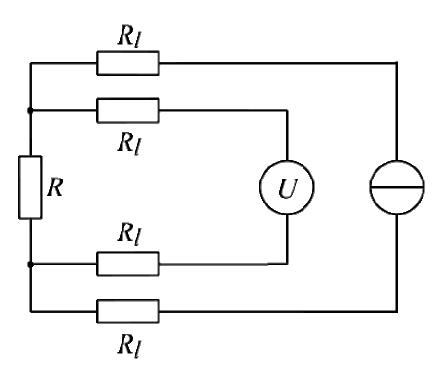


Fig. 16 low resistance measurement.

Resistive eclectic heating

"...Resistive eclectic heating employs methods of converting electric energy to heat energy by resisting the free flow of electric current. Electric heating has advantage to be precisely controlled to allow a uniformity of temperature within very narrow limits "(Chen, Dr. Mo-Shing Department of Electrical Engineering, University of Texas, Arlington. 2011 p.12) It is cleaner than other methods of heating because it does not involve directly any combustion and it is considered safe. Resistance heaters produce heat by passing an electric current through a resistance of conductive material the current pass through. Heaters of this kind have an inherent efficiency of 100% in converting electric energy into heat. The power of electric current is given by:

 $P = V \cdot I$

Where V - voltage applied and I - current. If the the Ohm's low is applied i.e. "...the current is directly proportional to the voltage and inverse proportional to resistance" (Ohms Law)

R:

$$I = \frac{V}{R}$$

The plover P will be:

$$P = R \cdot I^2$$

Since the efficiency of energy conversion in this case is 100%, The thermal power Q will be equal to input electric power:

$$Q = R \cdot I^2$$

This relationship is known as Joule's First Law. Joule heating, also known as ohmic heating and resistive heating, is the process by which the passage of an electric current through a conductor releases heat. "...*It was first studied by James Prescott Joule in 1841*" (*http://wpedia.goo.ne.jp/enwiki/Ohmic_heating*). It forms the basis for the practical applications involving electric heating.

"...Some times Joule heating is referred to as ohmic heating or resistive heating because of its relationship to Ohm's Law. It is now known that Joule heating is caused by interactions between the moving particles that form the current and the atomic ions that make up the body of the conductor ..."(

www.prema.coop/resistive_heating.html - 2010) Charged particles in an electric circuit are accelerated by an electric field but give up some of their kinetic energy

each time they collide with an ion. "..*The increase in the kinetic or vibrational energy of the ions manifests itself as heat and a rise in the temperature of the conductor. Hence, energy is transferred from the electrical power supply to the conductor and any materials with which it is in thermal contact.*" (http://english.turkcebilgi.com/Joule+heating -2008) Generally, the conductive polymer coatings follow the Ohm law

$$I = \frac{U}{R}$$

in moderate currents. The resistance is depends on temperature actually but for practical purposes we assumed it a constant in working temperature range. Having that fact I mind, we could control the energy supplied to the membrane surface varying the voltage applied and by choosing the distance between electrodes.

Assuming resistance to be constant, and varying the voltage, the thermal power will vary depending on square of applied voltage as follows:

$$Q = \frac{V^2}{R}$$

For the specific case of using surface resistance in calculations, the output thermal effect will strongly depend on geometry of terminals the voltage is applied. As it have been showed for parallel terminals the resistance will be will be:

$$R = \rho_s \frac{D}{L}$$

or

$$R = \rho_s \frac{D^2}{A},$$

where A is the surface area and L is the distance between terminals Then, form equation () the thermal power may be denoted as:

$$Q = \frac{V^2}{\rho_s \frac{D^2}{A}} = \frac{V^2 A}{\rho_s D^2}$$

The surface density QA heat in Watts per square meter may be expressed as

$$Q_A = \frac{1}{\rho_s D^2} V^2 \tag{1}$$

For particular voltage of 48 Volts and surface resistivity of 50 [Ω /sq] the heating power will be

$$Q_A = \frac{1}{50 \cdot 0.3^2} 48^2 = 512 [W \cdot m^{-2}]$$

For higher power levels, the eider surface resistance should be or distance between terminals should be decreased.

If a predefined power density is needed the equation (1) should be shoved against the electrode distance *D*:

$$D = V \sqrt{\frac{1}{\rho_s Q_A}} \tag{2}$$

Assuming $Q_A = 500W / m^2$

$$D = 48\sqrt{\frac{1}{50 \bullet 500}} = 0.3m$$

The similar dimensions have been used in experimental stand described further.

Practically, the terminals may be shaped as bus bars along the warp or along of weft of the fabric. Exact implementation of current supply circuit is a subject of further development an possibly patentable solutions. A simple possible circuit connectivity is shown on Fig. 17.

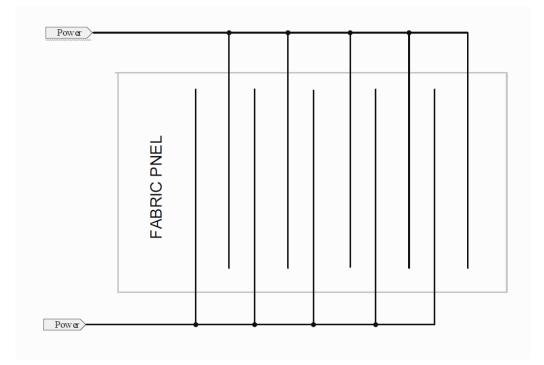


Fig. 17 Tape electrode connection.

Snow melting physics, thermal power requirements

Estimation of the surface density of energy needed for snow removal is not a part of this research. Nevertheless, we make some assumptions. Previously, it was shown that about 66 MJ was required to remove a 2.5 cm snowfall from 10 m2. of exposed surface. Thus, for a snowfall of 2.5 cm per hour (a considerable rate), 19 kWh would be required to clear the snow as fast as it fell. " ...*This heat rate is generally, considered excessive; design rates of 0.46 to 0.61 kW per m2per m2. are planned for areas that need to be cleared quickly, and up to about 0,46 kW per m2. for areas that can tolerate some accumulation during a snowfall."* (49. Newsletter/ETI Interface, January, 1997, Environmental Technology, Inc.)

Embedded in membrane eclectic heating allows operative snow removing which is the only scenario making possible reduction design loads (50).

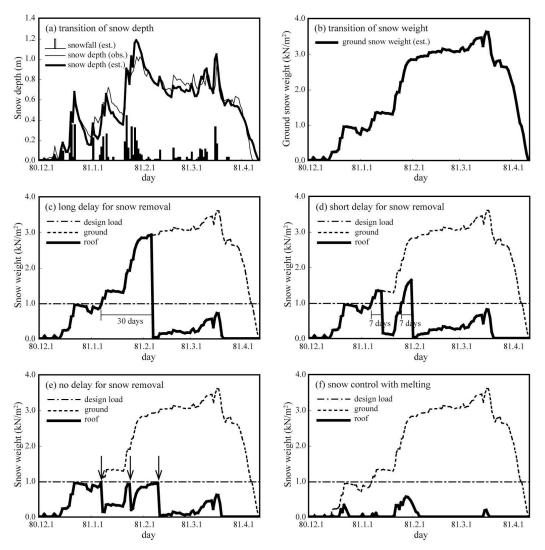


Fig. 18 Simulations of roof snow control (in case of Sapporo 1980-1981) [50]

Icing phenomenon, deicing techniques

De-icing is a procedure in which frost, ice, or snow is removed in order to provide clean surfaces. Anti- icing is a process that provides some protection against the formation of frost or ice for a limited period of time. There are various methods and systems that are used for de- icing and anti-icing. De- icing may be done by electrical heat and it is a preferable method in areas such aviation.

Targeting problem areas instead mass heating

The electric hating is highly flexible an allows precise control for maximum efficiency at minimum energy loses. The system performance may be greatly enhanced by embedding in membrane sensors based on smart polymers described in *smart polymers* section.

Chapter5 Experimental

5.1 Conductive polymer fabric properties

T-PI-65 Fabric data from supplier

EeonTex[™] T-PI-65 is a woven polyester fabric coated with a conductive polymer formulation.
This material is used in EMI shielding, artificial horizons and reducing radar reflection.
Parameters of EeonTex[™] conductive twill fabric
Part Number: EeonTex[™] T-PI-65
Approximate Construction: 70 ends/in x 55 picks/in
Yarn type: 2/150/34 polyester
Break Strength (warp x fill): 190 lb/in x 170 lb/in
Weight: 6.6 oz/yd² (223 g/m²)
Nominal width: 60 inches (1.52 m)
Thickness: ~20 mils (0.5 mm)

Surface Resistivity: 65 ohm/sq +/- 10% (50 to 105 ohm/sq per customer

specification)



Fig .19 Close view of conductive fabric specimen used in experiment.



Fig 20 Roll of conductive fabric specimen used in experiment.

5.2 Conductive polymer fabric sample preparation

The conductive polymer coated fabric sample have been provided by $\text{EeonTex}^{\text{TM}}$ The fabric sample was arranged for the experiment by sowing conductive buses (strips) according suggestions from fabric manufacturer. A conductive metallic thread has been used. Conductive strips are prepared using commercially available no insulated flat cable knitted by copper wires.

5.3 Experimental stand, materials and equipment used

The current source is a regulated AC/DC converter 24 - 42 V @ 10 Ampere. Applied voltage and current was monitored by voltmeter and amperemeter connected in simple circuit shown on Fig. 21:

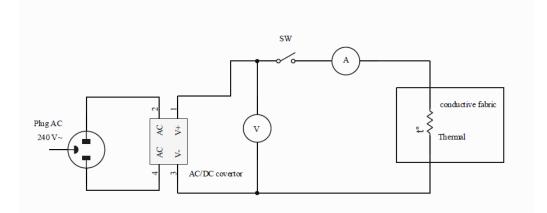


Fig. 21 Experimental stand electric circuitry.

The ambient temperature was measured by digital thermometer. The surface temperature was measured by thermal Imager "Fluke" TiR4.

5.4 Experimental data

Two experimental series was conducted at 24 and 42 V DC. The current direct reading was recorded after thermal equilibrium has been reached. There are averaged current readings at 24 and 42 V Table 3

Voltage [V]	Current [A]
24	0.35
42	0.61

The fabric shows larger than nominal resistance at increased temperature what is in accordance with positive temperature coefficient of resistance of conductive polymer. Rough calculation gains about 90 Ω square @ 50⁰ C. the power inserted in fabric is:

$$Q = UR = 24 \bullet 0.35 = 8.4W$$
,

or for 0.03 m³ the energy surface density is:

 $Q/A = Q_{A} = 8.4/0.03 = 280Wm^{-2}$

The actual temperature at thermal equilibrium in room conditions 20 $^{\circ}$ C, still air. Is about 50 $^{\circ}$ C (Fig. 27).

The second experimental serial was made at 42 V. Respective thermal power density is :

$$Q = UR = 42 \bullet 0.61 = 25.62W$$

 $Q/A = Q_A = 25.62/0.03 = 854Wm^{-2}$

5.5 Experimental data discussion

The theoretic power density calculated on nominal (provided by fabric supplier) surface resistance is significantly higher. Possible reasons are temperature dependence of resistance and additional contact resistance between conductive fabric and bus bars.

The positive temperature coefficient of resistance will as open loop thermo-regulator decreasing the thermal output at higher temperatures and preventing fabric overheating.

Equilibrium temperature is depends on radiative loses in first place if the convection and thermal conductivity are neglected. The power radiated by gray body according to Stefan–Boltzmann law is:

$$Q = A \varepsilon \sigma T^4$$

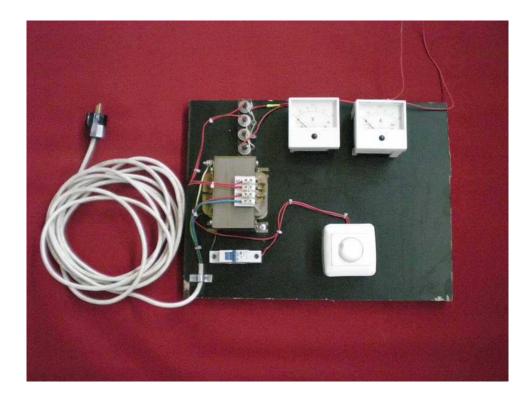
or

 $Q/A = \varepsilon \sigma T^4$,

where ε is the emissivity and σ =5.67x10⁻⁸Js⁻¹m⁻²K⁻⁴ is the Boltzmann constant. Solving against the absolute temperature we have.

$$T = \sqrt[4]{Q_A / \varepsilon \sigma}$$

It is very rough approximation and manipulation of emissivity is needed to attain accordance with experimental data.



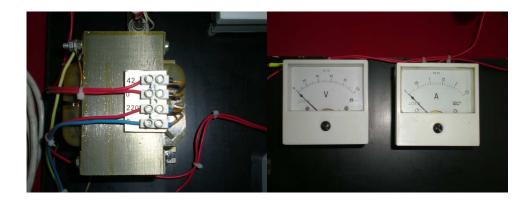


Fig. 22 The current source physical implementation.



Fig. 23 General view of current source and wired fabric sample.



Fig. 24 Wired fabric



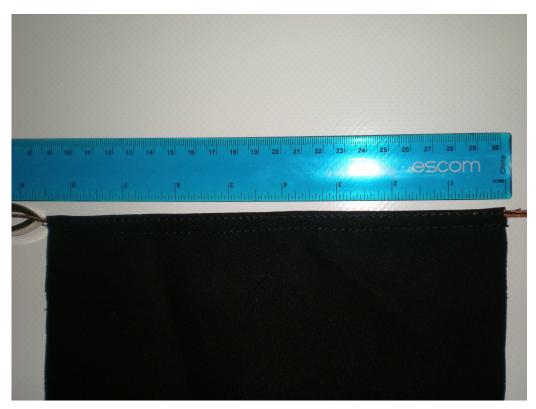


Fig.25 Wired fabric sample close view and dimensions.



Fig. 26 Current reading 0.4 A @ 24 V

Heater Formu	iia					
		9			Units	
Power _(density)	=	V ²		Power (density)	Watts/ft ²	
		R x L ²		V	Volts	
				R	Ohms/sq	
				L	ft	
Power (density)	=	V ²	Find <u>Power</u>			
		R x L ²				
				Length between bus bars (ft)	0.5	
				Resistance (ohms/sq)	65	
				Voltage (V)	24	
				Power (density)	35.44615	Watts/ft
R	=	V ²	Find <u>Resistance</u>			
		Power x L ²				
				Length between bus bars (ft)	0.5	
				Power (Watts/ft ²)	35.44615	
				Voltage (V)	24	
	_			Resistance	65.00001	Ohms/s
V	=	$(Power x R x L^2)^{1/2}$	Find <u>Voltage</u>			
				Length between bus bars (ft)	0.5	
				Power (Watts/ft ²)	35.44615	
				Resistance (ohms/sq)	65	
				Voltage	24	Volts
	_					
L ²	=	V ²	Find Length			
		R x Power	between bus			
				Voltage (Volts)	24	
				Power (Watts/ft ²)	35.44617	
				Resistance (ohms/sq)	65.00003	
				Length between bus bars (ft)	0.5	ft

Table 1. Tabulated fundamental data varying different parameters at 24V.

$P = A \epsilon \sigma T^4$			Power (density)	= V ²	Find Power			
				R x L ²				
P=Power (Watts)						Length between bus bars (m)	0.1524	
A=Area (m ²)						Resistance (ohms/sq)	65	
ε=constant (from 0.1 to 1.0)						Voltage (V)	24	
σ=5.67x10 ⁻⁸ Js ⁻¹ m	⁻² K ⁻⁴							
T=temperature (K)						Power (density)	381.5392	Watts/m ²
						Length	0.1524	m
Power	12.55385	Watts				Width of fabric	0.2159	m
А	0.032903	m ²						
3	0.6				Find Power			
σ	5.67E-08	Js ⁻¹ m ⁻² K ⁻⁴						
						Length between bus bars (ft)	0.5	
Т	52.42523	deg C				Resistance (ohms/sq)	65	
						Voltage (V)	24	
						Power (density)	35.44615	Watts/ft ²

Table 2 Theoretical power density and temperature at 24 V.

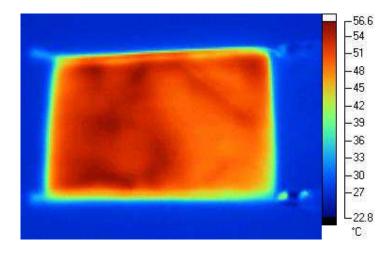


Fig. 27 Thermal-Image of polyester fabric with 24V made with thermal Imager "Fluke" TiR4

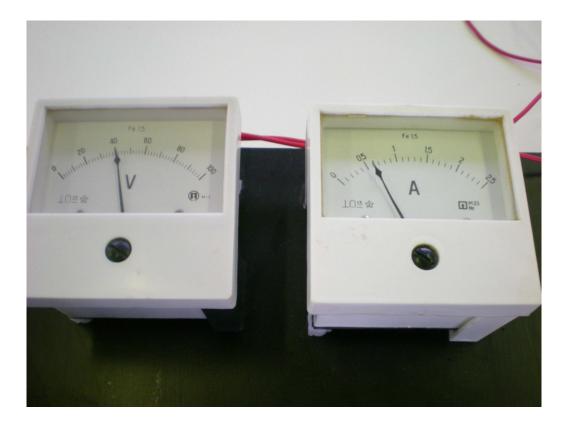


Fig. 28 Current readings at 42V.

Heater Formu	a				l Inita	
Power	-	V ²		Power	Units Watts/ft ²	
Power (density)	=	•		Power (density)		
		R x L ²		V	Volts	
				R	Ohms/sq	
				L	ft	
Power (density)	=	V ²	Find Power			
		R x L ²				
				Length between bus bars (ft)	0.5	
				Resistance (ohms/sq)	65	
				Voltage (V)	42	
				Power (density)	108.5538	Watts/ft
R	=	V ²	Find <u>Resistance</u>			
		Power x L ²				
				Length between bus bars (ft)	0.5	
				Power (Watts/ft ²)	108.5538	
				Voltage (V)	42	
				Resistance	65.00003	Ohms/s
v	=	(Power x R x L ²) ^{1/2}	Find <u>Voltage</u>			
		,				
				Length between bus bars (ft)		
				Power (Watts/ft ²)	108.5538	
	-			Resistance (ohms/sq)	65	
				Voltage	41.99999	Volts
. 2		<u></u>	Find Laws 4			
L ²	=	V ²	Find <u>Length</u> between bus			
	_	R x Power	between bus		40	
				Voltage (Volts)	42	
	-			Power (Watts/ft ²)	108.5538	
				Resistance (ohms/sq)	65.00003	
				Length between bus bars (ft)	0.5	ft

Table 3. Tabulated fundamental data varying different parameters at 42V

$P = A \epsilon \sigma T^4$			Power (density) =	V ²	Find Power			
				R x L ²				
P=Power (Watts)						Length between bus bars (m)	0.1524	
A=Area (m ²)						Resistance (ohms/sq)	65	
ε=constant (from 0.1 to 1.0)						Voltage (V)	42	
σ=5.67x10 ⁻⁸ Js ⁻¹ m	⁻² K ⁻⁴							
T=temperature (K)						Power (density)	1168.464	Watts/m ²
						Length	0.1524	m
Power	38.44615	Watts				Width of fabric	0.2159	m
A	0.032903	m ²						
3	1				Find Power			
σ	5.67E-08	Js ⁻¹ m ⁻² K ⁻⁴						
						Length between bus bars (ft)	0.5	
Т	84.61475	deg C				Resistance (ohms/sq)	65	
						Voltage (V)	42	
						Power (density)	108.5538	Watts/ft ²

Table 4 Theoretical power density and temperature at 42 V.

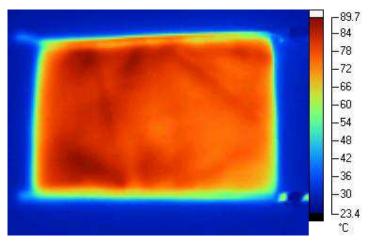


Fig. 29 Thermo-Image of polyester fabric with 42V made with thermal Imager "Fluke" TiR4

5.6 Further works

Further experiments in real winter conditions are scheduled for 2013/2014 winter.

Chapter 6

Conclusions

The conductive polymer coated textile is a promising new material in membrane structure design with multiple possible applications. Both sensors and actuators in smart material solution may be considered using conductive polymer coated textile.

Preferable method of coating is In Situ polymerization. Industrially, these polymerizations can be performed in textile dyeing equipment. The measured tensile and other physical properties of polypyrrole or polyaniline coated fabrics, on a number of different substrates, are virtually unchanged from untreated fabrics.

A long term stability may be achieved applying standard protective coatings like PVC, Silicon, Fluoropolymers etc.

Preliminary experimental data confirms feasibility of snow melting by electro conductive polymer coated fabric heater. Based on experimental data, a fabric with surface resistance 65 Ω = and voltage as low as 24 may be used to attain temperature difference of >30 $^{\circ}$ C. The thermal power density in this case is ~0.3 kW/m². It is about the power density reported for practical snow meting systems.

High reliable embedded electrical heaters may be produced by low resistive electro conductive polymer coating. The heat density would be large enough for snow melting systems.

Embedded temperature sensors would make snow melting system reactive and high efficient.

Bibliography

 Schlaich, Jörg ; Bergermann, Rudolf ; Sobek, Werner , *Tensile membrane* structures(1990) Bulletin of the International Association for Shell and Spatial Structures 31 (1990), S. 19-32

2. Nishi, Y., Nishikawa, K., Ishii, H., Analysis of snow melting process of the air supported structure -2, Summaries of Technical Papers of Annual Meeting, Vol. D, AIJ, pp.895 - 896, 1986.8

3. Shirakawa H, Louis EJ, MacDiarmid AG, Chiang CK, Heeger AJ (1977) J Chem Soc Chem Commun 579

4. Rupprecht, L.Conductive Polymers and Plastics: In Industrial Applications, Plastics Design Library, Elsevier Science, 2013

 Diaz A.F, Kanazawa K.K 1979 Electrochemical polymerisation of pyrrole. J. Chem. Soc. Chem. Commun 635

6. Diaz A 1981 Electrochemical preparation and characterisation of conducting polymers. Chemica Scripta. 17, 145–148.

 Kumar D, Sharma R.C 1998 Advances in conductive polymers. Eur. Polym. J. 34, 1053–1060.

 Otero T.F, Sansinena J.M 1995 Artificial muscles based on conducting polymers. Bioelectroch. Bioener. 38, 411–414.

9. Gao Z.Q, Zi M.X, Chen B.S 1994 The influence of overoxidation treatment on the permeability of polypyrrole films. J. Electroanal. Chem. 373, 141–148.

10. Armes S.P 1987 Optimum reaction conditions for the polymerization of pyrrole by iron (III) chloride in aqueous solution. Synth. Mat.

11. Duchet J, Legras R, Demoustier-Champagne S 1998 Chemical synthesis of polypyrrole: structure-properties relationship. Synth. Met. 98, 113–122.

12. Kumar D, Sharma R.C 1998 Advances in conductive polymers. Eur. Polym. J. 34, 1053–1060.

 Inzelt G, Pineri M, Schultze J.W, Vorotyntsev M.A 2000 Electron and proton conducting polymers: recent developments and prospects. Electrochim. Acta. 45, 2403– 2421.

14. Z.X.Ziang, X.M.Tao, "Smart Textiles" Textile Asia June 2001

 H.P. Haerri, and D Haenzi " UVabsorbers for Sun Protective Fabrics" International Textile Bulletin 5/2002 p 65-68 M.A. El-Sherif, J.M.Yuan and A. MacDiarmid, Fiber Optic Sensors and Smart
 Fabrics, Journal of Intelligent Materials Systems and Structures, (2000), 11(5): 351-359
 S. Ganjouhaghighi, Produce and Study the Hydrophilic and Photocatalytic Effect of

Au Dopped on TiO2 and SiO2 Films, M.Sc. Thesis, Sharif University (2007).

18. Richard P. Wool, Self-healing materials: a review, Soft Matter, 2008,4, 400-418

 Hayashi, "Properties and application of Polyurethane-based shape Memory Polymer" US-Japan workshop on Smart Materials and Structures held at University of Washington. Dec.3-4, 1995

20. S.Nato, Temperature-Sensitive Colouring Materials SWAY, Sen-1 Kikai Gakkaishi
(1989) 42 (9) 435-439 [D.A.Russel " Potential uses of Shape Memory films in clothing Technical Textile International October 1999, 17

21. Customer Info Nr 23 Sefar PowerMatrix, Sefar AG, CH-9410 Heiden, Switzerland

 Dr. Jamshid Avloni, Dr. Arthur Henn & Ryan Lau, Development and Applications of Nano- and Microscale Layers, Polymers in Electronics 2007, 30-31 January 2007 – Munich, Germany

23. Shirakawa, H., et al. 1977. Synthesis of electrically conducting organic polymers:24.Halogen derivatives of polyacetylene (CH)n. J Chem Soc Chem Commun 578.

24. Diaz, A.F., and J. Bargon. 1986. Handbook of conducting polymers, Vol. 1, ed. T.A. Skotheim, NY: Marcel Dekker, pp. 81–115.]

25. Andrieux, C.P., et al. 1991. Identification of the first steps of the electrochemical polymerization of pyrroles by means of fast potential step techniques. J Phys Chem 95:10158.

26. Diaz, A.F., et al. 1981. Electrooxidation of aromatic oligomers and conducting polymers. Electroanal Chem 121:355.

27. Wei, Y., J. Tian, and D. Yang. 1991. A new method for polymerization of pyrrole and derivatives. Makromol Chem Rapid Commun 12:617; Wei, Y., et al. 1991. Electrochemical polymerization of thiophenes in the presence of bithiophene or terthiophene: Kinetics and mechanism of the polymerization. Chem Mater 3:888.

28. Sonmez, G., P. Schottland, and K.K. Zong. 2001. Highly transmissive and conductive poly[(3,4-alkylenedioxy) pyrrole-2,5-diyl] (PXDOP) films prepared by air or transition metal catalyzed chemical oxidation. J Mater Chem 11:289.

29. Thomas, C.A., K. Zong, and P. Schottland. 2000. Poly(3,4-alkylenedioxypyrrole)s as highly stable aqueous-compatible conducting polymers with biomedical implications. Adv Mater 12:222.

30. Wang, P.C., Z. Huang, and A. MacDiarmid. 1999. Critical dependency of the conductivity of polypyrrole and polyaniline films on the hydrophobicity/hydrophilicity of the substrate surface. Synth Met 101:852.,39

31. M. Salmon, K. K. Kanazawa, A. F. Diaz, and M. Krounbi, A chemical route to pyrrole polymer films, J. Polym. Sci., Polym. Lett. Ed. 20:187).

R. V. Gregory, W. C Kimbrell, and H. H. Kuhn. Conductive textiles, Synth. Met.
2#:C823; H. H. Kuhn, and W. C. Kimbrell, Electrically conductive textile materials and method for making same, U.S. Patents 4,803,096 A989) and 4.975,317).

R. Jolly, C Petrescu, J. C. Thieblemont, J. C. Marechal, and F. D. Menneteau,Heating panels for accommodation obtained from textiles made electrically conductive by polypyrrole deposit, J. Coated Fabr.).

34. L. Maus, E. F. Witucki, and L. F. Warren. Process for applying an electrically conducting polymer to a substrate, U.S. Patent 4,696.835

R. B.Bjorklund and I. Lundstrom, Some properties of polypyrrole-paper composites,
 J. Electron. Mater. 13:211 (1984)

36. M. Ito, Y. Katagawa, H. Tajima, Y. Sawachika, M. Kimura, and I. Mizoguchi, Method of making electrically conductive composites, Jpn. Patent 62,275.137 91987)

37. M. Ito, Y. Katagawa, H. Tajima, Y. Sawachika, M.Kimura, and I. Mizoguchi, Method of making electrically conductive composites, Jpn. Patent 62,275.137 (1987)

38. K. Yasubaand M. Matsunaga, Manufacture of electrically conductive synthetic fiber textiles by coating with polypyrrole, Jpn. Patent 63,042,972 A2 (1988)

39. K. Yasubaand M. Matsunaga, Manufacture of electri- cally conductive synthetic fiber textiles by coating with polypyrrole, Jpn. Patent 63,042,972 A2 (1988).

40. H. H. Kuhn, W. C Kimbrell, G. Worrell, and C S. Chen, Properties of polypyrrole treated textiles for advanced applications, Tech. Pap.-Soc. Plast. Eng. 37:760(1991).

41. H. Munstedt, Ageing of electrically conducting organic matierals, Polymer 29:296 (1988).

42. B. Chen, J. Devaux, J.-P. Issi, and D. Billaud, The stability of polypyrrole electrical conductivity, Eur. Polym. J. 30:809 (1994).

43. J. C Thieblemont, J. L. Gabelle, and M. F. Planche, Polypyrrole overoxidation during its chemical synthesis, Synth. Met. 66:243 (1994).

44. W. A. Gazotti, Jr., V. F. Juliano, and M. A. De Paoli, Thermal and photochemical degradation of dodecyl- 97. sulfate-doped polypyrrole, Polym. Degrad. Stab. 42: 317(1993).
45. T. G. Vargo, J. M. Calvert, K. J. Vynne, J. K. Avloni, A. G. MacDiarmid and M. F.Rubner"Patterned Polymer Multilayer Fabrication by Controlled Adhesion of

Polyelectrolytes to Plasma-Modified Fluoropolymer Surfaces", Supramolecular Science, 2, 3-4, 169-174 (1995).

46. H. Kuhn and D. Child, in Handbook of Conducting Polymers, 2nd edition, T. A. Skotheim, R.L.Elsenbaumer, and J.R. Reynolds, eds., chap. 35, pp. 993-1013, Marcel Dekker, New York (1997).

47. Harlin A, Nousiainen P, Electrically and Optically Conductive Synthetic
PolymerFibre, 41. International Man-Made-Fibres Congress, 18–20 September 2002,
Dornbirn/Austria.

48. ASTM Standard D 257-99. Standard test methods for D-C resistance or conductance of insulating materials, 1999.; Michael B. Heaney. The Measurement, Instrumentation and Sensors Handbook, chapter Electrical Conductivity and Resistivity. CRC Press, 1999.

49. Newsletter/ETI Interface, January, 1997, Environmental Technology, Inc.

50. AIJ Recommendations for Loads on Building, CHAPTER 5 SNOW LOADS, 2006 Annual Meeting (Hokkaido) Annual Conference Architectural Institute of Japan

51. EeonTex (privat communication).

Books on conductive polymers:

- Edited by Hari Singh Nalwa, Handbook of Organic Conductive Molecules and Polymers, Volume 1 -Charge-Transfer Salts, Fullerenes and Photoconductors, Hitachi Research Laboratory, Hitachi Ltd. Ibaraki, Japan
- 2. Edited by TerjeA Skothenn et al., Handbook of Conducting Polymers Second Edition, MARCEL DEKKER, INC. 2998 N.Y.