IMPROVEMENT OF POLYPYRROLE COATING ADHESION
BY RADIO FREQUENCY PLASMA

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Submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

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I am the author of the thesis entitled

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Abstract

Polypyrrole (PPy) coatings offer wearer comfort and have applications in Electronic textiles. In this work, PPy was coated in solution, instead of incorporating conductive paths by weaving or knitting conductive yarns into the structure of the fabrics. Weak interfacial bonding with substrate and low conductivity is one of the major barriers for the applications of these coatings. To take these challenges, low pressure radio frequency plasma was used to functionalise the surface of polyester (PET), cotton and polyvinylidene fluoride (PVDF) substrates using different gases in plasma. PET and cotton were selected as they are commonly used as textile products and PVDF selected for its energy properties. A systematic study was conducted to understand how and why, plasma affects adhesion and conductivity of PPy coatings on these substrates. Both physical and chemical properties of substrate surfaces were studied using atomic force microscopy (AFM), scanning election microscopy (SEM), water contact angle measurements and X-ray Photoelectron spectroscopy (XPS) along with abrasion and electrical resistance measurements. Results show that addition of oxygen based functional groups (COOH, C=O etc.) on the textile substrate surface by plasma techniques increased wettability and surface roughness and were instrumental in improving adhesion and conductivity.

The first chapter provides background information on conducting polymers, polypyrrole coatings on textiles and presents the current challenges for commercial applications. An outline of existing conducting materials in the
The second chapter focuses on optimization of PPy coatings and thermal stability. Various concentrations of monomer, oxidant and dopant were employed and the durability of PPy coating was studied under heat. This study on coating optimization and thermal stability of PPy gave rise to a publication in “Fibres and Polymers” journal. In the third chapter, the plasma treatment was studied systematically, focusing on polyester fabric. PET fabric and PET thin film was treated with plasma using three different gases (argon, nitrogen and oxygen). The surface change is explored with different characterization tools to study the adhesion mechanism and conductivity enhancement. Results show that the PPy coating adhesion was enhanced in the case of oxygen plasma more than nitrogen and argon. The surface functionalization of PET proved to be more central than surface morphological changes. This work lead to a publication in “Plasma Processes and Polymers” and featured on cover page. In Chapter 4 oxygen plasma was further studied by varying coating conditions and these conditions were optimized for interfacial bonding enhancement with PET fabric and PET thin film. Cross sectional SEM imaging showed effectiveness of plasma adhesion improvement. This work resulted in a manuscript which is under review at the moment. The last chapter focuses on cotton and PVDF material. Scouring of cotton fabric incorporated electrophilic functional groups on the surface and adhesion was excellent even without plasma treatment. PVDF was treated by Ar and O₂ plasma gases for PPy coating adhesion. A combination of (Ar+O₂) plasma provided required functionalization and improved adhesion. A paper from this work is currently being finalized.


**Biography**

Tariq Mehmood was born on November 12\textsuperscript{th}, 1984 in Chiniot, Pakistan. He received his Bachelor of Science (honours) degree in Textile Engineering from National Textile University Faisalabad, Pakistan in 2007. After working as a textile engineer in a textile company in Lahore, Pakistan for a short period of time, he moved to Bahauddin Zakaria University, Multan Pakistan as a lecture teaching textile manufacturing subjects, here he was awarded scholarship by Higher Education Commission of Pakistan under faculty development programme and came to Australia to pursue his higher education. He joined the Ph.D. program at the Institute for frontier materials (then Institute for technology and research innovation) Deakin University Waurn ponds campus Geelong in July 2009.
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1. Introduction

1.1. Intrinsically conducting polymers

Intrinsically conductive polymers (ICP) are a class of materials with inherent ability to conduct owing to their chemical structure. ICPs have been a subject of intense research since their accidental discovery in 1977 due to their potential use in various fields. A key property of a conductive polymer is the presence of conjugated double bonds along the backbone of the polymer. The conjugated structure of the conducting polymer is reached simultaneously with polymerization of monomers via oxidation or reduction of electrons for the polymer backbone. A $\pi$-conjugated structure, alternating single and double bonds, with overlapping bond orbitals and the presence of charge carriers are pre-requisites for the ability of these materials for conduction [1].

Further conductivity enhancement can be made by doping, in which counter ions are introduced and incorporated in the material during the polymerization process. The dopant counter ions improve the intra chain charge transport within the polymer. The conductive polymers discovered to date have conductivities ranging from static dissipative ($\sigma = 10^{-7}$ S/cm) up to those of highly conducting materials [2] ($\sigma >1000$ S/cm), as shown in Figure 1.
The most commonly studied conducting polymers are polyaniline (PAni), polypyrrole (PPy), polythiophene (PT), polyacetylene (PAc) and poly (3, 4-ethylenedioxythiophene) (PEDOT).

1.2. Polypyrrole and its coating on textile

Intrinsically conductive polymers can be incorporated into textiles to render them conductive [3]. The conducting polymer selected for this work is PPy.
due to its ease of application, non-toxicity, good mechanical properties and high conductivity. The conductivity of the doped PPy can be tailored by adjusting synthesis parameters such as choice and concentration of oxidant and dopant, temperature and polymerization time [4] [5]. PPy can be deposited on textile materials by solution polymerization [6], vapor polymerization [7] and direct application methods using soluble conducting polymers [8]. Solution polymerization of PPy can occur in a number of organic solvents as well as in water, resulting in direct deposition of PPy on the surface of textile. Polymerization takes place simultaneously both on the substrate surface and in solution. The latter is referred to as bulk polymerization. In the case of vapor deposition, pyrrole monomer is applied in vapor phase to a pre oxidized fabric. The major benefit of the solution polymerization over the vapor polymerization method is low cost, ease of coating, and a possibility to make large samples. Solution polymerization method has been used in this work while employing water as solvent.

PPy coated textiles can be used for intelligent textiles [9], electrostatic charge dissipation [10], electromagnetic radiation absorption [11], heating [12] etc. Polypyrrole coated textiles are comfortable to human skin and environment friendly.

1.2.1. Chemistry of PPy polymerization

The stepwise polymerization of PPy is initiated at the most energetically favorable \( \alpha-\alpha' \) position by oxidation to yield a radical cation and can also be accomplished by reduction. Electrical conductivity values can be controlled by varying the type and amount of oxidant material [13]. Iron (III) chloride hexa-
hydrate \((\text{FeCl}_3)\) was used as oxidant material in this work. The process continues by coupling, accompanied by de-protonation and an electron oxidation of two free radical cations to form dimers. Combination of oligomeric radical cations forms higher molecular weight molecules (PPy) as shown in Figure 2

![Diagram](image)

**Figure 2: The growth of PPy on oxidation**

**1.2.2. Doping of polypyrrole**

In their native state, conducting polymers are semiconductors of wide band gap and a controlled increase of electrical conductivity over several orders of magnitude is possible through the doping process. The increase of the electrical conductivity by oxidation is typically based on incorporation of an anionic compound, normally called ‘dopant’, into the polymer matrix. The
mechanism of improvement in the electrical conduction via doping in PPy has been attributed to a redox interaction between the conducting polymer and the dopant. The original conjugated structure becomes disturbed with an abundance of ‘holes’ (p-doping), which become mobile upon influence of an external field and can generate electron flow in the material. The electric charge transport in conducting polypyrrole proceeds by charge hopping through two distinct conduction modes: intra-chain and inter-chain hopping. Many different dopants are available and bulky dopants are preferred due to their improved retention and stability as compared to small size anions (e.g. Cl⁻) [14]. If the dopant is large, its diffusion is prevented and it remains in the polypyrrole structure. Typical dopants employed in the PPy coatings on textiles are large organic molecules such as anthraquinone sulfonic acid (AQSA), dodecylbenzene sulfonic acid (DBSA), p-toluene sulfonic acid (pTSA), naphthalene di sulfonic acid (NDSA), benzene sulfonic acid (BSA), naphthalene sulfonic acid (NSA) and anthraquinone di sulfonic acid (AQDSA).

1.3. Substrate materials

PPy has been coated on various natural and synthetic textile substrates such as polyester[11], nylon lycra [15], cotton [16] and wool [17]. For this work polyester fabric was used as substrate. In addition to that; both cotton and poly vinylidene di-fluoride (PVDF) were also studied for PPy adhesion improvement.

We have used polyester, cotton and PVDF films as substrate material. Polyethylene terephthalate (PET) or Polyester is the most widely used
synthetic fibre and is available as filaments and fibres, both in woven and nonwoven form. PET fibre is strong due to its highly crystalline nature. It contains methylene, carbonyl and ester groups in the polymer chain and its highly crystalline nature makes it hydrophobic. PET fibres are available in a variety of types with special characteristics. These include different cross sectional shapes like round and multi-lobal [18]. PET fabrics have been coated with polypyrrole (PPy) by in situ polymerization [12]. Conducting polymer coated fabrics can generate heat when a voltage is applied to the fabric. These textiles can also be used as strain sensors, as they show cyclic decrease and increase in conductivity upon stretching and releasing.

Cotton is an important cellulosic textile fibre. The basic structural repeat unit is the cellobiose. Each ring unit contains three hydroxyls groups. These hydroxyls form hydrogen bonds within the macromolecule itself (intra-molecular) and between other cellulose macromolecules (intermolecular). The abundance of hydroxyl groups in cellulose molecules make cotton fibres, highly hydrophilic. Cellulose is highly crystalline and represents a tight packing of ordered chains wherein the hydrogen bonding is at a maximum [19].

Poly vinylidene di-fluoride (PVDF) is a highly non-reactive and pure thermoplastic polymer produced by the polymerization of vinylidene difluoride. PVDF is used generally in applications requiring the highest purity, strength, and resistance to solvents, acids, bases and heat and have applications as energy harvesting material due its piezo- and pyro-electric properties.
1.4. Optimization of reaction conditions

Electrical conductivity of PPy coatings is dependent on molar concentrations of reactants (pyrrole, oxidant and dopant) as well as reaction temperature, polymerization time, polymerization method, solvent and substrate [20]. The optimum molar ratios of reactants ensure the exhaustion of each chemical and improvement in overall process efficiency [21].

There are few earlier studies on optimization of PPy coatings on PET fabric. PET fabric was coated by PPy using FeCl$_3$ and NDSA [18] as oxidant and dopant and optimum molar ratios were reported [18]. Similarly, Kaynak et al. [22] studied the effects of concentrations of pyrrole, FeCl$_3$ and AQSA along with reaction time on the resultant electrical conductivity using PET fabrics. The reported optimum FeCl$_3$/pyrrole and AQSA/pyrrole molar ratios were 2.22 and 0.40 respectively. In this work, numerous PPy coating trials were carried out on PET fabric by varying reactant concentrations to determine the optimum concentrations of monomer pyrrole, oxidant FeCl$_3$ and the dopant pTSA. Results showed that molar concentrations of the reactants, polymerisation temperature and time had significant influence on the rate of polymerisation, ratio of bulk to surface polymerisation and electrical conductivity of the resulting fabric.

1.5. Long term stability of PPy conductivity

Durability is an important aspect in any technology that aims its transition from lab scale to the practical usage. The decrease in the electrical conductivity of PPy with time in ambient environment is referred to as aging. The degradation of conductivity can be caused by any process that changes or
hinders the charge hopping conduction mechanism. Different environmental variations like temperature, moisture, air and radiation distort chain continuity irreversibly [23] which leads to loss of conductivity. This decay was explained by quantum tunnelling of charge carriers [24].

Oxygen reaction with the main polymer chain or oxygen attack has been reported to be the major source of degradation and this is further substantiated by the studies showing better stability of PPy in inert atmosphere [25] [26]. Oxygen reaction imparts an irreversible loss of conjugation and conductivity [27].

The presence and concentration of different dopant molecules have an influence on the stability of PPy system during aging. In an earlier study [28], the conductivity of the highly doped PPy films was more stable with a lower rate of loss of conductivity compared to that of the lightly doped PPy films.

Electrical conductivity of PPy dropped slowly with time on exposure to atmospheric oxygen at room temperature, but the process could be accelerated by heating samples and measuring the decrease in conductivity as a function of time. Analysis of the kinetics of this process suggested a preliminary adsorption diffusion and final bulk diffusion mechanisms [29]. A stable interface between coated layer and atmosphere could be used as a barrier for the attack of oxygen and water [30].

Although aging leads to restrictions in use of PPy in some applications, at the same time, understanding the aging mechanism in PPy can help us forecast the lifetime and formulation of more stable products. There are a few accelerated aging studies available on PPy powder [31] and thin films [32] [33]. In this
thesis (chapter 2) a further study on the degradation of PPy coated PET fabric doped with pTSA is presented.

1.6. Interfacial bonding

The surfaces of two bonded materials in contact are held together by intermolecular forces present at the interface and examples of intermolecular forces are covalent, ionic, van der Waal, and hydrogen bonding. Nature of these forces determines the strength and life of overall bonding. Strong interfacial bonding is highly desirable for the durability of conductive coatings on textile materials. Conductive coating layer around fibre surface is depicted in Figure 3.

![Figure 3: Interfacial bonding between fibres and coating](image)

Weak interfacial bonding results in loss of coating material during normal wear and tear which in turn can lead to decrease in electrical conductivity and limit applications of these fabrics in commercial products. Adhesion dictates wash fastness of conductive coatings. Due to this, improving interfacial bonding strength has been an important research area. The main factors that
can also lead to adhesion failure of coatings on textile fibres are shrinkage, thermal or hygral expansion. So, the coating must have sufficient adherence to the textile to withstand these factors. Similarly both the surface chemistry and the topography of textile substrate are important for adhesion [34]. Surface properties can be evaluated by different methods in order to better understand the mechanisms governing the phenomenon of coating adhesion.

1.6.1. Mechanisms of Adhesion

The phenomenon of adhesion of one material onto another surface can be explained by taking into account the morphology, chemistry and surface mechanical properties of both materials at the interface. Currently there are a few theories of adhesion available as depicted in Figure 4 and a combination of these theories can be used to explain a particular case as no single theory can justify all cases. The mechanical theory describes that the coating material fills the voids or pores of the surface and bonding occurs due to interlocking of both adhering surfaces. The diffusion theory states that the adhesion occurs due to inter-diffusion of macromolecules across the interface and a number of chains crossing the interface between the two materials.
According to the electrostatic theory, when coating and substrate have substantial differences in their electronegativity, it is possible that electron transfer will occur, creating an electrostatic double layer at the interface. The strength of the adhesive bond comes from the force necessary to move the charged surfaces away from one another and lastly chemical bonding theory states that the adhesion strength is governed by the chemical bonds across the interface. Choice of adhesion theory depends on the nature of surface (morphology, charge, chemistry) and the structure of the textile. For example, in the case of smooth filament yarns, mechanical adhesion is much lower than yarns made of staple fibres [35].

Conductive coating can also be applied as dispersion in a binder, which is made of long chain macromolecules and produces a three dimensional network over textile upon curing. One of the main disadvantages of using binders in the application of conductive coatings to textile materials is the possible hindrance to charge transport.
1.6.2. Improving interfacial bonding

In order to improve the adhesion for a given coating material, different treatments can be carried out onto substrate surface. Intimate contact between adhering materials is a necessary condition for good adhesion but it is not sufficient on its own. The main techniques used for tailoring both surface chemistry and morphology are plasma and chemical, while use of mechanical and combustion methods are not possible due to fineness of textile fibre.

1.6.3. Chemical treatment

Chemical surface treatments of textile fibres have been widely used in industry. The presence of different functional groups at the interface can favour the chemical interactions. Surface oxidation of fibres serve mainly to remove the weak surface layer and roughen the surface, thereby enhancing the mechanical interlocking between the fibres and the matrix [36]. Meanwhile, chemical modification, particularly the production of carbonyl, carboxyl, and hydroxyl groups on the fibre surface occurs, which may also contribute to the adhesion of the coating to the fibre surface. Pre-treatment of PET with aqueous sodium hydroxide was observed to result in increased amount of deposited Polypyrrole (PPy) on the fibre surface [37] [38], this lead to improved electrical conductivity and heat generation capacity for the PPy coated PET fabrics. However, chemical treatment is time consuming, generally results in fibre strength reduction and environmental pollution [36].

1.6.4. Plasma treatment

Plasma is a surface sensitive dry technology and is intrinsically environment friendly. It can save large quantity of water, chemicals and energy without
producing toxic waste [40]. The plasma treatment changes chemical and physical structure of substrate surface and it can incorporate specific functional groups on the surface [34]. There are different methods to generate plasma by gas discharge. The most common methods used for textile surface modification are glow discharge, corona discharge and dielectric barrier discharge (DBD). There are two broad categories of plasma i.e. low pressure and atmospheric pressure. Only cold plasma (in which electrons get energy directly from the field and can have a much higher temperature than the gas) is suited for textile applications to avoid thermal damage of materials during the process. Glow discharge, both inductively coupled and capacitively coupled is generated at low pressure, while corona and dielectric barrier discharge are generated at atmospheric pressure. The other plasma parameters are process gas, treatment time, gas flow rate, plasma frequency and power. There are different types of power supply available to generate plasma, namely low frequency (50–450 kHz), radio frequency (RF) (13.56 MHz) and microwave (MW) (2.45 GHz).

We used inductively coupled RF source (13.56 MHz), throughout this work and detailed schematic diagram is shown in Figure 5 used here [41] as well. The reaction chamber, enclosed in a Faraday cage, was a cylindrical glass tube (30 cm long, 15 cm in diameter). The RF power generated the plasma via an external antenna around the inlet side of the chamber, leaving the rest of the chamber as the afterglow area. This antenna with an auto RF matching network could transfer 100% of the input RF power into the plasma. Samples were placed in the plasma source area.
The plasma used in this work is a partially/weakly ionised gas generated by an electric or electromagnetic field and it is electrically neutral (the number of positive charges is equal to the number of negative charges). In this weakly ionised gas, the electrons mostly collide with neutral molecules and atoms resulting in ionisation, excitation, and dissociation (gas phase reactions) [42]. During these reactions, various reactive species are generated, including charged particles (positive and negative ions and electrons), free radicals, neutral particles, and UV photons. These species react with the material surface and the surface/interface is changed.

Any gas can be used in plasma including vapour of a monomer, containing a desired functional group. One key issue is design of parameters, and how to select and control the reactive species for a specific application. All this requires a deep understanding of plasma physics, plasma chemistry, and material science [42].

There are different types of plasma processes that can take place on the surface depending on the external parameters and process gas selection such as cleaning, surface activation/functionalization, deposition and grafting. In
the cleaning process mostly inert (Ar, He) gases are used in the plasma chamber. The plasma cleaning process removes surface contaminants such as oils and dirt. In the activation/functionalization process, textile surface is treated with a reactive gas (O₂, N₂, NH₃ etc.) in plasma, which results in the incorporation of different moieties onto the textile surface and hence changes the surface chemistry. Similarly plasma can be used for material deposition by grafting.

There are many studies in the literature on the improvement of adhesion of various substrates using plasma. Armagan et al. [43] studied surface modification of polypropylene fabric by low pressure RF oxygen plasma treatment. The surface roughness of polypropylene (PP) fibres increased with the increase in plasma power and treatment time. XPS analysis showed that oxygen plasma treatment of polypropylene fibre surface led to a significant increase in atomic percentage of oxygen which gave rise to adhesion strength enhancement as confirmed by the Peel test. Shahidi et al. [44] compared oxygen and nitrogen gases in plasma, in relation to adhesion of copper coatings on PP fabric for antibacterial application. Improvement in adhesion was confirmed by both abrasion resistance and antimicrobial tests. In the field of composites, there are several examples of adhesion improvement of PET filaments with polymer and rubber matrix [45] [46] [47] [48] by plasma treatment, having applications in automotive industry. Different process gases (air, oxygen and nitrogen) resulted in formation of various chemical groups after plasma treatment and these groups subsequently led to covalent bonding by acid-base interactions [49].
Chemical modification of PET substrate surface after plasma treatment has been investigated. Costa et al. [50] studied low pressure RF plasma on PET fabric using different gases (O₂, N₂, CH₄, H₂) in plasma in order to investigate the influence of plasma composition on the surface characteristics, while Imor et al. [51] employed (N₂, N₂ + H₂O, N₂ + acrylic acid, CO₂) gas combinations in DBD to improve adhesion between sized PET fabric and polymer coatings. CO₂ gas resulted in improved adhesion as confirmed by the peel test. The PET fabrics treated with different plasma gases exhibited different morphological and hydrophilicity changes [51] [50] in both studies.

Oh et al. [52] studied the effect of plasma treatment on the surface of nylon-6 fabric for the adhesion and conductivity of PANi using oxygen, ammonia, and argon as process gas. Oxygen plasma added polar functional groups such as -OOH and -OOOH on the nylon 6 surface. Oxygen plasma treated fabrics showed the highest conductivity and it was more stable with respect to washing and abrasion than the same fabric without plasma pre-treatment.

The very first work on PPy adhesion was carried out by C.L. Heisey et al. [53] in 1994, using nylon fibres as substrate and interfacial strength was measured by micro-bond test. J. Molina et al. [54] treated polyester fabric with plasma by DBD using inorganic dopant (PW₁₂O₄₀³⁻), resulting in increased surface roughness and improved resistance to abrasion of the PPy coated substrate. Recently, Montarsolo et al [55] reported improved adhesion of PPy coating on PET with low temperature plasma treatment using oxygen and argon. Enhanced adhesion was confirmed by abrasion tests and subsequent surface resistivity and colour measurements. Aging of plasma treated surface was suggested to occur due to reorganization of surface groups or chains to
minimize total system energy [34]. The surface group reorientation seems to be reversible and depends on environmental conditions. In a hydrophobic environment (air) the surface groups tend to be hydrophobic whereas in a hydrophilic environment, such as water, the surface groups tend to be hydrophilic. Thus, it is very important to control the storage conditions (temperature, humidity) before and after treatment in order to obtain the desired final adhesion properties [34]. Thiophene and PPy have been successfully plasma polymerised using continuous and pulsed plasma techniques, however the grafting was non uniform and resulted in poor electrical conductivity [56] [57].

The major findings of non-thermal plasma surface modification and their relevance to textile adhesion are reviewed by Morent et al. [58]. During the aging process, the induced polar groups may re-orientate from the surface into the bulk of the material and mobile species diffuse from bulk towards the surface of material with time. This reorientation processes is dependent on surface treatment, crosslinking degree, temperature and environment (humidity, air) and results in an increase in the contact angle, thus it can change the adhesion and surface properties [34]. So it is important to coat plasma treated fabric soon after the plasma treatment in order to avoid the aging effect. Although plasma treatments generally enhance adhesion, however longer exposures can degrade the fibre, thus reducing the adhesion [59]. Takke et al. [60] studied the relationship of molecular weight of coatings with adhesion. Poly (ethylene glycol) with three different molecular weight variants deposition on Air-plasma treated PET fabrics surface. Washing
fastness test confirmed the relationship of molecular weight with adhesion, as high molecular weight PEG (1500 g/mol) gave the best fastness results.

1.7. Surface energy, wettability and roughness

The surface energy is the sum of all intermolecular forces present on the surface of a material and is measure of the degree of attraction or repulsion of a material surface for another material. When the substrate has a high surface energy, it tends to attract. Wettability of a textile surface is the measure of attraction or repulsion for liquid and is measured by water contact angle ($\theta$), which is the angle made by a liquid drop on a solid surface as shown in Figure 6. Young’s equation relates the solid/liquid contact angle with the solid/vapour ($\gamma_{SV}$), solid/liquid ($\gamma_{SL}$), and liquid/vapour ($\gamma_{LV}$) interfacial tensions [34].

\[ \gamma_{LV} \cdot \cos \theta = \gamma_{SV} - \gamma_{SL} \]

Figure 6: Schematic of water contact angle

The interfacial processes at the solid/liquid interface are important for coatings carried out in a liquid medium and these interactions across the interface can be physical or chemical in nature.
The plasma treatment can introduce water compatible functional groups (–COOH, –OH and –NH₂) on the textile surface, which speeds up wettability.

Figure 7: Wettability and surface energy (www.astp.com)

Water contact angle, which defines the wettability of one material, can also be used to find the surface energy of substrate (Figure 7). Substrates with a low surface energy are very difficult to wet and result in poor adhesion with coating material and vice versa. Similarly adhesion and surface energy are related to one another. Sometimes wettability of textile surfaces is monitored by indirect methods such as absorption time and wicking for porous textile structures that immediately absorb the liquid drop.

Surface roughness plays an important role in improving adhesion according to mechanical theory of adhesion. Many insect and lizard species possess adhesive organs on their feet that allow them to adhere to a wide variety of surfaces. An important aspect in adhesion is the true area of contact, which is
increased by the surface roughness [61]. Jang et al. [62] saw a linear increase of carbon fibre surface roughness up to 3 min of treatment time, however this trend changed for longer exposures. In addition to interlocking, added micro and nano pores on the substrate surface can improve interfacial bonding [63] due to availability of increased bonding sites.

1.8. Textile surface analysis techniques

1.8.1. Surface characterization

Plasma treatment induces chemical and physical structure changes on the textile surface in the near surface regions. Therefore, characterisation of plasma treated textiles requires techniques that will assess the surface properties in the near surface regions. There are two categories of techniques employed for characterization. Some techniques assess only surface physical and topographical properties and others only surface chemical properties [64].

Scanning electron microscopy (SEM) has been extensively used in analysis of the surface characteristics of plasma-treated textile fibres and woven materials. The information obtained from SEM is normally qualitative, simply providing an image of the surface at high magnification and good depth of field. Similarly, Atomic force microscopy (AFM) is frequently used for analysis of plasma treated surfaces. It contains a scanning probe, with a tip at the end of a cantilever. The probe scans in the very near surface region of a surface and the cantilever tip is made to approach the surface at a given rate. As soon as it contacts the surface, the cantilever deflects and this deflection is recorded as a function of the tip position relative to the surface. AFM is a quantitative as well as qualitative technique as compared with SEM. AFM can give us extra
numerical information e.g. line and area profiles and softwares can calculate root mean square roughness values from this information for further comparative analysis of various samples.

X-ray photoelectron spectroscopy (XPS) is a very powerful surface analysis technique in which chemical characterisation can be done in near surface regions of top 1–3 nm of the surface using etching by X-ray beam in an ultra-high vacuum condition. Fourier transform infrared (FTIR) can be used alongside XPS to provide a comprehensive analysis of how the surface chemical structure of the polymer is changed as a result of plasma treatment. The vibrational spectroscopy enables important information regarding the presence of important functional groups with a specific wavelength in the spectra [65].

1.8.2. Electrical resistivity

Surface resistance is used mostly for reporting electrical performance of a textile fabric and is an important performance indicator for conductive coatings on textiles. It is the ratio of DC voltage to the current flowing between two electrodes in contact with one side of fabric. On the other hand, surface resistivity is the ratio of voltage per unit length, to the surface current per unit width and is normally considered constant and ideally independent of measurement technique [66]. Conductivity and resistivity are both interchangeable for known configurations and heavily depend on the geometry, configuration and mechanical properties of fabric.

Conductive polymer coatings on textiles cannot be characterized by the volume resistivity due to the thickness of the conductive coating being much
smaller than the thickness of the textile substrate and due to geometry. The deformability of fabrics, intimacy of electrodes of the measuring device with the fabric and measuring environments can affect surface resistivity and its measurement.

The surface resistivity of the conducting fabrics can be measured by either two or four probe measurement setup.

Two probe measurement methods involve a configuration of two rectangular electrodes (parallel) (20 x 30 mm) or circular ring probes, which are pressed against the fabric surface with a 10 N pressure as shown in figure.

![Figure 8: Electrical resistance measurement setups. a) four probe b) concentric ring probe c) two probe [67] [68]](image_url)

In the four probe method, outer probes are used for the current supply, while the potential drop between the inner electrodes are measured. The four probe method provides results which are more reliable because it is not sensitive to contact resistance issues [69]. A comparison of surface resistivity is difficult when coating is carried on different fabric structures and there is a variation in measurement and coating method.

1.9. Interfacial bonding strength measurement
There are two categories of interfacial bonding strength measurement methods for coatings on textiles. First category include such methods, which are valid only, if the strength of the coating film exceeds the adhesive bond to the fabric; examples are grab test, cut strip test and Peel test (T-Peel, 90°, 180°)[70]. The coating of strip is separated from the backing using diagonal cut and knife. Second category includes methods which are valid for cases in which the coating is not sufficiently strong to be stripped off from the fabric or is are very thin (PPy coatings on fabric); Examples are bending [71], scratch [72] and abrasion [73] test. Similarly there are several interfacial adhesion strength measurement methods available for fibre polymer matrix based on tension, compression, pushing and pulling forces [74] as shown in Figure 9. One or more of these methods can be configured to server the purpose of investigating interfacial strength of PPy on fabric.

![Methods of fibre polymer matrix interfacial strength measurement](image)

Figure 9: Methods of fibre polymer matrix interfacial strength measurement [74]
In this work, abrasion test (0) and cross sectional examinations of textile fibre and PPy coating interface was employed to assess and compare the adhesion of coatings.

1.9.1. Abrasion resistance

The resistance of textile materials to abrasion is generally an indicator of wear performance or durability. Abrasion resistance is stated in terms of the number of cycles on a specified machine, using a specified method and is greatly affected by the conditions of the tests, such as the nature of abradant and the pressure between the specimen and abradant. It also depends on the inherent mechanical properties of the fibres, structure of the yarns and construction of fabric as well as on coatings. Good interfacial bonding enables fibres to hold conductive coatings despite repeated distortion during abrasion cycles. The crimp of the yarns in the fabric affects whether the warp or the weft is abraded the most [75].

Martindale abrasion tester is normally used to give a controlled amount of abrasion between two fabric surfaces in continuously changing directions. In the test, circular specimens of textiles fabric samples are abraded under constant weight. After the abrasion test, abrasion resistance can be evaluated and compared by visual appearance.
Figure 10: schematic of Martindale abrasion tester

The basic schematic of apparatus is shown in Figure 10. A circular cut sample is mounted in the sample holder. A spindle is inserted through the motion plate with weight placed on top of it and sample holder on the other side, while abradant fabric is securely mounted in abradant holder.

1.10. Conductive materials

A range of materials other than conductive polymers are under continuous investigation for the electronic functionality of textiles. The preferred properties of materials for electronic textiles vary greatly with the application area [76]. Some of the requirements are given in Table 1, Appendix 1. Few examples are metals and carbon based materials. Metals can be incorporated on textile using electroplating, coating and blending [77] in the form of metallic fibres and metal paste. Similarly metal coated fabrics (FlecTron) can be used for signal receiver [78]. In case of metal coated textiles, creasing the fabric can result cracks in the paste coating at the location of the bent [79].
Metals also result in irritations of the skin. Carbon fibres, graphene and carbon nanotubes are relatively newly discovered materials which can be used in conductive applications. CNTs were applied to fabric in different ways like coating on yarn [80], extrusion in a polymer, electro spinning and vacuum filtration[81] [82] and even a small amount of CNTs can result in high conductivities demonstrated in [83] due to its size. However, one of the major problems is the agglomeration of CNTs. Carbon nanotubes are carcinogenic too due to small size [84]. These can be dispersed by using surfactants to a certain extent. There are different techniques available to integrate conductive material into the nonconductive base at fibre, yarn and fabric level [84]. Some of the examples are depicted in Figure 11.

Figure 11: Integration of conductive material in textiles. a) blending [85], b) braiding [86], c) electro spinning [87], d) core-shell [88], e) surface coating [89], f) weaving [90], g) sewing [91], h) printing [92], i) solution dipping [83]
Conductive textiles conduct electricity and can be used for sensing and data transmission. Main applications of conductive textiles are found in Electronic textiles (e-textiles) also known as smart textiles; which are wearable clothing solutions with embedded electronics, computing and communication functions. These textiles perform intelligent applications in a wide range of possible scenarios (Figure 12) in addition to traditional function of climatic protection and cover. Textile based sensors have many advantages including ease of use, easy integration in daily life and round the clock operation [93].


Many different sensors can be integrated into these clothing including Pressure [99], Strain [100], temperature, chemical etc. These sensors when integrated into clothing help in training athletes, rehabilitation of patients, and constant monitoring of physiological state.
1.11. This work

In this work, adhesion of polypyrrole on PET, and cotton fabrics and PVDF films was investigated. A systematic study has been carried out using various gases to improve the adhesion of PPy coating and employing reference model surfaces. The changes in wettability, surface chemistry, surface morphology and roughness were studied in conjunction with adhesion and conductivity data. The main objective of this work is to improve adhesion and most importantly find the main factors that enhance adhesion. PPy coating optimization with a view to improve its thermal stability was also studied.

1.12. References


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2. Optimization of polymerization conditions and thermal degradation of conducting polypyrrole coated polyester fabrics

2.1. Abstract

PET fabric is coated with conducting polypyrrole (PPy) by oxidative polymerization from an aqueous solution of Pyrrole using ferric chloride hexahydrate (FeCl₃) as oxidant and p-toluene sulphonate (pTSA) as dopant. The optimum concentrations for monomer, oxidant and dopant were found to be 0.11, 0.857 and 0.077 mol/l respectively, which yielded a conductive fabrics with sheet resistance as low as 72 Ω/sq. PPy fabric gained sheet resistance less than one order of magnitude when aged for 18 months at room temperature. The stabilizing effect of the dopant pTSA against thermal degradation was demonstrated; the un-doped samples reached resistivities of around 40 kΩ, whereas doped samples reached less than 2kΩ at the same temperature and time.

2.2. Introduction

Conducting polymer polypyrrole (PPy) has been extensively studied for potential application in electronic textiles. PPy can be coated on textiles by solution or by vapour phase polymerization with a wide range of electrical conductivities. Simultaneous doping and polymerization of the pyrrole monomer occur on fabric, which give an oxidized polymer with a delocalized positive charge on the conjugated π-bond system. These fabrics can be used
as antistatic packing, capacitors, heating textiles, sensory fabrics and in intelligent applications [1].

A key drawback of conductive polymer coated fabrics is the decline in electrical performance with time due to aging, so one of the most important requirements of conducting polymers is the stability of conductivity [2]. Stability of electrical performance of PPy coated fabric depends on coating method, choice and concentrations of oxidant and dopant. Lower sheet resistance ($R_s$) and improved electrical stability are important for practical applications of PPy coated fabrics. Polyester was prove to be a better substrate than wool fibres [3] [4] in terms of surface resistance values and durability of coating and giving rise to deeper shades of black coating, which is indicative of a higher conductivity fabric surface.

There have been a few publications on the kinetics of electrical aging of chemically or electrochemically prepared free standing polypyrrole film [5] [6]. However, there is little work on determination of the optimum concentrations and decay of electrical performance of conductive polymer coated fabrics with temperature and time. In this work PPy coated PET fabrics were characterized with respect to optimization of reactant concentrations, accelerated aging tests and microscopic observations.

### 2.3. Materials & Methods

Plain weave 100% polyester (PET) fabric was used as the substrate material. The PET fabric was 168 grams per square meter and had 56 ends per inch in warp and 54 picks per inch in weft direction and was purchased from Spotlight Inc. Australia.
Monomer pyrrole (Py), oxidant iron chloride hexa hydrates (FeCl$_3$.6H$_2$O) and dopant p-toluene sulphonic acid mono hydrates (pTSA) were purchased from Sigma Aldrich Australia.

2.3.1. Polymerization

Fabric was cut into a square of 200 mm and washed in 1% non-ionic detergent (Hydrapol TN450) at 40°C for 10 min and then rinsed with deionized water for 5 mins so as to remove any oil or impurities. The cleaned fabric samples were conditioned under constant relative humidity (65 ± 2%) and temperature (20 ± 2°C) for at least 24 h prior to polymerization. Polypyrrole was coated on fabric by solution polymerization. Deionized water, dopant and pyrrole monomer were mixed in polymerization chamber, where the fabric sample was immersed in the solution. The reaction was carried out for two hours at room temperature with occasional stirring. The fabric was then washed with Luke warm water and subsequently dried at 25±2°C overnight in a fume hood. The samples were conditioned at 20±2°C at 65±2% humidity for 24 hours prior to measurements.

2.3.2. Surface Resistance

Resistance measurements were performed on all samples by a method similar to that reported in [7]. Two square copper electrodes (measuring 25.3 mm×25.3 mm) separated by 25.3 mm were placed on the sample (measuring 25.3 mm×50.60 mm) and pressed onto the fabric by constant force applied by a set of clamps. Resistance measurement were performed on samples at room temperature and then under fixed temperatures of 60, 80, 100 and 120°C as a function of time using Agilent 34401A digital multimeter, which was
connected to computer to record real time resistance values over time in aging experiments.

\[ R = R_s \left( \frac{l}{w} \right) \]

Here \( R, R_s, l, w \) is the resistance in ohms, ohms/square, the distance between electrodes, and the width of the each electrode respectively. As \((l/w)\) ratio was 1, the sheet resistance \( R_s \) was directly measured in ohms/square.

2.3.3. Scanning Electron Microscopy (SEM)

Scanning Electron Microscope Supra 55 VP was used to study the morphology and roughness of samples. Samples were gold coated prior to viewing. For cross sectional images, PPY coated samples were embedded in Polyester resin and then sliced with microtome.

2.4. Results and Discussion

The PPY deposition onto polyester fabrics was studied in detail to obtain optimum molar concentrations to produce highly conductive fabrics. In all experiments fabric to liquor ratio was fixed at 1:100 and polymerization time was set as 2 h. Three samples were prepared at each concentration and standard deviations were calculated to measure spread of results. In the first set of experiments chemical reagent concentrations to liquor ratio was studied. The molar ratios of monomer to oxidant and monomer to dopant were 1:3.53 and 1:0.34 respectively [8] [9]. Monomer concentrations were taken as reference and plotted.
In the second set of experiments molar concentration of FeCl$_3$ was varied, while the monomer and dopant concentration remained unchanged at 0.11 and 0.389 mol/l.

In the third set of experiments molar concentration of dopant was varied while oxidant and monomer remained at 0.857 and 0.110 mol/l respectively. The results of these experiments are shown in Figs. 1-3.

Sheet resistance decreased with increasing concentrations of reagents in the polymerization chamber due to increased deposition of polymer on fabric as shown in Figure 13. The optimum concentrations were reached at a monomer concentration of 0.14 mol/l.

![Figure 13: The effect of monomer concentrations in coating solution on PET fabric sheet resistance, oxidant to monomer and dopant to monomer molar ratios are 3.53 and 0.34 respectively](image)

At this point saturation occurred and no further decrease in resistance values was observed beyond this point. However, increasing concentrations beyond
0.14 mol/l contributed to the bulk polymerization of PPy, which subsequently deposited on the substrate. These dendritic depositions are loosely bound to the fabric surface and mostly can be removed by washing.

Figure 14: The effect of oxidant concentration on PET fabric sheet resistance; monomer and dopant concentrations are 0.11 and 0.389 mol/l

As seen in Figure 14, $R_s$ decreased rapidly by increasing molar concentration of oxidant in the solution and reached a plateau (near 0.857 mol/l). The effect of dopant concentration on the fabric resistance can be seen in the Figure 15 where $R_s$ decreased with the increase in dopant concentration until a plateau is reached at a concentration of 0.077 mol/l. Results indicate that the oxidant FeCl$_3$ had a more significant influence on the resulting fabric conductivity than the dopant pTSA, whilst keeping the remaining reactant concentrations constant. The pTSA in addition to increasing conductivity has been observed
to have a preserving effect on the electrical properties of the polymer reducing the rate of electrical degradation [10] [11].

Figure 15: The effect of dopant concentration on PET fabric sheet resistance, monomer and oxidant concentration are 0.857 and 0.110 mol/l

There has been a previous work [12] on the optimization of synthesis parameters of PPy coated PET fabrics using anthraquinone sulphonic acid (AQSA) as the dopant. In the present work higher molar concentrations and the effect of molar ratios were investigated and a threefold increase in the oxidant/pyrrole molar ratio resulted in a significant reduction in the values of $R_s$ to as low as 72 Ω/sq.

2.4.1. SEM Results

Polymerization takes place simultaneously both on the substrate surface and in the solution as bulk polymerization and is initiated by catalytically. Bulk
polymerized particles are loosely bound to the fabric surface and are present in the interstices of the woven structure shown in Figure 16.

![Figure 16: SEM image of PET fabric coated with pTSA doped PPy](image)

These dendritic particles are agglomerate of small PPy particles (Figure 17). A thorough washing of the coated samples is important to remove these particles from the surface and to get smooth PPy coating as shown in Figure 18.
Figure 17: SEM image of bulk polymerized particles on PET fabric surface coated with pTSA doped PPy

Surface morphology of PPy is also influenced by the preparation method, concentrations and choice of reactants, preparation time and temperature. Previous studies [13] [14] indicate that surface roughness of free standing conducting polymers increases with the increase in reactant concentration, polymerization time and temperature.
The average diameter of PET fibres can be determined by optical fibre diameter analyzer (OFDA) [15], which can also be used for determining the average thickness of the PPy coating on PET fibres by conducting experiments on uncoated and coated fibre snippets [7]. However, the $\pm 1$ micron accuracy of OFDA is not high enough to determine the average coating thickness of thin PPy layer (which is less than one micron in thickness), also the method is not suitable for non-circular fibres (Figure 19). Therefore scanning electron microscope was used to determine the average PPy coating thickness.

Figure 18: SEM image of PET fabric coated with pTSA doped PPy after washing.
Figure 19: SEM image of cross-section of PET fabric embedded in polyester resin before coating with PPy

PPy coating on PET fibre can be seen in the cross-sectional SEM images. Figure 19 and Figure 20 show the fibre cross sections before and after PPy coating respectively.
Figure 20: SEM cross-sectional image of PET fabric embedded in polyester resin after coating with pTSA doped PPy

The coating thickness of PPy film on the fabric surface was measured on a number of different SEM cross sectional images and averaged to obtain the thickness of PPy coating (Figure 21). The average PPy coating thickness was 612 nm.
2.4.2. Thermal Aging

A temperature profile is given to show performance of PPy coated fabric at different temperatures which has scope in heated textiles application.

Experiments were performed on the samples with concentrations of pyrrole, oxidant and pTSA as 0.11, 0.857 and 0.077 mol/l respectively. Sheet resistance of PET fabric samples recorded at room temperature was 72±2 Ω/sq. These samples were kept in an oven for accelerated aging at 60°C, 80°C, 100°C and 120°C for approximately 30 hours. The recorded $R_s$ values were plotted against time and then normalized as shown in the Figure 22 and Figure 23. At all temperatures $R_s$ initially decreased due to rise in temperature. Figure 22 shows first 100 hours of thermal aging results. This behaviour is not unexpected as the conductivity of electro-active polymers increases with temperature, similar to that of amorphous semiconductors;
however this trend is not persistent as effects of degradation soon manifest as increase in sheet resistance. So increase in $R_s$ is noted for the rest of time after initial period. The initial decrease of $R_s$ may be attributed to excitation of charge carriers in PPy to enter conduction band and after some time decrease in conduction is recorded due to de-protonation of polymer back bone [6] [16] [17].

According to Sixou et al. [18], a single expression can describes both the temperature and the aging time dependences of the conductivity for PPy film samples aged below 150 °C. This corresponds to a hopping process between conducting grains separated by expanding insulating barriers upon aging and a slight deviation above 150 °C occurs.

Reaction with oxygen was observed to be detrimental for electrical performance of PPy more than temperature alone [19], as PPy remained electrically stable at 200°C in the absence of oxygen [20]. Also oxygen to carbon ratios of PPy coated samples were observed to be higher after thermal treatment which suggested oxidative degradation due to heat [15] Temperature facilitates oxidation and aging, so rate of $R_s$ change is temperature dependent. The 120°C curve had much higher rate of aging than that of samples tested at 60, 80 and 100°C. In an earlier study [11], loss of conductivity with time was stated to obey first order kinetics for electrochemically synthesized conducting PPy films thermally aged [6], However, prolonged aging experiments at elevated temperatures indicated that the aging characteristics of these materials followed a multi order kinetics behaviour [21] [11]. According to Thieblemont et al.[22], at moderate temperatures (below 230°C), oxidation is a slow, limited by $O_2$ diffusion, however at high temperatures (typically $T >$
230°C) oxidation appears to be a bulk phenomenon [22]. So aging could not be attributed just to the reaction with oxygen and formation of carbonyl bonds that perturb the conjugation [23] but other factors like doping and temperature are found to be critical [24].

![Graph of normalized resistance (R/R₀) vs. time (first 100 mins) of pTSA doped PPy coated fabric aged at a) 60 b) 80 c) 100 and d) 120°C](image)

**Figure 22:** Graph of normalized resistance (R/R₀) vs. time (first 100 mins) of pTSA doped PPy coated fabric aged at a) 60 b) 80 c) 100 and d) 120°C

PPy coated PET fabrics differ significantly in morphology from electrochemically prepared PPy films. Thermal aging of PPy coated wool fabric using 2,6-naphthalenedisulfonic acid disodium salt as dopant and FeCl₃ as oxidant was reported in [15], where fabric gained 220 % increase in resistance in 100 hours of aging at 45°C whereas PPy coated fabric in this study gained 5 % resistance under similar conditions, which may be attributed to preserving effect of pTSA dopant. (Figure 22)
Figure 23: Graph of normalized resistance ($R/R_0$) vs. time (30 hours) of pTSA doped PPy coated fabric at aged a) 60 b) 80 c) 100 and d) 120°C

The graph in Figure 24 consists of in and out of oven combined resistance data of PPy coated fabric heated at 120°C for 30 hours in an oven, followed by observation of resistance at room temperature.
Resistance increased steadily in the oven from 0-2500 mins. When the sample was taken out, an immediate fourfold increase in resistance from 1441 to 6126 Ω/sq was observed. This sudden loss of conductivity may be attributed to the removal of the heat that causes increase in conductivity in amorphous semiconductors. Although the rate of degradation is accelerated at elevated temperatures, the higher level of in-oven conductivity may be attributed to constant supply of energy to the polypyrrole and the sudden jump in resistance upon removal of the sample from the oven may be attributed to the loss of energy supply that activate the charge carriers into the conduction band. Beyond this point, between 2600-5000 minutes, the degradation settled to a slower rate at room temperature than the initial period in the oven.
Room temperature aging at a longer time frame of up to 18 months is shown in Figure 25. Resistance was recorded after 0, 4, 10 and 18 months. The increase of resistance of PPy-coated PET fabric was evaluated from the resistance ratio $\frac{R_0}{R}$, where $R_0$ is the resistance at $t_0$ and $R$ is the resistance at $t_x$ ($x=\text{days}$). Patil and Deogaonkar [25] addressed the durability of PPy coatings on cotton fabric by atmospheric aging of conductivity over a period of 6 months. In a study of room temperature aging of AQSA doped PPy coated silk fabrics [23], gain in $R_s$ was quicker at the beginning and gradually reduced with time similar to results reported here, however PPy coated silk fabrics showed 330 % gain in resistance after one year whereas pTSA doped PPy coated PET fabric in this study showed 100 % increase in resistance in same time frame. This again may be attributed to the preserving effect of the dopant.
pTSA on the conductivity. Aging was less than one order of magnitude after 18 months; so the conductivity of fabrics reported here was more stable than PPy coated silk fabric doped with AQSA [23] under similar conditions.

![Graph of resistance vs. time of without pTSA dopant PPy coated PET fabric aged at 120°C](image)

Figure 26: Graph of resistance vs. time of without pTSA dopant PPy coated PET fabric aged at 120°C

The effect of concentration of pTSA dopant on the thermal stability of PPy coated PET fabric is also studied (Figure 26 and Figure 27). During thermal aging fabric resistance of the sample without dopant (polymerized by only FeCl₃) increased rapidly with time, as shown in Fig. 14. Dalas et al. [26] noted that the thermal degradation at elevated temperature is present due to the reduction of protonated conducting phase, similar was observed by Mohammad et al. [27]. Presence of dopant on the polypyrrole molecule obstructs, oxidation reaction.
In the next set of experiments three PPy coated PET samples were prepared using different dopant concentrations at 0.025 mol/l (sample a), 0.052 mol/l (sample b) and 0.077 mol/l (sample c). All the samples were aged at 120°C for approx. 20 hrs. and the results plotted in Fig. 15.

![Graph of resistance vs. time of PPy coated PET fabric aged at 120°C with different pTSA dopant concentrations; a) 0.025 mol/l b) 0.052 mol/l, c) 0.077 mol/l while pyrrole and FeCl₃ concentrations are 0.11, 0.857 mol/l respectively.](image)

Figure 27: Graph of resistance vs. time of PPy coated PET fabric aged at 120°C with different pTSA dopant concentrations; a) 0.025 mol/l b) 0.052 mol/l, c) 0.077 mol/l while pyrrole and FeCl₃ concentrations are 0.11, 0.857 mol/l respectively.

The preserving effect of the dopant can be seen in Figure 26 and Figure 27, which show that the resistance of the un-doped sample reached 40 kΩ whereas the samples (a), (b) and (c) doped with increasing concentrations of pTSA exhibited much lower rate of increase of resistance with time, not exceeding 1.7 kΩ within approximately the same time frame.
2.5. Conclusion

In this study, further improvements in the conductivity of chemically polymerized PPy coated PET fabrics were reported. Optimum concentrations were found as 0.14 mol/l for pyrrole (monomer), 0.857 mol/l for ferric chloride (oxidant) and 0.077 mol/l for p-toluene sulphonate (dopant). The resulting sheet resistance value was measured as low as 72 $\Omega$/sq. Oxidant concentrations had the most important effect on improving resistance of fabric. Room temperature electrical aging of PET sample for 18 months resulted in less degradation than previously reported [23] due to preserving effect of the dopant pTSA. The stabilizing effect of pTSA was demonstrated in a range of thermal degradation experiments where the un-doped samples reached resistivities in the range of 40 k$\Omega$, whereas doped samples reached 1.7 k$\Omega$ at the same temperature and approximately the same period in the oven.

2.6. References


CHAPTER TWO


3. Improved interfacial bonding between polyester and polypyrrole using argon, nitrogen and oxygen plasma treatment

3.1. Abstract

A systematic study was conducted using argon, oxygen and nitrogen plasma to improve the adhesion of polypyrrole coating to polyester fabric for improving conductivity and to understand the mechanisms involved. Polyester thin film was used as a reference sample. The changes in wettability, surface chemistry and morphology were studied by water contact angle, x-ray photoelectron spectroscopy and atomic force and scanning electron microscopy. It was found that both the highest conductivity and the strongest interfacial bonding were achieved by oxygen plasma treatment. The increase in hydrophilicity, surface functionalization and suitable nano-scale roughness gave improved adhesion.

3.2. Introduction

Conductive textiles can possess a wide range of mechanical and electrical properties depending on the properties of the textile structure and the conductive coating. These textiles have various applications such as bio-feedback, health monitoring and hepatics[1]. Polyester (PET) fibre is a widely used textile material due to its high strength, dimensional stability, as well as suitability for blending with other fibres [2] [3]. Friction causes abrasion of coatings during the product lifecycle. Improved interfacial bonding is essential
in applications involving the tensile and compressive forces that occur in electronic textile sensors [4] [5].

Adhesion of coatings to the PET surface can be improved by pre-treatment of PET with chemicals [6] [7], plasma[8] [9] [10] [11] or both [12]. Plasma treatment does not require use of water and chemicals, is an environment-friendly surface modification technique and it does not alter bulk properties of materials in contrast to chemical treatments [11]. Active species produced in the plasma interact with the PET surface and lead to a variety of possible processes: etching, cross-linking and chemical modification [13]. Functional groups incorporated in macromolecular chains during treatment enable stronger bonding between fibre and coating material [9]. Previously [8] we pre-treated PET and wool fabrics using an atmospheric pressure glow discharge plasma for the improvement of adhesion of polypyrrole (PPy) coating on the fabric surface using helium, acetylene and nitrogen gases. Plasma pre-treated samples showed lower sheet resistance and higher abrasion resistance compared to untreated samples. However, the bonding mechanism was not fully understood and so chemical and physical analysis of the plasma treated surface was needed to further improve binding strength of PPy coatings on a PET surface.

In order to understand the mechanisms involved three gases: argon (Ar), nitrogen (N₂) and oxygen (O₂) were used in a low pressure plasma set up to assess the changes in surface morphology, surface chemistry and surface wettability. PET thin film was used as a reference sample because of its flat surface but the same chemistry as PET fabric. The change in the surface hydrophilicity with varying plasma treatment time was studied by water
contact angle measurements. Surface morphology was assessed by atomic force microscopy (AFM) and scanning electron microscopy (SEM), while surface chemistry was determined by x-ray photoelectron spectroscopy (XPS). PPy was coated on PET fabric and thin film by in-situ polymerization. The interfacial strength of the PPy coating to the substrate was determined by sheet resistance ($R_s$) measurements, and by visual comparison, before and after abrasion with a Martindale abrasion tester. The effects of changes in the surface chemistry, physical structure and hydrophilicity were examined in conjunction with the abrasion results.

3.3. Materials & Methods

The PET fabric was of plain weave with 56 ends per inch and 54 picks per inch in warp and weft direction respectively and of 168 $g/m^2$ (GSM). It was ultrasonically cleaned in 1% non-ionic detergent (Hydrapol TN450) at room temperature for 20 minutes followed by rinsing and drying before being used in the experiments. In addition, PET thin film strips (35 x 100 mm) of 128 $\mu m$ thicknesses were ultrasonically cleaned in ethanol solution for 20 minutes, rinsed with deionized water and then dried with $N_2$ gas. The cleaned fabric and thin film samples were conditioned under standard atmospheric pressure at 65 $\pm$ 2% relative humidity and 21 $\pm$ 1 °C for at least 24 hours prior to further processing. Pyrrole (Py), ferric chloride hexahydrate ($FeCl_3.6H_2O$) and toluene sulphonic acid mono hydrate (pTSA) were purchased from Sigma-Aldrich.

3.3.1 Plasma treatment
Plasma treatment of both PET fabric and PET thin film was performed in a custom built 13.5 MHz inductively coupled reactor described in our previous work [14]. The base pressure $1 \times 10^{-3}$ mbar was achieved by use of a rotary pump. Ar plasma was used for the pre-treatment of the samples (100 W, $8 \times 10^{-2}$ mbar, 30 s) to activate and further clean the surface. The gas pressure ($8 \times 10^{-2}$ mbar) and power (100 W) were kept the same for all of the samples while treatment time was fixed at 120 s except for examining the effect on contact angle, where it was varied from 60 to 240 s.

The following abbreviations were used for the PET samples exposed to the 120 s plasma treatment in addition to surface activation with Ar for 30 s.

<table>
<thead>
<tr>
<th>tf</th>
<th>Pristine PET thin film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Artf</td>
<td>Argon plasma treated PET thin film</td>
</tr>
<tr>
<td>N$_2$tf</td>
<td>Nitrogen plasma treated PET thin film</td>
</tr>
<tr>
<td>O$_2$tf</td>
<td>Oxygen plasma treated PET thin film</td>
</tr>
</tbody>
</table>

3.3.2. PPy polymerization

PPy was coated on the PET fabric and PET thin film by a solution polymerization method at room temperature. Coating was carried out in a plastic container with liquor to fabric ratio of 50 to 1 and chemical concentrations of 0.11, 0.857 and 0.077 mol.l$^{-1}$ for Py, FeCl$_3$ and pTSA, respectively [15]. Firstly de-ionized water, pTSA and Py were mixed in the container and then plasma pre-treated samples were put in the container within 10 mins of plasma treatment. Finally FeCl$_3$ was introduced to start
polymerization. The coating was carried out for two hours with occasional stirring. PPy coated samples were then washed with warm water and subsequently dried at 25 ± 2 °C overnight in a fume hood. The same coating method was used for PET thin film samples.

3.3.3. Surface wettability measurement

Contact angle (CA) measurements were performed using a KSV CAM100 CA tester. All the measurements were done within ten minutes after the plasma treatment. 2 cm² specimens of PET thin films were cut and mounted on a glass slide and distilled water with droplet size of 2.5 µl was used. The camera frame interval was kept at 33 ms and KSV CAM100 software was used to calculate the contact angle from the captured images. All the plasma treatments in our experiments rendered polyester film hydrophilic, so a rapid spread of water drop over the surface was noted by numerous successive images. In order to compare hydrophilicity induced by different plasma gases contact angle was calculated for the images at 0.33 sec after droplet release[16]. At least three specimens of each sample were tested at six different positions to obtain an average value for the contact angle.

3.3.4. Surface chemical composition

XPS was used to investigate the chemical composition of the PET thin film surface before and after plasma treatment and were performed within 24 hrs of treatment. The XPS spectra was obtained using a K-Alpha X-ray photoelectron spectrometer from Thermo Fischer Scientific using monochromatic X-rays focused to a 400 nm spot size. Excessive charging of the samples was minimized using a flood gun. Survey spectra were obtained at
pass energy of 100 eV while high resolution peak scans were performed at 20 eV pass energy. The peak scans were employed to obtain the composition in terms of elemental C, N, and O. The C1s binding energies of the samples were accurately established by charge shift correcting the lowest binding energy peak of the C1s to 284.6 eV.

3.3.5. Surface physical morphology

A Supra 55 VP scanning electron microscope operated at 5 kV was used to study the surface morphology and roughness of PET thin film samples. All the samples were gold coated prior to viewing. SEM imaging was done within 3 hours of plasma pre-treatment.

A MultiMode 8 scanning probe microscope was used to study surface roughness of plasma pre-treated and untreated PET thin film samples. All the measurements were done within 2 weeks of plasma treatment.

3.3.6. Interfacial bonding strength

Interfacial bonding strengths were assessed using Martindale abrasion measurements described previously [17]. Round PPy coated PET fabric samples of 38 mm diameter were cut using a circular sample cutter used for GSM calculations. These samples were placed in the top holder and abraded under 9 kPa constant pressures by means of a head weight against a reference wool abradant fabric using the same Martindale sample head and base to avoid any experimental variation. Two different abrasion settings at (i) 200, (ii) 2000 cycles were applied on two sets of samples and results were compared with each other and the control sample. Photographs of the three samples, namely the control, 200 and 2000 cycles were taken together under the same lighting,
same exposure value and without any exposure compensation, so that the tonal changes due to abrasions could be visually compared. The images clearly show a tonal gradation between the samples due to the effect of the abrasive head.

In the case of PPy coated PET thin film samples, the abrasion tests were carried out for 2000 cycles by gluing them over a fabric sample held in the sample holder. The abraded thin film samples were then examined under an optical microscope (Olympus DP70) to assess the effects of abrasion at small scale.

3.3.7. Electrical resistance measurements

Electrical sheet resistance of the PET fabric samples was measured by a four probe technique before and after abrasion in a conditioned room (65 ± 2% R.H and 21 ± 1 °C). These samples were kept in conditioned room for at least 24 hours prior to resistance measurements. Our custom built four probe measurement device consist of an array of four rectangular copper probes, which were 15x3 mm in size and 4 mm apart, mounted on a plastic chip. The sample-probe contact pressure variation introduces considerable scatter to electrical resistance measurements. Therefore, fabric samples were clamped between the device and a plastic board using a Kakuta HV 350 clamp employing a constant pressing force every time. A constant voltage is applied from the outer probes to enable a stable current flow and the voltage drop was noted from the inner probes. This configuration enabled accurate and consistent measurements. Six measurements were taken for each sample and averaged. Resistance (R) in ohms was calculated from these values using
Ohm’s law. \( R_s \) values in ohms/sq were then calculated from following equation. \( R_S = R \times W/L \)

3.4. Results & Discussion

3.4.1. Surface wettability

The effect of plasma treatment time on hydrophilicity of the PET thin film samples was studied. The surface wettability test gives a high CA value indicates poor surface wettability, or hydrophobic surface while low CA indicates good wettability, or hydrophilic surface. The result of the CA measurements before and after plasma treatment are given in Figure 28 showing a CA value of 84.6° for untreated PET thin film sample. CA was reduced by all the gases used in this study and it further reduced with increased plasma treatment time but the oxygen plasma treatment resulted in the lowest CA value. The improvement in hydrophilicity was found to be in the order \( \text{O}_2 > \text{N}_2 > \text{Ar} \).
Figure 28: Water contact angle results for control and plasma treated PET thin film samples with treatment time 60-240 sec
CHAPTER THREE

Improvements in hydrophilicity of the PET thin film can be attributed to both changes in surface chemistry and physical morphology. Therefore XPS, AFM and SEM were used to examine the chemical and physical changes on the substrate surface after plasma treatment.

3.4.2. Surface chemical composition

The surface composition of PET thin film samples before and after plasma treatment using Ar, N₂ and O₂ are given in Table 1. Similarly overall XPS scan survey of all the samples is shown in Figure 29. Carbon (C) and oxygen (O) was detected in all the samples whereas nitrogen (N) was detected in N₂tf only.

C and O concentrations of the PET thin film sample surface were 75.0 % and 25.0 % prior to plasma treatment and the plasma treatments resulted in a decrease in percentage of carbon on the PET surface in the order of O₂>Ar>N₂.
Table 1: Atomic composition of untreated and plasma treated polyester samples with treatment time 120 sec.

<table>
<thead>
<tr>
<th></th>
<th>C-C/H (284.6 eV)</th>
<th>C-O (286.2 eV)</th>
<th>C-N (287.2 eV)</th>
<th>O=C-O (288.6 eV)</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>O/C</th>
<th>N/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>56.0</td>
<td>10.5</td>
<td>-</td>
<td>8.5</td>
<td>75.0</td>
<td>25.0</td>
<td>-</td>
<td>0.33</td>
<td>-</td>
</tr>
<tr>
<td>N₂tf</td>
<td>48.9</td>
<td>7.4</td>
<td>7.8</td>
<td>6.1</td>
<td>70.2</td>
<td>22.8</td>
<td>7.0</td>
<td>0.33</td>
<td>0.10</td>
</tr>
<tr>
<td>Arťf</td>
<td>38.3</td>
<td>15.5</td>
<td>-</td>
<td>13.3</td>
<td>67.1</td>
<td>32.9</td>
<td>-</td>
<td>0.49</td>
<td>-</td>
</tr>
<tr>
<td>O₂tf</td>
<td>32.4</td>
<td>18.2</td>
<td>-</td>
<td>15.4</td>
<td>66.0</td>
<td>34.0</td>
<td>-</td>
<td>0.52</td>
<td>-</td>
</tr>
</tbody>
</table>
The highest C drop was seen for O$_2$tf to 66% followed by 67.1% and 70.2% for Artf and N$_2$tf respectively. Oxygen concentration increased from 25% to 34% for O$_2$tf and to 32.9% for Artf samples, whereas it decreased to 22.8% for N$_2$tf sample.

Plasma treatments lead to introduction of O$_2$ and N$_2$ functional groups on the surface, therefore ratios of total O content/total C content (O/C) and total N content/total C content (N/C) were employed [1] to assess quantitative changes in chemical surface composition.

O/C rose to 0.52 from 0.33 after O$_2$ plasma and to 0.49 after argon plasma, however it stayed unchanged for N$_2$tf. N was only found in the N$_2$tf sample where the N/C ratio was 0.10.
Figure 29: Overall XPS scan survey of control, Artf, N₂tf and O₂tf samples
Quantitative information on the O functionalities on the surface structure was obtained from de-convolution of the C1s scan spectra mainly into three peaks as shown in Figure 30 (a, b, c, d). These peaks at 284.6, 286.2 and 288.6 eV were assigned to C-C/C-H, C-O and O-C=O groups [1] [2] [3] [4] respectively, and their relative concentrations are shown in Table 1.

The highest decline in the C-C/C-H peak was noted for O2tf from 56 to 32.4, followed by 38.3 and 48.9 for Artf and N2tf respectively.
The peak related to C-O groups increased to 18.2 and 15.5% for O2tf and Artf respectively from 10.5%, while it showed a decline for N2tf to 7.4%. Similarly, peak related to carboxylic groups was dropped to 6.1% for N2tf and increased for both Artf (13.3%) and O2tf (15.4%).

C1s spectra of N2tf revealed an additional peak at 287.2 eV as shown in Figure 30b. This new peak was assigned to the incorporation of amines on the PET surface [1] [4] [5]. Furthermore, presence of other nitrogen functionalities can be present beside C-O and O-C=O peaks due to overlapping [1].

The N1s scan of N2tf sample showed a broad peak centered around 399.6 eV (Figure 29 inset) which too indicates presence of amine groups. It is interesting to note the incorporation of oxygen based functional groups during argon plasma and a number of explanations can be given for this increase in O
% The oxygen may arise from the following sources: (i) as an impurity in Ar gas [6] (ii) that comes out from the PET during plasma treatment[7] (iii) exposure to air after the treatment[3] [8].

3.4.3. Surface morphology

The SEM images in Figure 31 (a, b, c, d) shows that the plasma treatment changed the surface morphology of the thin films, while the PET thin film was smooth before plasma treatment.

Some engraved features with voids, pores and ridges were observed on the thin film surface after plasma treatment. Changes in the surface morphology can be caused by ion bombardment and UV radiation in the plasma.
Figure 31: SEM images of a) control, b) Artf, c) N2tf and d) O2tf plasma treated PET thin film (120 sec)
AFM images enabled calculation of surface roughness values. The pristine PET thin film surface has a smooth morphology, compared to the plasma treated samples, with an average roughness value ($R_a$) of 0.79 nm (Figure 32).

Figure 32: AFM micrograph of control PET thin film sample (120 sec).
Figure 33: AFM micrograph of Ar plasma (120 sec) treated PET thin film sample
Substantial differences can be noticed among the control (Figure 32), Artf (Figure 33), N2tf (Figure 34) and O2tf (Figure 35) scanned AFM micrographs. It is worth emphasizing that the N2 plasma resulted in the highest roughness value of 3.61 nm. The surface roughness was changed moderately in the case of Artf to 1.99 nm, while it grew to 2.17 for O2tf. A unique feature is seen in O2tf, which consists of uniformly packed hillocks creating a three dimensional surface with increased surface area.

3.4.4. Interfacial bonding strength
PPy coated PET fabric samples abraded by the Martindale abrasion method were photographed (Figure 36) after 0, 200 and 2000 cycles of abrasion.
Figure 36: Martindale abrasion results of PPy coated a) control b) N2tf c) Artf and d) O2tf PET fabric samples after 0, 200 and 2000 abrasion cycles

The effectiveness of plasma treatments is clearly evident. O₂ and Ar plasma treated PET fabric samples showed a bigger improvement in coating fastness than N₂ treated fabric samples.

PPy coatings on untreated PET fabric samples faded away after 200 cycles of abrasion. Further abrasion was not possible as the PPy coating penetrated between warp and weft threads, into the interstices of the three dimensional textile structure, rendering parts of PPy coatings inaccessible to the abrasive disc of the Martindale abrasion tester. Therefore, for a more accurate assessment of the effect of each plasma treatment on the binding strength of the conducting polymer coating, flat PET films were used as substrate materials. The optical microscopy images of PPy coated PET film samples before and after 2000 abrasion cycles are shown in Figure 37.
Some of the coating for the untreated sample was already washed off (during washing subsequent to coating) even before the abrasion test due to weak interfacial bonding (Figure 37 a). Nearly all of the coating had faded away from the untreated sample after 2000 cycles of abrasion leaving the sample non-conductive (Figure 37 a*). Plasma treated samples clearly showed better abrasion resistance. Although the N$_2$ plasma sample showed some flaking off after 2000 cycles (Figure 37 b*), it was significantly better than the untreated sample. On the other hand the Ar and O$_2$ samples had strong binding as there was only small visible coating loss in the images (Figure 37 c*, d*).

### 3.4.5. Sheet resistance results

The resistance results after 0, 200 and 2000 abrasion cycles are presented in Figure 38.
All plasma gases lowered the $R_s$ values of the PPy coated PET fabric compared to the untreated sample. The lowest resistance values were noted for O$_2$ gas at 44 ohms/sq for 120 sec plasma treatment and there was a minor increase to 47.3 ohms/sq after 2000 abrasion cycles. The resistance value of the Ar plasma sample before abrasion was 50.3 ohms/sq and it also showed a slight rise to 53.3 ohms/sq after 2000 abrasion cycles.
Figure 38: Sheet resistance results of control, Ar, O₂ and N₂ plasma treated PET fabric samples (120 sec)
These results clearly show the effectiveness of O\textsubscript{2} and Ar plasma in lowering the resistance and improving the binding strength of the PPy coating. The N\textsubscript{2} treated sample also showed a lowered R\textsubscript{s} value of 55 ohms/sq (before abrasion) and after 2000 abrasion cycles; the resistance increased to 76.3 ohms/sq although it was still lower than the 90.2 ohms/sq of the untreated and abraded sample. It is interesting to note that the N\textsubscript{2} treated surface was rougher than the Ar treated one, and the treatment did not lower the R\textsubscript{s} value as much as that treated by Ar gas. This indicates that higher surface roughness is not the only factor affecting conductivity and coating fastness. The resistance data of PPy coated PET fabric samples in Figure 38 and photographs of abraded samples in Figure 36 and Figure 37, agree very well with each other and all confirm the order of plasma gas effectiveness as O\textsubscript{2}>Ar>N\textsubscript{2}.

These interfacial bonding results and the chemical composition data in Table 1 show that the incorporation of oxygen based functional groups were the main factor for improved PPy deposition as the same order of effectiveness was found by the analysis of O/C ratios (Table.1), also O\textsubscript{2} plasma was more efficient in incorporating oxygen functionalities than Ar plasma. Oxygen functionalization resulted in increased presence of ester functional groups (O-C=O), which are acid catalysed (electrophiles) and can attract nucleophilic nitrogen atom of pyrrole ring [1] [2]. This may be the reason for increased affinity of PPy molecules with PET surface. It is worth to mention that tried to use FTIR to confirm this, but the PPy coating was only around 200 nm, it was too thin to be measured by FTIR. The abrasion data suggest adequate strength of bonding with PET surface. The plasma induced increase in hydrophilicity,
surface functionalization and a nano-scale roughness all contributed to the improved coating adhesion and fastness.

3.5. Conclusion

A thorough investigation using Ar, O$_2$, N$_2$ plasma treatments on PET thin film and fabric revealed that better interfacial bonding between PPy and PET surface results in higher coating fastness. The interfacial bonding was enhanced by incorporation of COOH functional groups onto the PET surface, while uniform nanostructure formation also improved surface adhesion as depicted in below schematic.

The effectiveness of plasma gases was found to be in the order of O$_2$ > Ar > N$_2$. Oxygen plasma introduced the highest percentage of oxygen atoms and the highest level of oxygen functional groups, giving the highest interfacial bonding. This systematic approach has provided a better understanding of how and why the conductivity of PPy coated on a PET surface can be improved.
3.6. References


4.1. Abstract

In this work, improvement of binding of polypyrrole with polyethylene terephthalate (PET) thin films and fabrics using low pressure oxygen plasma was studied. A range of plasma treatment times were employed to investigate plasma induced effects on surface roughness, surface chemistry and hydrophilicity. Modifications of PET films were studied in respect to topography effects by means of atomic force microscopy and scanning electron microscopy and chemical effects of plasma treatment were studied using X-ray photoelectron spectroscopy. Results showed that the increase in surface functionalization by carboxylic groups and nano size roughness both contributed to improved adhesion and high conductivity.

4.2. Introduction

Plasma can be used to modify surfaces and deposit materials [1] [2]. Recently, there has been a surge in interest in the development of plasma technologies to improve the properties of textile surfaces without changing the bulk textile properties. Plasma treatment has shown an enhancement of dyeing/printing [3], color fastness [4], coating adhesion [5], and wicking [6], and can offer considerable savings of water, energy and effluents discharge to the environment [7] [8]. Intrinsically conducting polymers especially polypyrrole (PPy) possess a wide range of conductivity [9], easy processing, biocompatibility [10], environmental stability [11] [12] [13] and has potential
applications in electronic textiles [14] [15] [16] [17], heat generation [18] and electromagnetic interface shielding [19]. However, a key obstacle for practical application of PPy coated textiles has been poor adhesion of the coating to the fibre surface. Effect of plasma treatment on the surface properties of the substrate [20-25] and influence on the adhesion of the coating [26] [27] [28] have been investigated.

Garg et al. [26] pre-treated wool and polyester fabric using atmospheric pressure plasma and showed improvements in the ability of the substrate to bond with PPy coating. It was observed that bonding strength improvement was gas dependent. Montarso et al. [27] used oxygen (O₂) and argon (Ar) gases in low pressure radio frequency (RF) plasma for modification of PET fibre surface and improvement of its adhesion with PPy coatings. In our previous investigations [28], enhancement of PPy adhesion on PET surface by plasma treatment using Ar, O₂ and nitrogen (N₂) gases in low pressure RF plasma was reported. Abrasion data showed retention of PPy coatings even after 2000 abrasion cycles with better results observed in the case of O₂ when compared to N₂ and Ar. X-ray photoelectron spectroscopy (XPS) data showed enhancement of carboxylic (O-C=O) and ether groups (C-O) after O₂ plasma treatment. This enhanced concentration of electrophilic carboxylic groups on the surface of PET after plasma treatment provided additional bonding sites for nucleophilic nitrogen atom of the pyrrole ring [29] [30].

In this work, a wide range of oxygen plasma treatment conditions were explored to improve chemical functionalization and surface roughness for better polymer adhesion on the substrate. In conjunction with this, binding strength, electrical resistance, surface morphology, coating thickness, coating
interface, chemical composition and surface wettability were studied using a wide range of experimental techniques. PET thin film samples were chosen as a reference due to surface flatness in many measurements.

4.3. Materials & Methods

The substrate was a light weight plain weave, undyed PET fabric (168 GSM) with 56 ends per inch in warp and 54 picks per inch in weft direction and was purchased from Spotlight Australia. PET fabric was selected as the substrate due to its versatility, resilience and high strength [31].

A PET thin film with 128 μm thickness was used as a reference material. The fabric and thin film samples were washed in a solution of 5 g/l of ECE Phosphate reference detergent B in water at 50°C for 30 mins. The liquor ratio was kept at 10 l/kg and washing bath was continuously stirred with a plastic bar. Samples were then rinsed several times using deionised water and then air dried at room temperature. The cleaned fabric and thin film samples were conditioned under standard atmospheric pressure at 65 ± 2% relative humidity and 21 ± 1 °C for at least 24 h prior to further process.

Monomer (pyrrole), oxidant (ferric chloride FeCl₃·6H₂O) and dopant (toluene sulphonic acid mono hydrate pTSA) reagent quality were purchased from Sigma-Aldrich.

4.3.1. Plasma treatment

Plasma treatment of both PET fabric and PET thin film was performed in a custom built 13.5 MHz inductively coupled reactor [32]. The base pressure 1 x 10⁻³ mbar was achieved by use of a rotary pump. Ar plasma was used for the
pre-treatment of the samples (100 W, 8 x 10^{-2} mbar, 30 s) to activate and further clean the surface. The gas pressure (5 x 10^{-2} mbar) and power (100 W) were kept the same for all of the samples.

4.3.2. Contact angle measurement

Water contact angle (WCA) measurements were performed using a CAM100 WCA tester (KSV Instruments, Finland) and distilled water. At least three specimens of every PET thin film sample were tested six times each to get an averaged WCA measurement. The films were mounted on glass slides prior to measurement using double side adhesive tape. The interval of the frames captured by the camera was kept at 33 ms and 10 images were recorded for each sample. Attension theta v4.1.9.8 (Biolin scientific, Finland) software was used to calculate WCA from the captured images after 0.39 sec of water droplet contact time. All the measurements were carried out within 10 mins of plasma treatment.

4.3.3. X-ray photo spectroscopy (XPS)

Spectra were obtained using a K-Alpha X-ray photoelectron spectrometer (Thermo Fischer Scientific, USA) with monochromatic X-rays focused to a 400 μm spot size. Excessive charging of the samples was minimised using a flood gun. The C1s binding energies of the samples were accurately established by charge shift correcting the lowest binding energy peak of the C1s to 284.6 eV. Survey spectra were obtained at pass energy of 100 eV while high resolution peak scans were performed at 20 eV pass energy.

4.3.4. Microscopy and surface roughness
A Cypher AFM (Asylum Research, USA) was used to study surface roughness of plasma treated and untreated 1 μm PET thin film samples. All the measurements were done within 3 hours of treatment. AFM software calculated root mean square roughness values from each image. These images were analysed at different positions for each sample condition to get average roughness value. A Supra 55 VP (Carl Zeiss, Germany) scanning electron microscope (SEM) was used to study the surface morphology of deposited PPy on the PET fabric surface with and without plasma treatment. Similarly interfacial bonding of PPy and PET fabric surfaces was studied by cross sectional imaging. PPy coated samples were embedded in a polyester resin and then sliced by microtome to provide a flat cross section of the fibres for imaging. All the samples were gold coated prior to viewing.

A surface profiler (Bruker GT-K1) was used to measure the height/thickness of PPy coatings on PET thin film surface. PPy coated PET thin film square samples with dimension of 5 cm length and 5 cm width was used. One half of the sample surface was bonded with PET fabric using super glue; it was subsequently dried at room temperature for 1 hour. PET thin film was then peeled off the surface of PET fabric by force, this lead to sticking of half of PPy coating film on fabric and other half was bonded with PET film, PET film was then analysed using optical profilometer with half surface covered with PPy and half without PPy.

4.3.5. Abrasion resistance and sheet resistance

Circular PPy coated PET fabric samples were cut using a GSM cutter with 38 mm diameter and were abraded against a reference wool fabric under 9 kPa
head weight in Martindale abrasion tester (I.D.M instruments, Australia) for 5000 cycles. Photographs of the samples before and after abrasion were taken under the same lighting and exposure. Similarly, PPy coated PET thin film samples were abraded for 5000 cycles for the resistance measurement. Sheet resistance was measured using SP4 four point probe head (Signatone, USA) and source meter (Keithley 2400, USA) and employing same pressure for all the samples [33]. The thin film surface enabled stable contacts with probes compared to fabric. Three samples of each condition were measured at six different locations and averaged.

4.4. Results & Discussions

4.4.1. Contact angle measurement

Water contact angle (WCA) of the PET thin film surface was measured after 1, 3, 5, 10, 15, 30, 60, 120, 300 and 500 sec of O₂ plasma treatment. The average WCA value of the PET control sample was 81.9°, and it reduced to as low as 16.3° with increasing plasma treatment time (Figure 39). WCA reduction was directly related to the increase in the surface energy and O₂ plasma treatment increased the surface energy of PET samples. WCA dropped to 37.9° after 10 sec O₂ plasma treatment and it reached saturation after 120 sec treatment time.
Figure 39: Water contact angle results for control and oxygen plasma treated PET thin film samples with treatment time from 3 to 500 sec.

Prolonged exposure to plasma did not result in further decrease in WCA and it is interesting to note that even a few seconds of O₂ plasma treatment resulted in significant improvement of hydrophilicity of PET surface prior to saturation.

4.4.2. X-ray photo spectroscopy

XPS measurements were done for control, 3, 15, 60, 120, and 500 sec plasma treated samples. In all samples only carbon and oxygen were detected as shown in overall XPS scan in Figure 40 for control and O₂ plasma (500 sec) treated sample. An increase in height of the oxygen peak (around 530 eV) after plasma treatment was observed. High resolution C1s scans were performed to study the presence of different functional groups on the PET
surface. C1s peaks were curve fitted to calculate the relative concentration of present functional groups as shown in Figure 41. Three sub peaks at 284.6, 286.2 and 288.6 eV were assigned to C-C/C-H, C-O and O-C=O bonds, respectively.

Figure 40: Overall XPS scan survey of control and O2tf (500 sec) samples
The surface compositions of all the samples are given in Table 2. The C and O composition of the control sample at surface was 75.8 and 24.2, respectively, and oxygen to carbon ratio (O/C) stood at 0.36. An increase in oxygen percentage and decrease in carbon percentage with plasma treatment time was observed, and O/C ratio increased to 0.54 after 500 sec of O₂ plasma treatment.
Table 2: Atomic composition of untreated and treated PET thin film samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>C-C/C-H (284.6 eV)</th>
<th>C-O (286.2 eV)</th>
<th>C=O (288.6 eV)</th>
<th>C %</th>
<th>O %</th>
<th>O/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>48.39</td>
<td>12.73</td>
<td>12.15</td>
<td>73.3</td>
<td>26.7</td>
<td>0.36</td>
</tr>
<tr>
<td>O₂ 3 sec</td>
<td>40.41</td>
<td>15.83</td>
<td>14.86</td>
<td>71.1</td>
<td>28.9</td>
<td>0.41</td>
</tr>
<tr>
<td>O₂ 15 sec</td>
<td>41.00</td>
<td>12.85</td>
<td>14.48</td>
<td>68.3</td>
<td>31.7</td>
<td>0.46</td>
</tr>
<tr>
<td>O₂ 60 sec</td>
<td>39.80</td>
<td>12.77</td>
<td>15.26</td>
<td>67.8</td>
<td>32.2</td>
<td>0.48</td>
</tr>
<tr>
<td>O₂ 120 sec</td>
<td>38.13</td>
<td>13.22</td>
<td>14.02</td>
<td>65.4</td>
<td>34.6</td>
<td>0.53</td>
</tr>
<tr>
<td>O₂ 500 sec</td>
<td>35.67</td>
<td>14.22</td>
<td>14.93</td>
<td>64.8</td>
<td>35.2</td>
<td>0.54</td>
</tr>
</tbody>
</table>
The O/C ratio showed only a small increase after 120 sec treatment time. XPS data suggest that saturation of O₂ functionalization happened around 120 sec and this indication was supported by WCA measurements.

Oxidation of PET occurs by breaking of surface ester bonds by plasma, these chain scission reactions create radicals at the surface which then react with radicals present in the plasma gas and create carbonyl and carboxyl groups [1].
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b) $O_2$ 3 s

c) $O_2$ 15 s
Figure 41: C1s scan of control and oxygen plasma treated samples, Fig 3a; control, Fig 3b; 3s, Fig 3c; 15s, Fig 3d; 60s, Fig.3e; 120s and Fig 3f; 500s.

There was an increase in C-O and O-C=O peaks after plasma treatment and a decrease in the C-C/C-H peak. Relative concentrations of carbon sub peaks were changed after plasma treatment and the concentration of the peak related to C-C/C-H decreased from 49.4 % to 35.7 % after 500 sec of O₂ plasma, while peaks related to C-O and O-C=O both increased.

4.4.3. Microscopy and surface roughness

AFM images of PET thin film samples before and after oxygen plasma treatment are shown in Fig 4. A wide range of plasma treatment times were used (1, 5, 10, 30, 60, 120, 300 and 500 sec) to study the impact of plasma on PET surface morphology. Surface roughness was more pronounced at extended plasma exposures.
Figure 42: AFM scan of PET thin films before and after oxygen plasma treatments. Fig 4a control, Fig 4b 1s, Fig 4c 5s, Fig 4d 10s, Fig 4e 30s, Fig 4f 60s, Fig 4g 120s, Fig 4h 300s and Fig 4i 500s

Plasma treatment resulted in etching of the surface material creating uniform nano size features (Figure 42).

Figure 43: Surface roughness (r.m.s) (nm) of Oxygen plasma treated samples by AFM after 1, 5, 10, 30, 60, 120, 300 and 500s

Plasma treatment time was directly related to surface roughness and roughness kept on increasing with plasma exposure time without any saturation as shown in Figure 43.

Cross sectional SEM imaging of PPy coated PET fabric samples with and without plasma pre-treatment, in order to study PPy coating and PET fibre
interface, have been shown in Figure 44. In both the control and plasma treated samples a thin PPy coating was present around the PET fibre. In the control sample PPy was not physically bonded with PET surface, showing a gap between the fibre surface and coating observed (high magnification inset Figure 44).
Figure 44: SEM cross sectional images of PPy coated PET fibres without plasma pre-treatment (control) and after oxygen plasma (500 sec) pre-treatment

PPy bonded well in the oxygen plasma treated samples with no gap present. This depicts the effectiveness of binding of PPy with the PET surface after plasma treatment.

SEM images of the PPy coatings on PET fabric surface for the control and 120 sec O₂ plasma treated samples have been shown in fig. 6. The nano size PPy particles were similar in shape for both the treated and untreated samples.
There was no discernible difference in the PPy particle size. The average PPy particle size has been observed to depend on the reactant concentrations and polymerization time rather than the duration of plasma pre-treatment [2].

Figure 44: SEM images of the polypyrrole coating surface for control and 120 sec O2 plasma treated PET fabric
Figure 45: Surface optical profile of control PET thin film coated with PPy; raised half on the right is PPy coating

Figure 46: Surface optical profile of O₂ plasma (500 sec) treated PET thin film coated with PPy; raised half on the right is PPy coating

The optical surface profile of PET thin film with and without PPy coating is shown in Figure 45 for control sample without PPy coating and in Figure 46.
for oxygen plasma treated sample. The bright right side in each image is PPy coating. PET surface was relatively smooth before plasma treatment and it became rougher after plasma treatment. The peeling of PPy coating was uniform for control sample with straight edge, however in case of plasma treated sample, peeling was difficult and some material was strongly bonded that it still remained on the substrate. Veeco vision 4 surface profile software was used to assess the height of PPy coating by measuring step size, several measurements were made, however an exact measurement with a certain degree of accuracy was not possible to obtain due to the fact that, coating edge was raised by peeling and overall film was not flat at macro level. Anyhow coating thickness was in the range of 200-300 nm for both the samples.

4.4.4. Abrasion resistance and sheet resistance

Control and oxygen plasma treated samples with different treatment time (15, 120 and 500 sec) were abraded to assess the effectiveness of plasma pre-treatment. Figure 47 shows PPy coated PET fabric samples before any abrasion and after 5000 martindale abrasion cycles.
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Figure 47: PPy coated PET fabric before (a) control, b) 15 sec, c) 120 sec and d) 500 sec) and after (a*) control, b*) 15 sec, c*) 120 sec and d*) 500 sec) 5000 cycles of abrasion

Noticeable tonal change was evident after abrasion for all the samples; however the control sample showed the most coating loss. The tonal change in the 120 sec and 500 sec plasma samples was similar after plasma. Abrasion only removes the outermost PPy where a significant amount of conduction would be subsurface. Sheet resistance of the thin film samples was measured both before and after abrasion and results have been shown in Figure 48.

Figure 48: Sheet resistance values of PPy coated PET thin films before and after abrasion of 5000 cycles of control, 15, 120 and 500 sec plasma treatment times
Plasma treatment decreased sheet resistance with an increase in treatment time and this trend continued till 120 sec with no further significant decrease.

Almost all the PPy coating was lost from the control sample after abrasion making it impossible to measure a sheet resistance. Sheet resistance values of plasma treated samples show a small increase after abrasion and this gain was dependant on plasma treatment time. Sheet resistance values of 120 sec and 500 sec samples were similar before and after abrasion.

WCA measurements, XPS results and sheet resistance data show surface saturation with oxygen at 120 sec oxygen plasma treatment with no significant increase beyond 120 sec, however surface roughness data from AFM show no saturation at 120 sec treatment time with roughness increasing with increased plasma treatment time.

4.5. Conclusions

Low pressure Oxygen plasma treatments resulted in improved adhesion between PPy and PET. Plasma reactions changed the surface chemistry by decomposition of polymer chains and oxidation reactions forming additional C-O and O-C=O groups. Similarly, an increase in surface energy and roughness was observed. An increase in plasma treatment exposure time resulted in increased hydrophilicity and oxidation until a saturation point of 120 sec, while surface roughness never achieved saturation in the 500 sec maximum treatment undertaken in these experimental conditions and showed a linear relationship with treatment time. Improved PPy bonding is more dependent on surface chemistry than surface morphology.
This study provides valuable information for better understanding and predicting the effect of oxygen plasma treatments on physical and chemical properties of polyester fabric and thin films.

4.6. References


5. Study of radio frequency plasma treatment of PVDF film using Ar, O₂ and (Ar+O₂) gases for improved polypyrrole adhesion

5.1. Abstract

In this work, improvement of binding of polypyrrole with PVDF thin film using low pressure plasma was studied. Effects of various plasma gases i.e Ar, O₂ and Ar+O₂ gases on surface roughness, surface chemistry and hydrophilicity was noted. PVDF film’s topographical change was observed by means of scanning electron microscopy and chemical changes by X-ray photoelectron spectroscopy, while adhesion of polypyrrole by abrasion tests and sheet resistance measurements. Results showed that the increase in roughness and surface functionalization by oxygen functional groups contributed to improved adhesion and Ar+O₂ plasma gave better adhesion.

5.2. Introduction

PVDF poly (vinylidene fluoride) is a semi-crystalline polymer in which each monomer got two dipole moments, one due to CF₂ and the other due to CH₂. The most common and most studied crystal structures are α and β phases [1] [2]. The piezo- and pyro-electric properties of PVDF mainly depend on the β-phase content and its increment can be induced by several techniques, the most common being the mechanical stretching of the α-phase films at a suitable temperature [3]. Mechanical strains due to the bending, vibration or compression of the thin-film structure can be the source of the energy
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generation [4] [5]. PVDF sensor has been integrated into a seat cover fabric of automotive to obtain information about the car occupant [1]. Hutchison et al.[6] used platinum coating in between PVDF and PPy to get stable connection in their actuator device. Choi et al. [7] used conductive fabric and PVDF to monitor cardiorespiratory signals employing piezoelectric property of PVDF. The construction of PVDF based energy harvesting device require electrodes on both side of PVDF film, these electrodes are connected to electronic circuit to harvest electricity during motion. Different metal coatings can be used as electrode material [8] and are brittle and uncomfortable to skin. Polypyrrole (PPy) coatings can be used instead of metals for this purpose due to easy coating and comfort, conformity [9]. Bhat et al. [10] synthesized PVDF PPy composite film prepared by electrochemical polymerization and Mansouri et al. [11] coated PPy on PVDF microfiltration membranes by in-situ chemical polymerization method.

One of the perceived problems for PPy coating is poor adhesion due to low surface energy and chemical nature of PVDF. plasma can be used for the surface modification to improve adhesion and thus improving subsequent coating deposition and bonding [12] [13]. PVDF films were exposed [14] to Argon (Ar), Hydrogen (H₂), and Oxygen (O₂) remote plasma and it introduced various functional groups. Substitution of carbonyl or hydroxyl groups with fluorine atoms (de-fluorination) is central to adhesion improvement [15] [14] [16] [17]. Duca et al. [17] studied radio frequency (RF) Ar plasma treatment on PVDF and a decrease of fluorine to carbon (F/C) ratio and water contact angle and an increase in surface roughness was observed. Ar and O₂ plasma treatment [18] incorporated oxygen to the surfaces of PVDF. Our previous
investigation [19] on PET surface suggest that the improvement of adhesion of
PPy was mainly due to incorporation of oxygen based functional groups on the
surface after plasma treatment.

In this work, results of our investigations on PVDF under RF plasma for PPy
adhesion improvement is reported using Argon (Ar), Oxygen (O₂) and
(Ar+O₂) gases. The PVDF surface morphology, wettability and chemical
composition were studied before and after each plasma treatment. Similarly,
electrical resistivity and abrasion resistance of PPy coating was probed.
Possibility of application of plasma on cotton fabric for adhesion improvement
was studied too.

5.3. Materials & Methods

The substrate was a PVDF thin film with 50 micron thickness. Films were
immersed in acetone and ultrasonicated for 5 mins, then washed with
deionized water, several times and dried at room temperature. Plain woven
cotton fabric was purchased from spotlight Inc. Australia. The fabric was
washed using a recipe provided in table below.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>30 g/l</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>2 g/l</td>
</tr>
<tr>
<td>ECE Phosphate reference detergent B</td>
<td>5 g/l</td>
</tr>
<tr>
<td>Temperature</td>
<td>80° C</td>
</tr>
<tr>
<td>Time</td>
<td>40 mins</td>
</tr>
</tbody>
</table>
The liquor ratio was kept at 10 l/kg. Samples were then rinsed several times using deionised water and then air dried at room temperature.

All the substrate materials were then conditioned under standard atmospheric pressure at 65 ± 2% relative humidity and 21 ± 1 °C for at least 24 h prior to further processing.

Monomer (pyrrole), oxidant (ferric chloride FeCl₃.6H₂O) and dopant (para toluene sulphonic acid mono hydrate pTSA) reagent quality were purchased from Sigma-Aldrich.

5.3.1. Plasma treatment

Plasma treatment of both PVDF thin film was performed in a custom built 13.5 MHz inductively coupled reactor [20]. The base pressure 1 x 10⁻³ mbar was achieved by use of a rotary pump. Ar plasma was used for the pre-treatment of the samples (100 W, 8 x 10⁻² mbar, 30 s) to activate and clean the surface. The gas pressure was set at 8 x 10⁻² mbar for Ar and 8 x 10⁻² mbar for O₂ and Ar+O₂ samples. In case of Ar+O₂, the composition of both gases was kept 1:1 by volume. The plasma treatment time was fixed at 120 sec for all the samples.

5.3.2. Contact angle measurement

Water contact angle (WCA) measurements were performed using a CAM100 WCA tester (KSV Instruments, Finland) and distilled water. The films were mounted on glass slides prior to measurement using double side adhesive tape. At least six measurements of each PVDF sample condition were taken to get an averaged WCA measurement. Attension theta v4.1.9.8 (Biolin scientific)
The software was used to calculate WCA from the captured images after 0.80 sec of water droplet contact time. All the measurements were carried out within 10 mins of plasma treatment.

5.3.3. Scanning electron microscopy

A Supra 55 VP (Carl Zeiss, Germany) scanning electron microscope (SEM) was used to study the surface morphology of PVDF thin film surface before and after plasma treatment. All the samples were gold coated before viewing in the SEM.

5.3.4. X-ray photo spectroscopy (XPS)

Spectra were obtained using a K-Alpha X-ray photoelectron spectrometer (Thermo Fischer Scientific, USA) with monochromatic X-rays focused to a 400 μm spot size. Excessive charging of the samples was minimised using a flood gun. The binding energies of the samples were accurately established by charge shift; the binding energy peak of the F1s to 688.65 eV [14]. Survey spectra were obtained at pass energy of 100 eV while high resolution peak scans were performed at 20 eV pass energy. XPS measurements were done within one week of plasma treatment.

5.3.5. Abrasion resistance and sheet resistance

Circular PPy coated PVDF thin film samples were cut using a GSM cutter with 38 mm diameter and were abraded against a reference wool fabric under 9 kPa head weight in Martindale abrasion tester (I.D.M instruments, Australia) for 0, 200 and 2000 abrasion cycles. Micrographs of the samples before and after abrasion were taken under the same lighting and exposure by a microscope (Olympus DP-71, Japan). Sheet resistance was measured using
SP4 four point probe head (Signatone, USA) and source meter (Keithley 2400, USA) and employing same pressure for all the samples [21]. Sheet resistance values were obtained from six different locations of each sample and later average values were calculated.

### 5.4. Results & Discussions

Cotton fabric was coated with PPy with good success and resistivity values were as low as 240 ohm/sq. Martindale abrasion tests for 2000 cycles had no visible effect on the PPy coatings. This good fastness property of cotton may be due to the additional hydroxyl groups by scouring process. The material did not need any plasma treatment and only PVDF results are presented below.

#### 5.4.1. Contact angle measurement

Contact angle measurements show an improvement in the PVDF surface wettability after the plasma treatment. The average WCA value of the PVDF control sample was 84.55° and it reduced with plasma treatment irrespective to the gas used. WCA reduced to 68.36, 63.2 and 46.65 for Ar, O₂ and Ar+O₂ plasma samples respectively as shown in Figure 49. WCA is directly related to the surface energy, it is also dependent on surface morphology and chemical functional groups present on the surface.
Figure 49: Water contact angle of PVDF thin film before and after Ar, O\textsubscript{2} and (Ar+O\textsubscript{2}) plasma treatment

5.4.2. Scanning electron microscopy:

Changes in the surface morphology are normally caused by ion bombardment and UV radiation in the plasma and depend on plasma gas. The SEM images in Figure 50 (a, b, c, d, and e) show the surface of PVDF film before and after plasma treatment. The grainy features on the PVDF film surface were carried onward from film manufacturing process.
Figure 50: SEM micrograph of PVDF a) control, b) Ar plasma c) O$_2$ plasma d), and e) (Ar + O$_2$) plasma

There is not much noticeable etching by Ar plasma or O$_2$ plasma and only (Ar+O$_2$) plasma treatment significantly altered the morphology (Figure 50 d). The surface transformed to flat yet rougher surface as shown in higher resolution image (Figure 50 e). The roughness observed was uniform and nanosized and these observations are consistent with water contact angle measurements.
5.4.3. XPS measurement

XPS measurements were done for control, Ar, O₂ and (Ar + O₂) plasma treated PVDF samples. Carbon, fluorine and oxygen were detected in all the samples as shown in overall XPS scan in Figure 51: XPS survey scan of PVDF film before and after Ar, O₂ and Ar+O₂ plasma treatment & Table 3. Plasma treatment lowered the Fluorine content, however Oxygen is increased. There is a large difference in bonding energy between C–F and C–H bond. The bond energy for F–F bond is only 1.6 eV and that for H–F bonds is 5.85 eV, and that for C–F bonds is 4.42 eV [14]. High resolution C1s scans were performed to study the presence of different functional groups on the PVDF surface. C1s peaks were curve fitted to calculate the relative concentration of present functional groups. Three sub peaks C1s peak A, C1s peak B and C1s peak C at 286.4, 291.4 and 288 eV respectively were found. Peak A is assigned to CH₂-CF₂, CHF-CH₂-CF and O-CH₂ groups. Peak B is assigned to CF₂-CH₂, while peak C is assigned to CH₂-CF-CH₂, CH₂-CF-CHF, O-CH₂-CF₂ [22]. O 1s peak at 533.7 eV is assigned to C-O [23], while F1s peak at 688.65 eV to C-F bond.
Figure 51: XPS survey scan of PVDF film before and after Ar, O₂ and Ar+O₂ plasma treatment
Table 3: Atomic composition of untreated and plasma treated PVDF film samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>C1s Peak A (286.4 eV)</th>
<th>C1s Peak B (291.4 eV)</th>
<th>C1s Peak C (288 eV)</th>
<th>O1s peak A (533.7 eV)</th>
<th>F1s peak A (688.65 eV)</th>
<th>C</th>
<th>O</th>
<th>F</th>
<th>O/C</th>
<th>F/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>29.21</td>
<td>16.8</td>
<td>17.7</td>
<td>2.2</td>
<td>34.14</td>
<td>63.7</td>
<td>2.16</td>
<td>34.1</td>
<td>0.03</td>
<td>0.54</td>
</tr>
<tr>
<td>Ar</td>
<td>73.42</td>
<td>1.89</td>
<td>10</td>
<td>9.2</td>
<td>5.48</td>
<td>85.3</td>
<td>9.15</td>
<td>5.48</td>
<td>0.11</td>
<td>0.06</td>
</tr>
<tr>
<td>O₂</td>
<td>51.54</td>
<td>7.99</td>
<td>8.46</td>
<td>8.7</td>
<td>23.31</td>
<td>68</td>
<td>8.7</td>
<td>23.3</td>
<td>0.13</td>
<td>0.34</td>
</tr>
<tr>
<td>Ar+O₂</td>
<td>52.14</td>
<td>9.4</td>
<td>8.85</td>
<td>9.3</td>
<td>20.31</td>
<td>70.4</td>
<td>9.31</td>
<td>20.3</td>
<td>0.13</td>
<td>0.29</td>
</tr>
</tbody>
</table>
The untreated PVDF surface showed two main peaks at 291.4 eV (due to CF$_2$) and 286.4 eV (due to CH$_2$) components [11] [24]. Ar plasma was most effective in lowering the C1s peak B from 16.8 to 1.89, while O$_2$ and (Ar + O$_2$) resulted in moderate levels of de-fluorination (Table 3). The fluorine to carbon ratio (F/C) decreased from 0.54 to 0.06 for Ar and 0.34, 0.29 for O$_2$ and (Ar + O$_2$) respectively. Ar plasma also increased the surface oxygen content from 2.16 to 9.15 %, however other two plasma gases achieved similar results for oxygen incorporation. The oxygen to carbon ratio (O/C) rose to 0.13 for O$_2$ and (Ar + O$_2$) plasma from 0.03 for control sample. O/C value was 0.11 for Ar plasma. It is interesting to note the incorporation of oxygen based functional groups during argon plasma. The oxygen may arise from the following sources; (i) an impurity in Ar gas [25] (ii) exposure to air after taking out of plasma chamber before going to XPS measurement [17].
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b)

C1s scan (Ar)
C1s peak A
C1s peak B
C1s peak C

Counts / s (a.u.)

Binding energy (eV)

296 294 292 290 288 286 284 282

C1s scan (O₂)
C1s peak A
C1s peak B
C1s peak C

Counts / s (a.u.)

Binding energy (eV)

296 294 292 290 288 286 284 282
Figure 52: C1s scan spectra of PVDF a) control, b) Ar, c) O₂ and d) (Ar + O₂) plasma treatment

The C1s spectra of PVDF film before and after RF plasma show that plasma treatment causes de-fluorination and the incorporation of oxygen into the polymer surface (Figure 52: C1s scan spectra of PVDF a) control, b) Ar, c) O₂ and d) (Ar + O₂) plasma treatment). The C1s scans and overall composition (Table 3) indicates that CF₂ carbons were modified into CHF and CH₂ carbons and O-C carbons (O-CH₂ and O-CHF) during plasma exposure as evident by increase of oxygen content and decrease in C1s Peak A. Increase in hydrophilicity is important indication of incorporation of oxygen based functional groups. Although Ar plasma resulted in higher degree of de-fluorination, however this did not result in lowering WCA.

5.4.4. Abrasion resistance and sheet resistance
PPy coated PVDF film samples abraded by the Martindale abrasion tester are photographed by a microscope (Olympus DP71) after 0, 200 and 2000 cycles of abrasion (Figure 53). The magnification is set at 10 times for all the images. Some of the coating for the control sample was missing even before the abrasion test due to weak interfacial bonding and nearly all the coating faded away from the control sample after 200 and 2000 cycles of abrasion leaving surface non-conductive.

Plasma treated samples clearly showed better abrasion resistance. Ar plasma sample showed some flaking off after 2000 cycles, it was still significantly better than the control sample. On the other hand the O$_2$ and (Ar+O$_2$) plasma treated samples had strong binding as there was only small visible coating loss. The effectiveness of (Ar+O$_2$) plasma treatments is clearly evident, as it showed better coating fastness than using these gases alone. This is due to de-fluorination and mean time incorporation of oxygen based functional groups during plasma treatment [14].
Figure 53: PPy coated PVDF film sample after 0, 200 and 2000 abrasion cycles in martindale abrasion tester for control, Ar, O₂ and (Ar + O₂) samples; magnification 10 X
The Sheet resistance ($R_s$) results after 0, 200 and 2000 abrasion cycles are presented in Figure 54. $Ar$ and $Ar + O_2$ plasma gases lowered the $R_s$ values of the PPy coated PVDF films compared to the control sample (1600 ohms/sq), while $O_2$ plasma treatment resulted in small increase in initial $R_s$ values and it may be due to $O_2$ being less effected in de-fluorination as compared to $Ar$ and $(Ar+O_2)$ as shown in Table 3. The $R_s$ values could not be calculated for control samples with 200 and 2000 abrasion cycles. The lowest $R_s$ values were noted for $(Ar+O_2)$ gas at 1197 ohms/sq for 120 sec plasma treatment, which increased to 2589 ohms/sq after 2000 abrasion cycles. The $R_s$ value of $Ar$ plasma sample before abrasion was 1452; it rose to 2083 and 66523 ohms/sq after 200 and 2000 abrasion cycles respectively. Similarly $R_s$ values for $O_2$ plasma before abrasion were 2280; it rose to 4218 and 6989 ohms/sq after 200 and 2000 abrasion cycles respectively.

Figure 54: Sheet resistance of PPy coated PVDF samples; control, $Ar$, $O_2$ and $(Ar+O_2)$
The sheet resistance data of PPy coated PVDF samples in Figure 54 and photographs of abraded samples in Figure 53, agree very well with each other and all confirm the order of plasma gas effectiveness as \((\text{Ar+O}_2) > \text{O}_2 > \text{Ar}\). Contact angle measurements show an improvement in the PVDF surface wettability after the plasma treatment. The decrease of F/C ratio and water contact angle proves that both chemical and physical effects play an important role in the adhesion.

It is interesting to note that control, Ar and O\(_2\) plasma treated PVDF samples had a grainy surface morphology and it did not lower the \(R_s\) value as much as \((\text{Ar+O}_2)\) plasma treated surface having flat yet nano-sized surface roughness, similar trend was observed for bonding strength. Both XPS and surface imaging indicates that incorporation of oxygen functional groups and nano sized surface roughness is important for coating fastness. It was confirmed by the connection of abrasion resistance imaging, sheet resistance measurement and the chemical composition data in Table 3. Similar results were obtained in our previous work on Polyester fabric [19]. In this study we were able to use the advantages of both argon plasma (effective on de-fluorination) and oxygen plasma (effective on dehydration and introduction of oxygen functional group) to achieve improved bonding. In other words, the improved bonding of the combination may be attributed to the combined effect. Also the argon plasma produced more reactive sites on the substrate surface, which would enhance the binding of functional groups.

5.5. Conclusion
We have studied the improvement of binding of polypyrrole with PVDF thin film using low pressure plasma. Ar, O$_2$ and Ar+O$_2$ gases were used in plasma treatment. The abrasion data suggest adequate strength of bonding with PVDF surface after plasma treatment. The plasma induced increase in hydrophilicity, surface functionalization with oxygen based groups contributed to the improved coating adhesion and fastness. These results clearly show the effectiveness of Ar+O$_2$ plasma in lowering the resistivity and improving the binding strength of the PPy coating.

5.6. References


Summary and overall conclusion

In this work, the effect of low temperature radio frequency plasma pre-treatment on PET and PVDF surfaces has been studied with a view to improve the effectiveness of binding of PPy on these substrates. PPy coated textiles suffer from poor adhesion onto substrate surface. Plasma treatment is a surface sensitive environment friendly substitute to chemical treatment.

PPy coating optimisation and thermal stability was studied. Optimum concentrations were found to be 0.11, 0.857 and 0.077 mol/l for monomer, oxidant and dopant respectively and sheet resistance values for PPy coated PET fabric were recorded as low as 72 Ω/sq. PPy fabric gained resistance less than one order of magnitude when aged for 18 months at room temperature. Long term aging of PPy coating fabric at 120°C for 20 hours raised the resistance to 40 kΩ for un-doped and 1.7 for PTSA doped coatings. These results suggest the preserving effect of sulphonate based dopants. It was also noted that the oxygen attack on the polymer backbone is key factor of polymer degradation.

Low temperature plasma using Ar, O₂ and N₂ gases were used to improve the adhesion of PPy coating onto polyester fabric. The electrical conductivity and abrasion resistance results show significant improvement after plasma treatment and effectiveness of plasma gases was found to be in the order of O₂ > Ar > N₂. Plasma treatment introduced hydrophilicity and surface roughness, which was more significant in the case of oxygen. The wettability change is attributed to both chemical and physical changes on the substrate surface. Detailed XPS results indicate that the oxygen plasma treatment induced
oxygen based functional groups on the surface more than other gases. Surface functionalization by oxygen functional groups and a uniform nano-sized roughness was found to be the reason for PPy adhesion improvement. Oxygen plasma treatment on PET fabric and thin film was further studied by a range of plasma treatment conditions to find optimum conditions for better adhesion. Plasma resulted in surface oxidation which gave rise to depositions of additional oxygen functional groups. Increasing plasma exposure time resulted in more hydrophilicity and oxidation till a saturation point was reached at 120 sec, while surface roughness never achieved saturation even till 500 sec. Increase in surface functionalization by C-O and O-C=O groups and the formation of nano size roughness contributed to improved adhesion and high conductivity. These results show that improved PPy bonding is more dependent on surface chemistry than surface morphology.

Metal based electrode coatings are brittle and unconformable to skin and can be replaced by PPy coatings on energy generating PVDF films; however poor adhesion of PPy with PVDF is problematic. Surface functionalization was improved by the formation of oxygen groups on PVDF surface, reinforcing pervious results. Plasma altered surface roughness, chemistry and hydrophilicity of film. Electrical sheet resistance and abrasion resistance data clearly show that the combination Ar and O\textsubscript{2} gases were more effective in the improvement of coating and the binding strength of the PPy than Ar and O\textsubscript{2} alone.
Future Work

This work provides valuable information for better understanding the effect of oxygen plasma treatments on physical and chemical properties of PET and PVDF surface. This research has demonstrated the feasibility of effectively using plasma technology for coating adhesion with few textile substrates. These results can be used as guidelines for the substrate surface selection, coating optimisation and understanding PPy coating adhesion. A natural extension of this work would be to focus on other substrates like nylon, wool, silk etc. Improvement of coating adhesion by plasma has increased the scope of these conducting materials. There would be better utilization of PPy coated fabrics as sensors in intelligent textiles area and can envisage integration of these materials in physical and biological sensors in future. It would be interesting to study the vapour phase thin coatings and soluble conducting polymers in conjunction with plasma treatment and adhesion improvement. The degradation after plasma treatment has not been studied in this work.